SYNTHESIS AND CHARACTERIZATION OF BRANCHED POLYMERS VIA ANIONIC POLYMERIZATION BASED ON “STRATHCLYDE APPROACH”

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FACULTY OF SCIENCE
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Field of Study: **POLYMER CHEMISTRY**

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SYNTHESIS OF BRANCHED POLYMERS VIA ANIONIC POLYMERIZATION BASED ON "STRATHCLYDE APPROACH"

ABSTRACT

Branched polymers continue to attract interest in recent years due to their favorable properties over their linear counterparts. This work aimed at developing a synthetic route towards highly branched polymers from commercially available raw materials, in good yield and devoid of microgelation, i.e., to prepare a completely soluble polymer.In particular, anionic polymerization technique has been utilized to synthesize highly branched polymers of isoprene. The polymerizations were conducted under high vacuum conditions using *sec*-butyllithium as initiator at 50 °C in toluene. Toluene served both as a solvent and as a chain transfer agent while tetramethylethylenediamine (TMEDA) served as the polar modifier with a commercial mixture of divinylbenzene (DVB) employed as the branching agent for the "living" poly(isoprenyl)lithium anions. The nature of the reaction was studied on the TMEDA/Li ratio as well as the DVB/Li ratio. The obtained branched polymers were characterized by triple detection size exclusion chromatography (SEC), nuclear magnetic resonance (NMR) spectroscopy, melt rheology, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). The characterizations in terms of structural, rheological, thermal and morphological properties carried out on the branched polymers are hereby described and compared with those of the linear polymers. Broad molecular weight distributions have been obtained for the highly branched polymer products. ^{1}H NMR spectroscopy reveals the dominance of 3,4–polyisoprene microstructure. It was found that the complex viscosities and dynamic moduli of the branched samples were much lower compared to their linear counterparts. TEM studies show that the linear polyisoprene exhibited long-range order, which disappeared with increasing degree of branching. The branched polymers were thermally stable (up to ~ 387 °C) and completely soluble in common solvents. They decomposed via multistep reaction mechanism as manifested by the nonlinear relationship between the activation energy and the extent of conversion. The results also indicated that the trend of activation energy of the branched polymers studied increases with DVB content and decrease with increasing molecular weight distribution. The average E_a were found between 260.15–32031 kJmol^{-1}and the results showed that the average values of E_a obtained by KAS (262.34 kJ mol^{-1} to 314.65 kJ mol^{-1}) and FWO (260.15 kJ mol^{-1} to 309.67 kJ mol^{-1}) methods were in agreement with those obtained from the Kissinger method (265.79 kJ mol^{-1} to 282.75 kJ mol^{-1}). The results conform with earlier findings by the "Strathclyde team" for radical polymerization systems. This methodology has the potential of providing soluble branched vinyl polymers at low cost using the readily available raw materials.

Keywords: anionic polymerization, branched polymers, Strathclyde, isoprene, kinetics.

SINTESIS DAN PENCIRIAN POLIMER BERCABANG MELALUI PEMPOLIMERAN ANIONIK BERDASARKAN "PENDEKATAN STRATHCLYDE"

ABSTRAK

Polymer bercabang terus menarik minat kebelakangan ini, kerana cirinya yang memuaskan berbanding struktur linear. Kerja ini bertujuan untuk membangunkan laluan sintetik ke arah polimer yang bercabang tinggi dari bahan mentah yang tersedia secara komersil, dalam hasil yang baik dan tidak mempunyai mikrogelasi, iaitu menyediakan polimer yang larut sepenuhnya. Khususnya, teknik pempolimeran anionik telah digunakan untuk mensintesis polimer isoprena bercabang. Pempolimeran dilakukan di bawah keadaan vakum yang tinggi menggunakan sek-butillitium sebagai pemula pada 50 °C dalam toluena. Toluena bertindak sebagai pelarut dan sebagai agen pemindahan rantaian, sementara tetrametilenadiamina (TMEDA) pula berfungsi sebagai pengubah kutub dengan campuran komersial divinilbenzena (DVB) yang digunakan sebagai agen pencabang untuk anion poli(isoprenil)litium "hidup". Sifat tindak balas dikaji pada nisbah TMEDA/Li serta nisbah DVB/Li. Polimer bercabang yang diperolehi dicirikan oleh kromatografi penyisihan saiz tiga pengesanan (SEC), spektroskopi resonans magnetik nuklear (NMR), reologi cairan, analisis termogravimetri (TGA), kalorimetripengimbasan pembezaan (DSC) dan mikroskopi elektron transmisi (TEM). Ciri-ciri dari sifat-sifat struktur, reologi, haba dan morfologi yang dijalankan ke atas polimer bercabang dengan ini dihuraikan dan dibandingkan dengan polimer linear. Taburan berat molekul yang luas telah diperolehi untuk produk polimer yang bercabang tinggi. Spektroskopi ^{1}H NMR mendedahkan penguasaan mikrostruktur 3,4–polyisoprene. Didapati bahawa kelikatan kompleks dan modul dinamik bagi sampel bercabang jauh lebih rendah berbanding sampel yang berstruktur linear. Kajian TEM menunjukkan bahawa polyisoprene linear memamerkan susunan jangka panjang, yang hilang dengan peningkatan cawangan. Polimer bercabang adalah stabil (sehingga ~387 °C) dan larut sepenuhnya dalam pelarut biasa. Mereka memusnahkan melalui mekanisme reaksi multistep seperti yang ditunjukkan oleh hubungan tidak linear antara tenaga pengaktifan dan sejauh mana penukaran. Keputusan juga menunjukkan bahawa trend tenaga pengaktifan polimer bercabang dikaji meningkat dengan kandungan DVB dan menurun dengan pengagihan berat molekul yang semakin meningkat. Rata-rata E_a didapati antara 262.34–320.31 kJ mol^{-1} dan hasilnya menunjukkan bahawa nilai purata E_a diperolehi oleh KAS (262.34 kJ mol^{-1} hingga 314.65 kJ mol^{-1}) dan FWO (260.15 kJ mol^{-1} hingga 309.67 kaedah kJ mol^{-1}) sepadan dengan yang diperoleh daripada kaedah Kissinger (265.79 kJ mol^{-1} hingga 282.75 kJ mol^{-1}). Hasilnya sesuai dengan penemuan awal oleh "pasukan Strathclyde" untuk sistem pempolimeran radikal. Metodologi ini berpotensi untuk menyediakan polimer vinil bercabang yang melarut pada kos rendah dengan menggunakan bahan mentah yang sedia ada.

Kata kunci: pempolimeran anionik, polimer bercabang, Strathclyde, isoprena, kinetik.

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Shehu Habibu

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF SCHEMES

LIST OF TABLES

LIST OF SYMBOLS AND ABBREVIATIONS

°C : Degree Celsius

^{1}H NMR : Proton nuclear magnetic resonance

A : Pre-exponential factor

AIC : Advanced isoconversional

Ar : Aromatic

ATRP : Atom transfer radical polymerization

ATRP : Atom transfer radical polymerization

B : Branched

BHT : 2,6-di-tert-butyl-4-methylphenol

c : Concentration

$CDCl_3$: Deuterated chloroform

CMM : Coupled monomer methodology

CRCC : Controlled radical crosslinking copolymerization

CRP : Controlled radical polymerization

d : Doublet

Ð : Dispersity

DB : Degree of branching

DMM Double monomer methodology

dn/dc : Refractive index increment

DNA : Deoxyribonucleic acid

DP : Degree of polymerization

DRI : Differential refractive index

DSC : Differential scanning calorimetry

DVB : Divinylbenzene

E_a : Activation energy

FWO : Flynn-Wall-Ozawa

g : gram

g' : Branching factor

HBP : Hyperbranched polymer

HDPE : High-density polyethylene

HPLC : High performance liquid chromatography

HPLC : High performance liquid chromatography

HRTEM : High-resolution transmission electron microscopy

I : Initiator

ICTAC : International Confederation for thermal analysis and calorimetry

IFIRP : Initiator fragment incorporation radical polymerization

ISI : Institute of Scientific Information

KAS : Kissinger-Akahira-Sunose

Kg : Kilogram

k_i : Rate constant of initiation

kJ : Kilojoules

K_{LS} : Light scattering constant

k_p : Rate constant of propagation

K_{RI} : Refractive index constant

k_t : Rate constant of termination

K_V : viscometer constant

L : Linear

LDPE : Low-density polyethylene

Li : Lithium

LLDPE : Linear low-density polyethylene

M : Molar concentration

m : Multiplet

M : Monomer

m : Moles

m.p. : Melting point

M_0 : Initial monomer concentration (time = 0)

Me : Entangled molecular weight

Me_4Si : Tetramethyl silane

MeOH : Methanol

mg : milligram

MHz : Megahertz

MIMOS : Malaysian Institute of microelectronic system

min : minutes

ml : milliliters

mmol : millimol

M_n : Number averaged molecular weight

M_p : Peak molecular weight

M_w : Weight averaged molecular weight

MWD : Molecular weight distribution

n : Reaction order

N_2 : Nitrogen gas

N_A : Avogadro’s number

N_i : Number of molecules

nm : Nanometer

NMP : Nitroxide mediated polymerization

NMR : Nuclear magnetic resonance spectroscopy

PAMAM : Polyamidoamine

PC : Polycarbonate

PDI : Polydispersity index

PEO : Polyethylene oxide

PET : Polyethylene terephthalate

PI : Polyisoprene

PILi	:	Poly(isoprenyl)lithium
PMMA	:	Poly(methylmethacrylate)
PS	:	Polystyrene
PSLi	:	Poly(styryl)lithium
PTFE	:	Polytetrafluoroethylene
PTP	:	Proton transfer polymerization
PU	:	Polyurethanes
PVC	:	Polyvinylchloride
q	:	Quartet
R	:	Universal gas constant
r.t.	:	Room temperature
RAFT	:	Reversible addition fragmentation chain transfer polymerization
R_g	:	Radius of gyration
RI	:	Refractive index
RMS	:	Root mean square radius of gyration
ROMB	:	Ring-opening multi-branching
ROMP	:	Ring-opening metathesis polymerization
R_Θ	:	Rayleigh factor
s	:	singlet
SCROP	:	Self-condensing ring-opening polymerization
SCVP	:	Self-condensing vinyl polymerization
SEC	:	Size exclusion chromatography
sec-BuLi	:	*sec*-butyllithium
STA	:	Simultaneous thermal analyzer
t	:	triplet
T	:	Temperature
TEM	:	Transmission electron microscopy
T_g	:	Glass transition temperature

TG	:	Thermogravimetric
TGA	:	Thermogravimetric analysis
THF	:	Tetrahydrofuran
T_{max}	:	Temperature of maximum degradation
TMEDA	:	N,N,N’,N’-Tetramethylethylenediamine
TMP	:	1,1,1,1-tris(hydroxymethyl) propane
TPEs	:	Thermoplastic elastomers
UV	:	Ultraviolet
w.r.t.	:	With respect to
W_0	:	Initial weight
W_f	:	Final weight
wt	:	Weight
X	:	Degree of polymerization
$\bar{X}_n$	:	Number average degree of polymerization
$\bar{X}_w$	:	Weight average degree of polymerization
α	:	Degree of conversion
β	:	Heating rate
γ	:	Cross-linking index
δ	:	Chemical shift
η	:	Viscosity
η_0	:	Zero shear viscosity
λ_0	:	Wavelength of incident light
ρ	:	Fraction of double bonds present
ϕ	:	Volume fraction

CHAPTER 1: INTRODUCTION

1.1 Introduction

This chapter introduces the objectives of the Ph.D. research; the motivation behind the synthesis of branched polymers as well as the choice of anionic polymerization technique to accomplish the synthesis has been outlined. The problem to be addressed in this research (gel formation associated with the copolymerization of a vinyl monomer with multifunctional co-monomer) has been clearly defined. Objectives of the research, scope, limitations, as well as the organization of the thesis, have also been outlined.

1.2 Background

The occurrence of branching in polymers has been well known for many decades. Branched polymers represent an intermediate class of macromolecules between the linear and the network polymers. They have branch points in their structure from which two or more polymer chains originate. The branching phenomenon is also found in nature, for instance, deoxyribonucleic acid (DNA) and glycogen are naturally occurring proteins and polysaccharide respectively (Chou & Johnson, 1993; Russo *et al.*, 2013). Branching could also be deliberately introduced into 'linear' polymers to aid in processing or improve performance; an example is a preparation of linear low-density polyethylene (LLDPE) (Bork, 1984). Some levels of branching also occur inadvertently through side reactions taking place in the course of synthesizing many 'linear' polymers. Branching in polymers can be created by the addition of multifunctional monomers to difunctional monomers.

Highly branched polymers are among the most important class of synthetic polymers which have received constant attention from both industry and academic researchers. This constant attention is due to their unique chemical and physical properties. (Caminade *et al.*, 2015; Chisholm *et al.,* 2009; Voit & Lederer, 2009). Because of their distinctive and favorable properties such as increased solubility, solution and melt viscosities, as well as functional group density, branched polymers have found many potential applications in nanotechnology, catalysis and biomaterial fields (Chisholm *et al.*, 2009; Elkins & Long, 2004).

Apart from being good candidates for liquid coating industries due to their improved solubility and lower viscosity, (Campbell *et al.*, 2005; Liu *et al.*, 2013) branched and hyperbranched polymers have received much attention over the past decades due to their attractive features such as three-dimensional structures, and end-functionalized groups (Higashihara *et al.*, 2016; Hutchings, 2008; Yan *et al.*, 2011). Highly branched or hyperbranched polymers (HBPs) emerged to solve the problems of high cost and synthetic difficulties associated with dendrimers. Unlike dendrimers which are synthesized in multi-step approach, highly branched polymers are prepared in one-pot synthesis, making their potential applications in a large scale, commercially more viable (Caminade *et al.*, 2015; Kunamaneni *et al.*, 2003). There are several approaches to the synthesis of highly branched polymers, such as polycondensation (Segawa *et al.*, 2013; Zhang *et al.*, 2013), self-condensing vinyl polymerization (SCVP), (Alfurhood, Bachler, *et al.*, 2016; Alfurhood, Sun, *et al.*, 2016; Frechet, Henmi, Gitsov, & Aoshima, 1995; Graff *et al.*, 2015), high-temperature polymerization (Campbell *et al.*, 2005), and free-radical polymerization technique (Tobita, 2013). These techniques have been used to synthesize branched polymers of various types including graft polymers, star polymers, and miktoarm star-shaped polymers. While the polycondensation, self-condensing vinyl polymerization, and high-temperature methods are not cost-effective, the classical free radical copolymerization in the presence of an even small amount of multifunctional comonomer leads quickly to the formation of insoluble gels (Campbell *et al.*, 2005; Priddy, 1994). Thus, preparation of highly branched polymers in good yield, and without gelation remains a challenge to both industrial and academic polymer chemists and engineers. Various synthetic routes have been suggested. A straightforward and cost-effective approach to the synthesis of branched polymers via free radical polymerization was reported by Sherrington and his coworkers, a method known as “Strathclyde methodology.” Strathclyde approach employs the use of appropriate level of chain-transfer agents (thiols) to prevent gel formation during the free radical polymerization of vinyl monomers with difunctional comonomer (Baudry & Sherrington, 2006a, 2006b; Bütün *et al.*, 2005; Isaure *et al.*, 2004; O'brien *et al.*, 2000; Sherrington *et al.*, 2008). The addition of a difunctional comonomer results in chain branching but at the same time could also cause crosslinking and gel formation. However, the incorporation of a chain transfer step into this route causes the termination of the growing polymeric chains as well as the initiation of a new chain and consequently leads to the reduction in the molecular weight and hence, aids in overcoming the problem of gel formation.

Radical polymerization involving chain transfer to monomer has also been reported as a mean of producing highly branched polymers (Jiang *et al.*, 2012; Liu *et al.*, 2008; Liu *et al.*, 2013). The use of functionalized 1,1-diphenylethylene (DPE) derivatives in combination with anionic polymerization has been previously reported as one of the methods to synthesize highly branched polymers (Hirao *et al.*, 2006). For over six decades since the proof of its ‘living’ nature demonstrated by Szwarc et al., (Szwarc, 1983; Szwarc *et al.*, 1956) anionic polymerization remains the yardstick for measuring other living/controlled polymerizations. This superiority is due to the ability to synthesize well-defined structures of various architectures ranging from linear polymers to dendrimers with controlled molecular weights and several molecular weight distributions, which attracted the scientific community for years. However, the absence of natural death does not mean immortality either (Szwarc, 1983). Hence, the anionic polymerization technique could be explored in the preparation of highly branched polymers via chain transfer to solvent as an analogous to Strathclyde's approach.

This work was therefore aimed at synthesizing highly branched polyisoprene from commercially available raw materials, in good yield and devoid of microgelation. Copolymerization of isoprene and divinylbenzene (DVB) was carried out using *sec*-butyl lithium as the initiator, tetramethylethylenediamine (TMEDA) was added as the polar modifier, and gelation was prevented by chain transfer to solvent. Some experimental parameters were investigated such as the TMEDA/initiator ratio, as well as the proportion of the branching co-monomer to the initiator. The prepared linear and branched polymers were sufficiently characterized. Their thermal and rheological properties were assessed, and a comparison study has been made of the highly branched polymers and the linear polymers samples.

1.3 Research objectives

Recently, hyperbranched polymers (HBPs) have received increasing attention. However, radical copolymerization of vinyl monomers with multifunctional co-monomer even in small amounts lead to the formation of a cross-linked network (gel). Moreover, procedures such as self-condensing vinyl polymerization (SCVP) are complex and only allows for the use of a few specialized monomers. Therefore, developing a new synthetic route to HBPs in good yields using commercially available monomers is highly desirable. The primary focus of this thesis is on the design and synthesis of hyperbranched polymers through copolymerization of vinyl monomers with divinyl cross-linkers via anionic polymerization.

The thesis includes three objectives:

i. To develop novel synthetic protocols to synthesize branched polymers by anionic polymerization based on the general principles of the “Strathclyde approach” to the synthesis of branched polymers via free radical polymerization.
ii. To synthesize branched polymers of isoprene through copolymerization with divinylbenzene.
iii. To have full characterizations of the structural, thermal, and rheological properties of the synthesized polymers.

1.4 Significance of the study

The present research aimed at developing a new synthetic route to branched polymers using anionic polymerization employing a chain transfer mechanism. This methodology has the potential of providing soluble branched vinyl polymers at low cost using the readily available raw materials.

1.5 Scope of the research

The present work entails the synthesis and characterization of branched polymers using anionic polymerization technique exploiting chain transfer to solvent. Precisely, hyperbranched polyisoprenes were prepared and characterized using various analytical methods which include: triple detection size exclusion chromatography (SEC), nuclear magnetic resonance spectroscopy (NMR), melt rheology, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). The triple detection SEC facilitates the determination of molecular weight and the dispersity index as well as information about the degree of branching. NMR supplies information on the microstructure, while the DSC and TGA were employed to study the thermal properties of these polymers. Rheological and morphological information were respectively obtained from the rheology and transmission electron microscopy.

1.6 Thesis outline

This thesis consists of five (5) chapters; the structure of these five chapters is organized as follows:

Chapter 1: This chapter presents a clear picture of the present study. It gives a brief introduction highlighting the importance of branched polymers as well as the challenges associated with their synthesis. Hence, this chapter presents a background of the present study, the objectives, scope, as well as the limitations of the research. Also, the outline of the thesis is presented in this chapter.

Chapter 2: Chapter 2 presents a review of literature related to the synthesis, and characterization of branched polymers, the motivation behind the choice of the present technique (Strathclyde approach) and its application in anionic polymerization to synthesize the hyperbranched polymers has been given. The chapter also discussed on some applications of hyperbranched polymers.

Chapter 3: This chapter presents the experimental procedure used to synthesize and characterize the hyperbranched polymers as well as their linear precursors. Specifications of chemicals and reagents used as well as the purification procedure for the chemicals and glassware were also provided. Likewise, details of the instruments used to achieve the synthesis and characterizations as well as operating procedure were outlined.

Chapter 4: This chapter presents the results obtained from the experimental works carried out according to the procedures outlined in Chapter 3. The chapter also contains the discussion of the results as well as positioning it in the context of the existing literature.

Chapter 5: Chapter 5 gives a summary of significant findings of the present research and proffer some recommendations for future works.

1.7 Chapter summary

In this chapter, the motivation behind the synthesis of branched polymers as well as the choice of anionic polymerization technique to accomplish the synthesis has been outlined. The problem to be addressed in this research has been clearly defined. Objectives of the research, scope, limitations as well the organization of the thesis have also been outlined. An overview of the relevant literature will be provided in the next chapter.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

In the previous chapter, the objectives of the thesis were outlined. This chapter presents an overview of the relevant literature related to the concept of branching in polymer science. Also, the chapter highlighted the importance of anionic polymerization as one of the superior techniques for preparing polymers of various architecture and complexity. Discussion on the classification of polymers, brief on the synthesis, application, and importance of dendrimers is also highlighted. Finally, this chapter examined the literature related to the synthesis, characterization, and application of hyperbranched polymers.

2.2 Polymers

Polymers are high-molecular-weight chemical substances that constitute structural repeating subunits joined together by covalent chemical bonds (Young & Lovell, 2011). The word **polymer** is derived from the Greek words ***poly*** (many) and ***meros*** (parts). Polymer molecules have a molecular weight in the range of several thousand or more, and therefore, are referred to as macromolecules.

Polymers are found everywhere. So many of the things we purchase, wear, eat, consume, and dispose of are polymers. In fact, most of our body parts are polymers such as hair, skin, enzymes, DNA, bones, to mention just a few. We eat considerably polymeric materials or materials that contain polymers: cellulose (green vegetables), starch (potatoes), protein (milk and meat), etc. Polymers are used to modify many of our processed foods such as cheese, milkshakes, jams and ice creams.

Moreover, most of the materials we use to preserve and protect our foods from microorganisms and moisture, and to keep them warm or cold are polymers. All the clothes that we wear are made up of polymers, either natural such as wool, cotton, silk, or from synthetic sources like nylon and polyester. Materials used for medical applications including artificial organs, drug delivery devices, blood bags and surgical garments are all made from synthetic polymers. The building of our houses could not be possible without polymers; the wood we use consist of lignin and cellulose, the paints (acrylics), the plastic pipes for water supply, the tiles, the floor, and the furniture. For so many decades the interior of our automobiles contains a significant amount of polymers used purposely to reduce the weight of the automobiles and save energy from reduced fuel consumption (Patil *et al.*, 2017; Serrenho *et al.*, 2017; Marwana, 2017). The polyurethane foams used for the seat, the cover of the dashboard, wheel covers, lamp housings, electrical and electronic components as well as a number of automobile bodies are no longer prepared from metals. Bulletproof vests are made of exceptionally strong synthetic polymer fibers. We watch TVs, listen to CDs, communicate with our friends on cell phones, browse the internet with our computers, make payments with plastic cards, and travel with Touch & Go. All these materials consist of polymers, and the list goes on.

Polymers can easily be classified into two major groups, organic and inorganic. However, polymers can be classified in many ways based on the composition of monomers (homopolymers, copolymers), or the arrangement of chains in macromolecules (crystalline, semi-crystalline, amorphous), the process of polymerization (condensation, free radicals, anionic, cationic), the polymer structure and the areas of applications. They can also be classified based on their response to heat (thermosets, thermoplastics, elastomers), and according to their source, natural semi-synthetic or synthetic (Carraher, 2017; Stevens & Stevens, 1990; Young & Lovell, 2011). This thesis focused only on synthetic polymers and hence, brief classification of synthetic polymers is given in section 2.6.

2.3 Expressions of polymer molecular weights

Unlike simple organic compound that can be represented by molar masses, the molecular weights of polymers can only be represented as average since polymers are composed of units of different chain length. The degree of polymerization (X): expresses the number of units in a polymer chain and is given by equation 2.1 below.

$$X = \frac{M}{M_0} \qquad 2.1$$

In the above equation, M_0 and M represent the molar masses of the monomer and polymer, respectively.

Therefore, the molecular weight of the polymer and the chain length are related to the degree of polymerization. Polymer chains, however, are of different length and therefore better represented as an average degree of polymerization ($\bar{X}$), as a result, the molar masses of polymer chains in a given polymerization system are not the same therefore, the molecular weights of polymers are represented by average values such as number-average molecular weight (M_n) or weight average molecular weight (M_w) given by equations 2.2 and 2.3 respectively:

$$\langle M \rangle_n = \frac{\sum N_i M_i}{\sum N_i} \qquad 2.2$$

$$\langle M \rangle_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \qquad 2.3$$

Where N_i and M_i represent the number of molecules and molar mass respectively of species i. Figure 2.1 shows a schematic representation of the polymer molar mass distribution.

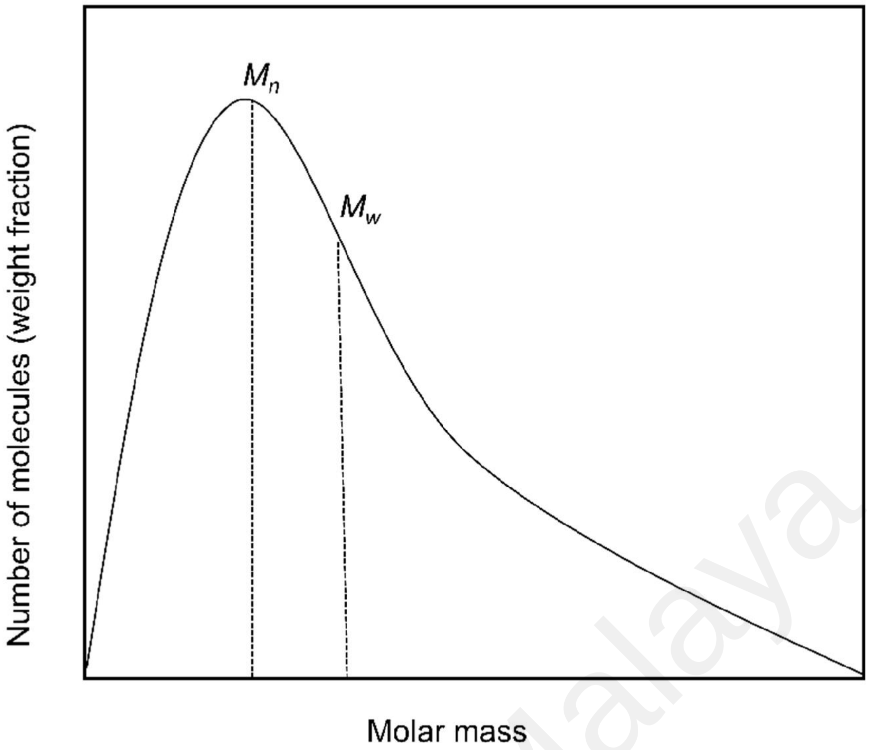


Figure 2.1: Schematic representation of the molecular weight distribution of synthetic polymers

Dispersity index (Đ) describes the extent of the distribution and is determined by the ratio of the weight average molecular weight to the number average molecular weight (Equation 2.4).

$$Đ = \frac{M_w}{M_n} \qquad \textbf{2.4}$$

The dispersity or dispersity index is an indication of the homogeneity in molecular weight of a given polymer. It also has a profound influence on the properties and processing of polymers (Gentekos *et al.*, 2016). A monodispersed polymer sample is the one in which all the chains are of the same lengths, hence, weight average and the number average molecular weights are the same (M_w = M_n, Đ =1). Polydisperse polymer, on the other hand, has molecules of varying chain lengths and the weight average molecular weight is higher than the number average molecular weight (M_w >

M_n, $Đ > 1$). Generally, naturally occurring polymers such as proteins are monodispersed ($Đ = 1$). While the dispersity of synthetic polymers is always greater than unity and is determined by the mechanism of polymerization employed (Gentekos *et al.*, 2016)

2.4 Mechanisms of polymer synthesis

A polymerization may either involve a stepwise reaction of polyfunctional monomers (step growth approach), or it may involve the growth of a polymer chain by a chain reaction (chain growth approach) (Carraher, 2017). Both approaches can be employed to synthesize polymers of various architecture such as linear, branched and networked polymers.

2.4.1 Step-growth mechanism

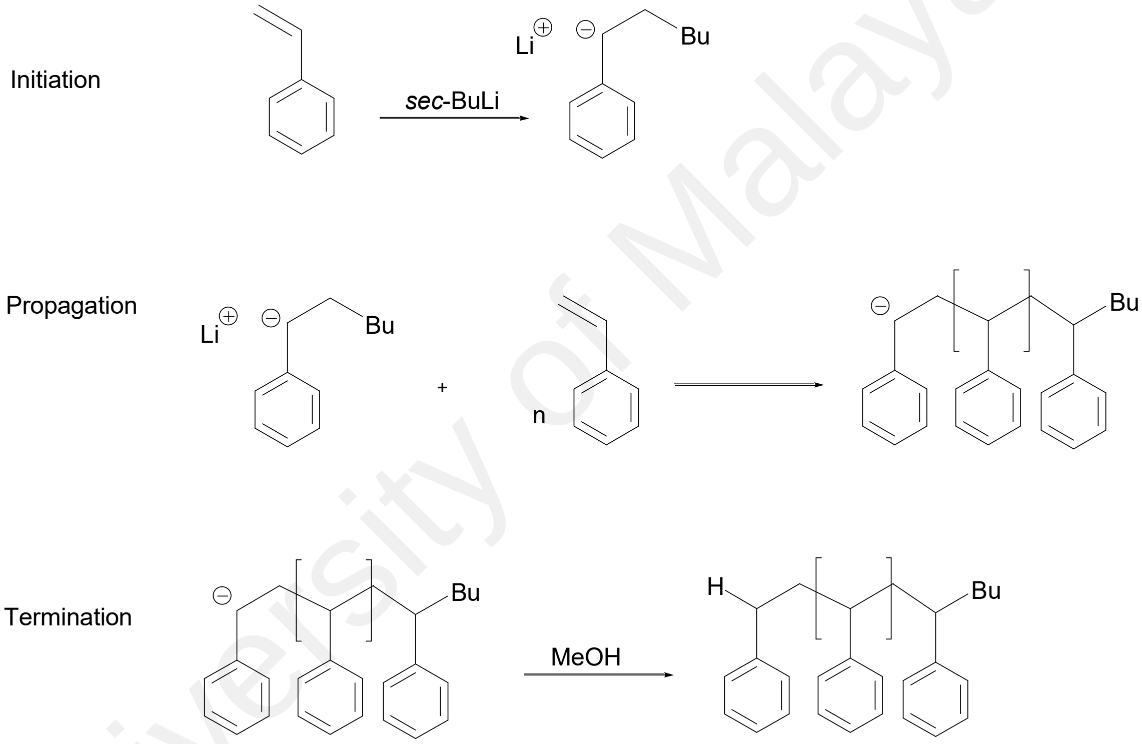
In step-growth polymerization, the polymer grows by step-wise reactions involving two molecular species of monomers or two functional groups of a monomer. They may be further divided into polycondensation or polyaddition reactions. In polycondensation usually, small molecule such as water or carbon dioxide are eliminated whereas in polyaddition, the monomers react together without any loss of small molecule. A typical example is the formation of polyurethanes by the reaction of diols with diisocyanates. Step-growth polymerization proceeds without an initiator but sometimes requires a catalyst. The monomers react at substantially the same rate until a mixture of polymers of high molecular weight is formed. The final architecture of the macromolecule produced via step-growth mechanism depends upon the number of reactive sites per monomer molecule. Hence, linear polymers are obtained if the reaction involves only bifunctional monomers whereas branched and network polymers are achieved if the reaction involves multifunctional monomers. Commercial polymers synthesized via step-growth polymerization include polycarbonate (PC), polyuria (PU), poly (ethylene terephthalate) (PET) as well as polyamides such as Nylon-6, 6, and Nylon-11.

2.4.2 Chain growth mechanism

Chain growth polymerization requires an initial reaction between an initiator (free radical or ionic) and a monomer. The reaction proceeds in three separate stages: initiation, propagation, and termination. The initial reaction between the initiator and the monomer is termed as initiation and marked the beginning of the polymerization reaction. Propagation stage is where the chains grow by joining each of the monomer molecules to the active chain. Termination marked the final stage of the polymerization where the chain growth ends (Carraher, 2017). When free radicals are involved in a chain growth reaction, the system is called free-radical polymerization. When ions are involved in the system, the polymerization is referred as ionic (anionic or cationic). When active organometallic centers are involved, the chain growth reaction is known as coordination polymerization. Examples of coordination polymerization include Ziegler-Natta, metallocene, as well as ring-opening metathesis polymerization. Various macromolecules, which include polystyrene (PS) polyisoprene (PI), polyvinyl chloride (PVC), polyethylene oxide (PEO), polymethylmethacrylate (PMMA), high-density polyethylene (HDPE) and low-density polyethylene (LDPE), are synthesized via chain-growth approach.

2.5 Anionic polymerization

First reported by Szwarc (Szwarc, 1956) in 1956, anionic polymerization is among the living polymerization techniques. Anionic polymerization involves a nucleophilic attack of a vinyl double bond by a carbanionic species that initiates the polymerization reaction. Anionic polymerization is true living polymerization since the active carbanionic species remains almost permanently present after the chain propagation. The polymerizations are usually carried out under an inert atmosphere or high vacuum conditions to prevent impurities and prepare polymers with controlled architecture and homogeneity (Hadjichristidis *et al.*, 2000). The most commonly used initiators in anionic polymerization are the anions generated from *tert*-butyl *sec*-butyl or *n*-butyl compounds that are generated from the respective alkyl lithium species. The nature of the alkyl group, as well as the solvent, affect the reactivity of the initiators (Hsieh & Quirk, 1996). These initiators are commonly used in anionic polymerization because of their efficiency, commercial availability, and ease of preparation. Scheme 2.1 demonstrates the anionic polymerization of styrene using *sec*-butyllithium as an initiator.



Scheme 2.1 Anionic polymerization of styrene initiated with *sec*-butyllithium

The monomers used in anionic polymerization must form a stable carbanionic species. Two major categories of monomers are vinyl or certain cyclic monomers. Examples include: styrene and derivatives (Liouni *et al.*, 1989), conjugated dienes (Nakamura *et al.*, 2001), lactones (Kricheldorf *et al.*, 1988; Kricheldorf & Rost, 2004), epoxides (Brocas *et al.*, 2013; Sanford *et al.*, 2018), acrylonitriles (Sivaram *et al.*, 1991), acrylates (Baskaran, 1996), vinyl pyridines (Fetters, 1983), etc. (Table 2.1).

Polymerizations of vinyl monomers involve stabilization by substituent groups capable of delocalizing the anionic species whereas cyclic monomers are polymerized via ring opening polymerizations in which the ring is opened by nucleophilic attacks to produce a living chain end (Hadjichristidis *et al.*, 2000; Morton & Fetters, 1975; Yu *et al.*, 1996). The ability of a monomer to undergo anionic polymerization defend on its reactivity, the stability of the initiator as well as the stability of the propagating carbanionic species.

Table 2.1: Monomers commonly used in anionic polymerization (Hsieh & Quirk, 1996)

Vinyl	Cyclic
Styrene and derivatives	Epoxides
Dienes	Sulfides
Vinyl pyridines	Lactides/Lactones
Alkyl acrylates and methacrylates	Carbonates
Acrylonitriles	Siloxanes
Vinyl ketones	Lactams
Nitroethylenes	

Generally, the presence of double bonds or groups such as an ester, cyano, carbonyl, sulfonic and aromatic rings promote the stabilization of the carbanions. On the contrary, electrophilic groups react with the living carbanionic chains. These groups include hydroxyl, carboxyl, primary amines, and secondary amines. However, the existence of such groups integrated on the monomer does not stop these monomers from being polymerized anionically, but there are some challenges associated. It is necessary to modify monomers containing electrophilic groups before undergoing anionic polymerization. This modification is achieved either by the protection of the electrophilic groups or by alternative polymerization procedures such as the use of selective initiators, specific counterions, or polymerizations at low temperature.

For over six decades since its discovery, anionic polymerization remains the best method for the preparation of complex macromolecular architecture because it provides access to numerous architectures via an outstandingly well-defined chemical reaction (Grubbs & Grubbs, 2017).

Interest in anionic polymerization continues to grow among both academic and industrial researchers and currently remains the "gold standard" for macromolecular synthesis with a high degree of control over molecular weight, molecular weight distribution, architecture and composition (Frey & Ishizone, 2018). Anionic polymerization has been utilized to prepare polymers of various architecture from simple to complex such as linear and block copolymers (Acar & Matyjaszewski, 1999; Hong *et al.*, 1999; Tanaka *et al.*, 2014; Yu *et al.*, 2018), star polymers (Ratkanthwar *et al.*, 2015), comb polymers (Frey & Ishizone, 2017), dendrimers (Hirao *et al.*, 2014; Mays, 2015) and hyperbranched polymers (Baskaran, 2003; Habibu *et al.*, 2018; Hadjichristidis *et al.*, 2001).

2.5.1 Living Anionic polymerization

Living polymerization was first declared by Szwarc (Szwarc, 1956) when he polymerized styrene in two steps using sodium naphthalene initiator. The experiment proceeded with approximately 100 % yield following the two monomer additions and that revealed the living nature of the polymeric chain ends. Szwarc and his co-workers later prepared tri-block copolymer styrene and isoprene of the type AAA-BBB-AAA to demonstrate the living nature of the reaction further. Complete polymerization of styrene monomer was carried out first followed by the addition of isoprene, and finally, styrene was added and allowed to propagate (Szwarc *et al.*, 1956).

Living anionic polymerization, therefore, refers to a polymerization approach that proceeds without chain transfer or termination reactions. Living anionic polymerization is the best synthetic method that offers the greatest control of molecular weight and architecture. Although other methods such as controlled radical polymerization can offer polymers with low molecular weight distribution, anionic polymerization is the method of choice when polymers of high molecular weight and complexity are desired. Living anionic polymerization also involves three stages of initiation, propagation, and termination. The initiation step in living anionic polymerization is usually faster than the propagation step, and this allows for low dispersity polymers to be obtained. Slow initiation results in broad molecular weight distribution. The most commonly used initiator is currently the *sec*-butyllithium due to its solubility in non-polar solvents such as benzene and cyclohexane. The reactivity of the initiators largely depends on the stability of the carbanion as well as the degree of aggregation of the alkyllithium initiators in solution. Generally, the less substituted the carbon of the carbanion, the less reactive the initiator and vice-versa. However, there are exceptions to this rule for instance, in the polymerization of styrene; *n*-butyllithium reacts faster than *tert*-butyllithium.

It was believed that ionic polymerizations (anionic and cationic) were the only existing "living" polymerization methods that offered efficient control of architecture of vinyl polymers (Hawker *et al.*, 2001). However, nowadays, controlled or living polymerizations are possible via a number of methods that include reversible addition-fragmentation chain transfer polymerization (RAFT), atom transfer radical polymerization (ATRP) and nitroxide-mediated polymerization (NMP).

2.5.1.1 Features of living anionic polymerization

The 60th birthday of living anionic polymerization was celebrated in 2016 (Ishizone & Frey, 2017; Szwarc, 1956; Szwarc *et al.*, 1956). Michael Szwarc himself concisely outlined the features of living anionic polymerization. Interestingly, living anionic polymerization does not involve termination step. This absence of termination or chain transfer reactions in the ideal living anionic polymerization is certainly a key feature of this technique that allows for preparation of polymers with incomparable accuracy. Prominent features of living anionic polymerization include (Ishizone & Frey, 2017).

(1) Synthesis of polymers with the lowest molecular weight distribution (1.1 or even lower).

(2) Excellent control of molecular weight governed by choice of monomer-initiator ratio, [Monomer] / [Initiator].

(3) Attainment of very high molecular weight polymers (up to 10^6 g mol^{-1}).

(4) Potential chain end functionalization of polymers which allows for the synthesis of copolymers containing diblock, triblock and even multiblock polymers, as well as a wide range of accurately end-functionalized macromolecules.

Living/controlled radical polymerizations such as ATRP, NMP and RAFT were inspired by anionic polymerization and since their emergence in the 19th century have been widely utilized to prepare polymers of various architectures (Grubbs & Grubbs, 2017). However, compared to living anionic methods, the living radical methods cannot offer polymers with exceptionally low dispersity and usually only molecular weights lower than 10^5 g mol^{-1} can be achieved (Ishizone & Frey, 2017).

2.5.1.2 Criteria for living polymerizations

For polymerization to be qualified as "living", the following seven criteria have to be satisfied (Quirk & Lee, 1992):

1) The polymerization continues until all the monomers available are consumed. Further addition of monomers should reinitiate the polymerization. The living nature of the polymerization can be tested through molecular weight determination of the polymer prior to and after the addition of the subsequent monomers. Any increase in the molecular weight after the monomer addition will confirm the living nature of the polymerization system.

2) As monomers are converted into polymers, the number average molecular weight (M_n) should continue to increase.
3) The number of active chains should be independent of conversion and should remain constant throughout the polymerization reaction.
4) Polymers can be prepared with targeted molecular weight by adjusting the stoichiometry of the reaction; this can be achieved by controlling the monomer-initiator ratio. However, the presence of impurities may cause variation between the theoretical and the experimental molecular weights. The impurities serve to reduce the number of active centers in the polymerization system. Likewise, the occurrence of termination or chain transfer may cause variations between the targeted molecular weight and the one obtained by size exclusion chromatography.
5) The polymerization should produce polymers with narrow molecular weight distributions. The rates of initiation and propagation compete in living polymerizations, and terminations are relatively absence. Consequently, low molar mass distributions (Đ~ 1.1) are obtained indicating that the polymer chains started growing at the same time. If initiation is slower compared to propagation, polymers will be obtained with broad molecular weight distribution (Elkins, 2005).
6) Preparing block copolymers via sequential addition of monomers is possible. This is due to the ability of the polymer chain ends to remain active throughout the polymerization. Moreover, this characteristic is often regarded as the defining feature of a living polymerization (Quirk & Lee, 1992).
7) Functionalization of chain-ends can be accomplished quantitatively. All active chain ends can be functionalized with the appropriate functional groups via quantitative termination of the reaction. Using techniques such as

NMR, it is possible to characterize the extent of the end-functionalization for low molecular weight polymers. For high molecular weight polymers, however, it may be difficult to quantify the functionalization reaction with reasonable accuracy (Quirk *et al.*, 2002).

However, it should be mentioned that none of the above criteria alone could qualify a given polymerization as a “living.” Therefore, more than one criterion are required to classify a polymerization as a “living.”

2.5.1.3 Commercial applications of anionic polymerization

The high vacuum conditions, tedious solvents, and monomer purifications required for anionic polymerization may serve as a deterrent for academic polymer synthesis. However, polymers synthesized via anionic polymerization technique have found many industrial applications. Examples of such polymers are thermoplastic elastomers (TPEs) obtained mainly from block copolymers involving isoprene, styrene and marketed under the brands Kraton® and Firestone (Hadjichristidis & Hirao, 2015; Hsieh *et al.*, 1981; Hsieh & Quirk, 1996). The advantage of these TPEs block copolymers is that they combine the properties of a diene-polymers with a glassy type polymer which offer the soft rubbery properties of the diene polymers and the strength of a glassy polymer (Hadjichristidis & Hirao, 2015; Hsieh *et al.*, 1981; Hsieh & Quirk, 1996). These types of polymers have many commercial applications including packaging, adhesives and bitumen modification. Anionic polymerization of diene using lithium initiators offered the opportunity to produce polyisoprene with a high content of cis– 1, 4–microstructure (> 90%) analogous to natural rubber and this contributed to the commercial success of anionic polymerization. Firestone begun to use lithium initiators since late 1950s and afterward in 1960s, shell employed alkyllithium initiators to prepare *cis*-polyisoprene in commercial quantity via anionic polymerization. A very high molecular weight and low dispersity polyisoprene were obtained which was devoid of any transition metals that may have adverse effects in some applications. Also, in the late 1960s, they employed the anionic polymerization to synthesize polybutadiene which was also useful for tyre manufacture (Hadjichristidis & Hirao, 2015; Hsieh *et al.*, 1981; Hsieh & Quirk, 1996). Ever since, the commercial applications of anionic polymerization technique have continuously increased. Surgical gloves having a lower modulus and outstanding tear strength have been produced from *cis*-polyisoprene lattices (Hadjichristidis & Hirao, 2015; Hsieh *et al.*, 1981; Hsieh & Quirk, 1996).

Another area of application of anionic polymerization is in the preparation of liquid hydrocarbon polymers (telomers). These polymers are usually synthesized from isoprene or butadiene with a metallic initiator. These materials possess relatively low viscosity and are used as sealants, surface coating agents, as well as adhesion promoters.

Anionic polymerization can also be employed to synthesize branched polymers using a polyfunctional linking agent after the polymerization. For example, divinylbenzene is used as either crosslinking agent or as a comonomer to commercially polymerized rubbers generating a long-chain branching or star polymers.

Telechelic polymers can be synthesized in commercial quantity via anionic polymerization because of its occurrence in the absence of termination and chain transfer. Examples include low molar mass hydroxyl- and carboxyl-telechelic polybutadiene prepared using a difunctional organolithium initiator and have many commercial applications (Hadjichristidis & Hirao, 2015; Hsieh *et al.*, 1981; Hsieh & Quirk, 1996).

Hence, anionic polymerization can be exploited to synthesize tailor-made polydienes that serve as alternatives to the natural rubber due to their enhanced properties and performances. In conclusion alkyllithium-initiated anionic polymerizations allow us to synthesize homopolymers, co-polymers as well as branched polymers from vinyl aromatic and dienes. Anionic polymerization techniques are exceptional in such a way that they allow for precise control over polymer properties such as molecular weight, dispersity, microstructure, composition, monomer sequence distribution in a copolymer as well as the nature of end functional groups.

2.6 Classification of synthetic polymers

Synthetic polymers can be classified as linear, branched, cyclic or cross-linked based on topological consideration (Hadjichristidis *et al.*, 2006). In linear polymers, the monomer units are connected in a long continuous string. Cyclic polymers, on the other hand, are characterized by the absence of polymeric chain ends and are therefore referred to as polymer rings (Semlyen, 2000; Tu *et al.*, 2016). Branched polymers are macromolecules characterized by the presence of *f*-functional points (f > 2) where branching can occur emanating from more than two linear chains (McNaught & McNaught, 1997). Hence more than two chain-end groups are present in one macromolecule. Branched polymers can further be classified in to dendrimers, hyperbranched polymers, brush/graft polymers, star polymers and randomly branched polymers depending upon the nature of the functional chain-end, the amount of branching points as well as how the branching points are arranged (Hadjichristidis *et al.*, 2006; Matyjaszewski *et al.*, 2007). Figure 2.2 shows the classification of polymers according to their topology.

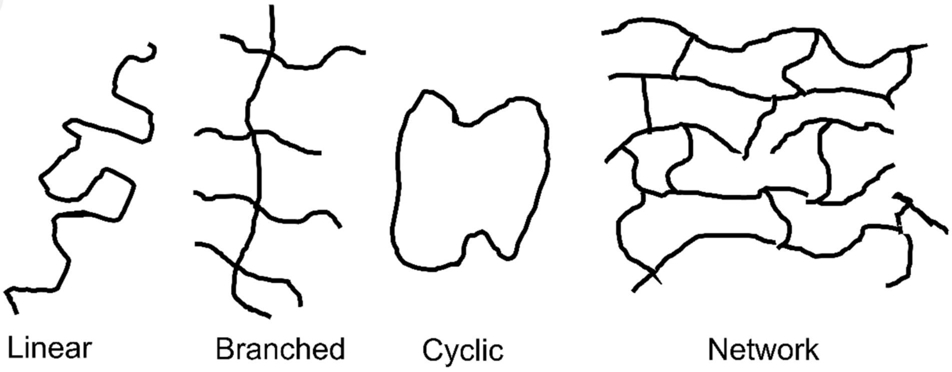


Figure 2.2: Topology of synthetic polymers

2.7 Branched polymers

The importance of branching in life as well as in polymer science was emphasized in 2007 when Frey tagged an editorial of the *Macromolecular Chemistry and Physics* as "Life is branched" (Frey, 2007). It is well established that polymer architecture plays a significant role in influencing the properties of polymers. As stated earlier, branched polymers are characterized by the presence of branching points emanating from the main chain, and branched polymers possess a higher number of chain-ends when compared to linear polymers. The history of branching in polymer science started with the synthesis of star polymers via polycondensation of AB-type monomers with multifunctional co-monomers by Flory in 1948 (Schaefgen & Flory, 1948). Since then, the interest in branched polymers has increased tremendously and currently branching plays a significant role in polymer science due to the chain-end functionality, which offers the macromolecules favorable properties such as improved solubility, lack of chain entanglement, as well as reduced melt and solution viscosities when compared to the linear polymers.

2.8 Dendrimers

Dendritic or dendritically branched polymers (Carlmark *et al.*, 2009) which were first synthesized in the late 1970s and early 1980s (Buhleier *et al.*, 1978; Newkome *et al.*, 1985; Newkome *et al.*, 1985; Tomalia *et al.*, 1985) are characterized by a tree-like three-dimensional architectures possessing a sizeable number of branching points. They represent a diverse class of macromolecules including hyperbranched polymers, dendrimers, dendronized polymers dendrons, and dendrigraft. In addition to branched, linear and cross-linked polymers, dendritic polymers are taken to be the fourth main class of macromolecules.

Dendritic polymers can be further divided in to those having a perfectly branched architecture with a DB (degree of branching) equals to 1.0 including dendrimers (Figure 2.3), dendronized polymers, and linear dendritic hybrids, or they can exhibit irregular and randomly branched structures such as in the case of multi-arm star polymers, hypergrafts, and hyperbranched polymers. The latter category possesses a lower degree of branching (Gao & Yan, 2004). The unique architecture of dendritically branched polymers makes them interesting for various applications.

The word "dendrimer" was coined from two Greek words *dendron* (tree-like) and *meros* (part). Dendrimers are perfectly branched, symmetrical, and monodisperse macromolecules consisting of branching points originating from a central core and possess a large number of surface or terminal end-groups (Konkolewicz *et al.*, 2011; Tomalia & Frechet, 2002). Since their earlier synthesis in the late 1970s and early 1980s, dendrimers have become one of the most highly researched topics in polymer science and Engineering.

Research interest in this area has increased dramatically, as evident by the number of yearly publications for the last 20 years when searching for "dendrimer" on SciFinder and ISI Web of Science (Figure 2.3).

Figure 2.3: Schematic representation of dendrimer

Because of their distinctive architectural and functional features, dendrimers have made a substantial contribution in many fields of biological and physical sciences and engineering, and have a vast scope of applications from nanotechnology to drug delivery (Fréchet, 2003; Hatton, 2015).

2.8.1 Synthesis of dendrimers

The growth of dendritic architecture can be accomplished in two ways: divergent or convergent strategies. In the divergent approach, the building of the dendrimer starts with a central core which continues with the sequential addition of branching units, which are called generations. After the growth of the required generations, the synthesis ended with the addition of surface end-groups (Tomalia *et al.*, 1985). The divergent approach to the dendrimer synthesis is presented in Figure 2.5 (a). This approach usually requires a series of protection–deprotection of functional groups before the reaction with the core and between the synthesis of one generation to the other. An example of this approach is the synthesis of series of poly(amidoamine) PAMAM dendrimers reported in 1985 by the research group of Tomalia (Tomalia *et al.*, 1985) via the Michael addition of methyl methacrylate to ammonia which served as the core.

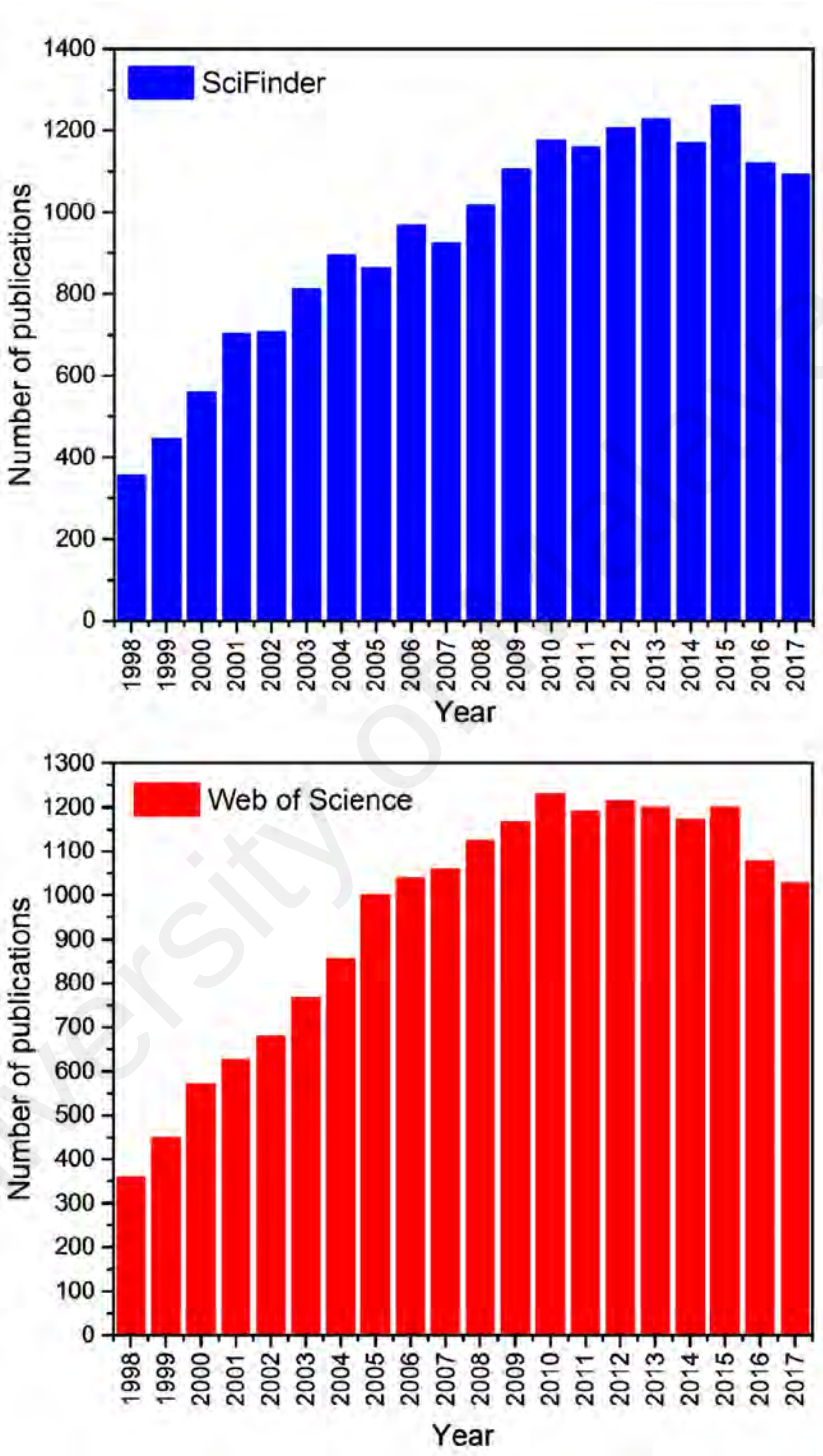


Figure 2.4: Number of publications (1998 to 2017) on SciFinder and ISI Web of science; using "dendrimer" as the search term

A large excess of ethylenediamine was used to achieve complete amidation of the resulting ether. A dendrimer was obtained with primary amine surface functionalities

(Scheme 2.2). If higher generations are desired with higher surface functionalities, the above procedure is repeated. This type of dendritic polymers is referred to as 'Starburst Dendrimer" and is obtainable in the market. However, there is a very high tendency of defects in this synthetic approach, and the probability increases with the number of generations synthesized (Tomalia *et al.*, 1985).

To reduce the difficulties encountered in the divergent approach and reduced the structural defects of dendrimers, the convergent approach was introduced (Hawker & Fréchet, 1990). In this approach, the surface functional group is first synthesized which is then coupled together with the branching unit and finally attached to the multifunctional core as shown in Figure 2.5 (b). This approach was first described in 1990 by Hawker and Fréchet (Hawker & Fréchet, 1990) who reported the synthesis of poly(aryl ether) dendrimers from 3,5-dihydroxy–benzyl alcohol as the monomer. They first prepared an aryl ether dendrons of up to 6 generations followed by coupling to a trifunctional core to produce the resulting dendrimer (Scheme 2.3).

The advantages of the convergent method over the divergent include: better synthetic control, reduces imperfection and requires no excess of reagent (Hawker & Frechet, 1990).

2.8.2 Applications of dendrimers

Since the discovery of dendrimers, they have over the years, demonstrated usefulness in many applications (Aulenta *et al.*, 2003). Some of these application areas include; catalysis (Caminade *et al.*, 2017; Deraedt *et al.*, 2017; Ye *et al.*, 2017), optics (Nádasi *et al.*, 2017; Tang & Li, 2017; Yao *et al.*, 2018) and medical fields (Abbasi *et al.*, 2014; Cloninger, 2002; Lee *et al.*, 2005; Stiriba *et al.*, 2002; Strašák *et al.*, 2017; Svenson & Tomalia, 2012; Wang *et al.*, 2018).

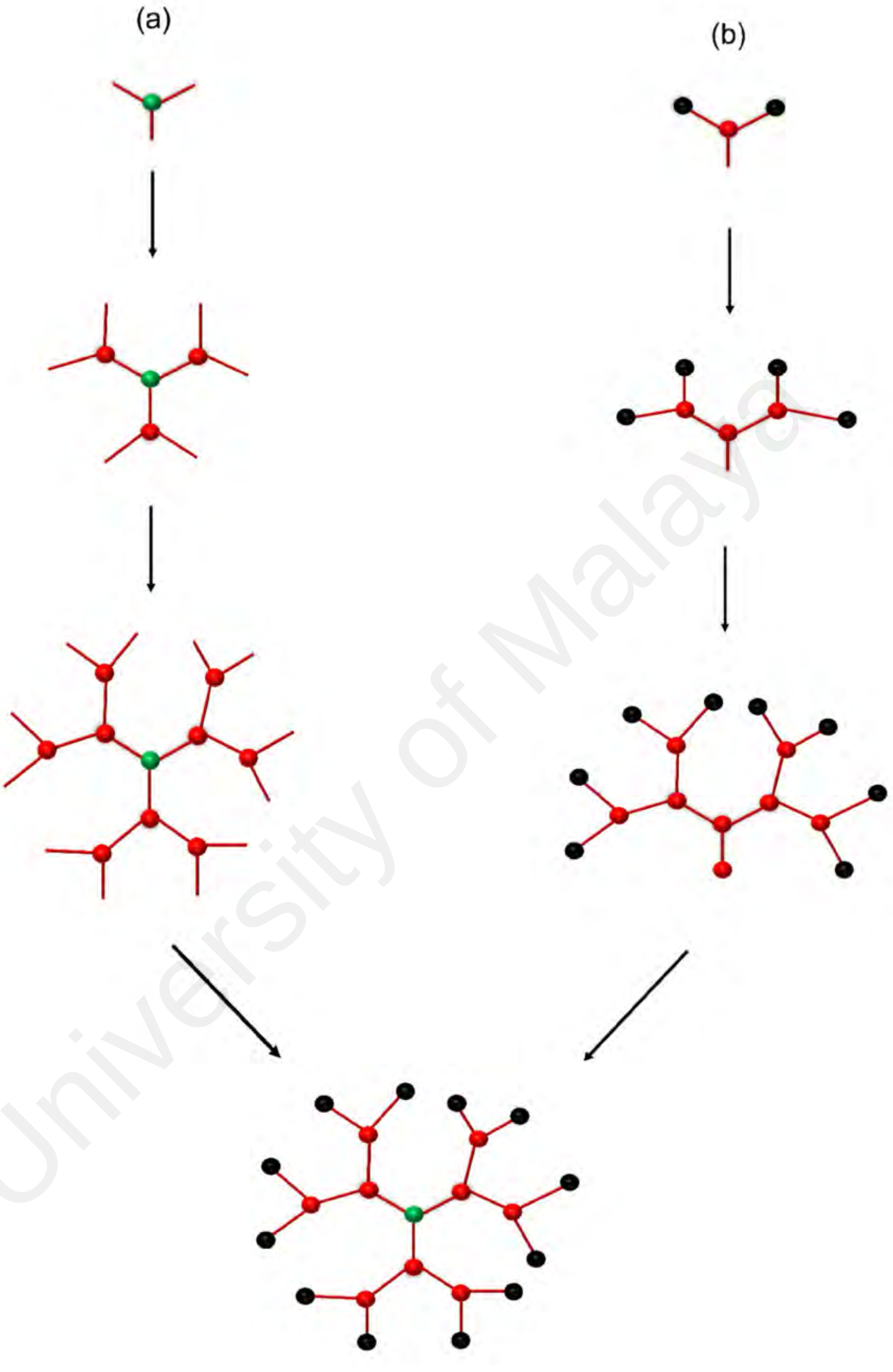
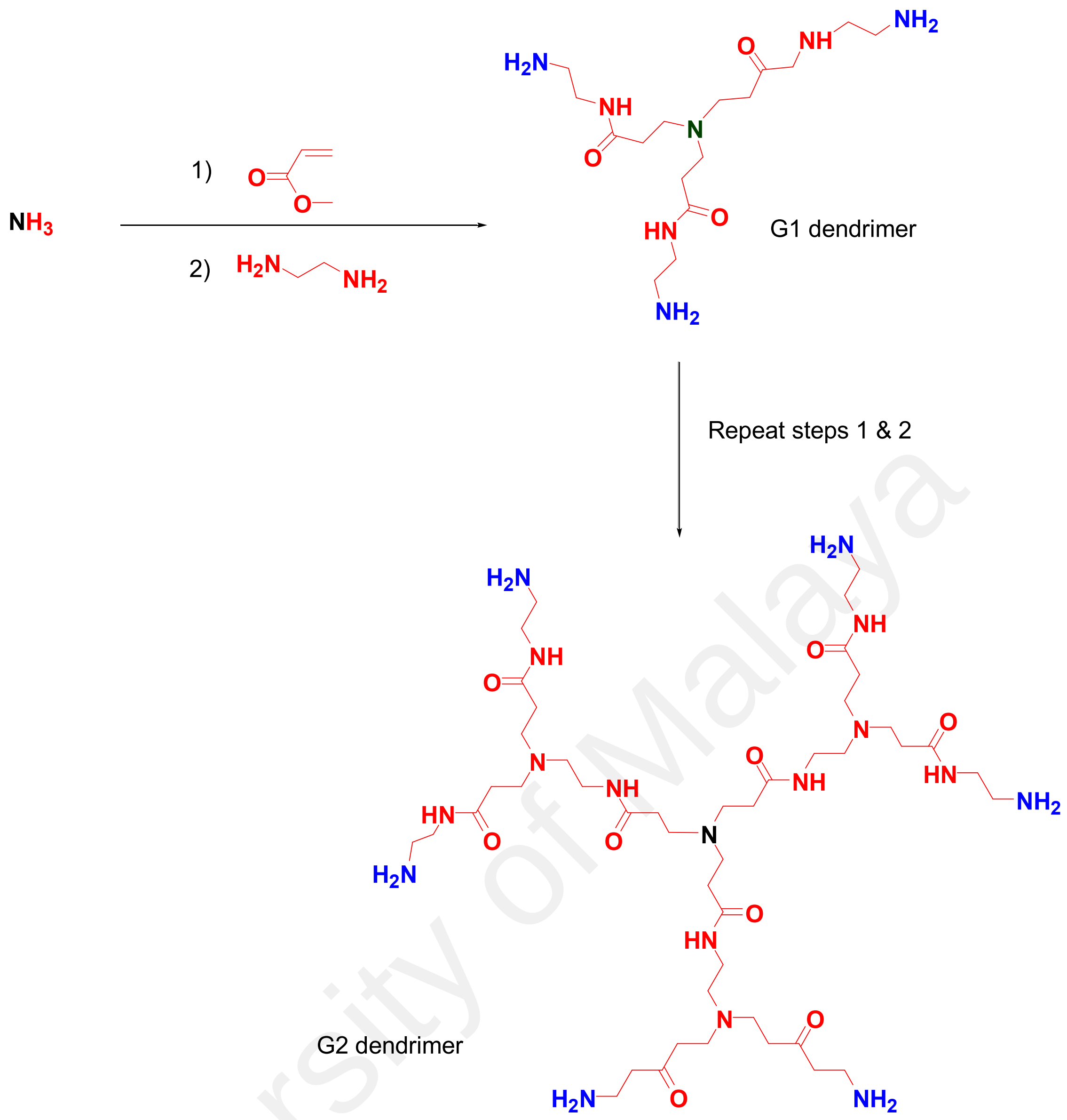
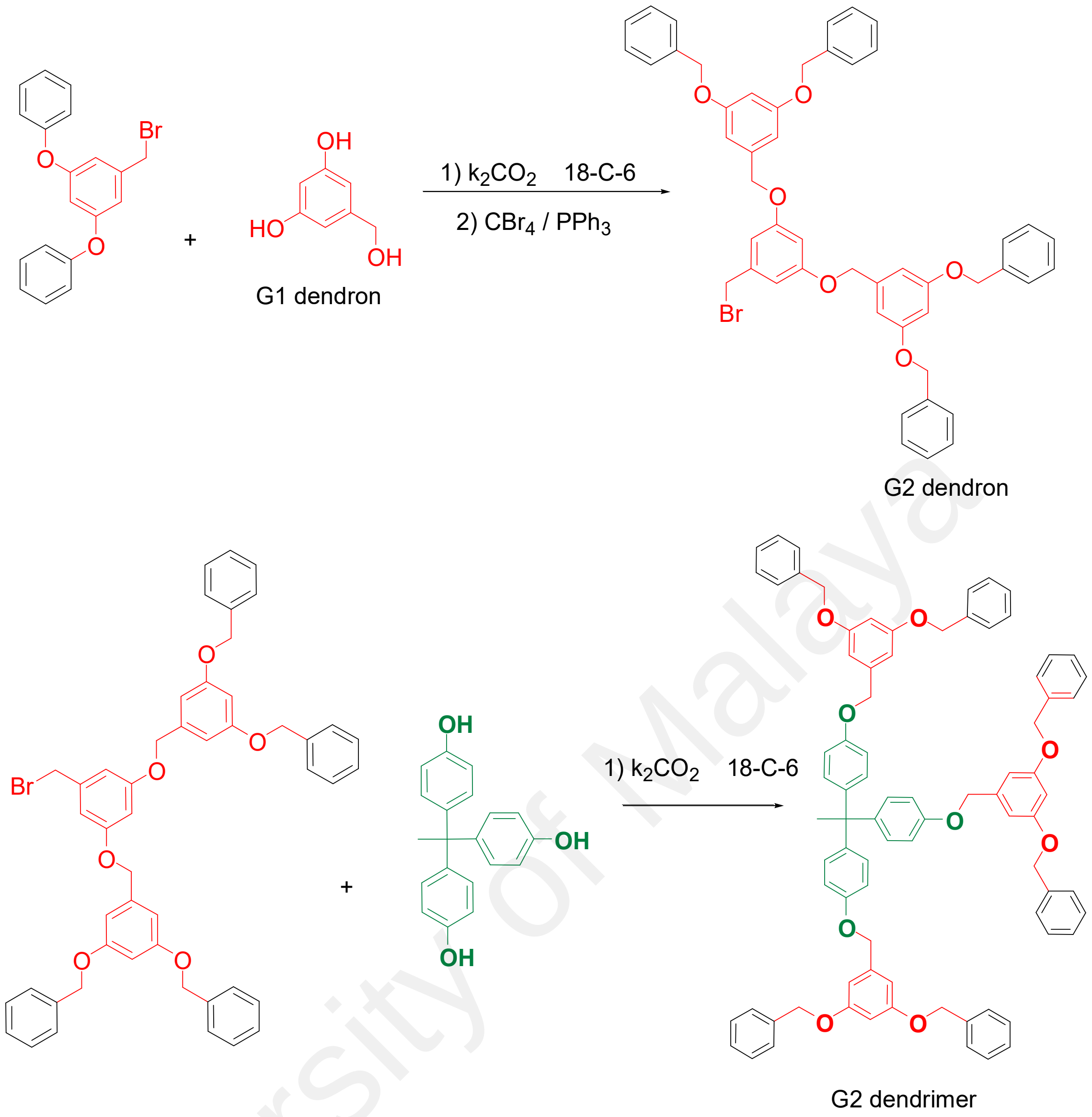


Figure 2.5: Divergent (a) and convergent (b) approaches to the synthesis of dendrimers



Scheme 2.2 Divergent synthesis of PAMAM dendrimers as reported by (Tomalia *et al.*, 1985)

The advantage of using dendrimers in catalysis is that they can combine the features of both homogeneous and heterogeneous catalyzes which are easy access to the catalytic site and ease of recovery, respectively (Astruc & Chardac, 2001; Astruc *et al.*, 2015; Reek *et al.*, 2006; Šebestík *et al.*, 2012; Ye *et al.*, 2017). Moreover, the catalytic function could be placed at the surface or the core of the dendrimer's molecule. The prospects of using dendrimers in medicine lie in their ability to bind through many surface groups. They could also be used in magnetic imaging chemistry (Chen *et al.*, 2015; Villaraza *et al.*, 2010; Langereis *et al.*, 2007).



Scheme 2.3 Convergent synthesis of poly(arylether) dendrimer as reported by Hawker and Fréchet (Hawker & Fréchet, 1990)

They are also used as nanosorbents for removal of heavy metals (Vunain *et al.*, 2016), as sensors (Soršak *et al.*, 2015; Staneva & Grabchev, 2018; Yordanova *et al.*, 2014), and in electronics (Bail *et al.*, 2016; Satoh & Yamamoto, 2018; Zhang, 2015; Zhao *et al.*, 2018). Dendrimer such as PAMAM Starburst is commercially available.

2.8.3 Limitations in the use of dendrimers

Despite the enormous potential applications of dendrimers, they have some major drawback which limits their applications. These difficulties are associated with the tedious and costly synthetic procedure. Both the convergent and divergent approaches to the synthesis of dendrimers involve multiple steps of purifications as well as protection and deprotection of some functional groups. The cost of production of dendrimers increases as the number of generations increases.

Although recently some improvements have been achieved in the synthesis of dendrimers due to the discovery of ‘click chemistry’ (Kempe *et al.*, 2012), the large-scale application of dendrimers is still limited. For example, the structure of the dendrimers produced via divergent route is generally limited to less than or equals to 10 generations. However, generation 13 dendrimers have been synthesized recently by Simanek and coworkers (Lim *et al.*, 2013).

The additional limitation which is associated with the divergent approach is the need for a large excess of reagents essential to achieve complete reaction for each generation. Hence, research on dendrimers is predominantly limited to those areas ready to accommodate the high cost of synthesis. Therefore, the research on dendrimers has mainly focused on three primary areas including catalysis, host-guest chemistry, and medicine, where these materials are high-valued, and only small quantities are required.

2.9 Hyperbranched polymers

The convergent approach was not sufficient enough in addressing the synthetic difficulties associated with dendrimers hence, despite enormous potential applications of dendrimers, it could not be available on a large industrial scale. For example, 2.5 g of PAMAM dendrimer cost 1,350 USD as at May 2018 (sigmaaldrich.com). Hence, only those high-value processes such as medicine and catalysis can afford. To address the synthetic difficulties associated with the dendrimers and pave the way for broader applicability, hyperbranched polymers (HBPs) emerged.

HBPs are randomly branched dendritic polymers synthesized via a one-pot polymerization. Hyperbranched polymers (Figure 2.6) are part of dendritic polymers; they are highly branched and possess a large number of surface groups (Gao & Yan, 2004). While dendrimers are monodispersed perfectly branched structures, HBPs, on the other hand, are polydisperse, irregular and imperfectly branched. Hyperbranched polymers have created a great deal of interest in academia and industry, as they form large polymeric structures in a one-pot synthesis. Hyperbranched polymers have broad molecular weight distributions due to lack of control in their synthesis. Excellent reviews on the fast and present research trends in hyperbranched polymers have been published by many research groups (Chen *et al.*, 2018; Gao & Yan, 2004; Hult *et al.*, 1999; Inoue, 2000; Jikei & Kakimoto, 2001; Kim, 1998; Voit, 2000, 2005; Voit & Lederer, 2009; Wang *et al.*, 2015; Wang & Gao, 2017; Yates & Hayes, 2004; Zheng *et al.*, 2015). The following sections give a brief insight into the history, synthetic methodology, properties and uses of HBPs.

2.9.1 History of hyperbranched polymers

The term "hyperbranched polymer" originated from DuPont in 1988 when it was coined by Kim and Webster. The limitation on the use of dendrimers in a large-scale application prompted Kim and Webster to produce these polymers in a rapid synthesis and at large quantities and this forced them to synthesize soluble dendritic polyphenylenes (Braunecker & Matyjaszewski, 2007; Kim & Webster, 1988; Kim, 1992; Kim & Beckerbauer, 1994; Kim & Webster, 1990).

However, the history of HBP date to the 19th century with the synthesis of resin from glycerol and tartaric acid. This development was followed by the reaction between glycerol and phthalic acid or phthalic anhydride in 1901 to produce hyperbranched polymers (Kienle & Hovey, 1929).

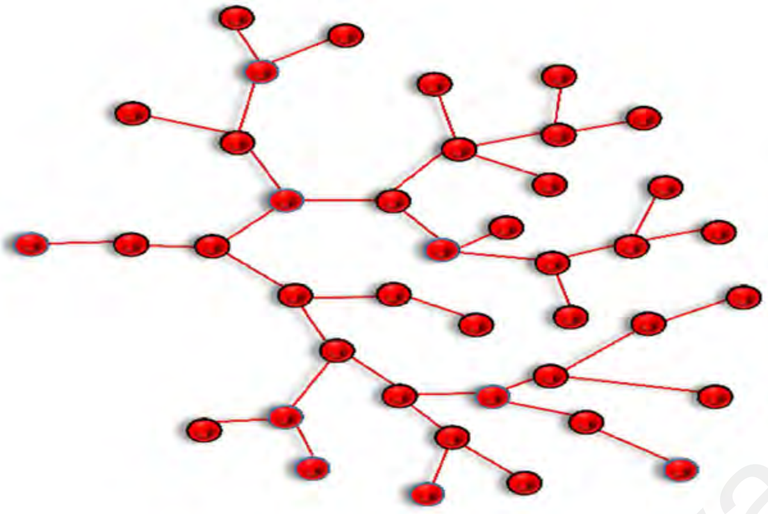


Figure 2.6: Schematic representation of hyperbranched polymer

In 1909, the Bakelite Company (U.S.A) reported the cross-linked phenolic resins, synthesized from phenol and formaldehyde. These resins possess a randomly branched structure of hyperbranched polymers before cross-linking (Gao & Yan, 2004). In 1941, Flory and his co-workers presented the idea of "highly branched species" when they studied the MWD of three-dimensional polymers with multifunctional branching units (Flory, 1941a, 1952), and came up with the critical conditions for gel formation. Flory also reported polycondensation of ABn monomer ($n \geq 2$) in 1952. A and B represent functional groups that can react with each other (Flory, 1952).

Although the works of Flory largely laid the theoretical basis for HBPs, the actual interest on HBPs was activated once dendrimers were discovered. Before 1995, it was conventionally thought that hyperbranched polymers could only be prepared via polycondensation technique. However,

In 1995 Fréchet prepared hyperbranched polyphenylene and hyperbranched polyesters utilizing self-condensing vinyl polymerization (SCVP) as a synthetic route to HBPs which is based on addition polymerization, as opposed to the previous methods which are based on the polycondensation technique (Fréchet & Hawker, 1995; Frechet, *et al.*, 1995).

In 2000, Sherrington and co-workers (Costello *et al.*, 2002; Sherrington *et al.*, 2000) developed the "Strathclyde route" as a facile and cost-effective way to the synthesis of hyperbranched polymers via radical copolymerization of vinyl monomers with a divinyl crosslinker and a suitable chain transfer agent. Similarly, in 2003, Sato prepared soluble hyperbranched polymers based on a method called initiator-fragment incorporation radical polymerization (IFIRP) (Sato *et al.*, 2005; Sato *et al.*, 2006; Sato *et al.*, 2003).

The IFIRP method was further improved using various controlled radical polymerization (CRP) techniques called controlled radical crosslinking copolymerization (CRCC). Table 2.2 provides a summary of the significant historical developments on the synthesis of HBPs.

Thus, interest in HBPs continues to increase since their first synthesis by Kim and Webster (Kim & Webster, 1990) due to their unique properties, ease of synthesis in large quantities and broader applicability compared to dendrimers. Presently over 1,000 articles are published yearly on hyperbranched polymers. Figure 2.7 shows the number of yearly publications for the last 20 years when searching for "hyperbranched polymer" on SciFinder and ISI Web of Science.

2.9.2 Properties of hyperbranched polymers

The key to the industrial applications of hyperbranched polymers is their unique properties. Polymer processing is one of the most critical factors for industrial applications of polymers. The relationship between rheological parameters and polymer architecture has been studied for decades. Viscosity is one of the remarkable physical properties of HBPs. The viscosity of hyperbranched polymers differs considerably from that of the linear polymers, and this is because of molecular architecture of the HBPs (Jikei & Kakimoto, 2001; Malmström & Hult, 1996; Yates & Hayes, 2004). When in solution, HBPs attain a maximum intrinsic viscosity as a function of molecular weight due to their more compact nature (Lyulin *et al.*, 2001).

For linear polymers, however, there is a linear relationship between the melt viscosity and the molecular weight up to a certain critical molar mass where there is an exponential increase in the viscosity due to the chain entanglement of polymer chains. However, for hyperbranched polymers and dendrimers, this phenomenon is not observed, and only a negligible entanglement takes place (Malmström & Hult, 1996; Yates & Hayes, 2004). A study was conducted to determine the effect of branching on the rheological properties of hyperbranched polystyrene and it was found that even though the molecular weight of the polymer molecule was well above the entanglement molecular weight (M_e), the formation of entanglement was prevented by the highly branching structure of the polymer (Clarke *et al.*, 2008).

Conformation and degree of branching (DB) are also among the fascinating properties of hyperbranched polymers. Hyperbranched polymers possess globular structure while dendrimers are spherical in nature as confirmed by small-angle neutron scattering and x-ray experiments (Prosa *et al.*, 1997). The degree of branching is a measure of flexibility of polymers and polymers with higher DB are usually of lower viscosity, and this affects the relative solubility of the polymer in various solvents (Jikei & Kakimoto, 2001; Yates & Hayes, 2004).

Table 2.2: History of hyperbranched polymers (Yan *et al.*, 2011)

Year	Case	Lead Authors	Reference
Before 1900	Tartaric acid + glycerol	Berzelius	(Gao & Yan, 2004; Kienle & Hovey, 1929)
1901	Glycerol + phthalic anhydride	Smith	(Kienle & Hovey, 1929)
1929-1939	Glycerol + phthalic anhydride	Kienle	(Kim, 1992; Kim & Beckerbauer, 1994; Ma *et al.*, 2009)
1941	Molecular size distribution in theory	Flory	(Flory, 1941a, 1952)
1952	AB_n polymerization in theory	Flory	(Flory, 1952)
1982	AB_2 + AB copolymerization	Kricheldorf	(Kricheldorf *et al.*, 1982)
1987 - 1991	AB_2 homopolymerization	Kim/Webstar	(Kim & Webster, 1990)
		Odian/Tomalia	(Gunatillake *et al.*, 1988)
		Fréchet/Hawker	(C. Hawker *et al.*, 1991)
1995	SCVP	Fréchet	(Frechet, Henmi, Gitsov, Aoshima, *et al.*, 1995)
		Matyjaszewski	(Matyjaszewski, Gaynor, Kulfan, *et al.*, 1997; Matyjaszewski, Gaynor, & Müller, 1997; Matyjaszewski *et al.*, 1998)
2000	Strathclyde Methodology	Sherrington	(Costello *et al.*, 2002; O'brien *et al.*, 2000)
2003	IFIRP	Sato	(Sato *et al.*, 2005; Sato *et al.*, 2006; Sato *et al.*, 2003)

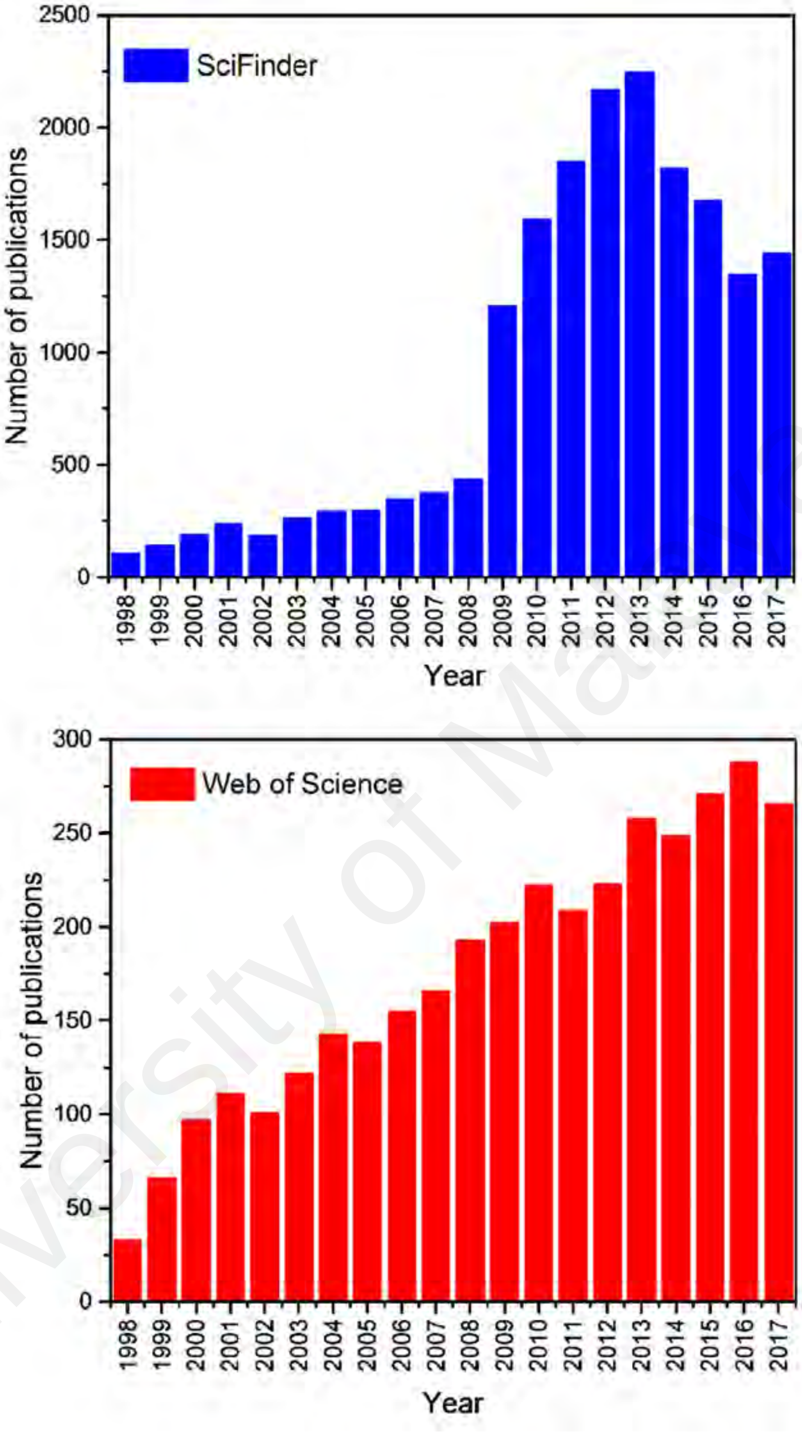


Figure 2.7: Number of publications (1998 to 2017) on SciFinder and ISI Web of science; using "hyperbranched polymer" as the search term

If L represents the number of partially reacted units and B the number of fully branched units, the degree of branching can be defined by Equation 2.5 as:

$$DB = \frac{2B}{2B + L} \qquad \textbf{2.5}$$

The values of the DB range from zero to one. For an entirely linear polymer, the DB is equal to 0 while for a perfectly branched polymer or a dendrimer the degree of branching is 1 (Holter *et al.*, 1997).

Moreover, the nature and number of end groups present in a hyperbranched polymer molecule significantly affect properties such as solubility and glass transition temperature. Generally, HBPs show excellent solubility in most of the organic solvents. Depending on the nature of the solvents, hydrodynamic radii of polymers varies. It is, therefore, necessary to point out that the molecular weight of dendrimers and HBPs measured by size exclusion chromatography using linear polymers such as polystyrene standards must be treated with care (Appelhans *et al.*, 2000). Because hyperbranched polymers possess smaller hydrodynamic radii than their linear counterparts of the same molecular mass. The polarity of chain end groups also influences the hydrodynamic radii of polymers.

Glass transition temperature (T_g) is among the most critical thermal properties of hyperbranched polymers. Due to their highly branched structure, hyperbranched polymers are generally amorphous. When amorphous polymers are heated, low molecular weight compounds change from glassy state to liquid state while high molecular weight substances change from glassy to rubbery state. Hyperbranched polymers exhibit significantly different thermal properties when compared to linear polymers as reported in various studies (Hawker & Chu, 1996; Anders Hult *et al.*, 1999; Benthem *et al.*, 2001; Voit, 2000; Voit, 2005). The end groups and backbone structure significantly affect the T_g of HBPs (Wooley *et al.*, 1993). Moreover, HBPs possess higher chemical reactivity over their linear analogs. They also display better compatibility when blended with other macromolecules (Yates & Hayes, 2004).

However, hyperbranched polymers display inferior mechanical properties due to the absence of chain entanglements. As a result, dendrimers and hyperbranched polymers show brittle nature, and this limits their application as thermoplastics (Kim & Webster, 1988; Yan & Chen, 2010). Nevertheless, it was reported that blending of aromatic hyperbranched polyester with linear bisphenol-A polycarbonate leads to a decrease in strain-to-break and toughness as well as an increase in tensile and compressive moduli compared to those of linear polycarbonate (Bolton & Wooley, 2002; Jikei & Kakimoto, 2001; Yates & Hayes, 2004).

Generally, hyperbranched polymers show numerous suitable properties, such as high solubility, low solution and melt viscosities, high compact structures, low chain entanglements, as well as multiple end-functional groups. They have been utilized in various fields such as adhesives, coatings, biomedicine, nanotechnology, composites, lubricants and photoelectric materials. A brief discussion on the applications of hyperbranched polymers is given in section 2.8.3.

2.9.3 Applications of hyperbranched polymers

Even though HBPs lack comprehensive and well-defined structure and molecular weights when compared to dendrimers, their one-pot synthesis allows for production on the large industrial scale. Moreover, suitable properties such as low solution and melt viscosities, excellent solubility, a significant amount of chain-end functionalities and high branching density, contribute significantly to the commercial success of hyperbranched polymers. They can be used in coatings (Gurunathan *et al.*, 2016), as additives (Cosimbescu *et al.*, 2016; Zheng *et al.*, 2015), in drug delivery (Kim & Webster, 1992), low–temperature curing agents (Román *et al.*, 2016; Sato *et al.*, 2014), as membranes (Tang *et al.*, 2016; Wang *et al.*, 2015; Zabolotsky *et al.*, 2015), sensors, in nanotechnology, as biodegradable materials and flame retardant (Arza *et al.*, 2018; Täuber *et al.*, 2014). Due to their unique properties, HBPs have been utilized as adhesive agents and as rheology modifiers (Jafarifard *et al.*, 2016; Sengupta *et al.*, 2018). For example, there was a significant decrease in the melt viscosity of the system when a small amount of hyperbranched polyphenylenes were added to polystyrene melt (Kim and Webster, 1990). Huber *et al.,* made similar observations when they added only 0.1 weight percent of hyperbranched aromatic-aliphatic poly(ether amide)s to linear polyamide-6 (Huber *et al.*, 1999). There was a substantial reduction in the melt viscosity without any tempering of the mechanical properties. HBPs consisting of ethylene glycol chains have been synthesized and applied as ion-conducting electrolytes because of their excellent electrochemical stability and high solvating and transportation power for appropriate ions (Gao & Yan, 2004; Itoh *et al.*, 2002).

Due to the high reactivity of HBPs resulted from a large number of surface functional groups they have found many applications in tissue engineering. Moreover, HBPs can form porous hydrogels and promote cell adhesion and proliferations (Frey & Haag, 2002; Wang *et al.*, 2015; Yu *et al.*, 2012). Largely, hyperbranched polymers show numerous suitable properties, which allow them to be used in various fields such as adhesives, coatings, biomedicine, nanotechnology, composites, and photoelectric materials.

2.9.4 Synthesis of hyperbranched polymers

It has been established that HBPs can be prepared either by polycondensation (Gunatillake *et al.*, 1988; Jikei *et al.*, 1999; Kim & Webster, 1990, 1992; Newkome, Baker*, et al.*, 1986; Newkome *et al.*, 1985; Newkome, Yao*, et al.*, 1986) or polyaddition (Frechet, *et al.*, 1995; Gaynor *et al.*, 1996; Guan, 2002; Li & Armes, 2005a, 2005b; Liu *et al.*, 2005a; Matyjaszewski, *et al.*, 1997; Matyjaszewski *et al.*, 1998; Müller *et al.*, 1997; O'brien *et al.*, 2000; Sato *et al.*, 2003) reaction mechanisms. Generally, there are two primary ways by which HBPs could be prepared; (1) single-monomer methodology (SMM) and (2) double-monomer methodology (DMM). The SMM involves polymerization of a single AB_n or latent AB_n-type monomers while in the DMM, two monomers are involved (Gao & Yan, 2004). Figure 2.8 summarizes the various routes to hyperbranched polymers (Gao & Yan, 2004; Jikei & Kakimoto, 2001; Yates & Hayes, 2004).

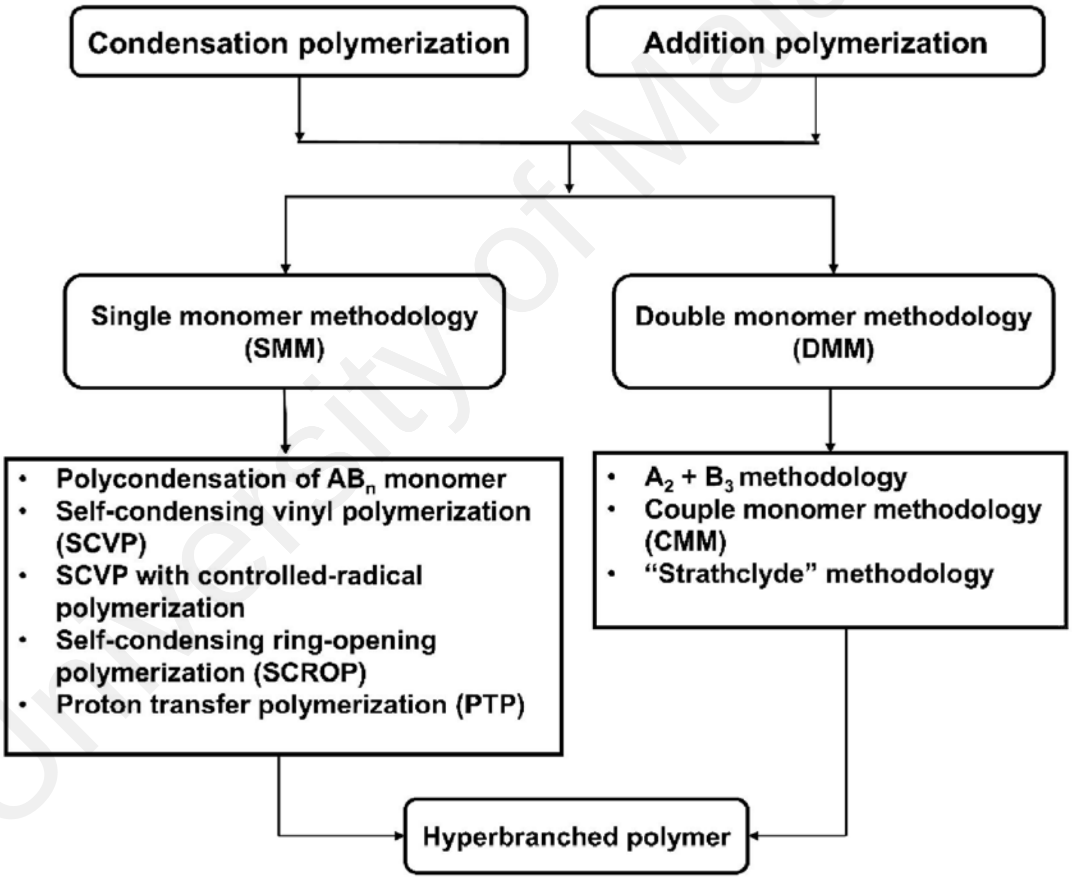


Figure 2.8: Various routes to hyperbranched polymers

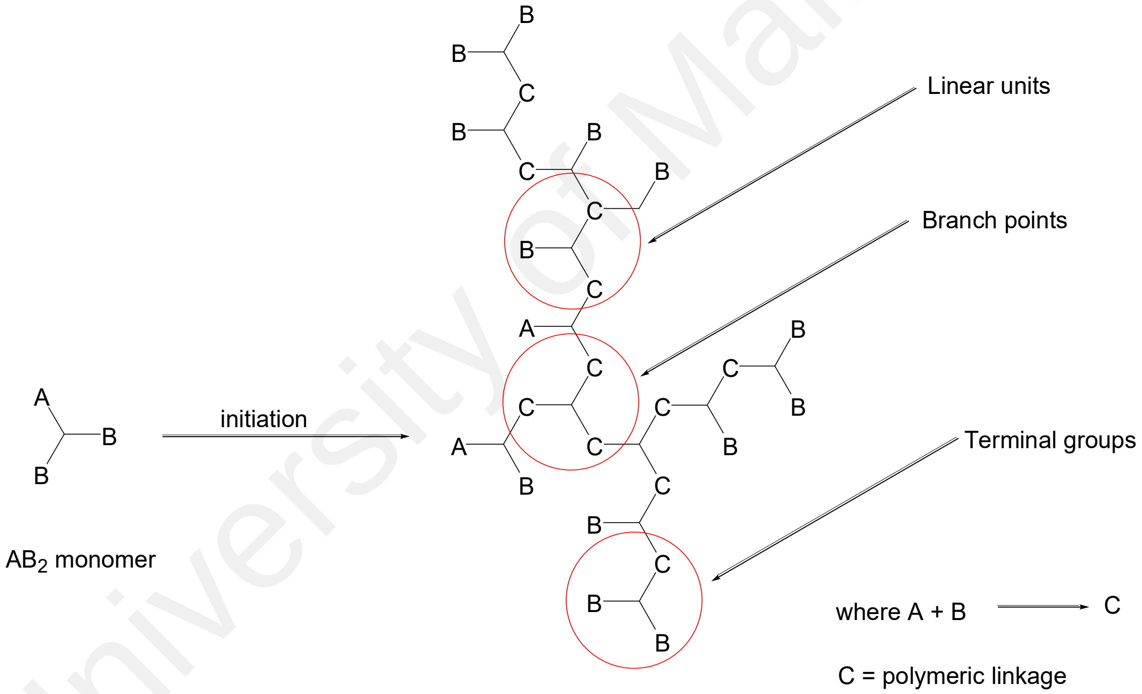
2.9.4.1 Hyperbranched polymers via polycondensation techniques

One of the most convenient ways to prepare HBPs is through the polycondensation of AB_n monomers (where $n \geq 2$) which was first demonstrated by Flory in 1952 (Astruc

& Chardac, 2001; Flory, 1952; Malmström & Hult, 1996; Malmström *et al.*, 1995; Moorefield & Vögtle, 2008). The most common monomers used are those having n = 2, but those with n > 2 such as AB_3, AB_4, and AB_6 are also used. In this type of polymerization, it is essential that the functional group A selectively reacts with B and that the B group be of equal reactivity to avoid the formation of side products due to cyclization reactions, and to produce hyperbranched polymers of high molecular weight. For example, the reaction between A–A or B-B functionalities even at a very low level can lead to gel formation at low conversion. Also, when highly functional monomers are involved, side reactions could cause gelation. Moreover, the polycondensation of AB_2 monomers usually proceeds without control of molecular weight which results in polymers with high dispersity indexes. The typical DB for these polymers ranges from 0.5 to 0.6 (Hawker *et al.*, 1991; Turner *et al.*, 1993; Voit, 2000). The addition of a core molecule Bn (n > 2) to the polycondensation of A-B type monomers was explored as one of the measures to achieve polymers with controlled molar mass (Frey *et al.*, 1998; Kricheldorf *et al.*, 1999; Kricheldorf *et al.*, 1982). Also, the copolymerization of AB_2 and B_n monomers allows for the control of molecular architecture as well as an increase in the degree of branching of the resulting HBPs. Scheme 2.4 presents a general mechanism for the formation of HBP via polycondensation technique which consists of four main parts namely: the branching points, the terminal groups, the linear units, and the focal point. The branching points (also called dendritic units) consist of all reacted B monomers, the terminal units also consist of B monomers, but with active functionality, the focal point consists of unreacted A monomers and the linear where only B functional group has reacted (Kim & Webster, 1988).

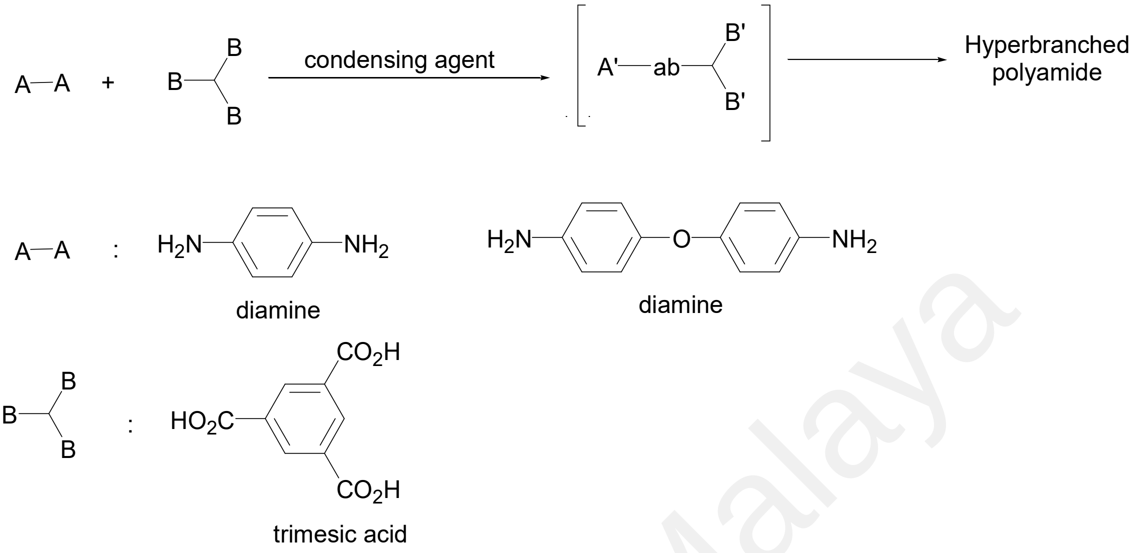
Many HBPs polymers have also been synthesized through the A_2+B_3 strategy (Emrick *et al.*, 2000; Fang *et al.*, 2000). A_2 + B_3 polymerization was first reported by Kakimoto and co-workers (Jikei *et al.*, 1999) as well as Fréchet (Emrick *et al.*, 1999) who prepared soluble HBPs by direct polycondensation of aromatic diamines and trimesic acid as shown in Scheme 2.5.

The advantage of '$A_2 + B_3$' approach over the conventional AB_2 polycondensation is that the monomers are commercially available in addition to the formation of polymers with improved structural composition. However, the $A_2 + B_3$ approach is associated with the formation of gel especially at a high concentration of monomer. Gelation is avoided when a dilute solution of the monomer is used or when the monomer is added slowly.



Scheme 2.4 Synthesis of hyperbranched polymer via the polycondensation of AB_2 monomers (Kim & Webster, 1988)

Furthermore, the polycondensation reaction could be stopped before reaching the gel point leading to incomplete monomer conversion (Cosulich *et al.*, 2000; Komber *et al.*, 2001; Monticelli *et al.*, 2001; Russo *et al.*, 1999; Tabuani, *et al.*, 2003). This problem prevents the manufacture of HBPs produced via ‘$A_2 + B_3$’ strategy on a large industrial scale.

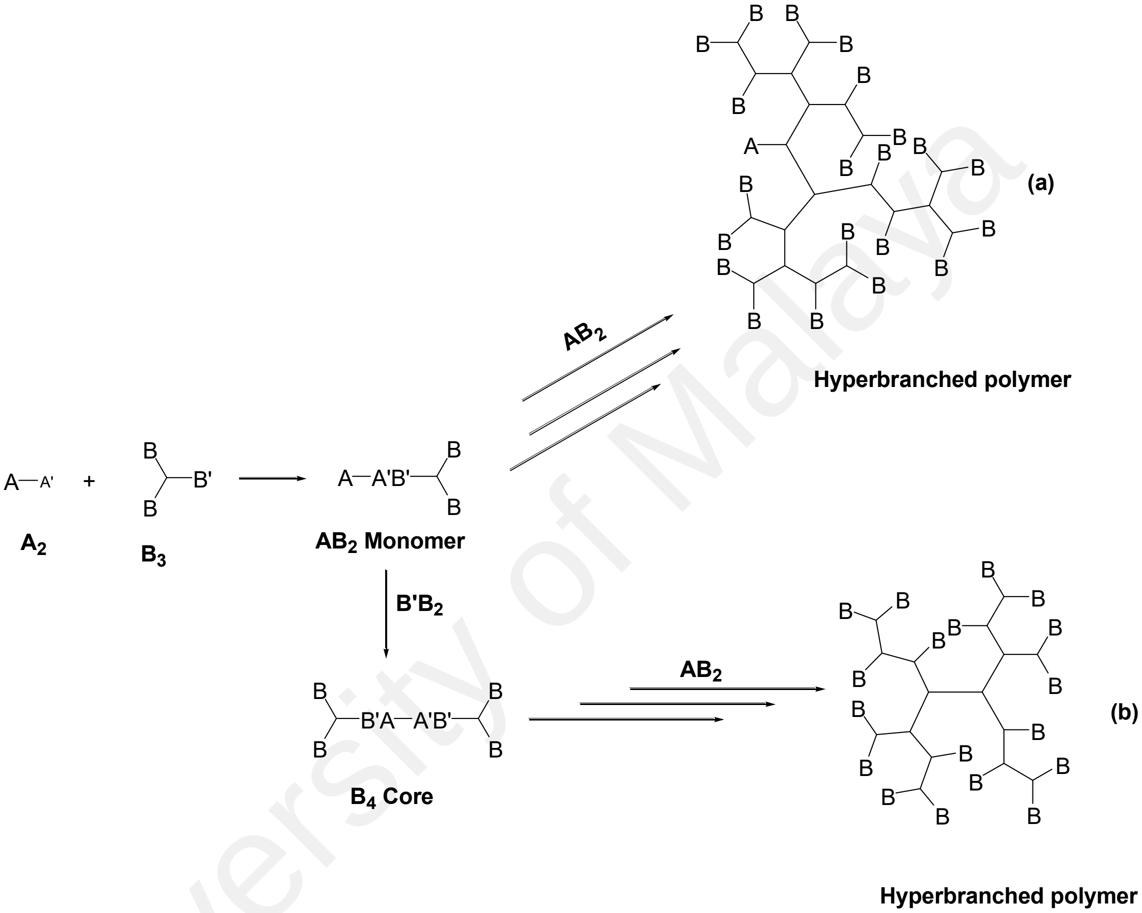


Scheme 2.5 Synthesis of hyperbranched polymer via $A_2 + B_3$ strategy (Emrick *et al.*, 1999; Mitsutoshi Jikei *et al.*, 1999)

Couple-monomer methodology (CMM) was reported as an improved strategy over the $A_2 + B_3$ approach (Froehling & Brackman, 2000; Benthem *et al.*, 2001; Yan & Gao, 2000). The CMM route works based on the unequal reactivity of the functional groups and the formation of an AB_n intermediate from a given pair of monomers. In this approach, two sets of monomers initially generate one type of AB_n intermediate *in situ* before the formation of HBP, hence the name couple-monomer methodology. Scheme 2.6 presents the general scheme for the CMM method.

In the reaction scheme presented in Scheme 2.6, the coupled monomers are A_2 and B_3, and in each case, the A and B functional groups are lower in reactivity than the corresponding A′ and B′, respectively. A′ and B′ functionalities react preferentially with each other and the AB_2 monomer is formed *in situ* which can go through self-polycondensation reaction to produce the HBP (a).

AB_2 monomers can also react with the $B'B_2$ molecules to form a B_4 core molecule, which in turn produce hyperbranched polymers of lower molecular weight distribution (b). Example of polymers that are synthesized via the CMM route includes hyperbranched poly(urea-urethane)s (Gao & Yan, 2003, 2004).



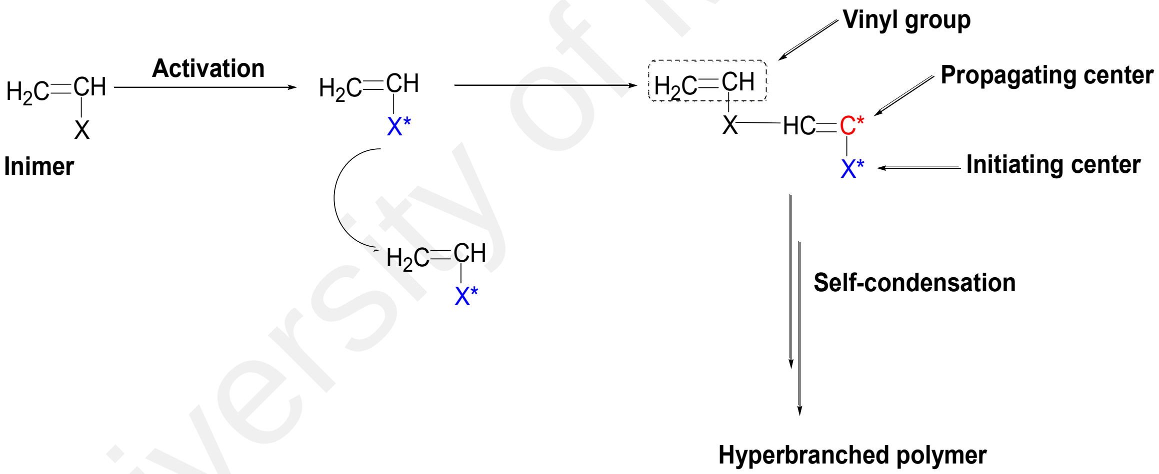
Scheme 2.6 General scheme for the synthesis of HBPs via the couple monomer methodology (Gao & Yan, 2004)

Initially, polyesters were the most commonly prepared HBPs via the polycondensation method. Later various hyperbranched polymers such as polyamides (Hu, 2017; Ohta *et al.*, 2016; Tang & Kong, 2014), polyimides (Yang *et al.*, 2017; Ying *et al.*, 2016), polyethers (Kricheldorf *et al.*, 2005; Kricheldorf & Schwarz, 2003), polyesters (Lin & Long, 2003), polycarbonates (Scharfenberg *et al.*, 2017; Scheel *et al.*, 2004; Sun *et al.*, 2017), and polyurethanes (Patel & Patel, 2015; Sathiyaraj *et al.*, 2017;

Unal *et al.*, 2004), have been synthesized via the polycondensation reactions of various monomers.

2.9.4.2 Synthesis of hyperbranched polymers via self-condensing vinyl polymerization (SCVP)

Self-condensing vinyl polymerization (SCVP) is one of the most widely used methods to synthesize hyperbranched polymers (Alfurhood *et al.*, 2016; Das *et al.*, 2018; Gao & Yan, 2004; Hawker *et al.*, 1995; Wang & Gao, 2017). SCVP was developed in 1995 by Frechet *et al.*, (Frechet, *et al.*, 1995) as a one-pot method that involves the use of an AB* inimer (where A is the vinyl group, and B* is the initiator fragment) to produce hyperbranched polymers.



Scheme 2.7: A general mechanism for the synthesis of hyperbranched polymers via self-condensing vinyl polymerization (SCVP) (Frechet, *et al.*, 1995)

In this type of polymerization, the initiator fragment is activated, then the active species react with the vinyl group, which propagates further to produce HBPs (Scheme 2.7). Assuming no chain transfer or termination occurs, the degree of polymerization is equal to the number of initiating sites in the hyperbranched polymer molecule, and only one pendant vinyl group is present. Also, only one cross-linkage or two cross-linking units are present at a given time, and the cross-linkages are not distributed across different chains. Hence, even at high conversions, there is no gel formation in the SCVP. The self-condensing vinyl polymerization and polycondensation that involves a trifunctional AB_2 monomer are very much alike, and in both cases, the degree of branching of about 0.5 can be achieved at high conversion with a very high dispersity (Simon & Müller, 2000; Yan *et al.*, 1997). However, SCVP also suffers some disadvantages such as the occurrence of gelation due to site reactions, as well as a high dispersity index.

Moreover, in the SCVP, a polymer with uniform chain end-functionality is difficult to obtain, and higher molecular polymers are obtained in other polymerization techniques as compared to the SCVP. Furthermore, the degree of branching cannot be readily determined using NMR spectroscopy (Gao & Yan, 2004). To control the molecular weight distribution and prevent gel formation, the SCVP method has been expanded to be used with control radical polymerization (CRP) technique. Some of the CRP techniques that incorporates SCVP are discussed below.

2.9.4.3 Synthesis of hyperbranched polymers via controlled radical polymerization techniques

The most commonly used technique to prepare polymers on a large industrial scale is free radical polymerization. However, the free radical method is not suitable to produce branched polymers especially when controlled branching is required. Usually, copolymerization of a vinyl monomer with a multifunctional comonomer, even in small amount, lead to the formation of a gel. In 1935, Staudinger and co-worker (Staudinger & Husemann, 1935), reported the first copolymerization of styrene with divinylbenzene. More recently, in 1991, Antonietti and Rosenauer studied further on the copolymerization of styrene with divinylbenzene (Antonietti & Rosenauer, 1991). The gelation behavior was studied in each case, and it was found that the gel content increased with the increase in the DVB content. To produce soluble branched polymers of high molecular weight via the free radical polymerization technique, high dilution is necessary. Therefore, it is difficult and uneconomical to produce branched polymers under the condition of high dilution. Hence, the use of controlled radical polymerization methods or chain transfer is necessary to prepare branched polymers via free radical techniques.

In a controlled radical polymerization, it is necessary to carefully control the ratio of the divinyl monomer to the initiator to avoid gelation. Flory and Stockmayer first explained the gelation theory for this type of copolymerization (Flory, 1941a, 1941b; Simha & Branson, 1944; Stockmayer & Jacobson, 1943). Assuming that the vinyl groups have equal reactivity, and in the absence of intramolecular cyclization, a gel will be formed when the number of cross-links per polymer chain (cross-linking index) is equal to one. Therefore to obtain soluble polymer of high molecular weight, the initiator–divinyl monomer ratio of 1:0.95 is usually employed (Isaure *et al.*, 2004). Practically, however, this theory can be influenced by other factors such as monomer concentration in the polymerization system (Li *et al.*, 2011; Rosselgong *et al.*, 2010). Further discussions on the Flory–Stockmayer's theory is given in section 2.9.2. Various controlled radical methods such as reversible addition-fragmentation chain transfer (RAFT) polymerisation (Wang *et al.*, 2003), nitroxide mediated polymerisation (NMP) (Hawker *et al.*, 1995), atom transfer radical polymerisation (ATRP) (Francoise Isaure *et al.*, 2004), can be employed in combination with self–condensing vinyl polymerisation (SCVP) to synthesize hyperbranched polymers. The use of a chain transfer agent ("Strathclyde approach") in a radical polymerization has also been reported (O'brien *et al.*, 2000).

(a) ***Nitroxide-mediated polymerization (NMP) with SCVP***

Hawker *et al*. investigated the SCVP–NMP using a styryl monomer and nitroxide-containing inimer attached to a benzylic carbon atom of the styryl group **1** (Figure 2.9). Hyperbranched polymers with M_w ranging from 65,000 to 300,000 gmol^{-1} and with PDI values ranging from 1.6 to 4.4 were prepared (Hawker *et al.*, 1995). These high molecular weight polymers with lower molecular weight distributions were achieved due to the living nature of the reaction. Tao *et al*. utilized two nitroxides **2** and **3** (Figure 2.9) to prepare a "weak-linked" hyperbranched polymers (Tao *et al.*, 2001). The weak-links resulted from the fact that the nitroxides are located at the branched points instead of at the chain ends. The branches could be disconnected from the main chain when thermal homolysis/recombination occur.

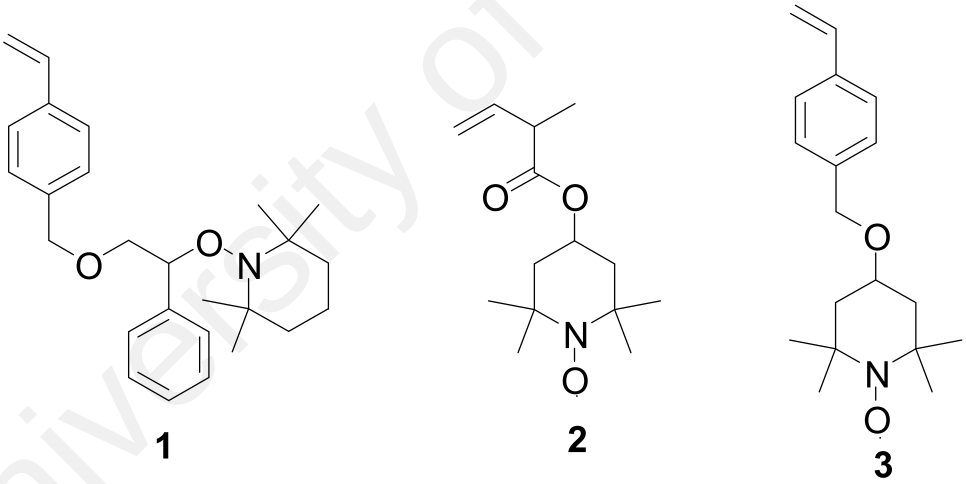
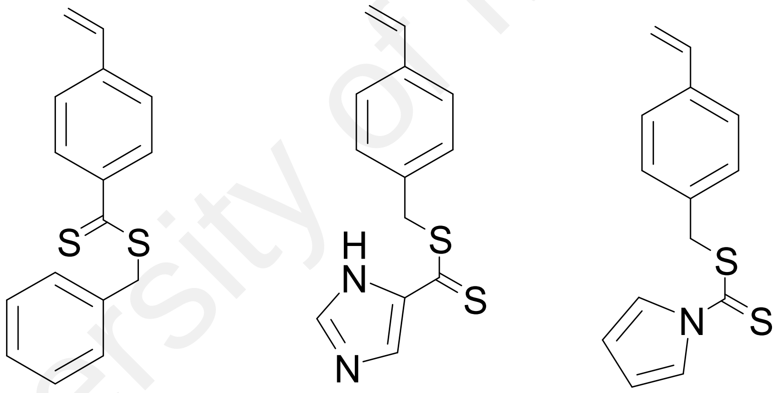


Figure 2.9: Monomers used for the synthesis of HBP via nitroxide SCVP

(b) ***Reversible addition-fragmentation chain transfer polymerization (RAFT) with SCVP***

Yang *et al.* first investigated the RAFT SCVP, in 2003 who incorporated a dithioester into a styrene monomer to synthesize an inimer (Wang *et al.*, 2003). However, similar to the NMP-SCVP work by Tao (Tao *et al.*, 2001), the branching agent **4**, (Figure 2.10) used by the Yang *et al.,* also created a "weak link" in the form of the dithioester in the subsequent hyperbranched polymers. Carter *et al.* later modified this method placing the dithioester such as **5** or **6** (Figure 2.10) at the chain ends (Carter, Hunt*, et al.*, 2005; Rimmer *et al.*, 2007).

RAFT SCVP route to hyperbranched polymers seems to be very promising, and this method was used to synthesize hyperbranched poly(N-isopropyl acrylamide-block-glycerol monomethacrylate) via copolymerization (Carter, Rimmer*, et al.*, 2005) however, the RAFT SCVP also suffers some disadvantages. The branched homopolymers produced by this method are much lower in molecular weight compared to the copolymers produced.



4 **5** **6**

Figure 2.10: Monomers used for the synthesis of HBP via RAFT SCVP

The final product contains a significant amount of dithiocarbonyl chain ends which can be removed by the reaction of the HBP with an excess of initiator radical (Perrier *et al.*, 2005). Moreover, radicals are formed by the decomposition of the initiator, and when the concentration of the initiator radicals exceeds that of the polymeric chain end radicals, the initiator radicals may combine with the polymer chain end radicals and cause the termination of the reaction. However, the nature of the initiator radical determines the structure of the polymer chain end groups, and this can be used for the synthesis of end-functionalized hyperbranched polymers.

Nevertheless, the RAFT SCVP method cannot be employed for the synthesis of hyperbranched polymers on a large industrial scale due to its strict reaction conditions and requirements.

(c) *Atom transfer radical polymerization (ATRP) with SCVP*

Various HBPs such as polymethacrylates, polyacrylates, polystyrene, and its derivatives have been produced by the use of ATRP technique (Bannister *et al.*, 2006; Gaynor *et al.*, 1996; Huang *et al.*, 2013; Matyjaszewski, Wei*, et al.*, 1997; Xia & Matyjaszewski, 1997); this has also been extended to SCVP. The ATRP-SCVP was first reported by Matyjaszewski *et al.*, in 1997 who used the normal ATRP condition (Copper (I) and 2,2'-bipyridyl) to polymerized 4–(chloromethyl) styrene (Matyjaszewski, *et al.*, 1997). The subsequent primary polymeric chain contains an end with a chlorine atom and a double bond at the other end. The double bond serves as a branching point when it is attached to the growing polymer chains. However, the reaction did not follow the ideal self-condensing vinyl polymerization technique because of unequal reactivity between the propagating and initiating species. Moreover, due to the low catalyst-monomer ratio, linear polymers are formed in favor of hyperbranched polymers. Also, for SCVP-ATRP to be achieved, high initiator concentration is necessary, and this shifts the equilibrium towards the active radicals, which in turns causes a large excess of radical concentration at the beginning of the reaction.

Consequently, an excess of X–Cu(II) is produced due to the termination of the excess radicals. These processes consume high amounts of the copper (I) and prevent activation or reactivation of the alkyl halides (R–X)s. Appropriate concentration of

Cu(I) has to be kept constant throughout the reaction to synthesize hyperbranched polymers at high conversion using self-condensing vinyl polymerization of the typical inimers shown in Figure 2.10. To achieve this, Matyjaszewski and his research team used zero valence state copper which decreases the X–Cu(II) complex and produces two equivalents of Cu(I) (Matyjaszewski *et al.*, 1998). Successful polymerizations of monomers **7, 8**, **9** and **10** shown in Figure 2.11 were achieved using this process.

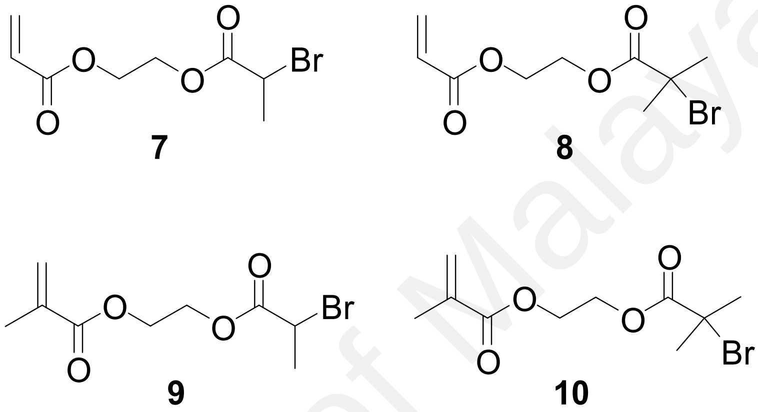


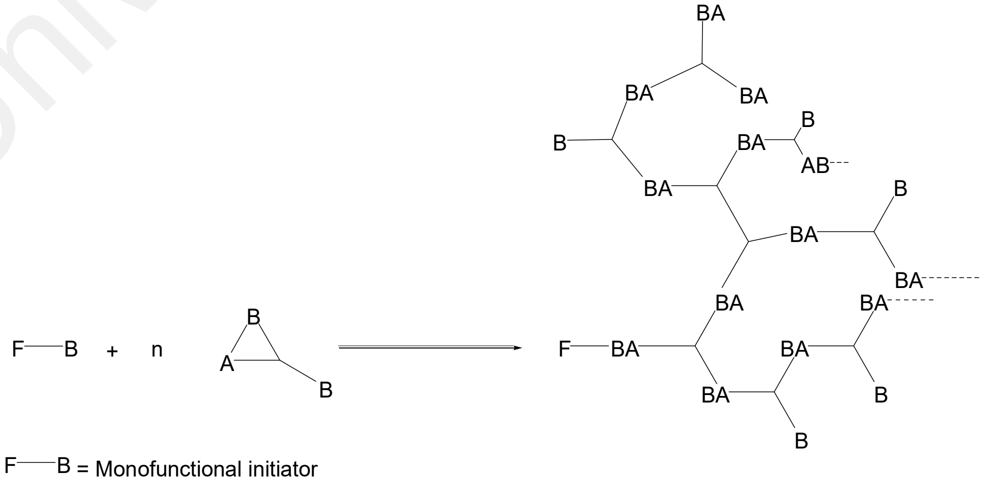
Figure 2.11: Monomers used for the synthesis of HBP via ATRP SCVP

Atom transfer radical polymerization in combination with SCVP can generate fluorinated HBPs with low energy surfaces. Hence, ATRP has been utilized in the copolymerization of 2,3,4,5,6–penta–fluorostyrene with either polyethylene glycol-containing inimer, 4-bromomethyl styrene or 4–chloromethyl styrene to prepare highly fluorinated hyperbranched polymers (Cheng *et al.*, 2005; Powell *et al.*, 2007). Additional initiators with better initiation capacity can also be added into the ATRP-SCVP system. For example, chloromethyl(styrene) was copolymerized with lauryl acrylate using a trifunctional initiator (Du *et al.*, 2008). A similar method has been employed in the synthesis of hyperbranched polymers with sugar functionality (Muthukrishnan *et al.*, 2005) as well as hyperbranched polyelectrolytes (Mori *et al.*, 2004). Again, it is difficult to control molecular weight distribution with SCVP but to achieve narrower distribution; a multi-step approach can be adopted where fragments are first prepared followed by modification via protection–deprotection process (Percec *et al.*, 2003). This approach was used by Percec *et al.* (Percec *et al.*, 2003) who carried out a multi-step synthesis of hyperbranched PMMA.

2.9.4.4 Self-condensing ring-opening polymerization (SCROP)

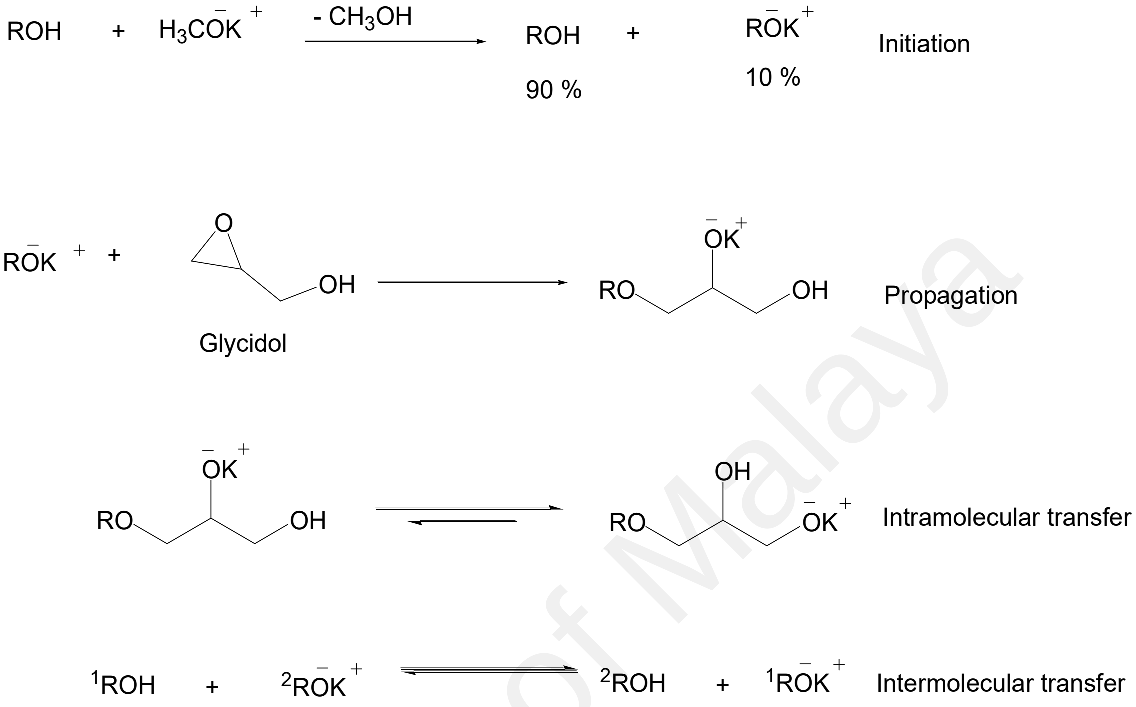
Self-condensing ring-opening polymerization, also known as the ring-opening multi-branching polymerization (ROMBP) proceeds via a similar approach to SCVP but employ a slightly different kind of monomers. Instead of the usual vinyl group of the inimer, the monomers used in the SCROP method consist of a heterocyclic group. Various hyperbranched polymers have been prepared by this method, which includes, polyesters, polyethers, and polyamines (Alkan *et al.*, 2015; Liu *et al.*, 1999; Sunder *et al.*, 1999; Trollsås *et al.*, 1999). A general reaction scheme for the SCROP polymerization is given in Scheme 2.8.

Frey *et al.,* (Sunder *et al.*, 1999) utilized this method in combination with living anionic polymerization to synthesize hyperbranched polyglycerols with low dispersity index ranging from 1.1 to 1.4 (Scheme 2.9).



Scheme 2.8: General scheme for the synthesis of hyperbranched polymers via the SCROP method

The glycidol served as a latent AB_2 monomer, which is the type of the monomers, employed in the SCROP synthesis.

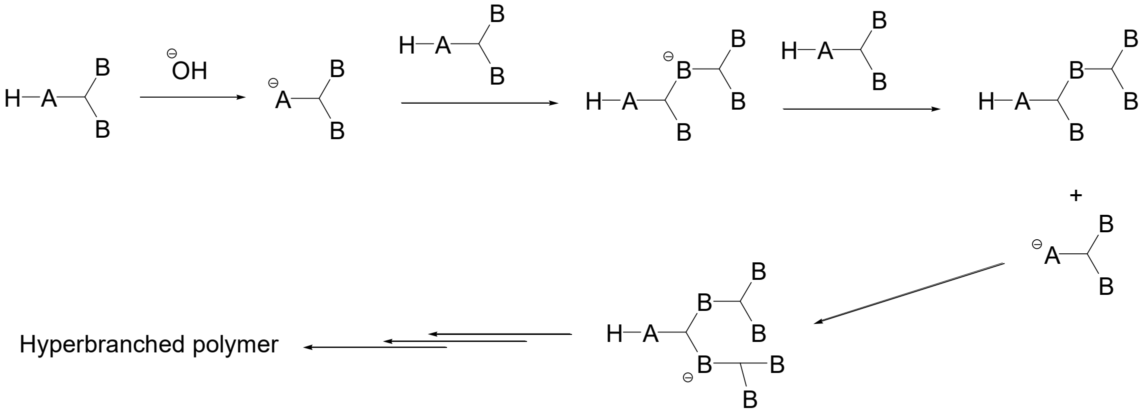


Scheme 2.9 Synthesis of hyperbranched polyglycerols via the SCROP method in combination with anionic polymerization

The ROH in scheme 2.9 is a trifunctional initiator known as 1, 1, 1-tris (hydroxymethyl)propane (TMP) that served as a core unit and lowered the molecular weight distribution of the resultant hyperbranched polymers. Moreover, cyclization was prevented via slow monomer addition strategy, and the resulting hyperbranched polymer contains several hydroxyl end-functionalized groups.

2.9.4.5 Proton-transfer polymerization (PTP)

The PTP method is used to synthesize hydroxyl or epoxy end-functionalized HBPs (Chang & Fréchet, 1999; Gong & Fréchet, 2000). Scheme 2.10 shows the general reaction mechanism for the PTP method.



Scheme 2.10 General scheme for the synthesis of hyperbranched polymers via proton-transfer polymerization

In the initiation step, a nucleophile is produced via proton abstraction by the hydroxide ion (OH^-). The nucleophile generated is then reacted with the second monomer followed by a proton transfer to generate a neutral dimer and a new nucleophile capable of reacting with another monomer. A proton transfer is involved in each of the subsequent propagation steps, and as a result, hyperbranched polymer is formed. The monomers used in the PTP fit into the AB_2 category, and they generally possess the hydroxyl (A) and epoxide (B) groups.

The following section (Section 2.10) discusses the copolymerization of vinyl monomers and the problem of gelation associated with it since the present research aims to prevent gel formation in the copolymerization of vinyl monomers.

2.10 Copolymerization of vinyl monomers

When two monomers are copolymerized, the resulting composition can be described by the Mayo-Lewis equation, otherwise known as the copolymer composition equation (Mayo & Lewis, 1944). By considering the reactivity ratios and the initial concentrations of the monomers involved in the copolymerization, the composition of the resulting copolymer can be determined by the Mayor–Lewis equation.

Copolymerization of two monomers give rise to the following set of equations (Hsieh & Quirk, 1996):

$$xM_1 + initior \quad \rightarrow \quad P_xM_1^{(-)} \tag{2.6}$$

$$P_xM_1^{(-)} + M_1 \quad \overset{k_{11}}{\rightarrow} \quad P_{x+1}M_1^{(-)} \tag{2.7}$$

$$P_xM_1^{(-)} + M_2 \quad \overset{k_{12}}{\rightarrow} \quad P_{x+1}M_2^{(-)} \tag{2.8}$$

$$P_xM_2^{(-)} + M_1 \quad \overset{k_{21}}{\rightarrow} \quad P_{x+1}M_2^{(-)} \tag{2.9}$$

$$P_xM_2^{(-)} + M_2 \quad \overset{k_{22}}{\rightarrow} \quad P_{x+1}M_2^{(-)} \tag{2.10}$$

where P_x is an active polymer chain consisting of x monomer units, M_1 and M_2 represent unreacted monomers 1 and 2, respectively, k is the rate constant for the reaction (Mayo & Lewis, 1944).

The rates of disappearance of monomers 1 and 2 are given by equation 2.11 and 2.12, respectively.

$$-\frac{d[M_1]}{dt} = k_{11}\left[P_{x+1}M_1^{(-)}\right][M_1] + k_{21}\left[P_{x+1}M_2^{(-)}\right][M_1] \tag{2.11}$$

$$-\frac{d[M_2]}{dt} = k_{22}\left[P_{x+1}M_2^{(-)}\right][M_2] + k_{12}\left[P_{x+1}M_1^{(-)}\right][M_2] \tag{2.12}$$

Dividing equation 2.11 by 2.12 gives the compositional ratio for the copolymerization. Thus;

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}\left[P_{x+1}M_1^{(-)}\right][M_1] + k_{21}\left[P_{x+1}M_2^{(-)}\right][M_1]}{k_{22}\left[P_{x+1}M_2^{(-)}\right][M_2] + k_{12}\left[P_{x+1}M_1^{(-)}\right][M_2]} \tag{2.13}$$

To simplify equation 2.13, the concentration terms $[P_{x+1}M_1^{(-)}]$ and $[P_{x+1}M_2^{(-)}]$ need to be removed from equation 2.13; this is done by introducing the steady-state approximation. This approximation requires that the rate of interconversion between two anionic chains $P_{x+1}M_1^{(-)}$ and $P_{x+1}M_2^{(-)}$ be the same. Hence,

$$k_{12}\left[P_{x+1}M_1^{(-)}\right]\left[M_2\right]=k_{21}\left[P_{x+1}M_2^{(-)}\right]\left[M_1\right] \qquad \textbf{2.14}$$

From equation 2.14, we have

$$\left[P_{x+1}M_1^{(-)}\right]=\frac{k_{21}\left[P_{x+1}M_2^{(-)}\right]\left[M_1\right]}{k_{12}\left[M_2\right]} \qquad \textbf{2.15}$$

Substituting Equations 2.14 and 2.15 in 2.13, we have:

$$\frac{d\left[M_1\right]}{d\left[M_2\right]}=\frac{\dfrac{k_{11}k_{21}\left[P_{x+1}M_2^{(-)}\right]\left[M_1\right]\left[M_1\right]}{k_{12}\left[M_2\right]}+k_{21}\left[P_{x+1}M_2^{(-)}\right]\left[M_1\right]}{k_{21}\left[P_{x+1}M_2^{(-)}\right]\left[M_1\right]+k_{22}\left[P_{x+1}M_2^{(-)}\right]\left[M_2\right]} \qquad \textbf{2.16}$$

To simplify equation 2.16, two parameters are introduced called reactivity ratios for the monomers and are defined by the ratios between the rate constants for self-propagation and the rate constants for cross-propagation (Equation 2.17).

$$r_1=\frac{k_{11}}{k_{12}} \text{ and } r_2=\frac{k_{22}}{k_{21}}. \qquad \textbf{2.17}$$

Now we divide the numerator and denominator of the right–hand side of Equation 2.16 and then substitute Equation 2.17 in the same equation. The result is given as Equation 2.18 and is called the Mayo-Lewis equation or the copolymer composition equation.

$$\frac{d\left[M_1\right]}{d\left[M_2\right]}=\frac{\left[M_1\right]}{\left[M_2\right]}\cdot\frac{r_1\left[M_1\right]+\left[M_2\right]}{\left[M_1\right]+r_2\left[M_2\right]}=\frac{m_1}{m_2}. \qquad \textbf{2.18}$$

According to this equation, the instantaneous composition of the copolymer being formed is determined by the concentration of the monomers used as well as their reactivity ratios (Hagiopol, 2012). The monomer reactivity explains the relative tendency for the two monomers to homopropagate or cross-propagate. If r = 0, for a given pair of monomer k_{11} will be equals to 0 and it means M_1 will prefer to cross-propagate with M_2. However, if $r_1 > 1$, M_1 will prefer to homopropagate.

2.10.1 The problem of gelation associated with copolymerization of vinyl monomers

Free radical copolymerization of a vinyl monomer with a small amount of multifunctional monomers has been widely used to synthesize branched polymers. Cross-linking occurs in the polymer chain when both the vinyl groups of a divinyl cross-linker have reacted via intermolecular or intramolecular reaction between the chain-end radicals and pendant vinyl groups. As the intermolecular cross-linking progressed, the size and molecular weight of the branched polymer increases exponentially until eventually an “infinite” value is reached and a polymeric network (gelation) occurs. The gel point is defined as a changeover from a viscous liquid (called sol) to an elastic gel. Statistical treatment for predicting the gel point is given by the Flory-Stockmayer’s theory discussed in the next section.

2.10.2 Flory-Stockmayer’s statistical theory: Prediction of the gel point

The process of gelation was first recognized in 1931 by Carothers who explained that gelation is joining of polymer molecules into a giant 3D–network (Carothers, 1936). In 1941 Flory pointed out a statistical method for predicting the extent of reaction at which gelation occurs (Flory, 1941a, 1953). Later, Stockmayer (W. H. Stockmayer, 1943) applied Flory’s method to a mixture of polyfunctional monomers and arrived at an expression (Equation 2.19), capable of predicting the gel–point in an addition polymerization system consisting of a monomer and divinyl crosslinker (Stockmayer, 1944).

The Flory-Stockmayer’s theory was built upon two assumptions:

(1) That same reactivity exists between the vinyl monomer and the divinyl cross-linker as well as the pendant double bonds.

(2) That intermolecular cyclization, involving the pendant vinyl bonds are neglected.

$$v_c = \alpha\rho(\bar{X}_w - 1) = 1 \qquad \textbf{2.19}$$

Where α is the extent of conversion of double bonds, ρ is the fraction of all double bonds present on divinyl monomer at the start of the reaction, and $\bar{X}_w$ is the weight-average degree of polymerization of the linear primary chains. According to the Equation 2.19, the critical gel point is attained when the weight-average number of cross–linking unit (v) per primary chain equals to 1.

When $\bar{X}_w >> 1$ and the polydispersity of the linear primary chain ($\bar{X}_w / \bar{X}_n$) is taken in to account, Equation. 2.19 is written as:

$$V_c = \alpha\rho\bar{X}_n \frac{\bar{X}_w}{\bar{X}_n} = 1 \qquad \textbf{2.20}$$

In which the $\alpha\rho\bar{X}_n$ is the cross–linking index *(γ)*. Since,

$$\rho = \left[\frac{2[X]_0}{[M]_0 + 2[X]_0}\right] \qquad \textbf{2.21}$$

$$\rho = \left[\frac{[M]_0 + 2[X]_0}{[PC]t}\right]\alpha \qquad \textbf{2.22}$$

Where $[M]_0$, $[X]_0$ represent the initial concentrations of the vinyl monomer and the cross-linker, respectively, while $[PC]_t$ represents the concentration of the primary chains at time *t*. Substitution of Equation 2.21 and Equation 2.22 into Equation 2.20 gives rise to Equation. 2.23 which can further be expressed as Equation 2.24.

$$V_c = \gamma \frac{\bar{X}_w}{\bar{X}_n} = \alpha \left[\frac{2[X]_0}{[M]_0 + 2[X]_0} \right] \left[\frac{[M]_0 + 2[X]_0}{[PC]t} \right] \alpha \frac{\bar{X}_w}{\bar{X}_n} = 1 \qquad \textbf{2.23}$$

$$V_c = \gamma \frac{\bar{X}_w}{\bar{X}_n} = \alpha^2 \frac{2[X]_0}{[PC]_t} \frac{\bar{X}_w}{\bar{X}_n} = 1 \qquad \textbf{2.24}$$

For a polydispersed system, Equation 2.24 shows that the number-average crosslinking units per primary chain *(γ)* equal to the weight-average crosslinking units per primary chain *(v)*.

For a copolymerization reaction with polydispersity equals 2, ($\bar{X}_w / \bar{X}_n = 2$), $\Upsilon_c = 1/2$ is required to attain the point of gelation. The critical conversion of double bonds at the gel point (α_c) is given by Equation 2.25.

$$\alpha_c = \sqrt{\frac{[PC]_t}{2[X]_0} \frac{1}{\frac{\bar{X}_w}{\bar{X}_n}}} \qquad \textbf{2.25}$$

According to the above equation, the theoretical gel point depends on the instantaneous concentration of the primary chains, its polydispersity, and the initial concentration of the crosslinker (Flory, 1953).

The Flory-Stock Mayer's theory offers essential guide for designing experiments with the aim of achieving highly branched polymers, even though the assumptions such as the absence of intramolecular cyclization, do not entirely agree with experimental findings (Dušek & Dušková-Smrčková, 2000; Gordon, 1954; Matsumoto, 2001; Walling, 1945). To avoid gel formation in the radical copolymerization of a vinyl monomer and multifunctional crosslinking agent, the polymerization reaction should be terminated before the critical gel point (α_c) to achieve a completely soluble product. Based on Equation 2.25, some strategies are used to postpone the gel formation to occur at higher conversion. These strategies include (Dušek & Dušková-Smrčková, 2000; Funke *et al.*, 1998; Matsumoto, 1995; Oh *et al.*, 2008):

(1) Early termination of the reaction at lower monomer conversion before reaching the critical gel point.
(2) The use of the low amount of crosslinker.
(3) Decreasing the primary chain length by employing a chain transfer agent or adding more initiator.

Point number (3) is particularly relevant to the present study where chain transfer to solvent is employed to achieve the desired branching and to prevent the gel formation in an anionic polymerization system.

2.10.3 The "Strathclyde" solution to the problem of gelation associated with the synthesis of HBPs via free radical polymerization techniques.

It has been well established that copolymerization of vinyl monomers with divinyl or multifunctional monomers via free radical polymerization leads to the formation of insoluble polymer network (gel). Evidently, for a particular monomer conversion to the polymer, as the degree of polymerization increases, the number of chains decreases, and gelation occurs even at lower conversion. It has been stated that even in a system with a very low monomer concentration (~10 % monomer), gelation can occur at any level significantly higher than 20 % conversion (Matsumoto, 1995). Therefore, synthesis of soluble branched polymers at high monomer conversion via the free radical copolymerization involving multifunctional comonomer had appeared to be impossible. However, in 2000, Sherrington and co-workers at the University of Strathclyde in the UK, developed a facile and cost-effective route to the synthesis of hyperbranched polymers and it was termed as the "Strathclyde approach" (Costello *et al.*, 2002; O'brien *et al.*, 2000). In the "Strathclyde approach", branched polymers are synthesized via free radical copolymerization of vinyl and multi-vinyl monomers by the use of chain transfer agents (CTA) to prevent gelation (O'brien *et al.*, 2000). Figure 2.12 shows the general reaction scheme for the synthesis of branched polymers via the "Strathclyde approach." The "Strathclyde route" employs an appropriate concentration of the vinyl monomer with a small amount of multi-functional comonomer and an equimolar amount of CTA.

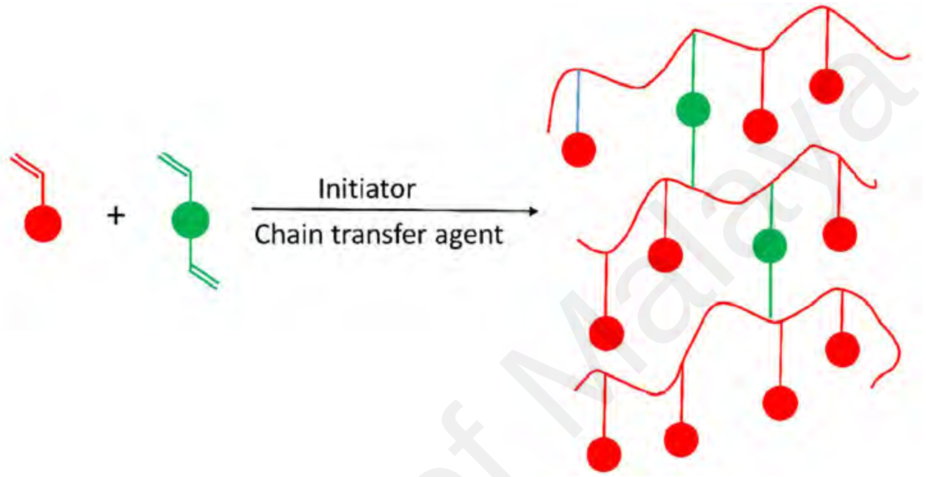


Figure 2.12: The "Strathclyde route" to the synthesis of hyperbranched polymers via free radical copolymerization using a free radical chain transfer agent (O'brien *et al.*, 2000)

The chain transfer agent decreases the degree of polymerization of the primary chain thereby reducing the number of branch points per primary chain as well as inhibiting the intermolecular reaction and consequently, gelation is prevented. This method makes it possible to obtain hyperbranched polymers in good yield without the problem of gelation. The "Strathclyde approach" can be used to tailor the molecular weight, architecture and the yield of branched polymers by choice of the chain transfer agent or changing the functionality of the vinyl monomer (Baudry & Sherrington, 2006b; Isaure *et al.*, 2004; Slark *et al.*, 2003). The thiol-based chain transfer agents employed by the Strathclyde team are suitable for the polymerization of acrylamides and methacrylates. However, when used with other monomers like N–vinyl pyrrolidinone or vinyl acetate, leads to the quenching of the polymerization (Baudry & Sherrington, 2006b). Also, the polymer chains will contain some functionalities of the chain transfer agent and the radical initiator used to initiate the polymerization reaction (Baudry & Sherrington, 2006b).

Moreover, the degree of polymerization is limited to some extent since a low concentration of the multifunctional comonomer, and a limited ratio of crosslinker to the initiator (≤ 1) are necessary to guarantee the formation of soluble branched polymers. Gelation occurs when the ratio of the crosslinker–initiator is higher than 1. The 'Strathclyde synthesis' was significantly improved with the development of controlled radical polymerization (CRP) techniques. Atom transfer radical polymerization being one of the most robust CRP methods was used to prevent gelation by regulating the polymer chain length (Isaure *et al.*, 2004). Also, the ATRP can offer better control of chain-end functionalities. Soluble hyperbranched polymethylmethacrylates (PMMA) were successfully prepared via one-pot synthesis using ATRP. Later, hydroxypropyl methacrylate was copolymerized with a cleavable disulfide dimethacrylate (Li & Armes, 2005a) or ethylene glycol dimethacrylate (Bannister *et al.*, 2006). Copolymerization of a vinyl monomer with multifunctional comonomer via reversible addition-fragmentation chain transfer polymerization (RAFT) was first reported by Liu *et al.* in 2005 (Liu *et al.*, 2005a; Liu *et al.*, 2005b). They later prepared soluble hyperbranched polymers of divinylbenzene by further exploring the RAFT method in homopolymerization (Koh *et al.*, 2011). RAFT polymerization of asymmetric divinyl monomers was also reported Dong *et al.* 2008, where they prepared hyperbranched PS consisting of numerous pendant vinyl groups using an asymmetric divinyl monomer having less reactive butenyl group and a more reactive styryl group. Further modifications of the polymer such as hydroxylation, amination, and epoxidation were possible due to the presence of the pendant vinyl groups. The gelation was avoided by reducing the cross-linking density since only small amounts of the butenyl vinyl groups were used up (Dong *et al.*, 2008).

2.11 Characterization of hyperbranched polymers

The developments in the synthesis of hyperbranched polymers so far largely depend on the distinctive characteristics that offer the possibilities for new applications (Burchard, 2004; Carlmark *et al.*, 2009; Gao & Yan, 2004; Voit, 2000; Yates & Hayes, 2004). Along with the synthetic evolution, considerable effort has been made to obtain information regarding the structure and properties of hyperbranched polymers via various characterization techniques. Moreover, most of the analysis of HBPs are based on the correlation of properties with the linear or perfectly branched polymers, to understand the differences and thus, the influence of the randomly branched architecture on the characteristics of these polymers.

In the following section, an overview of the various methods used for the structural, solution, rheological and thermal, characterization of hyperbranched polymers will be given.

2.11.1 Degree of branching (DB)

Information on the degree of branching (DB) of hyperbranched polymers is beneficial since the DB directly correlates with the compactness of the polymer structure as well as the location and the amount of the functional end groups. In contrast to the dendrimers, which are perfectly branched with only terminal units (T) and branched units (B), hyperbranched polymers possess additional linear units (L). Quantification of these different units in HBPs can be obtained either directly using techniques such as NMR spectroscopy (Chen *et al.*, 2006; Hawker *et al.*, 1991; Jia *et al.*, 2006), or indirectly via chromatographic techniques (Bolton & Wooley, 2002; Kambouris & Hawker, 1993). The degree of branching is expressed as the ratio of T, L, and B units in the polymer and can be used to compare between dendrimers and hyperbranched polymers. Dendrimers have DB of 1 and linear polymers DB of 0 while the DB of hyperbranched polymers varies from 0 to 1 and is commonly between 0.4 and 0.6 (Holter & Frey, 1997). Theoretically, polymerization of an AB_2 monomer in which the B groups have equal reactivity and no side reactions have occurred, the degree of branching of the resulting HBP is expected to have the value of 0.5 (Holter & Frey, 1997). The degree of branching for this type of hyperbranched polymer is defined by the Equation 2.26 (Hawker *et al.*, 1991):

$$DB_{Fréchet} = \frac{B+T}{B+L+T} \qquad \textbf{2.26}$$

For hyperbranched polymers particularly of AB_2 type, there is a relationship between the B and T units because for every branched unit formed there is a corresponding terminal unit hence, T = B+1 (Holter & Frey, 1997; Wooley *et al.*, 1994). Considering this relationship, even linear polymers will have DB > 0 if Equation 2.26 is used. Therefore, using this equation, only the degree of branching of polymers with a high degree of branching can be obtained accurately. Consequently, an alternative equation (Equation 2.27) was proposed for an AB_2 system, which takes in to account only the linear and branched units to overcome the drawback associated to the degree of polymerization (Holter *et al.*, 1997).

$$DB_{Frey} = \frac{2B}{2B+L} \qquad \textbf{2.27}$$

Side reactions such as cyclization can make the determination of the structural units for DB evaluation problematical (Komber *et al.*, 2001; Morikawa & Akagi, 2013; Parker & Feast, 2001; Unal *et al.*, 2005). Viscosity measurements with Mark–Houwink equation (Equation 2.28), allows for an indirect evaluation of the degree of branching (Hutchings *et al.*, 2005).

$$[\eta] = K.M^{\alpha} \quad \textbf{2.28}$$

were [η] is the intrinsic viscosity, α and K are the Mark–Houwink constants and M is the polymer molecular weight. In the synthesis of HBPs, it is vital to control the degree of branching since it affects the properties of hyperbranched polymers such as glass transition temperature, solution viscosity, and chain entanglements.

2.11.2 Molecular weight and molecular weight distributions

Size exclusion chromatography (SEC) is a valuable technique for obtaining the molecular weight and molecular weight distribution of hyperbranched polymers just as it is useful for linear polymers. However, it is difficult to determine the absolute molecular weight of hyperbranched polymers accurately. Moreover, when the SEC analysis is performed with only a differential refractive index (DRI) or UV–detector and calibrated with linear polymer standards, significant errors are unavoidable. This is due to the decrease in the hydrodynamic radius of hyperbranched polymers in solution resulting from their densely branched nature compared to the linear polymers (Lederer *et al.*, 2002).

It would be possible to obtain values that are more reliable if the calibration were to be carried using standards that are similar to the hyperbranched polymers in both chemical composition and architecture. However, such standards are not commercially available for hyperbranched polymers.

More accurate calculations of molecular weight can be performed using SEC machines equipped with differential viscometer detector and the calibration performed using universal calibration method. The universal calibration method calculates the molecular weight of polymers in relation to their intrinsic viscosity and hydrodynamic volumes and does not require the sample and the standard to have identical structure.

Therefore, using this approach, it is possible to obtain more accurate molecular weights than in SEC with RI detector alone. The relationship between intrinsic viscosity [η] and the molecular weight is described by the Flory–Fox equation (Equation 2.29).

$$[\eta] = \phi \left(\frac{R_g^3}{M_p} \right) \qquad \textbf{2.29}$$

Where ϕ is the volume fraction occupied by the polymer in solution, R_g is the radius of gyration, defined as the average squared distance of any point of the polymer coil from its center of mass, and M_P is the peak molecular weight related to a given retention volume. The structural parameters such as ϕ and R_g are constant for linear polymers, and therefore a linear relationship exists between the molecular weight and the intrinsic viscosity as given by the Mark–Houwink Equation (2.28 above).

Generally, K and α have implications for the compactness and shape of a given polymer in solution. The value of α is less than 0.6 for hyperbranched polymers and ranges from 0.6 to 0.8 for linear polymers (Frey, 1997; Turner *et al.*, 1994). Dendrimers and hyperbranched polymers, on the other hand, deviate from the linearity of the Mark–Houwink equation due to their more compact structures therefore, the universal calibration is also inaccurate for the calculation of their molecular weights (Garamszegi *et al.*, 2003; Kumar & Ramakrishnan, 1993; Lederer *et al.*, 2002; Schmaljohann & Voit, 2003; Richard Turner *et al.*, 1993; Voit, 2000). However, calculations of molecular weight using SEC equipped with viscometer and light scattering (Equation 2.30) eliminate the effect of the polymer structure.

$$R_\theta = \frac{4\pi^2 n_0^2 \left(\frac{dn}{dc} \right)^2}{\lambda_0^4 N_A} c M_w \qquad \textbf{2.30}$$

Where, n_0 is the refractive index of the solvent, *dn/dc* is the specific refractive index increment for a given polymer-solvent system, c is the concentration of the solution, λ_0 is the wavelength of incident light, and N_A is the Avogadro's constant. Equation 2.30 describes the relationship between the amount of light scattered from a polymer in solution (R_θ or Rayleigh factor), and the weight-average molecular weight, M_w. The intensity of the scattered light is proportional to both the molecular weight and the concentration of the polymer. Although information from light scattering can be reliable especially about the M_w of polymers, it is necessary to combine the light scattering with RI detector to obtain the *dn/dc* values of hyperbranched polymers accurately. The light scattering detector is undoubtedly the most powerful and accurate method for the determination of HBPs and does not require calibration with any standard.

In summary, a triple detector system with concentration, light scattering, and viscosity detectors provides the most detailed information about the molecular weight of HBPs. Due to their random nature HBPs often show a very broad molecular weight distribution (Kumar & Ramakrishnan, 1993; Pavlov *et al.*, 2001; Voit, 2000).

2.11.3 Rheological characterization of hyperbranched polymers

The key to the industrial applications of hyperbranched polymers is their unique properties. To fully utilize these materials, it is essential to gain insight on how architecture affects their rheological properties. Processing is one of the most critical factors for industrial applications of polymers, and good rheological property is one of the advantages enjoyed by the HBPs over linear polymers (Voit, 2005; Voit & Lederer, 2009). Researches have been carried out to investigate the rheological properties of hyperbranched polymers and it was discovered that HBPs strongly deviate from the established theories governing the behavior of linear and star polymers (De Gennes, 1975; Graessley & Roovers, 1979; Kharchenko & Kannan, 2003; Matyjaszewski *et al.*, 2007; McLeish & Milner, 1999; Vlassopoulos *et al.*, 1997). One of the remarkable conclusions was that HBPs are not entangled due to their compact nature and the presence of a high degree of branching. As a result, hyperbranched polymers are expected to behave like unentangled molecules (Farrington *et al.*, 1998; Sendijarevic & McHugh, 2000).

The leading indicator for the absence of entanglement is the existence of a linear relationship between weight–average molecular weight and zero shear viscosity (η_0). For entangled polymers, a linear relationship exists between η_0 and M_w while for unentangled polymers a deviation was observed and branching has a significant effect on this deviation (Muthukrishnan, Jutz*, et al.*, 2005). Hyperbranched polyethylenes with different branching topologies from virtually linear to dendritic were synthesized and evaluation was made of their rheological behavior via dynamic oscillations and steady shear experiments (McKee *et al.*, 2005; Patil *et al.*, 2005; Sheth *et al.*, 2005; Simon *et al.*, 2001; Ye *et al.*, 2004; Ye & Zhu, 2003). Newtonian flow behavior was observed in the case of highly branched polymers in contrast to the typical shear thinning for polymer sample that is almost linear. The investigation was carried out on the stress relaxation expressed by the storage (G') and the loss moduli (G'') and both linear and highly branched samples show similar behavior at lower frequency region in accordance with the scaling theory based on rouse model (De Gennes, 1976). However, in a higher frequency region, differences were observed. The nearly linear polymers show an elastic rubber plateau typical of polymers with chain entanglements. Similar behavior was observed for linear and branched poly(methyl methacrylate)s (Chisholm *et al.*, 2009) of comparable molecular weights (Figure 2.13).

Based on careful analysis of these findings and further rheological studies on hyperbranched polyesters and polystyrenes (Kharchenko & Kannan, 2003; Suneel *et al.*, 2002), it was concluded that highly branched polymers simultaneously behave as polymers and soft-colloids and display absence of or weak entanglements. Another critical factor that affects the rheological behavior of hyperbranched polymers is the amount and nature of end groups present (Schmaljohann *et al.*, 2000; Suneel *et al.*, 2002). For example, acetylation of hyperbranched poly(etheramide) containing a large number of OH end groups, and high viscosity at low-frequency regions resulted in a substantial reduction of the complex viscosity due to the relief of interactions between the polar functionalities (Bohme *et al.*, 2001).

In summary, the substantial reduction in melt viscosity of HBPs related to linear polymers is responsible for various interesting applications of HBPs. They have been blended with linear polymers not necessarily of similar composition to aid in processing (Gretton-Watson *et al.*, 2005; Mulkern & Tan, 2000; Rubinstein & Colby, 2003). Moreover, the rheological behavior of HBPs has given an awareness into their intermolecular interactions. Evidence from melt rheological studies of HBPs suggested the absence of entanglement for these materials, HBPs showed rouse-like behavior and no crossing over between the loss modulus, and storage modulus was observed at high frequency.

2.11.4 Thermal properties of hyperbranched polymers

Branching strongly influences the thermal properties of polymers like melting point and glass-transition temperature. Differences exist between the thermal transitions observed in hyperbranched polymers from those of the linear or even long–chain branched polymers, and a number of factors are responsible for these differences. Glass–transition temperature (*Tg*) is governed by the mobility of the polymer backbone, which in turn depend on the structure, or chemistry of the polymer backbone.

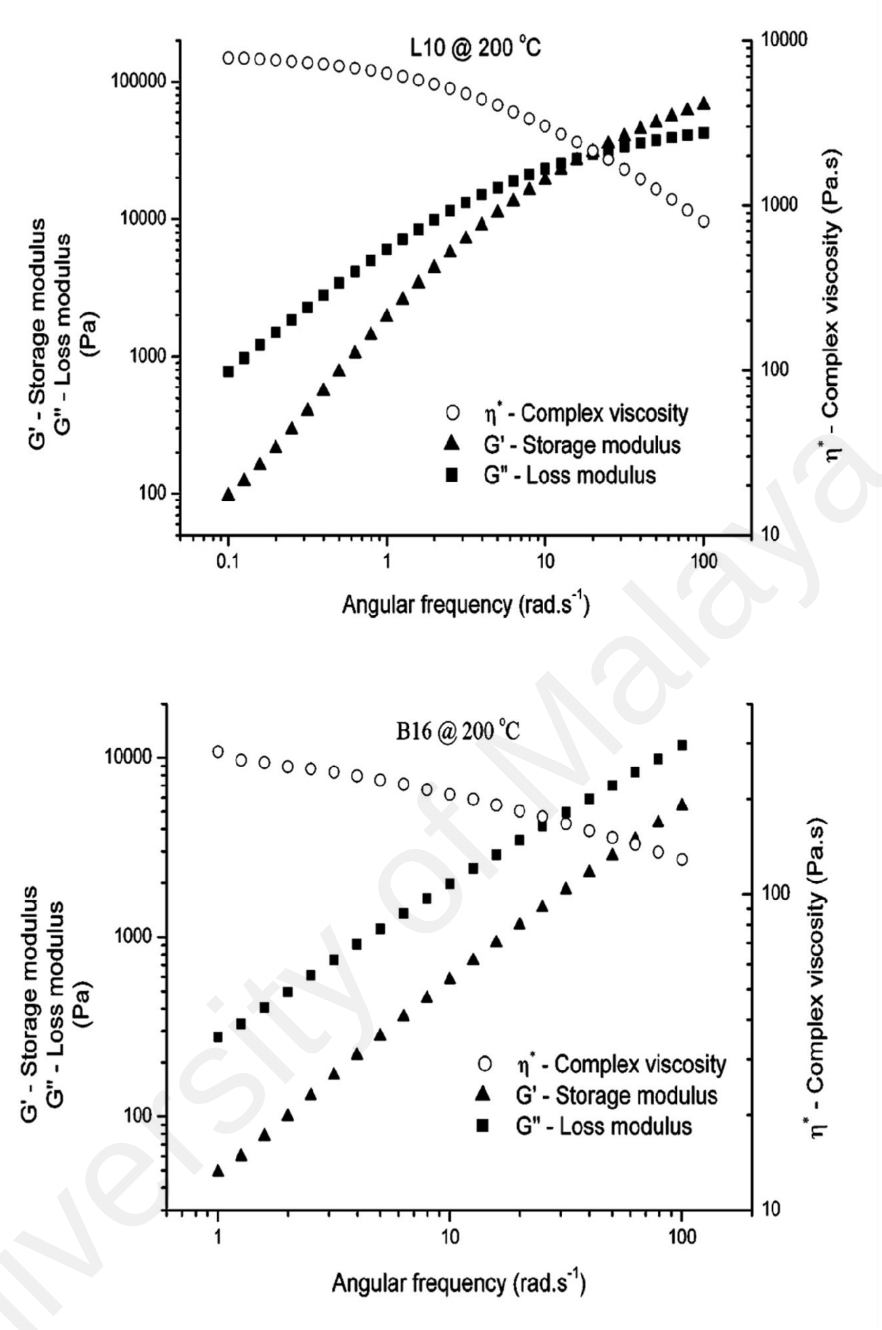


Figure 2.13: Storage modulus (*G'*), loss modulus (*G''*) and complex viscosity at 200 ˚C for (L10) linear and branched (B16) poly(methyl methacrylate)s. Reproduced with permission from (Chisholm *et al.*, 2009) Copyright © (2009), American Chemical Society

The degree of branching results in a decrease in the glass transition temperature of HBPs due to the restrictions of molecular mobility caused by the increase in compactness of the polymer molecules. This tendency was observed in hyperbranched polyetherimides where flexibility of the polymer molecules is tied to the degree of branching (Markoski *et al.*, 2001). However, increase in free volume due to branching can cause increase in the chain mobility and lowers the glass transition temperature. The effect of end groups on T_g of hyperbranched polymers is also significant. The end group effect on T_g has been found to be more evident in HBPs compared to the linear polymers. Moreover, the ability of end groups to participate in H-bonding also has a substantial effect on the glass transition of HBPs (Elrehim *et al.*, 2005; Hsieh *et al.*, 2001; Thompson *et al.*, 2000). However, identical T_g values were observed when linear and hyperbranched aromatic polyesters having a similar functional group, as well as identical backbone structure and chemistry, were compared (Behera *et al.*, 2005; Wooley *et al.*, 1994). This indicates that T_g mainly depends on the chemical nature of the polymer backbone while the branching topology has a lesser effect.

Moreover, while hyperbranched poly(phenylquinoxaline)s show a decrease in temperature for 5 % weight loss with a decrease in H–bonding ability, the opposite trend was observed for poly(aminoesters) (Ishida *et al.*, 2000; Powell *et al.*, 2005). Also, it was found that the thermal stability of linear poly(arylene etherketone) was improved upon incorporation of hyperbranched poly(arylene ether oxide) due to the presence of triarylphosphine oxide which imparts higher thermal stability to the hyperbranched copolymer than the linear homopolymers (Abdelrehim *et al.*, 2004).

Also, the degree of branching considerably affects the crystallization ability of polymers. The short and densely branched nature of HBPs, prevent the occurrence of crystallization. However, crystallization has been observed in some cases either as a result of branching dilution or due to modification with long chains or the possibility of some HBPs to form liquid crystals (Marcos *et al.*, 2007; Schallausky *et al.*, 2008; Schmaljohann *et al.*, 2000).

In summary, the thermal stability of hyperbranched polymers is usually not affected by their degree of branching alone. However, the type of end group present has a significant effect on their thermal stability (Baek & Harris, 2005; Chen & Yin, 2002; Peng *et al.*, 2005). The presence of end groups capable of forming hydrogen bonding usually behave differently with regards to thermal stability depending upon the chemistry of the main polymer chain. Nevertheless, when compared to linear polymers, the effect of the end groups on thermal stability is higher for HBPs.

2.11.4.1 Thermal degradation kinetics of hyperbranched polymers

Understanding the effect of molecular architecture on the properties of polymers is of interest from both theoretical and practical perspectives (Voit & Lederer, 2009). Recently, researchers have focused on the characterisation of hyperbranched polymers particularly about their structure-property relations, such as morphology, branching density, solution properties, crystallinity and glass transition temperature (Bai *et al.*, 2014; Frechet, 2003; Gao & Yan, 2004; Markoski *et al.*, 2001; Nishimura *et al.*, 2012; Zheng *et al.*, 2015). Many reports have been published on the chemical and physical changes that occur when polymers are exposed to heat over a wide range of temperature (Henrique *et al.*, 2015; Papageorgiou *et al.*, 2015; Speranza *et al.*, 2014; Yu *et al.*, 2016).

Thermal analysis of polymers is very vital to understanding the molecular architecture, degradation and mechanisms and in determining their application under various environmental conditions such as high–temperature. Extensive research on thermal degradation mechanism of the presently available macromolecules is available in the literature (Acar *et al.*, 2008; Arda *et al.*, 2017; Ciliz *et al.*, 2004; Holland & Hay, 2002; Peterson *et al.*, 2001). However, these studies have focused on the thermal properties of commercial homopolymers or blends of polymers. Moreover, there are few reports on this aspect related to hyperbranched and highly branched polymers.

Othman *et al.* (2015) gave some insight into the effect of terminal groups on the thermal decomposition of some flame-retardant hyperbranched polyimides (Othman *et al.*, 2015). Chen and coworkers (Chen *et al.*, 2016), studied the thermal degradation properties of the hyperbranched exopolysaccharide.

Thermal stability and the kinetics of thermal decomposition of polymers are usually studied using thermogravimetric analysis. TGA not only gives information on conversion as a function of temperature but also provides means to evaluate the thermal decomposition reactions or kinetic parameters. Quick evaluation of thermal stabilities and decomposition temperatures of different polymers, as well as the establishment of the thermal degradation mechanism, is also possible (Corazzari *et al.*, 2015; Ma *et al.*, 2015; Manafi *et al.*, 2015; Moussout *et al.*, 2016; Terzopoulou *et al.*, 2016; Tsanaktsis *et al.*, 2015).

Methods used for evaluating the kinetic parameters of various physicochemical processes from thermal analysis data can be classified into model fitting or model-free techniques. Principally, a fixed mechanism is assumed in the model–fitting approach with constant activation energy throughout the reaction. This technique consists of the fitting of kinetic data to some models to compute the kinetic triplets (activation energy, pre-exponential factor, and the reaction order). However; it is difficult to model complex reactions with reasonable accuracy. This is a limitation associated with the model–fitting approach. Model-free kinetics involves an isoconversional analysis on kinetic data obtained at a minimum of three heating rates, and activation energy is varied with temperature (Venkatesh *et al.*, 2013; Vyazovkin & Sbirrazzuoli, 2006). Thus, in model-free approaches, more than one mechanism is allowed during the course of the reaction. The principal disadvantage of the model-free method is that for a complete kinetic description, a reaction model is usually required. Regardless of which of the two approaches is employed, model-free or model fitting, it is unanimously assumed that the reaction rate has an Arrhenius–type dependence on temperature.

The primary objective of the Arrhenius–type of kinetic expressions is to determine the kinetic triplets experimentally. In the isoconversional methods, the complexity of a reaction is revealed via a functional interdependence between the activation energy and the extent of reaction *(α).* This approach allows for a reasonable prediction of kinetic information. When the activation energy of a process varies significantly with the conversion, it indicates that the process is complicated from a kinetic point of view.

2.12 Chapter summary

This chapter presented an overview of the relevant literature on the structural classification of polymers thereby highlighting the superiority of branched polymers over linear polymers. The chapter also discussed the various methods used to synthesize hyperbranched polymers as well as highlighting the importance of anionic polymerization as one of the techniques of choice for preparing polymers of various architecture and complexity. Concepts, theory, instrumentations and methods for the characterization of hyperbranched polymers were also presented. The problem of gelation and different methods of preventing it, achieving the synthesis of branched polymers were also reviewed. The chapter also presented an overview of some applications of hyperbranched polymers. Next chapter deals with the experimental methods used in the synthesis and characterization of hyperbranched polymers via anionic polymerization technique.

CHAPTER 3: EXPERIMENTAL

3.1 Introduction

The previous chapter (Chapter 2) presented an overview of the relevant literature on the structural classification of polymers, synthesis, characterization, application of hyperbranched polymers as well as highlighting the importance of anionic polymerization as one of the superior techniques for preparing polymers of various architecture and complexity. This chapter presents the experimental procedure used to synthesize and characterize the hyperbranched polymers as well as their linear precursors.

3.2 Materials

Isoprene (99%), *sec*–butyl lithium (1.4 M in cyclohexane), *n*–butyllithium (2.0 M in cyclohexane), and N, N, N’, N’–tetramethylethylenediamine (99.5 %) were obtained from Sigma-Aldrich. Toluene (HPLC grade), benzene (99.9%), isoprene and divinylbenzene were dried and degassed by several freeze–pump–thaw cycles over calcium hydride (CaH_2) (Aldrich). Dried methanol (99.9%) and divinylbenzene (98%, mixture of isomers), were purchased from Merck (Germany). Butylated hydroxytoluene (BHT), 99% was obtained from Fischer Scientific.

3.3 Preparation of reagents and glassware

All reactions were carried out in a customized reaction vessel designed for living anionic polymerization (“Christmas tree”) as shown in Figure 3.1.

This reaction vessel comprises of a sealed flask containing a cleaning solution of living polystyryl lithium in benzene (a), a washing vessel (b), small side flasks (c), and one main reaction flask (d). Anionic polymerization system does not tolerate any trace amount of impurities such as air or moisture hence, the reaction vessel has to be painstakingly prepared prior to use.

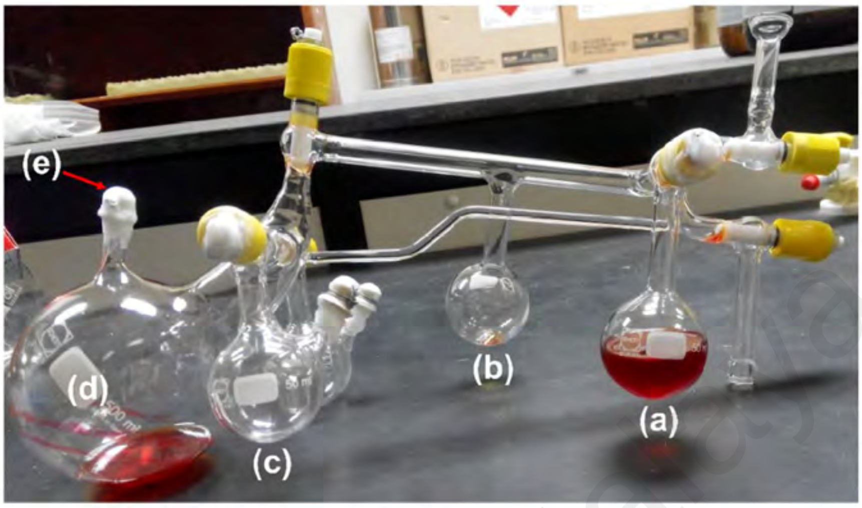


Figure 3.1: “Christmas tree” reaction vessel

The “Christmas tree” is first washed with four solvents (THF, toluene, methanol, acetone), respectively, and allowed to dry. After drying, septum (e) were tightly placed in to close the openings of the vessels with the help of metal wires. The vessel was then connected to the vacuum line (Figure 3.2) and evacuated for at least 1 hour to remove any traces of solvents, air, and moisture. After evacuation, the reaction vessel is then detached from the vacuum line. The living polystyryllithium solution contained in the flask (a) is then used to wash all parts of the reaction vessel in situ. After washing, the living solution is carefully moved back into flask (a), and the residual polystyryllithium solution on the walls of the Christmas tree is washed with benzene. The solvent was collected by distillation from the living solution in (a) into the (b) and poured back to (a) upon washing of any leftover solution. The washing is repeated as many times as possible until no orange color of the living polystyryllithium solution can be observed on the wall of the Christmas tree. After this washing, the living solution is frozen with liquid nitrogen and other parts of the Christmas tree are heated to distill any benzene left outside the flask (a). The Christmas tree is then attached to the vacuum line and evacuated overnight (Sarih, 2010).

Purification of solvents and monomers were achieved by drying and degassing that involves several freeze–pump–thaw cycles (Figure 3.3) over calcium hydride CaH_2.

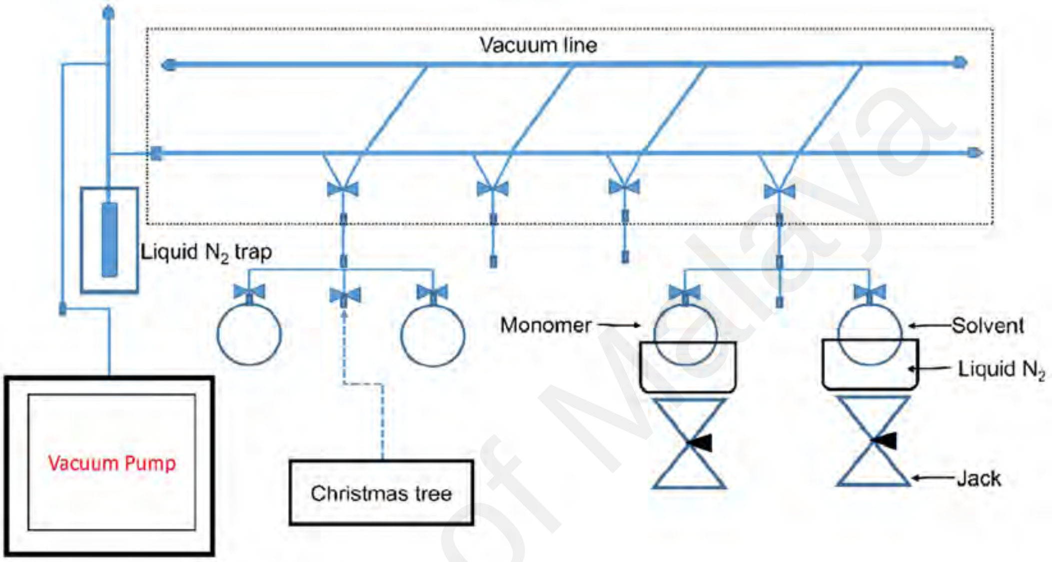


Figure 3.2: Schematic representation of the vacuum line used for purification of solvents, monomers

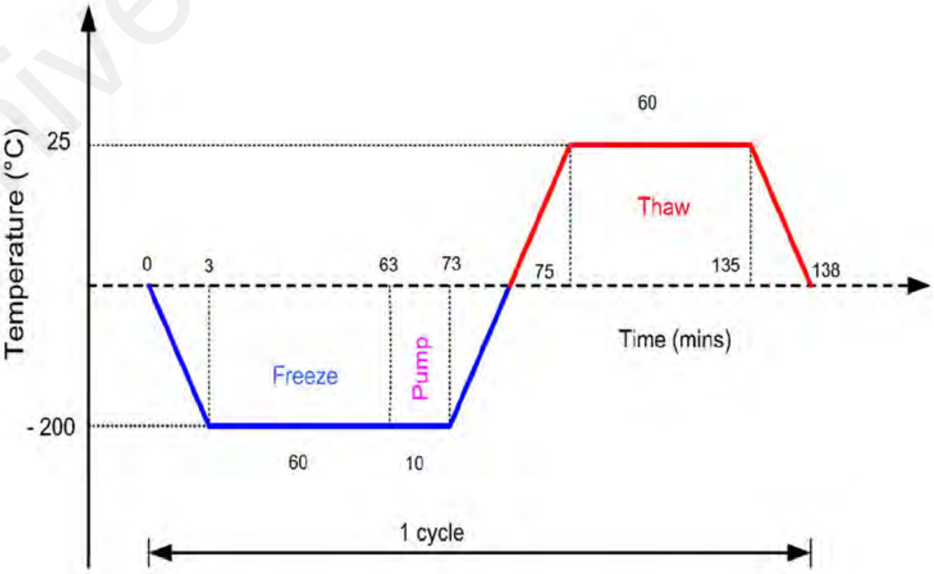


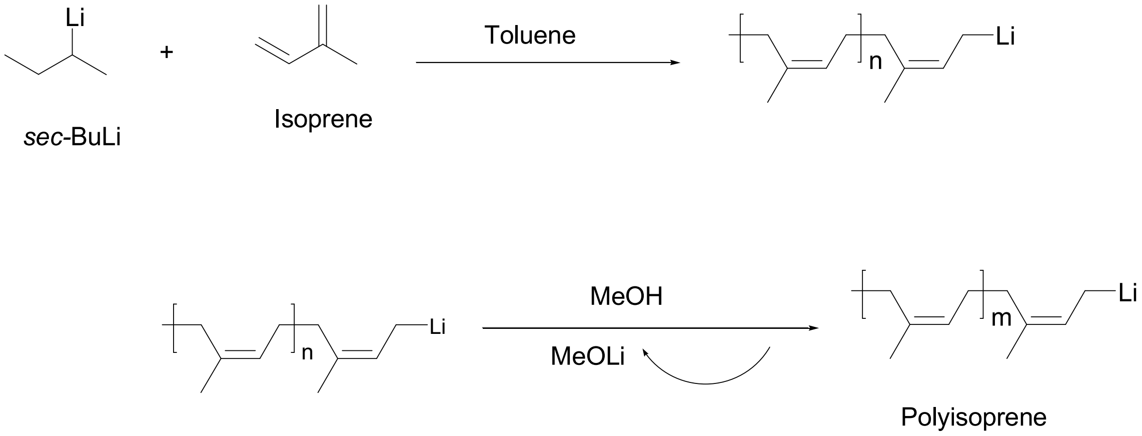
Figure 3.3: One cycle of freeze–pump–thaw for purification of solvents and monomers

3.4 Synthesis of linear and branched polyisoprene

All polymerizations were carried out by living anionic polymerization using standard high vacuum techniques similar to the one previously reported (Habibu *et al.*, 2018; Sarih, 2010).

3.4.1 Synthesis of linear polyisoprene

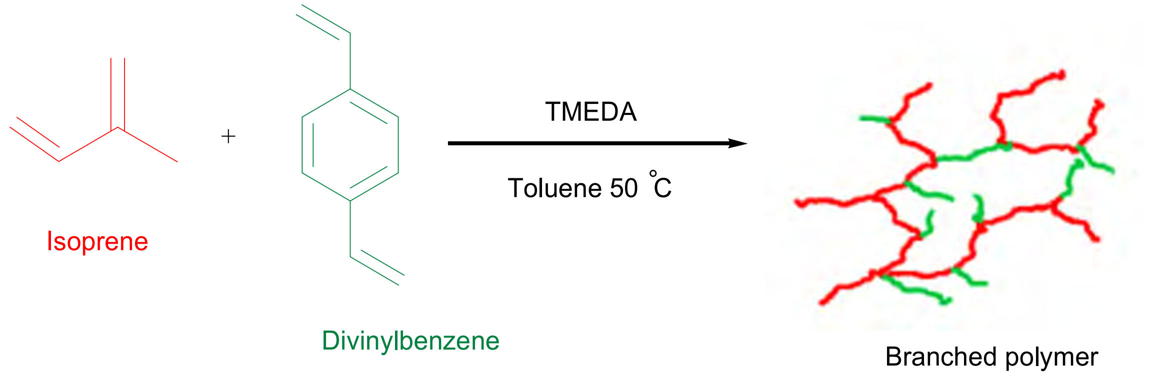
A typical procedure was as follows; toluene (100 ml) was distilled into the reaction vessel, followed by 5.2 g (0.0763 mole) of isoprene with the aid of an attachable flask. 0.1 ml (0.20 mol) of *n*–butyllithium was injected into the monomer in the attachable flask before being transferred to the reaction vessel. After the distillation of solvent and monomer, 0.22 ml (1.47 mol) of TMEDA (2 molar equivalent) was injected into the reaction followed by 0.52 ml (0.728 mol) of *s*-butyllithium to initiate the reaction. The reaction was maintained at 50 °C and was allowed to stir overnight. (0.1 ml, 2.47 mol) N_2–sparged methanol was used to terminate the reaction and produce homopolymers of isoprene that was collected by precipitation with excess methanol. BHT stabilizer was added after termination as well as before the precipitation to prevent oxidation. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) δH 1.32 (br, 3H, s, 1,4– *aliphatic*); 1.70 (br, 3H, s, 1,4–) 1.80 (br, 2H, m); 2.03 (4H, br, 1,4–, *aliphatic*); 2.26 (1H, br, 3,4–, *aliphatic*); 4.68 (1H, br, *olefinic*); 4.72 (1H, br, 3,4, *olefinic*); 5.12 (1H, s, 1,4–, *olefinic*). A similar procedure was adopted to prepare the remaining polymers by varying the TMEDA/Li from 0.5 to 2.0. Scheme 3.1 shows the synthetic route for the linear polyisoprene.



Scheme 3.1 Synthesis of linear polyisoprene homopolymers

3.4.2 Synthesis of branched polyisoprene

A typical procedure was as follows; 100 ml of toluene was distilled into the reaction vessel followed by 7.43 g (0.1091 mol) of isoprene with the aid of an attachable flask. 0.1 ml (0.20 mol) of n-butyllithium was injected into the monomer in the attachable flask before being transferred to the reaction vessel. After the distillation of solvent and monomer, 0.06 ml (0.4008 mol) (0.5 molar equivalent) TMEDA was injected into the reaction followed by 0.531 ml (0.743 mol) of *sec*-butyllithium to initiate the reaction. Divinylbenzene, 0.22 ml (1.5071 mol) was injected 5 minutes after initiation; the reaction was maintained at 50 °C and allowed to stir overnight (Scheme 3.2). The polymerization was terminated with 0.1 ml (2.47 mol) N_2–sparged methanol and recovered by precipitation in excess methanol containing a small amount of BHT. 1H NMR (400 MHz; $CDCl_3$; Me_4Si) δH 1.79–2.06 (14H, m, 1,4, *aliphatic*), 2.26 (1H, s, 3,4–, *aliphatic*), 4.64 (7H, br. s., 3,4), 4.67–4.76 (5H, m, 3,4), 4.77–4.94 (3H, m, 1,2), 4.94–5.12 (3H, m, 1,4–, *olefinic*),7.13–7.18 (3H, *m*, Ar). A similar procedure was adopted for all other branched polymer samples by varying the TMEDA/Li and the DVB/Li from 0.5 to 2.0 and 1.0 to 4.2 respectively.



Scheme 3.2 Synthesis of branched polyisoprene via anionic copolymerization of isoprene with DVB

3.5 Characterizations

3.5.1 Triple detection size exclusion chromatography (SEC)

SEC also known as GPC, gel permeation chromatography has been a powerful technique for the determination of polymer molecular weight and molecular weight distributions. The essential components of a SEC system comprise a solvent reservoir, pumps, an injection loop, columns, and detectors (Figure 3.4). The size exclusion chromatography is based on the separation of polymers by their size in an appropriate solvent (eluent). A dilute polymer solution is introduced into a solvent stream, which then passes through a series of columns containing porous beads of various pore sizes, which separate the polymers according to their chain lengths. Polymers with longer chain lengths are unable to penetrate the porous matrix and therefore have a shorter flow–path and are eluted earlier from the column. On the other hand, polymers with low molecular size have longer flow–path because they can penetrate the gel matrix and are therefore eluted at later retention times. Using triple detection system, consisting of differential refractive index (DRI), differential viscometer and light scattering detectors, it is possible to calculate the absolute molecular weight of the polymer without even the need for calibration. Each detector measures a different parameter, and the collection of these parameters give molecular weight information of the various molecular sizes in the sample. The data collected by the refractometer, viscometer and the light scattering detectors are calculated using Equations 3.1, 3.2 and 3.3 respectively.

$$Refractometer = K_{RI}\left(\frac{dn}{dc}\right)c \qquad \mathbf{3.1}$$

$$Viscometer\ = K_{V}\ ([\eta])\,c \qquad \mathbf{3.2}$$

$$Light\,scattering = K_{LS}\left(M_{w}\right)\left(\frac{dn}{dc}\right)^{2}c \qquad \mathbf{3.3}$$

Where *dn/dc* is the refractive index increment, *c* is the concentration, η is the intrinsic viscosity, M_w is the weight average molecular weight, and K_{RI}, K_V, and K_{LS} are instrument calibration constants. The differential refractometer calculates the *dn/dc* from the sample concentration entered during the injection of the sample; the intrinsic viscosity is determined by the viscometer also based on the sample concentration. The light scattering detector calculates the absolute molecular weight also based on the sample concentration as well as the value of the *dn/dc*. It is therefore essential to measure the sample concentration accurately when using triple detection system. However, if the *dn/dc* value of the polymer is known, it can be used to determine the concentration of the polymer in a given solvent. In the present study, the molecular weights and polydispersity indexes were determined using triple detection size exclusion chromatography (SEC) on a Malvern instrument (Viscotek 302) with refractive index, viscosity, and light scattering detectors, and 2 x 300 mm PLgel 5 µm mixed C columns. Tetrahydrofuran was used as the eluent with a flow rate of 0.8 - 1.0 ml min^{-1} and at a constant temperature of 35 ºC. The detectors were calibrated with a single polystyrene standard obtained from Polymer Laboratories, and values of *dn/dc* (ml g^{-1}) of 0.127 and 0.087 was used for linear polyisoprene and branched poly isoprene respectively. The *dn/dc* for the branched polymers were calculated from the instrument using a known concentration of the polymer.

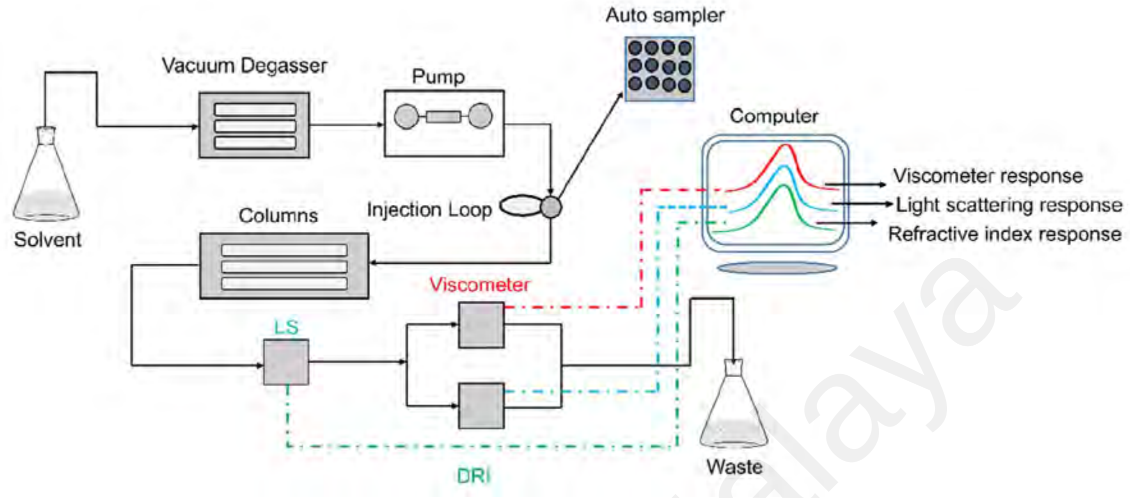


Figure 3.4: Schematic diagram showing the triple detection GPC/SEC system

3.5.2 Proton nuclear magnetic resonance spectroscopy (^{1}H NMR)

Proton Nuclear magnetic resonance (^{1}H NMR) spectroscopy is a well–established technique for the characterization of polymeric materials. It has been applied in the determination of microstructure, reactivity ratios, end-group composition as well as monomer sequence in copolymers (Izunobi & Higginbotham, 2011; Slichter, 1968). ^{1}H NMR spectra were recorded on 400 MHz JOEL–DELTA2 spectrometer using $CDCl_3$ as the solvent in 5 mm NMR tubes. Chemical shifts (in ppm) were recorded downfield relative to $CHCl_3$ ($\delta = 7.26$) as standard.

3.5.3 Melt rheology

Rheology has been extensively applied in the polymer science and engineering for investigating the structures and viscoelastic behavior of polymers, copolymers and polymer composites as a function of frequency or temperature. Linear Oscillatory measurements were performed on an Anton Paar MCR301 rheometer using a 25 mm parallel plate geometry with a gap of 1 mm and a convection temperature device (CTD). Amplitude sweep experiments were initially conducted to determine the linear viscoelastic regime. Frequency sweep measurements measured dynamic moduli for frequencies from 0.1 rad s^{-1} to 100 rad s^{-1} in the linear viscoelastic regime. Measurements were conducted over a temperature range of 40 to 120 °C, at 10° intervals for all samples. All the samples were stabilized with antioxidant (BHT) and vacuum dried to prevent oxidative degradation. The storage modulus, loss modulus as well as complex viscosity were evaluated.

3.5.4 Transmission electron microscopy (TEM)

The morphology and structural features of the branched polymers were analyzed using the high–resolution transmission electron microscopy (HRTEM). HRTEM is a powerful technique used in polymer science to analyze the shape, and structure of a polymeric material. HRTEM was used to investigate the effect of the branching on the morphology of the branched polymers and to compare them with linear polymers. Images were obtained by FEI TECNAI G2 F20 X–TWIN transmission electron microscope (TEM) operated at 200 kV. The analysis was performed at the Malaysian Institute of Microelectronic Systems (MIMOS). The samples were prepared and analyzed according to a similar procedure reported by Hutchings and coworkers in 2009 (Hutchings *et al.*, 2009).

3.5.5 Thermal analysis

Thermal properties of polymers and polymer composites are vital both for scientists and end users from different fields and allow for designing of polymers for desired applications. Thermal analysis techniques such as thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) provide valuable information regarding the thermal behavior of polymers. TGA determines the change in mass of a sample that is subjected to a programmed temperature in a well-defined atmosphere. Thermal properties of the branched polymers were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

3.5.5.1 Differential scanning calorimetry (DSC)

The glass transition temperature of the branched polymers was investigated by differential scanning calorimetry (DSC). Phase transition temperature was identified with a DSC 822e, Mettler Toledo calorimeter equipped with Haake EK90/MT intercooler. The calorimeter was calibrated using standard indium for temperature and enthalpy accuracy before experiments. All the samples tested were dried in a vacuum oven over di-phosphorous pentoxide for at least 48 hours. About 4-8 mg of each sample was heated under nitrogen atmosphere at a scanning rate of 10 ºC min^{-1} after the material was being encapsulated in the aluminum pans. The range for the measurement was from –40 to 200 °C and the samples were first heated from room temperature to 200 °C, and then cooled to –40 °C. The second heating cycle was performed in the range –40 °C to 200 °C and data from this cycle was used for the analysis. The data were analyzed using STARe thermal analysis system software.

3.5.5.2 Thermogravimetric analysis (TGA)

TGA analysis furnishes information on the mass change, about moisture content, thermal degradation temperature and stability of polymers. Thermogravimetric analyses of the linear homopolymers, as well as the branched samples, were performed with an STA 6000 Perkin Elmer simultaneous thermal analyzer (STA). Samples of about 10 *mg* were placed in alumina crucibles and heated from ambient temperature to 600 °C under nitrogen (N_2) atmosphere at a heating rate of 10 °C min^{-1} and a flow rate of 50 mL min^{-1}. Sample weight, sample temperature, heat flow, and first derivative, were continuously recorded.

3.5.6 Kinetics of thermal degradation

The TGA runs were performed under non-isothermal conditions as recommended by the kinetics committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) (Vyazovkin *et al.*, 2011). The experiments were carried out at the heating rate of 2, 5, 10 and 15 °C min^{-1} and a flow rate of 20 mL min^{-1}. Sample weight, sample temperature, and first derivative, and heat flow were continuously recorded. The use of non–isothermal thermogravimetric methods has a great capacity to unravel the mechanisms of chemical and physical processes that occur in the course of the degradation of polymers. The kinetic methods used in the thermal analysis of single-step reactions have been established over the years.

For systems that involve multi-step reactions, the use of inappropriate kinetic method can lead to misleading results. Nevertheless, it has been revealed that the use of isoconversional methods can provide meaningful values of activation energy in a wide-ranging environment. The isoconversional techniques allow for a model-free estimation of the activation energy. The isoconversional method is based on the isoconversional principle which states that at a given extent of conversion, the decomposition rate solely depends on the current sample temperature.

It has been concluded that model–free (isoconversional) methods are robust and most reliable tools to estimate the activation energy of thermally stimulated processes (Opfermann *et al.*, 2002; Starink, 2003; Vyazovkin *et al.*, 2011). In this research four isoconversional methods which include the Kissinger, Friedman, Flynn–Wall–Ozawa and Kissinger–Akahira–Sunose were employed to evaluate the dependence of activation energy (E_a) on conversion (α) for these polymers. Thermal degradation mechanism was also investigated using Coats–Redfern method.

The rate of thermal decomposition for the solid-state reaction dα/dt follows the equation (3.4).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad \mathbf{3.4}$$

Where $k\ (T)$ is the temperature-dependent rate constant, $f\ (\alpha)$ is the kinetic model that depends on the particular decomposition mechanism, and α is the degree of conversion represented by equation (3.5).

$$\alpha = \frac{w_o - w_t}{w_o - w_f} \qquad \mathbf{3.5}$$

where w_0 is the initial weight of the polymer sample, w_f is the final weight and w_t is the weight at a given time of the experiment.

The temperature-dependent rate constant was assumed to follow the Arrhenius equation (3.6):

$$k(T) = Ae^{-E_a/RT} \qquad \mathbf{3.6}$$

Where E_a is the apparent activation energy (kJ mol^{-1}), A is the pre-exponential factor (min^{-1}), and R is the gas constant (8.3142 $Jmol^{-1}K^{-1}$). Combining equations (3.3) and (3.5) gives rise to equation (3.7) which is the fundamental equation used to calculate the kinetic parameters based on the thermogravimetric analysis.

$$\frac{d\alpha}{dt} = f(\alpha)Ae^{-E_a/RT} \qquad \mathbf{3.7}$$

The most frequently used model for $f(\alpha)$ to analyze of thermogravimetric data is given by:

$$f(\alpha) = (1-\alpha)^n \qquad \mathbf{3.8}$$

in which n represents the reaction order. Substituting equation (3.8) in to (3.7) gives:

$$\frac{d\alpha}{dt} = (1-\alpha)^n A e^{-E_a/RT} \qquad \textbf{3.9}$$

For a non-isothermal thermogravimetric experiment at a constant heating rate $\beta = \frac{d\alpha}{dt}$, the above equation can be written as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}(1-\alpha)^n e^{-E_a/RT} \qquad \textbf{3.10}$$

Equation (3.10) is a differential form of the non-isothermal rate law. In the present study, model-free, non-isothermal methods were used to calculate the kinetic parameters.

3.5.6.1 Kissinger method

The Kissinger method involves the use of the maximum decomposition (T_{max}) temperature of which $d(d\alpha/dt)/dt$ is equal to zero. When equation (3.10) is differentiated with respect to *t* and the resultant expression set to 0 equation (3.11) is obtained.

$$\frac{E\beta}{RT_{\max}^2} = An(1-\alpha_{\max})^{n-1} e^{-E/RT_{\max}} \qquad \textbf{3.11}$$

According to Kissinger, the product $n(1-\alpha_{\max})^{n-1}$ does not depend on the heating rate β and equation (3.12) can be arrived at:

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \left\{\ln\frac{AR}{E} + \ln\left[n\left(1-\alpha_{\max}\right)^{n-1}\right]\right\} - \frac{E}{RT_{\max}} \qquad \textbf{3.12}$$

3.5.6.2 Friedman method

Friedman method is the most commonly used differential isoconversional process (Friedman, 1964; Venkatesh *et al.*, 2013). The following equation usually describes the temperature–dependent rate constant (k):

$$kf(\alpha) = \beta\left(\frac{d\alpha}{dT}\right) = Af(\alpha)e^{-Ea/RT} \qquad \textbf{3.13}$$

Taking the logarithm of both sides of equation (3.113) followed by simple rearrangement gives the Friedman's equation (3.14):

$$\ln\left(\beta\frac{d(\alpha)}{dT}\right) = \ln\left(\frac{d(\alpha)}{dt}\right) = \ln[Af(\alpha)] - \frac{E_a}{RT} \qquad \textbf{3.14}$$

The apparent activation energy (E_a) is obtained from the slope *($-Ea/R$)* of a plot of ln *($d\alpha/dt$)* against reciprocal temperature ($1000/T$) at constant conversion for a given set of heating rates.

3.5.6.3 Flynn–Wall–Ozawa method (FWO)

Flynn and Wall (Flynn, 1991) and Ozawa (Ozawa, 1965; Ozawa, 2000) proposed the FWO method. The main advantage of FWO method is that apart from the Arrhenius temperature–dependence equation no assumptions regarding the form of the kinetic model equations are required (Venkatesh *et al.*, 2013). The Flynn−Wall−Ozawa method is an integral model-free method, which involves the measurement of the temperature that corresponds to a fixed value of conversion at different heating rates. Integration of equation (3.13) and applying the Doyle approximation give rise to equation (3.15) in which the plot of ln β against $1000/T$ provides a straight line with slope equal to $-1.052Ea/R$ (Doyle, 1962; Venkatesh *et al.*, 2013).

$$\ln\beta = \ln\left(\frac{AE}{Rg(\alpha)}\right) = 5.331 - 1.052\left(\frac{E_\alpha}{RT}\right) \quad \textbf{3.15}$$

Where the kinetic model is *g (α) (i.e., kt = g (α)).* Therefore, when *g (α)* is known for a constant *α,* plots of ln *β* against the 1000/*T* taken at different *β* should give a straight line. The activation energy and the pre-exponential factor values are obtained from the slope and the intercept respectively.

3.5.6.4 Kissinger–Akahira–Sunose (KAS) method

The KAS method is an isoconversional method in which for a given conversion *(α),* the temperature *(T)* and the heating rate are related by the following equation (Chrissafis, 2008; Rajeshwari & Dey, 2014):

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - \left(\frac{E_a}{RT}\right) \quad \textbf{3.16}$$

In the KAS method, for each value of *α,* a straight line plot of $\ln\left(\frac{\beta}{T^2}\right)$ against 1000/*T* is obtained from the non-isothermal data acquired at various β (Idris *et al.*, 2010).

3.5.6.5 Coats–Redfern method

This is an integral method that involves the mechanism for thermal degradation. The activation energy is calculated based on the *f(α)* functions according to equation 3.17 derived by applying an asymptotic approximation (Coats & Redfern, 1964; Yang *et al.*, 2003).

$$\ln\frac{g(\alpha)}{T^2} = \ln\left(\frac{AR}{\beta E}\right) - \left(\frac{E_a}{RT}\right) \quad \textbf{3.17}$$

The Coats–Redfern assumes that the activation energy does not depend on the degree of conversion. The activation energy for each model is obtained using the slope obtained from the plot of $\ln\frac{g(\alpha)}{T^2}$ against 1000/T. Achievement of high correlation coefficient (R^2), as well as agreement between the activation energy obtained by this method compared to those obtained by previous methods al, lows for the selection of the kinetic model. The f*(α)* expressions for various mechanisms are listed in Table 3.1 (Coats & Redfern, 1964; Yang *et al.*, 2003).

Table 3.1: Expressions for *f(α)* for the most commonly used mechanisms of solid-state processes

Model	***f(α)***	**Mechanism**
A_2	$[-\ln(1-\alpha)]^{1/2}$	Nucleation and growth (Avrami equation 1)
A_3	$[-\ln(1-\alpha)]^{1/3}$	Nucleation and growth (Avrami equation 2)
A_4	$[-\ln(1-\alpha)]^{1/4}$	Nucleation and growth (Avrami equation 3)
R_2	$[1-(1-\alpha)^{1/2}]$	Phase boundary-controlled reaction (contracting area)
R_3	$[1-(1-\alpha)^{1/3}]$	Phase boundary-controlled reaction (contracting volume)
D_1	α^2	One-dimensional diffusion
D_2	$(1-\alpha)\ln(1-\alpha)+\alpha$	Two-dimensional diffusion
D_3	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion (Jander equation)
D_4	$(1-\frac{2}{3}\alpha)-(1-\alpha)^{2/3}$	Three-dimensional diffusion (Gingstling-Brounshtein equation)
F_1	$-\ln(1-\alpha)$	Random nucleation with one nuclei on the individual particle
F_2	$1/(1-\alpha)-1$	Random nucleation with two nuclei on the individual particle
F_3	$1/(1-\alpha)^2-1$	Random nucleation with three nuclei on the individual particle

3.6 Chapter summary

In this chapter, an outline of the experimental procedure used for the synthesis and characterization of the hyperbranched polymers as well as their linear precursors has been given. A summary of the procedure used is also presented in Figure 3.5.

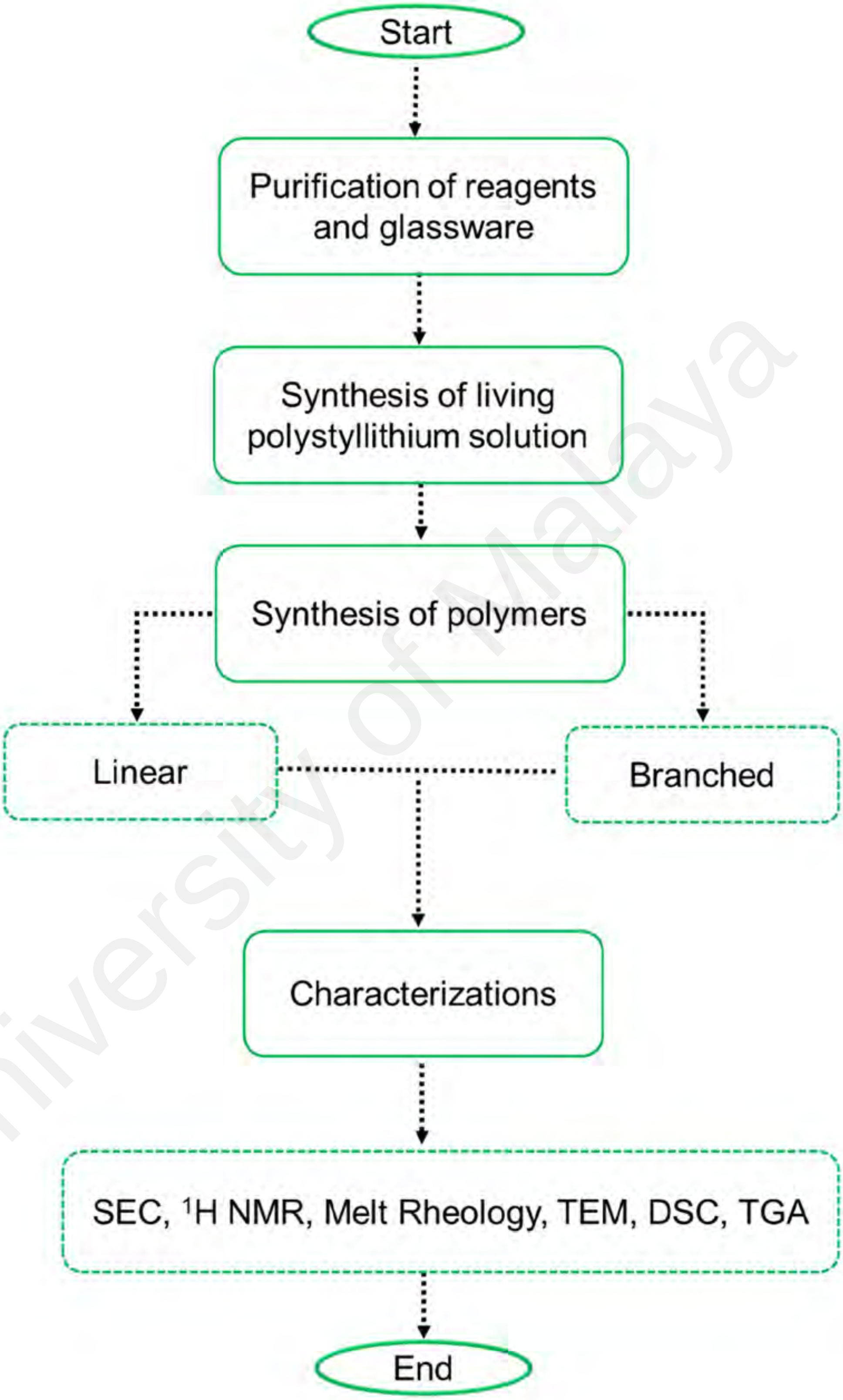


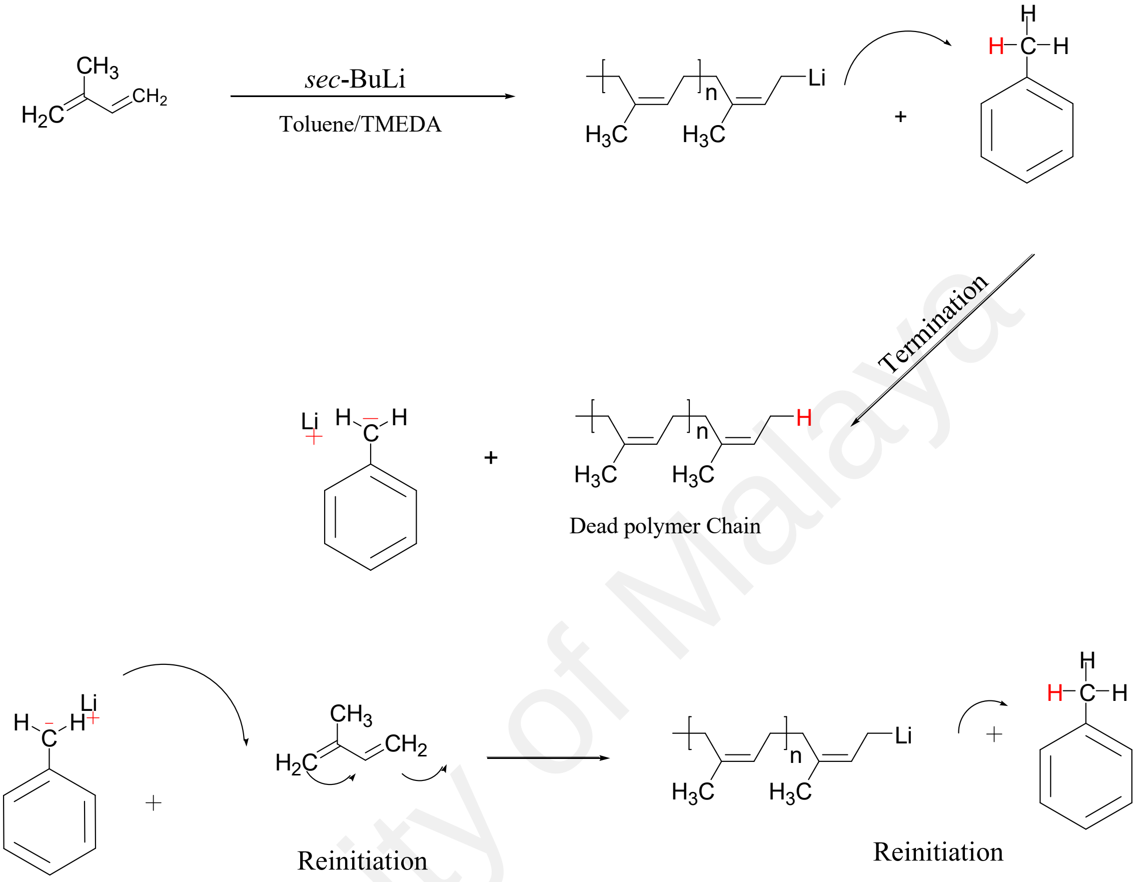
Figure 3.5: Summary of the experimental procedure

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

It is well-known that the type of solvent used strongly affects the anionic polymerization of diene monomers such as butadiene and isoprene. Moreover, the addition of Lewis bases such as TMEDA in a system containing lithium as a counter ion results in the formation of uncontrolled polymeric product with high dispersity index due to chain transfer reaction under appropriate conditions (Liu *et al.*, 2016). For example, when butadiene was polymerized in toluene at 40 °C in the presence of TMEDA, polymer with broad molecular weight and low 1,4–microstructure were obtained. (Hsieh & Quirk, 1996; Kraus *et al.*, 1967). However, due to the scarcity of reliable information on the effectiveness of the chain transfer process, the behavior of isoprene in toluene was initially investigated without the addition of the branching comonomer. Six linear samples (L1–L6) with varying amount of polar modifier were prepared (Table 4.1). These polymer samples were obtained in good yield (> 85%), and there was a remarkable decrease in the molecular weight as well as an increase in the dispersity index as the level of TMEDA/Li increases. The anionic polymerization of isoprene in toluene proceeds with chain transfer to solvent as depicted in Scheme 4.1, and the presence Lewis base, N,N,N'N'-tetramethylethylenediamine enhanced the chain transfer (Hsieh & Quirk, 1996).

The chain transfer process takes place in two stages, termination of the growing polymer chain followed by re-initiation. Since the point at which gelation occurs depend upon the polymer chain length as well as the crosslink density, in the absence of the termination, the polymerization would proceed with gel formation. Therefore, the termination stage of the chain transfer process serves to reduce the polymer chain length before it reaches the point of gelation. Figure 4.1 presents the molecular weight distribution curves for the linear samples, L1–L6. The curves were remarkably similar in their distribution and broadened with an increase in the amount of TMEDA.



Scheme 4.1 Mechanism of chain transfer to toluene in anionic polymerization of isoprene

Although there is no apparent systematic trend in the molar mass distribution of these linear polymers, the level of TMEDA used has an influence on the molar mass distributions. The branched polymers were synthesized with varying ratios of TMEDA/Li to understand the effect of the chain transfer process. The TMEDA/Li was varied from 0.5 to 2.0 to promote the chain transfer and obtain a favorable 1, 4-microstructure of the resulting branched polymer.

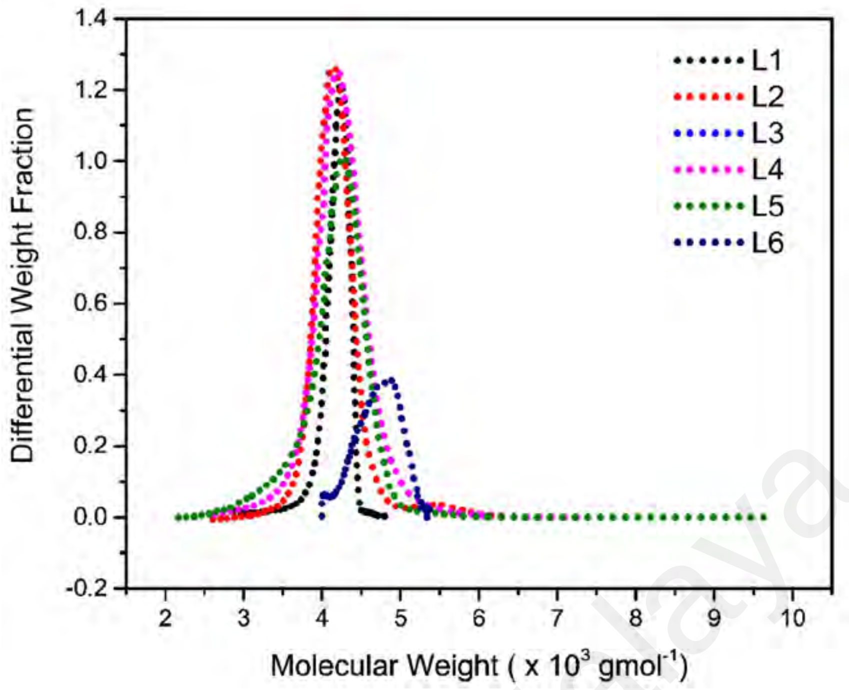


Figure 4.1: Molecular weight distribution curves for linear polymers prepared with varying amounts of TMEDA/Li: L1 (0); L2 (0.5); L3 (1); L4 (0.5); L5 (1.5); L6 (2)

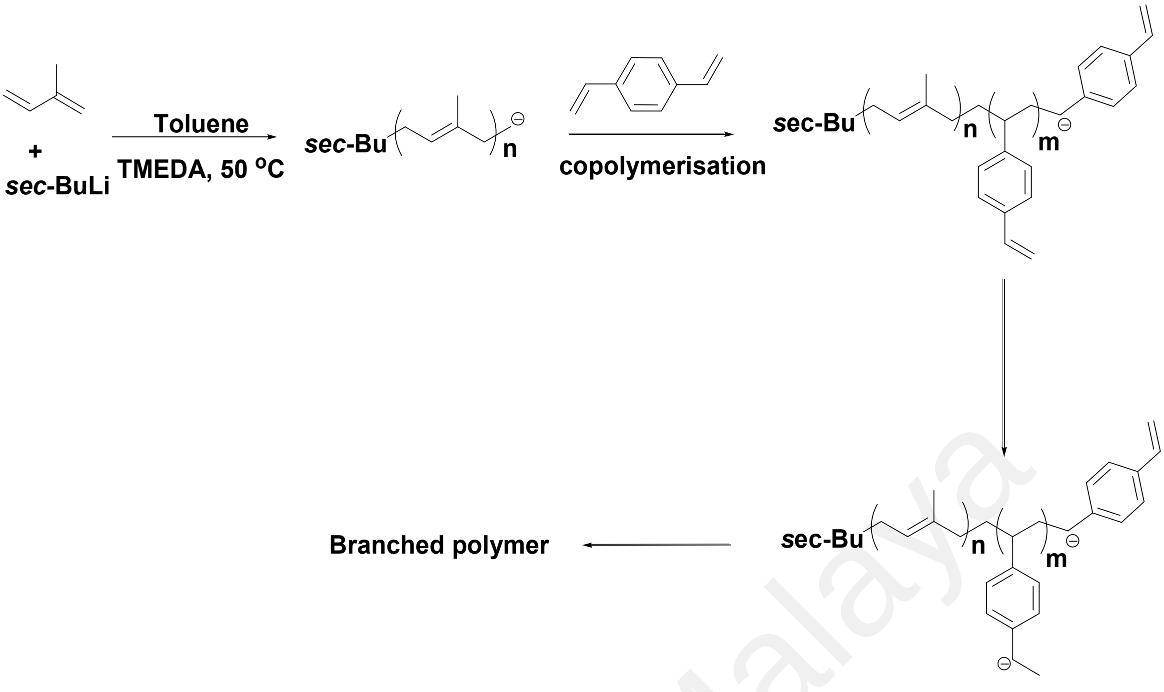
4.2 Synthesis of branched polymer

Copolymerization of isoprene and divinylbenzene was carried out to produce branched polyisoprene. Polymers were obtained in good yield (>85 %), and various ratios of TMEDA were employed for different DVB/Li ratios. The results of copolymerization of isoprene and divinylbenzene are summarized in Table 2, and the proposed branching mechanism is presented in Scheme 4.2.

Table 4.1: Synthesis and molecular characterization of linear polyisoprene

Sample	TMEDA/Li	M_n (g/mol)	Đ	Yield (%)[a]	Microstructure 1, 4 (%)	Microstructure 3, 4 (%)
L1	0	19,100	1.04	91	92	08
L2	0.5	11,300	2.1	92	11	79
L3	1	9,300	2.25	75	21	55
L4	0.5	57,500	1.88	84	12	78
L5	1.5	7,300	3.05	94	12	71
L6	2.0	9,700	5.04	72	09	67

[a] Calculated based on the amount of monomer used and the polymer product obtained using the formula: $Percentage\ yield = \frac{Experimental yield}{Theoretical yield}\ x\ 100$



Scheme 4.2 Proposed mechanism of formation of branched polyisoprene

4.3 Triple detection size exclusion chromatography

To illustrate the branching nature of the branched polymers (Table 4.2), their elution properties were compared with those of a linear sample L4 that was prepared with a TMEDA/Li ratio of 0.5 and Mw of 108,200 gmol^{-1}. Various amounts of TMEDA were used to prevent gelation in the synthesis of the branched polymers. All the branched polymers possess higher values of Mw than those of the linear ones.

It is evident from Fig. 2, 3, and 4 that the molar mass distributions (Đ) of the branched samples were broader when compared to the linear samples. Moreover, there were manifestations of multimodal spreading, and this is consistent with polymer samples having a randomly branched architecture (Baudry & Sherrington, 2006b; Michael Chisholm *et al.*, 2009; Graham *et al.*, 2007; Isaure *et al.*, 2004; Isaure *et al.*, 2003; O'brien *et al.*, 2000).

Table 4.2: Synthesis and molecular characterizations of branched polyisoprene

						PI-Microstructure					
Sample	**DVB: Li**	**TMEDA: Li**	***M_n* (g/mol)**	***Đ***	**Yield (%)[a]**	**1, 4 (%)**	**3, 4 (%)**	***$[\eta]_{hyper}$* (dlg^{-1})[b]**	***$[\eta]_{linear}$* (dlg^{-1})[c]**	**g'[d]**	**T_g[e]**
B1	1.0	1.0	86,800	2.49	98	14	57	0.5324	1.477	0.36	-14.85
B2	1.0	1.5	54,500	1.37	97	17	73	0.2802	0.658	0.43	-15.62
B3	1.0	0.5	17,900	2.04	89	18	72	0.2404	0.400	0.60	-19.53
B4	1.2	1.2	21,900	1.54	85	08	70	0.377	0.4272	0.88	-16.57
B5	1.2	1.5	34,800	6.51	82	11	60	0.4802	1.527	0.31	-12.06
B6	1.2	1.0	19,800	1.99	88	09	81	0.1896	0.424	0.45	-16.12
B7	2.0	1.5	17,500	3.17	78	14	76	0.313	0.542	0.58	-24.41
B8	2.0	0.5	79,600	3.88	85	16	77	0.724	1.917	0.38	-27.17
B9	3.0	1.0	141,600	2.19	98	15	67	0.2871	1.926	0.15	-9.52
B10	3.0	1.5	16,900	6.39	86	12	70	0.3151	0.885	0.36	-23.28
B11[f]	3.8	2.0	–	–	~100	–	–	–	–	–	–
B12[f]	4.2	0.8	–	–	~100	–	–	–	–	–	–
B13	2.0	1.5	82,400	1.87	~100	15	78	0.4811	1.149	0.42	–20.03

[a] Calculated based on the amount of monomer used and the polymer product obtained using the formula: *Percentage yield* = $\frac{\boldsymbol{Experimental yield}}{\boldsymbol{Theoretical yield}}$ *x 100.* [b] Measured by SEC in THF at 35°C. [c] Calculated using Mark-Houwink-Sakurada equation: $[\eta]lin = K M_w^{\alpha}$; $K = 0.000177\ dlg^{-1}$, $\alpha = 0.735\ dlg^{-1}$. [d] $g' = [\eta]hyper / [\eta]lin$. [e] Measured by DSC. [f] formed an insoluble gel.

It is clear that these branched polyisoprenes are complex both regarding molar mass and architectural distributions. It is evident from Figure 4.2 (a) (DVB/Li = 1), 4.3 (a) (DVB/Li = 2) and 4.4 (a) (DVB/Li = 3) that the branched samples possess broader distributions compared to the linear polymer. The molecular weight versus elution volume plots in Figure 4.2 (b), 4.3 (b), and 4.4 (b) all showed the branched samples at the upper right with respect to linear counterparts; this signifies the branched nature of these polymers once more. Similar observations were reported by other researchers (Baudry & Sherrington, 2006b; Chisholm *et al.*, 2009; Graham *et al.*, 2007; Hirao *et al.*, 2011; Isaure *et al.*, 2004; Isaure *et al.*, 2003; O'brien *et al.*, 2000). Furthermore, upon increasing the DVB ratio from 1 to 3, the gap between the linear and the branched samples on the molecular weight vs. elution volume plot becomes wider to indicate higher levels of branching (Baudry & Sherrington, 2006b; Michael Chisholm *et al.*, 2009).

The contraction factor, g that is the ratio of the mean square radius of gyration of the branched sample to that of the linear sample of the same molecular weight is one of the standard measures of polymer branching (Chisholm *et al.*, 2009; Zimm & Stockmayer, 1949). Since branched polymers are expected to be more compact than their linear counterparts of the same molecular weights, the g' value is unity for the linear polymers and decreases with the increase in the degree of branching.

The root-mean-square radius (RMS) of gyration could be measured by SEC coupled with light scattering detector. However, low molecular weight polymers have weak scattering, and it is, therefore, challenging to obtain a useful data for polymers with RMS radii ≤ 10–15 nm as reported by other researchers (Chisholm *et al.*, 2009; Grcev *et al.*, 2004). This, indeed a constraint, applies to most of the polymers synthesized in the present study. However, at an appropriately high molecular weight, some information could be derived. Comparing the molecular weights and RMS radii data of the linear sample L4 and the branched B9 having the highest molecular weights in their particular sets (Figure 4.5), reveals that the linear sample has larger radii than the branched polymer sample at any given molecular weight slice. A similar observation was reported by others (Michael Chisholm *et al.*, 2009; Graham *et al.*, 2007). A closer look at the polymerization composition reveals the formation of soluble branched polymers with up to DVB/Li ratios of up to 3.0 that is, three units of DVB molecules for every initiator fragment. Attempt to synthesize branched polymer with a DVB ratio of 3.8 resulted in the formation of cross-linked polymer even when the TMEDA/Li ratio was 2.0.

Usually, vinyl copolymerization involving divinyl benzene proceeds with crosslinking and gel formation even at an early stage of the polymerization. However, under appropriate conditions, soluble branched polymers could be obtained in the anionic polymerizations involving divinylbenzene or another multifunctional comonomer (Tanaka *et al.*, 2012). The solubility of the polymer formed is attributed to the fact that pendant vinyl groups in the polymer chain are much lower in reactivity than the vinyl group of the divinylbenzene. The chain transfer reaction may precede the pendant vinyl group attack by the chain end anion that would otherwise lead to crosslinking and gel formation. Dissimilarity in reactivity between the vinyl groups in divinylbenzene and other monomers was reported by a kinetic study of the model compounds (Shibasaki & Nakahara, 1979; Tanaka *et al.*, 2012). However, crosslinking may occur at the final stage of the polymerization, resulting in the formation of an insoluble gel.

Formation of soluble polymers in anionic polymerization involving divinylbenzene and lithium diisopropylamine was reported (Tsuruta, 1985), and it was suggested that the excess diisopropylamine would stabilize the chain-end carbanion thereby rendering it inactive towards the pendant double bonds. Similarly, chain end anions may be rendered more reactive in the presence of TMEDA due to the strong coordination between the Li^+ and TMEDA molecules thereby shifting the carbanionic chain end bearing the Li^+ to a highly reactive solvent-separated ion pair. Consequently, the system would be changed to non-living and the molecular weight of the resulting polymer would be different from the predicted by the ratio of the monomer–initiator (Voit & Lederer, 2009).

4.4 Effect of TMEDA on polyisoprene microstructure

Generally, when polymerizing isoprene, 3 types of isomeric microstructures are possible, 1,4–, 1,2– and 3,4– isomeric units (Scheme 4.3).

Polyisoprene produced by anionic polymerization using Li initiator has a high 1, 4– content (> 90%) analogous to natural rubber. That leads to the growth of the commercial importance of anionic polymerization (Baskaran & Muller, 2009). However, the addition of polar solvents especially THF to hydrocarbon media can drastically alter the microstructure from the high 1,4– to mainly 3,4– and some 1,2– units. Similarly, the addition of Lewis bases such as TMEDA, even in small amounts can significantly alter the microstructure (Agostini, 2014b). Four different combinations of TMEDA/initiator ratios were used in this study.

All polymerisations were achieved at a constant temperature of 50 °C; this ruled out the effect of temperature on the microstructure of polyisoprene (Kozak & Matlengiewicz, 2015a, 2015b, 2015c, 2015d; Uraneck, 1971).

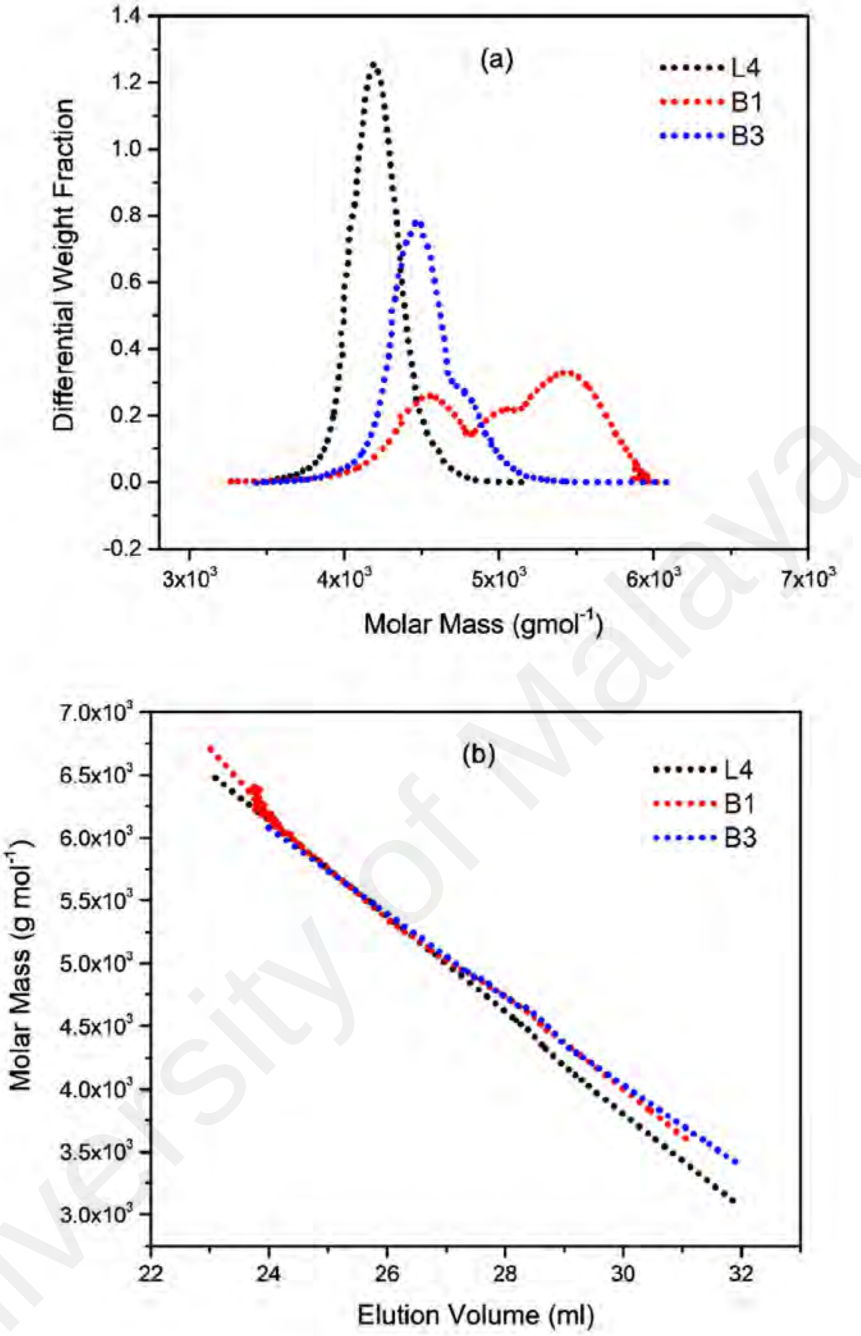


Figure 4.2: (a) Molar weight distribution curves; and (b) Molecular weight–elution volume plots for L4 (no DVB), B1 and B3 (DVB/Li = 1)

The content of isoprene isomeric units in the polymers synthesized was determined using ^{1}H NMR data (Table 4.2). According to the literature, the characteristic peaks of the alkene protons of the polyisoprene components exist in the range of 4.5–5.5 ppm. The peaks corresponding to 1,4–microstructure are visible at δ 5–5.2 ppm[$(CH_3)C{=}CH$], and those corresponding to 3,4–microstructure are found at δ 4.6–4.8 ppm [$(CH_3)C=CH_2$] (Agostini, 2014b; Shibasaki & Nakahara, 1979).

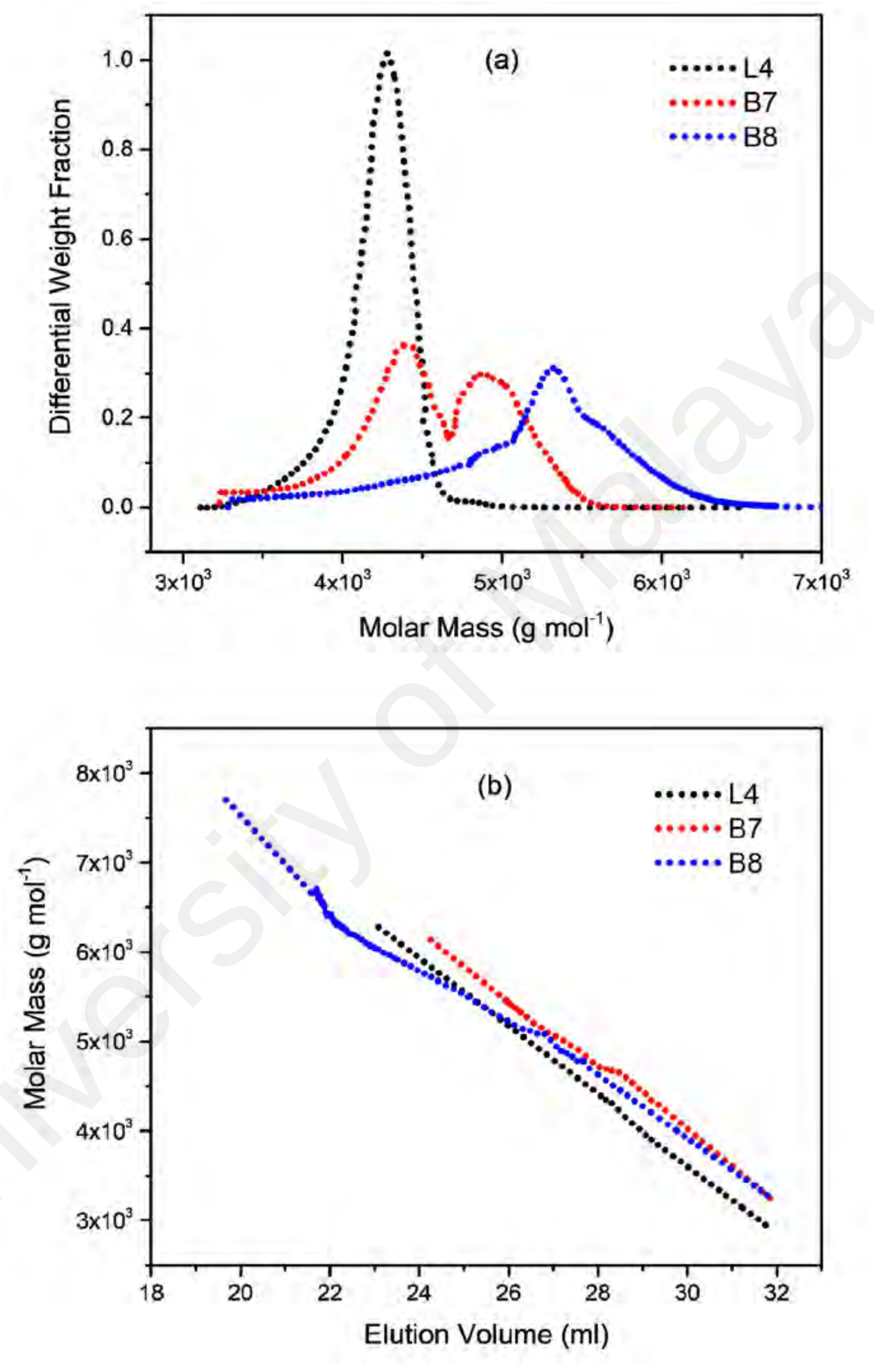


Figure 4.3: (a) Molecular weight distribution curves; and (b) Molecular weight–elution volume plots for L4 (no DVB), B7 and B8 (DVB/Li = 2)

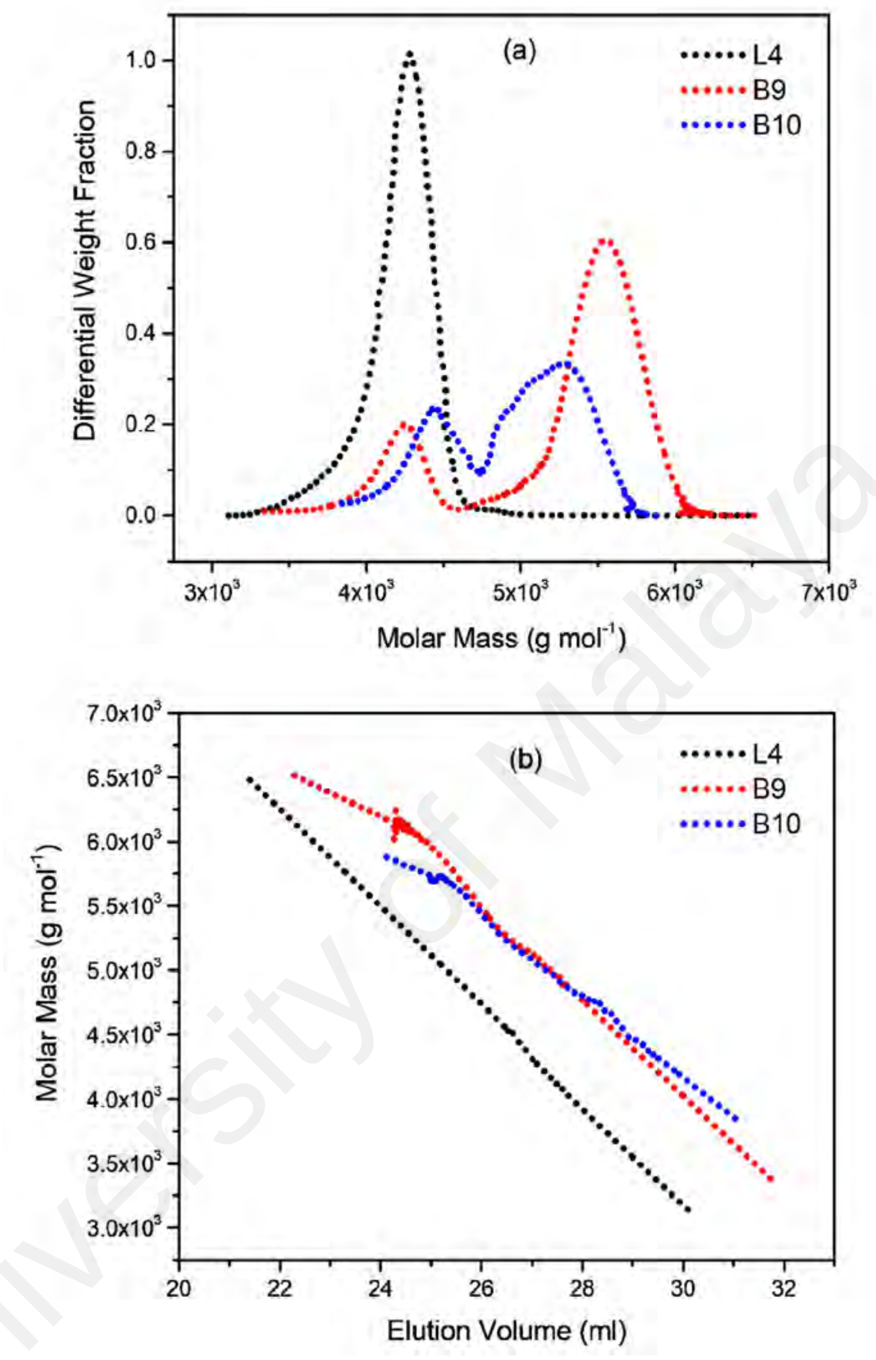


Figure 4.4: (a) Molecular weight distribution curves; and (b) Molecular weight–elution volume plots for L4 (no DVB), B9 and B10 (DVB/Li = 3)

The content of isoprene isomeric units in the polymers synthesized was determined using ^{1}H NMR data (Table 4.2). The percentage of 1,4–, 3,4– and 1,2–microstructural isomers in the polymer was calculated using the following equations:

$$I_{total} = I_{14} + I_{34} + I_{12} \qquad \mathbf{4.1}$$

where I is the total integrated peak area, $I_{1,4}$ $I_{3,4}$ and $I_{1,2}$ are the integrated peak areas of the 1,4–, 3,4– and 1,2– protons respectively (Burel *et al.,* 2011). Therefore,

$$\%\ 1{,}4\text{–microstructure} = \frac{I_{14}}{I_{total}} x100 \qquad \mathbf{4.2}$$

$$\%\ 3{,}4\text{–microstructure} = \frac{I_{34}}{I_{total}} x100 \qquad \mathbf{4.3}$$

$$\%\ 1{,}2\text{–microstructure} = \frac{I_{12}}{I_{total}} x100 \qquad \mathbf{4.4}$$

According to the literature, the characteristic peaks of the alkene protons of the polyisoprene components exist in the range of 4.5–5.5 ppm. The peaks corresponding to 1,4-microstructure are visible at δ 5–5.2 ppm[$(CH_3)C{=}CH$], and those corresponding to 3,4–microstructure are found at δ 4.6–4.8 ppm [$(CH_3)C{=}CH_2$] (Agostini, 2014b; Shibasaki & Nakahara, 1979). It was observed that the addition of TMEDA resulted in a shift in the microstructure from the mainly 1,4–microstructure to pre-dominantly 3, 4-microstructure (Figure 4.6).

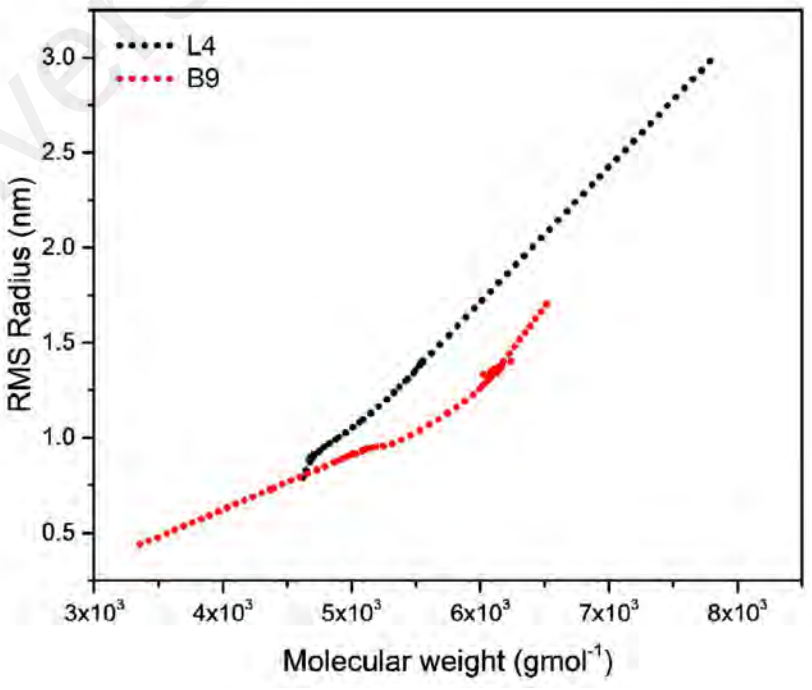
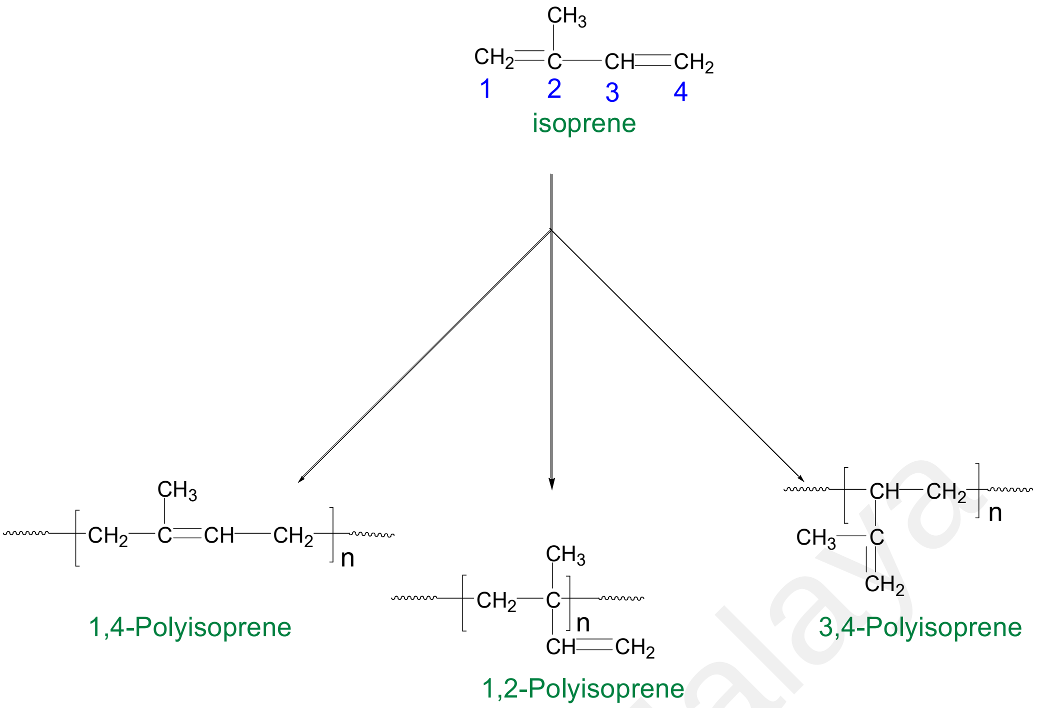


Figure 4.5: Root mean square radii of gyration versus molar mass for L4 and B9



Scheme 4.3 Microstructure of polyisoprene

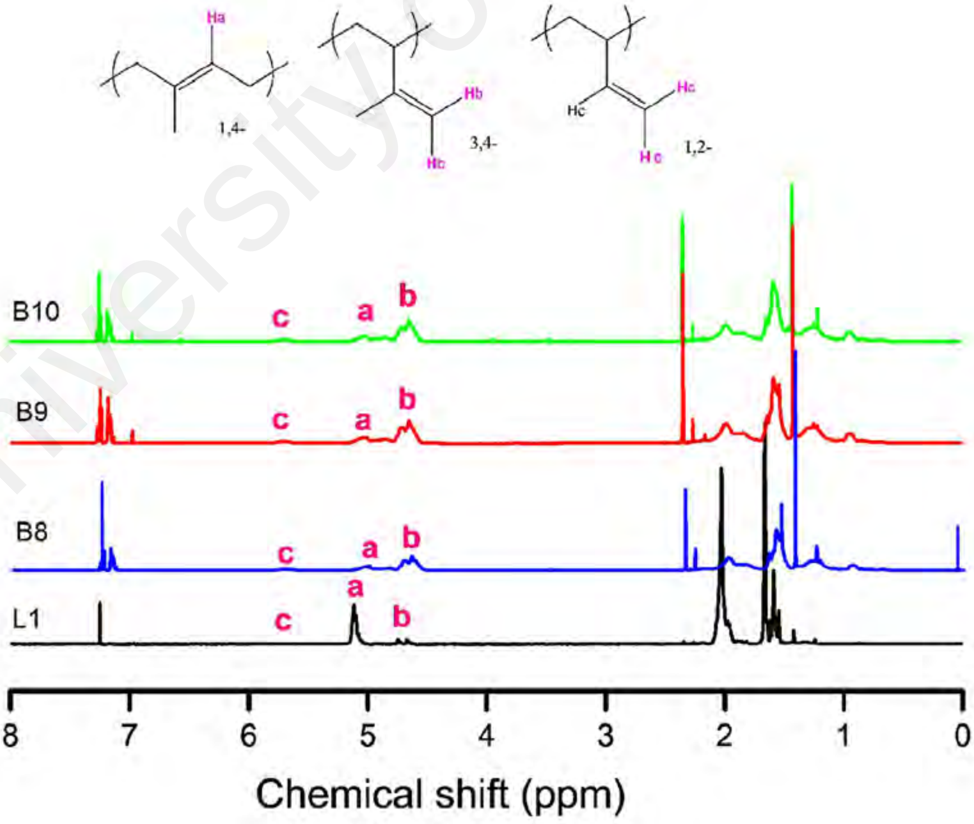


Figure 4.6: ¹HNMR 400MHz, $CDCl_3$, δ,) spectra of branched polymers prepared with different TMEDA/Li ratios

4.5 Melt rheological characteristics

In addition to their solution properties, the melt rheological behavior of branched polymers is one of their most essential features. Melt rheological properties of polymers are known to be influenced by three crucial molecular structural parameters for instance; molecular architecture (degree of branching), molecular weight as well as molecular weight distribution (Chisholm *et al.*, 2009; Janzen & Colby, 1999; Ren *et al.*, 2016; Wood-Adams *et al.*, 2000).

Linear oscillatory experiments were performed in an Anton Paar MCR 301 rheometer, and there was a strong relation between the melt rheological properties and the degree of branching of the branched polymers. Figure 4.7 shows the complex viscosity, η*, storage modulus, G', and loss modulus G", for (a) linear (L4) and (b) branched (B10) polymers respectively. It could be seen that the y-axis for L4 almost covers the range from 10^1– 10^5 Pa whereas for B10 it ranged from 10^{-1} and extended to slightly above 10^4 Pa. There is a decrease in the complex viscosity at high frequency for both the linear and branched samples which is a typical shear thinning behavior. The shear thinning behavior indicates the pseudoplastic behavior of the melt at this temperature. The complex viscosity, η* for the linear sample L4 was considerably higher than that of the branched sample B10, this is related to the nature of the molecular chains. Figure 4.7 (b) represents a typical curve for the branched polymers. The storage modulus, G' is a measure of the elasticity of materials, at low frequencies, the G' varies with frequency in approximately quadratic fashion for L4 but almost linearly for the branched sample, B10. However, at high frequency, there is a slight elastic rubber plateau in the case of linear sample L4 due to polymer chain entanglements (Doi & Edwards, 1978; Ren *et al.*, 2016). Meanwhile the loss modulus, G" reveals the viscous nature of the material which dominates and varies linearly with frequency for both the linear and branched samples. The G" indicates the energy lost to the viscous deformation in the course of the deformation of materials; it reveals the viscosity of materials. The higher the G'' value, the higher the viscosity of the polymer.

Polyisoprene possesses a flexible polymer backbone; it is easy for the linear samples with a long chain to entangle and prevents reorientation of the polymer chain, while the short molecular chains of the very high degree of branching are difficult to entangle. Therefore, there is a less steric hindrance during flow process hence decrease in complex viscosity for the highly branched samples.

Figure 4.8 shows the dependence of shear rate viscosity on molecular weight, Mw. The complex viscosity data at 1 rad s^{-1} for each branched sample were extracted at 70 °C. However, the data do not always represent the zero shear viscosity, η_0 values since they are difficult to obtain experimentally with reasonable accuracy. Nevertheless, it is useful for comparison. For linear polymers, the η_0 depends on the Mw if the polymer is entangled with a slope of about 3.4, as predicted by the classical Mark–Houwink–Sakurada equation: $[\eta] = KM^a$ (Chisholm *et al.*, 2009; Kharchenko *et al.*, 2003).

As the molecular weight of the polymer increases, there is a corresponding increase in internal friction during molecular motion. Also, the thermomechanical movement of the long chain molecules causes the whole molecule to entangle thereby making the flow of the entire molecular chain more difficult at high Mw, consequently η^* increases. This entanglement is a typical feature of linear polymers (Chisholm *et al.*, 2009; Kharchenko *et al.*, 2003). However, in contrast, the relationship between the η_0 and *Mw* for the branched polymers does not follow this equation. With a very low slope of 23×10^{-4} indicating the absence of entanglement.

This observation has been earlier reported for other hyperbranched polymers and dendrimers (Chisholm *et al.*, 2009; Fréchet *et al.*, 1996; Kharchenko *et al.*, 2003; Sendijarevic *et al.*, 2001).

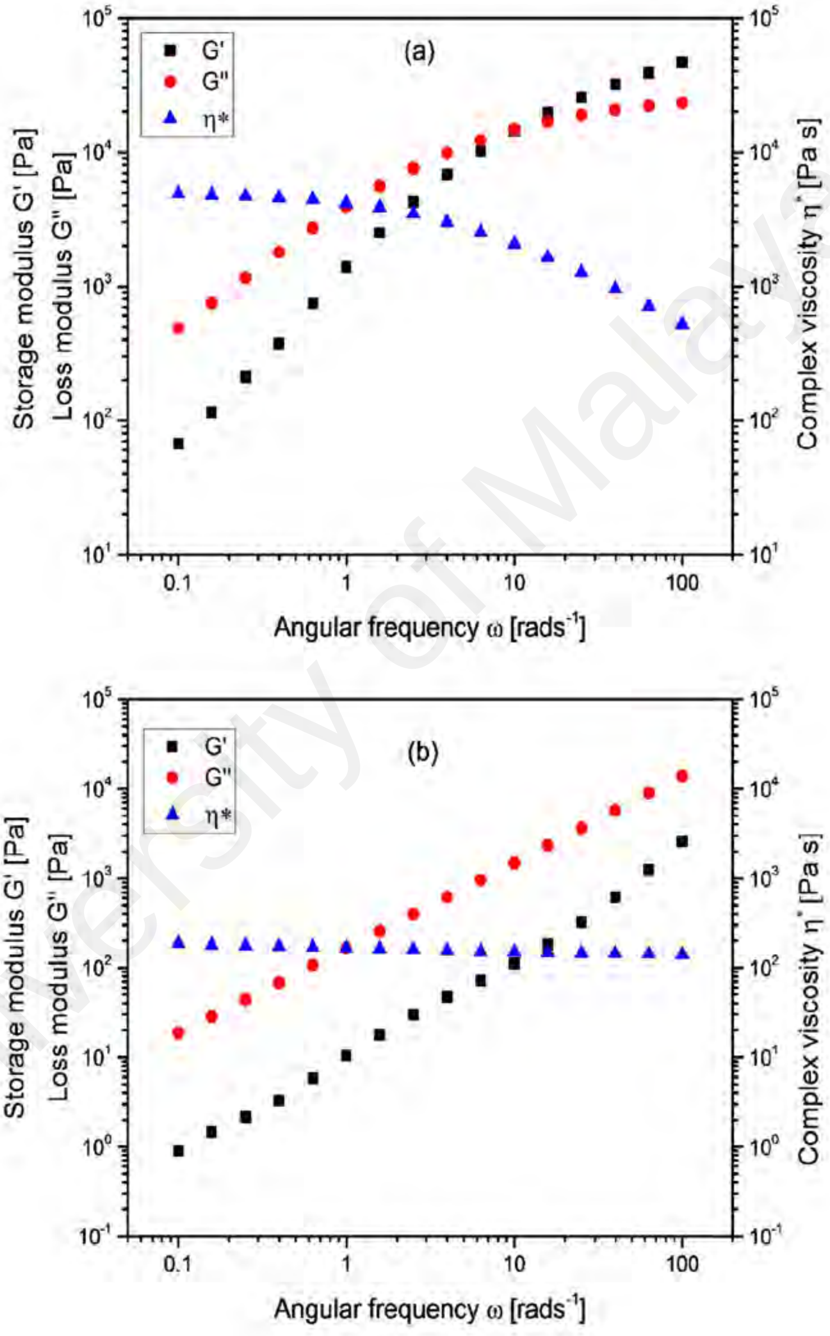


Figure 4.7: Complex viscosity (η,*) storage modulus G′, and loss modulus G″, for (a) linear, L4 and (b) branched, B10 polymers at 70 °C

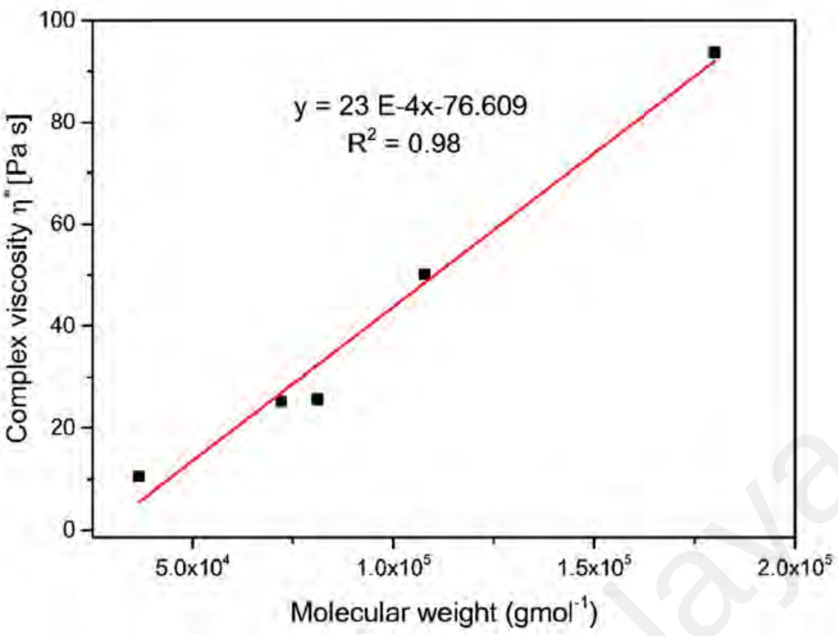


Figure 4.8: Complex viscosity, η* versus molecular weight, M_w for the branched polymers at 70 °C

4.6 Transmission electron microscopy (TEM)

The transmission electron microscope (TEM) has been widely used for many years to obtain information on the morphology of synthetic macromolecules.

In order to investigate the effect of the branched architecture upon the solid-state morphology and to compare with that of the linear sample, we carried out TEM analysis on the linear polymer (L4) and two branched polymers (B1 and B9). The investigation was carried out using high-resolution transmission electron microscopy (HRTEM), and the samples were prepared for imaging by cryo-ultramicrotomy. Typical data are shown in Figure 4.9 (a), (b) and (c) for the L4, B1, and B9 respectively. From the Figure, it is clear that the composition affects the morphology of these polymers. The increase in branching results in a less well-ordered morphology. It can be seen that the linear polymer shows a high degree of long-range order as expected (M. Matsen, 2000). However, the morphology of the branched polymers is dramatically different but, we can see some level of long-range order for the branched sample B1 which is entirely absent in the case of sample B9 Figure 4.9 (c).

Differences in degree of branching between these polymer samples have a role to play in the morphologies of these polymers. Highly branched architecture frustrates and inhibits any long-range order (Zhu *et al.*, 2006). A similar decrease in the long-range order was observed upon introduction of branched points into 'barbed wires' built from polystyrene arms and polyisoprene backbones. Beyer *et al.,* reported a similar observation of disordered morphologies in highly branched multigraft copolymers (Beyer *et al.*, 2000; Mays *et al.*, 2004; Staudinger *et al.*, 2006; Uhrig *et al.*, 2011; Weidisch *et al.*, 2001; Zhu *et al.*, 2006). Disordered morphology, could also occur due to the high dispersity of polymers (Uhrig & Mays, 2011; Wang *et al.*, 2015). Also, the results reported in the present study agree with those obtained previously by Hutchings (Hutchings *et al.*, 2015) where a similar change in morphology was observed due to the conversion of macromonomer into hyperblock.

It was established that irrespective of the molecular weight or structure of the linear precursor, the resulting branched polymer show the absence of long-range lattice order due to the branching architecture which impedes the development of defined long-range lattice order (Beyer *et al.*, 1997; Chiang, *et al.*, 2008; Hutchings *et al.*, 2015; Hutchings *et al.*, 2009; Matsen & Bates, 1996; Milner, 1994; Yang *et al.*, 2001; Zhu *et al.*, 2003).

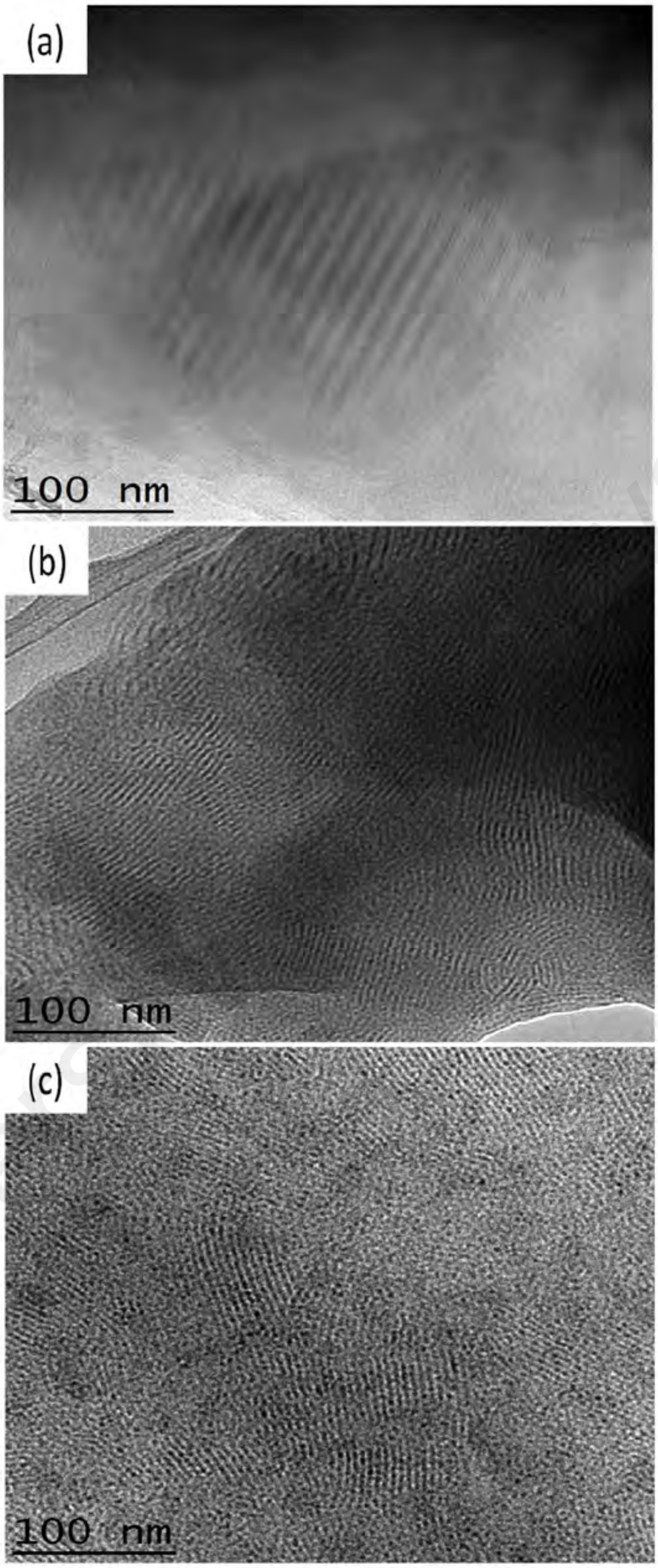


Figure 4.9: TEM images of (a) linear (L4: M_n = 57,500 gmol^{-1}, Đ = 1.88), (b) branched (B1: M_n = 86,800 gmol^{-1}, Đ = 2.49, DVB/Li = 1.0, g' = 0.36) and (c) branched (B9: (M_n = 141,600 gmol^{-1}, Đ = 2.19, DVB/Li = 3.0, g' = 0.15)

4.7 Differential scanning calorimetry (DSC)

DSC was the technique employed to determine the glass transition temperature (T_g) of the polymers.

T_g provides information about the mobility or rigidity of polymers. T_g also provides a temperature range of practical application, processing conditions as well as identification and comparison. The T_g values for the branched polymers were listed in Table 4.2 and ranged from –27.74 to –9.52 °C. The least values were obtained for the DVB–Li ratio of 2. The glass transition temperature is known to be affected by several factors that are related to the chemical structure of polymers. These factors include the molecular weight, the flexibility of the backbone, the molecular structure, as well as the existence of branching in a polymer (Cowie & Arrighi, 2007). In the case of polyisoprene, the microstructure also seems to play a significant role, and therefore different microstructures result in different T_g values (Widmaier & Meyer, 1981). Living anionic polymerization of isoprene in non-polar solvents using lithium initiator would be expected to produce polyisoprene with over 70 % 1,4 microstructure with T_g of about –73 °C (Ellis & Smith, 2008; Hsieh & Quirk, 1996; Kroschwitz, 1990; Widmaier & Meyer, 1981). However, in the present study, 3,4– microstructure dominates due to the presence of TMEDA and this 3,4–polyisoprene will cause an increase in the T_g of the resulting polymer. Parameters such as solvents, metal counterion as well as the presence of a Lewis base are known to strongly influence the microstructure of isoprene (Agostini, 2014). The use of lithium as counterion in the anionic polymerization of polyisoprene, results in the formation of polyisoprene with high 1,4– content (up to 90 %). Polydienes with high 1,4– microstructure possess low T_g values. However, when the polymerisation is conducted in a polar solvent or when a polar additive is added to a polymerization system involving non-polar solvent, the microstructure of the resulting diene is dramatically affected. The addition of Lewis base such as TMEDA, causes a change in the chain end configuration, the charge distribution as well as the distribution of contact ion pairs which govern the microstructure of the resulting polymer. Hence, in the presence of TMEDA, the 1,4– microstructure disappears and 3,4– or 1,2– microstructure dominate. Moreover, the mobility of the polymer backbone has a significant influence on the T_g of polymer, and this is primarily determined by the chemical composition and spatial structure. For example, the presence of aromatic rings hinders the free rotation of the polymeric chains. Hence, more thermal energy is required for chain mobility, and T_g increases. For highly branched polymers, several cooperative interactions are responsible for the variation of glass transition temperature. As the degree of branching increased the mobility of the molecular chain decreases due to the increase in compactness of the spatial distribution of the molecular structure. The increase in the degree of branching, at the same time, can cause an increase in the molecular mobility due to an increase in the free volume of the molecular chains (Ren *et al.*, 2016; Zhu *et al.*, 2009; Zhu *et al.*, 2011). As can be seen in Table 2, samples B7, B8 and B10 having the lowest g’ possess the lowest T_g values. Sample B9, on the other hand, has the highest T_g values possibly due to the high molecular weight as well as high DVB content.

4.8 Thermal degradation characteristics of branched polymers

Thermogravimetric analysis has been proved a valuable analytical method for the evaluation of the thermal stability of materials such as polymeric materials, copolymers, polymer blends, and polymer composites. This is because thermal property should be given special consideration when it comes to processing and usage of polymeric materials. Because upon heating a polymeric material, polymer breakdown and/or crosslinking can occur. Therefore, to understand the effect of DVB content on the thermal stability of branched polyisoprene, TGA analysis was employed to investigate the thermal degradation process of the branched polymers prepared.

Table 4.3: Thermal decomposition characteristics for the hyperbranched polyisoprene

Sample	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	$T_{70\%}$ (°C)	T_{max} (°C)	Residue at 580 °C
B3	388	427	444	444	1.34 %
B13	353	417	441	446	1.14 %
B10	377	423	442	445	0.8 %

TGA thermograms show the weight percentage of the experimental materials as a function of temperature. Initial degradation temperature, final decomposition temperature, and residual mass can be measured directly from the weight loss curve. Figure 4.10 (a) shows a typical TG curve obtained from the pyrolysis of branched polymers containing DVB: Li of 1, 2, and 3 at a heating rate of 15 °C min^{-1}. It showed that the DVB content and the molecular weight distribution affect the thermal stability of these branched polymers.

The thermal stability of the polymers improves with an increase in molecular weight. However, an increase in the dispersity lowers the thermal stability of these polymers (Yang *et al.*, 2003). The low molecular weight components of the more disperse samples could be the possible reason for the lower thermal stability of B10 compared to B13. It could be seen from Figure 4.10 that after about 580 °C, over 98 % conversion was achieved and there was less 2 % residue left in all the three samples.

The temperature of maximum decomposition (T_{max}) appears at 440 °C for B3 (DVB/Li = 1.0, Mw = 36,615 g mol^{-1}, Đ = 2.04) while for B13, (DVB/Li = 2.0, Mw = 153,913 g mol^{-1} Đ = 1.87) appeared at about 446 °C and that of B10 (DVB/Li = 3.0, Mw = 107,851 g mol^{-1} Đ = 6.39) was about 445 °C. Details of values are given in Table 4.3.

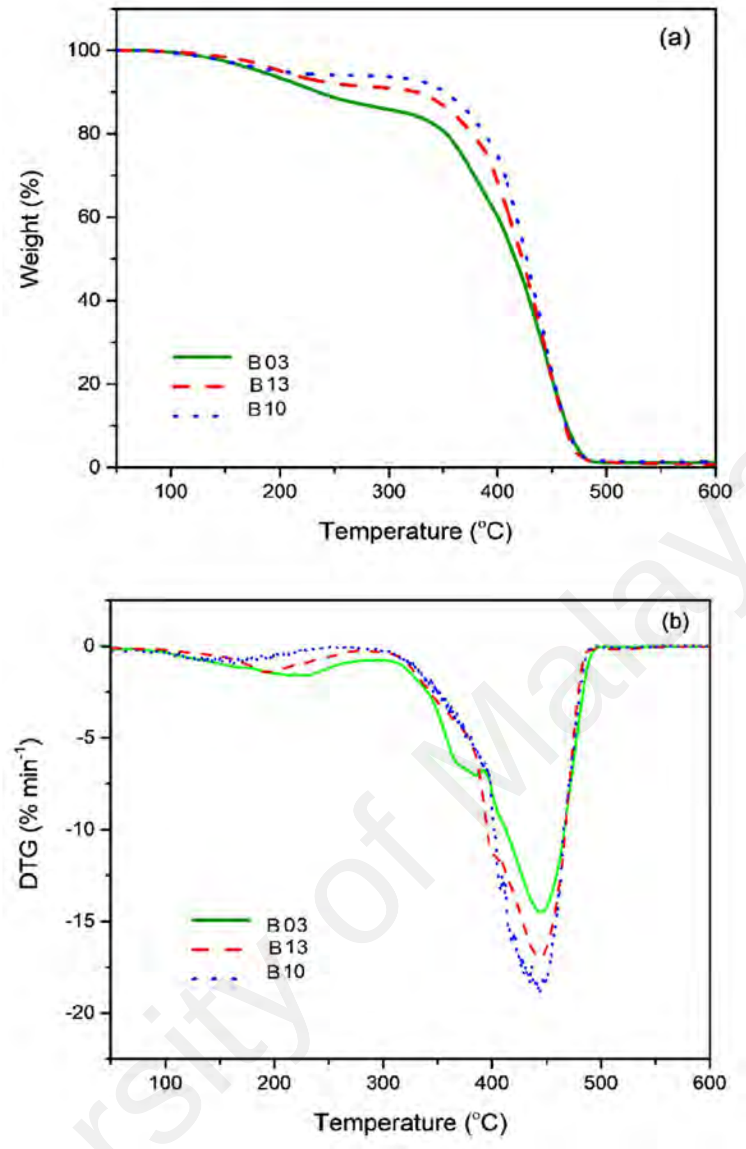


Figure 4.10: TGA (a) and DTG (b) curves at 15 °C min^{-1} for B03, B13, and B10

Moreover, at higher heating rates, there is a delay in the degradation process and the curves shift to higher temperatures as depicted by Figure 4.11.

4.9 Kinetics of thermal degradation of branched polymers

The TGA experiments with heating rates of 2, 5, 10, and 15 °C min^{-1} were conducted to investigate the thermal degradation kinetics of the highly branched polymers (B3, B13, B10) containing 1, 2, and 3 DVB: Li respectively. The most commonly used isoconversional methods in the study of thermal degradation kinetics include: The Kissinger, Friedman, Coats–Redfern, Flynn–Wall–Ozawa (FWO), Kissinger–Akahira–Sunose (KAS), as well as the Vyazokin's advanced isoconversional (AIC) (Chrissafis *et al.*, 2010; Vyazovkin, 2017). In this study, four different model-free methods, i.e. Kissinger, Friedman, FWO, and KAS were selected to analyze the experimental results obtained from the thermal degradation kinetics due to their ability to estimate the kinetic parameters with good accuracy and simplicity (Friedman, 1964; Rajeshwari & Dey, 2014).

Figure 4.11 (a–c) shows the typical TGA curves at different β for B3, B13, and B10 respectively.

To analyze the TG data, the Kissinger method was first employed since it is independent of any thermal degradation mechanism. Equation 3.9 was used to calculate the activation energy which can be obtained from the plots of ln (β/T_{max}^{2}) against the reciprocal of temperature 1000/T_{max} (Figure 4.12). The results are presented in and Tables 4.4, 4.5, and 4.6. The values of E_a for B3, B13 and, B10 are 282.75, 271.01, and 265.79 kJ mol^{-1} respectively.

The second method used was the Friedman method that is also, a derivative method. The Friedman's technique interrelates the rate of conversion *dα/dt* with various heating rates for a given conversion. Equation 3.11 has been employed to obtain the activation energy values from the plots of ln [β *(dα/dt)*] versus 1000/T over the conversion range of α = 0.2 – 08 (Figure 4.13). The results are also summarised in Table 4.4, 4.5, and 4.6 respectively. The average activation energies were almost similar to those obtained by the Kissinger method except for B13, which was about 49 kJ higher.

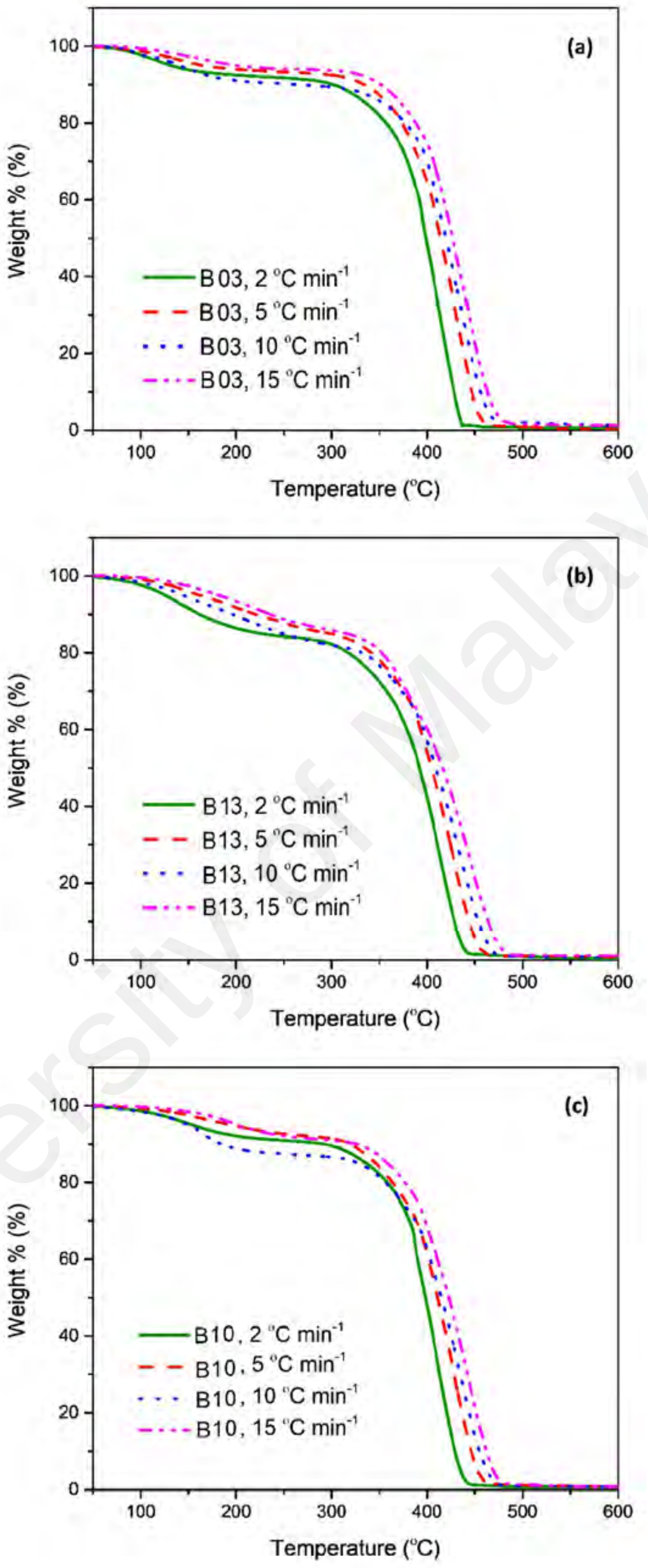


Figure 4.11: TGA curves at different heating rates for (a) B03, (b) B13 and (c) B10

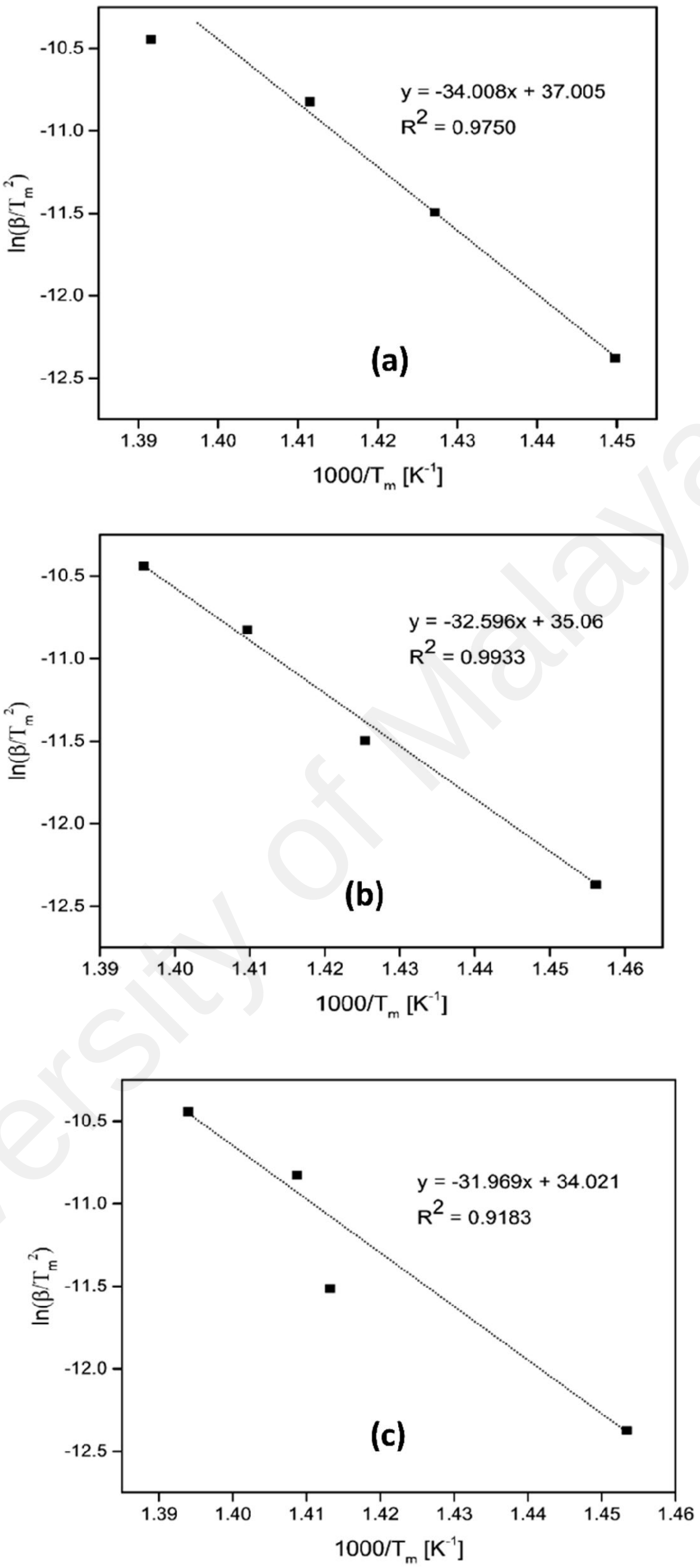


Figure 4.12: Kissinger plots (a) B3, (b) B13 and (c) B10 at various conversions *(α)*

Flynn–Wall–Ozawa method which is an integral method is a model-free method. Equation (3.12) was employed and the E_a was obtained from the plots of ln β against 1000/T for a fixed value of α. The slope equals to $-1.052Ea/R$ and the Doyle approximation was used for the integral values (Doyle, 1962; Venkatesh *et al.*, 2013). Similar values of α were used as in the case of Friedman's method. Results for the values of α between 0.2–0.8 are presented in Figure 4.14 while the activation energy values obtained are given in Tables 4.4, 4.5 and 4.6 respectively. The results for different samples show that the best fitting lines are nearly parallel for various heating rates which indicates that the activation energy values at the different extent of conversion are nearly similar. The average values of the activation energies obtained by the FWO method for B3, B13, B10 were 270.19, 309.67 and 260.15 kJ mol^{-1} respectively. Again, these values are relatively very close to those obtained by the Kissinger and Friedman methods.

Finally, the KAS method was also used to evaluate the activation energy from the experimental data obtained at different heating rates. The ln(β/T^2) versus 1000/T corresponding to different degrees of conversion (α) (0.2 – 0.8) for heating rates of 2, 5, 10, and 15 °C min^{-1} are presented in Figure 4.15 (a–c). A linear relationship is also observed by this method, and the apparent activation energy can be evaluated from slopes of straight lines with an excellent linear correlation coefficient (R^2 = 0.9127–0.9952). Tables 4.4, 4.5 and 4.6 also present the values of the activation energies obtained by the KAS method. The average values of the activation energies obtained by the KAS method for B3, B13, and B10 were 273.13, 314.65 and 262.34 kJ mol^{-1} respectively. Again, these values are very close to those obtained by the Kissinger and Friedman and FWO methods. In particular, approximately equal values of E_a were obtained by KAS and FWO methods, with slightly higher values obtained by the KAS method.

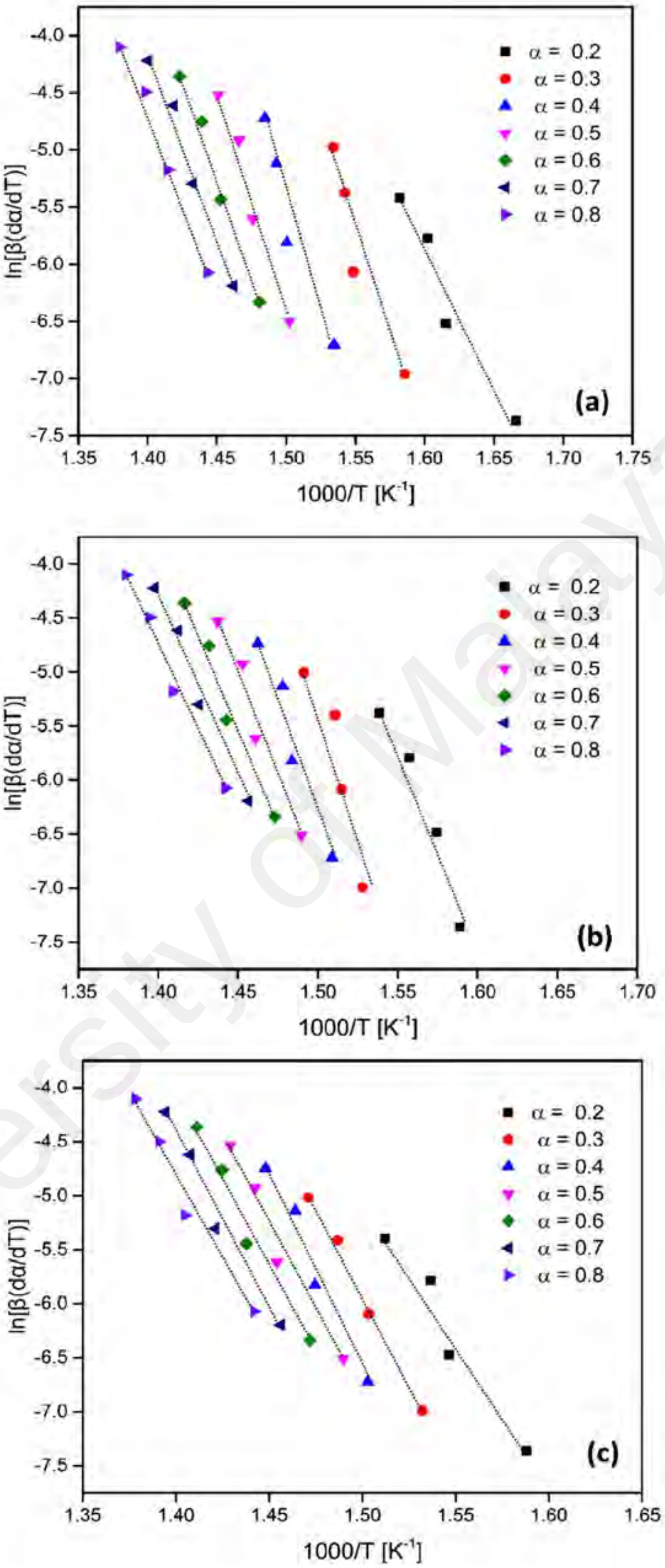


Figure 4.13: Friedman plots (a) B3, (b) B13 and (c) B10 at various conversions ***(α)***

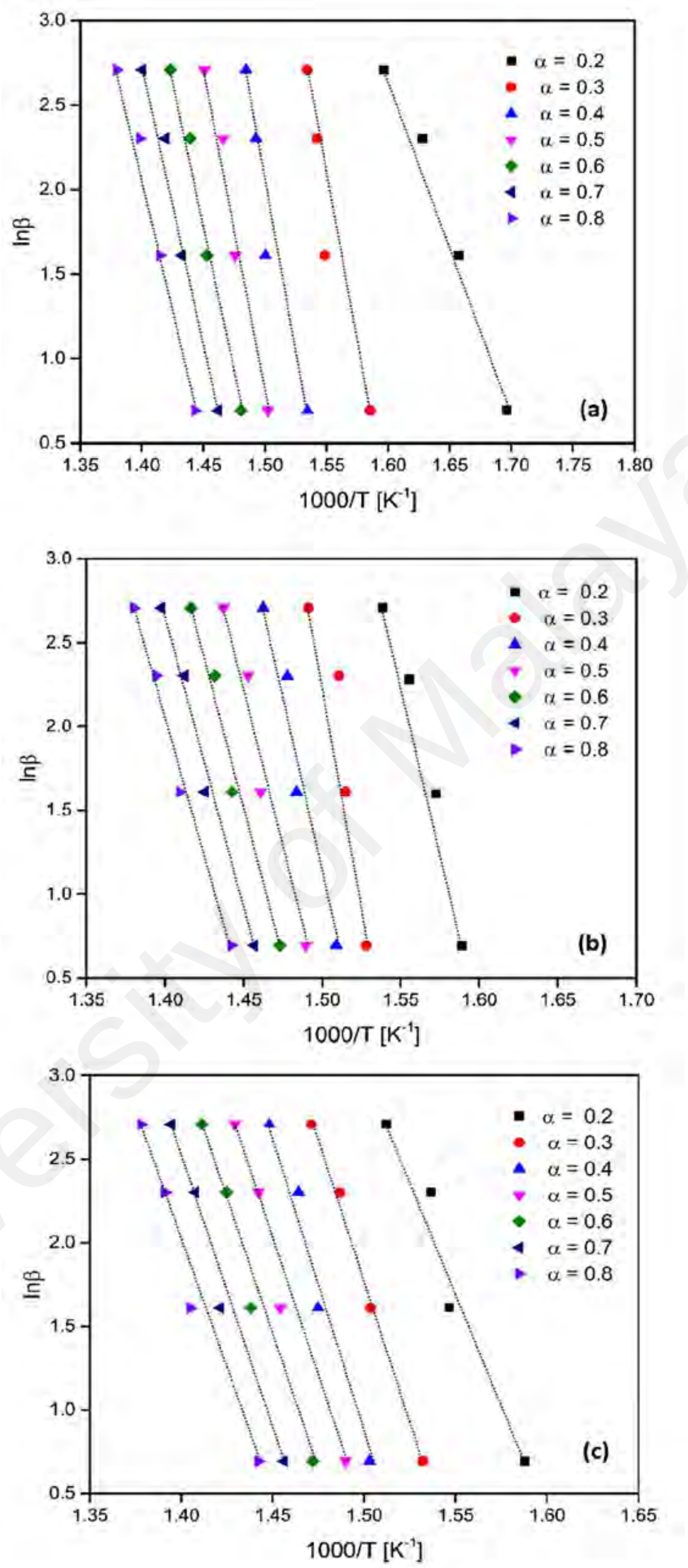


Figure 4.14: FWO plots (a) B3, (b) B13 and (c) 10 at various conversions *(α)*

Table 4.4: Activation energy for B3 obtained by the four non-isothermal methods

	Friedman		**FWO**		**KAS**	
α	**E(kJ mol^{-1})**	**R^2**	**E(kJ mol^{-1})**	**R^2**	**E(kJ mol^{-1})**	**R^2**
0.2	166.01	0.9840	162.59	0.9850	160.96	0.9829
0.3	304.69	0.9155	294.69	0.9181	299.38	0.9127
0.4	318.57	0.9373	308.04	0.9393	313.06	0.9353
0.5	328.68	0.9789	317.77	0.9796	323.05	0.9782
0.6	293.46	0.9885	284.38	0.9889	287.73	0.9880
0.7	274.79	0.9846	266.72	0.9853	268.98	0.9840
0.8	264.62	0.989	257.13	0.9895	258.72	0.9885
Average	278.69		270.19		273.13	
Kissinger	282.75	0.9750				

Table 4.5: Activation energy for B13 obtained by the four non-isothermal methods

	Friedman		**FWO**		**KAS**	
α	**E(kJ mol^{-1})**	**R^2**	**E(kJ mol^{-1})**	**R^2**	**E(kJ mol^{-1})**	**R^2**
0.2	257.57	0.9651	249.89	0.9037	252.26	0.9862
0.3	444.22	0.9873	427.48	0.9756	438.71	0.9871
0.4	365.78	0.9568	352.99	0.9581	360.18	0.9555
0.5	323.46	0.9678	312.86	0.9689	317.78	0.9667
0.6	298.21	0.9798	288.93	0.9806	292.46	0.9791
0.7	284.55	0.9859	276.01	0.9865	278.73	0.9854
0.8	268.35	0.9893	260.67	0.9897	262.46	0.9888
Average	320.31		309.67		314.65	
Kissinger	271.01	0.9933				

Table 4.6: Activation energy for B10 obtained by the four non-isothermal methods

	Friedman		**FWO**		**KAS**	
α	**E(kJ mol^{-1})**	**R^2**	**E(kJ mol^{-1})**	**R^2**	**E(kJ mol^{-1})**	**R^2**
0.2	221.97	0.9586	216.09	0.9605	216.62	0.9567
0.3	274.67	0.9954	266.35	0.9956	269.14	0.9952
0.4	309.01	0.9799	299.08	0.9806	303.38	0.9791
0.5	272.64	0.9740	264.56	0.9750	266.94	0.9729
0.6	273.75	0.9823	265.69	0.9830	267.98	0.9815
0.7	267.37	0.9816	259.69	0.9823	261.54	0.9808
0.8	256.68	0.9788	249.59	0.9797	250.79	0.9778
Average	268.01		260.15		262.34	
Kissinger	265.79	0.9183				

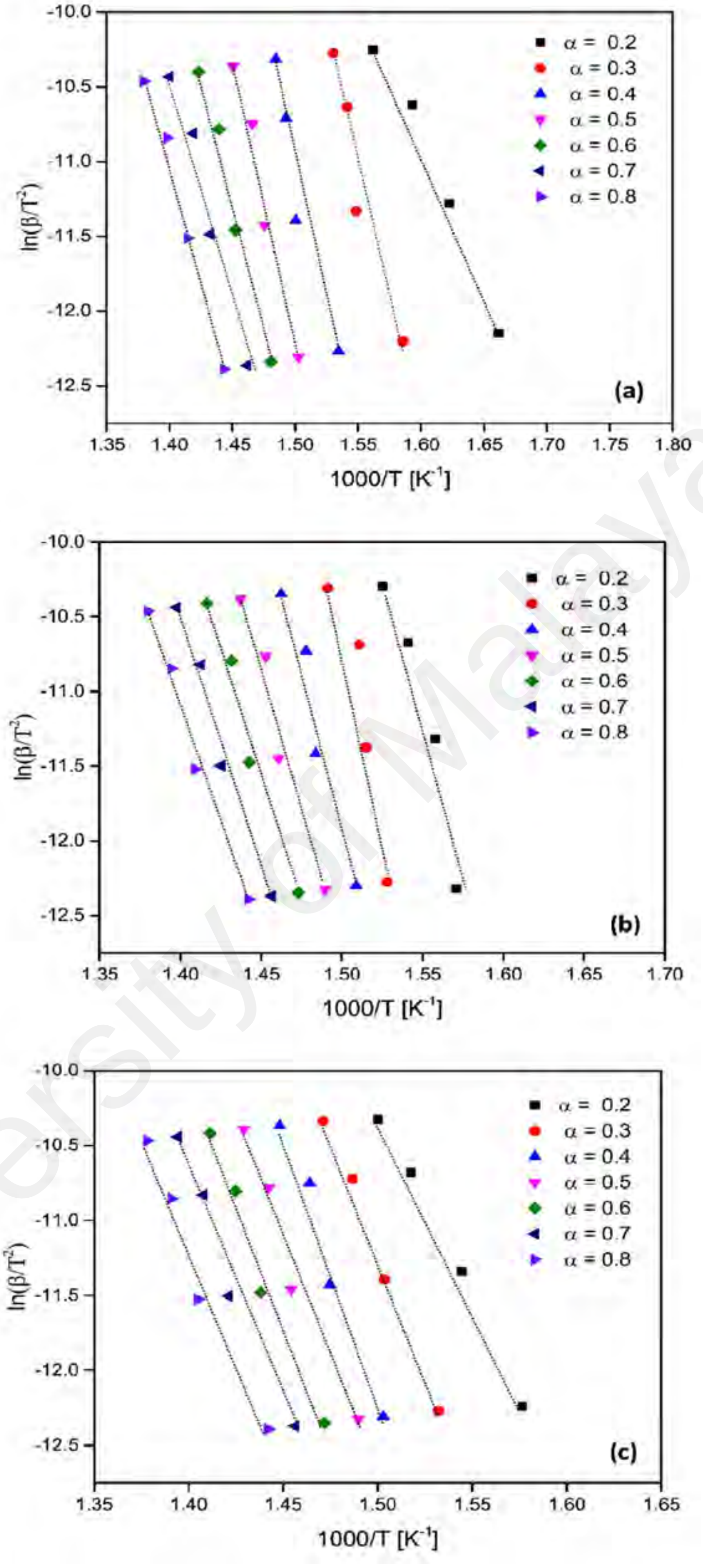


Figure 4.15: KAS plots (a) B3, (b) B13 and (c) B10 at various conversions *(α)*

Figure 4.16 presents the dependence of apparent activation energy *(E_a)* on the degree of conversion *(α)* for non-isothermal degradation process of polymers via the Friedman FWO, and KAS methods. The polymers are likely to degrade by a multi-step process as indicated by the nonlinear trend of E_a with *α*. It was established that if there is a difference between the values of E_a obtained by the isoconversional integral and differential methods, then there is a dependency between the activation energy and α. (Budrugeac *et al.*, 1996; Budrugeac & Segal, 1998; Opfermann *et al.*, 2002). It was also demonstrated that in both the FWO and the Friedman methods different values of E_a are obtained for a system of independent or competitive reaction mechanisms. However, if E_a and *α* are independent, then there is a high tendency of obtaining similar values of E_a by these approaches (Dowdy, 1987; Venkatesh *et al.*, 2013).

The numerical value of activation energy found using the Kissinger and Friedman methods, on the one hand, vary slightly with those obtained by the Flynn−Wall−Ozawa and the Kissinger–Akahira–Sunose methods on the other hand. These dissimilarities are possibly due to the temperature integrals approximations used during the derivation of the relationships for the nonlinear isoconversional techniques. The stability order of the branched polymers studied may be written as B13 > B3 > B10 based on the values of activation energy calculated.

Compared to the values of activation energy (223.4 kJ mol^{-1}) reported by Chen *et al.,* (Chen *et al.*, 2016), for hyperbranched exopolysaccharide, the values obtained in the present study are slightly higher. Similarly, average E_a values of 90.6 kJ mol^{-1} were reported for anhydride-terminated hyperbranched polymers with M_n and dispersity index ranging 16,000 g mol^{-1} to 19,000 g mol^{-1} and from 1.21 to 128 respectively (Othman *et al.*, 2015).

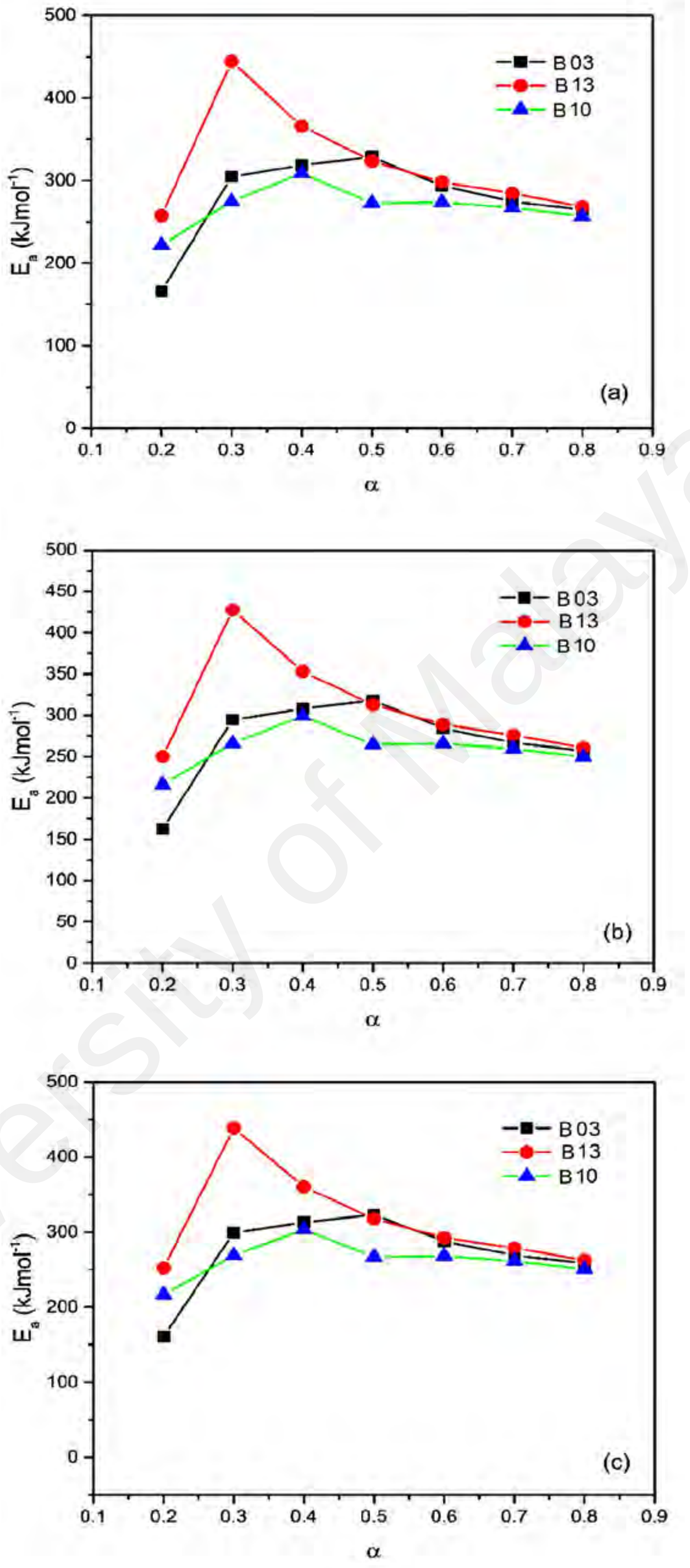


Figure 4.16: Plot showing the comparison of activation energy against the extent of conversion of B3, B13 and B10 obtained by the (a) Friedman, (b) FWO and (c) KAS methods

The dissimilarity may be explained in terms of differences in molecular weight, molecular weight distribution or the nature of the polymeric chains between the polymers used in the present study and the ones reported in the literature (Yang *et al.*, 2003).

The activation energy as a function of conversion could be estimated via the isoconversional methods without prior assumptions on the reaction model. Moreover, unlike the Kissinger method which produces a single value of the activation energy for the whole process isoconversional methods allow for detection of the multi-step kinetic dependence of activation energy on conversion which may not be revealed by the Kissinger Method (Vyazovkin & Wight, 1999).

To get an insight into the mechanism of thermal degradation of the branched polymers Coats–Redfern method was employed. The Coats–Redfern method is independent of the heating rate. The necessary data were computed for individual heating rates for each sample using similar values for the degree of conversion to those used in the isoconversional methods. The obtained kinetic parameters were presented in Tables 4.7, 4.8 and 4.9 for samples B03, B13 and B10, respectively.

Analyses of the activation energy together with the correlation coefficients for all designated kinetic models show that it is difficult to decide on the accurate degradation mechanisms for these branched polymers (Azimi *et al.*, 2014; Heidarzadeh *et al.*, 2017). Moreover, comparisons of values of activation energy between the Coats–Redfern method and those obtained by the isoconversional methods does not suggest the most likely reaction. Nevertheless, analyses of the data together with the high correlation coefficients may suggest the most likely reaction mechanisms.

Table 4.7: Activation energy for B03 obtained by Coats–Redfern method

	2 °C min^{-1}		**5 °C min^{-1}**		**10 °C min^{-1}**		**15 °C min^{-1}**	
	***E$_a$* (kJ mol^{-1})**	**R^2**	***E$_a$* (kJ mol^{-1})**	**R^2**	***E$_a$* (kJ mol^{-1})**	**R^2**	***E$_a$* (kJ mol^{-1})**	**R^2**
A_2	21.1	0.9594	22.5	0.9600	24.5	0.9299	25.8	0.9748
A_3	10.5	0.9790	11.4	0.9845	12.6	0.8922	13.5	0.9616
A_4	5.23	0.9152	5.8	0.9355	6.75	0.8127	7.30	0.9325
R_1	35.3	0.9509	37.5	0.9476	40.1	0.9843	41.7	0.9995
R_2	43.4	0.9281	45.9	0.9261	49.3	0.9695	51.5	0.9939
R_3	46.4	0.9199	49.1	0.9182	52.7	0.9635	55.0	0.9905
D_1	81.3	0.9613	85.7	0.9584	91.3	0.9872	94.6	0.9995
D_2	91.3	0.9493	96.2	0.9469	102.7	0.9800	106.7	0.9974
D_3	103.3	0.9333	108.9	0.9315	116.5	0.9691	121.3	0.9918
D_4	95.2	0.9439	100.4	0.9417	107.2	0.9765	111.5	0.9958
F_1	52.7	0.9029	55.8	0.9020	60.0	0.9504	62.8	0.9819
F_2	75.4	0.9527	79.7	0.9533	86.1	0.9081	90.5	0.9489
F_3	102.9	0.9115	108.6	0.9130	117.7	0.9709	124.2	0.9168

Table 4.8: Activation energy for B13 obtained by Coats–Redfern method

	2 °C min^{-1}		**5 °C min^{-1}**		**10 °C min^{-1}**		**15 °C min^{-1}**	
	***E$_a$* (kJ mol^{-1})**	**R^2**	***E$_a$* (kJ mol^{-1})**	**R^2**	***E$_a$* (k Jmol^{-1})**	**r**	***E$_a$* (kJ mol^{-1})**	**R^2**
A_2	46.0	0.9494	35.1	0.9314	35.2	0.9698	40.3	0.9898
A_3	27.0	0.9366	19.7	0.9076	19.7	0.9591	23.0	0.9868
A_4	17.5	0.9181	12.0	0.9687	12.0	0.9409	14.4	0.9820
R_1	70.7	0.9840	55.4	0.9789	55.2	0.9958	62.2	0.9985
R_2	85.6	0.9718	67.3	0.965	67.4	0.9890	75.9	0.9984
R_3	91.1	0.9679	71.7	0.9593	71.9	0.9854	81.0	0.9969
D_1	152.4	0.9860	121.9	0.9821	121.7	0.9964	135.9	0.9988
D_2	170.9	0.9784	136.6	0.9749	136.8	0.9933	152.7	0.9994
D_3	193.2	0.9711	154.6	0.9643	155.1	0.9871	173.4	0.9972
D_4	178.3	0.9761	142.6	0.9715	142.8	0.9915	159.6	0.9990
F_1	103.0	0.9586	81.2	0.9469	81.6	0.9766	91.9	0.9918
F_2	145.3	0.9248	115.0	0.9060	116.3	0.9436	131.1	0.9671
F_3	196.7	0.9823	156.1	0.9693	158.5	0.9115	178.8	0.9399

Table 4.9: Activation energy for B10 obtained by Coats–Redfern method

	2 °C min^{-1}		**5 °C min^{-1}**		**10 °C min^{-1}**		**15 °C min^{-1}**	
	E$_a$ **(kJ mol^{-1})**	**R^2**	***E$_a$*** **(kJ mol^{-1})**	**R^2**	***E$_a$*** **(kJ mol^{-1})**	**r**	***E$_a$*** **(kJ mol^{-1})**	**R^2**
A_2	45.9	0.9500	47.0	0.9849	45.9	0.9809	50.5	0.9920
A_3	26.9	0.9373	27.6	0.9811	26.8	0.9759	29.8	0.9902
A_4	17.5	0.9189	17.8	0.9755	17.3	0.9685	19.5	0.9875
R_1	70.8	0.9802	71.8	0.9986	70.4	0.9949	76.6	0.9958
R_2	85.5	0.9739	87.2	0.9961	85.5	0.9926	93.1	0.9978
R_3	91.0	0.9694	92.9	0.9938	91.1	0.9905	99.2	0.9969
D_1	152.5	0.9827	155.0	0.9988	152.1	0.9956	164.8	0.9964
D_2	170.6	0.9808	174.0	0.9980	170.8	0.9949	185.1	0.9981
D_3	192.9	0.9724	197.1	0.9944	193.6	0.9914	210.0	0.9972
D_4	178.0	0.9782	181.6	0.9971	178.3	0.9940	193.5	0.9981
F_1	102.7	0.9591	105.2	0.9876	103.2	0.9844	112.4	0.9933
F_2	144.8	0.9230	149.1	0.9605	146.4	0.9579	159.7	0.9724
F_3	195.9	0.9888	202.6	0.9317	199.0	0.9297	217.2	0.9476

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Highly branched polyisoprene has been successfully synthesized with a divinylbenzene in the presence of a chain transfer process in anionic polymerization to prepare a soluble polymer. The divinylbenzene introduces branching points into the polymer backbone, while the chain transfer mechanism decreases the molecular weight of the polymeric backbone. Since the gel point depends on the crosslink density as well as the chain length, the chain transfer can aid in preventing gelation through chain termination before gelation. This method was a modified approach to the "Strathclyde route" in which a free radical polymerization was employed. In the present study, anionic polymerization was used. Since anionic polymerization allows for the control of molecular weights through the utilization of an appropriate amount of initiator, chain transfer mechanism can be utilized as an added feature. Higher DVB/Li ratios resulted in cross-linked polymer products. ^{1}H NMR spectroscopy analysis reveals the dominance of 3,4–polyisoprene microstructure due to the addition of TMEDA. Size exclusion chromatography was used to demonstrate the branching nature of the prepared polymers. The branched polymers prepared in this study were compared to their linear counterparts and found to have favorable rheological, and solution properties hence could serve as rheological modifiers.

Investigations into the solid-state morphology of the resulting polymers, and in particular the impact of the hyperbranched architecture on morphology, were carried out by using HR-TEM. It was found that moving from the linear to the highly branched polymer samples, lead to the loss of the long-range, well-ordered morphologies associated with the linear polyisoprene. The highly branched architecture of the branched polymers is certainly responsible for preventing the long-range lattice order.

Thermogravimetric analysis was employed to investigate the thermal degradation kinetics of the branched polymers. The experiments were carried out under nitrogen at the flow rate of 20 mL min^{-1}. Four different model-free methods which include the Kissinger, Friedman, Flynn−Wall−Ozawa, and Kissinger–Akahira–Sunose methods were used to determine the values of activation energy. The values of activation energy obtained using the Kissinger and Friedman methods vary slightly with those obtained by the Flynn−Wall−Ozawa and the Kissinger–Akahira–Sunose methods. The activation energy for decomposition of the branched polymers depends upon the molecular weight as well as the dispersity index of these polymers. The branched polymers were decomposed via multistep kinetics as manifested by the lack of dependency between the activation energy with the degree of conversion.

5.2 Recommendations for future work

Further investigations of isoprene copolymerization with a divinyl crosslinkers may be carried out to examine the effect of other variables that were not investigated in the present study. Higher temperatures and low additive concentrations may be explored in order to achieve more chain transfer to solvent and at the same time preserving the microstructure of the resulting polyisoprene. Other polar additives such as potassium *tert*-butoxide may also be explored in order to assess their effect on chain transfer reaction. Other monomers different from isoprene can also be investigated. Alternatively, solvent mixtures or other solvents different from toluene may be used with different levels of polar additives in order to explore the possibility of chain transfer reactions. Also, a different multifunctional comonomer such as vinylbenzene chloride (VBC) which can also undergo chain termination and at the same time introduce branching may be employed. Furthermore, more characterizations of the branched polymer products can be carried out such as temperature gradient interaction chromatography (TGIC). The TGIC is capable of separating branched polymers not only by their molecular weight but also by their degree of branching. Finally, monomers such as 4–methyl styrene capable of undergoing chain transfer reactions can be exploited. In the case of 4–methyl styrene, the methyl group is likely to act in the same way as the methyl group in toluene. Under the appropriate condition, chain transfer, in this case, will also lead to the formation of branching. After establishing the extent of chain transfer of this monomer in anionic polymerization, it is possible to incorporate a divinyl crosslinker such as divinylbenzene or vinylbenzene chloride.

REFERENCES

Abbasi, E., Aval, S. F., Akbarzadeh, A., Milani, M., Nasrabadi, H. T., Joo, S. W., . . . Pashaei–Asl, R. (2014). Dendrimers: synthesis, applications, and properties. *Nanoscale Research Letters, 9*(1), 247.

Abdelrehim, M., Komber, H., Langenwalter, J., Voit, B., & Bruchmann, B. (2004). Synthesis and characterization of hyperbranched poly (urea–urethane) s based on AA* and B2B* monomers. *Journal of Polymer Science Part A: Polymer Chemistry, 42*(12), 3062–3081.

Acar, I., Pozan, G. S., & Özgümüş, S. (2008). Thermal oxidative degradation kinetics and thermal properties of poly (ethylene terephthalate) modified with poly (lactic acid). *Journal of Applied Polymer Science, 109*(5), 2747–2755.

Acar, M. H., & Matyjaszewski, K. (1999). Block copolymers by transformation of living anionic polymerization into controlled/"living" atom transfer radical polymerization. *Macromolecular Chemistry and Physics, 200*(5), 1094–1100.

Agostini, S. (2014). *Synthesis and characterisations of architecturally complex branched polymers.* (P.h.D), Durham University, 62–65.

Alfurhood, J. A., Bachler, P. R., & Sumerlin, B. S. (2016). Hyperbranched polymers via RAFT self–condensing vinyl polymerization. *Polymer Chemistry, 7*(20), 3361–3369.

Alfurhood, J. A., Sun, H., Bachler, P. R., & Sumerlin, B. S. (2016). Hyperbranched poly (N–(2–hydroxypropyl) methacrylamide) via RAFT self–condensing vinyl polymerization. *Polymer Chemistry, 7*(11), 2099–2104.

Alkan, A., Klein, R., Shylin, S. I., Kemmer–Jonas, U., Frey, H., & Wurm, F. R. (2015). Water–soluble and redox–responsive hyperbranched polyether copolymers based on ferrocenyl glycidyl ether. *Polymer Chemistry, 6*(40), 7112–7118.

Antonietti, M., & Rosenauer, C. (1991). Properties of fractal divinylbenzene microgels. *Macromolecules, 24*(11), 3434–3442.

Appelhans, D., Komber, H., Voigt, D., Häussler, L., & Voit, B. I. (2000). Synthesis and characterization of poly (ether amide) dendrimers containing different core molecules. *Macromolecules, 33*(26), 9494–9503.

Arda, B., Bal, A., & Acar, I. (2017). Characterization of the thermal oxidative degradation kinetics of thermoplastics. *Instrumentation Science & Technology, 45*(5), 558–576.

Arza, C. R., İlk, S., Demircan, D., & Zhang, B. (2018). New biobased non–ionic hyperbranched polymers as environmentally friendly antibacterial additives for biopolymers. *Green Chemistry, 20*(6), 1238–1249.

Astruc, D., & Chardac, F. (2001). Dendritic catalysts and dendrimers in catalysis. *Chemical Reviews, 101*(9), 2991–3024.

Astruc, D., Wang, D., Deraedt, C., Liang, L., Ciganda, R., & Ruiz, J. (2015). Catalysis inside dendrimers. *Synthesis, 47*(14), 2017–2031.

Aulenta, F., Hayes, W., & Rannard, S. (2003). Dendrimers: a new class of nanoscopic containers and delivery devices. *European Polymer Journal, 39*(9), 1741–1771.

Azimi, H. R., Rezaei, M., & Majidi, F. (2014). The non–isothermal degradation kinetics of St–MMA copolymers. *Polymer Degradation and Stability, 99*, 240–248.

Baek, J.–B., & Harris, F. W. (2005). Fluorine–and hydroxyl–terminated hyperbranched poly (phenylquinoxalines)(PPQs) from copolymerization of self–polymerizable AB and AB_2, BA, and BA_2 monomers. *Macromolecules, 38*(4), 1131–1140.

Bai, L.–b., Zhao, K., Wu, Y.–g., Li, W.–l., Wang, S.–j., Wang, H.–j., . . . Zhao, H.–c. (2014). A new method for synthesizing hyperbranched polymers with reductive groups using redox/RAFT/SCVP. *Chinese Journal of Polymer Science, 32*(4), 385–394.

Bannister, I., Billingham, N. C., Armes, S. P., Rannard, S. P., & Findlay, P. (2006). Development of branching in living radical copolymerization of vinyl and divinyl monomers. *Macromolecules, 39*(22), 7483–7492.

Baskaran, D. (1996). *Ligated and metal free initiating systems for the living anionic polymerization of alkyl (meth) acrylates.* University of Pune, 1–172.

Baskaran, D. (2003). Hyperbranched polymers from divinylbenzene and 1, 3–diisopropenylbenzene through anionic self–condensing vinyl polymerization. *Polymer, 44*(8), 2213–2220.

Baudry, R., & Sherrington, D. (2006a). Facile synthesis of branched poly (vinyl alcohol) s. *Macromolecules, 39*(16), 5230–5237.

Baudry, R., & Sherrington, D. (2006b). Synthesis of highly branched poly (methyl methacrylate) s using the “strathclyde methodology” in aqueous emulsion. *Macromolecules, 39*(4), 1455–1460.

Behera, G. C., Saha, A., & Ramakrishnan, S. (2005). Hyperbranched copolymers versus linear copolymers: A comparative study of thermal properties. *Macromolecules, 38*(18), 7695–7701.

Beyer, F. L., Gido, S. P., Büschl, C., Iatrou, H., Uhrig, D., Mays, J. W., . . . Tan, N. B. (2000). Graft copolymers with regularly spaced, tetrafunctional branch points: morphology and grain structure. *Macromolecules, 33*(6), 2039–2048.

Beyer, F. L., Gido, S. P., Poulos, Y., Avgeropoulos, A., & Hadjichristidis, N. (1997). Morphology of vergina star 16–arm block copolymers and scaling behavior of interfacial area with graft point functionality. *Macromolecules, 30*(8), 2373–2376.

Bohme, F., Clausnitzer, C., Gruber, F., Grutke, S., Huber, T., Potschke, P., & Voit, B. (2001). Hyperbranched poly (ether amide) s via nucleophilic ring opening reaction of oxazolines. *High Performance Polymers, 13*(2), S21–S32.

Bolton, D. H., & Wooley, K. L. (2002). Hyperbranched aryl polycarbonates derived from A2B monomers versus AB2 monomers. *Journal of Polymer Science Part A: Polymer Chemistry, 40*(7), 823–835.

Bork, S. (1984). Linear low–density polyethylene (LLDPE)–properties, processing and application. *Kunststoffe–German Plastics, 74*(9), 474–486.

Boskaran, D., & Muller, A. H. (2009). Anionic Vinyl Polymerization. *Controlled and living polymerizations: From mechanisms to applications*. John Wiley & Sons, 596.

Braunecker, W. A., & Matyjaszewski, K. (2007). Controlled/living radical polymerization: Features, developments, and perspectives. *Progress in Polymer Science, 32*(1), 93–146.

Brocas, A.–L., Mantzaridis, C., Tunc, D., & Carlotti, S. (2013). Polyether synthesis: From activated or metal–free anionic ring–opening polymerization of epoxides to functionalization. *Progress in Polymer Science, 38*(6), 845–873.

Budrugeac, P., Petre, A. L., & Segal, E. (1996). Some problems concerning the evaluation of non–isothermal kinetic parameters: Solid–gas decompositions from thermogravimetric data. *Journal of Thermal Analysis and Calorimetry, 47*(1), 123–134.

Budrugeac, P., & Segal, E. (1998). Thermal degradation of polychloroprene rubber under isothermal and non–isothermal conditions. *Journal of Thermal Analysis and Calorimetry, 53*(2), 441–447.

Buhleier, E., Wehner, W., & Vögtle, F. (1978). ′ Cascade′-and′ nonskid-chain-like′ syntheses of molecular cavity topologies. *ChemInform, 9*(25), 1–5.

Burchard, W. (2004). Angular dependence of scattered light from hyperbranched structures in a good solvent. A fractal approach. *Macromolecules, 37*(10), 3841–3849.

Bütün, V., Bannister, I., Billingham, N., Sherrington, D., & Armes, S. (2005). Synthesis and characterization of branched water–soluble homopolymers and diblock copolymers using group transfer polymerization. *Macromolecules, 38*(12), 4977–4982.

Caminade, A.–M., Ouali, A., Laurent, R., & Majoral, J.–P. (2017). Catalysis Within Dendrimers. In *Effects of Nanoconfinement on Catalysis* Springer, 173–207.

Caminade, A.–M., Yan, D., & Smith, D. K. (2015). Dendrimers and hyperbranched polymers. *Chemical Society Reviews, 44*(12), 3870–3873.

Campbell, J., Teymour, F., & Morbidelli, M. (2005). Production of hyperbranched polystyrene by high–temperature polymerization. *Macromolecules, 38*(3), 752–760.

Carlmark, A., Hawker, C., Hult, A., & Malkoch, M. (2009). New methodologies in the construction of dendritic materials. *Chemical Society Reviews, 38*(2), 352–362.

Carothers, W. H. (1936). Polymers and polyfunctionality. *Transactions of the Faraday Society, 32*, 39–49.

Carraher Jr, C. E. (2017). *Introduction to polymer chemistry*, CRC press, 1–5.

Carter, S., Hunt, B., & Rimmer, S. (2005). Highly branched poly (N–isopropylacrylamide)s with imidazole end groups prepared by radical polymerization in the presence of a styryl monomer containing a dithioester group. *Macromolecules, 38*(11), 4595–4603.

Carter, S., Rimmer, S., Sturdy, A., & Webb, M. (2005). Highly Branched Stimuli Responsive Poly[(N-isopropyl acrylamide)–co–(1, 2-propandiol–3–methacrylate)]s with Protein Binding Functionality. *Macromolecular Bioscience, 5*(5), 373–378.

Chang, H.–T., & Fréchet, J. M. (1999). Proton–transfer polymerization: a new approach to hyperbranched polymers. *Journal of the American Chemical Society, 121*(10), 2313–2314.

Chen, H., & Yin, J. (2002). Synthesis and characterization of hyperbranched polyimides with good organosolubility and thermal properties based on a new triamine and conventional dianhydrides. *Journal of Polymer Science Part A: Polymer Chemistry, 40*(21), 3804–3814.

Chen, L., Cheng, W. N., Zhang, B. B., & Cheung, P. C. K. (2016). Structural and thermal analysis of a hyper–branched exopolysaccharide produced by submerged fermentation of mushroom mycelium. *RSC Advances, 6*(113), 112260–112268.

Chen, L., Zhu, X., Yan, D., Chen, Y., Chen, Q., & Yao, Y. (2006). Controlling polymer architecture through host–guest interactions. *Angewandte Chemie International Edition, 45*(1), 87–90.

Chen, Q., Wang, H., Liu, H., Wen, S., Peng, C., Shen, M., . . . Shi, X. (2015). Multifunctional dendrimer–entrapped gold nanoparticles modified with RGD peptide for targeted computed tomography/magnetic resonance dual–modal imaging of tumors. *Analytical Chemistry, 87*(7), 3949–3956.

Chen, S. F., Xu, Z. J., & Zhang, D. H. (2018). Synthesis and application of epoxy–ended hyperbranched polymers. *Chemical Engineering Journal, 343*, 283–302.

Cheng, C., Wooley, K. L., & Khoshdel, E. (2005). Hyperbranched fluorocopolymers by atom transfer radical self–condensing vinyl copolymerization. *Journal of Polymer Science Part A: Polymer Chemistry, 43*(20), 4754–4770.

Chiang, W. S., Lin, C. H., Nandan, B., Yeh, C. L., Rahman, M. H., Chen, W. C., & Chen, H. L. (2008). Molecular Architecture Effect on the Self–Assembly Behavior of Comb–Coil Block Copolymers Displaying Lamellae–within–Lamellae Morphology. *Macromolecules, 41*(21), 8138–8147.

Chisholm, M., Hudson, N., Kirtley, N., Vilela, F., & Sherrington, D. C. (2009). Application of the “Strathclyde route” to branched vinyl polymers in suspension polymerization: architectural, thermal, and rheological characterization of the derived branched products. *Macromolecules, 42*(20), 7745–7752.

Chou, P. J., & Johnson, W. C. (1993). Base inclinations in natural and synthetic DNAs. *Journal of the American Chemical Society, 115*(4), 1205–1214.

Chrissafis, K. (2008). Kinetics of thermal degradation of polymers: complementary use of isoconversional and model–fitting methods. *Journal of Thermal Analysis and Calorimetry, 95*(1), 273–283.

Chrissafis, K., Paraskevopoulos, K., & Bikiaris, D. (2010). Thermal degradation kinetics and decomposition mechanism of two new aliphatic biodegradable polyesters poly(propylene glutarate) and poly(propylene suberate). *Thermochimica Acta, 505*(1–2), 59–68.

Ciliz, N. K., Ekinci, E., & Snape, C. E. (2004). Pyrolysis of virgin and waste polypropylene and its mixtures with waste polyethylene and polystyrene. *Waste Management & Research, 24*(2), 173–181.

Clarke, N., De Luca, E., Dodds, J. M., Kimani, S. M., & Hutchings, L. R. (2008). HyperMacs–long chain hyperbranched polymers: A dramatically improved synthesis and qualitative rheological analysis. *European Polymer Journal, 44*(3), 665–676.

Cloninger, M. J. (2002). Biological applications of dendrimers. *Current Opinion in Chemical Biology, 6*(6), 742–748.

Coats, A. W., & Redfern, J. (1964). Kinetic parameters from thermogravimetric data. *Nature, 201*(4914), 68.

Corazzari, I., Nisticò, R., Turci, F., Faga, M. G., Franzoso, F., Tabasso, S., & Magnacca, G. (2015). Advanced physico–chemical characterization of chitosan by means of TGA coupled on–line with FTIR and GCMS: Thermal degradation and water adsorption capacity. *Polymer Degradation and Stability, 112*, 1–9.

Cosimbescu, L., Robinson, J. W., & Bays, J. T. (2016). *Modified Thermoresponsive Hyperbranched Polymers for Improved Viscosity and Enhanced Lubricity of Engine Oils*. *Technical Report*, United states, 2–5.

Costello, P., Martin, I., Slark, A., Sherrington, D., & Titterton, A. (2002). Branched methacrylate copolymers from multifunctional monomers: chemical composition and physical architecture distributions. *Polymer, 43*(2), 245–254.

Cosulich, M., Russo, S., Pasquale, S., & Mariani, A. (2000). Performance evaluation of hyperbranched aramids as potential supports for protein immobilization. *Polymer, 41*(13), 4951–4956.

Cowie, J. M. G., & Arrighi, V. (2007). *Polymers: chemistry and physics of modern materials*: CRC press, 20–65.

Das, T., Sengupta, S., & Bandyopadhyay, A. (2018). Part II–Synthesis of Hyperbranched Polymers: Mixed Chain–Growth and Step–Growth Methods. In *Hyperbranched Polymers for Biomedical Applications* Springer, 65–108.

De Gennes, P. (1975). Reptation of stars. *Journal de Physique, 36*(12), 1199–1203.

De Gennes, P. (1976). Dynamics of entangled polymer solutions. I. The Rouse model. *Macromolecules, 9*(4), 587–593.

Deraedt, C., Ye, R., Ralston, W. T., Toste, F. D., & Somorjai, G. A. (2017). Dendrimer–Stabilized Metal Nanoparticles as Efficient Catalysts for Reversible Dehydrogenation/Hydrogenation of N–Heterocycles. *Journal of the American Chemical Society, 139*(49), 18084–18092.

Doi, M., & Edwards, S. (1978). Dynamics of concentrated polymer systems. Part 1–Brownian motion in the equilibrium state. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics, 74*, 1789–1801.

Dong, Z. M., Liu, X. H., Lin, Y., & Li, Y. S. (2008). Branched polystyrene with abundant pendant vinyl functional groups from asymmetric divinyl monomer. *Journal of Polymer Science Part A: Polymer Chemistry, 46*(18), 6023–6034.

Dowdy, D. (1987). Meaningful activation energies for complex systems II: Evaluation of the Friedman method when applied to multiple reactions, and comparison with the Ozawa–Flynn–Wall method. *Journal of Thermal Analysis and Calorimetry, 32*(4), 1177–1187.

Dowdy, D. (1987). Meaningful activation energies for complex systems: I. The application of the Ozawa–Flynn–Wall method to multiple reactions. *Journal of Thermal Analysis and Calorimetry, 32*(1), 137–147.

Doyle, C. (1962). Estimating isothermal life from thermogravimetric data. *Journal of Applied Polymer Science, 6*(24), 639–642.

Du, W., Nyström, A. M., Zhang, L., Powell, K. T., Li, Y., Cheng, C., . . . Wooley, K. L. (2008). Amphiphilic hyperbranched fluoropolymers as nanoscopic 19F magnetic resonance imaging agent assemblies. *Biomacromolecules, 9*(10), 2826–2833.

Dušek, K., & Dušková–Smrčková, M. (2000). Network structure formation during crosslinking of organic coating systems. *Progress in Polymer Science, 25*(9), 1215–1260.

Elkins, C. L. (2005). *Living Polymerization for the Introduction of Tailored Hydrogen Bonding.* (PhD) Virginia Tech., 100–170.

Elkins, C. L., & Long, T. E. (2004). Living anionic polymerization of hexamethylcyclotrisiloxane (D–3) using functionalized initiation. *Macromolecules, 37*(17), 6657–6659.

Ellis, B., & Smith, R. (2008). *Polymers: a property database*: CRC Press, 108–200.

Elrehim, M. A., Voit, B., Bruchmann, B., Eichhorn, K. J., Grundke, K., & Bellmann, C. (2005). Structural and end–group effects on bulk and surface properties of hyperbranched poly(urea urethane)s. *Journal of Polymer Science Part A: Polymer Chemistry, 43*(15), 3376–3393.

Emrick, T., Chang, H.–T., & Frechet, J. M. (1999). An A2+ B3 approach to hyperbranched aliphatic polyethers containing chain end epoxy substituents. *Macromolecules, 32*(19), 6380–6382.

Emrick, T., Chang, H. T., & Fréchet, J. M. (2000). The preparation of hyperbranched aromatic and aliphatic polyether epoxies by chloride–catalyzed proton transfer polymerization from ABn and A2 + B3 monomers. *Journal of Polymer Science Part A: Polymer Chemistry, 38*(S1), 4850–4869.

Fang, J., Kita, H., & Okamoto, K.–I. (2000). Hyperbranched polyimides for gas separation applications. 1. Synthesis and characterization. *Macromolecules, 33*(13), 4639–4646.

Farrington, P. J., Hawker, C. J., Fréchet, J. M., & Mackay, M. E. (1998). The melt viscosity of dendritic poly (benzyl ether) macromolecules. *Macromolecules, 31*(15), 5043–5050.

Fetters, L. (1983). *Synthesis and characterization of block polymers via anionic polymerization.* Paper presented at the Block Copolymers: Science and Technology: Papers Presented at the Ninth Midland Macromolecular Meeting Held August 20–24, 1979 in Midland, Michigan, 1–4.

Flory, P. J. (1941a). Molecular size distribution in three dimensional polymers. I. gelation1. *Journal of the American Chemical Society, 63*(11), 3083–3090.

Flory, P. J. (1941b). Molecular size distribution in three dimensional polymers. III. Tetrafunctional branching units. *Journal of the American Chemical Society, 63*(11), 3096–3100.

Flory, P. J. (1952). Molecular size distribution in three dimensional polymers. VI. Branched polymers containing A–R–Bf–1 type units. *Journal of the American Chemical Society, 74*(11), 2718–2723.

Flory, P. J. (1953). *Principles of polymer chemistry*: Cornell University Press.

Flynn, J. H. (1991). A general differential technique for the determination of parameters for d(alpha)/dt = f(alpha)a exp (–e/rt) – energy of activation, preexponential factor and order of reaction (when applicable). *Journal of Thermal Analysis, 37*(2), 293–305.

Fréchet, J. M. (2003). Dendrimers and other dendritic macromolecules: From building blocks to functional assemblies in nanoscience and nanotechnology. *Journal of Polymer Science Part A: Polymer Chemistry, 41*(23), 3713–3725.

Fréchet, J. M., & Hawker, C. J. (1995). Hyperbranched polyphenylene and hyperbranched polyesters: new soluble, three–dimensional, reactive polymers. *Reactive and Functional Polymers, 26*(1–3), 127–136.

Fréchet, J. M., Hawker, C. J., Gitsov, I., & Leon, J. W. (1996). Dendrimers and hyperbranched polymers: two families of three–dimensional macromolecules with similar but clearly distinct properties. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry, 33*(10), 1399–1425.

Frechet, J. M., Henmi, M., Gitsov, I., & Aoshima, S. (1995). Self–condensing vinyl polymerization: an approach to dendritic materials. *Science, 269*(5227), 1080.

Frechet, J. M., Henmi, M., Gitsov, I., Aoshima, S., Leduc, M. R., & Grubbs, R. B. (1995). Self–condensing vinyl polymerization: an approach to dendritic materials. *Science, 269*(5227), 1080–1083.

Frechet, J. M. J. (2003). Dendrimers and other dendritic macromolecules: From building blocks to functional assemblies in nanoscience and nanotechnology. *Journal of Polymer Science Part a–Polymer Chemistry, 41*(23), 3713–3725.

Frey, H. (1997). Degree of branching in hyperbranched polymers. 2. Enhancement of the DB: Scope and limitations. *Acta Polymerica, 48*(8), 298–309.

Frey, H. (2007). Special Issue ‘‘Branched Polymers’’Guest–Edited by Holger Frey. *Macromolecular Chemistry and Physics, 208*, 1613–1614.

Frey, H., & Haag, R. (2002). Dendritic polyglycerol: a new versatile biocompatible material. *Reviews in Molecular Biotechnology, 90*(3–4), 257–267.

Frey, H., & Ishizone, T. (2017). Living Anionic Polymerization Celebrates 60 Years: Unique Features and Polymer Architectures. *Macromolecular Chemistry and Physics, 218*(12), 1700217.

Frey, H., & Ishizone, T. (2018). Living Anionic Polymerization–Part II: Further Expanding the Synthetic Versatility for Novel Polymer Architectures. *Macromolecular Chemistry and Physics, 219*(1), 1–7.

Frey, H., Lach, C., & Lorenz, K. (1998). Heteroatom-Based Dendrimers. *Advanced Materials, 10*(4), 279–293.

Friedman, H. L. (1964). *Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic.* Paper presented at the Journal of Polymer Science: Polymer Symposia, 7–8.

Froehling, P., & Brackman, J. (2000). *Properties and applications of poly(propylene imine) dendrimers and poly(esteramide) hyperbranched polymers.* Paper presented at the Macromolecular Symposia, 1–10.

Funke, W., Okay, O., & Joos–Müller, B. (1998). Microgels–Intramolecularly Crossünked Macromolecules with a Globular Structure. In *Microencapsulation Microgels Iniferters,* Springer, 139–234.

Gao, C., & Yan, D. (2003). “A2 + CBn” approach to hyperbranched polymers with alternating ureido and urethano units. *Macromolecules, 36*(3), 613–620.

Gao, C., & Yan, D. (2004). Hyperbranched polymers: from synthesis to applications. *Progress in Polymer Science, 29*(3), 183–275.

Garamszegi, L., Nguyen, T. Q., Plummer, C. J., & Månson, J. A. E. (2003). Characterization of Hyperbranched Aliphatic Polyesters and Their Trimethylsilylated Derivatives by GPC-Viscometry. *Journal of Liquid Chromatography & Related Technologies, 26*(2), 207–230.

Gaynor, S. G., Edelman, S., & Matyjaszewski, K. (1996). Synthesis of branched and hyperbranched polystyrenes. *Macromolecules, 29*(3), 1079–1081.

Gentekos, D. T., Dupuis, L. N., & Fors, B. P. (2016). Beyond dispersity: deterministic control of polymer molecular weight distribution. *Journal of the American Chemical Society, 138*(6), 1848–1851.

Gong, C., & Fréchet, J. M. (2000). Proton transfer polymerization in the preparation of hyperbranched polyesters with epoxide chain–ends and internal hydroxyl functionalities. *Macromolecules, 33*(14), 4997–4999.

Gordon, M. (1954). Network Theory of the Gel Point and the "Incestuous" Polymerization of Diallyl Phthalate. *The Journal of Chemical Physics, 22*(4), 610–613.

Graessley, W., & Roovers, J. (1979). Melt rheology of four–arm and six–arm star polystyrenes. *Macromolecules, 12*(5), 959–965.

Graff, R. W., Wang, X., & Gao, H. (2015). Exploring Self–Condensing Vinyl Polymerization of Inimers in Microemulsion To Regulate the Structures of Hyperbranched Polymers. *Macromolecules, 48*(7), 2118–2126.

Graham, S., Rannard, S. P., Cormack, P. A., & Sherrington, D. C. (2007). One–pot synthesis of methacrylic acid–ethylene oxide branched block and graft copolymers. *Journal of Materials Chemistry, 17*(6), 545–552.

Grcev, S., Schoenmakers, P., & Iedema, P. (2004). Determination of molecular weight and size distribution and branching characteristics of PVAc by means of size exclusion chromatography/multi–angle laser light scattering (SEC/MALLS). *Polymer, 45*(1), 39–48.

Gretton–Watson, S. P., Alpay, E., Steinke, J. H., & Higgins, J. S. (2005). Hyperbranched polymers. Synthesis, modeling, experimental validation, and rheology of hyperbranched poly (methyl methacrylate) derived from a multifunctional monomer (MFM) route. *Industrial & Engineering Chemistry Research, 44*(23), 8682–8693.

Grubbs, R. B., & Grubbs, R. H. (2017). 50th Anniversary Perspective: Living Polymerization: Emphasizing the Molecule in Macromolecules. *Macromolecules, 50*(18), 6979–6997.

Guan, Z. (2002). Control of polymer topology through transition–metal catalysis: synthesis of hyperbranched polymers by cobalt–mediated free radical polymerization. *Journal of the American Chemical Society, 124*(20), 5616–5617.

Gunatillake, P. A., Odian, G., & Tomalia, D. A. (1988). Thermal polymerization of a 2–(carboxyalkyl) –2–oxazoline. *Macromolecules, 21*(6), 1556–1562.

Gurunathan, T., Mohanty, S., & Nayak, S. K. (2016). Hyperbranched polymers for coating applications: A review. *Polymer–Plastics Technology and Engineering, 55*(1), 92–117.

Habibu, S., Sarih, N. M., & Mainal, A. (2018). Synthesis and characterisation of highly branched polyisoprene: exploiting the "Strathclyde route" in anionic polymerisation. *RSC Advances, 8*(21), 11684–11692.

Hadjichristidis, N., & Hirao, A. (2015). *Anionic polymerization: principles, practice, strength, consequences and applications*: Springer, 5–106.

Hadjichristidis, N., Iatrou, H., Pispas, S., & Pitsikalis, M. (2000). Anionic polymerization: high vacuum techniques. *Journal of Polymer Science Part A: Polymer Chemistry, 38*(18), 3211–3234.

Hadjichristidis, N., Iatrou, H., Pitsikalis, M., & Mays, J. (2006). Macromolecular architectures by living and controlled/living polymerizations. *Progress in Polymer Science, 31*(12), 1068–1132.

Hadjichristidis, N., Pitsikalis, M., Pispas, S., & Iatrou, H. (2001). Polymers with complex architecture by living anionic polymerization. *Chemical Reviews, 101*(12), 3747–3792.

Hagiopol, C. (2012). *Copolymerization: toward a systematic approach*: Springer Science & Business Media, 208.

Hatton, F. L. (2015). *Hyperbranched Polydendrons: A New Macromolecular Architecture*: Springer, 10–15.

Hawker, C., & Fréchet, J. M. (1990). A new convergent approach to monodisperse dendritic macromolecules. *Journal of the Chemical Society, Chemical Communications* (15), 1010–1013.

Hawker, C., Lee, R., & Fréchet, J. (1991). One–step synthesis of hyperbranched dendritic polyesters. *Journal of the American Chemical Society, 113*(12), 4583–4588.

Hawker, C. J., Bosman, A. W., & Harth, E. (2001). New polymer synthesis by nitroxide mediated living radical polymerizations. *Chemical Reviews, 101*(12), 3661–3688.

Hawker, C. J., & Chu, F. (1996). Hyperbranched poly (ether ketones): manipulation of structure and physical properties. *Macromolecules, 29*(12), 4370–4380.

Hawker, C. J., & Frechet, J. M. (1990). Preparation of polymers with controlled molecular architecture. A new convergent approach to dendritic macromolecules. *Journal of the American Chemical Society, 112*(21), 7638–7647.

Hawker, C. J., Frechet, J. M., Grubbs, R. B., & Dao, J. (1995). Preparation of hyperbranched and star polymers by a" living", self–condensing free radical polymerization. *Journal of the American Chemical Society, 117*(43), 10763–10764.

Hawker, C. J., Lee, R., & Frechet, J. M. J. (1991). One–step synthesis of hyperbranched dendritic polyesters. *Journal of the American Chemical Society, 113*(12), 4583–4588.

Heidarzadeh, N., Rafizadeh, M., Taromi, F. A., del Valle, L. J., Franco, L., & Puiggali, J. (2017). Thermal degradation of random copolyesters based on 1,4–butanediol, terepthalic acid and different aliphatic dicarboxylic acids. *Thermochimica Acta, 654*, 101–111.

Henrique, M. A., Neto, W. P. F., Silvério, H. A., Martins, D. F., Gurgel, L. V. A., da Silva Barud, H., . . . Pasquini, D. (2015). Kinetic study of the thermal decomposition of cellulose nanocrystals with different polymorphs, cellulose I and II, extracted from different sources and using different types of acids. *Industrial Crops and Products, 76*, 128–140.

Higashihara, T., Ito, S., Fukuta, S., Miyane, S., Ochiai, Y., Ishizone, T., . . . Hirao, A. (2016). Synthesis and Characterization of Multicomponent ABC–and ABCD–Type Miktoarm Star–Branched Polymers Containing a Poly (3–hexylthiophene) Segment. *ACS Macro Letters, 5*, 631–635.

Hirao, A., Goseki, R., & Ishizone, T. (2014). Advances in living anionic polymerization: from functional monomers, polymerization systems, to macromolecular architectures. *Macromolecules, 47*(6), 1883–1905.

Hirao, A., Higashihara, T., Nagura, M., & Sakurai, T. (2006). Successive synthesis of well–defined many arm star–branched polymers by an iterative methodology using a specially designed 1, 1–diphenylethylene. *Macromolecules, 39*(18), 6081–6091.

Hirao, A., Tanaka, S., Goseki, R., & Ishizone, T. (2011). Living Anionic Polymerization of 1,4–Divinylbenzene. *Macromolecules, 44*(12), 4579–4582.

Holland, B., & Hay, J. (2002). The thermal degradation of PET and analogous polyesters measured by thermal analysis–Fourier transform infrared spectroscopy. *Polymer, 43*(6), 1835–1847.

Holter, D., Burgath, A., & Frey, H. (1997). Degree of branching in hyperbranched polymers. *Acta Polymerica, 48*(1–2), 30–35.

Holter, D., & Frey, H. (1997). Degree of branching in hyperbranched polymers. Enhancement of the DB: Scope and limitations. *Abstracts of Papers of the American Chemical Society, 214*, 261–PMSE.

Hong, K., Uhrig, D., & Mays, J. W. (1999). Living anionic polymerization. *Current Opinion in Solid State and Materials Science, 4*(6), 531–538.

Hsieh, H., Farrar, R., & Udipi, K. (1981). Anionic polymerization: some commercial applications. In: ACS Publications, 1–25.

Hsieh, H., & Quirk, R. P. (1996). *Anionic polymerization: principles and practical applications*: CRC Press, 17–205.

Hsieh, T.–T., Tiu, C., & Simon, G. (2001). Melt rheology of aliphatic hyperbranched polyesters with various molecular weights. *Polymer, 42*(5), 1931–1939.

Hu, X. (2017). Novel fluorescent porous hyperbranched aromatic polyamide containing 1, 3, 5–triphenylbenzene moieties: Synthesis and characterization. *Journal of Applied Polymer Science, 134*(8).

Huang, W., Yang, H., Xue, X., Jiang, B., Chen, J., Yang, Y., . . . Kong, L. (2013). Polymerization behaviors and polymer branching structures in ATRP of monovinyl and divinyl monomers. *Polymer Chemistry, 4*(11), 3204–3211.

Huber, T., Böhme, F., Komber, H., Kronek, J., Luston, J., Voigt, D., & Voit, B. (1999). New hyperbranched poly (ether amide) s via nucleophilic ring opening of 2–oxazoline–containing monomers. *Macromolecular Chemistry and Physics, 200*(1), 126–133.

Hult, A., Johansson, M., & Malmstrom, E. (1999). Hyperbranched polymers. *Branched Polymers II, Springer, 143*, 1–34.

Hutchings, L. R. (2008). DendriMacs and HyperMacs–emerging as more than just model branched polymers. *Soft Matter, 4*(11), 2150–2159.

Hutchings, L. R., Agostini, S., Hamley, I. W., & Hermida–Merino, D. (2015). Chain Architecture as an Orthogonal Parameter To Influence Block Copolymer Morphology. Synthesis and Characterization of Hyperbranched Block Copolymers: HyperBlocks. *Macromolecules, 48*(24), 8806–8822.

Hutchings, L. R., Dodds, J. M., Rees, D., Kimani, S. M., Wu, J. J., & Smith, E. (2009). HyperMacs to hyperblocks: a novel class of branched thermoplastic elastomer. *Macromolecules, 42*(22), 8675–8687.

Hutchings, L. R., Dodds, J. M., & Roberts–Bleming, S. J. (2005). HyperMacs: highly branched polymers prepared by the polycondensation of AB2 macromonomers, synthesis and characterization. *Macromolecules, 38*(14), 5970–5980.

Idris, S. S., Rahman, N. A., Ismail, K., Alias, A. B., Rashid, Z. A., & Aris, M. J. (2010). Investigation on thermochemical behaviour of low rank Malaysian coal, oil palm biomass and their blends during pyrolysis via thermogravimetric analysis (TGA). *Bioresource Technology, 101*(12), 4584–4592.

Inoue, K. (2000). Functional dendrimers, hyperbranched and star polymers. *Progress in Polymer Science, 25*(4), 453–571.

Isaure, F., Cormack, P. A., Graham, S., Sherrington, D. C., Armes, S. P., & Bütün, V. (2004). Synthesis of branched poly(methyl methacrylate)s via controlled/living polymerisations exploiting ethylene glycol dimethacrylate as branching agent. *Chemical Communications* 9, 1138–1139.

Isaure, F., Cormack, P. A., & Sherrington, D. C. (2003). Facile synthesis of branched poly(methyl methacrylate)s. *Journal of Materials Chemistry, 13*(11), 2701–2710.

Isaure, F., Cormack, P. A., & Sherrington, D. C. (2004). Synthesis of branched poly(methyl methacrylate)s: effect of the branching comonomer structure. *Macromolecules, 37*(6), 2096–2105.

Ishida, Y., Sun, A. C., Jikei, M., & Kakimoto, M.–A. (2000). Synthesis of hyperbranched aromatic polyamides starting from dendrons as ABx monomers: effect of monomer multiplicity on the degree of branching. *Macromolecules, 33*(8), 2832–2838.

Ishizone, T., & Frey, H. (2017). Living anionic aolymerization celebrates 60 years: unique features and polymer architectures. *Macromolecular Chemistry and Physics, 218*(12), 1–10.

Itoh, T., Ichikawa, Y., Hirata, N., Uno, T., Kubo, M., & Yamamoto, O. (2002). Effect of branching in base polymer on ionic conductivity in hyperbranched polymer electrolytes. *Solid State Ionics, 150*(3–4), 337–345.

Jafarifard, S., Bastani, S., Soleimani–Gorgani, A., & Sari, M. G. (2016). The chemo–rheological behavior of an acrylic based UV–curable inkjet ink: Effect of surface chemistry for hyperbranched polymers. *Progress in Organic Coatings, 90*, 399–406.

Janzen, J., & Colby, R. (1999). Diagnosing long–chain branching in polyethylenes. *Journal of Molecular Structure, 485*, 569–583.

Jia, Z., Chen, H., Zhu, X., & Yan, D. (2006). Backbone–thermoresponsive hyperbranched polyethers. *Journal of the American Chemical Society, 128*(25), 8144–8145.

Jiang, L., Huang, W., Xue, X., Yang, H., Jiang, B., Zhang, D., . . . Zhai, G. (2012). Radical polymerization in the presence of chain transfer monomer: an approach to branched vinyl polymers. *Macromolecules, 45*(10), 4092–4100.

Jikei, M., Chon, S.–H., Kakimoto, M.–a., Kawauchi, S., Imase, T., & Watanebe, J. (1999). Synthesis of hyperbranched aromatic polyamide from aromatic diamines and trimesic acid. *Macromolecules, 32*(6), 2061–2064.

Jikei, M., & Kakimoto, M. (2001). Hyperbranched polymers: a promising new class of materials. *Progress in Polymer Science, 26*(8), 1233–1285.

Kambouris, P., & Hawker, C. J. (1993). A versatile new method for structure determination in hyperbranched macromolecules. *Journal of the Chemical Society, Perkin Transactions 1*(22), 2717–2721.

Kempe, K., Krieg, A., Becer, C. R., & Schubert, U. S. (2012). “Clicking” on/with polymers: a rapidly expanding field for the straightforward preparation of novel macromolecular architectures. *Chemical Society Reviews, 41*(1), 176–191.

Kharchenko, S. B., & Kannan, R. M. (2003). Role of architecture on the conformation, rheology, and orientation behavior of linear, star, and hyperbranched polymer melts. 2. Linear viscoelasticity and flow birefringence. *Macromolecules, 36*(2), 407–415.

Kharchenko, S. B., Kannan, R. M., Cernohous, J. J., & Venkataramani, S. (2003). Role of architecture on the conformation, rheology, and orientation behavior of linear, star, and hyperbranched polymer melts. 1. Synthesis and molecular characterization. *Macromolecules, 36*(2), 399–406.

Kienle, R. H., & Hovey, A. (1929). The polyhydric alcohol–polybasic acid reaction. I. Glycerol–phthalic anhydride. *Journal of the American Chemical Society, 51*(2), 509–519.

Kim, Y. H. (1992). Lyotropic liquid crystalline hyperbranched aromatic polyamides. *Journal of the American Chemical Society, 114*(12), 4947–4948.

Kim, Y. H. (1998). Hyperbranched polymers 10 years after. *Journal of Polymer Science Part A: Polymer Chemistry, 36*(11), 1685–1698.

Kim, Y. H., & Beckerbauer, R. (1994). Role of end groups on the glass transition of hyperbranched polyphenylene and triphenylbenzene derivatives. *Macromolecules, 27*(7), 1968–1971.

Kim, Y. H., & Webster, O. W. (1990). Water soluble hyperbranched polyphenylene:" a unimolecular micelle?". *Journal of the American Chemical Society, 112*(11), 4592–4593.

Kim, Y. H., & Webster, O. W. (1992). Hyperbranched polyphenylenes. *Macromolecules, 25*(21), 5561–5572.

Koh, M. L., Konkolewicz, D., & Perrier, S. (2011). A simple route to functional highly branched structures: RAFT homopolymerization of divinylbenzene. *Macromolecules, 44*(8), 2715–2724.

Komber, H., Voit, B., Monticelli, O., & Russo, S. (2001). ^1H and ^{13}C NMR spectra of a hyperbranched aromatic polyamide from p–phenylenediamine and trimesic acid. *Macromolecules, 34*(16), 5487–5493.

Konkolewicz, D., Monteiro, M. J., & Perrier, S. (2011). Dendritic and hyperbranched polymers from macromolecular units: elegant approaches to the synthesis of functional polymers. *Macromolecules, 44*(18), 7067–7087.

Kozak, R., & Matlengiewicz, M. (2015a). Influence of polar modifiers on microstructure of polybutadiene obtained by anionic polymerization. Part 1: Lewis base (σ) amine–type polar modifiers. *International Journal of Polymer Analysis and Characterization, 20*(7), 502–511.

Kozak, R., & Matlengiewicz, M. (2015b). Influence of polar modifiers on microstructure of polybutadiene obtained by anionic polymerization. Part 2: Lewis base (σ) amine–ether and ether–type polar modifiers. *International Journal of Polymer Analysis and Characterization, 20*(7), 602–611.

Kozak, R., & Matlengiewicz, M. (2015c). Influence of polar modifiers on microstructure of polybutadiene obtained by anionic polymerization. Part 3: Lewis acid alkoxide (μ) and Lewis base amine, amine–ether, and ether mixed–type ($\sigma + \mu$) polar modifiers. *International Journal of Polymer Analysis and Characterization, 20*(8) 102–108.

Kozak, R., & Matlengiewicz, M. (2015d). Influence of polar modifiers on microstructure of polybutadiene obtained by anionic polymerization. Part 4: Acid–base polar modifiers forming σ–μ complexes: Amine–alkoxide, amine–ether–alkoxide, and ether–alkoxide. *International Journal of Polymer Analysis and Characterization 20*(6), 302–312.

Kraus, G., Childers, C., & Gruver, J. (1967). Properties of random and block copolymers of butadiene and styrene. I. Dynamic properties and glassy transition temperatures. *Journal of Applied Polymer Science, 11*(8), 1581–1591.

Kricheldorf, H. R., Berl, M., & Scharnagl, N. (1988). Poly (lactones). 9. Polymerization mechanism of metal alkoxide initiated polymerizations of lactide and various lactones. *Macromolecules, 21*(2), 286–293.

Kricheldorf, H. R., Bolender, O., & Wollheim, T. (1999). New polymer syntheses. 103. In situ end group modification of hyperbranched poly (3, 5–dihydroxybenzoate). *Macromolecules, 32*(12), 3878–3882.

Kricheldorf, H. R., Hobzova, R., Vakhtangishvili, L., & Schwarz, G. (2005). Multicyclic Poly (ether ketone) s by Polycondensation of 1, 3, 5-Tris (4-fluorobenzoyl) benzene with Various Diphenols. *Macromolecular Chemistry and Physics, 206*(21), 2133–2142.

Kricheldorf, H. R., & Rost, S. (2004). Polylactones, 67. *Macromolecular Chemistry and Physics, 205*(8), 1031–1038.

Kricheldorf, H. R., & Schwarz, G. (2003). Cyclic polymers by kinetically controlled step-growth polymerization. *Macromolecular Rapid Communications, 24*(5-6), 359–381.

Kricheldorf, H. R., Zang, Q.–Z., & Schwarz, G. (1982). New polymer syntheses: 6. Linear and branched poly (3–hydroxy–benzoates). *Polymer, 23*(12), 1821–1829.

Kroschwitz, J. (1990). Poly(arylene sulfide)s. *Concise Encyclopedia of Polymer Science and Engineering.*

Kumar, A., & Ramakrishnan, S. (1993). A novel one–pot synthesis of hyperbranched polyurethanes. *Journal of the Chemical Society, Chemical Communications 18*, 1453–1454.

Kunamaneni, S., Buzza, D. M. A., Parker, D., & Feast, W. J. (2003). Size exclusion chromatography and rheology of AB/AB 2 hyperbranched polymers. *Journal of Materials Chemistry, 13*(11), 2749–2755.

L. Villaraza, A. J., Bumb, A., & Brechbiel, M. W. (2010). Macromolecules, dendrimers, and nanomaterials in magnetic resonance imaging: the interplay between size, function, and pharmacokinetics. *Chemical Reviews, 110*(5), 2921–2959.

Langereis, S., Dirksen, A., Hackeng, T. M., Van Genderen, M. H., & Meijer, E. (2007). Dendrimers and magnetic resonance imaging. *New Journal of Chemistry, 31*(7), 1152–1160.

Lederer, A., Voigt, D., Clausnitzer, C., & Voit, B. (2002). Structure characterization of hyperbranched poly(ether amide)s–I. Preparative fractionation. *Journal of Chromatography A, 976*(1–2), 171–179.

Lee, C. C., MacKay, J. A., Fréchet, J. M., & Szoka, F. C. (2005). Designing dendrimers for biological applications. *Nature Biotechnology, 23*(12), 1517.

Li, W., Yoon, J. A., Zhong, M., & Matyjaszewski, K. (2011). Atom transfer radical copolymerization of monomer and cross–linker under highly dilute conditions. *Macromolecules, 44*(9), 3270–3275.

Li, Y., & Armes, S. P. (2005a). Synthesis and chemical degradation of branched vinyl polymers prepared via ATRP: use of a cleavable disulfide–based branching agent. *Macromolecules, 38*(20), 8155–8162.

Li, Y., & Armes, S. P. (2005b). Synthesis of branched water–soluble vinyl polymers via oxyanionic polymerization. *Macromolecules, 38*(12), 5002–5009.

Lim, J., Kostiainen, M., Maly, J., da Costa, V. C., Annunziata, O., Pavan, G. M., & Simanek, E. E. (2013). Synthesis of large dendrimers with the dimensions of small viruses. *Journal of the American Chemical Society, 135*(12), 4660–4663.

Lin, Q., & Long, T. E. (2003). Polymerization of A2 with B3 monomers: a facile approach to hyperbranched poly (aryl ester) s. *Macromolecules, 36*(26), 9809–9816.

Liouni, M., Touloupis, C., Hadjichristidis, N., & Mays, J. W. (1989). Viscosity–temperature relationships for linear and 12-arm star polystyrenes in dilute solution. *Journal of Applied Polymer Science, 37*(9), 2699–2708.

Liu, B., Kazlauciunas, A., Guthrie, J. T., & Perrier, S. (2005a). One–pot hyperbranched polymer synthesis mediated by reversible addition fragmentation chain transfer (RAFT) polymerization. *Macromolecules, 38*(6), 2131–2136.

Liu, B., Kazlauciunas, A., Guthrie, J. T., & Perrier, S. b. (2005b). Influence of reaction parameters on the synthesis of hyperbranched polymers via reversible addition fragmentation chain transfer (RAFT) polymerization. *Polymer, 46*(17), 6293–6299.

Liu, J., Wang, Y., Fu, Q., Zhu, X., & Shi, W. (2008). Branched polymer via free radical polymerization of chain transfer monomer: a theoretical and experimental investigation. *Journal of Polymer Science Part A: Polymer Chemistry, 46*(4), 1449–1459.

Liu, J., Xiong, X., Liu, R., Jiang, J., & Liu, X. (2013). One–pot synthesis of branched alternating copolymers p (St–*alt*–MAn) via free radical polymerization in the presence of chain transfer monomer. *Polymer Bulletin, 70*(6), 1795–1803.

Liu, K., He, Q., Ren, L., Gong, L. J., Hu, J. L., Ou, E. C., & Xu, W. J. (2016). Synthesis and characterization of the well–defined polypentadiene via living anionic polymerization of (E)–1, 3–pentadiene. *Polymer, 89*, 28–40.

Liu, M., Vladimirov, N., & Fréchet, J. M. (1999). A new approach to hyperbranched polymers by ring–opening polymerization of an AB monomer: 4–(2–hydroxyethyl)–ε–caprolactone. *Macromolecules, 32*(20), 6881–6884.

Lyulin, A. V., Adolf, D. B., & Davies, G. R. (2001). Computer simulations of hyperbranched polymers in shear flows. *Macromolecules, 34*(11), 3783–3789.

Ma, X., Tang, J., Shen, Y., Fan, M., Tang, H., & Radosz, M. (2009). Facile synthesis of polyester dendrimers from sequential click coupling of asymmetrical monomers. *Journal of the American Chemical Society, 131*(41), 14795–14803.

Ma, Z., Chen, D., Gu, J., Bao, B., & Zhang, Q. (2015). Determination of pyrolysis characteristics and kinetics of palm kernel shell using TGA–FTIR and model–free integral methods. *Energy conversion and Management, 89*, 251–259.

Malmström, E., & Hult, A. (1996). Kinetics of formation of hyperbranched polyesters based on 2, 2–bis (methylol) propionic acid. *Macromolecules, 29*(4), 1222–1228.

Malmström, E., Johansson, M., & Hult, A. (1995). Hyperbranched aliphatic polyesters. *Macromolecules, 28*(5), 1698–1703.

Manafi, P., Ghasemi, I., Karrabi, M., Azizi, H., Manafi, M. R., & Ehsaninamin, P. (2015). Thermal stability and thermal degradation kinetics (model–free kinetics) of nanocomposites based on poly (lactic acid)/graphene: the influence of functionalization. *Polymer Bulletin, 72*(5), 1095–1112.

Marcos, M., Martín–Rapún, R., Omenat, A., & Serrano, J. L. (2007). Highly congested liquid crystal structures: dendrimers, dendrons, dendronized and hyperbranched polymers. *Chemical Society Reviews, 36*(12), 1889–1901.

Markoski, L. J., Moore, J. S., Sendijarevic, I., & McHugh, A. J. (2001). Effect of linear sequence length on the properties of branched aromatic etherimide copolymers. *Macromolecules, 34*(8), 2695–2701.

Matsen, M. (2000). Equilibrium behavior of asymmetric ABA triblock copolymer melts. *The Journal of Chemical Physics, 113*(13), 5539–5544.

Matsen, M. W., & Bates, F. S. (1996). Unifying weak–and strong–segregation block copolymer theories. *Macromolecules, 29*(4), 1091–1098.

Matsumoto, A. (1995). Free–radical crosslinking polymerization and copolymerization of multivinyl compounds. In *Synthesis and Photosynthesis* : Springer, 41–80.

Matsumoto, A. (2001). Polymerization of multiallyl monomers. *Progress in Polymer Science, 26*(2), 189–257.

Matyjaszewski, K., Gaynor, S. G., Kulfan, A., & Podwika, M. (1997). Preparation of hyperbranched polyacrylates by atom transfer radical polymerization. 1. Acrylic AB* monomers in “living” radical polymerizations. *Macromolecules, 30*(17), 5192–5194.

Matyjaszewski, K., Gaynor, S. G., & Müller, A. H. (1997). Preparation of hyperbranched polyacrylates by atom transfer radical polymerization. 2. Kinetics and mechanism of chain growth for the self–condensing vinyl polymerization of 2–((2–bromopropionyl)oxy)ethyl acrylate. *Macromolecules, 30*(23), 7034–7041.

Matyjaszewski, K., Gnanou, Y., & Leibler, L. (2007). *Macromolecular Engineering*: Wiley Online Library, 150–200.

Matyjaszewski, K., Pyun, J., & Gaynor, S. G. (1998). Preparation of hyperbranched polyacrylates by atom transfer radical polymerization, 4. The use of zero-valent copper. *Macromolecular Rapid Communications, 19*(12), 665–670.

Matyjaszewski, K., Wei, M., Xia, J., & McDermott, N. E. (1997). Controlled/“living” radical polymerization of styrene and methyl methacrylate catalyzed by iron complexes. *Macromolecules, 30*(26), 8161–8164.

Mayo, F. R., & Lewis, F. M. (1944). Copolymerization. I. A basis for comparing the behavior of monomers in copolymerization; the copolymerization of styrene and methyl methacrylate. *Journal of the American Chemical Society, 66*(9), 1594–1601.

Mays, J. W., Uhrig, D., Gido, S., Zhu, Y., Weidisch, R., Iatrou, H., . . . Lach, R. (2004). *Synthesis and structure–property relationships for regular multigraft copolymers.* Paper presented at the Macromolecular Symposia, 203.

McKee, M. G., Elkins, C. L., Park, T., & Long, T. E. (2005). Influence of random branching on multiple hydrogen bonding in poly(alkyl methacrylate)s. *Macromolecules, 38*(14), 6015–6023.

McLeish, T. C., & Milner, S. T. (1999). Entangled dynamics and melt flow of branched polymers. Springer, 195–256.

McNaught, A. D., & McNaught, A. D. (1997). *Compendium of chemical terminology* (Vol. 1669): Blackwell Science Oxford.

Milner, S. T. (1994). Chain architecture and asymmetry in copolymer microphases. *Macromolecules, 27*(8), 2333–2335.

Monticelli, O., Mariani, A., Voit, B., Komber, H., Mendichi, R., Pitto, V., . . . Russo, S. (2001). Hyperbranched aramids by the A~ 2+ B~ 3 versus AB~ 2 approach: influence of the reaction conditions on structural development. *High Performance Polymers, 13*(2), S45–S60.

Moorefield, C. N., & Vögtle, F. (2008). *Dendritic molecules: concepts, syntheses, perspectives*: Wiley VCH, 88–107.

Mori, H., Walther, A., Andre, X., Lanzendörfer, M. G., & Müller, A. H. (2004). Synthesis of highly branched cationic polyelectrolytes via self–condensing atom transfer radical copolymerization with 2–(diethylamino) ethyl methacrylate. *Macromolecules, 37*(6), 2054–2066.

Morikawa, A., & Akagi, M. (2013). Hyperbranched poly (ether ether ketone) s: preparation and comparison of properties with the corresponding dendrimers. *Polymer Journal, 45*(6), 614.

Morton, M., & Fetters, L. J. (1975). Anionic polymerization of vinyl monomers. *Rubber Chemistry and Technology, 48*(3), 359–409.

Moussout, H., Ahlafi, H., Aazza, M., & Bourakhouadar, M. (2016). Kinetics and mechanism of the thermal degradation of biopolymers chitin and chitosan using thermogravimetric analysis. *Polymer Degradation and Stability, 130*, 1–9.

Muhamad–Sarih, N. (2010). *Synthesis of Well–Defined Multi–End Functionalized Polymers via Living Anionic Polymerization.* (PhD), Durham University, 108.

Mulkern, T., & Tan, N. B. (2000). Processing and characterization of reactive polystyrene/hyperbranched polyester blends. *Polymer, 41*(9), 3193–3203.

Müller, A. H., Yan, D., & Wulkow, M. (1997). Molecular parameters of hyperbranched polymers made by self–condensing vinyl polymerization. 1. Molecular weight distribution. *Macromolecules, 30*(23), 7015–7023.

Muthukrishnan, S., Jutz, G., Andre, X., Mori, H., & Müller, A. H. (2005). Synthesis of hyperbranched glycopolymers via self–condensing atom transfer radical copolymerization of a sugar–carrying acrylate. *Macromolecules, 38*(1), 9–18.

Muthukrishnan, S., Mori, H., & Müller, A. H. (2005). Synthesis and characterization of methacrylate–type hyperbranched glycopolymers via self–condensing atom transfer radical copolymerization. *Macromolecules, 38*(8), 3108–3119.

Nádasi, H., Stannarius, R., Eremin, A., Ito, A., Ishikawa, K., Haba, O., . . . Araoka, F. (2017). Photomanipulation of the anchoring strength using a spontaneously adsorbed layer of azo dendrimers. *Physical Chemistry Chemical Physics, 19*(11), 7597–7606.

Nakamura, Y., Wan, Y., Mays, J. W., Iatrou, H., & Hadjichristidis, N. (2001). Radius of Gyration of Polystyrene Combs and Centipedes in Solution. *Macromolecules, 34*(6), 8323–8328.

Newkome, G., Yao, Z.–Q., Baker, G., & Gupta, V. (1985). Preparation of highly branched cascade molecules. *Journal of Organic Chemistry, 50*, 2004–2006.

Newkome, G. R., Baker, G. R., Saunders, M. J., Russo, P. S., Gupta, V. K., Yao, Z.–q., . . . Bouillion, K. (1986). Two–directional cascade molecules: synthesis and characterization of [9]–n–[9] arborols. *Journal of the Chemical Society, Chemical Communications, 10*, 752–753.

Newkome, G. R., Yao, Z., Baker, G. R., & Gupta, V. K. (1985). Micelles. Part 1. Cascade molecules: a new approach to micelles. A [27]–arborol. *The Journal of Organic Chemistry, 50*(11), 2003–2004.

Newkome, G. R., Yao, Z., Baker, G. R., Gupta, V. K., Russo, P. S., & Saunders, M. J. (1986). Chemistry of micelles series. Part 2. Cascade molecules. Synthesis and characterization of a benzene [9] 3–arborol. *Journal of the American Chemical Society, 108*(4), 849–850.

Nishimura, N., Shibasaki, Y., Ozawa, M., & Oishi, Y. (2012). High refractive coating materials using hyperbranched polymers. *Journal of Photopolymer Science and Technology, 25*(3), 355–358.

O'brien, N., McKee, A., Sherrington, D., Slark, A., & Titterton, A. (2000). Facile, versatile and cost effective route to branched vinyl polymers. *Polymer, 41*(15), 6027–6031.

Oh, J. K., Drumright, R., Siegwart, D. J., & Matyjaszewski, K. (2008). The development of microgels/nanogels for drug delivery applications. *Progress in Polymer Science, 33*(4), 448–477.

Ohta, Y., Sakurai, K., Matsuda, J., & Yokozawa, T. (2016). Chain–growth condensation polymerization of 5–aminoisophthalic acid triethylene glycol ester to afford well–defined, water–soluble, thermoresponsive hyperbranched polyamides. *Polymer, 101*, 305–310.

Opfermann, J., Kaisersberger, E., & Flammersheim, H. (2002). Model–free analysis of thermoanalytical data–advantages and limitations. *Thermochimica Acta, 391*(1–2), 119–127.

Othman, M. B. H., Ahmad, Z., Osman, H., Omar, M. F., & Akil, H. M. (2015). Thermal degradation behavior of a flame retardant melamine derivative hyperbranched polyimide with different terminal groups. *RSC Advances, 5*(112), 92664–92676.

Ozawa, T. (1965). A new method of analyzing thermogravimetric data. *Bulletin of the Chemical Society of Japan, 38*(11), 1881–1886.

Ozawa, T. (2000). Thermal analysis – review and prospect. *Thermochimica Acta, 355*(1–2), 35–42.

Papageorgiou, G. Z., Tsanaktsis, V., Papageorgiou, D. G., Chrissafis, K., Exarhopoulos, S., & Bikiaris, D. N. (2015). Furan–based polyesters from renewable resources: Crystallization and thermal degradation behavior of poly (hexamethylene 2, 5–furan–dicarboxylate). *European Polymer Journal, 67*, 383–396.

Parker, D., & Feast, W. J. (2001). Synthesis, structure, and properties of hyperbranched polyesters based on dimethyl 5–(2–hydroxyethoxy)isophthalate. *Macromolecules, 34*(7), 2048–2059.

Patel, R. H., & Patel, K. S. (2015). Synthesis and characterization of flame retardant hyperbranched polyurethanes for nano–composite and nano–coating applications. *Progress in Organic Coatings, 88*, 283–292.

Patil, A., Patel, A., & Purohit, R. (2017). An overview of Polymeric Materials for Automotive Applications. *Materials Today: Proceedings, 4*(2), 3807–3815.

Patil, R., Colby, R. H., Read, D. J., Chen, G., & Guan, Z. (2005). Rheology of polyethylenes with novel branching topology synthesized by a chain–walking catalyst. *Macromolecules, 38*(25), 10571–10579.

Pavlov, G., Errington, N., Harding, S., Korneeva, E., & Roy, R. (2001). Dilute solution properties of lactosylated polyamidoamine dendrimers and their structural characteristics. *Polymer, 42*(8), 3671–3678.

Peng, H., Lam, J. W., & Tang, B. Z. (2005). Facile synthesis, high thermal stability, and unique optical properties of hyperbranched polyarylenes. *Polymer, 46*(15), 5746–5751.

Percec, V., Barboiu, B., Grigoras, C., & Bera, T. K. (2003). Universal iterative strategy for the divergent synthesis of dendritic macromolecules from conventional monomers by a combination of living radical polymerization and irreversible terminator multifunctional initiator (TERMINI). *Journal of the American Chemical Society, 125*(21), 6503–6516.

Perrier, S., Takolpuckdee, P., & Mars, C. A. (2005). Reversible addition− fragmentation chain transfer polymerization: end group modification for functionalized polymers and chain transfer agent recovery. *Macromolecules, 38*(6), 2033–2036.

Peterson, J. D., Vyazovkin, S., & Wight, C. A. (2001). Kinetics of the thermal and thermo–oxidative degradation of polystyrene, polyethylene and poly (propylene). *Macromolecular Chemistry and Physics, 202*(6), 775–784.

Powell, K. T., Cheng, C., Gudipati, C. S., & Wooley, K. L. (2005). Design, synthesis, and characterization of linear fluorinated poly(benzyl ether)s: A comparison study with isomeric hyperbranched fluoropolymers. *Journal of Materials Chemistry, 15*(48), 5128–5135.

Powell, K. T., Cheng, C., & Wooley, K. L. (2007). Complex amphiphilic hyperbranched fluoropolymers by atom transfer radical self–condensing vinyl (co) polymerization. *Macromolecules, 40*(13), 4509–4515.

Priddy, D. (1994). Recent advances in styrene polymerization. In *Polymer Synthesis* Springer, 67–114.

Prosa, T. J., Bauer, B. J., Amis, E. J., Tomalia, D. A., & Scherrenberg, R. (1997). A SAXS study of the internal structure of dendritic polymer systems. *Journal of Polymer Science Part B: Polymer Physics, 35*(17), 2913–2924.

Quirk, R. P., & Lee, B. (1992). Experimental criteria for living polymerizations. *Polymer International, 27*(4), 359–367.

Quirk, R. P., Mathers, R. T., Wesdemiotis, C., & Arnould, M. A. (2002). Investigation of ethylene oxide oligomerization during functionalization of poly(styryl) lithium using MALDI− TOF MS and NMR. *Macromolecules, 35*(8), 2912–2918.

Rajeshwari, P., & Dey, T. (2014). Structural and thermal properties of HDPE/n–AlN polymer nanocomposites. *Journal of Thermal Analysis and Calorimetry, 118*(3), 1513–1530.

Ratkanthwar, K., Zhao, J., Zhang, H., Hadjichristidis, N., & Mays, J. (2015). Schlenk techniques for anionic polymerization. In *Anionic Polymerization* Springer, 3–18.

Reek, J. N., Arévalo, S., van Heerbeek, R., Kamer, P. C., & Van Leeuwen, P. W. (2006). Dendrimers in catalysis. *Advances in Catalysis, 49*, 71–151.

Ren, Y., Wei, Z., Leng, X., Wu, T., Bian, Y., & Li, Y. (2016). Relationships between Architectures and Properties of Highly Branched Polymers: The Cases of Amorphous Poly (trimethylene carbonate) and Crystalline Poly (ε–caprolactone). *The Journal of Physical Chemistry B, 120*(17), 4078–4090.

Rimmer, S., Carter, S., Rutkaite, R., Haycock, J. W., & Swanson, L. (2007). Highly branched poly–(N–isopropylacrylamide) s with arginine–glycine–aspartic acid (RGD)–or COOH–chain ends that form sub–micron stimulus–responsive particles above the critical solution temperature. *Soft Matter, 3*(8), 971–973.

Román, F., Colomer, P., Calventus, Y., & Hutchinson, J. M. (2016). Molecular mobility in hyperbranched polymers and their interaction with an epoxy matrix. *Materials, 9*(3), 192.

Rosselgong, J., Armes, S. P., Barton, W. R., & Price, D. (2010). Synthesis of branched methacrylic copolymers: comparison between RAFT and ATRP and effect of varying the monomer concentration. *Macromolecules, 43*(5), 2145–2156.

Rubinstein, M., & Colby, R. H. (2003). *Polymer physics* (Vol. 23): Oxford university press New York, 108–200.

Russo, S., Boulares, A., Da Rin, A., Mariani, A., & Cosulich, M. E. (1999). *Hyperbranched aramids by direct polyamidation of two reactant systems: synthesis and properties.* Paper presented at the Macromolecular Symposia, 1–12.

Russo, V., Liberati, E., & Cazzolla, N. (2013). Glycogen–based cationic polymers. In: Google Patents, 1–5.

Sanford, M. J., Van Zee, N. J., & Coates, G. W. (2018). Reversible–deactivation anionic alternating ring–opening copolymerization of epoxides and cyclic anhydrides: access to orthogonally functionalizable multiblock aliphatic polyesters. *Chemical Science, 9*(1), 134–142.

Sathiyaraj, S., Shanavas, A., Kumar, K. A., Sathiyaseelan, A., Senthilselvan, J., Kalaichelvan, P., & Nasar, A. S. (2017). The first example of bis (indolyl) methane based hyperbranched polyurethanes: Synthesis, solar cell application and anti–bacterial and anti–oxidant properties. *European Polymer Journal, 95*, 216–231.

Sato, E., Uehara, I., Horibe, H., & Matsumoto, A. (2014). One–step synthesis of thermally curable hyperbranched polymers by addition–fragmentation chain transfer using divinyl monomers. *Macromolecules, 47*(3), 937–943.

Sato, T., Arima, Y., Seno, M., & Hirano, T. (2005). Initiator–Fragment Incorporation Radical Polymerization of Divinyl Adipate with Dimethyl 2, 2 '–Azobis (isobutyrate): Kinetics and Formation of Soluble Hyperbranched Polymer. *Macromolecules, 38*(5), 1627–1632.

Sato, T., Nakamura, T., Seno, M., & Hirano, T. (2006). Soluble hyperbranched copolymer via initiator–fragment incorporation radical copolymerization using a trivinyl monomer. *Polymer, 47*(13), 4630–4637.

Sato, T., Sato, N., Seno, M., & Hirano, T. (2003). Initiator-fragment incorporation radical polymerization of divinylbenzene in the presence of glyoxylic oxime ether: Formation of soluble hyperbranched polymer. *Journal of Polymer Science Part A: Polymer Chemistry, 41*(19), 3038–3047.

Satoh, N., & Yamamoto, K. (2018). Dendrimers and Their Application to Organic Electronics Devices. In *Nanoparticle Technology Handbook (Third Edition)* Elsevier, 559–562.

Schaefgen, J. R., & Flory, P. J. (1948). Synthesis of multichain polymers and investigation of their viscosities1. *Journal of the American Chemical Society, 70*(8), 2709–2718.

Schallausky, F., Erber, M., Komber, H., & Lederer, A. (2008). An Easy Strategy for the Synthesis of Well-Defined Aliphatic-Aromatic Hyperbranched Polyesters. *Macromolecular Chemistry and Physics, 209*(22), 2331–2338.

Scharfenberg, M., Hofmann, S., Preis, J., Hilf, J., & Frey, H. (2017). Rigid Hyperbranched Polycarbonate Polyols from CO_2 and Cyclohexene–Based Epoxides. *Macromolecules, 50*(16), 6088–6097.

Scheel, A., Komber, H., & Voit, B. (2004). *Hyperbranched thermolabile polycarbonates derived from a A2+ B3 monomer system.* Paper presented at the Macromolecular Symposia, 1–6.

Schmaljohann, D., Häußler, L., Pötschke, P., Voit, B. I., & Loontjens, T. J. (2000). Modification with alkyl chains and the influence on thermal and mechanical properties of aromatic hyperbranched polyesters. *Macromolecular Chemistry and Physics, 201*(1), 49–57.

Schmaljohann, D., & Voit, B. (2003). Kinetic evaluation of hyperbranched A2 + B3 polycondensation reactions. *Macromolecular Theory and Simulations, 12*(9), 679–689.

Šebestík, J., Reiniš, M., & Ježek, J. (2012). Dendrimers in Catalysis. In *Biomedical Applications of Peptide–, Glyco–and Glycopeptide Dendrimers, and Analogous Dendrimeric Structures,* Springer, 99–102.

Segawa, Y., Higashihara, T., & Ueda, M. (2013). Synthesis of hyperbranched polymers with controlled structure. *Polymer Chemistry, 4*(6), 1746–1759.

Semlyen, J. A. (2000). *Cyclic polymers*, Springer, 1–50.

Sendijarevic, I., Liberatore, M. W., McHugh, A. J., Markoski, L. J., & Moore, J. S. (2001). Effect of branching on the rheological properties of solutions of aromatic etherimide copolymers. *Journal of Rheology, 45*(5), 1245–1258.

Sendijarevic, I., & McHugh, A. J. (2000). Effects of molecular variables and architecture on the rheological behavior of dendritic polymers. *Macromolecules, 33*(2), 590–596.

Sengupta, S., Das, T., & Bandyopadhyay, A. (2018). Structure–Property Relationship of Hyperbranched Polymers. In *Hyperbranched Polymers for Biomedical Applications*, 109–134.

Serrenho, A. C., Norman, J. B., & Allwood, J. M. (2017). The impact of reducing car weight on global emissions: the future fleet in Great Britain. *Phil. Trans. R. Soc. A, 375*(2095), 20160364.

Sherrington, D. C., Bouhier, M. H., Cormack, P. A. G., & Graham, S. (2008). POLY 267–Exploitation of the Strathclyde methodology in synthesizing branched vinyl polymers. *Abstracts of Papers of the American Chemical Society,* 235.

Sheth, J. P., Unal, S., Yilgor, E., Yilgor, I., Beyer, F. L., Long, T. E., & Wilkes, G. L. (2005). A comparative study of the structure–property behavior of highly branched segmented poly (urethane urea) copolymers and their linear analogs. *Polymer, 46*(23), 10180–10190.

Shibasaki, Y., & Nakahara, H. (1979). Polym Sci Polym Chem Ed 1979, 17, 2387;(b) Shibasaki, Y.; Fukuda, K. *Journal of Polymer Science, Polymer Chemistry Education, 17*, 2947.

Simha, R., & Branson, H. (1944). Theory of chain copolymerization reactions. *The Journal of Chemical Physics, 12*(6), 253–267.

Simon, P. F., & Müller, A. H. (2000). Molecular parameters of hyperbranched polymers made by self-condensing vinyl polymerization of macroinimers. *Macromolecular Theory and Simulations, 9*(8), 621–627.

Simon, P. F., Müller, A. H., & Pakula, T. (2001). Characterization of highly branched poly (methyl methacrylate) by solution viscosity and viscoelastic spectroscopy. *Macromolecules, 34*(6), 1677–1684.

Sivaram, S., Dhal, P., Kashikar, S., Khisti, R., Shinde, B., & Baskaran, D. (1991). Tailoring carbanion structures for controlled anionic polymerization of acrylonitrile. *Macromolecules, 24*(7), 1697–1698.

Slark, A. T., Sherrington, D. C., Titterton, A., & Martin, I. K. (2003). Branched methacrylate copolymers from multifunctional comonomers: the effect of multifunctional monomer functionality on polymer architecture and properties. *Journal of Materials Chemistry, 13*(11), 2711–2720.

Soršak, E., Valh, J. V., Urek, Š. K., & Lobnik, A. (2015). Application of PAMAM dendrimers in optical sensing. *Analyst, 140*(4), 976–989.

Speranza, V., De Meo, A., & Pantani, R. (2014). Thermal and hydrolytic degradation kinetics of PLA in the molten state. *Polymer Degradation and Stability, 100*, 37–41.

Staneva, D., & Grabchev, I. (2018). Heterogeneous sensors for ammonia, amines and metal ions based on a dendrimer modified fluorescent viscose fabric. *Dyes and Pigments, 155*, 164–170.

Starink, M. (2003). The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of isoconversion methods. *Thermochimica Acta, 404*(1–2), 163–176.

Staudinger, H., & Husemann, E. (1935). Über hochpolymere Verbindungen, 116. Mitteil.: Über das begrenzt quellbare Poly-styrol. *Berichte der deutschen chemischen Gesellschaft (A and B Series), 68*(8), 1618–1634.

Staudinger, U., Weidisch, R., Zhu, Y., Gido, S., Uhrig, D., Mays, J., . . . Hadjichristidis, N. (2006). *Mechanical properties and hysteresis behaviour of multigraft copolymers.* Paper presented at the Macromolecular symposia, 7–8.

Stevens, M. P., & Stevens, M. P. (1990). *Polymer chemistry: an introduction*: oxford university press New York, 1–104.

Stiriba, S. E., Frey, H., & Haag, R. (2002). Dendritic polymers in biomedical applications: from potential to clinical use in diagnostics and therapy. *Angewandte Chemie International Edition, 41*(8), 1329–1334.

Stockmayer, W., & Jacobson, H. (1943). Gel Formation in Vinyl-Divinyl Copolymers. *The Journal of Chemical Physics, 11*(8), 393.

Stockmayer, W. H. (1943). Theory of molecular size distribution and gel formation in branched-chain polymers. *The Journal of Chemical Physics, 11*(2), 45–55.

Stockmayer, W. H. (1944). Theory of molecular size distribution and gel formation in branched polymers II. General cross linking. *The Journal of Chemical Physics, 12*(4), 125–131.

Strašák, T., Malý, J., Wróbel, D., Malý, M., Herma, R., Čermák, J., . . . Cuřínová, P. (2017). Phosphonium carbosilane dendrimers for biomedical applications– synthesis, characterization and cytotoxicity evaluation. *RSC Advances, 7*(30), 18724–18744.

Sun, J., Aly, K. I., & Kuckling, D. (2017). A novel one–pot process for the preparation of linear and hyperbranched polycarbonates of various diols and triols using dimethyl carbonate. *RSC Advances, 7*(21), 12550–12560.

Sunder, A., Hanselmann, R., Frey, H., & Mülhaupt, R. (1999). Controlled synthesis of hyperbranched polyglycerols by ring–opening multibranching polymerization. *Macromolecules, 32*(13), 4240–4246.

Suneel, Buzza, D., Groves, D., McLeish, T., Parker, D., Keeney, A., & Feast, W. (2002). Rheology and molecular weight distribution of hyperbranched polymers. *Macromolecules, 35*(25), 9605–9612.

Sunusi Marwana, M. (2017). Microstructural evolution and mechanical properties of magnesium alloy/austenitic stainless steel joints produced by resistance spot welding techniques (PhD). University of Malaya, 1–10.

Svenson, S., & Tomalia, D. A. (2012). Dendrimers in biomedical applications – reflections on the field. *Advanced Drug Delivery Reviews, 64*, 102–115.

Szwarc, M. (1956). ‘Living’polymers. *Nature, 178*(4543), 1168.

Szwarc, M. (1983). Living polymers and mechanisms of anionic polymerization. In *Living Polymers and Mechanisms of Anionic Polymerization* Springer, 1–177.

Szwarc, M., Levy, M., & Milkovich, R. (1956). Polymerization initiated by electron transfer to monomer. A new method of formation of block polymers1. *Journal of the American Chemical Society, 78*(11), 2656–2657.

Tabuani, D., Monticelli, O., Chincarini, A., Bianchini, C., Vizza, F., Moneti, S., & Russo, S. (2003). Palladium nanoparticles supported on hyperbranched aramids: synthesis, characterization, and some applications in the hydrogenation of unsaturated substrates. *Macromolecules, 36*(12), 4294–4301.

Tabuani, D., Monticelli, O., Komber, H., & Russo, S. (2003). Preparation and characterisation of Pd nanoclusters in hyperbranched aramid templates to be used in homogeneous catalysis. *Macromolecular Chemistry and Physics, 204*(12), 1576–1583.

Tanaka, S., Goseki, R., Ishizone, T., & Hirao, A. (2014). Synthesis of well–defined novel reactive block polymers containing a poly (1, 4–divinylbenzene) segment by living anionic polymerization. *Macromolecules, 47*(7), 2333–2339.

Tanaka, S., Matsumoto, M., Goseki, R., Ishizone, T., & Hirao, A. (2012). Living anionic polymerization of 1, 4–divinylbenzene and its isomers. *Macromolecules, 46*(1), 146–154.

Tang, R., & Li, Z. (2017). Second-Order Nonlinear Optical Dendrimers and Dendronized Hyperbranched Polymers. *The Chemical Record, 17*(1), 71–89.

Tang, X. D., & Kong, Q. M. (2014). *Synthesis and characterization of the hyperbranched polyamide with triphenyl phosphorus structure and the influence* *on mechanical property of nylon–6.* Paper presented at the Advanced Materials Research, 1–5.

Tang, Y. P., Yuwen, S., Chung, T. S., Weber, M., Staudt, C., & Maletzko, C. (2016). Synthesis of hyperbranched polymers towards efficient boron reclamation via a hybrid ultrafiltration process. *Journal of Membrane Science, 510*, 112–121.

Tao, Y., He, J., Wang, Z., Pan, J., Jiang, H., Chen, S., & Yang, Y. (2001). Synthesis of branched polystyrene and poly (styrene–b–4–methoxystyrene) by nitroxyl stable radical controlled polymerization. *Macromolecules, 34*(14), 4742–4748.

Täuber, K., Marsico, F., Wurm, F. R., & Schartel, B. (2014). Hyperbranched poly (phosphoester) s as flame retardants for technical and high performance polymers. *Polymer Chemistry, 5*(24), 7042–7053.

Terzopoulou, Z., Tsanaktsis, V., Nerantzaki, M., Achilias, D. S., Vaimakis, T., Papageorgiou, G. Z., & Bikiaris, D. N. (2016). Thermal degradation of biobased polyesters: Kinetics and decomposition mechanism of polyesters from 2, 5–furandicarboxylic acid and long–chain aliphatic diols. *Journal of Analytical and Applied Pyrolysis, 117*, 162–175.

Thompson, D. S., Markoski, L. J., Moore, J. S., Sendijarevic, I., Lee, A., & McHugh, A. J. (2000). Synthesis and characterization of hyperbranched aromatic poly (ether imide)s with varying degrees of branching. *Macromolecules, 33*(17), 6412–6415.

Tobita, H. (2013). Free-Radical Polymerization with Long-Chain Branching and Scission in a Continuous Stirred-Tank Reactor. *Macromolecular Reaction Engineering, 7*(5), 181–192.

Tomalia, D. A., Baker, H., Dewald, J., Hall, M., Kallos, G., Martin, S., . . . Smith, P. (1985). A new class of polymers: starburst–dendritic macromolecules. *Polymer Journal, 17*(1), 117.

Tomalia, D. A., & Frechet, J. M. (2002). *Introduction to the dendritic state*, Wiley Online Library, 1–20.

Trollsås, M., Kelly, M. A., Claesson, H., Siemens, R., & Hedrick, J. L. (1999). Highly branched block copolymers: design, synthesis, and morphology. *Macromolecules, 32*(15), 4917–4924.

Tsanaktsis, V., Vouvoudi, E., Papageorgiou, G. Z., Papageorgiou, D. G., Chrissafis, K., & Bikiaris, D. N. (2015). Thermal degradation kinetics and decomposition mechanism of polyesters based on 2, 5–furandicarboxylic acid and low molecular weight aliphatic diols. *Journal of Analytical and Applied Pyrolysis, 112*, 369–378.

Tsuruta, T. (1985). Molecular design of functional polymers having amino groups. *Die Makromolekulare Chemie, 13*(S19851), 33–46.

Tu, X. Y., Liu, M. Z., & Wei, H. (2016). Recent progress on cyclic polymers: Synthesis, bioproperties, and biomedical applications. *Journal of Polymer Science Part A: Polymer Chemistry, 54*(11), 1447–1458.

Turner, S. R., Voit, B. I., & Mourey, T. H. (1993). All–aromatic hyperbranched polyesters with phenol and acetate end groups: synthesis and characterization. *Macromolecules, 26*(17), 4617–4623.

Turner, S. R., Walter, F., Voit, B. I., & Mourey, T. H. (1994). Hyperbranched aromatic polyesters with carboxylic–acid terminal groups. *Macromolecules, 27*(6), 1611–1616.

Uhrig, D., & Mays, J. (2011). Synthesis of well–defined multigraft copolymers. *Polymer Chemistry, 2*(1), 69–76.

Uhrig, D., Schlegel, R., Weidisch, R., & Mays, J. (2011). Multigraft copolymer superelastomers: Synthesis morphology, and properties. *European Polymer Journal, 47*(4), 560–568.

Unal, S., Oguz, C., Yilgor, E., Gallivan, M., Long, T., & Yilgor, I. (2005). Understanding the structure development in hyperbranched polymers prepared by oligomeric A2+ B3 approach: comparison of experimental results and simulations. *Polymer, 46*(13), 4533–4543.

Unal, S., Yilgor, I., Yilgor, E., Sheth, J., Wilkes, G., & Long, T. (2004). A new generation of highly branched polymers: hyperbranched, segmented poly (urethane urea) elastomers. *Macromolecules, 37*(19), 7081–7084.

Uraneck, C. (1971). Influence of temperature on microstructure of anionic-initiated polybutadiene. *Journal of Polymer Science Part A-1: Polymer Chemistry, 9*(8), 2273–2281.

van Benthem, R. A., Meijerink, N., Gelade, E., de Koster, C. G., Muscat, D., Froehling, P. E., . . . Zwartkruis, T. J. (2001). Synthesis and characterization of bis (2–hydroxypropyl) amide–based hyperbranched polyesteramides. *Macromolecules, 34*(11), 3559–3566.

Venkatesh, M., Ravi, P., & Tewari, S. P. (2013). Isoconversional kinetic analysis of decomposition of nitroimidazoles: Friedman method vs Flynn–Wall–Ozawa method. *The Journal of Physical Chemistry A, 117*(40), 10162–10169.

Vlassopoulos, D., Pakula, T., Fytas, G., Roovers, J., Karatasos, K., & Hadjichristidis, N. (1997). Ordering and viscoelastic relaxation in multiarm star polymer melts. *EPL (Europhysics Letters), 39*(6), 617.

Voit, B. (2000). New developments in hyperbranched polymers. *Journal of Polymer Science Part A: Polymer Chemistry, 38*(14), 2505–2525.

Voit, B. (2005). Hyperbranched polymers—all problems solved after 15 years of research? *Journal of Polymer Science Part A: Polymer Chemistry, 43*(13), 2679–2699.

Voit, B. I., & Lederer, A. (2009). Hyperbranched and Highly Branched Polymer Architectures: Synthetic Strategies and Major Characterization Aspects. *Chemical Reviews, 109*(11), 5924–5973.

Vunain, E., Mishra, A., & Mamba, B. (2016). Dendrimers, mesoporous silicas and chitosan–based nanosorbents for the removal of heavy–metal ions: a review. *International Journal of Biological Macromolecules, 86*, 570–586.

Vyazovkin, S. (2017). Isoconversional kinetics of polymers: The decade past. *Macromolecular Rapid Communications, 38*(3), 1–6.

Vyazovkin, S., Burnham, A. K., Criado, J. M., Pérez–Maqueda, L. A., Popescu, C., & Sbirrazzuoli, N. (2011). ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochimica Acta, 520*(1–2), 1–19.

Vyazovkin, S., & Sbirrazzuoli, N. (2006). Isoconversional kinetic analysis of thermally stimulated processes in polymers. *Macromolecular Rapid Communications, 27*(18), 1515–1532.

Vyazovkin, S., & Wight, C. A. (1999). Model–free and model–fitting approaches to kinetic analysis of isothermal and nonisothermal data. *Thermochimica Acta, 340*, 53–68.

Walling, C. (1945). Gel Formation in Addition Polymerization1. *Journal of the American Chemical Society, 67*(3), 441–447.

Wang, D., Zhao, T., Zhu, X., Yan, D., & Wang, W. (2015). Bioapplications of hyperbranched polymers. *Chemical Society Reviews, 44*(12), 4023–4071.

Wang, D. L., Zhao, T. Y., Zhu, X. Y., Yan, D. Y., & Wang, W. X. (2015). Bioapplications of hyperbranched polymers. *Chemical Society Reviews, 44*(12), 4023–4071.

Wang, L., Yang, Y., Shi, X., Mignani, S., Caminade, A.–M., & Majoral, J.–P. (2018). Cyclotriphosphazene core–based dendrimers in biomedical applications: An update on recent advances. *Journal of Materials Chemistry B, 6*(6) 884–895.

Wang, N., Wang, L., Zhang, R., Li, J., Zhao, C., Wu, T., & Ji, S. (2015). Highly stable "pore–filling" tubular composite membrane by self–crosslinkable hyperbranched polymers for toluene/n–heptane separation. *Journal of Membrane Science, 474*, 263–272.

Wang, W., Wang, W., Li, H., Lu, X., Chen, J., Kang, N.–G., . . . Mays, J. (2015). Synthesis and characterization of graft copolymers poly(isoprene–g–styrene) of high molecular weight by a combination of anionic polymerization and emulsion polymerization. *Industrial & Engineering Chemistry Research, 54*(4), 1292–1300.

Wang, X., & Gao, H. (2017). Recent progress on hyperbranched polymers synthesized via radical–based self–condensing vinyl polymerization. *Polymers, 9*(6), 188.

Wang, X. F., & Gao, H. F. (2017). Recent progress on hyperbranched polymers synthesized via radical–based self–condensing vinyl polymerization. *Polymers, 9*(6), 188.

Wang, Z., He, J., Tao, Y., Yang, L., Jiang, H., & Yang, Y. (2003). Controlled chain branching by RAFT–based radical polymerization. *Macromolecules, 36*(20), 7446–7452.

Weidisch, R., Gido, S., Uhrig, D., Iatrou, H., Mays, J., & Hadjichristidis, N. (2001). Tetrafunctional multigraft copolymers as novel thermoplastic elastomers. *Macromolecules, 34*(18), 6333–6337.

Widmaier, J., & Meyer, G. (1981). Glass transition temperature of anionic polyisoprene. *Macromolecules, 14*(2), 450–452.

Wood–Adams, P. M., Dealy, J. M., Degroot, A. W., & Redwine, O. D. (2000). Effect of molecular structure on the linear viscoelastic behavior of polyethylene. *Macromolecules, 33*(20), 7489–7499.

Wooley, K., Hawker, C., Lee, R., & Fréchet, J. (1994). One–step synthesis of hyperbranched polyesters. Molecular weight control and chain end functionalization. *Polymer Journal, 26*(2), 187.

Wooley, K., Hawker, C., Pochan, J., & Frechet, J. (1993). Physical properties of dendritic macromolecules: a study of glass transition temperature. *Macromolecules, 26*(7), 1514–1519.

Wooley, K. L., Fréchet, J. M., & Hawker, C. J. (1994). Influence of shape on the reactivity and properties of dendritic, hyperbranched and linear aromatic polyesters. *Polymer, 35*(21), 4489–4495.

Xia, J., & Matyjaszewski, K. (1997). Controlled/"living" radical polymerization. Atom transfer radical polymerization using multidentate amine ligands. *Macromolecules, 30*(25), 7697–7700.

Yan, D., Gao, C., & Frey, H. (2011). *Hyperbranched polymers: synthesis, properties, and applications* John Wiley & Sons, 8, 15–35.

Yan, D., Müller, A. H., & Matyjaszewski, K. (1997). Molecular parameters of hyperbranched polymers made by self–condensing vinyl polymerization. 2. Degree of branching. *Macromolecules, 30*(23), 7024–7033.

Yan, D. Y., & Gao, C. (2000). Hyperbranched polymers made from A(2) and BB '(2) type monomers. 1. Polyaddition of 1–(2–aminoethyl)piperazine to divinyl sulfone. *Macromolecules, 33*(21), 7693–7699.

Yan, H., & Chen, Y. (2010). Blends of polypropylene and hyperbranched poly (phenylene sulphide) for production of dyeable PP fibres, *Iranian Polymer Journal*, *19*(10), 791–799.

Yang, K.–K., Wang, X.–L., Wang, Y.–Z., Wu, B., Jin, Y.–D., & Yang, B. (2003). Kinetics of thermal degradation and thermal oxidative degradation of poly (p–dioxanone). *European Polymer Journal, 39*(8), 1567–1574.

Yang, L., Hong, S., Gido, S. P., Velis, G., & Hadjichristidis, N. (2001). I5S miktoarm star block copolymers: packing constraints on morphology and discontinuous chevron tilt grain boundaries. *Macromolecules, 34*(26), 9069–9073.

Yang, Z., Wang, Q., & Wang, T. (2017). Engineering a hyperbranched polyimide membrane for shape memory and CO_2 capture. *Journal of Materials Chemistry A, 5*(26), 13823–13833.

Yao, D., Zhang, X., Abid, S., Shi, L., Blanchard–Desce, M., Mongin, O., . . . Paul–Roth, C. O. (2018). New porphyrin–based dendrimers with alkene linked fluorenyl antennae for optics. *New Journal of Chemistry, 42*(1), 395–401.

Yates, C., & Hayes, W. (2004). Synthesis and applications of hyperbranched polymers. *European Polymer Journal, 40*(7), 1257–1281.

Ye, R., Zhukhovitskiy, A. V., Deraedt, C. V., Toste, F. D., & Somorjai, G. A. (2017). Supported Dendrimer–Encapsulated Metal Clusters: Toward Heterogenizing Homogeneous Catalysts. *Accounts of chemical research, 50*(8), 1894–1901.

Ye, Z., AlObaidi, F., & Zhu, S. (2004). Melt rheological properties of branched polyethylenes produced with Pd-and Ni–diimine catalysts. *Macromolecular Chemistry and Physics, 205*(7), 897–906.

Ye, Z., & Zhu, S. (2003). Newtonian flow behavior of hyperbranched high–molecular–weight polyethylenes produced with a Pd−diimine catalyst and its dependence on chain topology. *Macromolecules, 36*(7), 2194–2197.

Ying, L., Guo, X., & Fang, J. (2016). Synthesis, freestanding membrane formation, and properties of novel sulfonated hyperbranched polyimides. *High Performance Polymers*, *30*(1), 3–15.

Yordanova, S., Grabchev, I., Stoyanov, S., & Petkov, I. (2014). New detectors for metal cations and protons based on PAMAM dendrimers modified with 1, 8–naphthalimide units. *Journal of Photochemistry and Photobiology A: Chemistry, 283*, 1–7.

Young, R. J., & Lovell, P. A. (2011). *Introduction to polymers*: CRC press, 12–102.

Yu, J., Sun, L., Ma, C., Qiao, Y., & Yao, H. (2016). Thermal degradation of PVC: A review. *Waste Management, 48*, 300–314.

Yu, X., Liu, Z., Janzen, J., Chafeeva, I., Horte, S., Chen, W., . . . Brooks, D. E. (2012). Polyvalent choline phosphate as a universal biomembrane adhesive. *Nature Materials, 11*(5), 468.

Yu, Y.–G., Chae, C.–G., Kim, M.–J., Seo, H.–B., Grubbs, R. H., & Lee, J.–S. (2018). Precise Synthesis of Bottlebrush Block Copolymers from ω–End–Norbornyl Polystyrene and Poly (4–tert–butoxystyrene) via Living Anionic Polymerization and Ring–Opening Metathesis Polymerization. *Macromolecules*, *51*(2), 447–455.

Yu, Y., Dubois, P., Jérôme, R., & Teyssié, P. (1996). Difunctional initiator based on 1, 3-diisopropenylbenzene. IV. Synthesis and modification of poly(alkyl methacrylate-b-styrene-b-butadiene-b-styrene-b-alkyl methacrylate (MSBSM)) thermoplastic elastomers. *Journal of Polymer Science Part A: Polymer Chemistry, 34*(11), 2221–2228.

Zabolotsky, V., Utin, S., Bespalov, A., & Strelkov, V. (2015). Modification of asymmetric bipolar membranes by functionalized hyperbranched polymers and their investigation during pH correction of diluted electrolytes solutions by electrodialysis. *Journal of Membrane Science, 494*, 188–195.

Zhang, G. (2015). *Surface–core–functionalized polyphenylene dendrimers for organic electronics.* Johannes Gutenberg–Universität Mainz, 2–45.

Zhang, Y.–R., Spinella, S., Xie, W., Cai, J., Yang, Y., Wang, Y.–Z., & Gross, R. A. (2013). Polymeric triglyceride analogs prepared by enzyme–catalyzed condensation polymerization. *European Polymer Journal, 49*(4), 793–803.

Zhao, L., Wang, S., Ding, J., & Wang, L. (2018). Solution processible distyrylarylene–based fluorescent dendrimers: Tuning of carbazole–dendron generation leads to nondoped deep–blue electroluminescence. *Organic Electronics, 53*, 43–49.

Zheng, Y., Li, S., Weng, Z., & Gao, C. (2015). Hyperbranched polymers: advances from synthesis to applications. *Chemical Society Reviews, 44*(12), 4091–4130.

Zhu, Q., Wu, J., Tu, C., Shi, Y., He, L., Wang, R., . . . Yan, D. (2009). Role of branching architecture on the glass transition of hyperbranched polyethers. *The Journal of Physical Chemistry B, 113*(17), 5777–5780.

Zhu, X., Zhou, Y., & Yan, D. (2011). Influence of branching architecture on polymer properties. *Journal of Polymer Science Part B: Polymer Physics, 49*(18), 1277–1286.

Zhu, Y., Burgaz, E., Gido, S. P., Staudinger, U., Weidisch, R., Uhrig, D., & Mays, J. W. (2006). Morphology and tensile properties of multigraft copolymers with regularly spaced tri–, tetra–, and hexafunctional junction points. *Macromolecules, 39*(13), 4428–4436.

Zhu, Y., Gido, S. P., Moshakou, M., Iatrou, H., Hadjichristidis, N., Park, S., & Chang, T. (2003). Effect of junction point functionality on the lamellar spacing of symmetric (PS)n (PI)n miktoarm star block copolymers. *Macromolecules, 36*(15), 5719–5724.

Zimm, B. H., & Stockmayer, W. H. (1949). The dimensions of chain molecules containing branches and rings. *The Journal of Chemical Physics, 17*(12), 1301–1314.

LIST OF PUBLICATIONS AND PAPERS PRESENTED

List of publications

- **Habibu, S.,** Sarih, N. M., & Mainal, A. (2018). Synthesis and characterisation of highly branched polyisoprene: exploiting the "Strathclyde route" in anionic polymerisation. *RSC Advances*, *8*(21), 11684–11692.

List of presentations

- **Shehu Habibu**, Norazilawati Muhamad Sarih, and Lian R. Hutchings; Exploiting the "Strathclyde Route" in Anionic Polymerization for the Synthesis of Branched Polymers; 25th POLYCHAR 2017 World Forum on Advanced Materials, Putra World Trade Centre, Kuala Lumpur, Malaysia, 9th – 13th October 2017, (Oral).
- **Shehu Habibu**, Norazilawati Muhamad Sarih, and Lian R. Hutchings; Highly branched soluble poly (isoprene). Lunching of industry linkage fund and presentation to MREPC scholarship awards. Malaysian Rubber Export Promotion Council (MREPC), One World Hotel, Petaling Jaya, Malaysia, 26 September 2017, (Poster).
- **Shehu Habibu**, Norazilawati Muhamad Sarih, and Lian R. Hutchings; Synthesis and Characterization of Branched Polyisoprene via Living Anionic Polymerization UM #111 Chemistry Symposium Department of Chemistry, Faculty of Science, University of Malaya, Kuala Lumpur, Malaysia. 3rd March 2016 (Poster).