PREPARATION OF STYRENE ACRYLIC COPOLYMER TONER RESIN BY SOLUTION POLYMERIZATION

NEO SU SIANG

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ABSTRACT

This project has investigated solution polymerization to produce toner resins. There are three stages: (i) synthesis of low molecular weight styrene acrylic copolymer; (ii) synthesis of high molecular weight styrene acrylic copolymer; (iii) mixing high and low molecular weight copolymers. Gel Permeation Chromatography (GPC) was used to study molecular weight distributions, Melt Flow Index (MFI) Instrument to study the flowability of resin, Differential Scanning Calorimetry (DSC) to study the thermal properties of resin, and acid number to quantitate the amount of acidic group in the resin. A comparison of properties between the experimental samples, patent's claims, and commercial resins had been carried out. Preparation of low molecular weight resin has carried out by using monomers, initiator and solvent. The effects of initiator concentration on the resin's properties of low molecular weight resin had been studied. High molecular weight resin was produced by using monomers, initiator, solvent and crosslinking agent in the system. The process started with bulk polymerization followed by solution polymerization. The variation on amount of tetra(ethylene glycol)diacrylate (TD) during solution polymerization was carried out to study the effects on resin's properties. Commercial toner resins contain a high molecular weight portion and a low molecular weight portion. The commercial resins have glass transition temperature in the range of 63~66°C, Melt Flow Index in the range of 4~10 g/10 min, and acid number in the range of 8.5~10.2 mg KOH g^{-1}. As for high molecular weight portion, M_n is in the range of 1.93×10^5~3.02×10^5 $gmol^{-1}$, M_p in the range of 8.07×10^5~1.7×10^6 $gmol^{-1}$, M_w in the range of 5.5×10^5~6.77×10^5 $gmol^{-1}$, M_z in the range of 1.2×10^6~1.5×10^6 $gmol^{-1}$, polydispersity in the range of 2.24~3.92. While for low molecular weight portion, M_n is roughly 4×10^3 $gmol^{-1}$, M_p around 5×10^3 $gmol^{-1}$, M_w in the range of 6×10^3~7×10^3 $gmol^{-1}$, M_z in the range of 9×10^3~1.1×10^4 $gmol^{-1}$, polydispersity in the range of 1.68~1.80. The ratio of low molecular weight portion to high molecular weight portion varies from 36:64 to 60:40. In this project, the low and high molecular weight portions were synthesized separately and they were mixed at various proportions to achieve the required properties as toner resins.

ABSTRAK

Tujuan utama projek ini adalah untuk menghasilkan resin toner yang melibatkan tiga peringkat eksperimen. (i) sintesis kopolimer stirena akrilik berberat molekul rendah; (ii) sintesis kopolimer stirena akrilik berberat molekul tinggi; (iii) percampuran kedua-dua kopolimer berberat molekul rendah dan tinggi. Kromatograf Penelapan Gel (GPC) telah diguna untuk mengkaji taburan berat molekul; Alat Indeks Aliran Leburan (MFI) diguna untuk mengkaji keupayaan leburan resin beralir; Kalorimetri Pengimbasan Pembezaan (DSC) untuk mengkaji sifat therma and nombor asid (AN) untuk mengkaji kandungan asid yang terdapat dalam resin. Satu perbandingan di antara resin perdagangan, paten US dan sampel eksperimen telah dianalisiskan. Resin berberat molekul rendah adalah disintesis melalui proses pempolimeran larutan dengan menggunakan hanya pelarut, monomer dan initiator. Manakala, resin berberat molekul tinggi adalah disediakan melalui proses pempolimeran bulk diikuti dengan pempolimeran larutan dengan menggunakan monomer, pelarut, initiator dan juga agen crosslinking. Dengan merujuk kepada resin perdagangan, terdapat dua bahagian dalam resin tersebut; bahagian berberat molekul rendah dan bahagian berberat molekul tinggi. Merujuk kepada resin perdagangan, T_g adalah dalam linkungan 63~66°C, MFI dalam linkungan 4~10 g/10 min, dan AN dalam linkungan 8.5~10.2 mg KOH/g. Keputusan GPC untuk bahagian berberat molekul tinggi, M_n dalam linkungan $1.93 \times 10^5 \sim 3.02 \times 10^5$ gmol^{-1}, M_p dalam linkungan $8.07 \times 10^5 \sim 1.7 \times 10^6$ gmol^{-1}, M_w dalam linkungan $5.5 \times 10^5 \sim 6.77 \times 10^5$ gmol^{-1}, M_z dalam linkungan $1.2 \times 10^6 \sim 1.5 \times 10^6$ gmol^{-1} dan I_p dalam linkungan 2.24~3.92. Manakala untuk bahagian berberat molekul rendah, M_n adalah dalam linkungan $3.5 \times 10^3 \sim 3.8 \times 10^3$ gmol^{-1}, M_p dalam linkungan $4.7 \times 10^3 \sim 4.9 \times 10^3$ gmol^{-1}, M_w dalam linkungan $5.9 \times 10^3 \sim 6.9 \times 10^3$ gmol^{-1}, Mz dalam linkungan $9 \times 10^3 \sim 1.1 \times 10^4$ gmol^{-1} dan Ip dalam linkungan 1.68~1.80. Nisbah bahagian berberat molecul tinggi kepada bahagian berberat molecul rendah berubah daripada 36:64 kepada 60:40. Dalam projek ini, bahagian resin berberat molekul tinggi dan rendah adalah disintesis berasingan dan dicampurkan dalam pelbagai nisbah untuk mencapai sifat-sifat yang diperlukan oleh toner resin.

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MAA	Methacrylic acid
TD	Tetra ethylene glycol diacrylate
GPC	Gel permeation chromatography
DSC	Differential scanning calorimetry
MFI	Melt flow indexes
TSC	Total solid content
AN	Acid number
MWD	Molecular weight distribution
T_g	Glass transition temperature
M_n	Number average molecular weight
M_w	Weight average molecular weight
M_z	Z average molecular weight
M_p	Peak value for molecular weight distribution
I_p	Polydispersity of molecular weight
Al	aluminium
THF	Tetrahydrofuran

CHAPTER ONE: INTRODUCTION

1.1. Laser Printer

Nowadays, colour laser and inkjet printers have become common facilities to almost all big companies that require printings of various types. A laser printer can print faster and with better quality compared with an inkjet printer. This is due to the unvarying diameter of the laser beam that makes laser printer prints sharper. The toner powder which is used in laser printers is cheaper and lasts a long time. Moreover, the printed image is water resistant.

The main components of a laser printer are; a photoconductive drum (OPC drum) and laser within a highly precise optic-mechanical ray system. Other components are to ensure the correct functioning of the two main components[1]. Figure 1.1 shows the basic components of a laser printer, which included discharge lamp, corona wire, toner hopper, laser scanning unit, fuser, photoreceptor drum assembly and developer roller.

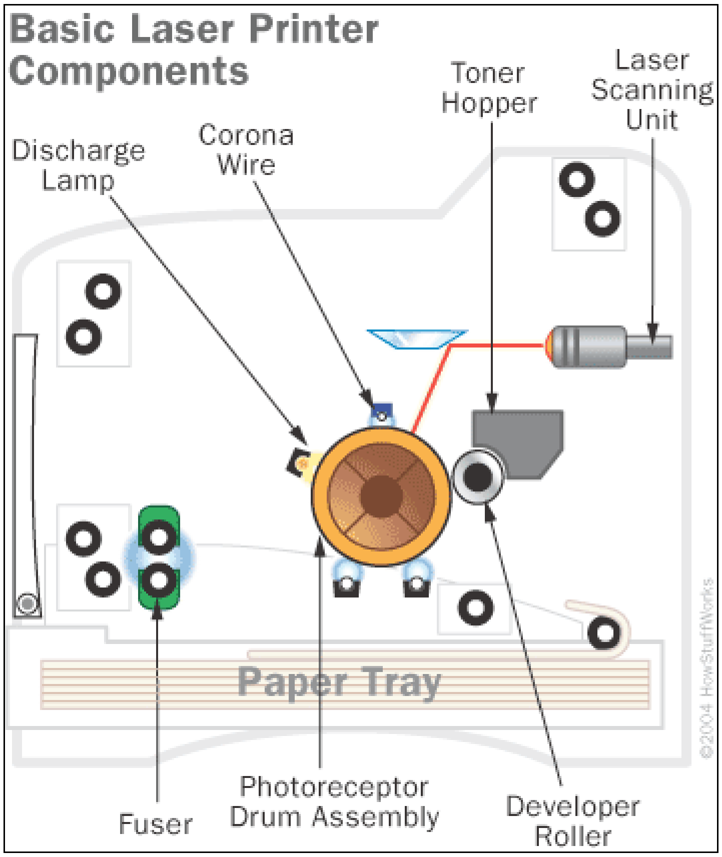


Figure 1.1 The basic components of a laser printer includes fuser, photoreceptor drum assembly, developer roller, laser scanning unit, toner hopper, corona wire and discharge lamp

Initially, the charged corona wire (a wire with an electrical current running through it) gives a total positive charge to the drum. As the drum revolves, the printer shines a tiny laser beam across the surface to discharge certain points. In this way, the laser "draws" the letters and images (which is also known as electrostatic image) to be printed as a pattern of electrical charges. The system can also work with the charges reversed, where a positive electrostatic image is “drown” on a negative background.

After setting the pattern, a positively charged toner will be coated on the drum and cling on the negative discharged areas of the drum.

With the powder pattern affixed, the drum rolls over a sheet of paper, which is given a negative charge by the transfer corona wire (charged roller). This charge is stronger than the negative charge of the electrostatic image, so the paper can pull the toner powder away. Since it is moving at the same speed as the drum, the paper picks up the image pattern exactly. The paper is discharged by the detac corona wire immediately after picking up the toner to avoid it from clinging to the drum.

The paper was passed through the fuser (a pair of heated rollers) which apply heats on the paper to melt down the toner powder and fuse with the fibers in the paper. The fuser rolls the paper to the output tray, and one complete printing image is obtained.

After depositing toner on the paper, the drum surface passes through the discharge lamp, where bright light exposes the entire photoreceptor surface, erasing the electrical image. The drum surface then passes the charge corona wire, which reapplies the positive charge.

1.2. Toner

Toner is a pigmented powder used in laser printers and photocopiers to form the text and picture images on the printed paper. In its earliest form it was simply carbon black powder. Then, to improve the quality of the printout the carbon black was blended with a polymer. Toner particles are melted by the heat of the fuser, causing them to bind to the paper. The specific polymer used varies from one manufacturer to another but can be a styrene acrylic copolymer or a polyester resin.

Toner formulations vary from one manufacturer to manufacturer to meet the requirements of different machine designs. Toner usually contains resin, imaging dye, stabilizer, charger, antioxidants and substances preventing particles from spontaneous sticking together. There are now two main types of toner in the market; conventional (traditional) toner and chemically produced toners (CPT).

Conventional toner is manufactured through mechanical milling of the carbon black mixture. A large solid mass of carbon black mixture is crushed and ground to a fine powder with a fairly narrow particle size distribution. Meanwhile, CPT is the toner synthesized chemically through processes such as emulsion aggregation process or suspension polymerization process. Although CPT is better than the conventional toner in terms of quality, but the manufacturing of CPT is still a costly process. Comparison between the processes to produce conventional toner and CPT is shown in Figure 1.2. [2, 3]

Most of the commercial resins contain two fractions: a high and a low molecular weight portions. The low molecular weight portion imparts a good fixing property on paper during printing process. The low molecular weight faction has M_n in the range 1×10^3 $gmol^{-1}$ to 5×10^3 $gmol^{-1}$ (preferably 1.5×10^3 $gmol^{-1}$ to 2.8×10^3 $gmol^{-1}$) and T_g in the range 40 to 75°C in order to provide heat melting ability at low temperature. [4]

Meanwhile, the high molecular weight portion has sufficiently high molecular weight to ensure a good offset property for printing quality. [5-23]

The mixed resin should have M_n in the range of 2×10^3 $gmol^{-1}$ to 1.5×10^4 $gmol^{-1}$ (preferably 2×10^3 $gmol^{-1}$ to 1×10^4 $gmol^{-1}$) to provide heat melting ability at low temperature. In case M_n was less than 2×10^3 $gmol^{-1}$, this would lead to poor dispersion of the colouring agent due to the viscosity reduction during kneading process. In case M_n was more than 1.5×10^4 $gmol^{-1}$, this would result in poor fixing ability.

M_z value for mixed resin should be higher than 4×10^5 $gmol^{-1}$ (preferably higher than 5×10^5 $gmol^{-1}$) to enhance resin strength, increased viscosity during the hot kneading, improved the dispersability of colouring agent, reduced the variation of electrostatic changed during the duplication, maintained the image concentration more constantly, and reduced fogging problem.

The polydispersity, I_p, which is the ratio of M_w: M_n, should be in the range of 5 to 15 to make sure the resin having good offset and fixing properties. In case I_p was too low, the toner resins typically exhibit a viscosity profile wherein viscosity decreased sharply at higher temperatures which lead to poor offset properties. Conversely, if the polydispersity was too high, the fixing properties of the toner resins were adversely affected. Lastly, T_g should be in the range of 40°C to 90°C (preferably 50°C to 80°C) in order to provide heat melting ability at low temperature. [4, 19]

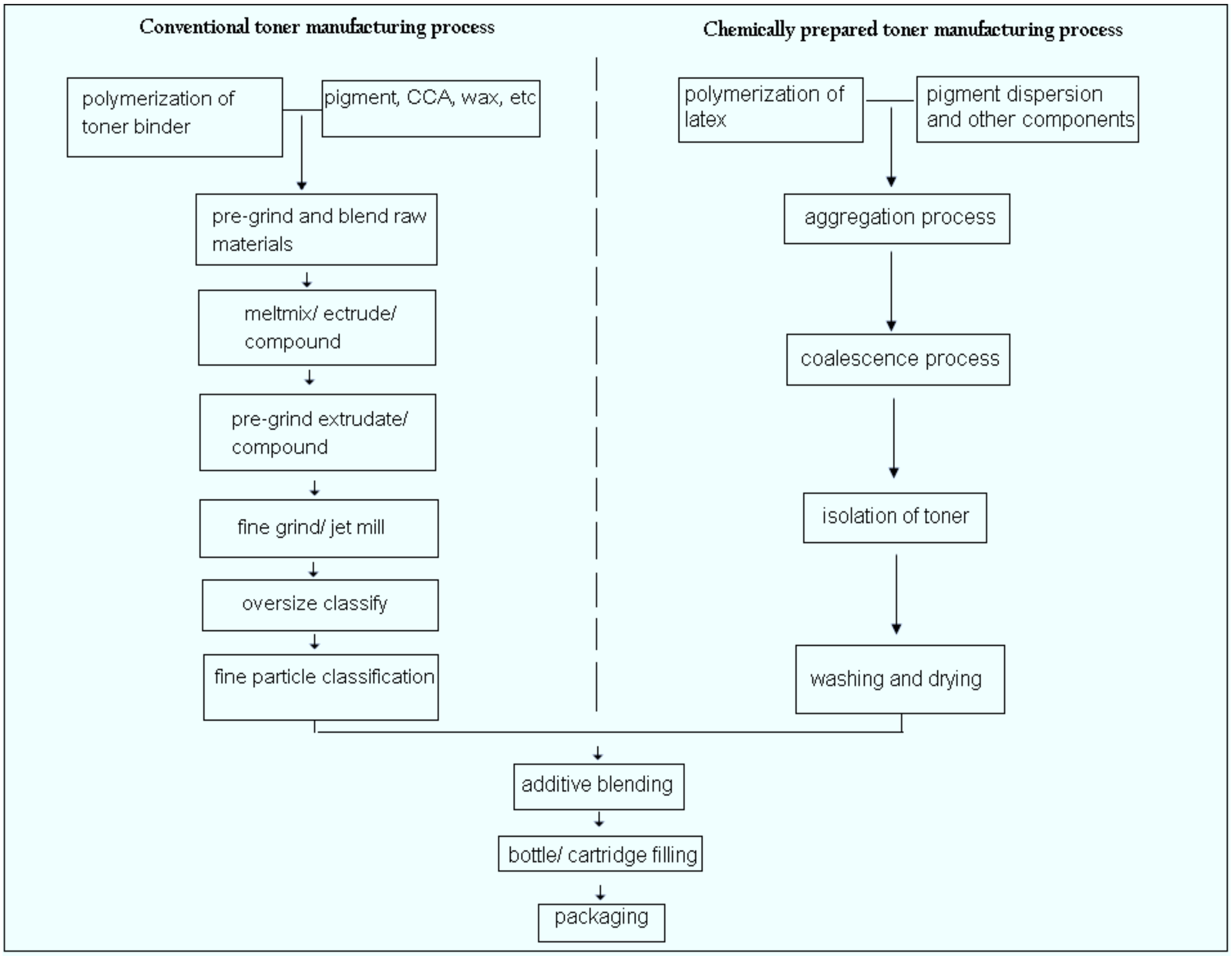


Figure 1.2 Comparison between manufacturing processes of conventional toner with chemically prepared toner [24]

Certain characteristics of the toner are critical to the performance of the toner. Charge properties of toner are crucial for the proper transfer of the toner particles. Improper charge properties of the toner leading to print defects such as background, blasting or light print. This is strongly affected by the toner particle size and shape.

Another important characteristic of the toner is the fusing ability which requires specific melting and adhering properties. The toner must be able to melt at the proper temperature to be compatible with the fusing system where it will be used. The melting point as well as the fusing rate is also very important. Improper fusing leads to print defects such as cold offset or hot offset, ghost image picked up in the fuser and low density of prints.

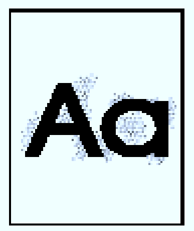
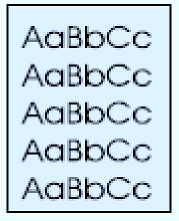
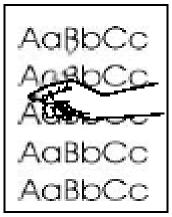
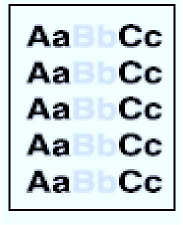
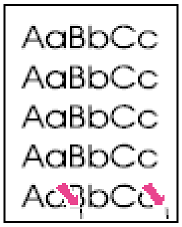
All of the previously mentioned properties are important to the imaging quality of the print out. Toner must charge, transfer, and fuse properly to produce a good image. Therefore, the use of suitable resin in toner production is very important in order to produce finished toners with the required properties. Figure 1.3 shows the appearance of conventional toner, SJ700, which clearly showed that the conventional toner particles are irregular in shape and size.

Figure 1.3 Picture of conventional toner resin particles under 3 Mega Pixel camera by magnification 10×

1.3. Print defects

Some of the common print defects are shown in Table 1.1.

Table 1.1 Examples of common print defects

Print defect	**Description**
	Background is scatter.
	Background is gray in colour.
	The toner fixing is poor; toner is loose and easy rubs out from paper.
	The printing is too light, too dark or fade.
	There are some repetitive defects obtain in the printing.

1.4. Bulk and Solution Polymerization

Binder resin is the major component in the toner accounting for 50-90%, therefore, the properties of the binder resin that strongly affects the properties of finished toner are molecular weight, softening point, melting point and melt flow indexes.

There are various methods of manufacturing conventional binder resin such as solution polymerization, bulk polymerization, suspension polymerization and dispersion polymerization. In this study, we are using the bulk polymerization and solution polymerization processes to produce the binder resin.

Bulk polymerization of a pure monomer offers the simplest process with minimum contamination of the product. However, this process is difficult to control due to the characteristics of radical chain polymerization, which is highly exothermic, coupled with the rapid increase in viscosity leading to difficulty on heat dissipation. [25]

Free-radical polymerization is an important commercial method to produce acrylic resins for paints, adhesives and coatings.

Solution polymerization takes place in a solvent where the monomers and initiator are dissolved in. The solvent must have suitable boiling points for the conditions of the polymerization, and any subsequent solvent-removal step. Selection of solvent may be also influenced by other factors such as flash point, cost, and toxicity. The initiator dissolves in the solvent and decomposes to form free radicals which initiate the polymerization of the monomer to produce the polymer particles. [26, 27]

Solution polymerization offers an easier temperature control compare to the bulk polymerization because of the added heat capacity of solvent and lower viscosity. The level of impurities in the copolymer can be low since the initiators residues can be removed. The disadvantages of solution polymerization are firstly, the removal of solvent and unreacted monomer can be difficult. Secondly, polymers are usually in lower molecular weight because of certain amount of chain transfer reaction. Thirdly, the reaction temperature is limited by the boiling point of the solvent used. Finally, the organic solvent used in the polymerization process is often expensive, toxic and flammable and the solvent recovery process is costly. [26, 27, 28, 29]

In this study, both solution and bulk polymerization were investigated, the high molecular weight polymer can easily built up by undergo bulk polymerization and the difficulties of heat dissipation can be solved by switching the bulk polymerization to solution polymerization after certain percentage of conversion.

The comparison on the advantages and disadvantages of different polymerization processes is shown in Table 1.2.

Table 1.2 Comparison between various processes of polymerization

Polymerization processes	**Bulk**	**Solution**	**Suspension**	**Emulsion**
Materials	Monomer + initiator + water	Monomer + initiator + organic solvent	Monomer + oil soluble initiator + inorganic stabilizer + water	Monomer + water soluble initiator + surfactant + water
Advantages	• Separation of polymer from the solvents/dispersion medium is easy because of the absence of added substance. • The molecular weight of the polymer is high because of the absence of solvent (which acts as chain transfer agent) in the polymerization reaction.	• Overcome problems of intractably viscous and heat dissipation thus produces an easier temperature control system. • Product precipitate gradually as reaction proceeds in a heterogeneous system. (product not soluble in solvent) • Level of impurities can be very low, since the initiator residues can be washed out. • In a system that polymer soluble in solvent, with provided sufficient solvent present, system remain fluid right up to the completion of the reaction.	• System properly conducted, where it will remain completely fluid over the entire course of the reaction. • Heat dissipation problem better than in bulk polymerization process. • If water is used as the medium, problems of inflammability, toxicity and expense are minimized. • Product polymer is easy to be separate from the dispersion medium.	• Easier temperature control, since the viscosity changes very little with conversion. • Water is used as the medium, thus provide better thermal conductivity.

Table 1.2, continued

Polymerization processes	Bulk	Solution	Suspension	Emulsion
Disadvantages	• System becomes intractably viscous as the reaction proceeds. • Dissipation of the heat of polymerization • Product polymer often branched/cross linked.	• Solvents are usually expensive, toxic and often flammable. • Molecular weight of product polymer seriously curtailed by the reaction of radical transfer-to-solvent. • Removal of last traces of solvent and unreacted monomer can be difficult.	• The purity of the product polymer is lower than those obtained by bulk polymerization, but is better than those obtained by emulsion polymerization. • Careful attention to stirring is necessary. • The product polymer has very large particles size.	• Removal of monomer can be difficult without coagulating the latex. • Impurities levels are usually rather high because surfactant and coagulant residues are hard to remove.

1.5. Mechanism for free-radical additional polymerization

There are two fundamental polymerization mechanisms; free-radical addition polymerization and step-growth polymerization. Preparations of binder resin in this study undergo the additional polymerization. Additional polymerization involves three district steps: initiation, propagation and termination.

Initiation involves the dissociation of initiator (usually at the suitable temperature) to generate free-radical entities, and followed by the addition of a monomer molecule to the initiating radical as shown in equation 1.1a and 1.1b where k_d is the constant for the initiation dissociation and k_i is the rate constant for initiation.

$$\mathbf{I} \xrightarrow{k_d} \mathbf{2R\bullet} \qquad \mathbf{[1.1a]}$$

$$\mathbf{R\bullet + M} \xrightarrow{k_i} \mathbf{RM_1\bullet} \qquad \mathbf{[1.1b]}$$

The propagation step is the step where the monomer units are added to the initiated monomer species, this can be represent in equation 1.2a to 1.2c. The propagation rate constant is denoted as k_p.

$$\mathbf{RM_1\bullet + M} \xrightarrow{k_p} \mathbf{RM_2\bullet} \qquad \mathbf{[1.2a]}$$

$$\mathbf{RM_2\bullet + M} \xrightarrow{k_p} \mathbf{RM_3\bullet} \qquad \mathbf{[1.2b]}$$

$$\mathbf{RM_{n-1}\bullet + M} \xrightarrow{k_p} \mathbf{RM_n\bullet} \qquad \mathbf{[1.2c]}$$

The propagation step is the fundamental reaction in any polymerization. Compared to condensation polymerization, the propagation rate for addition polymerization is very rapid. Very high molecular-weight polymer can be formed in relatively short time. This propagation step will continue until some termination process occurs.

One of the obvious termination mechanism occurs when two propagating radical chains of arbitrary degrees of polymerization of x and y meet at their free-radical ends. This kind of termination occurs by combination (by the formation of covalent bond between two radical chains) to give a single terminated chain of degree of polymerization (x + y) as illustrated by equation 1.3. The rate of termination in this manner is denoted as k_{tc}.

$$\mathbf{RM_m\bullet + RM_n\bullet \xrightarrow{k_{tc}} RM_{m+n}R} \qquad \mathbf{[1.3]}$$

Termination can also occurs by a disproportionation reaction, where one terminated chain will have an unsaturated carbon group, and another fully saturated terminated end. This reaction is illustrated as in equation 1.4, where the rate of termination by disproportionation is denoted as k_{td}. [30, 31]

$$\mathbf{RM_m\bullet + RM_n\bullet \xrightarrow{k_{td}} RM_n + RM_m} \qquad \mathbf{[1.4]}$$

1.6. Thermal Initiation in Absence of an Initiator

Monomers such as styrene and acrylate are known to be capable of self initiated polymerization at elevated temperatures. In most cases of thermal spontaneous polymerization, the initiation mechanism and the kinetics involved appear obscure and sometimes irreproducible because of the presence of traces or uncertain amount of impurities and their direct or indirect role in radical forming reactions with or without involvement of monomer molecules. [31]

The mechanism of thermal polymerization for styrene with no added initiator is shown as Figure 1.4.

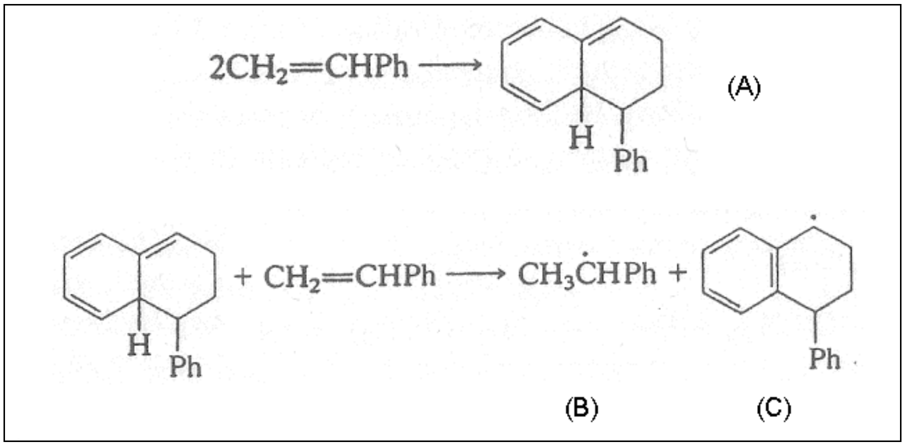


Figure 1.4 Mechanism of thermal polymerization for styrene, which involve initial formation of Diels-Alder dimmer (compound **A** in Figure 1.4), which transfers a hydrogen atom to monomer to yield an initiator styryl radical (compound **B** in Figure 1.4) and a benzylic radical (compound **C** in Figure 1.4). [32]

1.7. Radical Initiator

Radical initiators refer to substances that can produce radical species under specific conditions and kick start the radical polymerization reactions. These substances generally possess weak bonds with low bond dissociation energies; examples like halogen molecules, azo compounds, and organic peroxides.

Halogens can generate two free radicals resulting from the homolysis of the bond easily, for example, chlorine molecule can generate two chlorine radicals (Cl•) by irradiation with ultraviolet light. This process is used for chlorination of alkanes.

Azo compounds (R-N=N-R') tends to generate two carbon-centered radicals (R• and R'•) and nitrogen gas upon decomposition by heating or irradiation.

Organic peroxides each have a peroxide bond (-O-O-), which is readily cleaved to give two oxygen-centered radicals. The radicals are rather unstable and believed to be transformed into relatively stable carbon-centered radicals. For example, benzoyl peroxide

($(PhCOO)_2$) generates benzoyloxyl radicals ($PhCOO\bullet$), each of which loses carbon dioxide to be converted into a phenyl radical ($Ph\bullet$).

Radical initiators, especially azo compounds and organic peroxides, are inherently unstable. They must be kept in a cool place or refrigerated. Care should be taken with the handling of the compounds or an explosion may occur. Figure 1.5 shows the chemical structure of benzoyl peroxide which is used as the initiator in this study.[30, 31, 32]

1.8. Transfer Constants in Free Radical Polymerization

Transfer reaction in radical polymerization means a process in which the polymer radical reacts with another species in the system (such as monomer, polymer, catalyst, solvent or modifier) to form a dead polymer and new radical which can continue the kinetic chain by following equations:

$$\mathbf{P\bullet_{n-1} + M \xrightarrow{k_p} P\bullet_n} \qquad \mathbf{[1.5a]}$$

$$\mathbf{P\bullet_n + RX \xrightarrow{k_{tr}} P_nR + X\bullet} \qquad \mathbf{[1.5b]}$$

$$\mathbf{X\bullet + M \xrightarrow{k_i} P\bullet_I} \qquad \mathbf{[1.5c]}$$

By making the following assumptions:

a) All new radicals $X\bullet$ react only by formation of growing polymer radicals;

b) All polymer radicals have equal reactivity independent of their size;

c) All rate constants are independent of solvent;

d) The consumption of monomer by initiation and transfer is negligible compared with propagation;

e) A steady-state concentration of polymer radicals is quickly established ($d[P\bullet]/dt = 0$).

Then we can define the dimensionless transfer constant, C_x, by using the equation as followed:

$$\mathbf{C_x = \mathit{k_{tr}/k_p}} \qquad [1.6]$$

Where k_p is the rate constant of propagation,

k_{tr} is the rate of chain transfer,

k_i is the rate of chain reinitiation. [34, 36]

1.9. Crosslinking Reaction in Free Radical Polymerization

Both addition and condensation polymers can be linear, branched, or crosslinked. Linear polymers are made up of one long continuous chain, without any excess appendages or attachments.

There are two types of chemical crosslinking. The first type is crosslinking during polymerization by use of polyfunctional instead of difunctional monomers; the crosslinks may contain the same repeating structure as the main chains. Second type of chemical crosslinking occurred in a separate processing step after the linear (or branched) polymer is formed, the crosslinks may have an entirely different structure.

There are number of significant changes that accompany chemical crosslinking. At high level of crosslinking, the polymer cannot be dissolved or molded, thus difficult to recycle. The polymers are no longer dissolve but swelling in the present of solvent except for some ionically crosslinked polymers. A solvent swollen crosslinked polymer is referred to as gel. Covalently crosslinked polymers also lose their flow properties. They may still undergo deformation, but the deformation will be reversible; that is, the polymer will exhibit elastic properties.

Crosslinking density, Γ , refers to the number average molecular weight of uncrosslinked polymer, $(M_n)_0$, divided by the number average molecular weight between crosslinks, $(M_n)_c$, as shown in equation 1.7.

$$\Gamma = (M_n)_0/(M_n)_c \qquad [1.7]$$

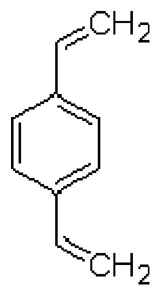
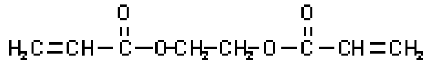
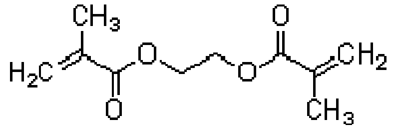
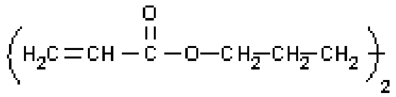
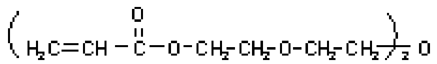
The higher the crosslink density, the polymer becomes more rigid. Very high crosslink densities lead to embrittlement because crosslinking reduces segmental motion; it is frequently employed to increase the glass transition temperature.

On the other hand, there could be the physical crosslinking, which is due to strong secondary bonding attraction between polymer chains such that the polymer exhibits properties of a thermosetting material while remaining thermoplastic.

Many of the mechanical and solution properties of crystalline polymers resemble those of crosslinked amorphous polymers due to the very strong secondary forces arising from close chain packing. The existing of intermolecular hydrogen bonding in certain materials also behaves like crosslinked polymers, example like gelatin (an animal-derived protein that exhibits elastomeric properties).[32, 33]

Table 1.3 shows some examples of crosslinking agents that used for synthesis of styrene acrylic copolymer.

Table 1.3 Examples of crosslinking agents for synthesis of styrene acrylic copolymer

Cross linking agent	Chemical structure
Divinylbenzene	
Ethylene glycol diacrylate	 $H_2C{=}CH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-CH{=}CH_2$
Ethylene glycol dimethacrylate	
1,6-Hexanediol diacrylate	 $\left(H_2C{=}CH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_2-\right)_2$
Tetra(ethylene glycol) diacrylate	 $\left(H_2C{=}CH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-CH_2-CH_2-\right)_2O$

1.10. Styrene acrylic Copolymerization

There are four separate propagation steps (equation 1.8a, 1.8b, 1.8c, 1.8d) in a free-radical copolymerization (with their own rate constant).

$$\sim M_1\bullet + M_1 \xrightarrow{k_{11}} \sim M_1M_1\bullet \qquad [1.8a]$$

$$\sim M_1\bullet + M_2 \xrightarrow{k_{12}} \sim M_1M_2\bullet \qquad [1.8b]$$

$$\sim M_2\bullet + M_1 \xrightarrow{k_{21}} \sim M_2M_1\bullet \qquad [1.8c]$$

$$\sim M_2\bullet + M_2 \xrightarrow{k_{22}} \sim M_2M_2\bullet \qquad [1.8d]$$

The rates of disappearance of comonomers M_1 and M_2 can be obtained by considering the individual steps by which M_1 and M_2 are consumed. The rate equations are shown in equation 1.9a and 1.9b.

$$-d[M_1]/d_t = k_{11}[M_1\bullet][M_1] + k_{21}[M_2\bullet][M_1] \qquad [1.9a]$$

$$-d[M_2]/d_t = k_{12}[M_1\bullet][M_2] + k_{22}[M_2\bullet][M_2] \qquad [1.9b]$$

Where M_1 = styrene monomer, and

M_2 = n-butyl acrylate monomer

Under steady-state, the concentration of $M_1\bullet$ and $M_2\bullet$ remaining constant, the rates of interconversion of chain radicals are equal, which prescribes that rates of reactions for equation 1.8b and 1.8d are equal,

$$k_{12}[M_1\bullet][M_2]= k_{21}[M_2\bullet][M_1] \qquad [1.10]$$

Therefore, combining equation 1.9a and 1.9b and expressing $[M_1\bullet]$ in terms of $[M_2\bullet]$ (or vice versa) with the help of equation 1.10, the ratio of disappearance of monomers $M_1$and M_2 is described by

$$\frac{d[\mathrm{M}_1]}{d[\mathrm{M}_2]} = \frac{[\mathrm{M}_1]}{[\mathrm{M}_2]}\left(\frac{k_{11}[\mathrm{M}_1^{\bullet}]+k_{21}[\mathrm{M}_2^{\bullet}]}{k_{12}[\mathrm{M}_1^{\bullet}]+k_{22}[\mathrm{M}_2^{\bullet}]}\right) \qquad [1.11]$$

The copolymer composition can be predicted by considering the comonomer reactivity and concentration. The relative change in the comonomer composition is given by the instantaneous copolymerization equation (obtained by dividing equation 1.9a by equation 1.9b), thus the monomer reactivity ratio can be defined as equation 1.12a and 1.12b. [27]

$$r_1 = k_{11}/k_{12} \qquad [1.12a]$$

$$r_2 = k_{22}/k_{21} \qquad [1.12b]$$

Where r_1 = reactivity ratio for styrene monomer, and

r_2 = reactivity ratio for n-butyl acrylate monomer

The reactivity ratios for many important combinations of monomers had been determined and been tabulated in several reference sources. [30, 31, 32, 34] The reactivity ratios for less common monomer pairs can be calculated by using the Q-e scheme (shown in equation 1.13a and 1.13b) which proposed by Alfrey and Price.

$$\mathbf{r_1 = (Q_1/Q_2)exp[-e_1(e_1-e_2)]} \qquad \mathbf{[1.13a]}$$

$$\mathbf{r_2 = (Q_2/Q_1)exp[-e_2(e_2-e_1)]} \qquad \mathbf{[1.13b]}$$

Where Q_1, Q_2 = reactivity of the monomer M_1 and M_2, and

e_1, e_2 = polarity of the radical $M_1\bullet$ and $M_2\bullet$

The r_1, r_2 value for styrene and n-butyl acrylate monomers respectively are calculated as followed.[34]

$$\mathbf{r_1 = (Q_1/Q_2)exp[-e_1(e_1-e_2)]}$$

$$\mathbf{= (1.00/0.38)exp[0.80(-0.80-0.85)]}$$

$$\mathbf{= 0.70}$$

$$\mathbf{r_2 = (Q_2/Q_1)exp[-e_2(e_2-e_1)]}$$

$$\mathbf{= (0.38/1.00)exp[-0.85(0.85+0.80)]}$$

$$\mathbf{= 0.09}$$

The reactivity ratio $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, the copolymer equation on the composition of the copolymer can be obtained by substitute r_1, r_2 into equation 1.11.

$$n = \frac{d[M_1]}{d[M_2]} = \left(\frac{r_1[M_1]/[M_2]+1}{r_2[M_2]/[M_1]+1}\right) = \frac{r_1 x + 1}{(r_2 x) + 1} \qquad \mathbf{[1.14]}$$

Where n = composition of the copolymer

x = composition of the feed

Therefore, an equimolar ratio of styrene and n-butyl acrylate would produce a styrene-rich copolymer in which there would be three molecules of styrene to every two molecules of n-butyl acrylate in the polymer chain. [30] The calculation is shown as below.

$$n = \frac{r_1 x + 1}{(r_2 x) + 1} = \frac{0.70(1) + 1}{(0.09 \times 1) + 1} = \frac{1.7}{1.09} = 1.56$$

Copolymer can have several configurations or arrangements of the monomers along the chain. The four main configurations are depicted as in Figure 1.5 and the configuration for copolymer produced from this study is in random form.

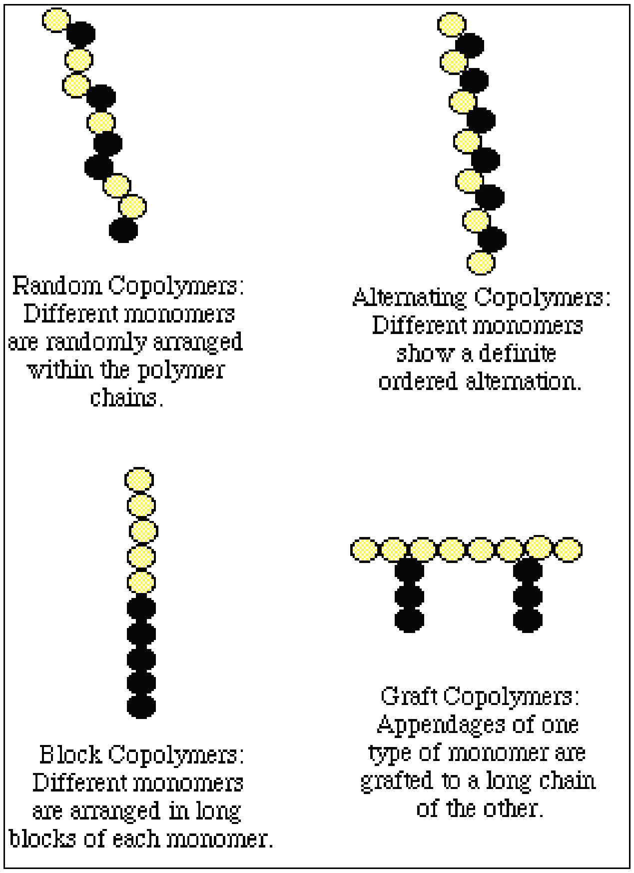


Figure 1.5 Copolymer configurations can be either in random, alternating, block or graft configuration depends on the comonomer reactivity and concentration as well as the polymerization condition and processes

1.11. Selection of Monomer

The two main monomers used in this study are styrene and n-butyl acrylate. Acrylic esters such as n-butyl acrylate are commercially important in the synthesis of acrylic resins because of their optical clarity, mechanical properties, adhesion and chemical stability to apply in paints, adhesives and coatings.

Polystyrene comprise about 14% of the total thermoplastic market. An especially important application for styrenic polymers is the manufacturing of foam-insulation and packaging materials. Polystyrene provides better high temperature performance, toughness, lower permeability, provide higher strength and good chemical resistance.[27]

1.12. Scope of Study

The objective of this study is to investigate the production of binder resin that could be used for toner manufacturing. Both bulk and solution polymerization processes were investigated. A series of styrene acrylic copolymer samples with different amount of methyl methacrylic acid and tetra (ethylene glycol) diacrylate were prepared to undergo a series of characterization tests. The result of each test was collected and the comparisons with the commercial resins had been carried out.

CHAPTER TWO: EXPERIMENTAL

2.1 Synthesis of Low Molecular Weight Styrene acrylic Copolymer

2.1.1 Materials

Industrial grade xylene, styrene, n-butyl acrylate, industrial grade methanol, and benzoyl peroxide (moistened with 25% water) were used to synthesize the low molecular weight styrene acrylic copolymer.

2.1.2 Apparatus

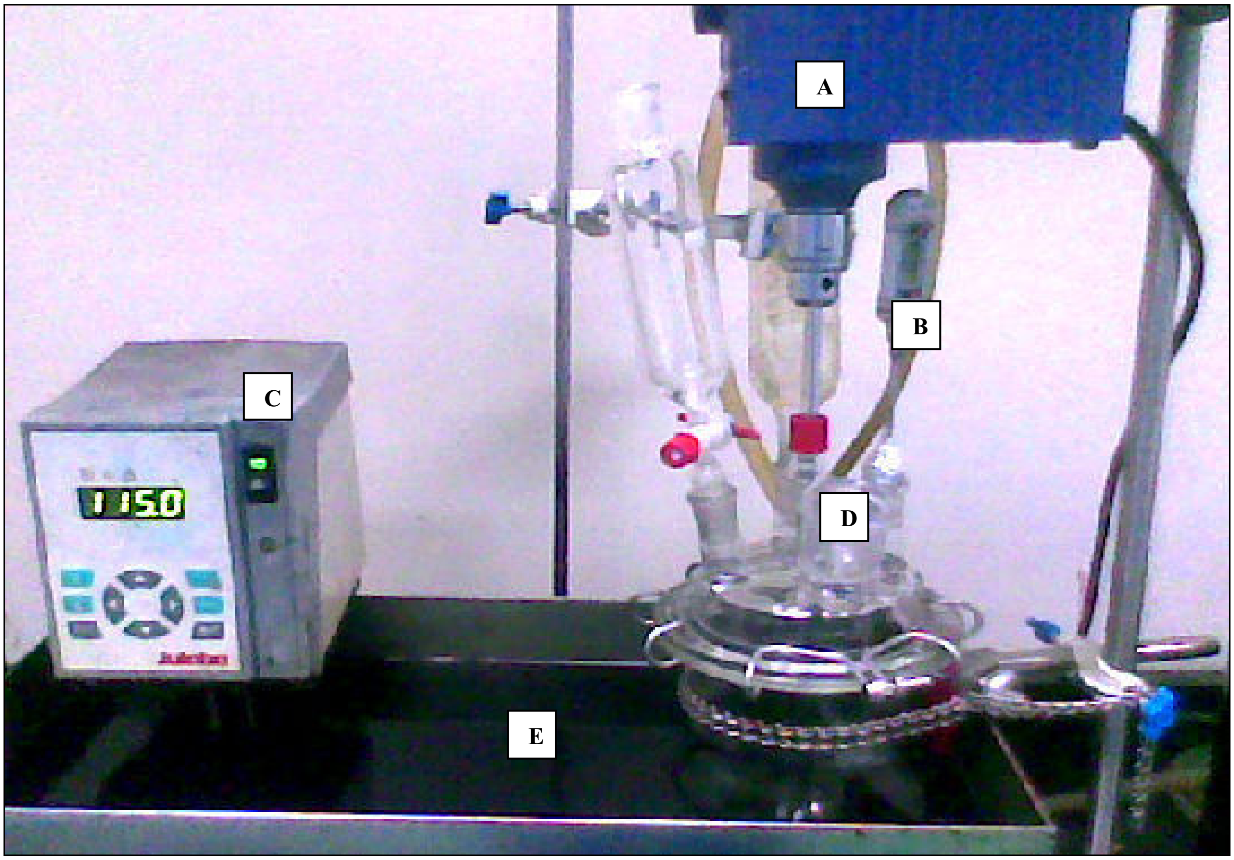


Figure 2.1 Apparatus set up for preparation of low molecular weight resin (A: mechanical stirrer, B: digital thermometer, C: heater, D: reactor flask, E: oil bath)

2.1.3 Formulations

The formulations of low molecular weight resins are shown in Table 2.1.

Table 2.1 Formulation for preparation of low molecular weight resin by solution polymerization at 130°C.

Code	**L10**	**L11**	**L12**
Formulation/ Parts per 100 parts of monomer			
Styrene	90	90	90
n-butyl acrylate	10	10	10
Benzoyl peroxide	10	12.5	15
Xylene	100	100	100
Total	210	212.5	215

2.1.4 Process

The initial formulation and process in this study was adapted from a patent literature [4]. A flask was charged with 100 parts of xylene and heated to 130ºC in an oil bath. A mixture of 90 parts of styrene, 10 parts of n-butyl acrylate and 10 parts of benzoyl peroxide (for experiment L12) was being purge by nitrogen gas for 3 minutes to displace dissolved oxygen. The mixture was continuously added into the reactor flask drop-wise over 5 hours. The reaction was carried on for another 2 hours to ensure complete polymerization. The reactor was allowed to cool down to room temperature before the product was isolated.

2.1.5 Sample Drying

The copolymer was precipitated by addition of methanol. The precipitated copolymer was spread on a glass tray (A4 x A4 size) and dried in an oven at 130ºC for 10 hours. The dried film was collected and used to run the series of property tests.

2.2 Synthesis of High Molecular Weight Styrene acrylic Copolymer

2.2.1 Materials

Industrial grade xylene, styrene, n-butyl acrylate, methacrylic acid, methanol and benzoyl peroxide, and analytical grade tetra (ethylene glycol) diacrylate, were used to synthesize the high molecular weight styrene acrylic copolymer.

2.2.2 Apparatus

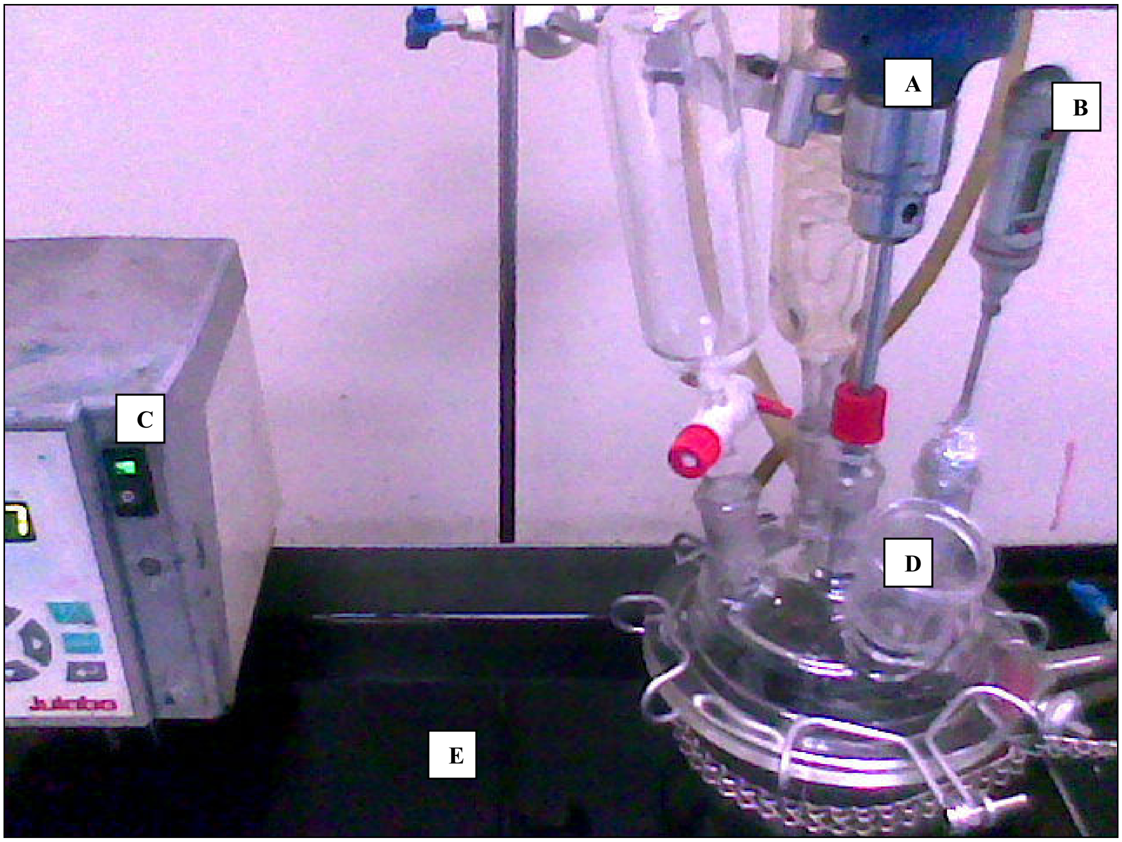


Figure 2.2 Apparatus set up for preparation of high molecular weight resin (A: mechanical stirrer, B: digital thermometer, C: heater, D: reactor flask, E: oil bath)

2.2.3 Formulations

The preparation of high molecular weight resins are listed in Table 2.2.

Table 2.2 Formulation for preparation of high molecular weight resin

Code	**H55**	**H59**	**H56**	**H58**	**H57**	**H60**	**H61**	**H62**	**H63**	**H64**
Formulation/ Parts per 100 parts of monomer										
Styrene	73.5	73.5	73.5	73.5	73.5	72.8	72.8	72.8	72.8	72.8
n-butyl acrylate	24.5	24.5	24.5	24.5	24.5	24.2	24.2	24.2	24.2	24.2
Methacrylic acid	2	2	2	2	2	3	3	3	3	3
Tetra ethylene glycol diacylate	0.5	0.6	0.7	0.8	0.9	0.5	0.6	0.7	0.8	0.9
Benzoyl peroxide	1	1	1	1	1	1	1	1	1	1
Xylene (A)	40	40	40	40	40	40	40	40	40	40
(B)	60	60	60	60	60	60	60	60	60	60

2.2.4 Process

The initial formulation and processes in this study was adapted from a patent literature[4, 35]. A flask was charged with 73.5 parts of styrene, 24.5 parts of n- butyl acrylate and 2 parts of methacrylic acid (for experiment H55). The mixture was being purge by nitrogen gas for 10 minutes to displace dissolved oxygen. The mixture was heated in an oil bath and polymerized in bulk for 4 hours by maintaining the reaction temperature at 120ºC. A conversion of around 50% was obtained by the bulk polymerization in the absence of polymerization initiator.

In the next step, 0.5 parts of tetra (ethylene glycol) diacrylate in 60 parts of xylene was poured into the system. A mixture of 1 part of benzoyl peroxide in 40 parts of xylene was dripped in continuously over 2 hours into the system at 130ºC. The polymerization was left for further 3 hours while maintained the temperature at 130ºC. The reactor was then allowed to cool down to 70ºC before the copolymer was isolated.

2.2.5 Sample Drying

The copolymer was precipitated by adding methanol. The precipitated polymer was spread on a glass tray (A4 x A4 size) and dried in an oven at 130ºC for 10 hours. The dried film was collected and used to run the series of property tests. Figure 2.3 shows a glass tray contained precipitated polymer.

Figure 2.3 Glass tray contained precipitated polymer (before dried in oven)

2.3 Mixing of High and Low Molecular Weight Styrene acrylic Copolymer

2.3.1 Materials

Low molecular weight polymer solution (polymer A, as described in section 2.1) and high molecular weight polymer solution (polymer B, as described in section 2.2) were used in mixing of high and low molecular weight styrene acrylic copolymer.

2.3.2 Apparatus

The apparatus set up for mixing is as described in Figure 2.4.

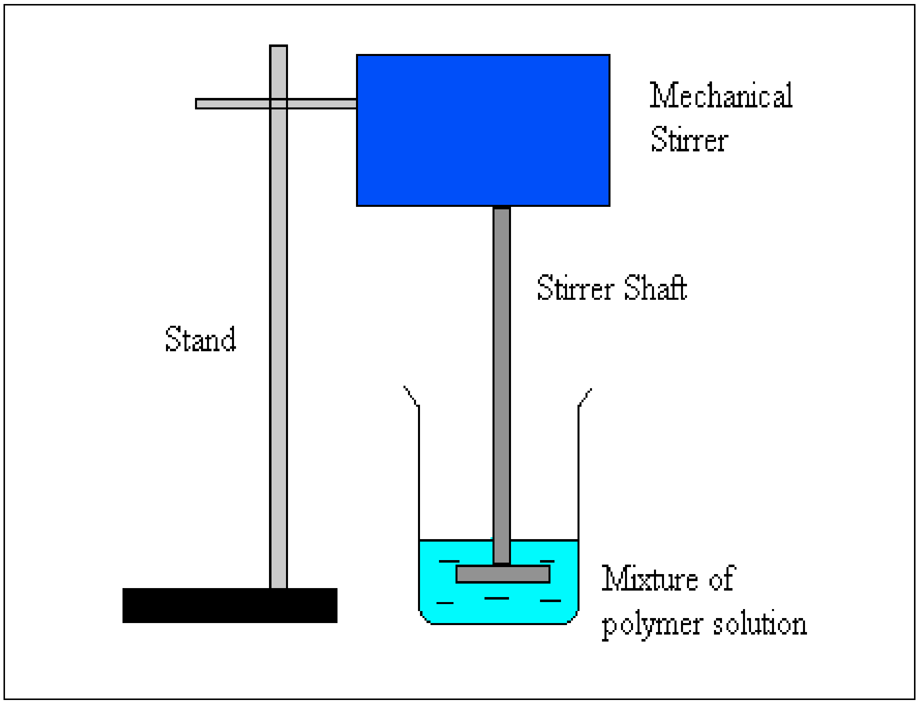


Figure 2.4 Apparatus for mixing of high and low molecular weight resins

2.3.3 Formulations

The formulations of the mixing samples were shown in Table 2.3.

Table 2.3 Formulation for preparation of mixing between high and low molecular weight resins

Code	**Mixing ratio /% in TSC**	
	H58	**L12**
M28	50	50
M29	60	40
M30	70	30
M31	80	20
Code	**Mixing ratio /% in TSC**	
	H63	**L12**
M40	50	50
M41	60	40
M42	70	30
M43	80	20

2.3.4 Processes

Polymer A and B were mixed in different ratios into a 250 ml beaker. The mixture was stirred under mechanical stirrer at 300 rpm for first 2 minutes and then at 100 rpm for 20 minutes.

2.3.5 Sample Drying

The copolymer was precipitated by adding the industrial grade methanol. The precipitated copolymer was spread on a glass tray (A4 x A4 size) and dried in oven under temperature 130ºC for 10 hours. The dried film was collected and used to run the series of property tests.

2.4 Characterization for Series of Styrene acrylic Copolymer

2.4.1 Differential Scanning Calorimetry (DSC)

DSC test was carried out by using Mettle Toledo DSC822^{e}. DSC furnace was calibrated by using Indium. Around 10 mg of sample was weighed accurately and be pressed into the aluminium crucible (40 μl). The sample was inserted into the DSC machine and heated from 25 to 100°C at heating rate 10°C min^{-1}, the scan was repeated for second time.

The first scan of the DSC represent the thermal history of the sample, therefore, the second scan was took parts in the results interpretation.[37]

Figure 2.5 shows a DSC furnace.

Figure 2.5 Differential Scanning Calorimetry (DSC)

2.4.2 Gel Permeation Chromotography (GPC)

GPC measuring furnace was built up from Water 1515 Isocratic HPLC Pump, Water 2414 Refractive Index Detector, and Water HPLC columns (one of Styragel®HR 4 THF 7.8 x 300 mm column and two of Styragel®HR 5E THF 7.8 x 300 mm column). Those parts were all connected to a normal PC and were operated by using Breeze software.

Standard solutions were prepared by dissolving 0.0 5g of monodisperse polystyrene standard with known molecular weights into 5 ml of THF. Measurements of these standard solutions were carried out to establish the calibration curve. Polymer samples were also prepared in the same way by dissolving 0.05 g of each sample into 5 ml of THF. Each sample was filtered by Minisart NY 0.45 μm single filter before injected manually into the GPC column. Figure 2.6 shows a GPC furnace.

Figure 2.6 Gel Permeation Chromotography (GPC)

2.4.3 Melt Flow Indexer (MFI)

MFI was determined by using a Rayran Melt Flow Index Instrument. This testing was started by taking a small amount (around 8 to 10 grams) of the polymer sample and put into the specially designed MFI apparatus (which is a miniature extruder consists of a small die inside). The polymer sample was packed inside the extruder barrel. A piston would act as the medium which caused the extrusion of the molten polymer. The sample was then preheated for a specified duration of time under certain temperature (360 s at 150ºC for raw resin samples). A weight shear was exerted on the molten polymer and immediately started the flow through the die. Sample of the melt was taken after desired period of time (recorded as t) and is weighed accurately (recorded as w). The MFI could be calculated through the following equation.

MFI = (w/t) x 600 g/10 min **[2.1]**

Where w = weight of sample collected after flow through the die

t = time of sample used to flow the melt

Figure 2.7 Melt Flow Indexer (MFI)

2.4.4 Acid Number (AN)

0.5 g potassium hydrogen phthalate was titrated with kalium hydroxide (KOH) solution. The volume of KOH was recorded down and titration was repeated for three times to get the average value. The concentration of KOH could be calculated through the following equation.

$$\mathbf{N = (1000 \times W_{KHP})/(204.23 \times V_{eq})} \qquad \textbf{[2.2]}$$

Where N = Normality for the standardized NaOH solution

W_{KHP} = weight (in g) of potassium hydrogen phthalate in 50 ml solution

V_{eq} = volume of titrant consume (in ml)

204.23 = molecular weight of potassium hydrogen phthalate

A blank titration was carried on the solvent. 0.5 ml of phenolphthalein (Hln) was added into 50 ml of xylene and was titrated with 0.05 N standardized KOH solution, the volume was recorded down as V_{blank}. Titration was repeated for three times to get the average value.

About 1 g of resin sample was weighed accurately and dissolved in 50 ml of xylene in a 250 ml Erlenmeyer flask. 0.5 ml of phenolphthalein (Hln) was added and the solution was titrated with standardized KOH solution. Titration was repeated three times. The average of three determinations was reported. The acid number for samples could be calculated by using the following equation.

$$\textbf{Acid Number} = \mathbf{AN = (V - V_{blank} \times N \times 56.1)/ W} \qquad \textbf{[2.3]}$$

Where V= KOH solution required for titration, ml

V_{blank}= KOH solution required for blank titration, ml

N= Normality for the standardized KOH solution

W= Weight of the specimen

2.4.5 Total Solid Content (TSC)

1 g monomer should produce 1g polymers at 100% conversion, thus the solid content for sample obtained from both bulk and solution polymerization could be calculated by using the following equation.

$$\text{TSC} = \frac{\text{Weight of monomer polymerized}}{\text{Weight of copolymer solution}} \times 100\,\% \qquad [2.4]$$

As the polymerization may not achieve 100% conversion, there is a need to determine the experimental total solid content. The weight of an empty aluminium cup was weighed and recorded down as W_0. About 2 g of solution sample was weighed accurately into the aluminium cup and recorded as W_1. The weighed sample was then dried in oven at 130 ºC for 4 hours and the final weight was W_2. The experimental TSC was calculated by using the following equation.

$$\text{TSC} = (W_2 - W_0) / (W_1 - W_0) \text{ X } 100\% \qquad [2.5]$$

Where W_0 = weight of empty container

W_1 = weight of resin sample used

W_2= dry weight for resin sample plus container

From the total solid content obtained from experiment, the percentage conversion of the polymer can be calculated through the following equation.

Percentage conversion of copolymer

$$= \frac{\text{wt of dried copolymer isolated experimentally x 100\%}}{\text{Wt of monomer in the copolymer solution assuming all converted to polymer}} \qquad [2.6]$$

The followed figure shows three aluminium cups contained dried polymer samples.

Figure 2.8 Aluminium cups contained dried polymer samples

2.5 Preparation of Finished Toner by using Pilot Plant

2.5.1 Materials

Mixed resin M30 (as described in section 2.3.3), Bayoxide E8706 (magnetite pigment), N30 CCA (charge control agent), Viscol 550P (wax), RY200-L2 (surface treatment silica), and Zinc Stearate (lubricant).

2.5.2 Formulations

Table 2.4 and 2.5 shows the formulation for pilot line processing and the formulation for final blending accordingly.

Table 2.4 Formulation for pilot line processing to produce raw toner

Materials	Amount/%	Weight/g
M30	54.5	1635
Bayoxide E8706 (magnetite pigment)	44	1320
N30 CCA (charge control agent)	0.5	15
Viscol 550P (wax)	1	30
Total	100	3000

Table 2.5 Formulation for final blending to produce finished toner

Materials	Amount/%	Weight/g
Raw toner	97.925	293.775
RY200-L2 (surface treatment silica)	1	3
Bayoxide E8706 (magnetite pigment)	1	3
Zinc Stearate	0.075	0.225
Total	100	300

2.5.3 Pilot Line Processes

Resin need to go through a series of processes in pilot line to produce a raw toner before it can further produced to finished toner. The flow charts of this series of processes are shown in Figure 2.9.

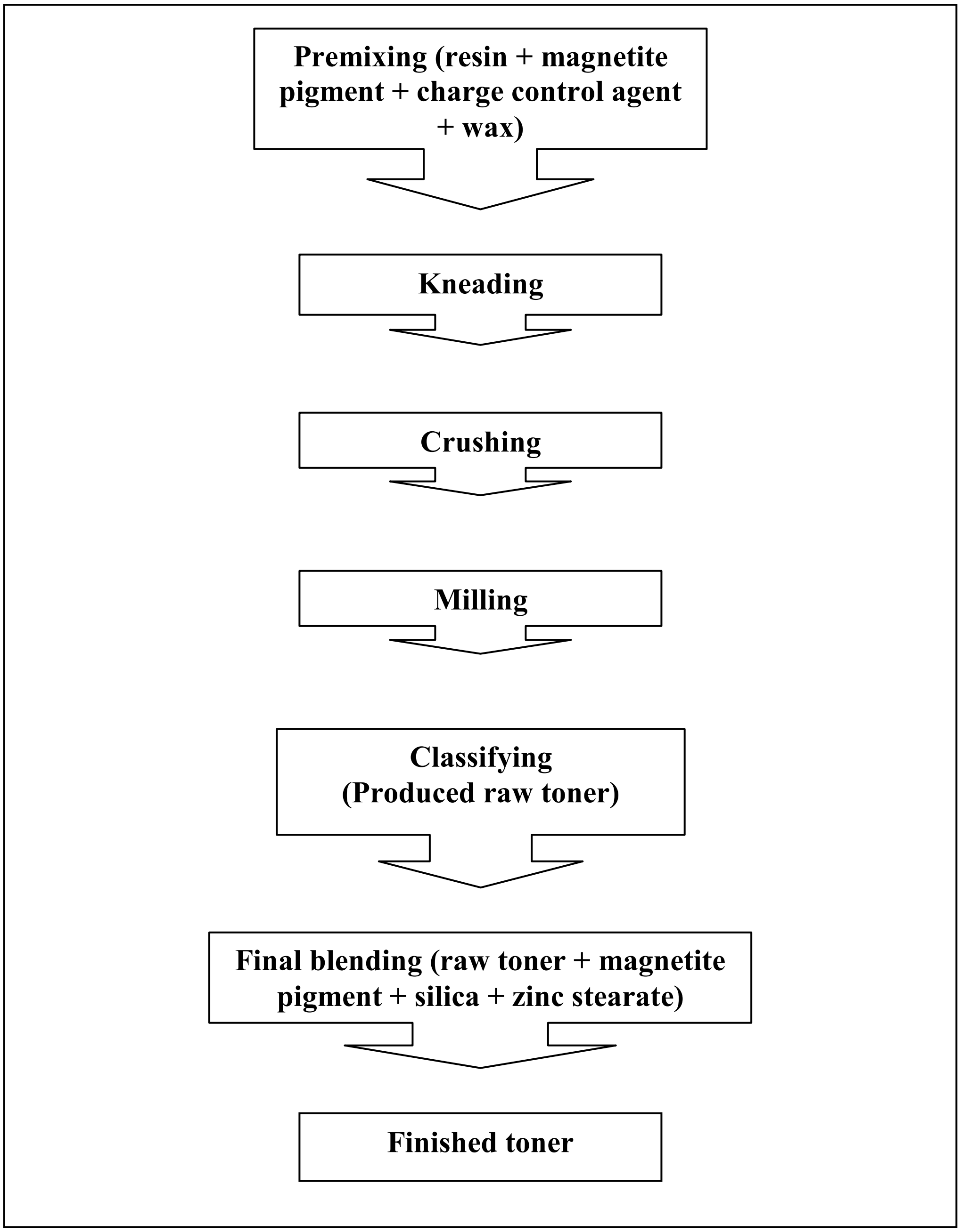


Figure 2.9 Processes to produce finished toner

The toner resin, pigment (magnetite type), wax and charge control agent were mixed in a mechanical mixer. The mixture was transferred into a kneading machine (extruder) and temperature was raised to melt and extrude the mixture into flat pieces. The extruded sample was then crushed into small pieces before being fed into the milling machine to grind down to very fine powder.

The powder was then subjected to a classifying process by sieving. Larger particles were returned for further crushing, and the undersize particles were recovered for melting and extrusion.

Raw toner particles of fairly even size between 8-10 microns were than blended with additives of around 1-2% of magnetite pigment, silica and zinc stearate to produce the finished toner. Physical properties of the toner were checked. These include the apparent density, flowability, tribocharge, magnetic content, and particle size distribution.

The diagrams of the series of instruments were shown in Figure 2.10 to 2.14.

Figure 2.10 Mixer used to mix the resin, magnetite pigment, wax and charge control agent.

Figure 2.11 Extruder was used to melt the mixture and extrude the mixture of resin, magnetite pigment, wax and charge control agent.

Figure 2.12 Crusher was used to crush down the extruded mixture into rough powder

Figure 2.13 Miller was used to reduce the size of the rough powder, wherein classifier was used to produce toner powder in more even sizes.

Figure 2.14 Blender was used to blend the toner powder together with magnetite pigment, silica and zinc stearate to produce a finished toner.

2.6 Print Test

After final blending, the finished toner was filled in to a toner cartridge and carried out a series of print test (ISO-IEC 19752 monochrome print test).

2.7 Toner Characterization

2.7.1 Apparent Density

Apparent density was studied to obtain the density of finished toner in gcm^{-3}. The toner powder was allowed to flow into a weighed steel container, w_0; after the powder was fully filled up the container, recorded down the weight of sample with container, w_1. The apparent density can be calculated using following equation.

Apparent density = $(w_1 - w_0)/100$ [2.7]

Figure 2.15 showed the equipment used to measure the apparent density.

Figure 2.15 Apparent density equipment (A: sample hopper, B: sample container)

2.7.2 Flowability

The ability of flow for a toner powder was determined by using disc method; toner powder was tested on the ability to flow through discs with different pore sizes within 10 seconds. The equipment was shown in Figure 2.16.

Figure 2.16 Flowability equipment (A: sample hopper, B: sample container, C: disc with different pore size)

2.7.3 Tribocharge

Keithley Instruments 610C solid state electrometer was used to determine the tribocharge of finished toner. The charge content was measured in μCg^{-1}. 0.1 g sample was mixed with 2 g of carrier; the mixture was then being blow by oxygen continuously until a stable reading can be obtained. Figure 2.17 indicated the diagram of electrometer.

Figure 2.17 Keithley Instruments 610C solid state electrometer (A: sample container)

2.7.4 Magnetic Content

The percentage of magnetic component contained inside a toner resin was measured by using Tectron Ag. 916 Fluxmeter. 1.5 g of sample was filled into a test tube, the test tube was then be inserted into fluxmeter. The testing was repeated 2 times to get a stable value.

The diagram of a fluxmeter was as indicated in Figure 2.18.

Figure 2.18 Tectron Ag. 916 Fluxmeter

2.7.5 Particle Size Distribution

The particle size distribution of toner particles was determined by using SILAS 1064. 0.5 g of toner powder was dispersed into 50 ml of dilute detergent solution. The dispersion was then being poured into the CILAS 1064 particle size analyzer (As shown in Figure 2.19) to go through osmometry light scattering measurement.

Figure 2.19 CILAS 1064 particle size analyzer

CHAPTER THREE: RESULTS AND DISCUSSION

3.1 Characterization for Low Molecular Weight Styrene acrylic Copolymer

3.1.1 Different Scanning Calorimetry (DSC)

DSC is most often used for characterizing the glass transition temperature, T_g, melting point, T_m, crystallization point, T_c, and heat of fusion of polymers, ΔH. T_g is important in describing the properties and potential end use of a polymer. [30, 37]

The test sample and the reference material are heated separately by individually controlled units. The power input to these heaters are controlled and continuously adjusted consequent to any thermal effect in the test sample as to maintain the two at identical temperatures. The differential power or heat energy required to achieve this state of affairs is recorded against the programmed temperature of the system.[38]

3.1.2 Gel Permeation Chromatography (GPC)

GPC is used to determine the molecular weight distribution of a polymer sample. GPC functions by separates the polymers according to size or hydrodynamic radius. A small amount of polymer solution was injected into a set of columns that are packed with porous beads. Smaller molecules can penetrate the pores and therefore retain to a greater extent than the larger molecules which continue down the columns and is eluted faster. [37]

The following are some equations that are important in interpreting the curve for GPC. Number-average molecular weight, M_n, is the number of molecules present in a given weight of a sample.

$$\mathbf{M_n = (\sum N_i M_i)/\sum N_i} \qquad \mathbf{[3.1]}$$

Where N_i = number of molecules with molecular weight M_i

M_i = molecular weight of i^th fraction

The evaluation of number average molecular weight is useful in analysis of kinetic data to examine the effects of many side reactions including chain transfer, inhibition, retardation, autoacceleration or gel effect in vinyl polymerization.

Weight-average molecular weight, M_w, is the sum of the contributions based on the weight fraction of each species.

$$\mathbf{M_w = (\sum w_i M_i)/\sum w_i = (\sum N_i M_i^2)/(\sum N_i M_i)} \qquad [3.2]$$

w_i = weight of i species having molecular weight M_i

Weight average molecular weight is important in relation to bulk properties of polymers that reflect their load bearing capacity. Softening, hot deformation, tensile and compressive strength, modulus and elongation, toughness and impact resistance and some other related bulk properties of polymer are better appreciated on the basis of weight average molecular weight.[38]

The polydispersity index, I_p, indicates the distribution of individual molecular masses in a given polymer sample. The I_p is calculated by using weight average molecular weight divided by number average molecular weight.

$$\mathbf{I_p = M_w/M_n} \qquad [3.3]$$

Melt elasticity properties of polymer sample is more closely dependent on the Z average molecular weight, M_z. As for toner resin, melt elasticity properties is the main key in the toner resin process ability. M_z is the third power average and is shown mathematically as equation 3.4. [30]

$$\mathbf{M_z = (\sum n_i M_i^3)/(\sum n_i M_i^2)} \qquad [3.4]$$

Figure 3.1 shows the M_n, M_w, M_p, and M_z in a GPC curve. [32, 38]

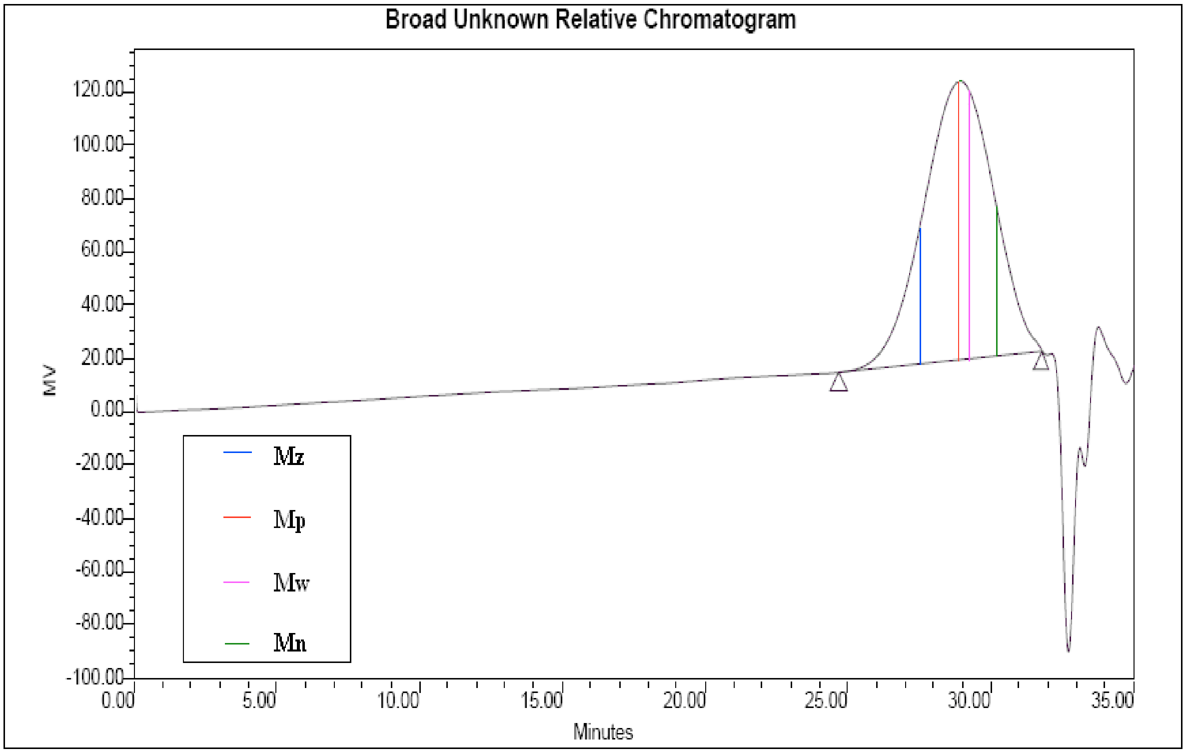


Figure 3.1 GPC curve for low molecular weight resin

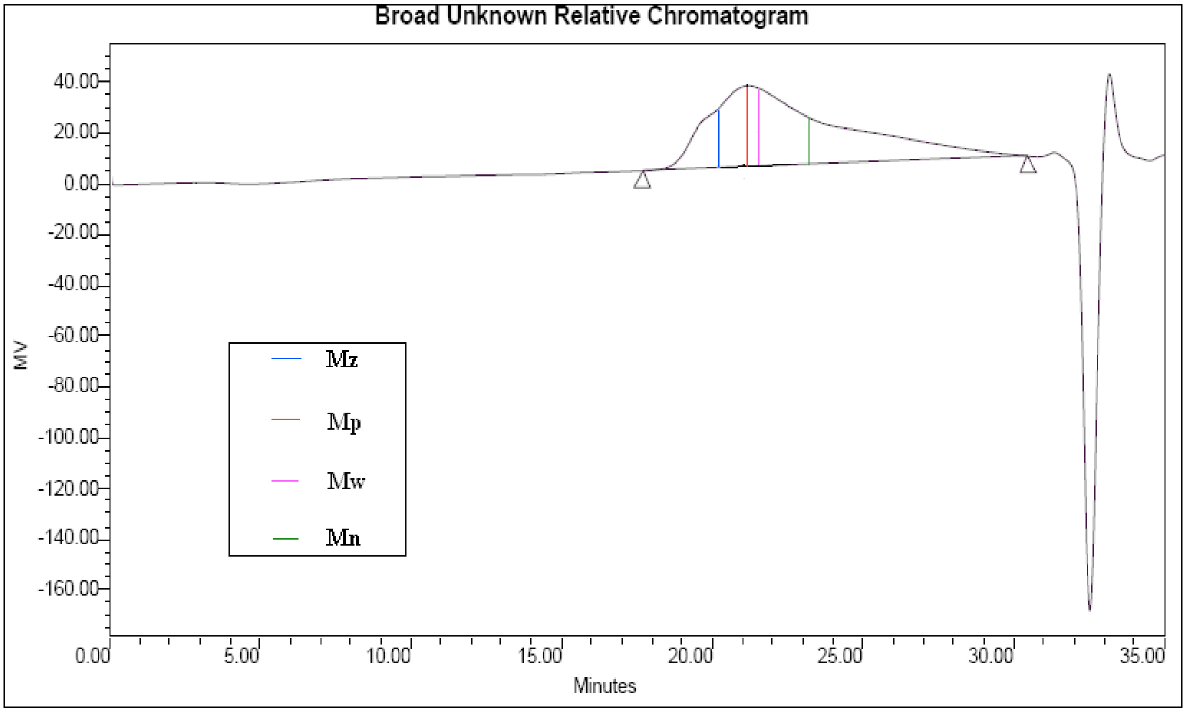


Figure 3.2 GPC curve for high molecular weight resin

3.1.3 Melt Flow Indexes (MFI)

Melt flow index is carried out to test the ability of molten resin to flow under pressure. The test polymer can be used in any convenient from; powder, granules or moulded pieces. The polymer sample is contained in a vertical metal cylinder, subjected to controlled heating at required temperature and then extruded through a jet by a loaded piston. MFI is defined as the amount of polymer in gram extruded in 10 minutes. The melt flow index for a resin can be calculated by using the following equation. The calculation of flow rate (given by RayRan Melt Flow Indexer) is given by the equation 3.5a.

$$\textbf{Flow rate} = (427 \times L \times d)/t \qquad [3.5a]$$

Where,

427 = Mean of areas of Piston and cylinder x 600

L = length of piston travel, cm

d = density of sample at test temperature, g/cm^3

t = time of piston travel for L in seconds

MFI is calculated by using equation 3.5b.

$$MFI = \frac{w}{t} x600 \qquad [3.5b]$$

Where, w = weight of sample flown through (g)

t = time for sample flow (s)

Melt flow rate is an indirect measure of molecular weight, high melt flow rate corresponding to low molecular weight. At the same time, melt flow rate is a measure of the ability of the material's melt to flow under pressure. Melt flow rate is inversely proportional to viscosity of the melt at the conditions of the test.

3.1.4 Acid Number (AN)

Acid number test is carried out to check the acidity of resin samples in mg KOH/g of samples. In order to assure the accuracy of the acid number, the molarity of KOH used need to be standardized by undergoes titration with potassium hydrogen phthalate, KHP, by known concentration. Before taking on the testing, the solvent which used to dissolve samples also need to be standardized to determine the amount of impurities present in the solvent.

In this study, phenolphthalein was used as the indicator for the titration and the changes of colour in different pH is shown in figure below. [40, 41]

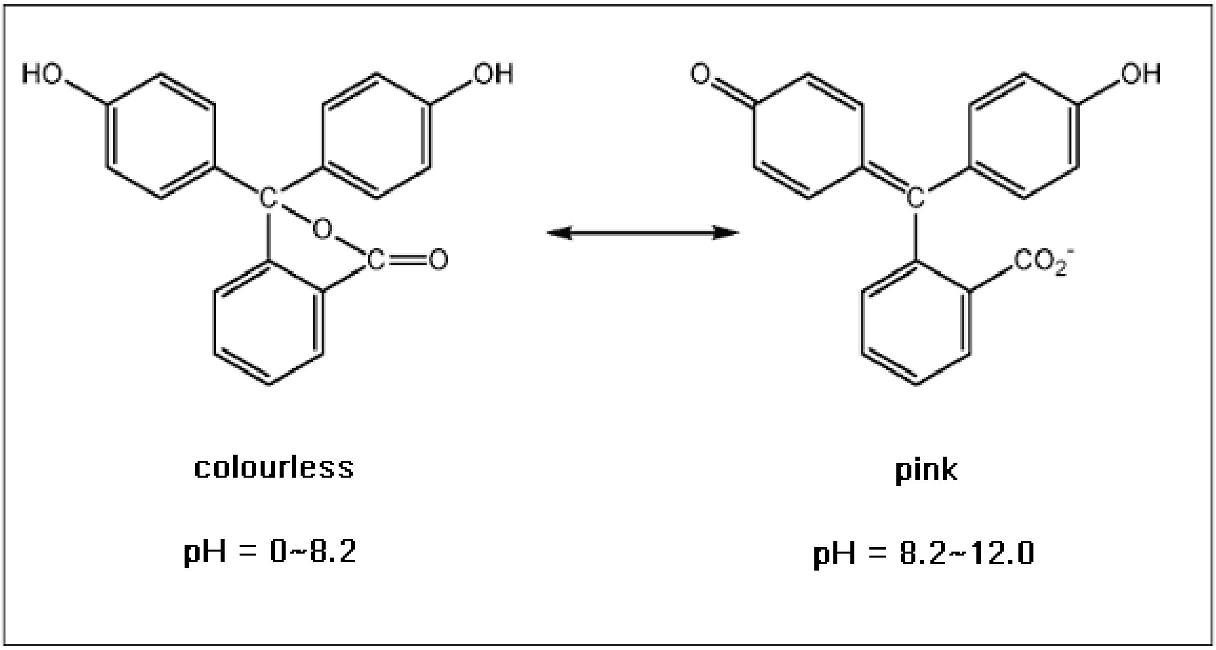


Figure 3.3 Phenolphthalein appear colourless in acidic system (pH 0 to 8.2) and appear in pink colour when the system change to alkaline (pH 8.2 to 12)

Standardization of KHP

Amount of KHP used = 0.5g

	Amount of KHP used/g	**Initial burette reading/ml**	**Final burette reading/ml**	**Volume used/ml**	**Normality for KOH**
First determination	0.50	0.80	45.10	44.30	0.055
Second determination	0.50	0.00	44.85	44.85	0.055
Average normality					0.055

Standardization of KOH can be done by applying the following equation.

$N = (1000 \times W_{KHP})/(204.23 \times V_{eq})$ [3.6]

Where N = Normality for the standardized KOH solution

W_{KHP} = weight of KHP in 50 ml solution, g

V_{eq} = volume of titrant consume, ml

204.23 = molecular weight of KHP

Blank titration of xylene

	Initial burette reading/ml	**Final burette reading/ml**	**Volume used/ml**
First determination	0.85	1.00	0.15
Second determination	1.00	1.15	0.15
Average volume (V_{blank})			0.15

Titration of sample (example, L10)

	Amount of L10 used/g	**Initial burette reading/ml**	**Final burette reading/ml**	**Volume used/ml**
First determination	1.00	29.30	29.50	0.20
Second determination	1.00	29.50	29.70	0.20
Average volume (V)				0.20

The acid number for samples can be obtained by using the following calculation, and the results for low molecular weight samples are displayed in Table 3.4.

$$\textbf{Acid Number = AN=} \{(V-V_{blank}) \times N \times 56.1\}/ W \qquad \textbf{[3.7]}$$

Where V= KOH solution required for titration, ml

V_{blank}= KOH solution required for blank titration, ml

N= Normality for the standardized KOH solution

W= Weight of the specimen, g

Acid number for sample, example L10

$$AN= \{(V-V_{blank}) \times N \times 56.1\}/ W$$

$$= \{(0.20-0.15)\times 0.055\times 56.1\}/1$$

$$= \mathbf{0.2\ mg\ KOHg^{-1}}$$

3.1.5 Total Solid Content (TSC)

Total solid content is used to determine the percentage of solid material present in the samples; as well as to calculate the percentage of conversion for those samples (As shown by equation 2.4 and 2.6)

The experimental TSC results and percentage of conversion for low molecular weight resins are shown in Table 3.1

Calculation for TSC (experimental method) for example L12

	Weight of container/g	**Weight of sample L12/g**	**Dry weight for (sample + container)/g**	**TSC/%**
Experimental Determination	94.34	95.87	95.11	50.3

$$\text{TSC} = \frac{\text{Wt of dried copolymer isolated experimentally}}{\text{Weight of copolymer solution}} \times 100\ \%$$

$$= (W_2 - W_0) / (W_1 - W_0) \text{ X } 100\% \qquad \textbf{[2.5]}$$

Where W_0 = weight of empty container

W_1 = weight of resin sample used plus container

W_2= dry weight for resin sample plus container

= 100 x (95.11-94.34)/(95.87-94.34)

= **50.3%**

Calculation for percentage of conversion, for example L12

Percentage conversion of copolymer

$$= \frac{\text{Wt of dried copolymer isolated experimentally} \times 100\%}{\text{Wt of monomer in the copolymer solution assuming all converted to polymer}} \qquad \textbf{[2.6]}$$

= 0.77/0.818 x 100%

= **94.1%**

3.1.6 Summary for Low Molecular Weight Resin

The formulation together with properties results for low molecular weight resins in terms of T_g, molecular weight, acid number, total solid content and percentage of conversion were summarized in Table 3.1.

Table 3.1 Formulation and properties results for low molecular weight resin

Code	**L10**	**L11**	**L12**
Formulation/ Parts per 100 parts of monomer			
Styrene	90	90	90
n-butyl acrylate	10	10	10
Benzoyl peroxide	**10**	**12.5**	**15**
Xylene	100	100	100
Properties results			
$M_n \times 10^3$ /$gmol^{-1}$	4.5	4.0	3.4
$M_w \times 10^3$ / $gmol^{-1}$	8.5	7.2	6.0
$M_p \times 10^3$ / $gmol^{-1}$	6.0	5.3	4.0
$M_z \times 10^4$ / $gmol^{-1}$	1.4	1.1	1
I_p	1.87	1.78	1.78
T_g/°C	54	54	53
MFI (130ºC)/(g/10min)	34.2	46.7	57.4
Acid number/mg $KOHg^{-1}$	0.2	0	0
Experimental TSC/%	50.7	50.4	50.3
Conversion/%	98.9	97.7	94.1

Resins L10 to L12 were prepared by using solution polymerization for 7 hours at reaction temperature 130°C. The GPC, DSC, MFI, and AN results were obtained by using dried resin which have been dried in oven for 130°C for 10 hours.

By referring to Table 3.1, the amount of initiator used was increased from L10 to L12. The increase in the amount of initiator had no significant effects on the glass transition temperature of the copolymer. The T_g was determined by the structure of the copolymer. [30]

The GPC result for low molecular weight resin was shown in Table 3.1 above. The narrow GPC peak meant that the molecular weight distribution for the resins was quite narrow. The increased in the initiator amount tends to lower down the overall molecular weight of copolymer. This might be due to the increased amount of initiator used tends to increase the concentration of free radicals in the system; therefore the termination of polymer chain occurred faster. As a result from this, the overall molecular weight of copolymer was shifted lower. [39]

The melt flow index for low molecular weight resins increased in inversed proportional to molecular weight. The higher the overall molecular weight of copolymer, the harder was the copolymer. Therefore, the melt flow index became high when the overall molecular weight for resin was low. [38]

Overall, the acid numbers for the low molecular weight resins were near to zero. This is because there were no acid group present in the system (the monomers used are styrene and n-butyl acrylate); hence, the acidity for the system was near to neutral.

In commercial production, higher conversion will ensure lower lost due to unreacted monomer. Percentage conversion for the three samples were exceeded 90%, this value was more than satisfactory. [5-23]

In this study, with the intention to obtain heat-melting ability of the toner resin composition at lower temperatures; the low molecular weight fraction was prepared by solution polymerization of styrene and n-butyl acrylate in xylene using benzoyl peroxide as initiator. Meanwhile, the overall molecular weight of resins were adjusted to a satisfactory low extend by varying the amount of initiator used during reaction.

In a radical polymerization, an increase in initiator concentration causes an increase in the number of radicals. A termination reaction is second order; therefore, the average molecular weight reduces with simultaneous increase in rate of reaction; consequently, rate of polymerization would tend to increase while the average degree of polymerization decreases.[39]

In the experiment, by lowering the molecular weight of resins, the glass transition temperature, percentage of conversion, and acid number still remain the same. The Melt flow index was affected by the molecular weight of resins, the value of MFI increased with the reduction of the molecular weight.[38]

3.2 Characterization for High Molecular Weight Styrene acrylic Copolymer

Testing procedures of properties tests and the determination of GPC, DSC, AN, MFI, TSC and percentage of conversion are same as described in section 3.1.1 to 3.1.5.

3.2.1 Summary for High Molecular Weight Resin

The formulation together with properties results for high molecular weight resins were summarized in Table 3.2 and 3.3.

Table 3.2 Formulation and properties results for high molecular weight resin prepared by using 2 parts methacrylic acid by weight

Code	**H55**	**H59**	**H56**	**H58**	**H57**
Formulation/ Parts per 100 parts of monomer					
Styrene	73.5	73.5	73.5	73.5	73.5
n-butyl acrylate	24.5	24.5	24.5	24.5	24.5
Methacrylic acid	**2**	**2**	**2**	**2**	**2**
Tetra ethylene glycol diacrylate	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**
benzoyl peroxide	1	1	1	1	1
Xylene (A)	40	40	40	40	40
(B)	60	60	60	60	60
Properties results					
T_g /°C	62	60	65	61	Formed insoluble gel
$M_n \times 10^4$/gmol^{-1}	2.91	3.20	3.42	3.12	
$M_w \times 10^5$/gmol^{-1}	2.44	2.24	2.06	3.42	
$M_p \times 10^5$/gmol^{-1}	2.87	2.77	2.83	3.03	
$M_z \times 10^5$/gmol^{-1}	6.73	6.13	5.39	12.41	
I_p	8.38	7.01	6.02	10.94	
MFI (150°C)/(g/10min)	1.8	2.4	4.7	1.5	
Acid number /mgKOHg^{-1}	13.5	14.0	13.7	13.7	
Experimental TSC Part (A) /%	58.4	52.3	47.5	47.2	
Experimental TSC Part (B) /%	48.7	48.9	48.2	48.7	
Conversion Part (A) /%	58.4	52.5	47.5	47.2	
Conversion Part (B) /%	95.8	96.1	94.7	95.5	

Table 3.3 Formulation and properties results for high molecular weight resin prepared by using 3 parts methacrylic acid by weight

Sample name	**H60**	**H61**	**H62**	**H63**	**H64**
Formulation/ Parts per 100 parts of monomer					
Styrene	72.8	72.8	72.8	72.8	72.8
n-butyl acrylate	24.2	24.2	24.2	24.2	24.2
Methacrylic acid	**3**	**3**	**3**	**3**	**3**
Tetra ethylene glycol diacrylate	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**
benzoyl peroxide	1	1	1	1	1
Xylene (A)	40	40	40	40	40
(B)	60	60	60	60	60
Properties results					
T_g /°C	60	64	63	63	Formed insoluble gel
$M_n\times10^4$/gmol^{-1}	4.08	3.97	3.69	3.24	
$M_w\times10^5$/gmol^{-1}	2.48	3.51	3.19	2.87	
$M_p\times10^5$/gmol^{-1}	2.91	3.40	2.96	2.75	
$M_z\times10^5$/gmol^{-1}	6.55	10.93	10.84	9.59	
I_p	6.08	8.83	8.63	8.85	
MFI (150 °C) /(g/10 min)	2.2	0.9	Too hard to flow	Too hard to flow	
Acid number/ mg KOHg^{-1}	19.4	19.7	19.1	19.5	
Experimental TSC Part (A) /%	49.7	45.9	50.0	49.4	
Experimental TSC Part (B) /%	49.8	51.1	50.0	49.2	
Conversion Part (A) /%	49.7	45.9	50.0	49.4	
Conversion Part (B) /%	97.4	99.9	97.8	96.1	

Sample H55 to H59 and sample H60 to H64 were prepared by using bulk polymerization for 4 hours under reaction temperature 120°C followed by solution polymerization for 5 hours under reaction temperature 130°C. The DSC, GPC, MFI and AN tests were carried out by using dried copolymers, which had dried in oven for 10 hours at 130°C.

The properties results for samples prepared by using 2 and 3 parts methacrylic acid incorporated with 0.5 to 0.8 parts tetra ethylene glycol diacrylate were listed in Table 3.2 and 3.3. The glass transition temperature for samples prepared by using 2 and 3 parts methacrylic acid incorporated with 0.5 to 0.8 parts tetra ethylene glycol diacrylate were in the range of 60 to 64°C. In these experiments, the resulting copolymer should be of random structure (by referring to section 1.10) and the monomer used was just different in 1 part of methacrylic acid. T_g was mostly depend on the structure of polymer. Consequently, the T_g for all the samples were quite close to each others. Nevertheless, the samples with 2 and 3 parts methacrylic acid incorporated with 0.9 parts tetra ethylene glycol diacrylate encountered gelation problem in the system.

The GPC curve for high molecular weight resin was shown as Figure 3.3. The GPC peak was broad which meant the molecular weight distribution for the sample was also broad. The polydispersity, I_p, which indicates how broad the molecular weights were distributed, were in the range of 6 to 10. [38]

Overall, the M_z for those samples prepared by using 2 and 3 parts methacrylic acid incorporated with 0.5 to 0.8 parts tetra ethylene glycol diacrylate were in increasing trend when the amount of tetra ethylene glycol diacrylate were increased. This was due to the tetra ethylene glycol diacrylate which incorporated into the system act as crosslinking agent; it crosslinked the polymers by free radical reaction. [42] However, the M_n, M_w and M_p did not have much change with the increased amount of tetra ethylene glycol diacrylate.

MFI for all samples were quite low, which was in the range of 0.9 g/ 10 min to 4 g/ 10 min. The MFI was inversely related to average molecular weight. The higher the overall molecular weight of copolymer, the harder was the copolymer; hence, melt flow index became lower when overall molecular weight of copolymer increased. [38] MFI for samples H62 and H63 were too low to be detected, which meant the two samples were very hard, the copolymers were unable to melt and flow at 150°C.

Acid number for samples prepared by using 2 parts methacrylic acid incorporated with different amount of tetra ethylene glycol diacrylate produced very similar results, which were around 13 mg KOH/g of sample. In the meantime, the samples prepared by using 3 parts methacrylic acid incorporated with different amount of tetra ethylene glycol diacrylate also gave very similar acid number results, which were around 19 mg KOH/g of sample. The acid number increased significantly when the amount of methacrylic acid used was increased from 2 parts to 3 parts, this phenomenon was due to the increasing of acid group in the polymer sample which provided by methacrylic acid. [42] The incorporation of methacrylic acid, MAA, into the copolymer was randomly through free radical reaction and the mechanism was shown in Figure 3.4.

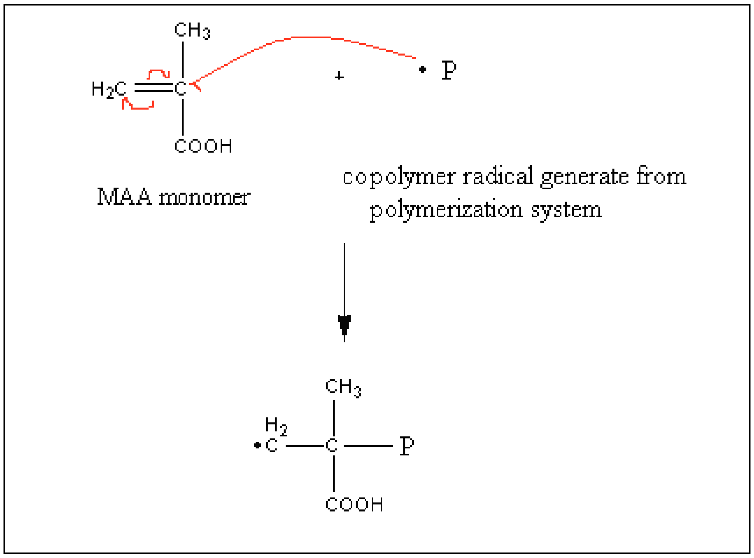


Figure 3.4 Mechanism of methacrylic acid incorporated into the copolymer

The percentage of conversion after bulk polymerization (part A) was roughly around 46% to 58%. After continued with solution polymerization, the percentage of conversion at the end of reaction was in the range of 95% to 99%. Percentage conversions for all samples were higher than 95%, the high percentage of conversion meant indicating that the polymerization process was near completion; therefore very little free monomer remained in the system.

There were two ways to prepare an ultra-high molecular weight polymer; firstly by addition of 0.01 to 1 parts by weight of divinyl compound (kind of ethylenically unsaturated monomer) into the termination stage of bulk polymerization or solution polymerization stage. The addition of this divinyl compound could increase the M_z accompanying with three dimensional crosslinking reactions. The greater amount used would result a higher M_z; however, when the amount used was more than 1 part, a gel like insoluble matter would be formed. [5-23]

The second way to prepare an ultra-high molecular weight polymer was by addition of methacrylic acid in the range of 1 to 15 parts by weight of the ethylenically unsaturated monomer employed in the bulk polymerization stage. This addition of methacrylic acid after completion of bulk polymerization would no longer affect the M_z. [4]

In these studies, 2 to 3 parts of methacrylic acid were added into the system during bulk polymerization stage, and followed by the addition of 0.5 to 0.9 parts of tetra (ethylene glycol) diacarylate, tetra ethylene glycol diacrylate, into the solution polymerization stage to increase the M_z of the copolymer. For both series with 2 and 3 parts methacrylic acid incorporated with 0.5 to 0.8 parts of tetra ethylene glycol diacrylate, the M_z had been increased effectively from 6×10^5 gmol^{-1} to over 1×10^6 gmol^{-1}. Samples which incorporated with 0.9 parts of tetra ethylene glycol diacrylate formed a gel like insoluble matter in the system. The occurrence of the gelation problem might due to the over crosslinked process between methacrylic acid and tetra ethylene glycol diacrylate. When the amount of tetra ethylene glycol diacrylate was increased, the level of crosslinking was increased correspondingly. Once the amount of tetra ethylene glycol diacrylate exceeded 0.8 parts, the crosslinked level became too high that the copolymer no longer soluble in the xylene and formed an insoluble matter in the system. [32, 42]

In a copolymerization system of methacrylic acid and tetra ethylene glycol diacrylate, TD, which contained multiacrylates, two types of network chains might take part in the crosslinking reaction. The first type of network chain was the poly(acrylate-co-acrylic acid) chain that was built up as the polymerization proceeded by radical propagation through acrylate and methacrylic acid double bonds (As shown in Figure 3.4). The chain was marked as chain A in Figure 3.6. The second type of network chain was the tetra ethylene glycol diacrylate chain which connected acrylate functionalities within each macromer unit (As shown in Figure 3.5). The chain was marked as chain B in Figure 3.6. [42]

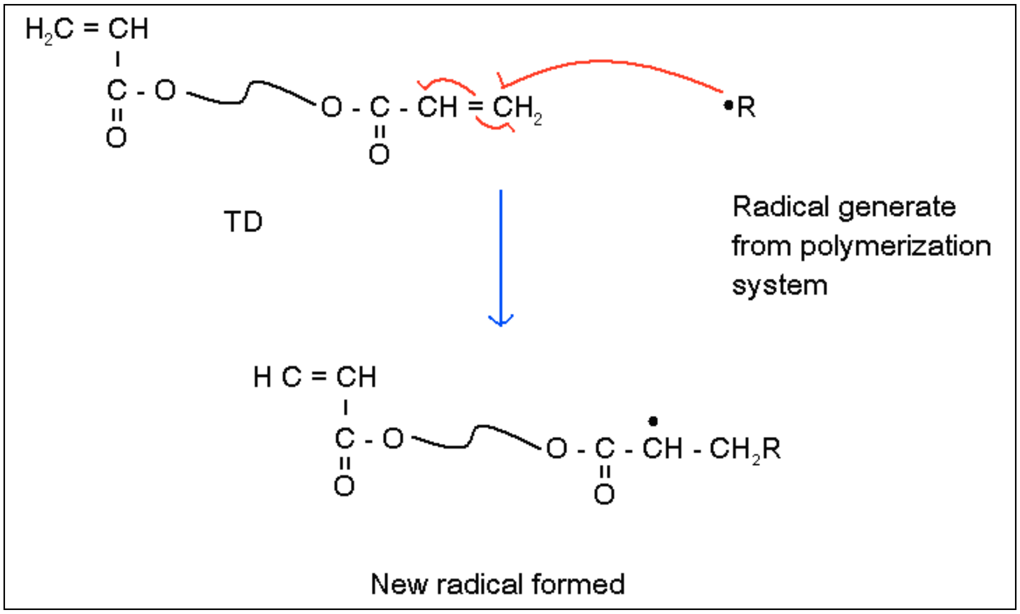


Figure 3.5 Generation of radical for tetra ethylene glycol diacrylate in the polymerization system

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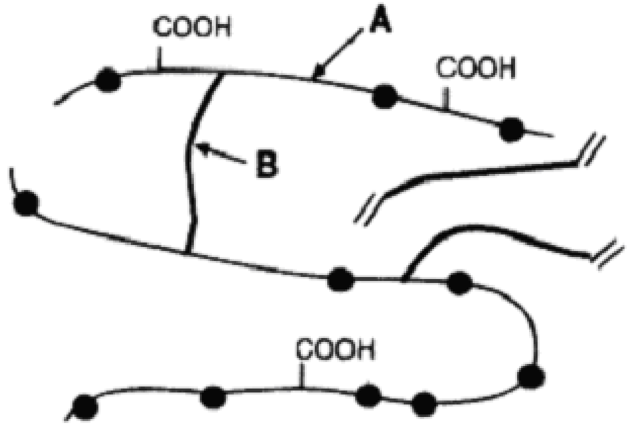

Network structure of the poly(multiacrylate-*co*-AA) system.

Figure 3.6 Network morphology in the crosslinking reaction [42]

3.3 Characterization for Mixture of High and Low Molecular Weight Styrene acrylic Copolymer

As refer to section 3.1.2, the melt elasticity properties of resins are determined by the M_z value. M_z for high molecular weight sample should be high enough to make sure toner resin is not stick on the roller during toner production; M_z for low molecular weight should be low enough to make sure toner resin is able to stick on the paper during printing process. Therefore, in this study, H58 and H63 (As described in section 2.2.3) were chose due to the highest value of M_z in the high molecular weight series; at the meanwhile, L12 (by referring to section 2.1.3) was chose due to the lowest value of M_z in the low molecular weight series. Testing procedures of GPC, AN, DSC, TSC and percentage of conversion are same as described in section 3.1.1 to 3.1.5. The determination of AN and MFI are same as described in section 3.1.3 and 3.1.4, whereas the determination of GPC peak ratio and the calculation for mixing ratio are described as below.

3.3.1 Determination of GPC Peak Ratio

As for sample M28, GPC peak area for high molecular weight fraction = 4109305; whereas GPC peak area for low molecular weight fraction = 8174495.

ratio for high molecular weight fraction =

$$\frac{\text{peak area for high molecular weight portion}}{\text{peak area for high molecular weight portion} + \text{peak area for low molecular weight portion}} \times 100\%$$

$$= \frac{4109305}{4109305 + 8174495} \times 100\%$$

= 33%

GPC peak ratio for low molecular weight fraction =

$$\frac{\text{peak area for low molecular weight portion}}{\text{peak area for high molecular weight portion} + \text{peak area for low molecular weight portion}} \times 100\%$$

$$= \frac{8174495}{4109305+8174495}\times 100\%$$

$$= 67\%$$

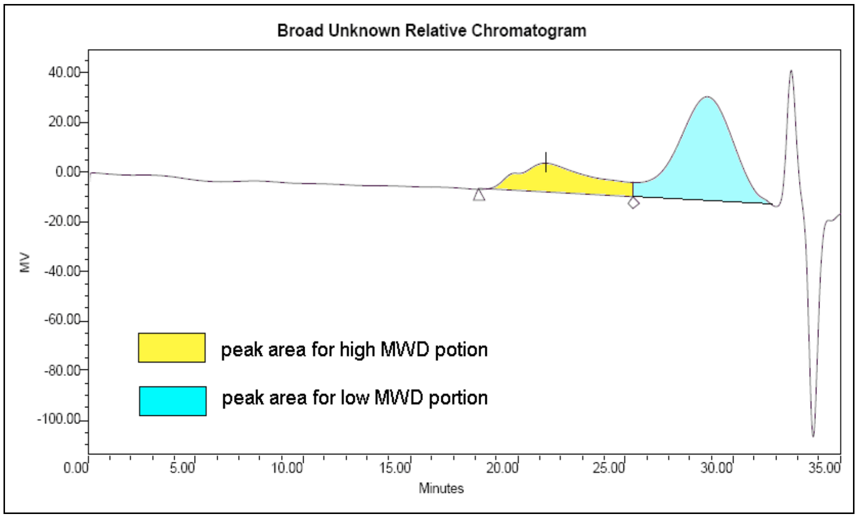

Figure 3.7 GPC curve of mixed sample

In a GPC system, smaller molecules can penetrate the pores of the columns and are therefore retained to a greater extent than the larger molecules which continued down the columns and eluted faster (as shown in Figure 3.8). With regards to Figure 3.7, there were two major peaks; high molecular weight fraction which eluted out first (yellow colour peak) and low molecular weight fraction (blue colour peak) which eluted out later. [37]

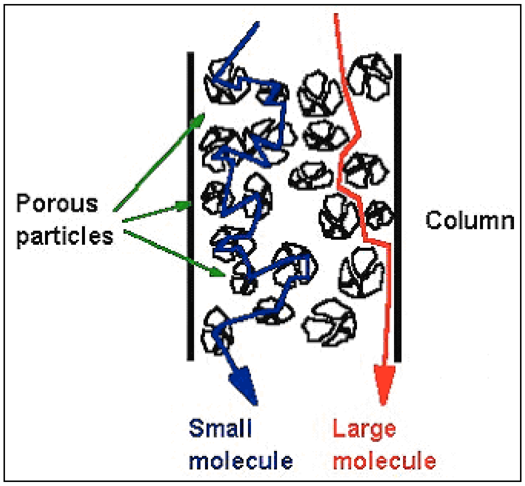

Figure 3.8 The figure shows that larger molecules which continued down the columns and eluted faster whereas smaller molecules can penetrate the pores of the columns and are therefore retained to a greater extent than the larger molecules.

3.3.2 Calculation for Mixing Ratio

TSC Calculation for L12 (experimental method)

	Weight of Al pan /g	Weight of sample L12 /g	Dry weight (for sample + Al pan) /g	TSC /%
First determination	0.1215	2.0215	1.2568	56.16
Second determination	0.1174	2.0036	1.2423	56.14
Third determination	0.1113	2.0070	1.2398	56.23
Average TSC				56.2

TSC Calculation for H58 (experimental method)

	Weight of Al pan /g	Weight of sample H58 /g	Dry weight (for sample + Al pan) /g	TSC /%
First determination	0.1124	2.0074	1.1140	49.90
Second determination	0.1335	2.0745	1.1577	49.37
Third determination	0.1170	2.0100	1.1245	50.12
Average TSC				49.8

TSC Calculation for H63 (experimental method)

	Weight of Al pan /g	Weight of sample H63 /g	Dry weight (for sample + Al pan) /g	TSC /%
First determination	0.1181	2.0757	1.1962	52.0
Second determination	0.1212	2.0399	1.1722	51.5
Third determination	0.1063	1.9676	1.1192	51.5
Average TSC				51.7

Calculation for mixing weight-M28 (ratio H:L = 50:50)

Weight of L12 used for mixing

Ratio needs = 50

By referring to the TSC test, 100g L12 copolymer solution contained 56.2 g solid, therefore,

Weight need to get 50g solid = 50/56.2 x 100

= 89.0g

Weight used to get 50g of mixture =

$$\frac{\text{weight need for high MW sample}}{\text{weight need for high MW sample} + \text{weight need for low MW sample}} \times \text{total weight of mixture}$$

$$= \frac{89.0}{89.0 + 100.4} \times 50$$

= **23.5** g (in solution)

Weight of H58 used for mixing

Ratio needs = 50

By referring to the TSC test, 100g H58 solution polymer contained 49.8 g solid, therefore,

Weight need to get 50g solid = 50/49.8x100

= 100.4 g

Weight used to get 50g of mixture =

$$\frac{\text{weight need for high MW sample}}{\text{weight need for high MW sample} + \text{weight need for low MW sample}} \times \text{total weight of mixture}$$

$$= \frac{100.4}{89.0 + 100.4} \times 50$$

= **26.5** g (in solution)

Calculation for TSC after mixing

Theoretical TSC for sample M28

TSC M28 =

$$\frac{(\text{weight used} \times \text{TSC})\text{of high MW sample} + (\text{weight used} \times \text{TSC})\text{of low MW sample}}{\text{total weight used for high and low MW sample}}$$

$$= \frac{(23.5 \times 56.2) + (26.5 \times 49.8)}{50} = 52.8\%$$

3.3.3 Summary for Mixed Resins

Formulation and properties results for mixed resins were summarized in Table 3.4 and 3.5 below.

Table 3.4 Formulation and properties results for mixed sample M28 to M31

Code		**M28**		**M29**		**M30**		**M31**	
Mixing ratio /% in TSC	**H58**	**50**		**60**		**70**		**80**	
	L12	**50**		**40**		**30**		**20**	
T_g /°C		62		60		60		62	
MFI (150°C) / (g/10 min)		33.0		32.2		20.1		9.1	
Acid number / mg $KOHg^{-1}$		6.7		7.9		9.3		10.6	
Theoretical TSC /%		52.8		51.8		51.3		51.0	
Molecular weight		**High**	**Low**	**High**	**Low**	**High**	**Low**	**High**	**Low**
M_n×10^3/ $gmol^{-1}$		216	4	176	4	146	4	150	5
M_w×10^3/ $gmol^{-1}$		530	9	471	9	449	8	437	10
M_p×10^3/ $gmol^{-1}$		329	5	318	5	300	5	284	6
M_z×10^3/ $gmol^{-1}$		1254	16	1209	18	1245	14	1190	17
I_p		2.45	1.94	2.67	2.20	3.06	2.00	2.91	2.05
GPC peak ratio /%		33	67	41	59	54	46	60	40

Table 3.5 Formulation and properties results for mixed sample M40 to M43

Code		**M40**		**M41**		**M42**		**M43**	
Mixing ratio /% in TSC	**H63**	**50**		**60**		**70**		**80**	
	L12	**50**		**40**		**30**		**20**	
T_g /°C		62		64		62		62	
MFI (150°C) / (g/10 min)		38.3		40.1		9.4		7.2	
Acid number / mg $KOHg^{-1}$		9.8		11.6		13.6		15.9	
Theoretical TSC /%		53.4		53.0		52.7		52.3	
Molecular weight		**High**	**Low**	**High**	**Low**	**High**	**Low**	**High**	**Low**
$M_n \times 10^3$/ $gmol^{-1}$		191	4	158	4	197	5	149	5
$M_w \times 10^3$/ $gmol^{-1}$		447	10	374	10	454	12	382	12
$M_p \times 10^3$/ $gmol^{-1}$		318	5	286	5	331	5	301	6
$M_z \times 10^3$/ $gmol^{-1}$		1049	20	875	19	1017	23	937	21
I_p		2.35	2.29	2.37	2.25	2.30	2.47	2.57	2.38
GPC peak ratio /%		31	69	41	59	47	53	59	41

The glass transition temperature for all the mixed samples were almost the same (by referring to Table 3.4 and 3.5), in the range of 60 to 63°C. For all mixed samples, the low molecular weight sample used was the same, the only difference was the high molecular weight sample (differ in 1 part of methacrylic acid) used and the ratio of mixing. T_g is mostly depends on the structure of polymer, thus the T_g for all samples were quite close to each others.

The GPC results for samples M28 to M31 were shown in Table 3.4. The average molecular weights for samples were similar to each others for both high and low molecular weight fraction. This result showed that the changing in mixing ratio did not affect much on the molecular weight. The only difference observed from the GPC results was the GPC peak ratio. The GPC peak ratio for high molecular weight fraction was in increasing trend while the mixing ratio changed from H:L=50:50 to H:L=80:20.

By referring to Table 3.5, we noticed that the average molecular weight for samples M40 to M43 were also close to each others for both high and low molecular weight fraction. This result showed that the changing in mixing ratio did not have significant effects on the molecular weight. The GPC peak ratio for high molecular weight fraction was in increasing trend while the mixing ratio changed from H:L=50:50 to H:L=80:20. This phenomenon was as expected; when the amount of high molecular weight resin used increased in a sample, the percentage of high molecular weight fraction should increase accordingly.

MFI value was in decreasing trend while the mixing ratio changed from H:L=50:50 to H:L=80:20. The result showed that the changing in mixing ratio had significantly lower down the ability of resin to flow. Increased amount of high molecular weight resin used in the sample tends to harden the sample and thus brought down the MFI value.

By referring to Tables 3.4 and 3.5, TSC and acid number for mixed resins were increased when the mixing ratio changed from H:L=50:50 to H:L=80:20. By increasing the amount of high molecular weight resin used in the sample, the properties of the mixed product would become closer to the properties of the high molecular weight resin; hence, TSC and acid number was increased consequently because the TSC and AN of high molecular weight resin was higher than TSC and AN of low molecular weight resin.

3.4 Characterization for Styrene acrylic Commercial Resin

Three commonly used styrene acrylic commercial resins (SJ 700, CPR 350 and CPR 400) had been chosen to undergo a series of characterization tests to compare the properties between commercial resins and the experimental mixed samples.

3.4.1 Summary for Commercial Resins

Table 3.6 shows the properties results for commercial resin.

Table 3.6 Properties results for commercial resins

Commercial resin	**SJ700**		**CPR350**		**CPR400**	
T_g /°C	63		67		64	
MFI (150°C) /(g/10 min)	4.4		4.2		10.3	
Acid Number /mg $KOHg^{-1}$	10.2		9.1		8.5	
Molecular weight	**High**	**Low**	**High**	**Low**	**High**	**Low**
$M_n \times 10^3$/ $gmol^{-1}$	159	4	193	4	302	4
$M_w \times 10^3$/ $gmol^{-1}$	625	6	550	7	677	7
$M_p \times 10^3$/ $gmol^{-1}$	1074	5	807	5	892	5
$M_z \times 10^3$/ $gmol^{-1}$	1521	9	1199	11	1309	10
I_p	3.92	1.68	2.85	1.80	2.24	1.73
GPC peak ratio /%	36	64	50	50	60	40

T_g for three commercial resins were quite closed to each others; in the range of 63 to 67 °C.

The results in the Table 3.6 obviously showed that all the three commercial resins, as for their high molecular weight fraction, contained extra high average molecular weight.

As for low molecular weight fraction, all three resins showed very similar molecular weight with each others. The only difference that could be observed was the GPC peak ratio. This ratio for high molecular weight fraction was varied from 40% to 64% from resin to resin.

MFI results were shown as in Table 3.6. MFI values for SJ700 and CPR350 were quite similar to each others, while the CPR400 had a higher MFI. This result showed that the ability of flow for CPR400 was greater than the rest.

With regards to Table 3.6, acid numbers for the three commercial resins were in the range of 8 to 10 mg KOH/g of sample. By comparing the Table 3.4, 3.5 and 3.6, we found that the properties for mixed sample M30 was closed to commercial resin SJ700 in term of T_g, M_z, and AN.

Table 3.7

Comparison between commercial resins, patent literature and experimental samples

Sample name		**Properties**														
		Tg (°C)	**Molecular weight**										**GPC peak ratio**		**MFI / (g/10 min)**	**AN / (mg KOH/g)**
			Mn (gmol^{-1}/ 10^3)		**Mw (gmol^{-1} / 10^3)**		**Mp (gmol^{-1} / 10^3)**		**Mz (gmol^{-1} / 10^3)**		**Ip**					
			H	**L**	**H**	**L**	**H**	**L**	**H**	**L**	**H**	**L**	**H**	**L**		
Commercial resin	SJ700	63.0	155	4	618	6	992	5	1,509	9	4.00	1.68	36	64	4.4	10.2
	CPR350	66.6	193	4	550	7	807	5	1,199	11	2.85	1.80	50	50	4.2	9.1
	CPR400	64.4	302	4	677	7	892	5	1,309	10	3.24	1.73	60	40	10.3	9.5
Experimental sample	M28	62.4	216	4	530	9	329	5	1,254	16	2.45	1.94	33	67	33.0	6.7
	M29	60.4	176	4	471	9	318	5	1,209	18	2.67	2.20	41	59	32.2	7.9
	M30	60.2	146	4	449	8	300	5	1,245	14	3.06	2.00	54	46	20.1	9.3
	M31	61.8	150	5	437	10	284	6	1,190	17	2.91	2.05	60	40	9.1	10.6
	M40	62.4	191	4	447	10	318	5	1,049	20	2.35	2.29	31	69	38.3	9.8
	M41	63.5	158	4	374	10	286	5	875	19	2.37	2.25	41	59	40.1	11.6
	M42	61.8	197	5	454	12	331	5	1,017	23	2.30	2.47	47	53	9.4	13.6
	M43	62.2	149	5	382	12	301	6	937	21	2.57	2.38	59	41	7.2	15.9
US patent 5,084,368		40~90	2~15	1~5					≥400							

3.5 Print Test

M30 and SJ700 were used as the resin binder in the toner formulation to produce the finished toners. Sample M30 were chose because of its closest properties with the commercial resin SJ700 (in terms of T_g, M_z, and AN). Print tests were carried out for the two toners to compare the quality of the two resins. Table 3.7 indicated the comparison of properties between finished toner produced by using M30 and SJ700.

Table 3.8 Comparison of properties between finished toner produced by using M30 and SJ700.

	Toner M30		**Toner SJ700**	
Particle size distribution				
5% / µm	4.10		5.29	
50% / µm	8.52		9.95	
95% / µm	16.12		18.43	
5 µm / %	7.93		4.02	
24 µm / %	99.72		99.55	
Sharpness Index, D95/D5	3.93		3.48	
Tribocharge / μCg^{-1}	-18.5		-17.0	
Magnetic Content / %	48		50	
Flowability / mm	5		5	
Apparent Density / gcm^{-3}	0.594		0.579	
Melt Flow Index 160°C, (g/10 min)	29		26	
Glass Transition Temperature / °C	60		62	
Molecular weight	**High**	**Low**	**High**	**Low**
$M_n \times 10^3$/ $gmol^{-1}$	195	4	213	3
$M_w \times 10^3$/ $gmol^{-1}$	388	8	499	6
$M_p \times 10^3$/ $gmol^{-1}$	270	5	929	5
$M_z \times 10^3$/ $gmol^{-1}$	801	12	924	8
I_p	1.99	1.85	2.34	1.66

With reference to Table 3.7 above, all the properties for toner prepared by using resin M30 (referred to Table 3.4) was similar with the properties of toner prepared by using commercial resin, SJ700.

The print out of toner prepared by using resin M30 was found to have a better colour tone by comparing to resin SJ700. However, there were minor background problem existed for both toner M30 and SJ700 (by referring to section 1.3, Table 1.1). The print out results were attached in Appendix I and II respectively. Figure 3.9 and Figure 3.10 show the diagrams of finish toner prepared by using resin M30 and SJ700 respectively.

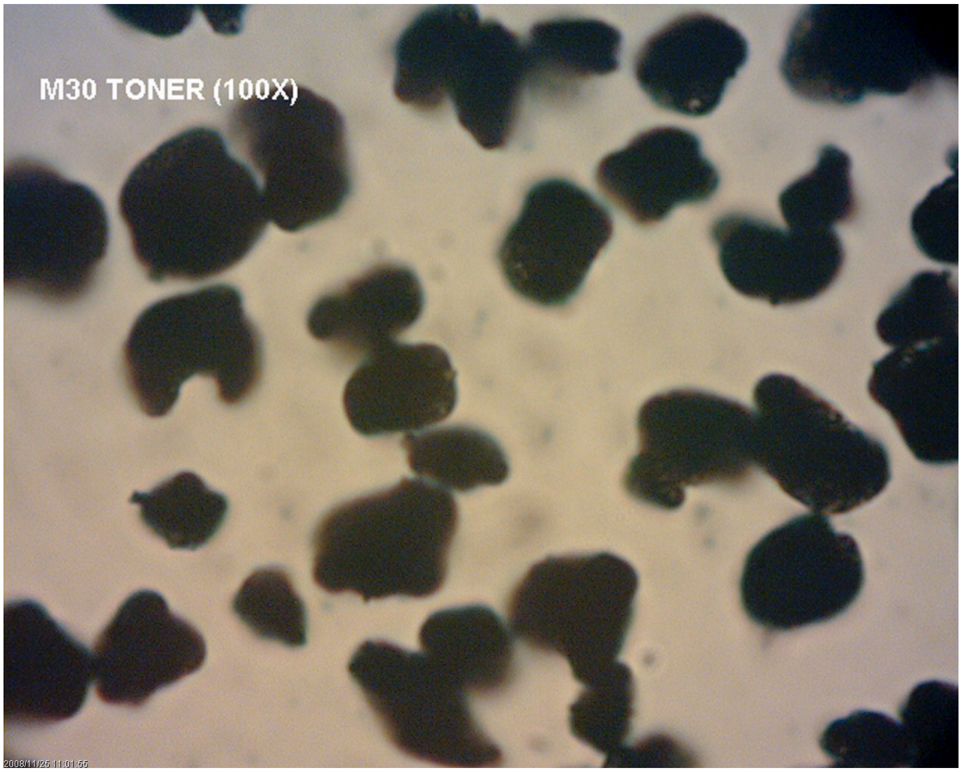

Figure 3.9 Finish toner prepared by using resin M30 was observed by using microscope under magnification 100×, the toner particles were found in irregular shape.

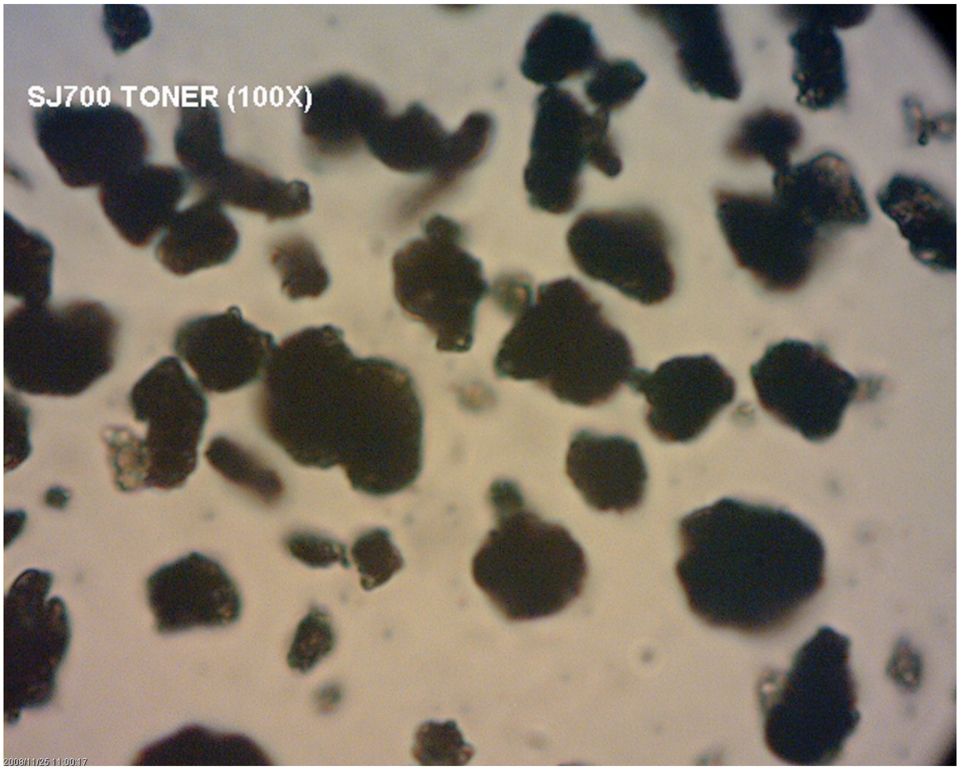

Figure 3.10 Finish toner prepared by using resin SJ700 was observed by using microscope under magnification 100×, the toner particles were found in irregular shape.

CHAPTER 4: CONCLUSION

4.1 Summary

With reference to Table 3.8 in section 3.4.1, all the properties for toner prepared by using resin M30 (referred to Table 3.4) were similar with the properties of toner prepared by using commercial resin, SJ700.

Particle size distribution for toner M30 at 5%, 50% and 95% were 4.1 µm, 8.52 µm and 16.12 µm; the percentage at 5 µm and 24 µm was 7.93% and 99.72% relatively. As for toner SJ700, particle size distribution at 5%, 50% and 95% were 5.29 µm, 9.95 µm and 18.43 µm, it was slightly higher than toner M30; the percentage at 5 µm and 24 µm was 4.02% and 99.55% respectively. Sharpness index was similar; 3.93 for toner M30 and 3.48 for toner SJ700.

Tribocharge for toner M30 was slightly stronger than toner SJ700; -18.5 and -17 μCg^{-1} correspondingly. Magnetic content was similar for both toners; 48% for toner M30 and 50% for toner SJ700. Flowability for both toners was identical; 5 mm for both toners.

As for apparent density, the results for toner M30 was 0.594 gcm^{-1}, this result was similar with apparent density for toner SJ700, 0.579 gcm^{-1}. The melt flow index for both toners were also comparable with each other, where melt flow index for toner M30 was 29 g/ 10 min and results for toner SJ700 was 26 g/ 10 min. This similarity was also observed for glass transition temperature where results for toner M30 and SJ700 were 60°C and 62°C respectively.

The low molecular weight distributions for both toners were similar in terms of M_n, M_w, M_p, M_z and I_p. As for high molecular weight distribution, M_n, M_w, M_z and I_p for both toners were comparable to each others, only M_p value for toner M30 was lower than toner SJ700; 2.7×10^5 $gmol^{-1}$ for toner M30 and 9.29×10^5 $gmol^{-1}$ for toner SJ700.

In terms of the print test, toner M30 produced a good printing colour tone by comparing to the performance of the commercial toner SJ700, which was chosen as the benchmark for the present project. There was minor background problem for both samples of toners made from M30 and SJ700. (by referring to section 3.5).

4.2 Further Works as Extension to the Project

a) In the preparation of high molecular weight sample, copolymerization process by using crosslinking agents other than tetra ethylene glycol diacrylate can be carried out.

b) Instead of preparing the high and low molecular weight resin separately, the experiment can also be carried out to prepare resin sample which contained high and low molecular weight fraction in a single polymerization system.

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