CHAPTER 4: COPOLYMERIZATION OF PALM OLEIC ACID-BASED MACROMERS WITH METHYL METHACRYLATE AND BUTYL ACRYLATE

Alkyd-acrylate hybrid systems can be synthesized in several different ways. Typically they are synthesized by free radical polymerization of acrylic monomers in the presence of different kinds of unsaturated alkyd resins. In this chapter, copolymerization of the macromers with different ratios of MMA and BA are studied. The aim of the present work is to investigate kinetic of the reactions and thermal properties of the copolymers on their surface coating application. The formation of copolymer was confirmed by ^{1}H-NMR, FT-IR spectroscopy, solvent extraction as well as thermal analysis results. The performances of these copolymers as coatings were evaluated using standard test methods which will be discussed in the next chapter.

4.1 Preparation of macromer-methyl methacrylate copolymers (MMC)

4.1.1 Effect of macromer content on the conversion (%)

The macromers were copolymerized with MMA monomer at different macromer/MMA ratios as described in Section 2.3. Two plausible schemes for the synthesis of the copolymers are represented by Figure 4.1.

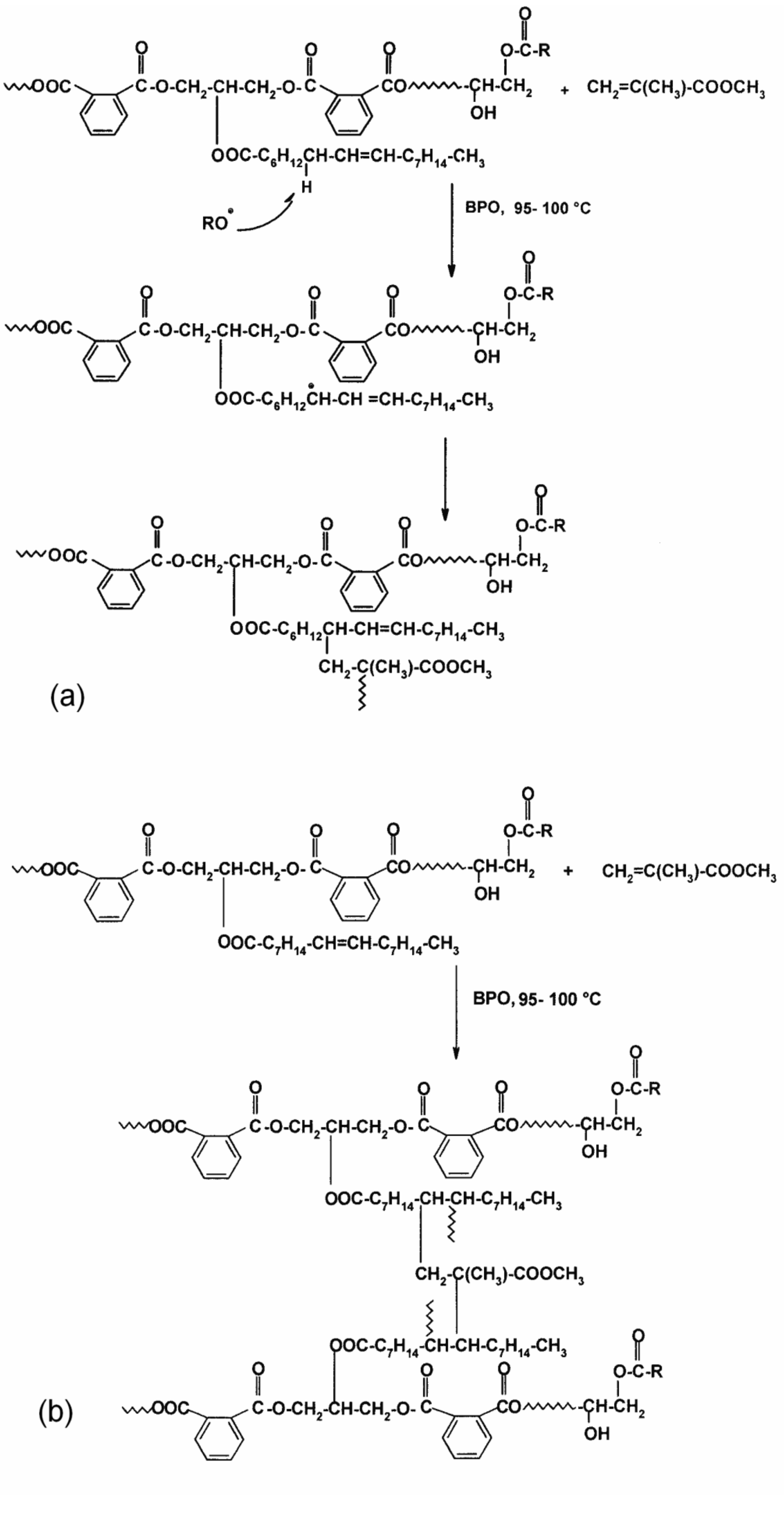


Figure 4.1 : Two plausible reaction mechanisms for the synthesis of the copolymers, proton abstraction (a), and addition mechanism to C=C (b).

The effect of the AlkOA/MMA ratio on conversion (%) is presented in Figures 4.2, 4.3 and 4.4 for copolymers of AlkOA65, AlkOA40 and AlkOA28 with MMA respectively. For each macromer, the polymerization rate decreases when the macromer content is increased. This is similar to the observations in other alkyd-acrylics systems as reported by Wang et al. [94] and Uschanov et al. [95].

The macromer contains one or more attached oleate branches that have -C=C- double bonds, which serve as the sites for copolymerization with MMA.

The effect of steric hindrance needs to be considered. The -C=C- in the oleate side chain of the macromer has more steric hindrance than that of MMA, consequently the propagating radical would react more with MMA than the macromer. As the macromer/MMA ratio is increased the rate of copolymerization as well as the conversion would decrease. In addition, the conversion is also influenced by the fact that as the polymerization system becomes viscous after reaching certain conversion level, the mobility of monomers and propagation radicals is slowed down. The same trend was also observed by using AIBN whereby 100% conversion could not be reached [125].

As the polymerization is initiated by free radicals, the unsaturated double bonds can stabilize the radicals through the allylic hydrogens. This will slow down the polymerization rate as shown in the Figure 4.1(a). Alternative addition mechanism (b) in Figure 4.1 is supported by ^{1}HNMR results which shows the reduction of -C=C- after copolymerization.

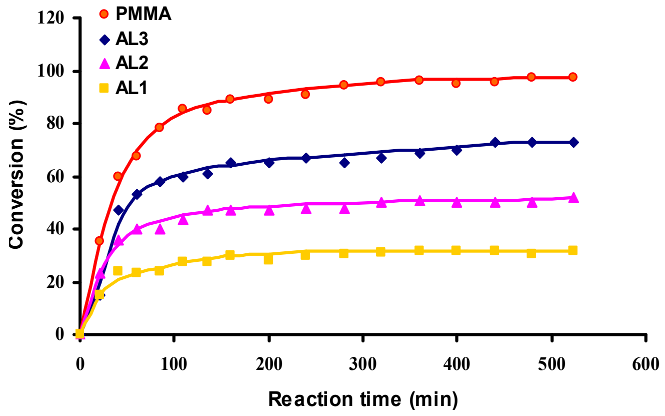


Figure 4.2 : Conversion of copolymers of AL1, AL2 and AL3 with ratios 50%, 35% and 20% of AlkOA65 respectively

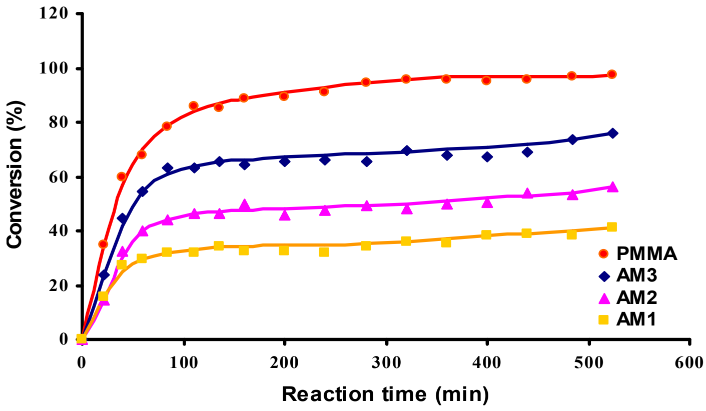


Figure 4.3 : Conversion of copolymers of AM1, AM2 and AM3 with ratios 50%, 35% and 20% of AlkOA40 respectively

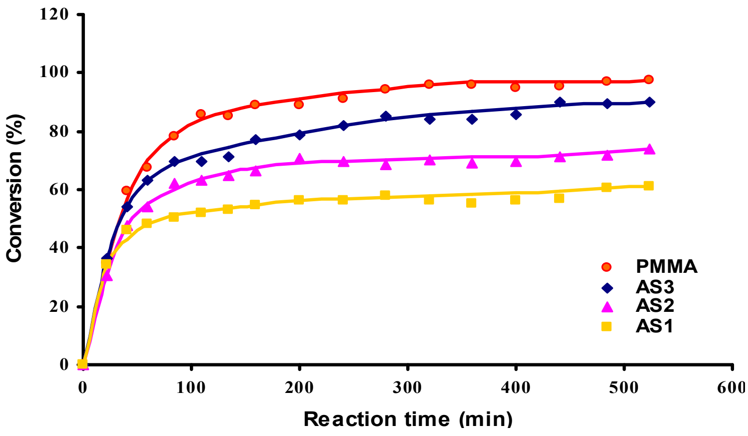


Figure 4.4 : Conversion of copolymers of AS1, AS2 and AS3 with ratios 50%, 35% and 20% of AlkOA28 respectively

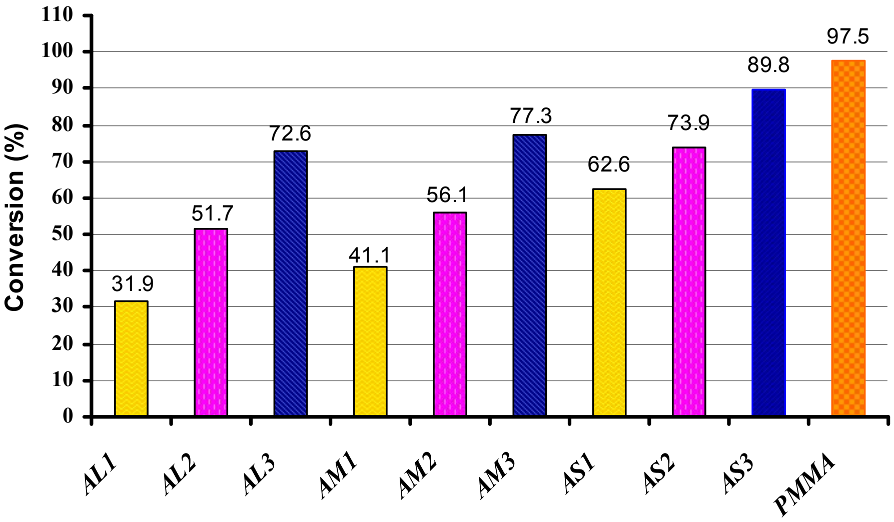


Figure 4.5 : Conversion (%) of PMMA and copolymers (MMC)

The conversion results for all samples were compared in Figure 4.5. Copolymerization of short oil length macromer with 80% MMA (AS3) exhibited the highest conversion (%), because it has the lowest percentage of oleic acid (28%), and consequently less steric hindered -C=C-, thus increasing the observed copolymerization rate.

4.2 Evidence on formation of true copolymer

The formation of copolymer was confirmed by FTIR, ^{1}H-NMR spectroscopies and solvent extraction, as discussed below.

4.2.1 FTIR spectroscopy

The overlaid FTIR spectra of AS copolymers (copolymer of AlkOA28 with MMA), related macromer and PMMA are displayed in Figure 4.6. Assignments of important peaks are shown in Table 4.1. Overall the spectrum of the copolymers resembled that of the PMMA with a couple of extra peaks.

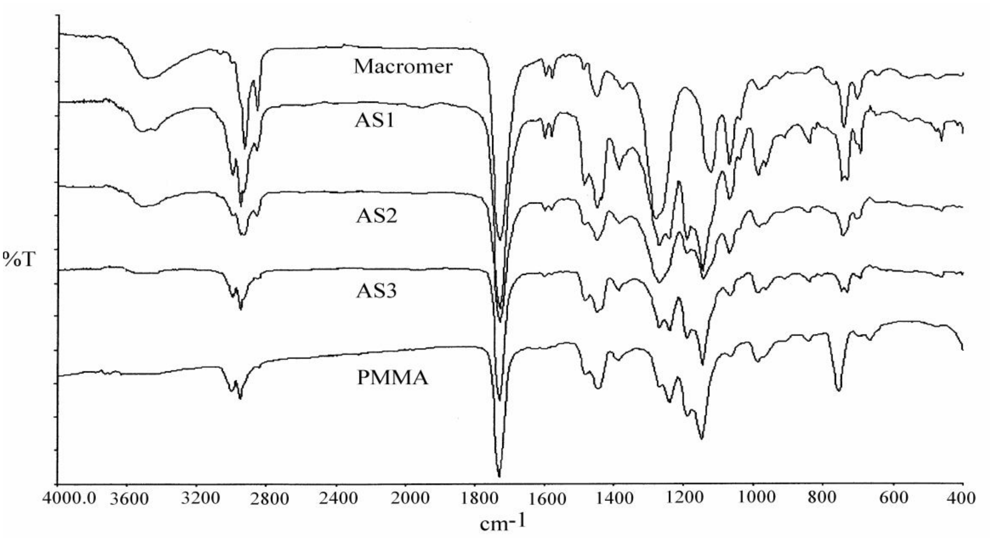


Figure 4.6 : The FTIR spectra of AS copolymers, AlkOA28 macromer and PMMA

The two weak peaks at 1580 and 1599 cm^{-1} arising from C=C are due to the aromatic rings in PA, while the broad bands at 3458-3524 cm^{-1} can be attributed to the hydroxyl groups present in the macromer and its copolymers. The peak intensity of the -OH stretching band also decreases with increasing MMA content in the copolymers. FTIR spectra of the AlkOA40 and AlkOA65, and related copolymers were displayed in Appendix C.

Table 4.1 : The absorption peaks of AS copolymers, AlkOA28 and PMMA

Bonding	**Wave number/cm^{-1}**
OH stretching	3458- 3524
C-H stretching aromatic	2993
Methyl (-CH_3), methylene C-H and methoxy (OCH_3)	2843, 2949, 2927
Methylene –$(CH_2)_n$- rocking	720-750
C=O stretching carbonyl groups	1726
C=C stretching aromatic rings(PA)	1580, 1599
Methylene C-H bending	1448-1485
Aromatic =C-H bending	744
C-O-C stretching of ester groups	1071-1285

4.2.2 ^{1}H-NMR Spectroscopy

Reaction of double bonds in the resulting copolymers was identified and confirmed using the ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectra of oleic acid, AlkOA40 and one of its copolymer (AM2) are shown in Figures 4.7(A), (B) and (C) respectively. The assignments of the various protons are as shown in the figures and Table 4.2. In particular δ= 5.3 ppm due to -CH=CH- (b, c), and 0.89 ppm due to $-CH_3$ (a), are attributed to the oleate unit in the macromer structure.

The ratio of peak integrations of these two peaks in the macromer is 2:3 (≈0.67), but in the copolymer it was less than 0.02, which indicating that -C=C- of the macromer was involved in the radical addition reactions. With reference to the ^{1}H-NMR spectrum of the copolymer in Figure 4.7(C), the peak at 3.7 ppm is the $-OCH_3$ of the MMA unit, while that at 0.89 is the $-CH_3$ from the oleate chain of macromer. The same results were observed for copolymer AM1 and AM3. Thus the ^{1}H-NMR spectra have provided evidence that the copolymer contained both MMA and the macromer units. ^{1}HNMR spectra of copolymers of AlkOA28 macromer and AlkOA65 macromer were shown in Appendix A.

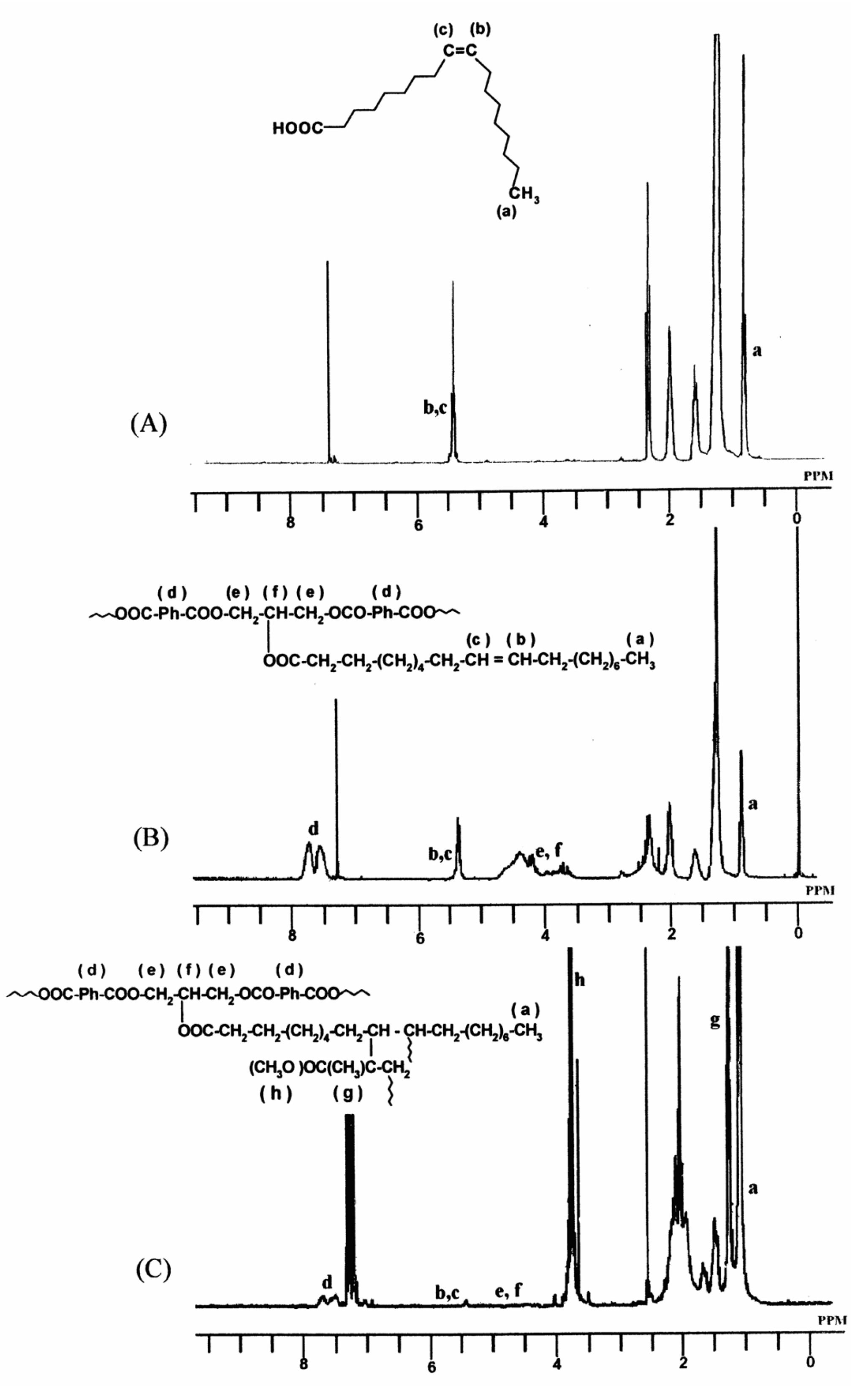


Figure 4.7 : ^{1}H-NMR spectra of oleic acid (A), AlkOA40 (B) and copolymer AM2 (C)

Table 4.2 : Chemical shifts of ^{1}H-NMR spectra of AlkOA40, AM2 and oleic acid

Chemical shift (δ)/ ppm	Structure
0.89 (protons of methyl groups)	$\mathbf{CH_3}$-$(CH_2)_7$-CH=CH-
1.0 (protons of methyl groups)	CH_2=C($\mathbf{CH_3}$)-$COOCH_3$
1.2, 1.3 (methylene protons)	–($\mathbf{CH_2}$)$_6$-CH_2-CH=CH-CH_2-($\mathbf{CH_2}$)$_6$-CH_3
3.6 - 4.7: protons of glycerol moiety	-O-$\mathbf{CH_2}$-**CH**(O)-$\mathbf{CH_2}$(O)-
5.3	–C**H**=C**H**-
3.7	-(O$\mathbf{CH_3}$)C=O
7.5-7.7	-Ph-

4.2.3 Solvent extraction

The formation of true copolymer is further confirmed by a separate solvent extraction experiment. Ethyl ether was chosen as it is a good solvent for the macromers and bad solvent for the polyacrylate. Samples were extracted with diethyl ether under continued reflux for 2 days to remove any unreacted macromer, and the ^{1}H-NMR spectrum was unaltered. Figure 4.8 shows ^{1}H-NMR spectrum of copolymer AM2 after solvent extraction. From Figure 4.8, a chemical shift at 7.5-7.8 ppm contributed by the aromatic ring protons of the macromer is observed together with a broad peak at 4.2-4.6 ppm from hydroxyl proton belonging to the macromer and at 3.7 ppm is assigned to -OCH_3 in MMA units. All these results are in accordance to the fact that a copolymer was really formed and that the product is not just a blend of macromer and PMMA.

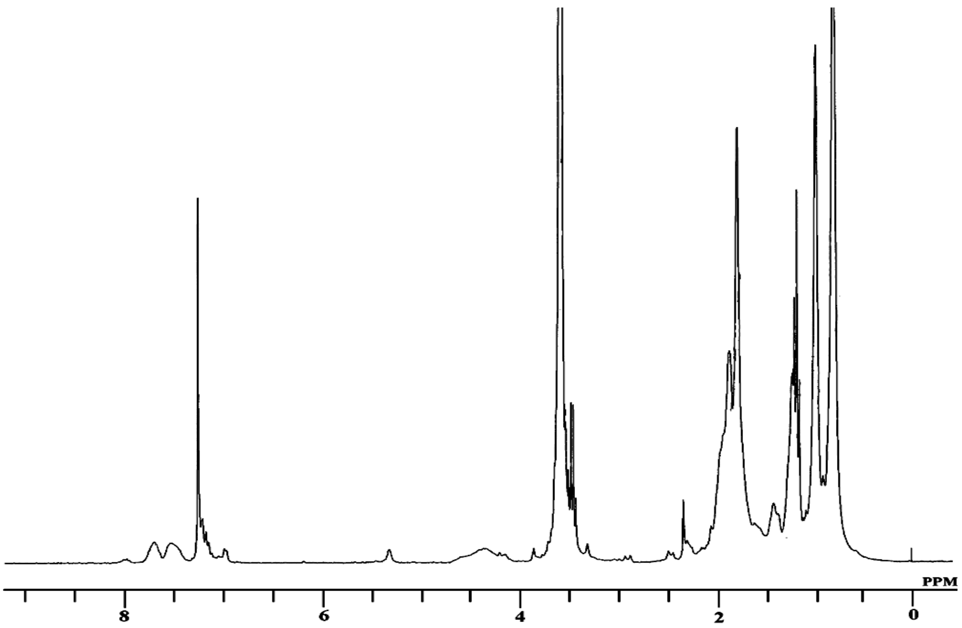


Figure 4.8 : ^{1}H-NMR spectrum of copolymer AM2 after solvent extraction

4.3 Percentage of swelling in toluene for MMC copolymers

The copolymer samples were dried beforehand at 100°C for 24 h. They were then tested for their solubility in toluene at room temperature. Most of the samples could be dissolved in toluene between one to four hours. The AL series samples dissolved in toluene between 30 min to one hour. AM3 and AS2 dissolved in toluene after 4 hours. Only AS1 was found to form gel. The percentage of swelling of the copolymer is defined by the following equation.

$$\text{Swell}\,(\%) = \frac{\text{swollen weight} - \text{initial weight}}{\text{initial weight}} \times 100 \qquad [4.1]$$

With reference to equation [4.1], the percentage of swelling could be calculated only for AS1. The swelling results for AS1 display in Table 4.3. Presumably AS1 is highly crosslinked due to its highest functionality among the copolymers.

Table 4.3 : Swelling (%) in crosslinked copolymer of AS1

	First trial	**Second trial**
Initial weight	0.2867	0.3041
Swollen weight	0.8985	0.9023
Swell (%)	213.4	196.7
Average Swell (%)	205.1	

4.4 Molecular weight distributions

The GPC results of macromer (AlkOA40), related copolymers (AM series) and PMMA are shown in Figure 4.9.

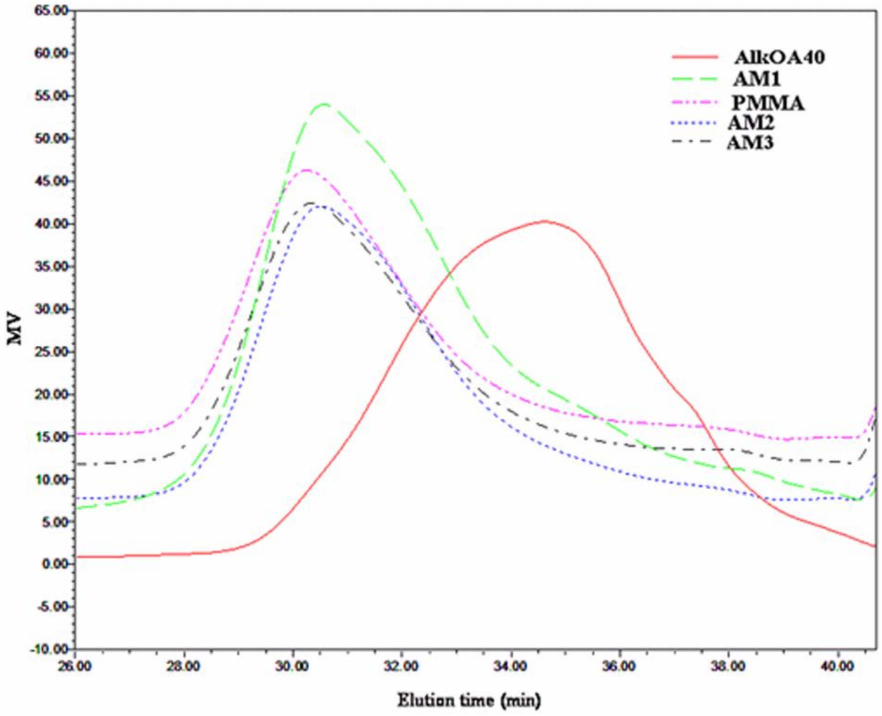


Figure 4.9 : Chromatograms of AlkOA40, AM copolymers and PMMA

The GPC trace of AlkOA40 shows a peak at low relative molecular weight, with peak at elution time of 34.7 min while the copolymers and homopolymer of PMMA all have much higher molecular weights, as indicated by the peaks at shorter elution times. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity for the copolymers and PMMA are tabulated in Table 4.4. The overlaid GPC chromatograms of macomers of AlkOA28 and AlkOA65 and related copolymers were shown in Appendix D.

Table 4.4 : M_n, M_w and polydispersity of the copolymers (MMC) and PMMA based on GPC chromatograms

Sample code	**M_n**	**M_w**	**M_w/M_n**
AL1	3252	17705	5.4
AL2	4353	16024	3.7
AL3	5111	19958	3.9
AM1	4384	13060	3.0
AM2	5183	18607	3.6
AM3	5444	20754	3.8
AS1	5467	32535	6.0
AS2	5938	18815	3.2
AS3	7533	15277	2.0
PMMA	8536	16895	2.0

4.5 Thermal analysis

4.5.1 DSC analysis

DSC technique is frequently used for polymer characterization to provide evidence on formation of true copolymer. The T_g is dependent on the polymer structure, intermolecular and intramolecular interactions as well as molecular weight. Figure 4.10 displays the overlaid DSC thermograms of the copolymers of macromer AlkOA40 with MMA (AM series) and PMMA. DSC traces of rest of the samples were shown in Appendix E.

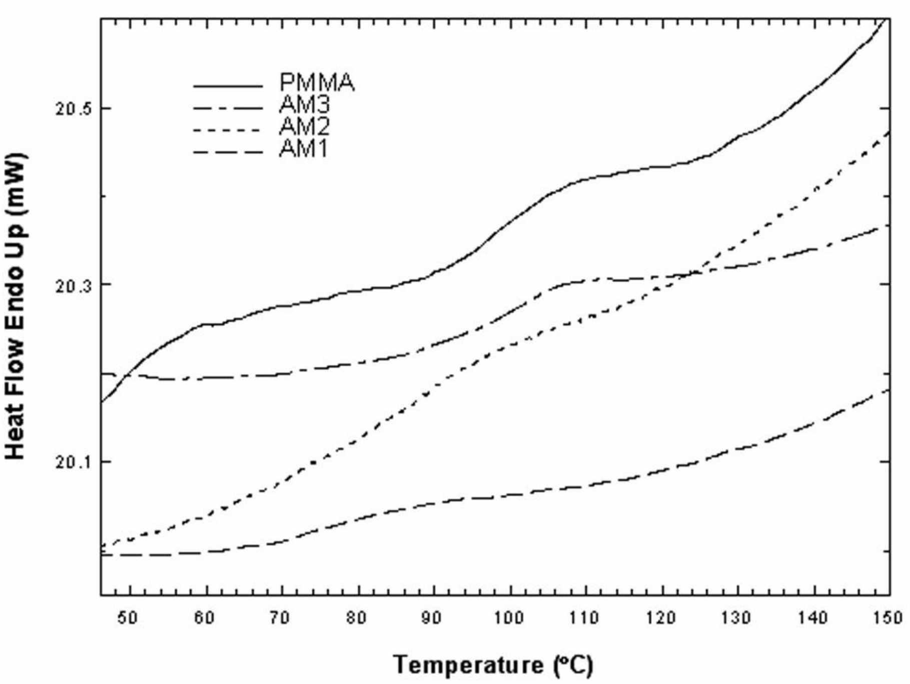


Figure 4.10 : Overlay of DSC thermograms for the copolymers of AM series and PMMA

DSC thermogram of each copolymer showed a single broad T_g, without any melting peak, indicating the amorphous nature of the copolymers. From the results shown in Table 4.5, the copolymers exhibit a single T_g in the range of 65.1- 95.6°C (338.1-368.6 K), while T_g of PMMA is at 101.6°C (374.6 K) and that of the macromers are between -39˚C to -36˚C (234-237 K). This suggests that the macromer and MMA are quite compatible. Higher T_g values are related to strong dipolar interaction between side substituents of the polymeric chain, which restricts segmental motion while the T_g of low molecular weight compounds depends on the intermolecular interaction of individual molecules exclusively, being controlled by the molar volume and dipolar connectivity, hydrogen bonds, and van der Waals interactions between molecules. This was observed in AL1 and AM1 that possess lower T_g values. The introduction of more oleate branches will introduce some flexibility in these structures. An increase in the concentration of branching agent is accompanied by a reduction in the T_g. It has been reported that alpha substituents such as methyl group, also hinders segmental motion and can affect the stiffness and flexibility of the polymer [126].

The glass transition temperature for two compatible components can be described by the Gordon-Tailor equation [4.2] [127].

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \qquad [4.2]$$

where w_1 and w_2 are the weight fractions of the two components of the copolymer and k is the Gordon-Taylor constant, which is a model specific parameter. T_{g1} and T_{g2} are glass transition temperature values of individual component 1 and 2, respectively.

An example of calculation using Gordon-Tailor equation to determine the T_g (theory) of AM series is shown below.

$$T_g = \frac{(0.35 \times 234.14 + k \times 0.65 \times 374.6}{0.35 + k \times 0.65} = 361.5$$

$$k=5.2$$

where T_{g1} and T_{g2} are 234.14 K and 374.6 K by assuming the components AlkOA40 and PMMA, respectively; and w_1 and w_2 are 0.35 and 0.65; T_g refers to the T_g (experimental) of AM2.

According to the calculated Gordon-Taylor constant (k), T_g (theory) of AM1 and AM3 were obtained as following.

For AM1 $$T_g = \frac{(0.5 \times 234.14 + 5.2 \times 0.5 \times 374.6)}{0.5 + 5.2 \times 0.5} = 351.9K$$

For AM3 $$T_g = \frac{(0.2 \times 234.14 + 5.2 \times 0.8 \times 374.6)}{0.2 + 5.2 \times 0.8} = 368.2\,\mathrm{K}$$

The calculated glass transition temperatures, T_g (calculated) using equation [4.1] together with the T_g (Exp.) that obtained from DSC measurements are tabulated in Table 4.5.

Table 4.5 : T_g (Expt.) and T_g (Cal.) of copolymers, T_g (Expt.) of PMMA

Copolymers code	**Macromer/MMA**	**Glass transition temperature, K**		**Gordon-Taylor constant (k)**
		T_g (Expt.)* ± 2 /°C	**T_g (Cal.)**	
AL1	50/50	338.1	338.2	2.8
AL2	35/65	359.5	352.3	
AL3	20/80	363.1	363.0	
AM1	50/50	350.9	351.9	5.2
AM2	35/65	361.5	361.5	
AM3	20/80	368.2	368.2	
AS1	50/50	353.2	353.2	5.6
AS2	35/65	364.6	362.3	
AS3	20/80	368.6	368.6	
PMMA	0/100	374.6	-	-

T_g (Expt.)* refers to T_g from DSC measurements

4.5.2 Thermogravimetry Analysis (TGA)

The thermal degradation behaviour of the three series of copolymers with three different macromer/MMA ratios at a heating rate of 10°C has been investigated by TGA analysis. Table 4.6 shows the decomposition temperature at various stages of weight loss. Four to six degradation stages are observed for the nine copolymer samples. The minimum temperature the copolymers start to degrade was at 131°C and up to 647°C. TGA curves of the copolymer samples were displayed in Appendix F.

Table 4.6 : Thermal behaviour of three series of copolymers (MMC)

Sample	**Stage**	**Decomposition Temperature (˚C)**		**Weight loss (%)**
		T1	**T2**	**Δ W**
AL series (copolymers AlkOA65 and MMA)				
AL1	1	141	240	7.60
	2	240	309	24.4
	3	309	440	65.0
	4	440	**573**	2.4
AL2	1	136	208	7.0
	2	208	249	7.6
	3	249	312	30.7
	4	312	386	36.9
	5	386	**548**	17.6
AL3	1	133	184	4.9
	2	184	204	3.5
	3	204	247	8.9
	4	247	277	9.3
	5	277	312	23.5
	6	312	**450**	49.5
AM series (copolymers AlkOA40 and MMA)				
AM1	1	145	241	7.7
	2	241	310	25.2
	3	310	447	64.9
	4	447	**591**	1.2
AM2	1	140	241	12.9
	2	241	312	30.2
	3	312	434	55.0
	4	434	**548**	1.6
AM3	1	131	198	8.1
	2	198	246	10.2
	3	246	314	34.4
	4	314	**501**	47
AS series (copolymers AlkOA28 and MMA)				
AS1	1	160	233	5.1
	2	233	309	22.8
	3	309	447	68.5
	4	447	**647**	2.8
AS2	1	146	236	10.3
	2	236	311	27.9
	3	311	437	58.3
	4	437	**582**	2.2
AS3	1	139	196	8.5
	2	196	243	6.4
	3	243	309	24.9
	4	309	**439**	58.1

Results in Figure 4.11 and Table 4.6 showed that the onset temperature of the degradation has increased significantly with the increase in macromer content.

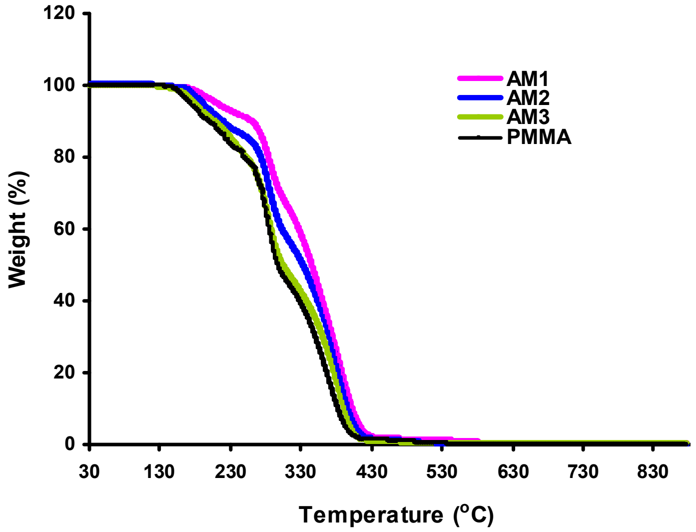


Figure 4.11 : The overlay TG thermograms AM series copolymers and PMMA

AM1 starts to degrade at 145°C, AM2 at 140°C, and AM3 at 131°C. The increase in the macromer content could lead to higher amount of intermolecular interactions as the macromer is polyfunctional. All copolymer samples showed the similar trend in thermodegradation.

There are many published references which provide extensive discussions of thermal stability. The following general trends are observed: [119]

1. The strength of the covalent bonds in the polymer, and especially of the weakest bond of the polymer chain, is the most important factor in determining the thermal stability.

2. Secondary chemical interactions, such as van der Waals interactions, hydrogen bonding, and the resonance stabilization of aromatic rings, increase the average effective bond strength and/or the intermolecular attraction, and thus stabilize the polymer against degradation.

3. Chemical crosslinks increase the number of bonds that must be broken and consequently crosslinking increases the thermal stability.

4. Structural defects and/or irregularities are weak points. They may function as initiation sites for degradation and thus usually decrease the thermal stability.

5. Ordering of polymer chains, and especially crystallinity, usually increases the thermal stability.

6. Molecular symmetry, and the resulting regularity of the chemical structure, also usually increases the thermal stability.

7. Aromatic functionalities incorporated into the chain backbone increase the thermal stability.

In addition, the decomposition conditions, which include temperature, the atmosphere used, heating rate, the sample size, impurities, and the aggregate state are important factors to note.

4.6 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was employed to study the properties of the copolymer samples over the temperature range of -60 to 110°C unless stated otherwise. One of the most important applications of DMA is to determine the glass transition temperature of polymer.

4.6.1 Peak analysis of DMA

At low temperatures, the polymer chains in an amorphous thermoplastic are immobile and they cannot resonate with the oscillatory loads and thus remain stiff. The polymer is said to be in the glassy state (Figure 4.12). The macromolecular segments are unable to change shape through rotation around C-C bonds in this rigid state. At higher temperatures, in the rubbery state the molecular segments become readily mobile and can easily resonate with the load. A change from the glassy state to the rubbery state is called the glass transition.

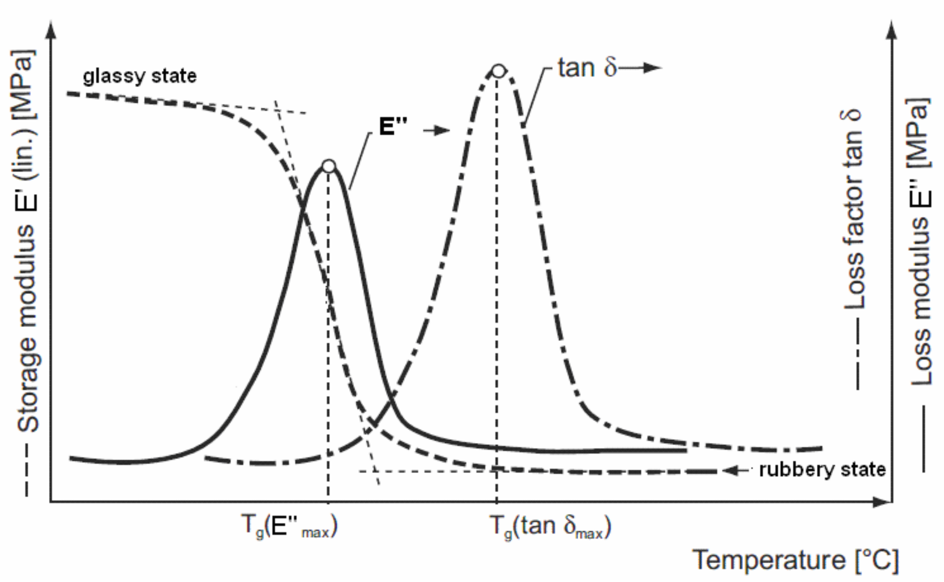


Figure 4.12 : Glass transition temperature as the maximum tan δ_{max} and maximum E''_{max} (Adapted from Dynamic Mechanical Analysis: A Practical Introduction [103])

Above the T_g, polymer has rubbery properties and the storage modulus of the material will decrease dramatically with increasing viscosity whereas the loss modulus and tan δ reach a maximum when the polymer sample is heated up through the T_g region (Figure 4.12).

DMA is a more sensitive technique to determine the T_g compared to DSC, as transitions are detected through temperature dependence of the loss tangent (tan δ_{max}) and the loss modulus (E''_{max}). Such graphs are easier to evaluate than step graphs. Figure 4.12 displays how the various methods are compared and how the different T_g are evaluated. As tan δ is the ratio of loss modulus (E'') to storage modulus, thus larger value of tan δ indicates greater energy loss. In the other words, a lower value shows that a polymer is more elastic. Three relaxations (γ, β and α-transitions) may be seen from DMA curves. The γ-relaxation commonly appears in the temperature range between -150˚C to -120˚C with higher intensity than T_β. The β-relaxation temperature is typically located between -50˚C and room temperature while α-relaxation is above room temperature. It is noted that in this experiment only the loss modulus peaks are used. This is because the ASTM D 4065-2001 recommends that the T_g be based on the temperature of maximum loss modulus.

4.6.2 Glass transition temperature and mechanical properties of the copolymers (MMC) using DMA

The characteristics of polymer strongly depend on their molecular structures. The viscoelasticity of a polymer is a result of a material simultaneously possessing both solid-like and liquid-like characteristics. Every polymer exhibits this nature to some extent. As noted earlier, the modulus, or stiffness of the polymer is a function of the intermolecular forces such as hydrogen bonds and is also influenced by the presence of stiffening groups such as phenyl groups in the polymer backbone.

The T_g of the copolymers with different macromer/MMA ratios obtained from DMA measurement, (temperature of the maximum loss modulus, E''_{max}), are summarized in Table 4.7. Variations of loss modulus for copolymer samples as a function of temperature are given in Appendix G. From Table 4.7, increase in the macromer/MMA ratio results in decrease in T_g. The methyl group in the MMA moiety may have hindered segmental motion and affect the flexibility of the polymer. Thus higher MMA content in the copolymer leads to less flexibility and higher loss modulus. On the other hand, increment of oleic acid content, which presumably functions as a plasticizer, introduces more flexible side chain in the macromer. Consequently this will decrease the loss modulus of the copolymer samples. The synergy of all these factors is reflected in the overall properties of copolymers as obtained in Table 4.7.

Table 4.7 : T_g at the maximum loss modulus for the three series of MMC copolymers

Copolymer	**Macromer/MMA**	**E’’ ± 2 /°C**	**E’’/MPa**
AL series			
AL1	50/50	-7.20 (T_β)	205.7
		51.29	122.5
AL2	35/65	10.33 (T_β)	78.95
		84.83	365.3
AL3	20/80	16.93 (T_β)	40.90
		88.61	324.0
AM series			
AM1	50/50	85.14	281.4
AM2	35/65	89.26	282.3
AM3	20/80	91.28	233.8
AS series			
AS1	50/50	85.88	114.4
AS2	35/65	92.55	194.6
AS3	20/80	95.78	326.1

The β-relaxation is ascribed to the existence of segmental mobility of the side groups or pendant components in the amorphous regions. Though, there is no consensus in the literature about its mechanism. It has been reported that β-relaxation could possibly due to the motions of long chain branches [128]. Referring to Table 4.7, T_β values for the AL series show relaxations are in the temperature range of -7.20°C to 16.93°C. Only AL series shows these relaxations (T_β) as higher proportion of oleic acid is present in the AlkOA65 composition. Therefore it has more flexible side chains in this AL series compared to AM and AS series.

A similar trend is observed in the AM and AS series. With increasing macromer/MMA ratio, the T_g is reduced. AlkOA28 has higher glycerol content leading to higher functionality (a factor to produce crosslinking or branching) and also higher PA content compared to AlkOA40 and AlkOA65. Generally, it can be seen that the copolymers of the AS series have higher T_g than AM and AL series. The DMA results are in good agreement with the T_g as determined by DSC (Table 4.5).

It is also important to note that the T_g values obtained from DMA analysis are different from those from the DSC. Such a difference is not unexpected because of the differences in the nature of the two methods. DSC measures the change in the heat capacity from frozen to unfrozen chains whereas DMA measures the change in mechanical response of these chains.

4.7 Modification of synthesized copolymers (MMC) with BA monomer: effect of macromer content on conversion (%)

The properties of the macromer-acrylate copolymers can be altered by changing or adjusting the acrylate or macromer or their ratio. For this purpose copolymers with different macromer/MMA ratios are modified by addition of small amount of BA as a comonomer (10 wt.% and 5 wt.% of BA were used to replace part of MMA). Two plausible reaction mechanisms for preparation of copolymers (MMBC) with macromer, MMA and BA monomers are depicted in Figure 4.13.

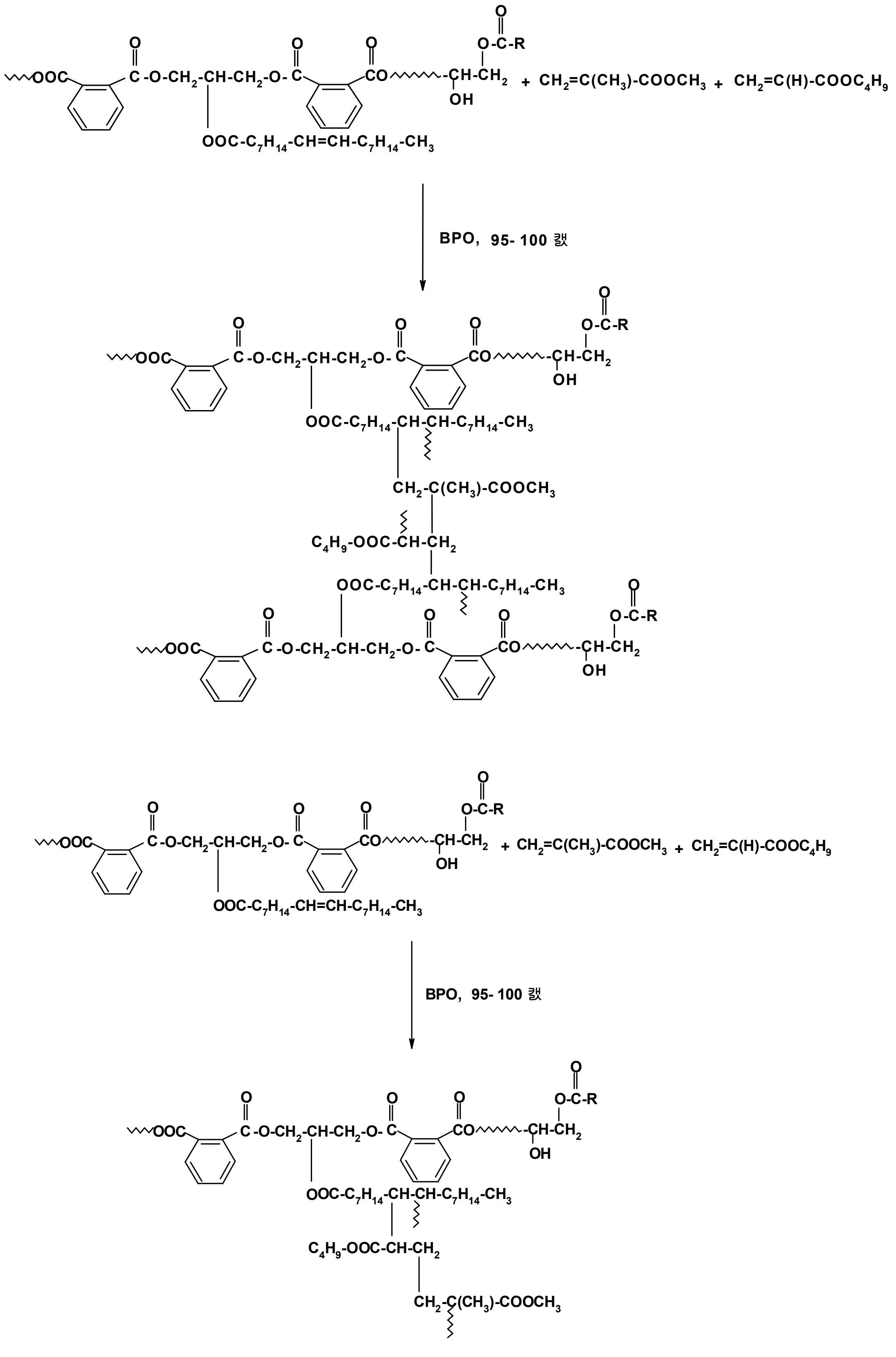


Figure 4.13 : Two plausible reaction mechanisms for preparation MMBC copolymers

The effect of macromer/acrylate ratio and role of the BA on conversion are given in Figures 4.14 to 4.17. Regardless of the type of macromer used, conversion and polymerization rate increase when the amount of macromer decreases (the same trend as that observed for the copolymerization rate of macromers with MMA alone). In addition, conversion (%) is greater compared to conversion when only MMA was used (Section 4.1).

Figure 4.18 presents the comparison of the conversion (%) for all the samples. Copolymerization rate of the AlkOA28 with MMA and 10 wt.% BA, AS3B(10%), exhibits the highest conversion (%), while copolymerization rate for AlkOA65 is the lowest.

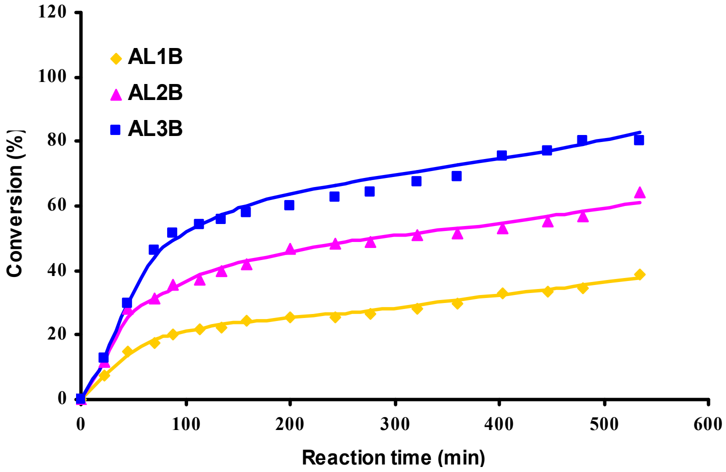


Figure 4.14 : Conversion of modified copolymers with different ratios of AlkOA65/acrylate with 10 wt.% BA

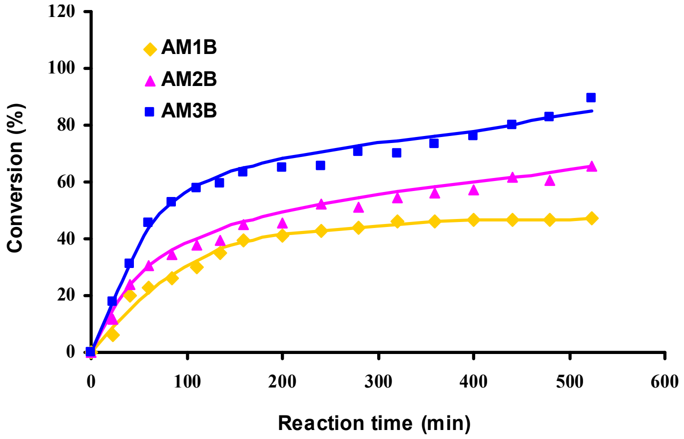


Figure 4.15 : Conversion of modified copolymers with different ratios of AlkOA40/acrylate with 10 wt.% BA

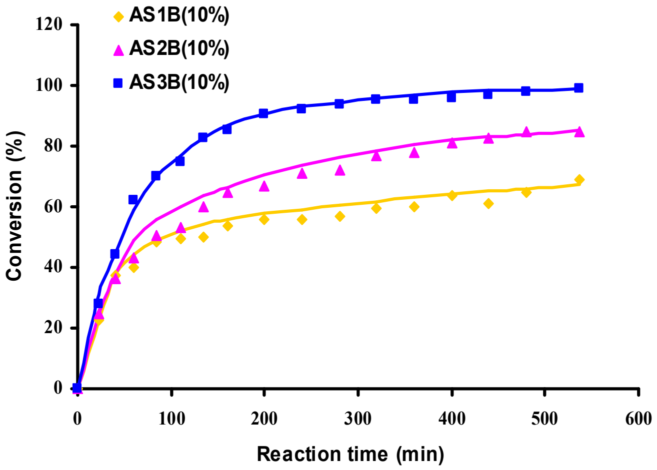


Figure 4.16 : Conversion of modified copolymers with different ratios of AlkOA28/acrylate with 10 wt.% BA

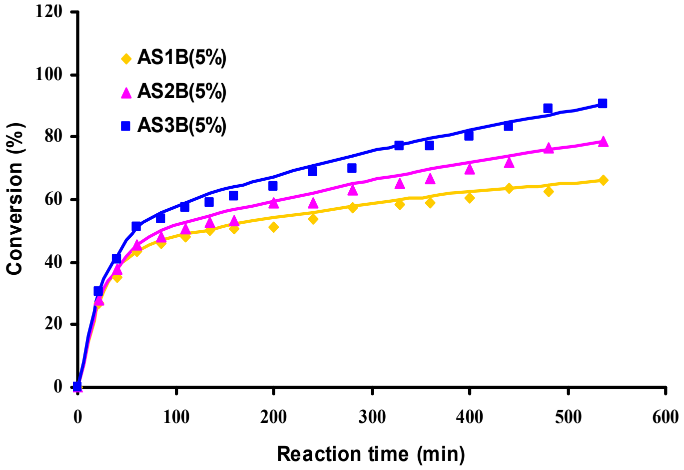


Figure 4.17 : Conversion of modified copolymers with different ratios of AlkOA28/acrylate with 5 wt.% BA

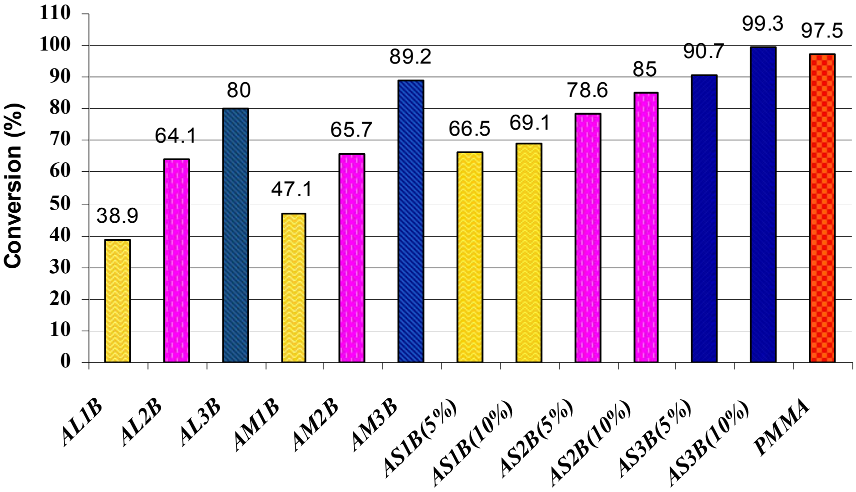
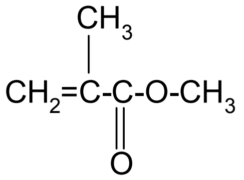


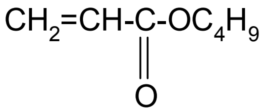
Figure 4.18 : Conversion (%) MMBC copolymers

The high conversion level of AS3B is a consequence of reducing of steric hindrance when some MMA was replaced with BA in the composition. When the structure of MMA (Figure 4.19) is compared to that of BA (Figure 4.20), it can be seen that the BA has less steric hindrance across the -C=C-.



$CH_2=C(CH_3)-C(=O)-O-CH_3$

Figure 4.19 : Chemical structure of MMA



$CH_2=CH-C(=O)-OC_4H_9$

Figure 4.20 : Chemical structure of BA

If only the energy required to interact with a π-bond versus a σ-bond is considered, addition to a double bond will be energetically favoured over abstraction of an allylic hydrogen. On the other hand, steric features of the attacking monomer or chain and the structure of groups that surround the reactive polymer site, often affects the choice to make abstraction the more preferred site of attack [129]. Gonzalez et al. explained this phenomenon in the following ways: (i) the propagation rate constant of MMA is lower as compared to that of BA, (ii) the MMA radicals are tertiary radicals and hence are much less reactive for hydrogen abstraction than the secondary BA radicals since the alkyl groups are electron donating, (iii) MMA units in the polymer backbone do not have labile hydrogens to be abstracted [130]. This suggests that the routes of attack for BA to the macromer through direct addition to a double bond on a macromer. Also hydrogen abstraction from macromer is more likely to occur in BA to macromer than that of MMA, thus supporting the results and trends shown in Figure 4.18.

4.8 FTIR Spectroscopy of MMBC copolymers

Figure 4.21 shows the a overlaid FTIR spectra of the modified ASB(10%) series; in this case ASB from AlkOA28 with MMA and 10 wt.% BA monomer. Typically there are six major bands. The strong band, at 1728 cm^{-1} is characteristic of carbonyl bond from esteric linkages. The double weak bands at 1579 and 1599 cm^{-1} are due to the -C=C- of the aromatic rings in PA, while strong bands around 1272-1143 cm^{-1} can be attributed to the

C-O-C stretching of ester groups. In addition, a broad band around 3473 cm^{-1} arising from hydroxyl groups and triplet medium bands at 2993 cm^{-1}, 2931 cm^{-1} and 2848 cm^{-1} which are characteristic of C-H stretching aromatic and aliphatic bands respectively are also observed. The presence of bands at 741 cm^{-1} and 987 cm^{-1} correspond to the C-H out-of-plane vibrations of $C-CH_3$ and $O-CH_3$. There were no significant changes in the FTIR spectra of the modified copolymers before and after using BA because of similar functional groups present in copolymers. The FTIR spectra of the rest of the modified copolymers are shown in Appendix H.

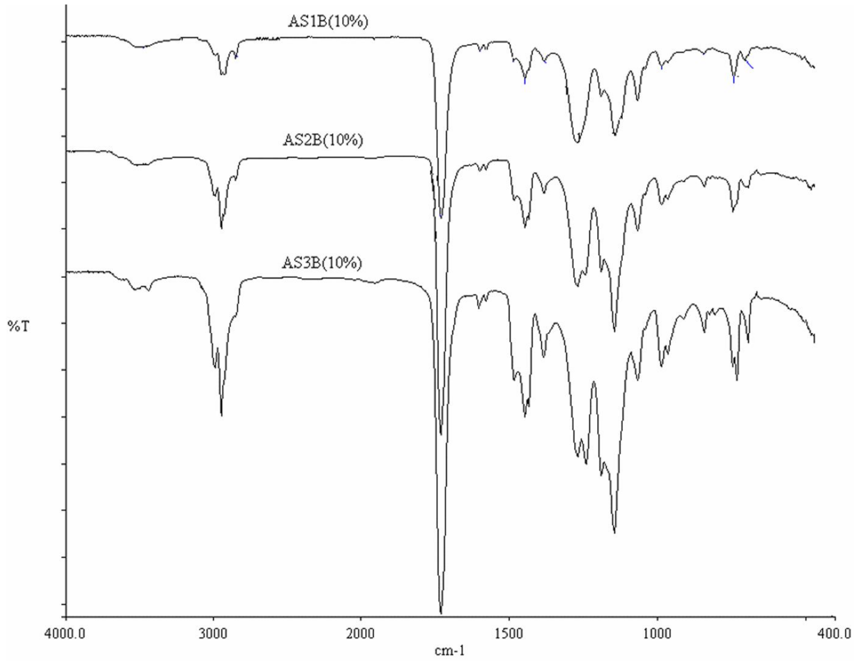


Figure 4.21: FTIR spectra of AS1B(10%), AS2B(10%) and AS3B(10%) copolymers

4.9 ^{1}H-NMR Spectroscopy of MMBC copolymers

^{1}H-NMR was used to confirm structure of MMBC copolymers. Figure 4.22 shows the ^{1}H-NMR spectrum of AM2B together with its molecular structure. Although the ^{1}H-NMR spectrum of AM2B has very similar appearance to that of AM2 due to the existence of similar functional groups and very low percentage of BA in the copolymer structure but the BA unit in the copolymer can be identified by the appearance of peaks at 3.98 and 0.94 ppm arising from –OCH_2 and -CH_3 respectively. These peaks are identified in all the modified copolymers. The chemical shifts of the major peaks are tabulated in Table 4.8 and ^{1}HNMR spectra of samples were demonstrated in Appendix I.

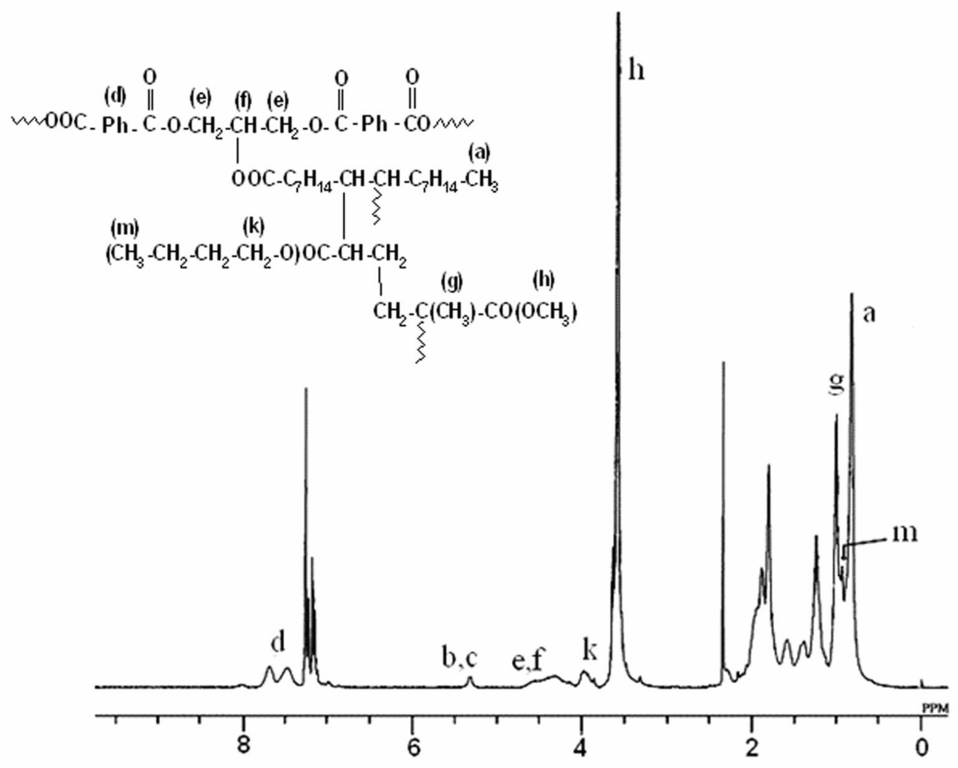


Figure 4.22: ^{1}H-NMR spectrum of AM2B and one of the plausible its molecular structure

Table 4.8 : Characteristic peaks and chemical shifts of ^{1}H-NMR spectrum of AM2B

Chemical shift (δ)/ ppm	**Structure**
0.84 (protons of methyl groups)	**CH_3**-$(CH_2)_7$-CH=CH- (a)
1.02 (protons of methyl groups)	CH_2=C(**CH_3**)-$COOCH_3$ (g)
0.94 (protons of methyl groups)	**CH_3**-CH_2-CH_2-CH_2-OC(O)- (m)
4.3 (protons of glycerol moiety)	-O-**CH_2**-**CH**(O)-**CH_2**-O- (e,f)
3.7 (protons of methoxy groups)	-(O**CH_3**)C=O (h)
3.98 (protons of methyleneoxy groups)	CH_3-CH_2-CH_2-**CH_2**-OC(O)- (k)
5.3	–CH=CH- (remaining) (b,c)
7.5-7.7	-Ph- (d)

4.10 DSC analysis of MMBC copolymers

The T_g is related to chain stiffness and the geometry of polymer chain. Flexible polymers with methylene and oxygen atoms in the chain have relatively low T_g [126]. Also, the T_g decreases as the size of the pendant groups increases. Thus, the T_g values for polymers of ethyl, propyl and butyl acrylates are -24, -48, and -55°C, respectively [126].

In this study, DSC analyses of the twelve copolymer samples (MMBC) were carried out to study the effects of incorporating small amounts of BA on T_g of the copolymers. The data are tabulated in the Table 4.9 which disclose no melting point and that the each sample shows T_g with smaller value than that of copolymer synthesized without BA (MMC). DSC thermograms for the modified copolymers were shown in Appendix J.

Table 4.9 : Values of T_g resulting from DSC and molecular weight characteristics of MMBC copolymers

Sample code	**Macromer/ (MMA+BA)**	**$T_g \pm 2$/°C**	**M_n**	**M_w**	**M_w/M_n**
AL1B	50/50	65.66	4493	16987	3.8
AL2B	35/65	66.68	5084	20879	4.1
AL3B	20/80	67.98	5687	22118	3.9
AM1B	50/50	66.95	5399	19695	3.6
AM2B	35/65	50.38, 67.04	5915	19452	3.3
AM3B	20/80	49.62, 68.19	6286	21483	3.4
AS1B(10%)	50/50	48.48, 67.10	6824	46717	6.8
AS2B(10%)	35/65	49.85, 67.88	11571	39147	3.4
AS3B(10%)	20/80	49.15, 69.01	14088	27960	2.0
AS1B(5%)	50/50	48.87, 68.28	6820	33878	5.0
AS2B(5%)	35/65	48.99, 68.75	10669	40152	3.8
AS3B(5%)	20/80	49.04, 80.25	12223	38416	3.1

4.11 Percentage of swelling in toluene for MMBC copolymers

The copolymer samples (MMBC) containing 10% BA were dried at 100˚C for 24 h. The dried samples were then immersed in toluene at room temperature. Among of the copolymers only AS1B(10%) formed swollen gel, and the rest of the samples dissolved in toluene before four hrs. The percentage of swelling for the AS1B was calculated using the equation [4.1] in Section 4.3 at sixth hour. The results for AS1B(10%) are displayed in Table 4.10.

Table 4.10 : Swelling (%) in crosslinked copolymer of AS1B(10%)

	First trial	**Second trial**
Initial weight	0.3199	0.3055
Swollen weight	1.0023	0.9890
Swell (%)	213.32	223.73
Average Swell (%)	218.5	

4.12 GPC results of MMBC copolymers

Molecular weight and polydispersity of modified copolymers using BA monomer (MMBC) were measured by GPC. The results, tabulated in Table 4.9, reveal that the molecular weight of MMBC samples is higher than those of the MMC samples. Overlays of chromatograms of MMBC samples were displayed in Appendix K. Molecular weight of the modified copolymers increases with increasing the acrylate content, the higher the acrylate content, the higher molecular weight (the same trend as the increasing of molecular weight (M_n) in MMC samples).

4.13 Thermogravimetry Analysis (TGA) of MMBC copolymers

TGA analyses were performed to study effect of BA monomer on thermal stability behaviour of four series of the modified copolymers. The normalized weight loss (TG) and differential fractional weight loss profiles (DTG) for MMBC samples at a heating rate of 10°C min^{-1} are shown in Appendix L. Decomposition temperatures and percentage of weight losses in various steps of decomposition process are presented in Table 4.11. Three to five decomposition steps are observed for the twelve copolymers containing BA (MMBC).

In discussing the thermal decomposition of polymers, it should be emphasized that decomposition is a complex multi-stage process. It consists of a series of sequential and simultaneous reactions of depolymerisation, initiation, scission of side-chain and the main chain of macromolecules, recombination, chain termination, etc. Therefore, each specific process has its own distinct mechanism depending on a number of factors. Weight loss by the thermal degradation of a polymer perpetually requires the breakage of chemical bonds. Once chemical bonds start to break, reactive chain ends and other free radicals are created, and decomposition can proceed either by depolymerization or by random chain scission [131,132]. In any case, weight loss can only start after the first bond breakage event. The first bond to break will usually be the weakest bond in the polymer.

In addition to explanation referred in Section (4.5.2), the backbone of organic polymers mostly consist of carbon and hydrogen atoms. The strongest intramolecular forces (covalent bonds) join these atoms together, which definitely influence on the thermal behaviour of the polymers.

The secondary forces (as intermolecular forces) are classified as van der Waals forces, dipole interaction, hydrogen bonding and ionic bonding with dissociation energies equal to 0.5-2 kcal mol^{-1}, 1.5-3 kcal mol^{-1}, 3-7 kcal mol^{-1} and 10-20 kcal mol^{-1} respectively [133].

Table 4.11 : Decomposition temperatures and weight loss (%) in the MMBC copolymers

Sample	**Stage**	**Decomposition Temperature (°C)**		**Weight loss (%)**
		T1	**T2**	**Δ W**
ALB series (copolymers AlkOA65, MMA and BA)				
AL1B	1	141	234	3.5
	2	234	319	21.8
	3	319	**451**	73.5
AL2B	1	141	231	3.1
	2	231	319	24.7
	3	319	**445**	71.1
AL3B	1	141	233	5.4
	2	233	321	29.0
	3	321	**444**	65.0
AMB series (copolymers AlkOA40, MMA and BA)				
AM1B	1	156	241	4.4
	2	241	311	15.8
	3	311	458	78.5
	4	458	**625**	0.8
AM2B	1	148	235	5.1
	2	235	313	20.5
	3	313	451	72.4
	4	451	**606**	0.6
AM3B	1	148	200	3.0
	2	200	249	4.1
	3	249	313	23.7
	4	313	447	68.6
	5	447	**604**	0.4
ASB series (copolymers AlkOA28, MMA and BA 10 wt.%)				
AS1B(10%)	1	166	251	2.4
	2	251	311	12.3
	3	311	457	82.4
	4	457	**651**	1.2
AS2B(10%)	1	151	242	5.2
	2	242	313	19.3
	3	313	452	73.4
	4	452	**623**	0.8
AS3B(10%)	1	143	236	7.3
	2	236	315	25.2
	3	315	444	65.6
	4	444	**601**	0.2
ASB series (copolymers AlkOA28, MMA and BA 5 wt.%)				
AS1B(5%)	1	160	247	3.3
	2	247	312	17.2
	3	312	450	77.4
	4	450	**640**	1
AS2B(5%)	1	162	233	2.8
	2	233	314	23.8

‘Table 4.11, continued’

	3	314	448	70
	4	448	**599**	2
AS3B(5%)	1	142	210	3.5
	2	210	241	2.9
	3	241	318	29.8
	4	318	**440**	62.8

Referring to Table 4.11 and comparing to the Table 4.6, the results reveal that thermal stability of modified copolymers after using BA monomer (MMBC) were improved compared with MMC copolymers. In the case of AM1B sample, degradation process starts from 156˚C until 625˚C and main weight loss occurs between 311˚C to 458˚C (78.5%), while for AM1 (Table 4.6) degradation process occurs between 145˚C to 591˚C and main weight loss takes place between 310˚C to 447˚C (64.9%). This suggests that presence of BA in the copolymer composition for all samples gives higher thermal stability.

This may be due to the fact that modified copolymers (MMBC) contain additional extended chain than MMC copolymers, using the data in Table 4.12, calculating bond dissociation energy of MMBC samples (8150 kJ mol^{-1}) relative to MMC copolymers (5800 kJ mol^{-1}). In addition, one the reasons for higher thermal stability of MMBC samples is higher molecular weight than that of MMC samples.

Table 4.12 : Some bond dissociation energy [134]

Bond	**Bond dissociation energy (kJ mol^{-1})**
C-H	414
C-C	347
C-O	351
C=O	745

Figure 4.23 compares thermal stability of each macromer and its copolymer with macromer/acrylate ratio of 35/65 before modification and after modification with 10 wt% of BA. It can be seen that thermal stabilities of each macromer and its modified copolymer with BA are almost similar. As noted earlier, thermal stability of modified copolymers (MMBC) are higher than MMC copolymer.

From Figure 4.24, it is very clear that copolymer containing 10 wt.% BA show higher thermal stability compared to copolymer containing 5 wt.% BA.

This observation may be explained due to the differences in the molecular weights as molecular weight has been reported to affect the thermal degradation behaviour of polymers and improve thermal stability [135]. In study on thermal degradation PMMA, poly butyl acrylate, and their copolymers, Vinod Kumar and Giridhar observed that degradation temperature increased with mole percentage of BA in the copolymer, indicating the increase in activation energy and consequently in thermal stability of the copolymer [136].

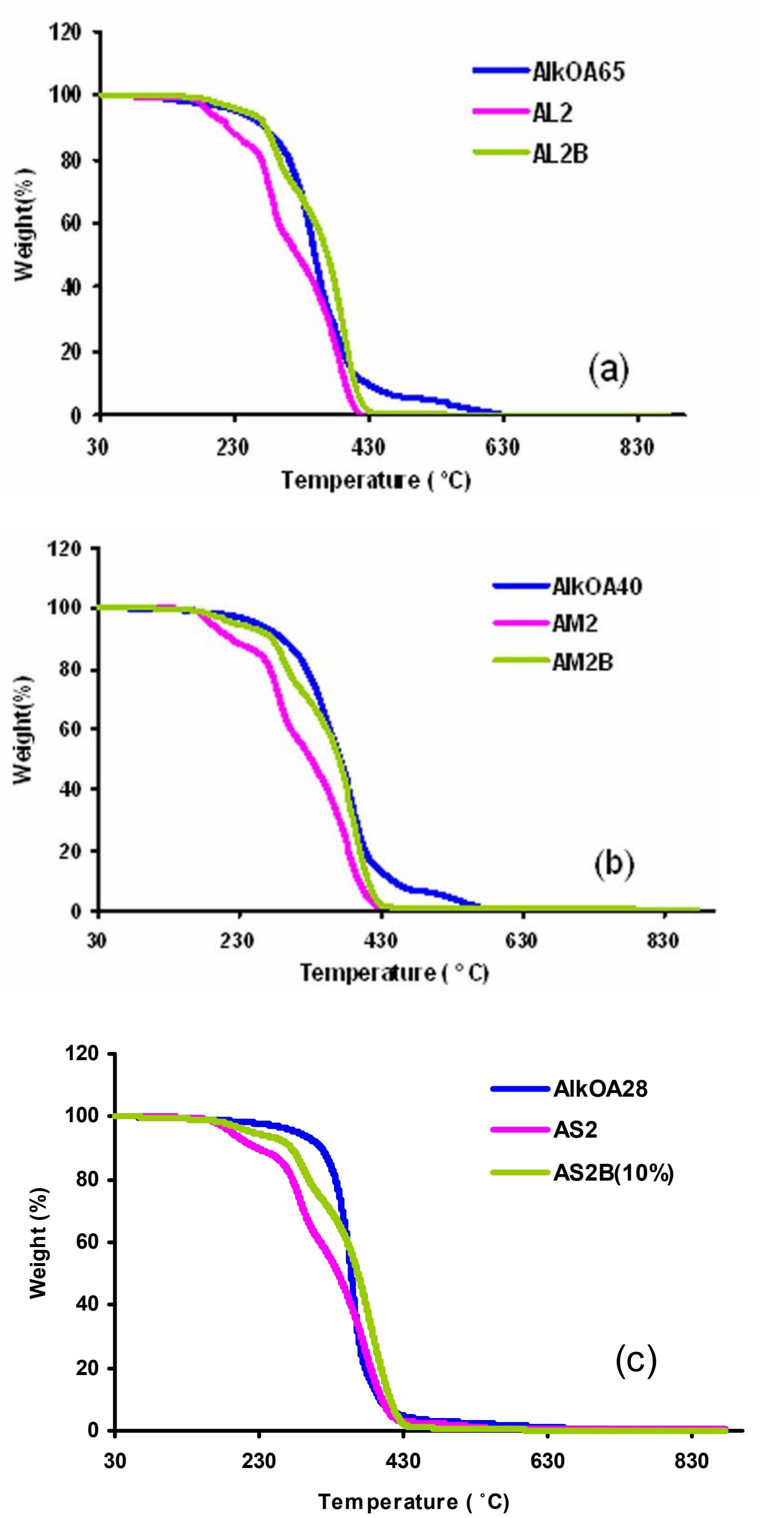


Figure 4.23 : Thermal stability of AlkOA65, AL2 and AL2B (a), AlkOA40, AM2 and AM2B (b), AlkOA28, AS2 and AS2B(10%) (c).

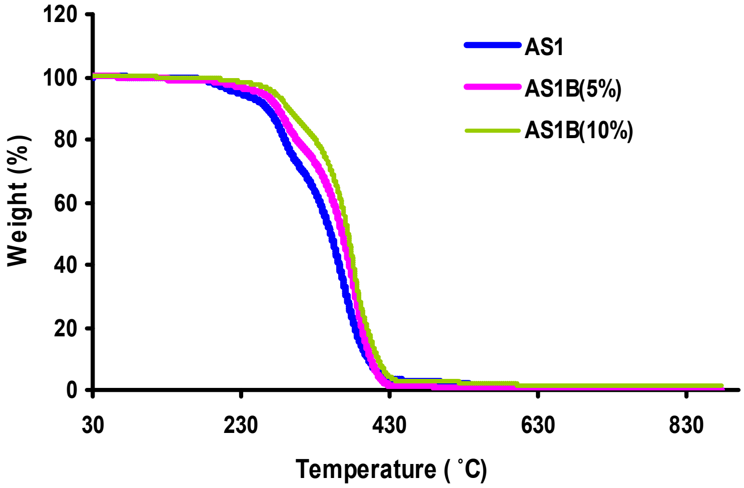


Figure 4.24 : Effect of different percentages of BA on thermal stability of modified copolymers of AS1

4.14 Glass transition temperature and mechanical properties of MMBC copolymers using DMA

In this study, T_gs were determined through the temperature dependence of the maximum at the loss modulus (E'') peaks. Appendix M displays variations of dynamic mechanical characteristics as a function of temperature, while the values of these T_gs are shown in Table 4.13. Generally, MMBC samples show lower loss modulus at maximum peak and consequently higher elasticity compared to the MMC samples. This is due to the existence of the long side group of BA in the structure that allows flexibility of the copolymer.

In all the four series of modified copolymers, most of the samples exhibit secondary relaxation (T_β). The existence of T_β is generally attributed to the onset of a significant amount of some kinds of motions of the polymer chains and/or the side groups attached to them, on a much smaller and more localized scale than the large-scale cooperative motions of chain segments associated with T_α [119].

Table 4.13 : DMA data for four series of MMBC copolymers using BA

Designation code	**Macromer/acrylate**	**E" ± 2/°C**	**E"/MPa**
ALB Series			
AL1B	50/50	-40.61 (T_β)	35.36
		1.33 (T_β)	46.40
		48.30	46.29
AL2B	35/65	-40.59 (T_β)	39.86
		72.74	350.7
AL3B	20/80	-13.21 (T_β)	38.36
		77.32	269.8
AMB series			
AM1B	50/50	-10.05 (T_β)	41.66
		39.26	69.16
		72.99	227.2
AM2B	35/65	18.43 (T_β)	46.85
		74.69	267.0
AM3B	20/80	14.10 (T_β)	38.66
		78.65	469.0
ASB series using 10 wt.% BA			
AS1B(10%)	50/50	-10.07 (T_β)	39.41
		36.10	62.80
		78.38	253.0
AS2B(10%)	35/65	5.18 (T_β)	41.46
		79.79	232.8
AS3B(10%)	20/80	-0.60 (T_β)	46.08
		81.04	261.3
ASB series using 5 wt.% BA			
AS1B(5%)	50/50	0.9 (T_β)	29.99
		53.56	38.76
		85.68	208.0
AS2B(5%)	35/65	2.53 (T_β)	22.93
		53.84	42.22
		88.03	122.8

‘Table 4.13, Continued’

AS3B(5%)	20/80	2.79 (T_β)	44.10
		93.66	360.0

The ALB series exhibits the lowest T_β due to existence of longer oil length i.e. AlkOA65. Tasic et al. stated that the increment of alkyl chains is one of the reasons which reduces the polar interactions and decreases T_g [137].

4.15 Summary

Synthesis and characterizations of copolymers of MMA and a palm oil-based macromer have been carried out by free radical polymerization in toluene solution. The structure of copolymers synthesized (MMC) was confirmed by FTIR and ^{1}H-NMR spectra.

Increasing the amount of macromer has led to a decrease in the polymerization rate. On the other hand, increasing the amount of MMA leads to increasing molecular weight, lower thermal stability, higher T_g values and decreasing elasticity.

The properties of the MMC copolymers were found to change when BA was used. The presence of BA has led to increment in the polymerization rate, increase molecular weight, higher thermal stability, lower T_g values and increased elasticity compared to similar properties of the MMC samples.