Thermal and Mechanical Analysis of Urethane Acrylate Graft Copolymer
Part A: Urethane Macromonomer Base on TDI and EG

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Abstract

Urethane macromonomers (UMs) having different urethane chain lengths (X) were synthesized by the reaction of an isocyanate-terminated prepolymer with 2-hydroxy ethyl methacrylate (HEMA) and isopropanol. The existence and the structural identification of the UMs were verified by FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy. Various percentages of the respective UMs (0-40 wt % acrylate monomers) were then incorporated into methyl methacrylate (MMA) and n-butyl methacrylate (n-BMA) backbones via solution free-radical copolymerization. The resulting methyl methacrylate-g-urethane and n-butyl methacrylate-g-urethane copolymers were characterized by GPC, ^{1}H NMR, ^{13}C NMR, FTIR, TGA and DMA. Phase separation between the urethane segment and the acrylate segment in the graft copolymerization products was investigated by DMA and TEM. DMA results showed that in most graft copolymer products the two respective component parts of PMMA-g-urethane or n-PBMA-g-urethane were compatible as only one T_g was observed. Two glass transitions, at temperatures of 22 and 76 °C, corresponding to the n-PBMA and urethane moieties, were observed when the chain length of the UMs was increased from X=4 to X=32. Microphase separation was also evident in TEM measurement.

Keywords: acrylic-urethane copolymer, acrylic-urethane graft copolymer, urethane macromonomer

1. Introduction

Polymethacrylates such as n-butyl methacrylate (n-PBMA) and methyl methacrylate (PMMA), which are prepared by free-radical polymerization, exhibit high transparency, weather resistance, and low toxicity (Wilks, 1988; Elvers et al., 1992). However, their poor cohesive strength, low thermal stability and low abrasion resistance limit their applications, especially when compared to two-phase composites. The properties of the methacrylate can be improved by combining them with other polymers such as polyurethanes. Polyurethanes (PUs) possess many unique properties, such as a wide range of flexibility combined with toughness, high abrasion resistance, good chemical resistance, high acid etch resistance, excellent weather ability, and very low temperature cure (Yao et al., 2002). PUs do however have some disadvantages. They are considered to be expensive polymers, especially when considered for use in solvent based adhesives.

The objective of this study was to use PUs as grafts in polymethacrylates and to study the influence of an increase in the chain length and the amount of UMs on the enhancement of physical properties of the graft copolymer.

Literature reports that methacrylate monomers have been incorporated into di- or poly methacrylate functional polyurethanes using aqueous free-radical initiators. Both anionic and cationic polyurethanes containing unsaturated polyester polyols in their backbones have been used and methacrylate monomers have been grafted onto the main chains (Durrieu et al., 2005). Block copolymers of polyurethanes have been made by crosslinking polyurethane dispersions using difunctional amines as chain extenders. For instance, vinyl-terminated aqueous polyurethane dispersions were prepared from an aliphatic diisocyanate, a polyol and a hydroxyl acrylate, and then suitable vinyl monomers and an initiator were added (Kim & Lee, 1996; Nair et al., 1999).

Graft copolymers are an important class of polymeric materials. They have a wide range of applications, derived from the ability to tailor their properties through appropriate selection of the combination of respective monomers that form the backbone and the side chains (Adrian et al., 2003).

The macromonomer technique is a simple method by which to prepare graft copolymers as it is a one-step process. Macromonomers are usually linear polymeric species having one or more reactive end groups that can participate in polymerization reactions (Milkovich & Chiang, 1975). Such end groups include acrylic, vinylic, allylic, propenylic, or isopropenylic functionality (Henschke et al., 1997; Shiho & Desimone, 2000), so the macromonomers can either homopolymerize to give regular comb-shaped polymers or copolymerize with conventional monomers to give graft copolymers (Se et al., 2005).

Macromonomers have been widely and successfully used as building blocks for the synthesis of various branched polymer architectures (also on a commercial scale). Macromonomers can be readily copolymerized with conventional monomers to afford graft copolymers with well defined structures. The structure of the polymer chain of the macromonomer affects the properties of the graft copolymer while the polymerizable end group controls the reactivity during polymerization. Many functional groups with chemical reactivity have been studied for various types of polymerizations, including conventional free radical (Roos et al., 1999), group transfer (Ishizu & Kuwahara, 1994), anionic (Sanda et al., 2001), cationic (Yamada et al., 1999), controlled free radical (Nomura et al., 2000), and ring-opening metathesis (Nagasaki et al., 1994) polymerizations.

To our knowledge this is the first report concerning monofunctional urethane macromonomers. Lee et al. (2005) and Jung et al. (2005) have reported the synthesis of linear type vinylurethane macromonomers with difunctionality by the reaction of isocyanate-terminated prepolymers with methacrylamide. The vinylurethane macromonomers were then used in dispersion polymerization with styrene and methylmethacrylate to yield crosslinked microgels. In this present study, UMs were synthesized to be predominantly monofunctional. The UMs were then incorporated into methacrylate by solution free-radical polymerization. Although difunctional urethane macromonomers are well known, to our knowledge the grafting of monofunctional urethane macromonomers has not yet been reported.

2. Experimental

2.1 Materials

Following chemicals were dried over molecular sieve: ethylene glycol (Sigma-Aldrich, 99.9%); (Bayer, 95%); 2-hydroxyethylmethacrylate (BASF, USA, 98%); isopropanol (Sigma-Aldrich, 99.5%), methyl ethyl ketone (MEK) (Sigma-Aldrich, 99%); methanol (MeOH, 99.5%); dimethylformamide (DMF, 99.5%); 2,2'-azobis(isobutyronitrile) (AIBN) (Delta Scientific, 98%). Toluene diisocyanate (consisting of a mixture of 20% of the 2,6 isomer and 80% of the 2,4 isomer) was used as received. n-BMA (Aldrich) and MMA (ICI Chemicals and Polymers, 98%) were washed with a 0.3 M potassium hydroxide (KOH) solution, followed by distillation under reduced pressure to remove the inhibitor. The monomers were stored at 0 $^{\circ}$C over molecular sieves (4 Å).

2.2 Synthesis of Urethane Macromonomers (Ums)

UMs with different average chain lengths (X) and with the following general structure were synthesized by addition polymerization: HEMA-(TDI-EG) X-TDI-isopropanol (formula 1), where HEMA is 2-hydroxyethylmethacrylate, EG is ethylene glycol, TDI is toluene diisocyanate, and X is 4, 8, 12 or 32.

The synthesis of the UMs was carried out under a nitrogen atmosphere. Scheme 1 shows the synthesis procedure used for the preparation of the UMs with average chain lengths X=4 to X=32, using a three-step addition reaction. The formulations used are tabulated in Table 1. TDI and MEK were added to the flask and the mixture cooled to below 10 $^{\circ}$C. The reactor was then sealed and purged with nitrogen gas. This was followed by addition of the ethylene glycol, under stirring (400-500 rpm). The temperature was increased to 15-18 $^{\circ}$C and held for 30-60 minutes. In the second step, the reaction temperature was increased to 20-30 $^{\circ}$C and HEMA was added. The reaction was allowed to run for 60 minutes. In the final step, the reaction temperature was first increased to 30-35 $^{\circ}$C, excess isopropanol was added, and then the reaction temperature was increased to 55 $^{\circ}$C to ensure that all previously unreacted isocyanate reacted. The degree of the reaction was verified by measuring the isocyanate group (2270 cm^{-1}) that disappears as result of reaction with hydroxyl group, using IR spectroscopy. The isocyanate group was no longer visible in the IR spectrum of the reaction product, as shown in measurements. The obtained UMs were dried in a vacuum oven at 45 $^{\circ}$C for 24 hours and then stored in a desiccator until required for use in further polymerization.

$$X+1 \left[OCN-R-NCO \right] + X \left[HO-CH_2-CH_2-OH \right]$$

Step 1

$$OCN\left[R-\underset{H}{N}-\underset{O}{C}-O-CH_2-CH_2-O-\underset{O}{C}-\underset{H}{N}\right]_X R-NCO$$

HEMA **Step 2**

$$CH_3-\underset{CH_2}{C}-\underset{O}{C}-O-CH_2-CH_2-O-\underset{O}{C}-\underset{H}{N}\left[R-\underset{H}{N}-\underset{O}{C}-CH_2-CH_2-O-\underset{O}{C}-\underset{H}{N}\right]_X R-NCO$$

Isopropanol **Step 3**

$$H_3C-\underset{CH_2}{C}-\underset{O}{C}-O-CH_2-CH_2-O-\underset{O}{C}-\underset{H}{N}\left[R-\underset{H}{N}-\underset{O}{C}-O-CH_2 CH_2-O-\underset{O}{C}-\underset{H}{N}\right]_X R-\underset{H}{N}-\underset{O}{C}-O-\underset{CH_3}{CH}-CH_3$$
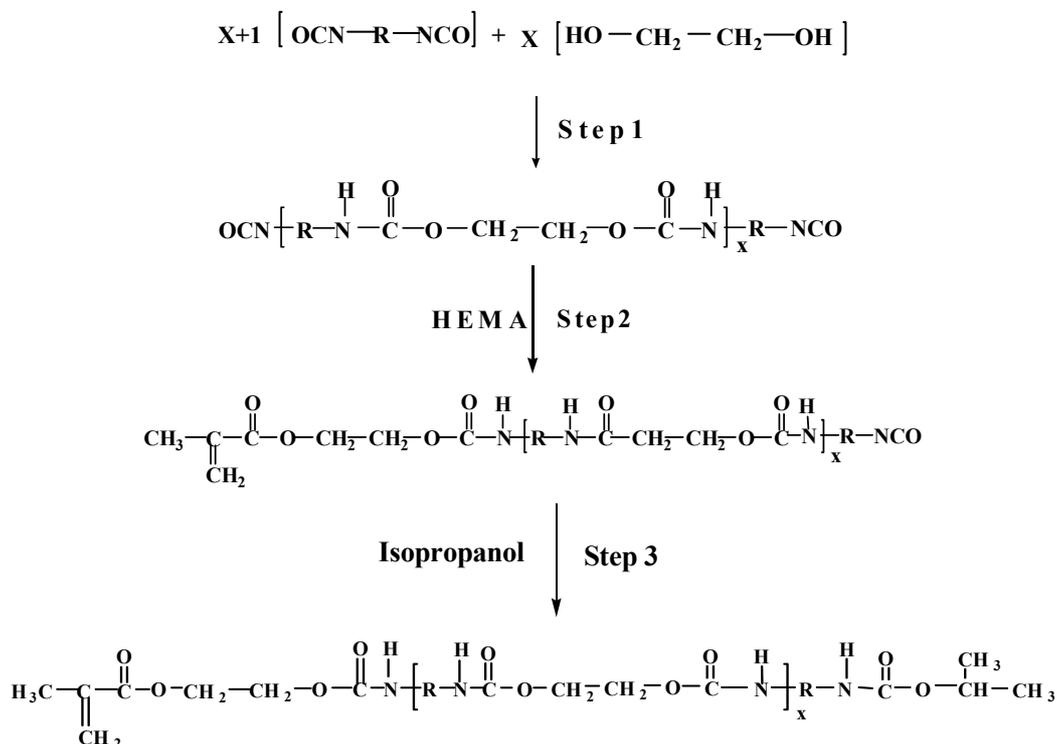
Scheme 1. Procedure for the preparation of difunctional urethane macromonomers

Table 1. Formulations used for the preparation of polyurethane macromonomers

Raw material	UM having X=4	UM having X=8	UM having X=12	UM having X=32
TDI (g)	33.61	34.98	35.54	21.79
EG (g)	9.58	11.08	11.69	7.53
HEMA (g)	4.01*	2.32*	1.63*	0.41*
Isopropanol (g)	2.78*	1.60*	1.13*	0.29*
Excess of Isopropanol (g)	3.54**	3.66**	3.72**	2.06**
[OH]/[NCO]	1.15	1.15	1.14	1.13

* Amounts of HEMA, isopropanol, TDI and EG used to synthesize UMs were calculated as mole % according to Formula 1, at [OH]/ [NCO] mole ratio 1:1, in which HEMA was calculated as 40 mole % of the UM chain end and isopropanol was calculated as 60 mole % of the UM chain end.

** An excess of isopropanol was needed to ensure that all reactive NCO groups were fully reacted. (If this is not the case, then secondary reactions take place, to ultimately form an desirable cross linked structures). Thus, the minimum quantities of excess isoproponal were experimentally determined to be 0.15 moles (using FTIR) to ensure that all the NCO groups reacted.

Besides the desired UMs with only one polymerizable end group, i.e. HEMA on one chain end and isopropanol on the other, the obtained UMs can also have undesirable chemical structures. One such undesirable product occurs when HEMA reacts on both sides of the urethane pre-polymers (urethane chain with excess isocyanate); this product will lead to crosslinking. Another undesirable product is formed when isopropanol reacts on both chain ends of the urethane pre-polymer, rendering the UM unreactive. Thus it is very important to optimize reaction conditions in an attempt to maximize the yield of the desired product that has HEMA on one chain end and isopropanol on the other.

Three different methods were used to optimize the reaction conditions to obtain the desired product. After the polyurethane with excess isocyanate was prepared (Step 1 in Scheme 1) the temperature was decreased to 10 °C and then the following different procedures were followed:

1) Method 1: All of the HEMA was added at once at the start of the reaction and the temperature was held at between 20-25 °C for 45-60 minutes to obtain a homogeneous mixture. This was followed by the addition of all of the isopropanol. The reaction was allowed to proceed at 25-30 °C for a further 45-60 minutes.

2) Method 2: HEMA was added dropwise at 20 °C, and the reaction temperature was kept at 20-25 °C for 45-60 minutes. This was followed by the addition all the isopropanol. The reaction was allowed to proceed at 30-35 °C for a further 45-60 minutes.

3) Method 3: HEMA and isopropanol were added together, in fractions, at 20 °C. The reaction temperature was kept at 20-30 °C and the reaction time was 60-90 minutes.

Due to similarity in the end group in the structure of UMs in all three fractions that are possible form, it was not possible to separate these three fractions by using chromatography techniques, and it was otherwise not possible to measure the yield of each fraction. Thus all comparisons between the above three methods were made after free radical copolymerization of the synthesized UMs and after the unreacted and unreactive UMs were removed (as confirmed by GPC) which will be discussed later.

Table 2 compares the yields of the products of the copolymerization using synthesized UMs, the three different methods that were used to obtain the UMs. Method 1 gave the highest yields of both PMMA-g-urethane and n-PBMA-g-urethane copolymers under similar copolymerization conditions. Method 1 was therefore considered to be the best of the three methods and was therefore used to synthesize the further UMs in this study.

Table 2. Comparisons of yields of graft copolymers prepared as result of using different methods used to prepare the UMs

Method	Feed polymerization (g)			PMMA-g-urethane (g)	Yield (%)	PBMA-g-urethane (g)	Yield* (%)
	UM X=8	MMA	n-BMA				
1	0.25	4.75	4.75	3.79	76	3.86	77
2	0.25	4.75	4.75	3.65	73	3.75	75
3	0.25	4.75	4.75	3.59	71	3.64	73
1	0.50	4.50	4.50	3.75	75	3.89	78
2	0.50	4.50	4.50	3.62	72	3.80	76
3	0.50	4.50	4.50	3.54	70	3.66	73

* Yield % = PMMA-g-urethane (g)/MMA (g) + UM (g)

2.3 Synthesis of Acrylic-G-Urethane Copolymers

Solution free-radical copolymerization was carried out in a 250-ml three-neck round-bottom flask under a nitrogen atmosphere. DMF was first introduced into the reactor, followed by MMA or n-BMA, and then by UM in specified concentrations (0, 5, 10, 15, 20, 25, 30, and 40 wt % relative to MMA or n-BMA), and of each of the different chain lengths of urethane macromonomers (X = 4, 8, 12, 32) were used for each synthesis. The polymerization temperature was raised to 75 °C and AIBN (1 wt % relative to the monomer) was charged into the reactor. The reaction was allowed to proceed for 18 hours. The resulting solution was poured into 400 ml methanol to precipitate the polymer. The copolymers were dried overnight in a vacuum oven at 40 °C and then analyzed by NMR and FTIR spectroscopy, GPC, TGA, TEM, and DMA.

2.4 Characterization of Urethane Macromonomer and Acrylic-G-Urethane Copolymers

The urethane macromonomers with different chain lengths and the acrylate-g-urethane copolymers were characterized by FTIR and NMR spectroscopy, and GPC.

FTIR spectroscopy was used to monitor the disappearance of various functional groups during UM synthesis, and also to characterize the synthesized UMs and graft copolymers. 32 scans were accumulated for each specimen. A Perkin Elmer 1650 apparatus was used.

^{1}H and ^{13}C NMR spectroscopy were also used to determine the structures of the synthesized UMs and the PMMA-g-urethane and n-PBMA-g-urethane copolymers. ^{1}H NMR spectra were measured on a Varian 300 MHz or 600 MHz instrument, using $CDCl_3$ or DMSO as solvents, depending on the solubility of the material being analyzed. DMSO was used as solvent for UM samples and $CDCl_3$ as solvent for all graft copolymer samples. All spectra were referenced to tetramethylsilane (TMS) at 0 ppm. ^{13}C NMR spectra were obtained in a similar manner to the ^{1}H NMR spectra, but at a frequency of 125 MHz.

GPC was used to determine the molecular weights and molecular weight distributions (polydispersities) of the UMs and graft copolymers. Samples of UMs were dried at 40 ˚C for 24 h under vacuum and then dissolved in THF. Samples of graft copolymers were obtained by precipitation in methanol and redissolving in THF. GPC analyses were carried out using a Waters model 610 pump, Waters model WISP 717 autoinjector, model 410 refractive index detector and model 486 UV detector (at 254 nm). Two PLgel 5-μm mixed-C column (300×7.5 mm) as a pre-column (Polymer Laboratories), and a PLgel 5-μm guard (50-7.5 mm) (Polymer Laboratories) were used. THF was used as solvent at a flow rate of 1.0 ml/min. The column was calibrated with narrow PMMA standards (5mg/1ml THF), ranging from 2,500 to 898,000 g mol^{-1}.

Thermogravimetric analysis (TGA) was carried out on dried samples of the UMs and acrylate-g-urethane copolymers to investigate their thermal stabilities. Analyses were carried out using a TGA-50 SHIMADZU thermogravimetric instrument with a TA-50WSI thermal analyzer, connected to a computer. Samples (10-15 mg) were degraded in nitrogen (flow rate 50 ml/min) at a heating rate of 5 °C /min.

Dynamic mechanical analysis (DMA) was used first to determine the T_g values of the UMs and graft copolymer samples, and second to investigate the phase separation between urethane and acrylate segments of the synthesized acrylate-g-urethane copolymers. DMA was carried out on a Perkin Elmer DMA 7e using the thin-film extension mode. The frequency was 1 Hz and the heating rate was 5 °C/min. Samples were about 0.3 mm thick. The solution-cast films were dried before testing.

Transmission electron microscopy (TEM) was used to directly visualize the morphology of the acrylate-g-urethane copolymers. Bright-field TEM images were recorded on a TEM 200CX (JEOL Tokyo, Japan) at an accelerating voltage of 120 kV. Prior to analysis, samples of acrylate-g-urethane copolymers were stained with OsO_4, embedded in epoxy resin, and then cured at 60 °C for 24 h. The embedded samples were ultra-microtomed with a diamond knife on a Reichert Ultracut S ultra-microtome at room temperature. This resulted in sections with a nominal thickness of ~ 100 nm. The sections were transferred from water at room temperature to 300-mesh copper grids, which were then transferred to the TEM apparatus.

3. Results and Discussion

3.1 Urethane Macromonomers

Figure 1 shows the FTIR spectra of UMs with average chain length X=12. In Figure 1(a) the peaks observed at 3312, 1532 and 1711 cm^{-1} are characteristic peaks of N-H, and the C=O stretching and vibration from the urethane group, respectively. The strong peak observed at 2275 cm^{-1} is characteristic of the isocyanate group (-N=C=O) (first-step intermediate in Scheme 1). The FTIR spectrum of the end-capped UM with average chain length X=12 is seen in Figure 1(b). In addition, the characteristic peak of the isocyanate groups (-N=C=O) associated with the first step (Figure 1(a)) at 2275 cm^{-1} has completely disappeared in Figure 1(b), confirming that (-N=C=O) reacts with HEMA and isopropanol to form the urethane group.
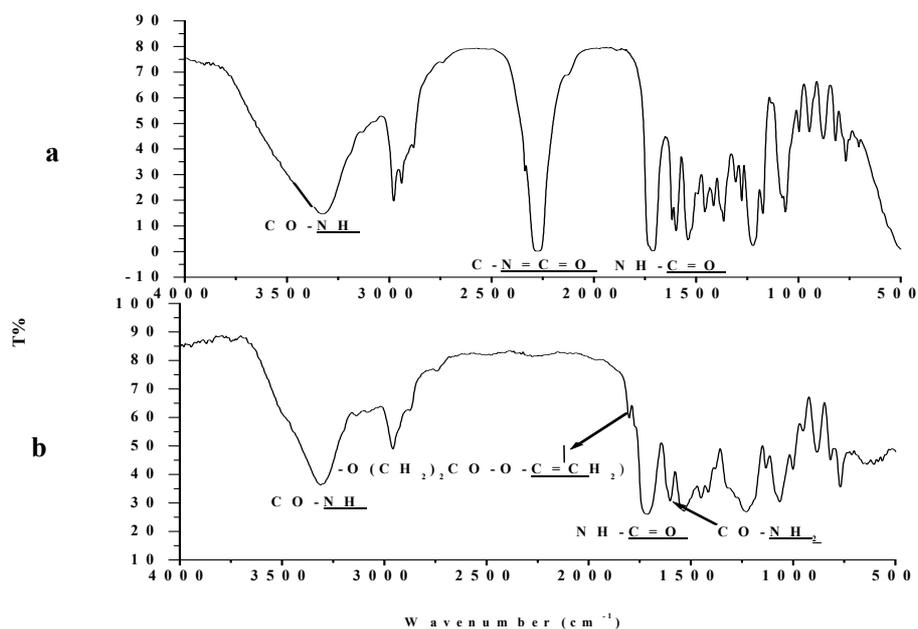
Figure 1. FTIR spectra of UM (average chain length X=12): (a) before addition of isopropanol + HEMA (b) after addition of isopropanol + HEMA

Figure 2 shows the 1H NMR spectrum of the synthesized UM of average chain length X=12, prepared by the reaction of the isocyanate-terminated urethane prepolymer, HEMA and isopropanol. The signal assignments are as follows. The aromatic ring protons are in the region 7.13-7.56 ppm (a), whereas the resonance signals for the methylene protons of the UM appear in the region 3.41-4.92 ppm (b), depending on the position of the methylene protons with respect to the neighboring urethane groups. Characteristic signals of urethane N-H protons appear in the region 8.67-9.74 ppm (c). The signals of the methyl group attached to the aromatic ring appear at 2.07 ppm (d) and the signals at 1.23 and 1.88 ppm (e and f) correspond to the methyl groups of the isopropanol and HEMA components. The important characteristic signals of the vinyl-terminated protons in the UM are detected in the region 5.71-6.08 ppm (g), indicating the existence of acrylate groups in the UM structures. 1H NMR spectra of other UMs of different chain lengths that were synthesized showed similar results.

A typical ^{13}C NMR spectrum of the UM having a urethane average chain length X=12 (and the peak assignments) is shown in Figure 3, ^{13}C NMR spectra of all of the UMs prepared in this study show aromatic carbons at 115-137 ppm, whereas the resonance signals for the methylene carbons appear in the region 59-66 ppm, depending on the position of the methylene carbon with respect to neighbouring urethane groups. The characteristic signal of the urethane ester appears in the region 167-153 ppm. The signal of the methyl group attached to the aromatic ring of TDI appears at 17.45 ppm, whereas the peaks at 16.76-18.41 ppm correspond to the methyl groups of isoproponal and HEMA. The important characteristic signal of the vinyl-terminated group of the UM was detected in the region 122.5 and 125.6 ppm, indicating the existence of acrylate groups in the UM structure.
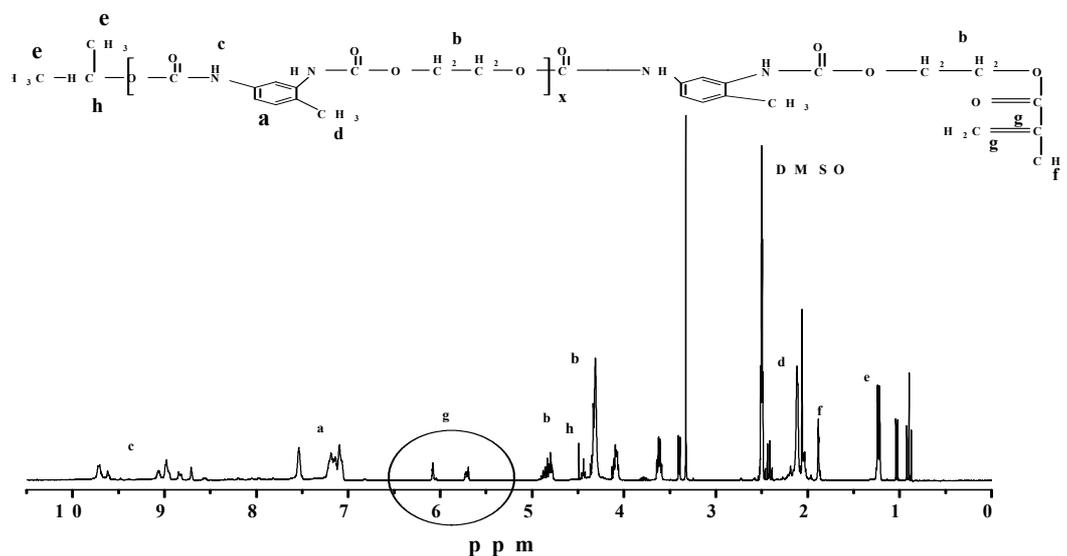
Figure 2. ^{1}H NMR spectrum of synthesized urethane macromonomer (X=12), dissolved in DMSO

The number-average molecular weights values ($\overline{M_n}$) and polydispersity index (PDI) of the four UMs having different urethane average chain lengths were determined by GPC (based on PMMA standards). Results are tabulated in Table 3. Good correlation between theoretical and experimental values of $\overline{M_n}$ was obtained.

3.2 Synthesized Methacrylate-G-Urethane Copolymers

The ability of UMs to undergo copolymerization was determined using MMA and n-BMA as comonomers. Four different lengths of UMs were copolymerized with different quantities of MMA and n-BMA under free radical copolymerization conditions. The resulting graft copolymers were isolated by precipitation from DMF into methanol. Methanol was a solvent for UM and a non-solvent for PMMA, n-PBMA and the corresponding acrylate-g-urethane copolymers.

The graft copolymers were characterized by GPC (using a double detector system of UV [254 nm] and RI). The UV detector detected the UMs, but not the PMMA and n-PBMA (the absorptions of which were too low at this wavelength).
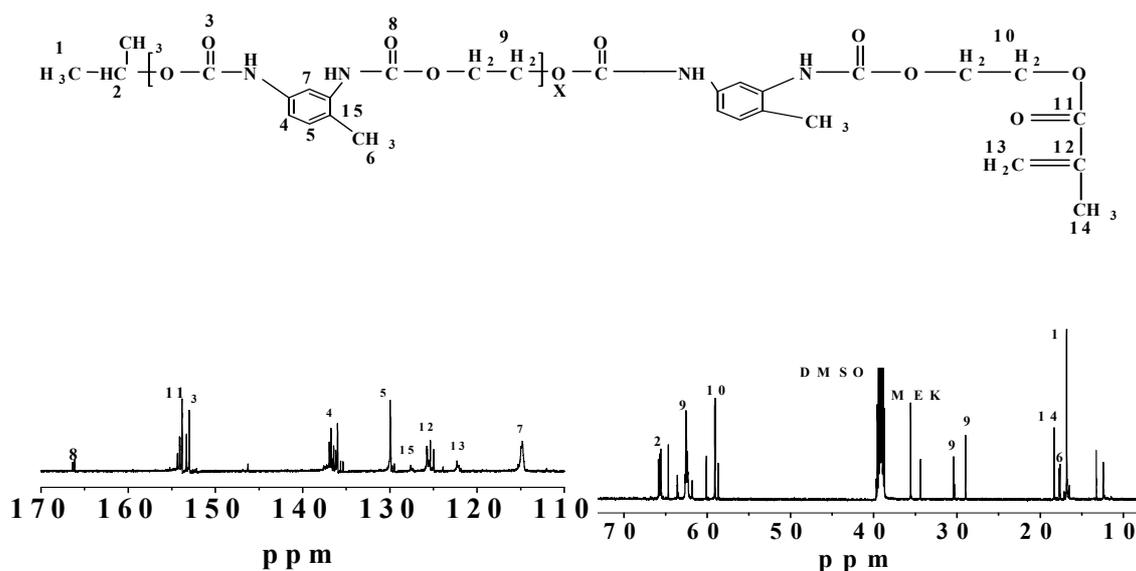
Figure 3. ^{13}C NMR spectrum of synthesized urethane macromonomer (X=12), dissolved in DMSO

Table 3. Number average molecular weight ($\overline{M_n}$) and polydispersity index ($\overline{M_w}/\overline{M_n}$) the UMs of different average chain lengths, as determined by GPC

Urethane length (X)	Theoretical molecular weight*	$\overline{M_n}$	Polydispersity
4	1280	1260	1.64
8	1480	1810	1.85
12	1810	2100	2.16
32	7310	7840	2.32

* Calculating according to formula 1.

Unreactive UMs (UMs containing isopropanol at both ends, and unreacted UMs) were extracted, by filtration, after precipitation of the polymer in methanol. It was however expected that some unreactive and unreacted UMs might precipitate along with the graft copolymer after a single precipitation, as can be seen the example in Figure 4 for X=32 (shoulder at low molecular weight). A further three or more precipitations from methanol were required to completely remove unreacted and unreactive UMs from the copolymers.
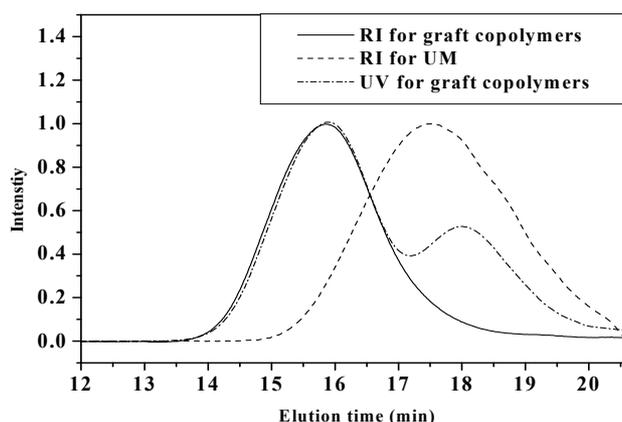
Figure 4. GPC traces of MMA copolymerized with 5% UM (X=32) after a single precipitation

The molecular weights and molecular weight distributions of UMs and both PMMA-g-urethane and n-PBMA-g-urethane copolymers were determined by GPC. GPC results confirmed the syntheses of PMMA-g-urethane and n-PBMA-g-urethane copolymers. Figure 5 and Figure 6 are examples of GPC traces showing the extracted graft copolymers of PMMA-g-urethane and n-PBMA-g-urethane copolymers, respectively, after removal of all the unreacted and unreactive UM. UV peaks for unreacted UM were not observed and the graft copolymer signals were shifted to lower elution time compared to the starting material. This indicated that the molecular weights of the graft copolymer samples increased due to the grafting reaction, and also that no homopolymers of PMMA or n-PBMA, or UMs, were present. In the absence of unreacted UMs, the UV response almost mirrored the RI response in all graft copolymers.

$\overline{M_n}$, $\overline{M_w}$ and PDI obtained for both PMMA-g-urethane and n-PBMA-g-urethane copolymers are tabulated in Tables 4 and 5, respectively. All of the PMMA-g-urethane and n-PBMA-g-urethane copolymers had $\overline{M_n}$ values of about 30,000. Although expected, these values were considered to be slightly low, because DMF has a high chain transfer constant for MMA and n-BMA (5.01×10^{-4} and 4.38×10^{-4}) (Boyer et al., 2004). Tables 5 and 6 also show that the $\overline{M_n}$ values of all of the graft copolymers were similar to those of the PMMA and n-PBMA homopolymers and copolymers.

Analysis by GPC with a UV detector was also used as technique to know how match UM was incorporated into PMMA or PBMA during free–radical copolymerization. The calculation was done by taking the same concentrations of UM and graft copolymer to GPC with a UV detector and compares the integration absorption peak of graft copolymer to integration absorption peak of UM and all results are given in Table 6.
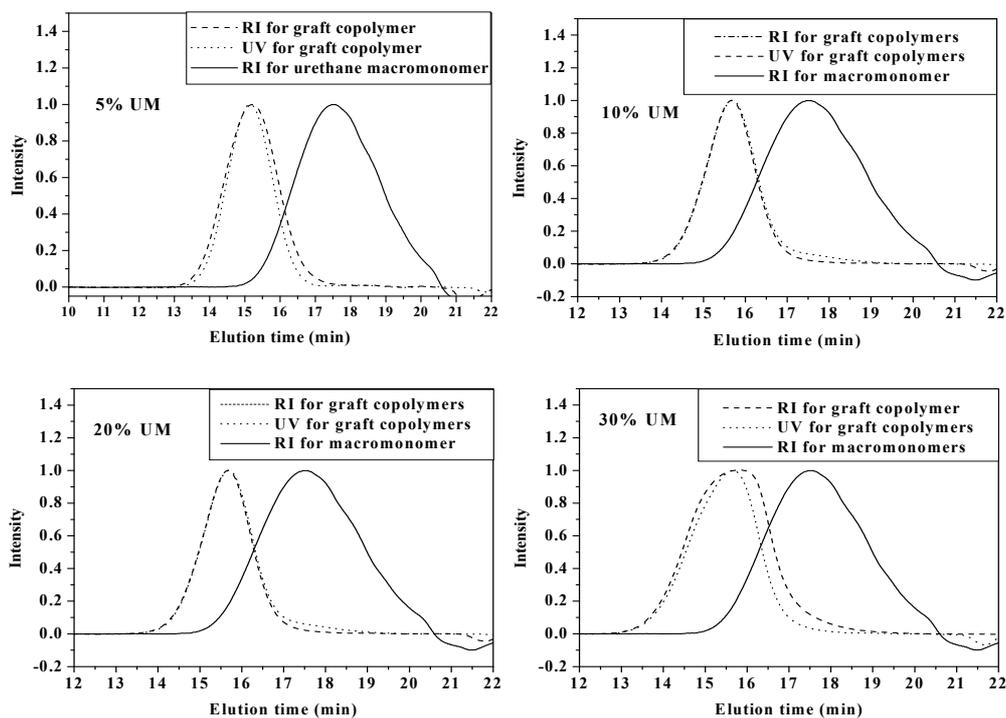
Figure 5. GPC traces of MMA copolymers containing various amounts of UM (5, 10, 20, 30%) of average chain length X=12
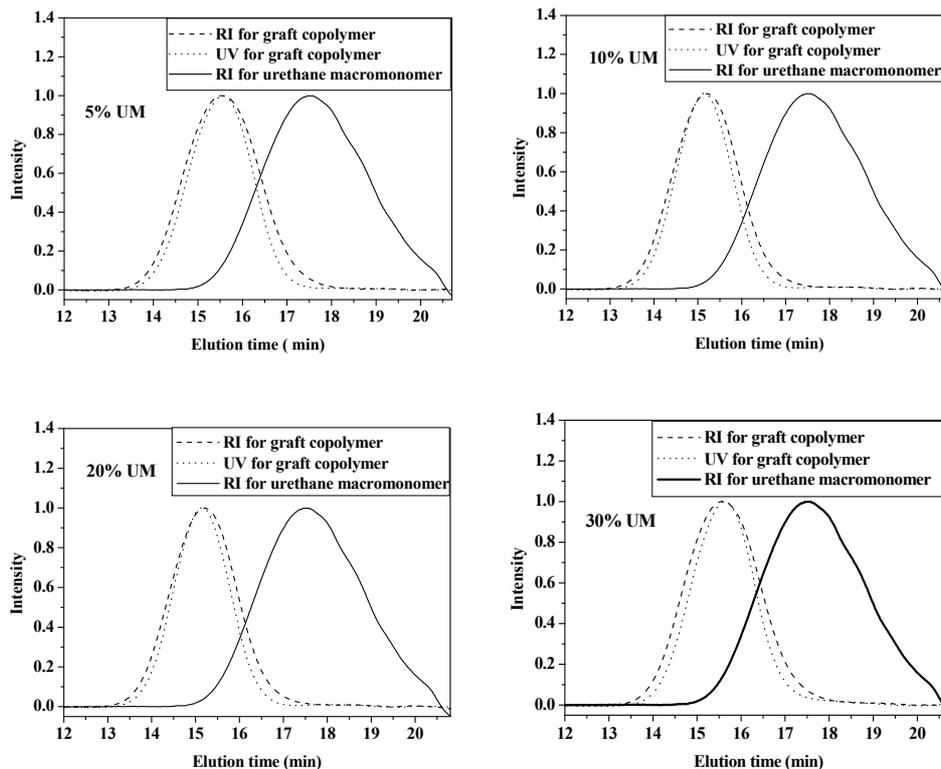
Figure 6. GPC traces of n-BMA copolymers with various amounts of UM (0, 10, 20, 30%) of average chain length X=4

Table 4. Apparent number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$) and polydispersity ($\overline{M}_w / \overline{M}_n$) for n-PBMA-g-urethane copolymers

Ums	Feed ratio by wt%* MMA/Macromonomer	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	PDI	Yield of product PMMA-g-urethane (g)	Yield (%)
X=4	100/0	35	55	1.54	3.98	79.6
	95/5	27	44	1.59	3.65	73.0
	90/10	25	42	1.66	3.55	71.0
	85/15	34	46	1.36	3.32	64.4
	80/20	26	40	1.53	3.12	62.4
	75/25	35	48	1.38	3.06	61.2
	70/30	19	33	1.70	3.01	60.2
X=8	95/5	24	48	1.96	3.53	70.6
	90/10	29	44	1.53	3.38	67.6
	85/15	29	47	1.59	3.20	64.0
	80/20	28	41	1.46	3.11	62.2
	75/25	22	39	1.78	3.04	60.1
	70/30	24	34	1.40	2.99	59.8
X=12	95/5	26	52	1.94	3.42	68.4
	90/10	25	45	1.78	3.22	64.4
	85/15	20	41	2.04	3.13	62.6
	80/20	25	47	1.85	3.01	60.2
	75/25	19	42	2.11	2.98	59.6
	70/30	16	35	2.14	2.85	57.0
X=32	90/10	20	44	2.17	3.28	65.4
	80/20	22	41	1.84	3.09	60.4
	70/30	25	42	1.69	2.92	58.8
	60/40	22	34	1.49	2.61	51.4

* The total quantities of UM and MMA in all copolymerization feeds were based on 5.00 g.

Table 5. Apparent Number average molecular weight ($\overline{M_n}$), weight average molecular weight ($\overline{M_w}$) and polydispersity ($\overline{M_w}/\overline{M_n}$) for n-PBMA-g-urethane copolymers

Ums	Feed ratio by wt%* BMA/Macromonomer	$\overline{M_n} \times 10^{-3}$	$\overline{M_w} \times 10^{-3}$	PD	Yield of product n-PBMA-g-urethane	Yield%
X=4	100/0	38	68	1.77	3.85	77.0
	95/5	26	52	1.96	3.63	72.6
	90/10	33	51	1.53	3.51	70.2
	85/15	28	47	1.65	3.33	66.6
	80/20	28	48	1.67	3.11	62.6
	75/25	22	41	1.87	3.07	61.4
	70/30	17	37	2.08	3.01	60.2
X=8	95/5	28	51	1.79	3.55	71.0
	90/10	21	49	2.30	3.33	66.6
	85/15	20	45	2.22	3.21	64.2
	80/20	27	48	1.74	3.11	62.6
	75/25	28	43	1.55	3.04	60.8
	70/30	17	39	2.30	2.98	59.6
X=12	95/5	19	55	2.78	3.45	69.0
	90/10	33	52	1.51	3.27	65.4
	85/15	30	48	1.57	3.19	63.8
	80/20	29	49	1.66	3.11	62.6
	75/25	20	47	2.28	3.01	60.2
	70/30	16	38	2.26	2.99	59.8
	60/40	17	37	2.12	2.91	58.2
X=32	90/10	20	44	2.17	3.32	66.4
	80/20	22	41	1.84	3.12	62.4
	70/30	25	42	1.69	2.94	58.8
	60/40	19	40	2.15	2.85	54.3

* The total amounts of UM and n-BMA in all copolymerization feeds were based on 5.00 g.

Table 6. Percentage UM incorporated into the graft copolymer as determined by ^{1}H NMR spectroscopy

UM	Feed ratio by wt%* MMA/UM	% UM* By H[1] NMR	% UM By GPC	Feed ratio by wt%* n-BMA/UM	% UM By H[1] NMR	% UM By GPC
X=4	90/10	1.2	0.6	90/10	1.7	1.2
	80/20	5.8	5.9	80/20	6.2	5.8
	70/30	10.2	10.9	70/30	8.7	8.9
X=8	90/10	0.8	1.1	90/10	1.1	0.9
	80/20	6.7	6.5	80/20	5.6	5.9
	70/30	10.3	9.2	70/30	8.3	9.1
X=12	90/10	3.2	2.9	90/10	2.6	1.6
	80/20	4.1	3.8	80/20	5.1	4.3
	70/30	9.3	9.2	70/30	9.2	8.6
X=32	90/10	-	0.4	90/10	0.9	0.6
	80/20	7.5	6.3	80/20	3.63	4.3
	70/30	9.7	8.7	70/30	7.83	7.8
	60/40	15.3	12.7	60/40	11.67	10.9

* Since only 40% HEMA was used to UMs only, 80% of the UM was expected to react.

Figure 7 shows GPC with a UV of UM with X=4 and one series of GPC traces isolated graft copolymers i.e. PMMA–graft-urethane, and from this may be note that the more amount was used form UM in free copolymerization feed, the more absorption was detected by UV detector, the more incorporation into PMMA molecular chain. It may be due to the more amount of UM in free radical copolymerization feed the more vinyl terminated double bond a valuable the more chance to undergo to free radical polymerization.
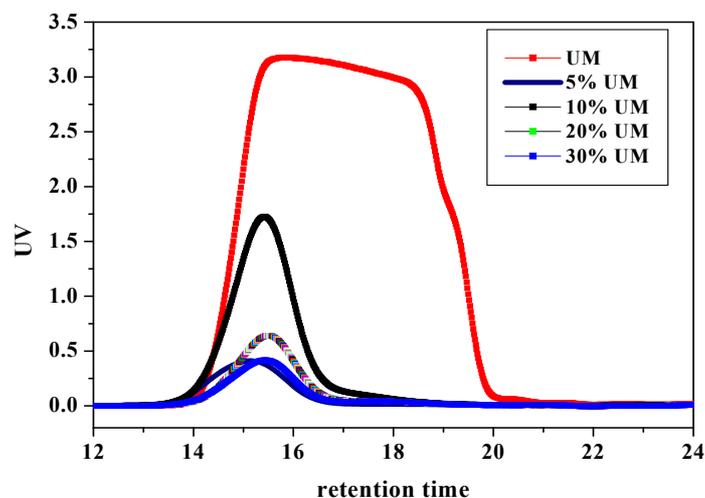
Figure 7. GPC traces of UM with X=4 and GPC traces of MMA copolymerization with urethane macromonomer with X=4 (a) 5 %, (b) 10%, (c) 20%, (d) 30%

Figure 8 compares the FTIR spectra of PMMA-g-urethane copolymer and n-PBMA-g-urethane copolymer with those of the UM, and PMMA and n-PBMA homopolymers. New absorption peaks were observed in the spectra of the graft copolymers. The band at 3313 cm^{-1} was assigned to the hydrogen-bonded N-H stretching band of the urethane groups. The amide vibration appeared at 1531 cm^{-1} and the aromatic ring of the TDI repeat unit appears at 1601 cm^{-1}. This structure was also confirmed by ^{1}H NMR and ^{13}C NMR. These results confirmed that the UM was successfully incorporated into the PMMA and n-PBMA polymer structures. This was supported by GPC results.

W a v e l e n g t h   (c m $^{-1}$)
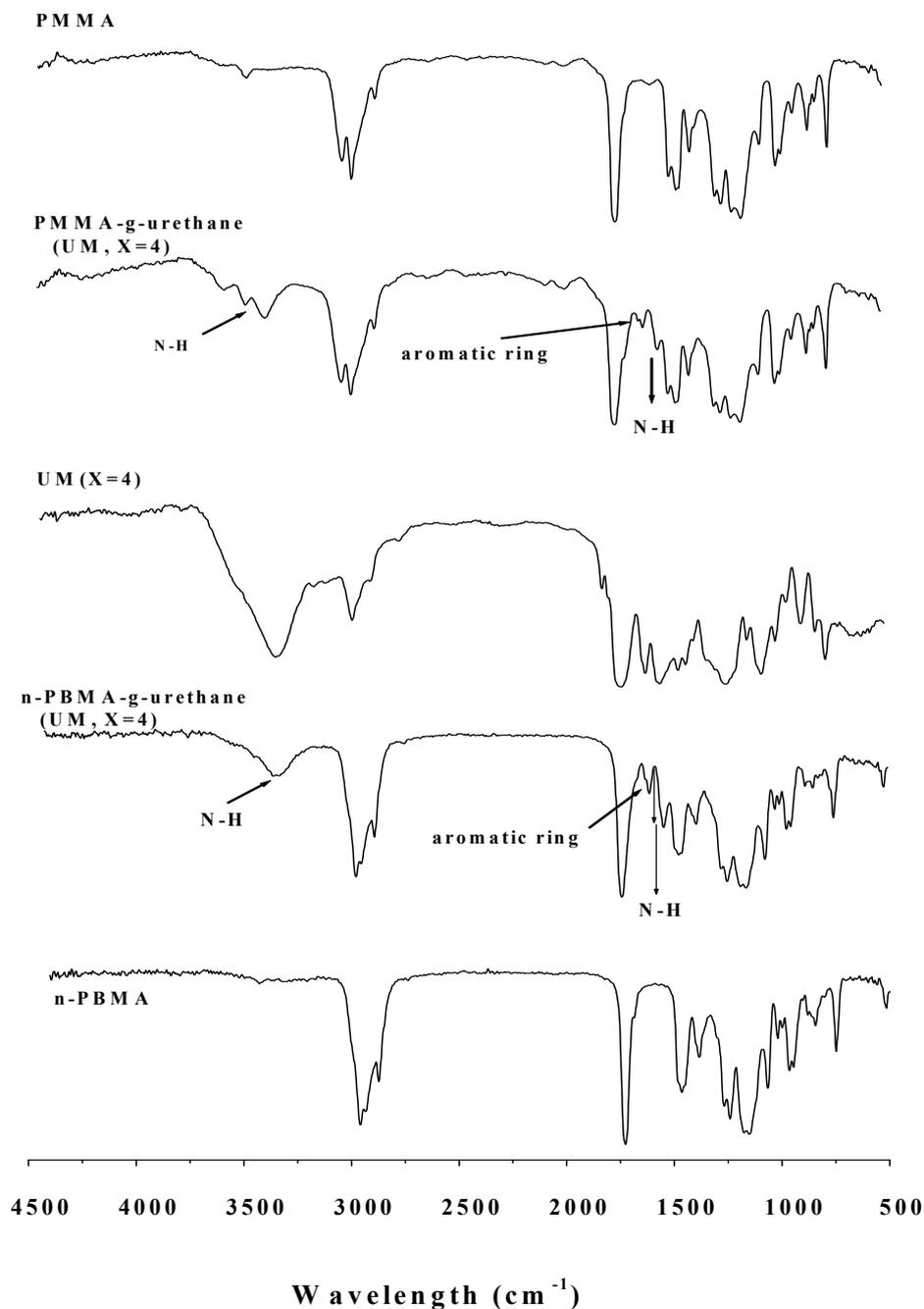
Figure 8. FTIR spectra comparing PMMA-g-urethane with UM and PMMA homopolymer, and n-PBMA-g-urethane with UM and n-PBMA homopolymer

Figure 9 compares the 1H NMR spectrum of a PMMA-g-urethane copolymer with the ^{1}H NMR spectra of UM and PMMA homopolymer, and the ^{1}H NMR spectrum of n-PBMA-g-urethane copolymers with ^{1}H NMR spectra of UM and n-PBMA homopolymer (after all of the unreacted and unreactive UMs were removed, as confirmed by GPC). New signals were observed in the graft copolymer spectrum (compared with the PMMA or n-PBMA spectra). The two broad signals in the region 6.8-8.0 ppm in the case of the graft copolymers were attributed to the aromatic protons of the TDI repeat unit in the UMs. The signals at 3.49-4.32 ppm originated from the methylene proton of EG in the UMs; the intensity of these peaks were low due to the small amount of UM that was incorporated into the graft copolymers. Furthermore, the signals ascribed to the vinylic protons of the UMs in the region 5.71-6.08 ppm were observed to have completely disappeared upon copolymerization of MMA or n-BMA. These results were consistent the UM being successfully incorporated into the PMMA and n-PBMA polymer structures, as supported by GPC results.
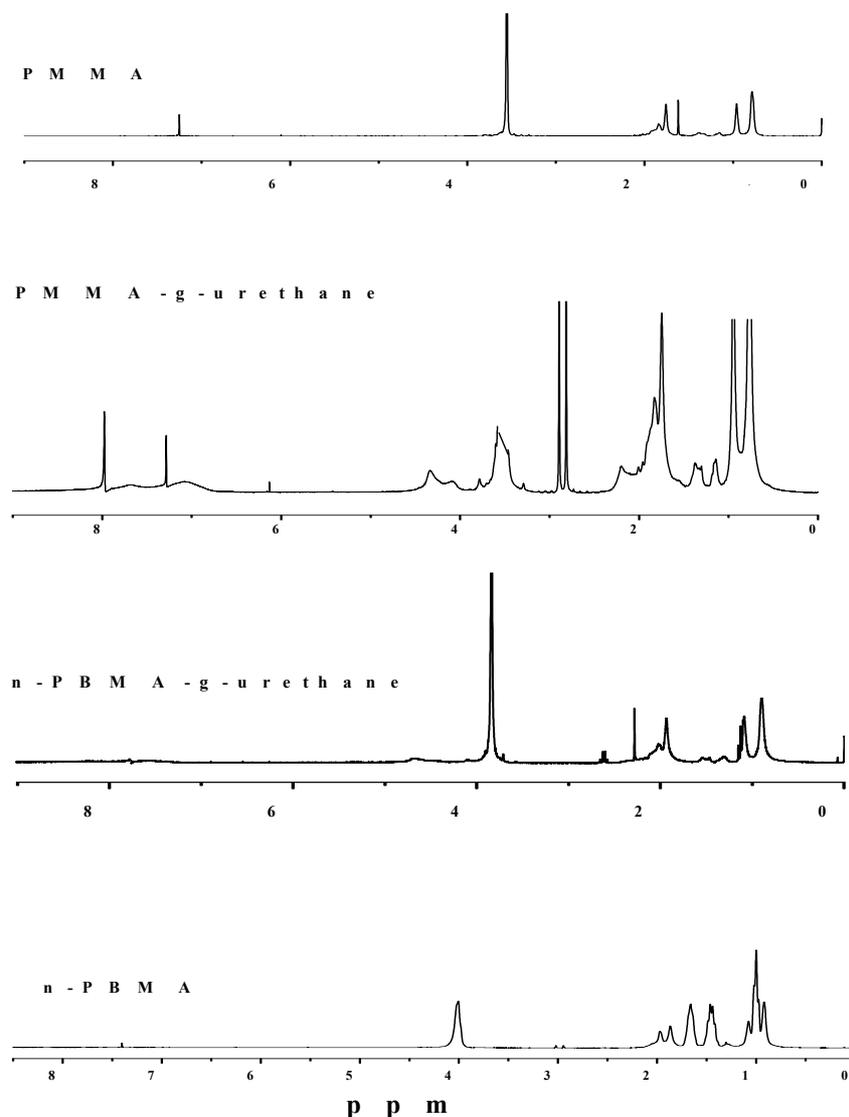
Figure 9. ^{1}H NMR spectra comparing PMMA-g-urethane with PMMA homopolymer, and n-PBMA-g-urethane with n- PBMA homopolymer

The amount of the UM that was incorporated into the two copolymers was also determined by ^{1}H NMR spectroscopy. Calculations were based on the integration of the aromatic ring signal of the UM (6.8-8.0 ppm) in graft copolymers, the methoxy group of PMMA (3.54 ppm) in the PMMA-g-urethane copolymers, and the methyleneoxy group of n-PBMA (3.62 ppm) in the n-PBMA-g-urethane copolymers. The results are given in

Table 6.

As the amount of UM added during graft copolymerization increased so the percentages of UMs incorporated into both PMMA-g-urethane and n-PBMA-g-urethane copolymers also increased. Part of the added UM was unreactive (i.e. when there were isopropanol groups at both ends), and was extracted with solvent. (This also contributed to the low incorporation level of UM into graft copolymers). Very low concentrations of UMs could not be reliably detected spectroscopically as it was difficult to clearly identify the broad UM peaks in the spectra.

Figure 10 compares the ^{13}C NMR spectrum of a PMMA-g-urethane copolymer with the ^{13}C NMR spectra of UM and PMMA, and the ^{13}C NMR spectrum of n-PBMA-g-urethane copolymer with the ^{13}C NMR spectra of UM and n-PBMA homopolymer. New signals were observed in the graft copolymer spectra (compared to the PMMA or n-PBMA homopolymers). The signals in the regions 129.06, 135.78 and 153.36 ppm were mainly attributed to the aromatic carbons of TDI in the urethane macromonomer. The signals at 27.07, 36.36 and 64.73 ppm originated from the methylene carbons of EG and HEMA in the UM. In addition, the ^{13}C NMR signals assigned to the vinylic carbons of the UMs in the region 126.0-129.6 ppm were observed to have completely disappeared upon copolymerization with MMA or n-BMA. These results were consistent with the UM being successfully incorporated into the PMMA and n-PBMA polymer structures, as was supported by GPC results.
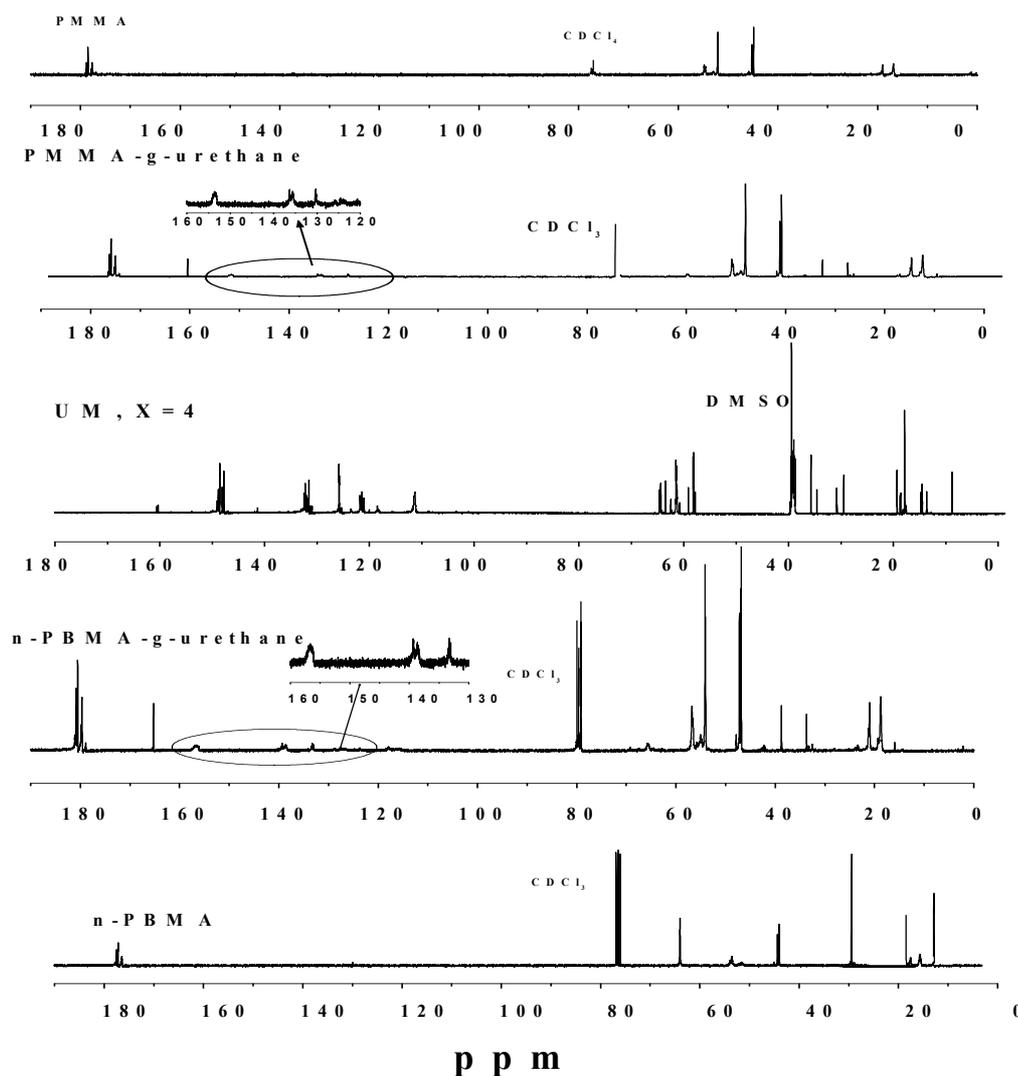
Figure 10. ^{13}C NMR spectra comparing PMMA-g-urethane with UM and PMMA homopolymer, and n-PBMA-g-urethane with UM and n-PBMA homopolymer

Primary TGA curves for MMA and n-BMA copolymerized with different amounts of UMs (ranging from 0-30% by weight according to MMA and n-BMA) from UMs having different average chain lengths (X= 4, 8, 12, and 32) were recorded. The decomposition patterns for all of the graft copolymers were similar. There was a slight improvement in thermal stability as the amount of UMs increased. There was also a slight improvement in thermal stability as the average chain length of the UMs increased as shown in Figure 11 and Figure 12.
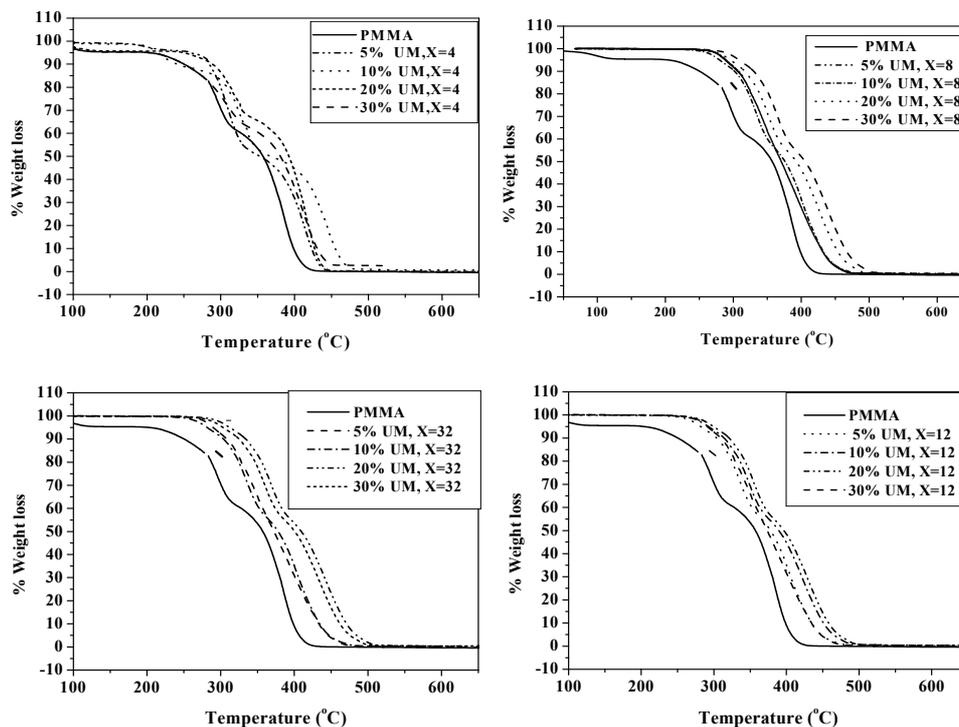
Figure 11. TGA curves of MMA copolymerized with different amount of the UMs of various average chain lengths: (a) X=4, (b) X=8, (C) X=12 and (d) X=32

The TGA curves of PMMA-g-urethane copolymers recorded under nitrogen compared with those of PMMA homopolymers are shown in Figure 11 (solid line). PMMA degraded in three steps, and was virtually completely degraded by 420 $^{\circ}$C. The first stage of degradation occurred in the temperature range 205-290 $^{\circ}$C. The second stage of the degradation occurred in the temperature range 290-390 $^{\circ}$C. The third stage of degradation occurred above 390 $^{\circ}$C. However, the graft copolymers degraded at a slower rate as the UM content and average chain length in the graft copolymers increased.

The TGA curves of n-PBMA-g-urethane copolymers recorded under nitrogen compared with those of PBMA homopolymers are shown in Figure 12 (solid line). n-PBMA degraded in three steps, and was virtually completely degraded at 450 $^{\circ}$C. The first stage of degradation occurred in the temperature range 175-250 $^{\circ}$C. The second stage of the degradation took place in the temperature range 250-350 $^{\circ}$C. The third stage of degradation occurred above 390 $^{\circ}$C. However, the graft copolymers degraded at a slower rate as the UM content and average chain length in the graft copolymers increased.
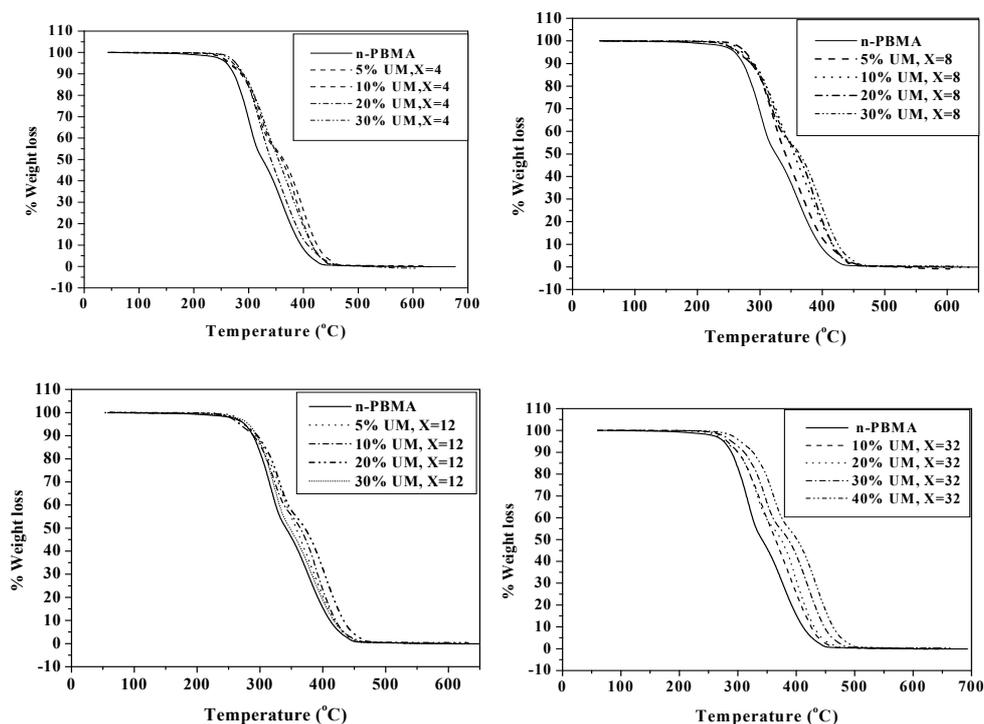
Figure 12. TGA curves of n-BMA copolymerized with different amounts of UMs of various average chain lengths: (a) X=4, (b) X=8, (C) X=12 and (d) X=32

3.3 Phase Separation

DMA analysis was used to determine the T_g values of the samples of UM and graft copolymer, and to investigate the phase separation between urethane and acrylate segments of the synthesized acrylate-g-urethane copolymers.

Figure 13 shows the tan δ curves of UMs having different average chain lengths, as detected by DMA. The tanδ traces of the UMs showed only a single T_g (i.e. the onset of the long-range, coordinated molecular motion), which suggested homogeneity of the polymer. T_g increased with increasing UM average chain length. Table 7 gives the T_g data for UMs having different average chain lengths, as determined by DMA.
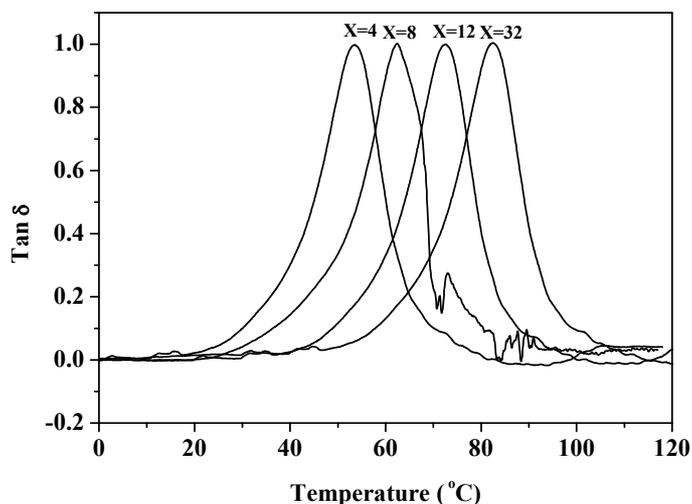
Figure 13. Tan δ curves of UMs of different average chain lengths

Table 7. T_g values of UMs of different average chain lengths, as determined by DMA

UM	T_g (°C)	T (°C)
	at onset*	at max peak height
X=4	39	53
X=8	45	62
X=12	57	72
X=32	63	80

In the PMMA-g-urethane copolymers PMMA is more abundant than the UM component. PMMA homopolymer had a glass transition temperature of ± 115 °C. When MMA was copolymerized with UM the T_g of the copolymer shifted to a lower temperature, to between the T_g values of the UM and PMMA. The tanδ traces of the UMs showed only a single peak between the PMMA and UM peaks, which suggested a homogeneous (i.e. not phase separated) material. Figure 14 shows tan δ traces of PMMA-g-urethane copolymers containing different amounts of UMs (average chain length X=12). The T_g was measured as the onset temperature, and the T_g values of the PMMA-g-urethane copolymers varied between 76-115 °C. The T_g values of all the synthesized PMMA-g-urethane copolymers are tabulated in Table 8.
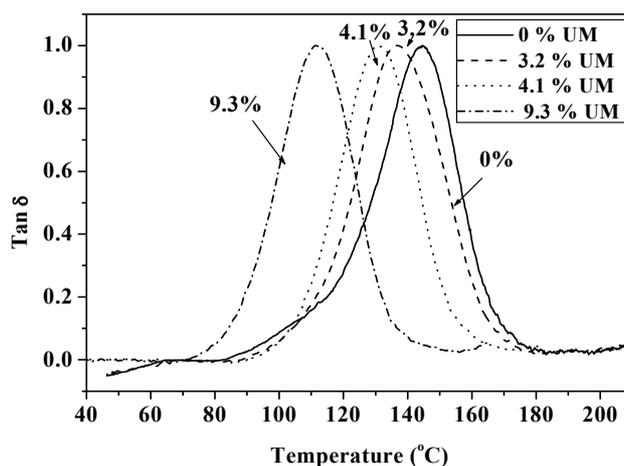
Figure 14. Tan δ curves of PMMA-g-urethane copolymers containing different amounts of UM of average chain length X=12

Data in Table 8 show that PMMA-g-urethane graft copolymers had single T_g values and that T_g decreased with increasing UM content. This confirmed that the UMs and PMMA segments in the PMMA-g-urethane copolymer are either completely compatible or that there was no large scale phase separation. In addition, the T_g values of the graft copolymers were shifted to lower temperatures because of the presence of pendant groups of the UMs (graft chain). It was further noted that the T_g of PMMA-g-urethane copolymers decreased as the amount of UM incorporated into graft copolymers increased and as the urethane average chain length increased.

In the n-PBMA-g-urethane copolymers, the n-PBMA segment is the more abundant and flexible chain in the copolymer. n-PBMA homopolymer had a glass transition temperature of ± 25 °C, which is lower than the T_g of the UMs (Table 7).

Table 8. T_g values of PMMA-g-urethane copolymers, as determined by DMA

UM	Feed ratio by wt MMA/UM (%)	UM% in PMMA-g-urethane	T_g (°C) at onset	T (°C) at max peak height
	100/0	0.0	115	144
	90/10	3.0	110	137
X=4	80/20	4.7	104	131
	70/30	10.7	95	122
	90/10	-	108	133
X=8	80/20	5.3	100	127
	70/30	9.2	93	117
	90/10	3.2	106	129
X=12	80/20	4.1	95	121
	70/30	9.3	88	113
	90/10	-	102	125
X=32	80/20	5.2	96	118
	70/30	8.7	85	108
	60/40	10.9	80	101

Figure 15 shows typical tanδ curves of n-PBMA-g-urethane copolymers containing different amounts of UMs of average chain length X=12. The copolymers each had only one T_g (measured as the onset temperature) at 19-45 °C. This confirmed that the UM and n-PBMA segments were largely compatible and that copolymers were formed.

The T_g values of all the synthesized n-PBMA-g-urethane copolymers are tabulated in Table 9. The T_g values increased as the amount of UM incorporated into the graft copolymers increased. Lower T_g values were observed when the UM average chain length increased due to the increasing the average chain length, forcing demixing, probably on the nanoscale. This would imply that the n-PBMA domains are pure and the T_g will decrease, and approach the T_g value of n-PBMA (instead of one homogeneous peak there are now two peaks close together, forming a peak envelope).
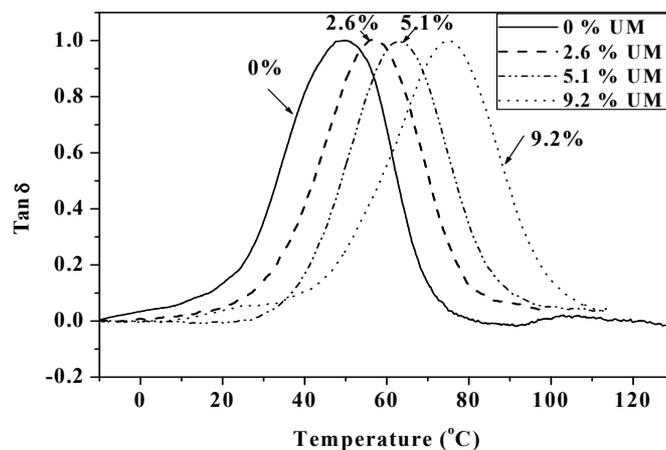
Figure 15. Tan δ curve of n-PBMA-g-urethane copolymers containing different amounts of UM of average chain length X=12

When the average chain length of UM was increased to X=32 and the amount of UM increased to 40% during copolymerization (at 11.7% UM incorporation into the graft copolymers), microphase separation occurred. Two T_g values are observed in Figure 16. The tan δ curve shows only one peak, as it is less sensitive to incompatibilities, but the loss and storage modulus curves show two peaks (which shows only one peak on all other graft copolymers that were synthesized in this study) at different temperatures (19 and 76 °C), which are due to the softer n-PBMA and harder UM, respectively. This indicated that there was a degree of micro-phase separation. Detection of glass transition temperatures associated with each of the respective homopolymers indicated that the UM segments and n-PBMA segments in the above case were locally separated (microphase separation) into distinct regions. This result is supported by the TEM image presented in Figure 17, which shows nanosegregated regions of dark UM segments and lighter n-PBMA.

Table 9. T_g values of n-PBMA-g-urethane copolymers, as determined by DMA

UM	Feed ratio by wt%	UM in	T_g (°C)	T (°C)
	n-BMA/UM	n-PBMA-g-urethane (%)	at onset	at max peak height
	100/0	0.0	19	49
	90/10	3.1	30	61
X=4	80/20	5.6	37	68
	70/30	10.9	42	80
	90/10	-	28	59
X=8	80/20	4.7	36	65
	70/30	9.1	40	78
	90/10	2.6	25	58
X=12	80/20	5.1	34	64
	70/30	9.2	41	77
	90/10	-	22	53
X=32	80/20	3.7	30	58
	70/30	8.1	38	70
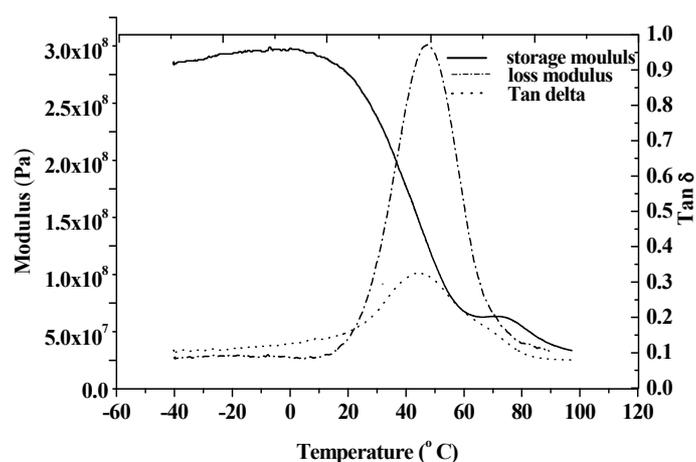
Figure 16. Tanδ, loss and storage modulus curves of n-BMA copolymerized with 40% UM of average chain length X=32
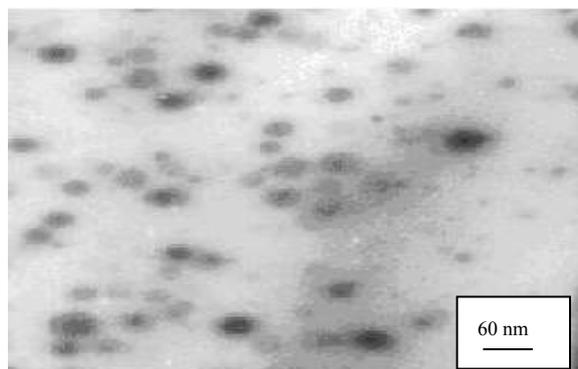
Figure 17. TEM image of n-PBMA-g-urethane copolymer tinted with osmium tetroxide. The light regions are soft n-PBMA domains and the dark regions are hard urethane domains

4. Conclusion

Novel urethane macromonomers, predominantly monofunctional, and having different urethane average chain lengths, were successfully synthesized and then used in solution free-radical copolymerization of MMA and n-BMA. The existence of the grafted urethane macromonomer with PMMA and n-PBMA was confirmed using FTIR, ^{1}H NMR, ^{13}C NMR and GPC (with UV and RI detectors) and DMA. The yield of both graft copolymers decreased as the concentration of the urethane macromonomers in the copolymerization feed increased. As the concentration of urethane macromonomer in the copolymerization feed increased, more urethane macromonomer was incorporated into the PMMA and n-PBMA backbones, and better thermal stability was found in both PMMA-g-urethane and n-PBMA-g-urethane. In most of the graft copolymers a large measure of compatibility was observed. The T_g values of the PMMA-g-urethane decreased as the concentration of urethane macromonomer increased in the copolymerization feed while, the T_g values increased as the concentration of urethane macromonomer was increased in the n-PBMA-g-urethane copolymer. A single peak, indicating compatibility, was observed in all of these cases. In the case of the highest UM content for the longest UM in an n-PBMA-g-urethane copolymer there were two glass transition temperatures, corresponding to the n-PBMA and urethane fractions, respectively. The result also indicated that n-PBMA and urethane moieties exhibited microphase separation when the average chain length of UM was adequately long at sufficient UM content UM content, as confirmed by TEM.

Acknowledgments

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