International Journal of Engineering Research-Online
A Peer Reviewed International Journal
Articles available online http://www.ijoer.in; editorijoer@gmail.com

Vol.10, Issue.1, 2022
Jan-Feb.

RESEARCH ARTICLE

ISSN: 2321-7758

Synthesis and Characterization of Methacrylic/Urethane Graft Copolymer, Urethane Macromonomer (UM1) Based on 4, 4 Diphenylmethane Diisocyanate and Ethylene glycol

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DOI: 10.33329/ijoer.10.1.1

ABSTRACT

Various percentages of the respective UM2 (0_55 wt % of methacrylate monomers) were incorporated into polymethyl methacrylate (PMMA) and poly n-butyl methacrylate (PnBMA) backbones via solution free-radical copolymerization. The resulting methyl methacrylate-g-urethane and n-butyl methacrylate-g-urethane copolymers were characterized by ^{1}H-NMR,^{13}C-NMR, FTIR, SEC with double detectors (UV and RI), light scattering, UV-Vis, HPLC. Weight percentages of UM1 incorporated into the methyl methacrylate-g-urethane copolymers were calculated using FTIR, UV-Vis and ^{1}H-NMR techniques.

Keyword; polyurethane, polyacrylate and graft copolymer

Introduction

Historically, polyacrylates have found extensive use as adhesives and coatings1. Most polyacrylates generally have a low glass transition temperature (Tg), which makes them suitable to handle, process, and purify. In addition, the wide range of available acrylate monomers allows the physical properties of their polymers to be tailored. Polyacrylates are less expensive than PUs. However, a problem associated with polyacrylates is that their flexible backbones impart limited thermal stability and mechanical strength.

Properties and applications of polymers can be extended by copolymerization with other polymers to give new materials with tailored properties and performances[2]. The ability to produce polymers with well-defined and controlled structures has led to the study of structure-property relationships in polymer materials. An understanding of this relationship is essential in predicting polymer properties and in designing materials with new properties.

Graft copolymers with a backbone of one polymer and branches of other polymer exhibit material properties that are a combination of both homopolymer constituents. There are several reviews of graft copolymers[3,4,5,6]. The presence of long chain branching has a dramatic effect on the dynamic and rheological behavior of well-entangled polymers.[7,8]

The macromonomer technique is the simplest way to prepare graft copolymers[9]. Macromonomers are polymers end-capped with a polymerizable end group able to copolymerize with low molecular weight monomers, so the macromonomers can either homopolymerize to

give a regular comb polymer or copolymerize with a suitable monomer to give a graft copolymer. These end-functional polymers can be prepared by modifying polymer end groups or, very conveniently, by using functional initiators in living/controlled polymerizations[10].

Many researchers have studied creating specialized copolymers of various architectures, for offering new properties[11,12,13,14,15] One of the most attractive copolymers is graft copolymers, which contain polymer units that are incorporated as side chains on a backbone polymer, and which cause that polymer to exhibit good phase separation[16,17] Graft copolymers have been used for a variety of applications, such as impact-resistant plastics, thermoplastic elastomers, compatibilizers, polymeric emulsifiers, hydrogels, drug delivery polymers, and gas permeation membranes[18,19,20] Graft copolymers are generally prepared by three general methods: the grafting-onto, grafting from, and the macromonomer method.[21]

The "grafting onto" method involves a coupling reaction between the backbone and the branches, which are prepared separately by living polymerization methods[22.] Functional groups are distributed along the chain backbone, and can react with the living branches. In the "grafting from" method, active sites are required along the main chain backbone that are able to initiate the polymerization of the second monomer, resulting in the formation of branches and the final graft copolymer. In the macromonomer method, polymer chains having polymerizable end groups, known as "macromonomers", are copolymerized with another monomer in order to produce the graft copolymer[23].

To the best of the author's knowledge this is the first report on the use or synthesis of monofunctional urethane macromonomers. In this present study, urethane macromonomers (UM1) which was synthesized in our previous study[24] to be predominantly monofunctional, UM1 will be used as grafts in solution free-radical copolymerization with methacrylate monomers.

Experimental

Various quantities of UM1 were copolymerized with various quantities of MMA, and with various quantities of n-BMA, respectively, using solution free radical copolymerization

Choice of solvent

The choice of a good solvent for the acrylate and UM1 was done by trail and error. Many different solvents were tried, such as benzene, toluene, acetone, acetonitrile, methanol, ethanol, dimethylformamide (DMF) and dimethylsulfoxide (DMSO). Complete solubilization of the UM1 and acrylate was achieved by using DMF or DMSO. However, DMSO could not readily be used because it crystallizes at room temperature and needs to be heated before use. Therefore DMF was chosen as the solvent for all the copolymerization reactions of methacrylate and UM1

Materials

n-BMA (Aldrich, 99%) and MMA (ICI Chemicals and Polymers, 99.9%) were washed with a 0.4potassium hydroxide solution (KOH, Associated Chemical Enterprises, 85%), followed by distillation under reduced pressure to remove the inhibitor. The monomers were stored for hours at ^{0} ^{o}C over molecular sieve (4 Å). The following materials were also used: potassium persulphate (KPS, 99%), methanol (MeOH, 99.8%), dimethylformamide (DMF, 99.5%), distilled and deionized water (DDI, from a Millipore milli-Q purification system) and silicon oil (SA Silicones). 2,2'-Azobis(isobutyronitrile) (AIBN, Delta Scientific, 98%) was recrystallized from methanol.

Purification of the monomers

MMA and n-BMA monomers were first washed with 0.4 M KOH followed by distillation under reduced pressure to remove any other impurities using potassium persulfite. The monomers were first washed with 0.4 M KOH solution to remove the hydroquinone inhibitor. The distillation was carried out under reduced pressure and low heat (about 45 ^{o}C) to avoid self polymerization of the monomers. The distilled fractions were collected and dried over anhydrous magnesium sulfate to ensure a completely dry

monomer. The monomers were stored at -8 °C prior to use.

Methacrylic-urethane copolymer formulations

Formulations used to prepare the different PMMA-g-UM1 copolymers and PnBMA-g-UM1 copolymers are shown in Table 1

Table1: Formulations used for the preparation of PMMA-g-UM1 and PnBMA-g-UM1 copolymers

Reagent	Mass of reagents used in various experiments			
	EXP.1* (g)	EXP.2* (g)	EXP.3* (g)	EXP.4* (g)
MMA	5.00	4.50	3.75	2.25
AIBN**	0.05	0.045	0.047	0.025
UM	0.00	0.50	1.25	2.75
DMF	35.00	35.20	35.45	35.00
n-BMA	5.00	4.50	3.75	2.25
AIBN**	0.05	0.045	0.047	0.025
UM	0.00	0.50	1.25	2.75
DMF	35.00	35.20	35.45	35.00

*The concentrations of the UM1 were between 0 and 55 wt % (relative to MMA or n-BMA), and the quantities of UM1 and MMA or UM1and n-BMA in all copolymerization feeds were based on 5 g.

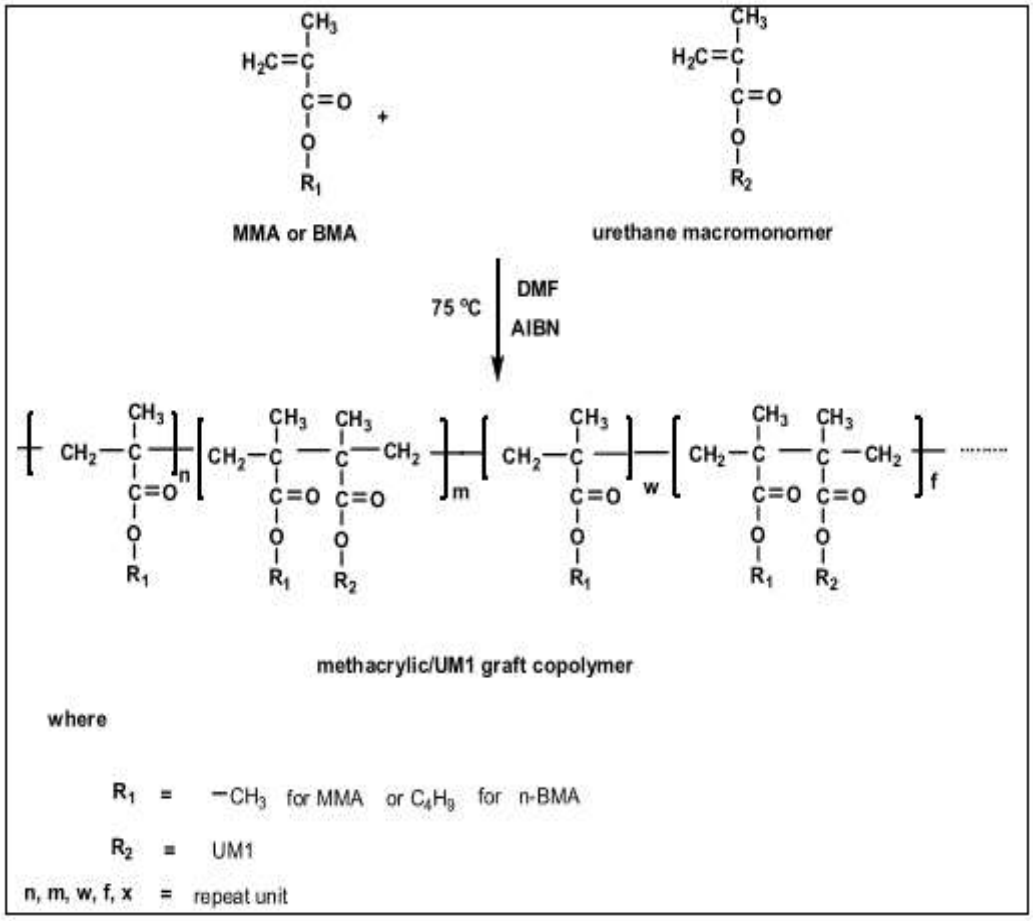
** The concentration of initiator (AIBN) was varied between 0.7 to 1% by weight according to n-BMA. (This is actually considered high, and will affect the molecular weight of graft copolymers). These concentrations of initiator were chosen because at low concentration of initiator the yield of graft copolymer is very low (as can be seen in Table 2) because of the high chain transfer constant to DMF, the solvent used.

Table 2: Effect of the concentration of initiator on yield of graft copolymers

Concentrationof AIBN (wt %)	Feed polymerization			Graft yield from PMMA-g-urethane(g)	Graft yield from PnBMA-g-urethane(g)
	UM1 (g)	MMA (g)	nBMA (g)		
0.1	0.50	4.50	4.50	1.54	1.92
0.4	0.50	4.50	4.50	2.42	2.81
0.5	0.50	4.50	4.50	2.71	3.15
0.7	0.50	4.50	4.50	4.74	4.94
1	0.50	4.50	4.50	4.85	4.01
1.4	0.50	4.50	4.50	4.18	4.42

Experimental procedure

Solution free radical copolymerization was carried out in a 250-ml three-neck reactor with magnetic stirring, under a nitrogen atmosphere. Scheme1 shows the synthesis procedure for the graft copolymers. DMF was first introduced into the reactor. MMA or n-BMA, and AIBN (1% wt relative to the monomer), were then charged into the reactor, followed by the UM1. Various concentrations of UM1 were used: 0, 10, 25 and 55 wt % relative to MMA or n- BMA. The polymerization temperature was 75 oC and the reaction time was 24 h. The copolymers were precipitated in MeOH, then separated by filtration and dried under vacuum at room temperature overnight. The unreacted UM1 was removed by precipitation using DMF as solvent and THF and MeOH as non-solvent. The removal of the unreacted macromonomer was tracked using SEC with UV and RI detectors.



Scheme 1: Formation of methacrylic-urethane graft copolymer

Characterization methacrylate-g-urethane copolymers

Different techniques were used in this study to analyze and characterize the UM1 and methacrylate-g-urethane copolymers

Fourier-transform infrared spectroscopy FTIR

During the synthesis of the UM1, FTIR samples were prepared by extracting some polymer (dissolved in DMF) from the reactor at various time intervals. The samples were then run against a DMF background between sodium chloride discs. This was done to monitor the NCO content during the UM1 synthesis. Other IR analyses were performed on a Perkin Elmer Paragon 1000 FTIR instrument at 32 scans, using a photo-acoustic (PAS) cell, so eliminating sample preparation. FTIR spectra were recorded in the range 3500-500 cm^{-1}, with a resolution of 4 cm^{-1}. Samples were prepared by grinding about 2-5 mg of the graft copolymer (after extraction) with 120 mg KBr, followed by pressing to form transparent disks

Matrix-assisted laser mass spectrometry MALDI-TOF-MS

MALDI-TOF-MS were recorded on a Voyager–DE STR (Applied Biosystems, Framingham) equipped with a nitrogen 337 nm laser in the reflector mode, at 25 kV accelerating voltage, and with delayed extraction. The matrix was trans-2-[3-(4-tert- butylphenyl)-2-methyl-2-propenylidene] malononitrile (Aldrich) and potassium trifluoro acetate (KTFA) (Aldrich) was used as the cationizing agent. For each analysis, the analyte sample was prepared by first making up the following concentrations of the matrix, KTFA, and sample, in DMF, separately: 35 mg/mL matrix; 5 mg/mL KTFA; 1 mg/mL sample, before mixing them in the ratio of 4:1:4 and hand spotting on the target plate. One thousand laser shots were obtained for each spectrum. All the MALDI-TOF-MS results reported in this work were obtained as described here

Proton NMR ^{1}H-NMR

^{1}H-NMR spectra were recorded in deuterated-DMSO, using a Varian Unity INOVA 400 MHz NMR instrument, and a Varian VXR 300 MHz NMR instrument. The NMR spectra were used to determine the chemical composition of macromonomer and to characterize the graft copolymers. All spectra were referenced to tetramethylsilane (TMS) at 0 ppm.

Carbon NMR ^{13}C-NMR

^{13}C-NMR spectra were obtained in the same manner as the proton ^{1}H-NMR spectra, but at a frequency of 600 MHz, using a Varian Unity INOVA NMR instrument. Long runs (overnight) were used

Size exclusion chromatography SEC

Number average and weight average molecular mass (Mn) as well as polydispersity indices were obtained through the use of SEC with two concentration dependent detectors, UV and RI. The UV was adjusted to 254 nm, corresponding to the absorption of the aromatic ring. Therefore this detector only detects a response when there are aromatic rings in the sample, for example the urethane macromonomer. UM1 and methacrylate-g-urethane copolymers were dissolved in dimethylactamide (DMAc) (5 mg/ml) and filtered through a 0.45-µm nylon filter. Analyses were carried out with a system comprising Waters 610 fluid Unit, Waters 410 differential refractometer at 30 °C, Waters 717plus auto sampler and Waters 600E system controller. Plgel columns 5 µm Mixed-C 300X7.5 mm (Polymer Laboratories) was used. The column oven was set at 30 °C. The DMAc solvent flow rate was 0.5 mL/min, and the injection volume was 100-µl. The system was calibrated with narrow polystyrene standards. Millennium 2005 was used for data acquisition and data analysis

Light scattering LS

The dn/dc values of the graft copolymers were determined for pure graft copolymers, using a Scan Ref monocolor instrument at a wavelength 633 nm. The dn/dc value for each graft polymer was determined by measuring the refractive indices of a series of prepared polymer samples in DMAc, of various concentrations, prepared from single stock solution (0.5 1.0mg/mL, 2.0 mg/mL, 3.0 mg/mL and 4.0 mg/mL). Samples of each graft (2.0 mg/mL) were injected in the SEC which is coupled to a multiangle light scattering (MALLS) detector, for the determination of the absolute molar mass of the graft copolymers.

Gradient polymer elution chromatography GPEC

HPLC is used to separate molecules under high pressure in a stainless steel column filled with a suitable matrix. The solvent/nonsolvent combination is an important parameter in gradient HPLC. The separation takes place with respect to the polarity of the different components. The nonpolar polymer elutes as the first component from the stationary phase; this is normally the acrylic homopolymers e.g. PMMA or PnBMA, if present. This component is followed by the graft copolymer, which is the most polar component in the product and which may contain unreacted urethane macromonomer as the second component.

The gradient HPLC system comprised a Waters 2690 separation module Alliance equipped with a Nucleosil CN column, pore size 100 Å, particle size 5µm, 12.5×4 (ID) cm. A constant column temperature of 40 °C was maintained through the use of an oven. The detector used was an evaporative light scattering detector (ELSD) PL-ELS 1000 from Polymer Labs, which was operated at 80 °C, with an N2 carrier gas flow rate of 1 SLM (standard litres per min). Data collection and processing were performed using PSS Win SEC7 from Polymer Standards Service.

Separation of a complex mixture with respect to the chemical composition distributions (CCDs) of the different species can be achieved by gradient HPLC. To determine the CCD of the graft copolymers CCl3/THF or THF/DMF gradient was used as the mobile phases, and a cyano-modified silica gel (Nucleosil CN) as the polar stationary phase.

Ultraviolet/visible spectroscopy UV/Vis

A Perkin Elmer UV/visible Lambda 20 Spectrometer was used to identify the UV absorption band of the aromatic ring bond in the structure of the urethane macromonomer. The data were analyzed with UV

W in lab v.4.2 software. Quartz cuvettes (supplied by CND Scientific) with a 10 mm path length were used.

Results and discussion

SEC analysis

The PMMA-g-UM1 and PnBMA-g-UM1 copolymers were synthesized by solution free radical polymerization. The molecular structure was confirmed using SEC with double detectors UV and RI.

The ability of UM1 to undergo copolymerization was determined using MMA and n-BMA respectively as monomers. Different amounts of UM1 were copolymerized with different amounts of MMA and n-BMA under free radical copolymerization conditions. The resulting graft Yield of graft copolymer equals the amount of graft copolymer after extracting unreacted UM1 (g) divided by 5 (g) which is the total amount of UM1 and methacrylic monomer in the copolymerization feed. Copolymers were isolated by precipitation from DMF solution into excess methanol

Table 3 illustrates the formulations used to prepare the graft copolymer with different amounts of macromonomer. The yield was determined gravimetrically after extraction of the unreacted macromonomer. The yield of the PMMA-g-UM1 copolymers ranged between 70% and 84% and that of the PnBMA-g-UM1 copolymers range between 69% and 81% (all the calculations were done after extraction of the unreacted UM1.

Table 3 shows that all PMMA-g-UM1 and PnBMA-g-UM1 copolymers had molecular weights of about 70,000, which is higher than of the starting UM1 (Table 2). In addition to this, the molecular weight values of the graft copolymers obtained by SEC measurements were generally much lower than the absolute molecular weight because linear polystyrene has a much larger hydrodynamic volume than the corresponding graft copolymers of the same molecular weight[25].

Table 3: Formulation and characterization of graft copolymers

	Samplecode	UM1 (g)	crylate(g)	Graft copolymer Mn (g/mol)	Graft copolymer Mw (g/mol)	PDI	Yield* % of graft copolymer
			MMA				
PMMA-g-	G10M	0.50	4.50	$7.39 X10^4$	$1.15 X10^5$	1.56	84
	G25M	1.25	3.75	$7.25 X10^4$	$1.36 X10^5$	1.83	76
	G55M	2.75	2.25	$7.13 X10^4$	$1.47 X10^5$	2.07	70
			n-BMA				
PnBMA-g-	G10B	0.50	4.50	$7.02 X10^4$	$1.17 X10^5$	1.68	81
	G25B	1.25	3.75	$6.82 X10^4$	$1.38 X10^5$	2.03	77
	G55B	2.75	2.25	$6.34 X10^4$	$1.47X10^4$	2.33	69

Yield of graft copolymer equals the amount of graft copolymer after extracting unreacted UM1 (g) divided by 5 (g) which is the total amount of UM1 and methacrylic monomer in the copolymerization feed.

Figure 1 shows SEC traces for UM1, PMMA and PnBMA, characterized by SEC with a UV detector (254 nm). The UV detected the UM1 but not the PMMA and PnBMA absorptions, which were too small to detect at this wavelength. The UM1 has a strong UV absorption due to the aromatic ring in the polymer chain.

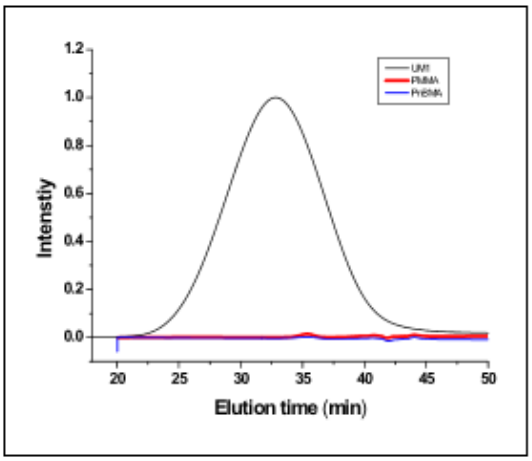


Figure 1: SEC traces of UM1, PnBMA and PMMA (UV detector).

Figure 2 and Figure 3 are examples of SEC traces of the graft copolymer of PMMA-g- UM1 and PnBMA-g-UM1 (25 wt % macromonomer), respectively, before extraction. A bimodal distribution curve was obtained after the copolymerization reaction. The first peak at a lower retention time is attributed to the graft copolymer. The red line represents the RI response corresponding to the graft copolymers PMMA-g-UM1 and PnBMA-g-UM1. The UV detector response is shown by the blue line, and the lower retention peak shows the presence and distribution of the UM1 in the PMMA or PnBMA backbone. The second peak is attributed to the presence of the unreacted UM1, since there is a strong UV response for this peak. This is expected as UM1 contains two terminated groups.

The segment and repeat unit density around the propagating radical site of the formed copolymer is relatively large, and increases with the degree of polymerization, making the insertion of the macromonomer more difficult. The incompatibility issue between the backbone and the branches also plays a large role in decreasing the reactivity of the macromonomer, as discussed by Ito and Kawaguchi,3 Hong et. al,[26] and Meijs and Rizzardo[27].

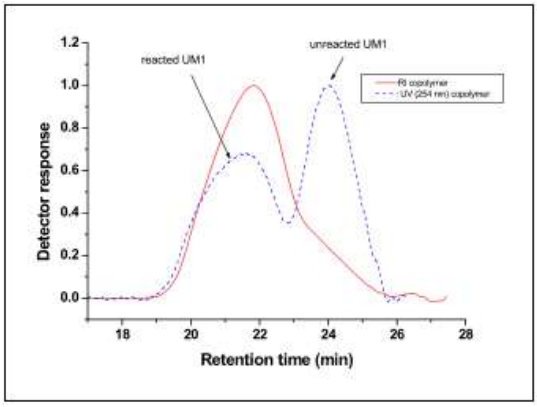


Figure2: SEC traces of unextracted graft copolymer PMMA-g-UM1 (25 wt %).(RI and UV detector responses have been normalized

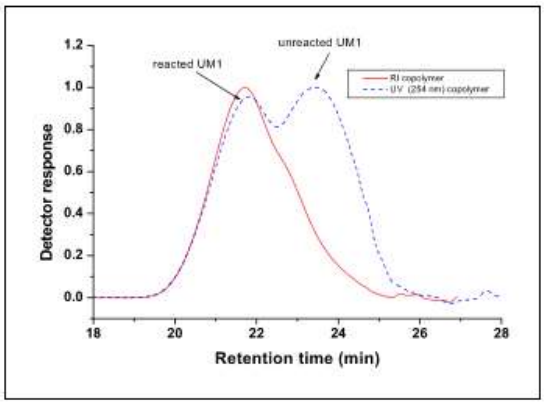


Figure 3: SEC traces of unextracted graft copolymer PnBMA-g-UM1. (Note: RI and UV detector responses have been normalized.)

The repeat unit density around the propagating radical site in the copolymer is relatively large, and increases with the degree of polymerization, making the insertion of the macromonomer more difficult. This is especially so if there is an incompatibility issue between the backbone and the graft as this will play a large role in decreasing the reactivity of the macromonomer, as discussed by Ito et al.[19] Hong et al.,[26] Meijs and Rizzardo.[27]This may not be a major issue as there is a large fraction of unreactive UM1.

Extraction of unreacted macromonomer

Methanol is a nonsolvent for PMMA, PnBMA and the corresponding methacrylate-g-urethane copolymers. However, there is some unreacted UM1 (UM1 containing both MeOH end groups which cannot react during graft

copolymerization or urea side reaction and some unreacted UM1 (UM1 containing at least one 2-HEA end group, which did not react during graft copolymerization) were extracted by precipitation in methanol. However a little unreactive and unreacted UM1 also precipitated along with the graft copolymer, as indicated by the slight shoulder at low molecular weight in Figures 2 and 3 . The unreacted UM1 was further removed by precipitation using DMF as solvent and THF and MeOH as nonsolvent. A sample of about 0.5 g of graft copolymer was dissolved in about 10 ml DMF and precipitated in THF. The solution was filtered, and then precipitated again in MeOH. The resultant graft copolymer and PMMA or PnBMA homopolymers precipitated out of solution, while the unreacted macromer remained soluble. The extraction of the unreacted macromer was tracked using SEC with a RI detector, as shown in Figures 5 and 6.

Figure 4 is an example of MALDI-TOF-MS showing (a) UM1 before using the UM1 in a free radical copolymerization and (b) extracted unreacted UM1 after using the UM1 in a free radical copolymerization. The percentage of graft formation was calculated gravimetrically after extraction of the unreacted macromer. The formulation and characterization of the grafts are tabulated in Table 1. The yields of the graft polymers were 69-84% and all the calculations were done after removing all unreacted macromere

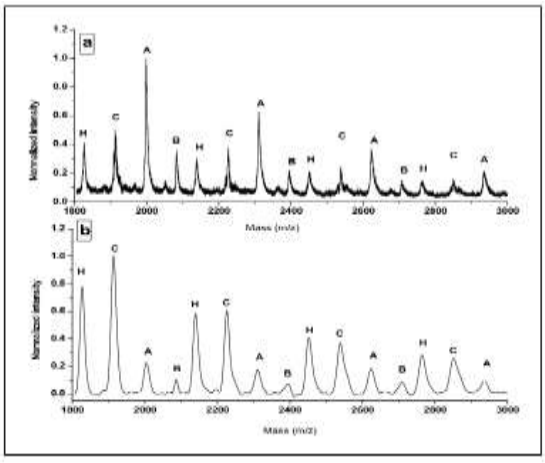


Figure 4: MALDI-TOF-MS (a) before using UM1 in free radical copolymerization and (b) extracted UM1 after free radical copolymerization

Characterization of graft copolymers after extraction

SEC analysis

SEC equipped with a dual detector system (RI and UV) was used to characterize the graft copolymers. The UV detector was set up at a wavelength of 254 nm, which is suitable for detecting UM1 the aromatic rings. A UV response was observed for all the graft copolymers. The distribution of the UV response gives an idea of the branch content in the graft. Figures

5and 6 are examples show the SEC of the graft copolymers PMMA-g-UM1 and PnBMA-g-UM1 after extraction of the unreacted macromer. The distribution of the UV response associated with the UM1 branches on the MMA or n-BMA backbones indicates that the UM1 branches are distributed evenly throughout the graft polymer, and no UV peaks for unreacted UM were observed at high retention time and also the retention time of the graft copolymer samples were shifted to lower time compared to the retention time of the starting materials (e.g. retention time of UM1). This result indicates that the molecular weights of the graft copolymer samples increased due to the grafting reaction. This was observed for all the synthesized grafts, with different macromonomer contents. In the two Figures below the UV response almost mirrors the RI response, but there is a significant difference at the longer retention times (note that the detector response has been normalized). This is an indication that there may not be a totally uniform distribution of the graft in the polymer

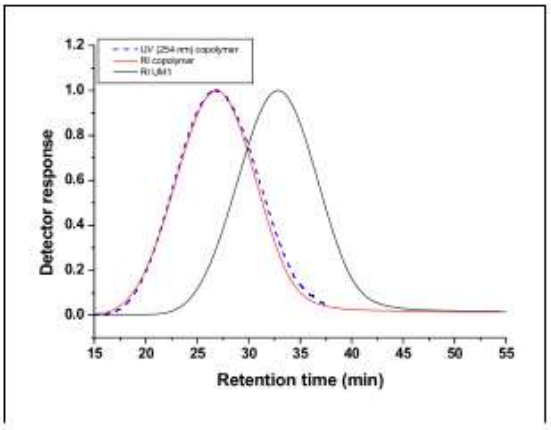


Figure 5: SEC traces of PMMA-g-UM1 (25 wt % UM1) illustrating the UM1 distribution

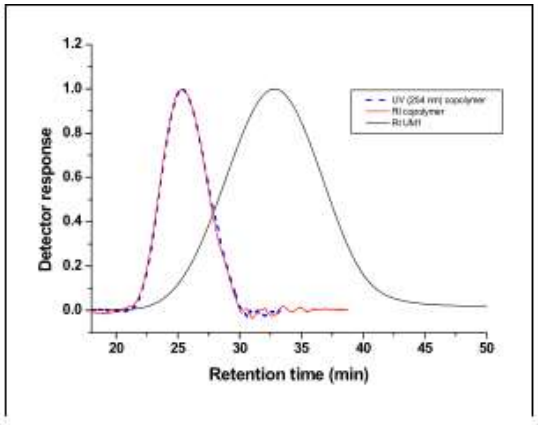


Figure 6: SEC traces of PnBMA-g-UM1 (25 wt % UM1) illustrating the UM1 distribution

The yields of the copolymerization reactions for both PMMA-g-UM1 and PnBMA-g-UM1 copolymers are shown Table 1.

The yields of both PMMA-g-UM1 and PnBMA-g-UM1 copolymers decreased as the quantities of the UM1 are increased. This is because as the weight fraction is increased, so too does the weight fraction of the unreactive UM1 increase, which, after removal with methanol, resulted in a decrease in the percentage yield of the graft copolymers.

GPEC analysis

It is well known that graft copolymers synthesized, using a low molecular weight monomer and a macromonomer, by radical polymerization display heterogeneity in terms of both molecular mass and chemical composition. Therefore, the characterization of these materials by a single technique (for example SEC) is made difficult by the effects of both the molecular The yields of the copolymerization reactions for both PMMA-g-UM1 and PnBMA-g-UM1 copolymers are shown Table 1.

The yields of both PMMA-g-UM1 and PnBMA-g-UM1 copolymers decreased as the quantities of the UM1 are increased. This is because as the weight fraction is increased, so too does the weight fraction of the unreactive UM1 increase, which, after removal with methanol, resulted in a decrease in the percentage yield of the graft copolymers. Mass and chemical composition on the separation mechanism. Techniques such as SEC, with selective detection, cannot be used to fully characterize copolymers due to the fact that the hydrodynamic volume, necessary for characterization, is dependent on the chemical composition. Gradient Elution High Performance Liquid Chromatography also known as Gradient Polymer Elution Chromatography (GPEC) is a good technique for separating via chemical composition.

Graft copolymers may contain ungrafted homopolymer and unreacted macromonomer, as well as copolymer that vary in composition. In this study GPEC was used to analyze the copolymers and monitor the extraction of unreacted macromer, as well as to determine the chemical composition distribution of synthesized graft copolymers.

HPLC analysis was performed with a combination of precipitation HPLC and adsorption or retention HPLC. By starting with a non-solvent and increasing the percentage of a good solvent, on a stationary phase possessing strong adsorption interactions with small-pore column packings, copolymer retention was achieved that resulted in compositional separations. In this study a Nucleosil C18; 100Å (25 x 0.46) column was used. A compromise between copolymer solubility and chromatographic solvent strength was used to ensure copolymer separation over a broad chemical composition distribution.

GPEC of PMMA-g-UM1 copolymers

The premise on which the GPEC separation works can be explained as follows: PMMA homopolymer is completely soluble in chloroform

and is therefore unretained on the silica packing. The graft copolymer however is insoluble in the starting solvent, chloroform. The mode of retention is therefore the governing factor in determining the actual separation. The retention process in the case of the PMMA-g-UM1 copolymer, using chloroform/DMF as solvent system over silica packing, relies on initial precipitation, followed by adsorption retention after redissolution of the graft copolymer in the solvent gradient.

Several gradients were tested before optimal separation was obtained. Variables that were investigated included: the rate at which the percentage of non-solvent to good solvent was added and the quantity of sample injected, furthermore both linear and non-linear gradients were tested. Figure 7 shows examples of some of the gradients that were tested (but not used, because they either resulted in bad separation or variable separation). Profile #1, for example, yielded good separation but results were not consistent and therefore this was unusable. For all profiles the quantity of sample injected on the GPEC column was varied from 8 µl to 20 µl. Profile #4 yielded good separation between PMMA, PMMA-g-UM1 copolymer and unreacted UM1, and more, importantly, results were consistent for multiple runs. Here it was also found that a sample injection volume of 10 µl provided optimal results. Throughout the development of the gradient profile a sample flow rate of 1 mL/min was used runs. Here it was also found that a sample injection volume of 10 µl provided optimal results. Throughout the development of the gradient profile a sample flow rate of 1 mL/min was used

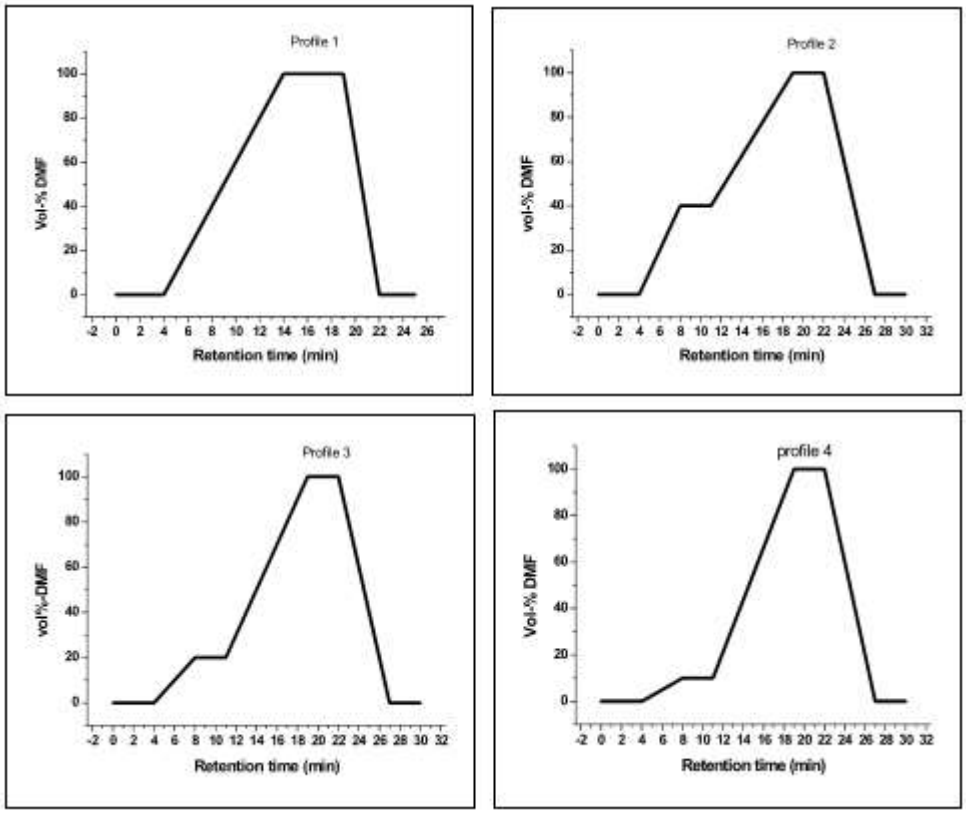


Figure 7: Example of gradient elution profiles considered for the separation of PMMA-g-UM1 copolymer: stationary phase: Nucleosil C18; 100Å; eluent:chloroform/DMF

PMMA standard and UM1 synthesized in this study were used to identify their retention times in the elution profile. Figure 8 shows the retention times of these components. PMMA elutes between 2 and 4 min whereas UM1 elutes between 13 and 17 min

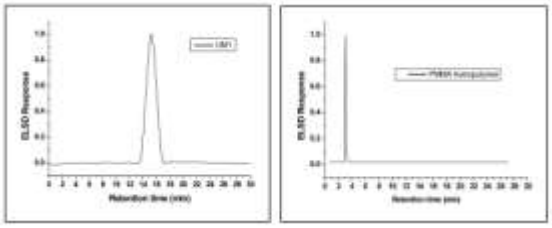


Figure 8 : Gradient HPLC elution plots of UM1 and PMMA homopolymer

The gradient HPLC chromatogram of the typical example of the PMMA-g-UM1 copolymer after gradient profile separation is presented in Figure 9. The assignment of the peaks was carried out by comparison with the chromatographic behaviour under similar conditions used for UM1 and PMMA separation using a reversed phase column (Nucleosil C18; 100Å). The first peak was assigned to PMMA homopolymer, followed by the graft copolymer PMMA- g-UM1, and finally unreacted UM1

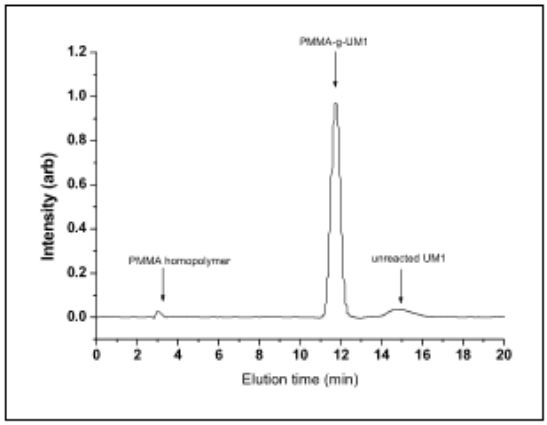


Figure 9: Gradient HPLC chromatogram of the PMMA-g-UM1 copolymer (G55M). (Stationary phase: Nucleosil C18; 100Å; eluent: chloroform/DMF; detector: ELSD

GPEC of PnBMA-g-UM1 copolymers

PnBMA homopolymer is completely soluble in toluene and is therefore not retained on the silica packing. The graft copolymer is however insoluble in the starting solvent toluene. The mode of retention is therefore the governing factor in determining the actual separation. In this case (PnBMA-g-UM1 copolymer), for the toluene/DMF system on silica the retention relies on initial precipitation, followed by adsorption retention after redissolution of the graft copolymer in the solvent gradient. Linear gradients were used here, as shown in Figure 10

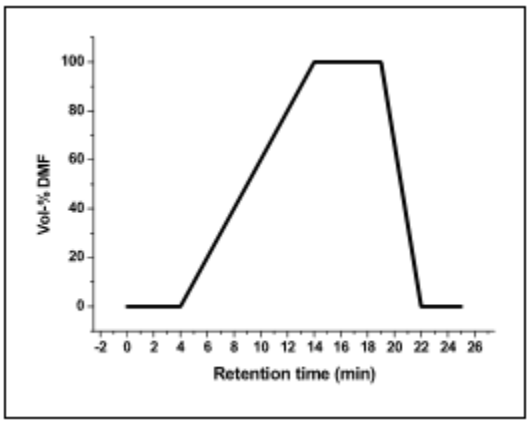


Figure 10: Gradient elution profiles considered for the separation of PnBMA-g-UM1 copolymer (Stationary phase: Nucleosil C18; 100Å, eluent: toluene/DMF

Separation is a function of component polarity. Here PnBMA is much less polar than UM1, therefore when using a reversed phase column (Nucleosil C18; 100Å) PnBMA is expected to elute first in a low polar solvent (toluene), followed by the UM1. PnBMA and UM1 were used to identify their retention times in the elution profile. Figure11 shows the retention times of these components. PnBMA elutes between 2 and 4 min, whereas UM1 elutes between 15 and 18 min

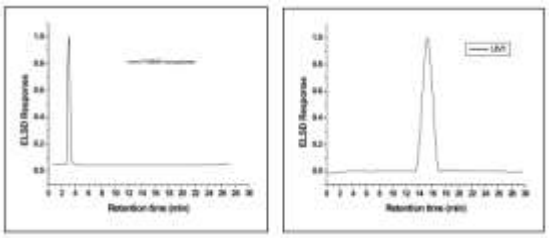


Figure 11: HPLC elution plots of UM1 and PnBMA homopolymer

A gradient HPLC chromatogram showing a typical PnBMA-g-UM1 copolymer before extractions is illustrated in Figure 12. It shows that very good separation into three fractions was obtained. The assignment of the peaks was carried out by comparison with the homopolymer and chromatographic behaviour of UM1 and PnBMA homopolymer using a reversed phase column (Nucleosil C18; 100Å). The three elution peaks

visible are assigned to the sample constituents PnBMA, UM1 and PnBMA-g-UM1. PnBMA is eluted quickly and leaves the column first. The second peak, which is significantly retained is PnBMA-g-UM1, and the third peak is assigned to unreacted UM1. As was expected, it is retained the most on the stationary phase. A gradient HPLC chromatogram showing a typical PnBMA-g-UM1 copolymer after extracting almost all of the PnBMA homopolymer and unreacted UM1 is illustrated in Figure 13

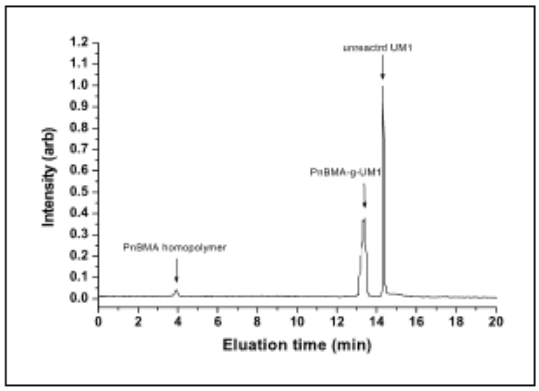


Figure 12: Gradient HPLC chromatogram of the PnBMA-g-UM1 copolymer (G55B) before extracting unreacted UM1 and PnBMA homopolymer. (Stationary phase: Nucleosil C18; 100Å; eluent: toluene /DMF; detector: ELSD

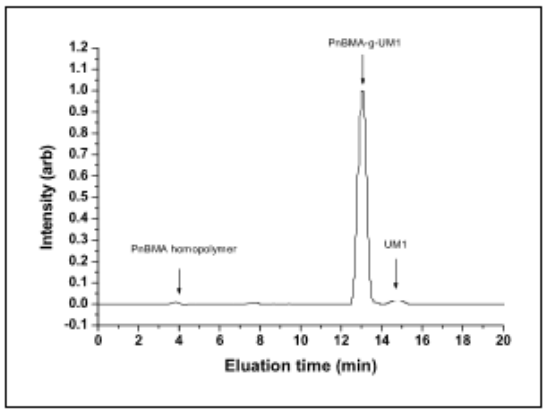


Figure 13: Gradient HPLC chromatogram of the PnBMA-g-UM1 copolymer (G55B) after extracting unreacted UM1 and PnBMA homopolymer. (Stationary phase: Nucleosil C18; 100Å; eluent: toluene /DMF; detector: ELSD.

Light scattering

The graft copolymers were also characterized using a multi-angle light scattering detector (MALLS) to determine the absolute molecular mass, as the Mn result obtained from SEC calibrated with linear polystyrene standards could be misleading. These results are presented and discussed below. To be able to use the MALLS detector the specific refractive index increment, usually referred to as the dn/dc value, was determined for each of the individual graft copolymers in dimethylacetamide (DMAc), by calculaitng from the refractive index detector signal and the concentration of the polymer solution. The molecular weights and molecular weight distributions (Mw/Mn) were calculated using Wyatt Technology Astra software. Peak areas were selected based on the width of the light-scattering peaks.

Table 4 shows the weight average molecular weight and number average molecular weight of the graft copolymers obtained by MALLS. The molecular weight distributions of the graft copolymer were relatively narrower than those obtained from the normal SEC. The molar mass values obtained by MALLS are consistently higher than the molar mass obtained relative to polystyrene. This indicates a difference in molecular size of the graft copolymer in the better solvent for copolymers of same molar mass

Table 4 : The number average molar weight and weight average weight mass of the graft copolymers obtained via SEC-MALLS

	Sample code	dn/dc	Graft copolymer		
PMMA-g-UM1			Mn (g/mol)	Mw (g/mol)	PDI
	G10M	0.113	$9.23 X10^4$	$1.64 X10^5$	1.77
	G25M	0.133	$9.14 X10^4$	$1.85 X10^5$	2.02
	G55M	0.146	$8.45 X10^4$	$1.94 X10^5$	2.29
PnBMA-g-UM1	G10B	0.102	$9.18 X10^4$	$1.73 X10^5$	1.88
	G25B	0.141	$9.07 X10^4$	$1.78 X10^5$	1.96
	G55B	0.162	$8.94 X10^4$	$1.94X10^5$	2.17

FTIR analysis

The FTIR spectra of the graft copolymers provide proof that the UM1 was actually grafted to PMMA or PnBMA through the double bond (which disappears) during free-radical copolymerization. After all the unreacted and unreactive UM1 (UM1 with MeOH in both chain ends were removed as confirmed by SEC the graft copolymers samples were analyzed by FTIR.

PMMA-g-urethane copolymers

Figure 14 shows a comparison of the FTIR spectra of the PMMA-g-UM1 copolymers and PMMA homopolymer. New peaks were observed in the spectra of the graft copolymers. The band at 3331 cm^{-1} is assigned to the hydrogen-bonded N-H stretching absorption peak of the urethane groups. The amide absorption peak appears at 1528 cm^{-1} and aromatic band of the MDI repeat unit at 1601 cm^{-1}. These results show that the UM1 was successfully incorporated into the PMMA polymer structure. This was also confirmed by GPEC and SEC.

The peaks at 936 cm^{-1} ascribed to the double bond in the UM1, disappear. This indicates that UM1 has fully reacted with MMA

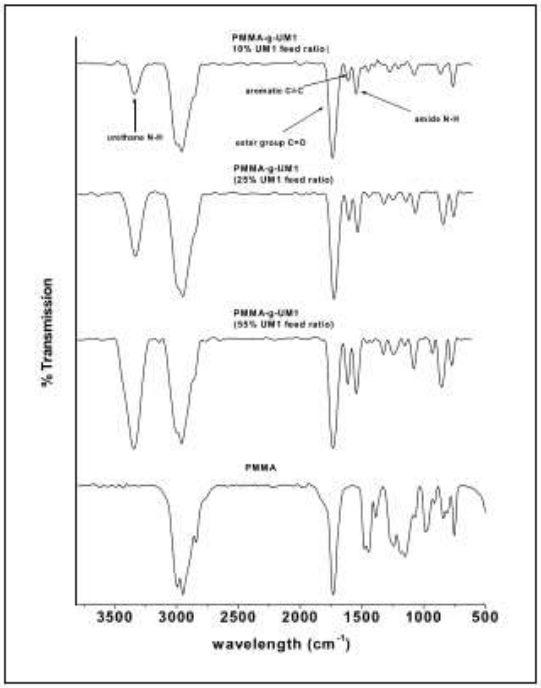


Figure 14: FTIR spectra showing comparisons between PMMA-g-UM1 and PMMA homopolymer

PnBMA-g-UM1 copolymers

Figure 15 shows a comparison of the FTIR spectra of the PnBMA-g-UM1 copolymers and the PnBMA homopolymer. New peaks were observed in spectra of the graft copolymers. The absorption peak at the 3329 cm^{-1} is assigned to the N-H stretching band of the urethane group. The amide vibration absorption peak appears at 1546 cm^{-1} and the aromatic absorption peak of the MDI repeat unit appears at 1605 cm^{-1}. These results show that

the UM1 was successfully incorporated into the PnBMA polymer chain, which was also confirmed by GPEC and SEC. The peak at 936 cm^{-1} for the double bond in the UM1 disappears. This indicates that UM1 has fully reacted with n-BM

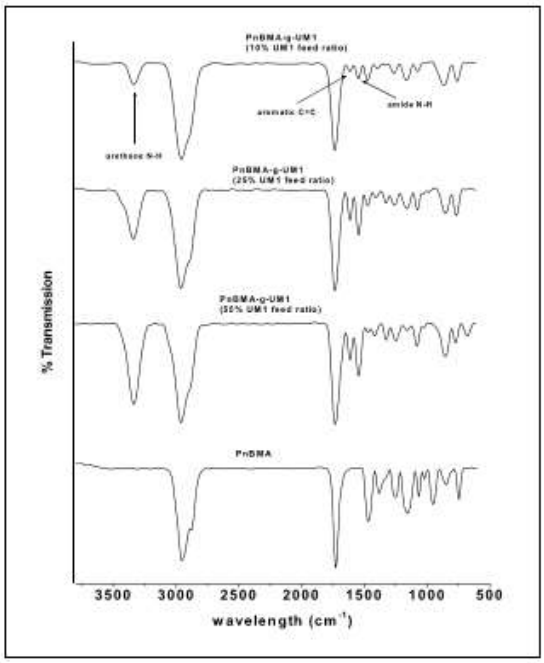


Figure 15: FTIR spectra showing comparisons between PnBMA-g-UM1 and PnBMA homopolymer

Effect of the UM1 content on copolymerization

Figures 14 and 15 above clearly show that as the amount of UM1 was increased in the feed of the copolymerization reactions, the percentage of UM1 being incorporated into the PMMA-g-UM1 and PnBMA-g-UM1 copolymers also increased. This is indicated by an increase in the intensity of the areas of the UM1 absorption peaks in these spectra, such as NH stretching at 3330 cm-1, NH absorption at 1546 cm-1, the aromatic absorption peak at 1605 cm-1 and C=O at 1742 cm-1.

The weight percentages of UM1 incorporated into the graft copolymers were determined from FTIR spectra, using calibration curves. The calibration curves were drawn up by mixing different percentages of UM1 with PMMA and PnBMA homopolymers, respectively (without polymerization). The percentages of UM1 to PMMA and UM1 to PnBMA homopolymers that were used were: 9%, 12%, 21%, 32%, 43 % and 51% by weight.

Figures 16 shows calibration curves for PMMA and PnBMA homopolymers which were separately mixed with different amounts of UM1. The calibration curves were obtained by plotting the UM1 content on the X axis and the transmission area of the N-H area of the urethane groups at 3345 cm^{-1} on the Y axis

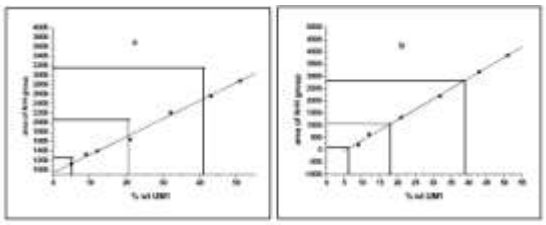


Figure 16: Calibration curve of (a) PMMA and (b) PnBMA mixed with different amounts of UM1

From the calibration curves in Figures 16 (a) and (b), the weight percentages of UM1 calculated to be incorporated into both PMMA-g-UM1 and PnBMA-g-UM1 copolymers are shown in Table 5. It can noted that as the amount of UM1 used during graft copolymerization increased, the weight percentages of UM1 incorporated into both PMMA-g-UM1 and PnBMA-g-UM1 copolymers also increased. This was also confirmed by UV-Vis and ^{1}H-NMR

Table 5 : Weight percentages of UM1 incorporated into the graft copolymers, as calculated from FTIR data

	Sample code	UM1/MMA feed ratio (wt %)	NH absorption peak area in FTIR spectrum	UM1 incorporated into copolymers (wt %)
PMMA-g-UM1	G10M	10-90	1155	4.2
	G25M	25/75	1740	20.4
	G55M	55/45	2494	41.04

		UM1/n-BMA feed ratio (wt %)		
PnBMA-g-UM1	G10B	10-90	94.5	6.18
	G25B	25/75	1065	18.02
	G55B	55/45	2852	39.09

UV-Vis spectroscopy analysis

The graft copolymers were further characterized using UV-Vis spectroscopy, after extracting the unreacted macromer. UV spectroscopy is a method that is used to determine the absorption wavelength (λmax) of UV-absorbing species. Here UM1 was expected to absorb at 254 nm, where the aromatic ring of UM1 absorbs. The UV spectra of the UM1, PMMA, PnBMA, PMMA-g-UM1 and PnBMA-g-UM1 copolymers are presented in Figures 17 and 18

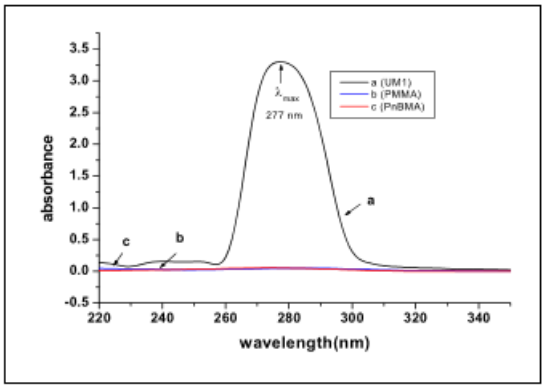


Figure 17: UV/Vis spectrum: (a) UM1 (b) PMMA and (c) PnBMA [DMF was used as solvent (UV-cutoff 200 nm)] wavelength

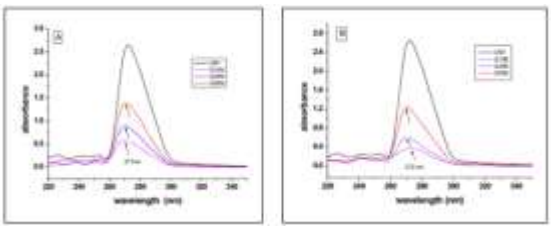


Figure 18: UV/Vis spectra of UM1 copolymerized with different amounts of acrylate [(A) PMMA and (B) PnBMA, DMF was used as solvent (UV-cutoff 200 nm

UV/Vis analysis of the PMMA-g-UM1 and PnBMA-g-UM1copolymers (Figure 18) showed that graft copolymers had strong absorption peaks in the region where the UM1 absorbs. The strong absorption peak was absent in this region in the PMMA and PnBMA homopolymers 17 Figure

A calibration curve was used to determine the equivalent amounts of the UM1 in the PMMA- g-UM1 and PnBMA-g-UM1copolymers. Solutions of various concentrations of the UM1 using DMF as solvent, were prepared and their UV absorbance measured. A plot of absorbance versus quantity of the UM1, in mg/mL, was constructed (Figure 19). Three samples of different known masses per each graft copolymer were dissolved in DMF and their absorbances were measured at a concentration of 0.2 mg/ml. The corresponding equivalent amount of UM1 in both copolymers was determined from the calibration curve see Table 6

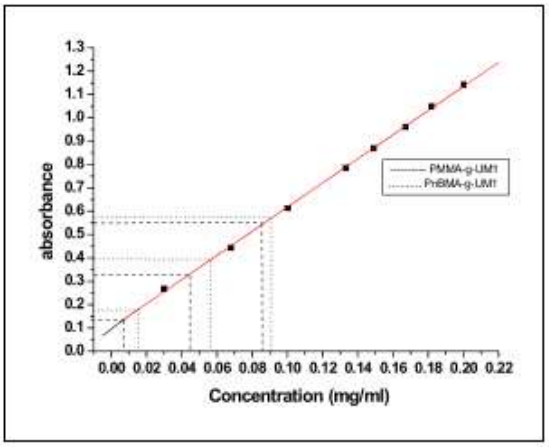


Figure 19: Calibration curve for the determination of percentage of UM1 incorporated into PMMA or PnBMA. [The dotted lines are extrapolation lines for PnBMA-g-UM1 copolymers and the dashed lines for PMMA-g-UM1 copolymers see Table 6.

Table 6.: UV data for the determination of the weight percentages of UM1 incorporated into PMMA or PnBMA

	Sample code	Feed ratio		Absorbance	Equivalent amount of graftcopolymer (mg/ml)	UM1 incorporatedinto copolymers(wt %*)
		UM1 (g)	MMA (g)			
PMMA-g-UM1	G10M	0.50	4.50	0.14	0.007	3.5
	G25M	1.25	3.75	0.33	0.045	22.0
	G55M	2.75	2.25	0.55	0.088	44.0
		UM1 (g)	n-BMA (g)			
PnBMA-g-UM1	G10B	0.50	4.50	0.18	0.015	7.5
	G25B	1.25	3.75	0.39	0.055	20.5
	G55B	2.75	2.25	0.57	0.091	44.5

*wt % UM1 was calculated by dividing the equivalent amount of graft copolymer by the equivalent amount of UM1, which is 0.2 mg/ml (absorbance of all graft copolymers was measured at this concentration.)

C-NMR analysis of graft copolymers after extraction was also used to confirm the presence of the branched UM1 in the graft copolymers.

^{13}C-NMR analysis

PMMA-g-UM1 copolymers

Figure 20 shows a comparison of the ^{13}C-NMR spectra of PMMA-g-UM1 copolymer to that of the PMMA homopolymer. New peaks were evident in the graft copolymer spectra. The peaks in the region between δ = 117 and δ =140 ppm are mainly attributed to the aromatic carbons of the MDI in the UM1. The peaks at δ = 61.4 ppm originate from methylene carbon of the EG in the UM1. In addition, the ^{13}C-NMR peaks ascribed to the vinylic carbon of the UM1 at δ = 127.55 and δ = 131.49 ppm were observed to have completely disappeared upon copolymerization with MMA. This result shows that the UM1 was successfully and totally incorporated into PMMA-g-UM1 copolymers, and confirms the results that of analysis by FTIR and SEC.

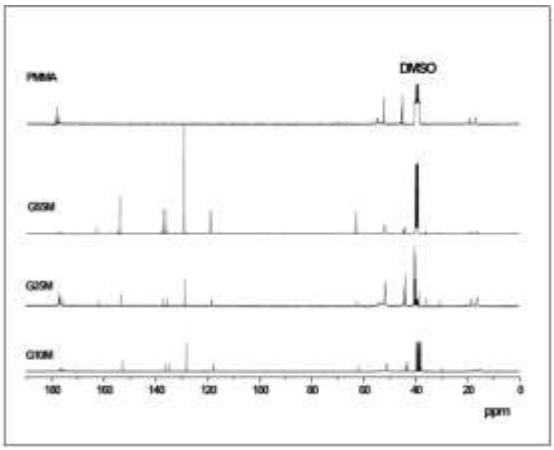


Figure 20: ^{13}C-NMR spectra of PMMA-g-UM1 copolymers and PMMA homopolymer dissolved in DMSO. (See Table 4.10 for explanation of G10M, G25M and G55M codes.)

PnBMA-g-UM1 copolymers

Figure 21 shows a comparison of the ^{13}C-NMR spectra of PnBMA-g-UM1 copolymers and PnBMA homopolymer. New peaks were evident in the graft copolymer spectra. The peaks in the MDI in the UM1. The peaks at δ = 62.5 ppm originate from methylene carbons of the EG in the UM1. In addition, the ^{13}C-NMR peaks ascribed to the vinylic carbon of the UM1 at δ= 127 and δ = 131.49 ppm were observed to have completely disappeared upon copolymerization with n-BMA at all ratios used. This result shows that the UM1 was successfully and totally incorporated into PnBMA-g-UM1 copolymers.

Analysis of graft copolymers after extraction also confirmed the presence of the branched UM1 in the copolymers, and allowed the calculation of the percentage of UM1 incorporated into the graft copolymers.

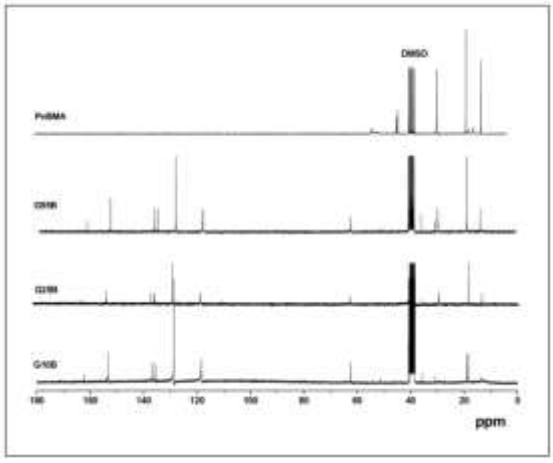


Figure 21: 13C-NMR spectra of PnBMA-g-UM1 copolymers and PnBMA homopolymer dissolved in DMSO. (See Table 4.10 for explanation of G10B, G25B and G55B codes)

PMMA-g-UM1 copolymers

Figure 22 shows a typical ^{1}H-NMR spectrum of the graft copolymer, after extraction of the unreacted macromonomer, and PMMA homopolymer. The^{1}H-NMR spectrum of PMMA-g-UM1 shows a characteristic peak at δ = 3.6 ppm, which originates from the methoxy group (CH3-O) of the methyl methacrylate. The appearance of peaks of MDI in regions of δ = 6.2 of UM1 branches in the copolymer after extraction. In addition, the 1H-NMR peaks ascribed to the vinylic protons of the UM1 at δ = 5.95 ppm, δ = 6.25 ppm and δ = 6.47 ppm were observed to have disappeared upon copolymerization with MMA. These results show that the UM1 was successfully incorporated into PMMA-g-UM1 copolymers and confirm the FTIR, ^{13}C-NMR and SEC results

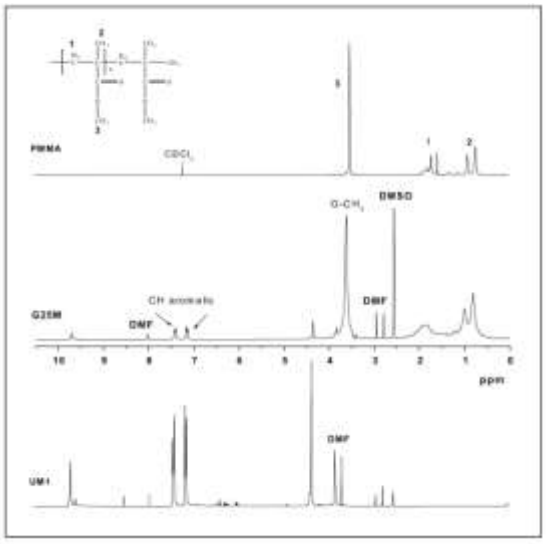


Figure 22: ^{1}H-NMR spectra of PMMA-g-UM1 copolymer, PMMA homopolymer and UM1 dissolved in DMSO

PnBMA-g-UM1 copolymers

Figure 23 shows a typical ^{1}H-NMR spectrum of the graft copolymer, after extraction of the unreacted macromonomer and PnBMA homopolymer. The spectrum of PnBMA-g-UM1 shows a characteristic peak at δ = 3.6 ppm which originates from the methylene oxy group (CH2-O) of the methyl methacrylate. The appearance of peaks of MDI in regions at δ = 6.2 ppm and δ = 7.5 ppm, which originate from aromatic ring of UM1, indicates the presence of UM1 branches in the copolymer after extraction. In addition, the ^{1}H-NMR peaks ascribed to have disappeared upon copolymerization with n-BMA. These results show that the UM1 was successfully incorporated into PnBMA-g-UM1 copolymers and confirm FTIR, ^{13}C-NMR and SEC results

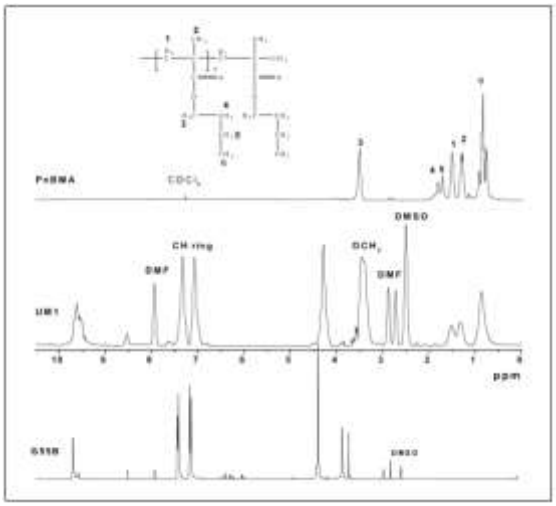


Figure 23: ^{1}H-NMR spectra of PnBMA-g-UM1 copolymer, PnBMA homopolymer and UM1 dissolved in DMSO.

Determination of the UM1 percentage in the graft copolymers, using 1H-NMR

The percentages of UM1 that were incorporated into the graft copolymers were determined from the1H-NMR spectra of each copolymer by the integration of the peaks for the methoxy group (at δ = 3.6 ppm) for the PMMA (backbone) or methyleneoxy group for the PnBMA (backbone) versus the protons of the aromatic ring (at δ = 7.08 and 7.29 ppm) of the UM1(branch),[42,43] taking into account the number of protons in each peak

$$UM1\% = \left[\frac{\delta_{ring} / (N_{ring} * (n+1))}{\delta_{ring} / (N_{ring} * (n+1)) + \delta_{CH_3O} / N_{CH_3O}} \right] \times 100$$

$$UM1\% = \left[\frac{\delta_{ring} / (N_{ring} * (n+1))}{\delta_{ring} / (N_{ring} * (n+1)) + \delta_{CH_2O} / N_{CH_2O}} \right] \times 100$$

where UM1 % is the percentage of UM1 which was incorporated into graft copolymers.

δ ring, δCH_3O and δ CH_2O are the integration intensities of the aromatic ring, CH_3O and CH_2O protons. N ring, N CH_3O and N CH2O are the number of protons in each group.

n is the average urethane macromonomer chain length equal to 4 as calculated using ^{1}H-NMR

Table 7 shows a summary of the graft copolymers synthesized and the corresponding mol %and wt % of UM2 incorporated into graft copolymers

Table 7 : Percentage UM1 incorporated into graft copolymers, as determined by ^{1}H-NMR

	Sample code	UM1 feed ratio (wt %)	Integration of CH_3O protons	Integration of aromatic ring protons	UM1 incorporated into copolymers (mol %)	UM1 incorporated into copolymers (wt %) (Mw of UM1 by ^{1}HNMR=1646 g/mol)	UM1 incorporated into copolymers (wt %) (Mw of UM1 by SEC=2218 g/mol)
PMMA-g-UM1	G10M	10	1	0.061	0.44	4.26	6.91
	G25M	25	1	0.192	1.47	19.8	24.81
	G55M	55	1	0.687	4.96	40.44	47.57
			Integration of CH_2O protons	Integration of aromatic ring protons			
PnBMA-g-UM1	G10B	10	1	0.094	0.47	4.16	4.49
	G25B	25	1	0.4	1.96	18.81	24.65
	G55B	55	1	0.851	4.08	42.55	49.7

The results in Table 7 shows that the percentage of UM1 incorporated into both PMMA-g- UM1 and PnBMA-g-UM1 copolymers increased as the quantities of UM1 increased during graft copolymerization. The UM1 content in the graft copolymers, as determined by 1H-NMR, was 4.26-40.44 by weight for PMMA-g-UM1 and 4.16-42.55 by weight for PnBMA-g-UM1. These results are close to the results that were determined by UV/Vis and FTIR using calibration curves

Conclusions

The urethane macromonomer was used in solution free-radical copolymerization with MMA and with n-BMA. The existence of the grafted urethane macromonomer with PMMA and PnBMA, respectively was confirmed using FTIR, and SEC (with UV and RI detectors), HPLC. 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 PnBMA backbones.

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