

N,N-diethyl Dithiocarbamate Group Induced Photografting of Methyl Methacrylate onto Polyurethane

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ABSTRACT: The *N,N*-diethyl dithiocarbamate group present in a variety of compounds acts as an initiator in the photopolymerization processes. The photolability of this group is due to the cleavage of the C—S bond by UV irradiation. *N,N*-Diethyl dithiocarbamate-(1,2)-propane diol with a pendent *N,N*-diethyl dithiocarbamate group was prepared from 3-chloro-(1,2)-propane diol and sodium diethyl dithiocarbamate. A polyurethane macrophotoinitiator was then synthesized by a two-step process, where *N,N*-diethyl dithiocarbamate-(1,2)-propane diol was used as the chain extender. Other components used included 4,4'-diphenylmethane diisocyanate and poly(propylene glycol) (molecular weight = 1000). The polyurethane thus synthesized had pendent *N,N*-diethyl dithiocarbamate

groups. This polyurethane macrophotoinitiator was then used to polymerize methyl methacrylate in a photochemical reactor (Compact-LP-MP 88) at 254 nm. The resulting graft copolymer, polyurethane-*g*-poly(methyl methacrylate), was freed from the homopolymer by a standard procedure. The graft copolymer was characterized by Fourier transform infrared spectroscopy, ¹H-NMR spectroscopy, thermogravimetric analysis, differential scanning calorimetry, solution viscometry, and scanning electron microscopy. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 64–71, 2009

Key words: graft copolymers; irradiation; photopolymerization; polyurethanes; thermogravimetric analysis (TGA)

INTRODUCTION

Graft copolymers are considered promising heteropolymeric functional materials. These compounds are widely used to control the stability of disperse systems, as compatibilizers for improving the compatibility of polymer mixtures, thickeners, film-forming coatings, protective coatings, and so on.¹ Polyurethane-*g*-polyvinyl copolymers constitute an important class of copolymers that is both academically and commercially important. The commercial importance arises from its wide-ranging applications in coating materials, adhesives, and sealing compounds.

Polyurethane-*g*-polyvinyl copolymers are generally synthesized with an ethylenically unsaturated monomer containing an isocyanate reactive group in the synthesis of polyurethane macromonomers. The olefinically unsaturated groups are pendent in the macromonomer. The polyurethane macromonomers with pendent unsaturation are then thermally reacted with vinylic monomers in the presence of thermal initiators.^{2–6} Another method of graft copolymerization is through a photografting proce-

dures,^{7,8} where the polyurethane macromonomers have pendent photolabile groups, through which the grafting of the vinylic monomers is attained by UV irradiation. The introduction of a photolabile group into the polyurethane backbone may be achieved through a diisocyanate or short-chain diol containing the photolabile group. The *N,N*-diethyl dithiocarbamate group is known as an important photoinitiator, and the graft copolymerization of polyurethane through this group has not been studied so far.

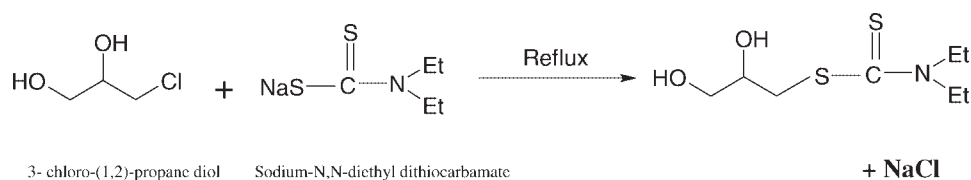
In this article, we report the introduction of pendent photolabile *N,N*-diethyl dithiocarbamate groups into a polyurethane macromonomer. This product was then UV-irradiated in the presence of methyl methacrylate (MMA) to synthesize polyurethane-*g*-poly(methyl methacrylate) (PMMA).

EXPERIMENTAL

Materials and methods

4,4'-Diphenylmethane diisocyanate (MDI; Aldrich, St. Louis, MO), 3-chloro-(1,2)-propane diol (CPD; E. Merck, Germany), and poly(propylene glycol) (PPG; molecular weight = 1000, Aldrich) were distilled under reduced pressure before use. MMA (E. Merck) was washed first with 5% NaOH followed by distilled water and then dried over CaCl₂ (fused). Finally, it was distilled under reduced pressure.

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Scheme 1 General reaction scheme for the synthesis of DCPD.

Dimethyl sulfoxide (DMSO; E. Merck) and dimethylformamide (E. Merck) were distilled before use. Ethanol (absolute) and acetone (E. Merck) were used as received.

Fourier transform infrared (FTIR) spectra were recorded in PerkinElmer spectrum RX 1 FTIR spectrophotometer (Norwalk, CT). The $^1\text{H-NMR}$ spectra were recorded in a Varian FT NMR AS 400-MHz spectrometer (the Netherlands). Thermogravimetric analysis (TGA) was carried out with a TA Instruments series STD 2960 simultaneous differential thermal analysis-TGA analyzer (Switzerland) in a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. Differential scanning calorimetry (DSC) studies were carried out in a TA Instruments series DSC Q 10 V 9.0 Build 275 instrument under a nitrogen atmosphere. Scanning electron microscopy (SEM) studies were carried out with a Leo 1430 VP electron microscope (Cambridge, UK).

Synthesis of *N,N*-diethyl dithiocarbamato-(1,2)-propane diol (DCPD)

DCPD was synthesized from an equimolar mixture of CPD and sodium *N,N*-diethyl dithiocarbamate. The mixture was refluxed for 6 h in a solvent mixture of acetone and absolute ethanol (Scheme 1). At the end of the reaction, the sodium chloride produced was filtered out, and the solvents were removed in a Bucci rotavapor. The crude product

was purified with column chromatography and finally distilled under reduced pressure.

DCPD was characterized by elemental analysis and UV-vis, FTIR, and $^1\text{H-NMR}$ spectroscopy, the results of which were reported elsewhere.⁹

Synthesis of the polyurethane macrophotoinitiator (PU-SR₁)

PU-SR₁ was synthesized from MDI, PPG, and DCPD by a two-step procedure. MDI (2.0002 g) and PPG (2.6602 g) were reacted first at 70°C for 1.5 h under a nitrogen atmosphere. Then, the temperature of the reaction mixture was lowered to 50°C . The chain-extender diol DCPD (1.1880 g) was dissolved in 25 mL of DMSO and slowly added from a pressure-equalizing funnel to the reaction mixture. This was followed by the addition of the catalyst dibutyl tin dilaureate (two drops). The reaction mixture was again heated at 90°C for 5 h. At the end, the resulting polymer was recovered by precipitation in water and dried in a vacuum oven.

Photograft copolymerization

The photograft copolymerization reactions were carried out in a Heber multilamp photochemical reactor (Chennai, India) at 254 nm. PU-SR₁'s with pendent *N,N*-diethyl dithiocarbamato groups were used to synthesize polyurethane-*g*-PMMA copolymers [(PU-SR₁)-*g*-PMMA]. A mixture of PU-SR₁ (0.1046 g) and

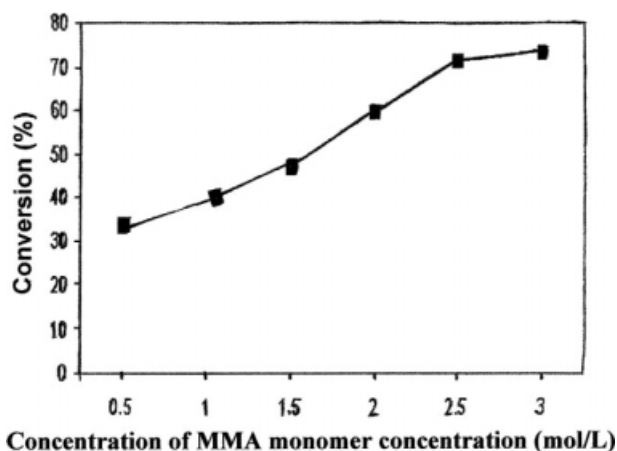


Figure 1 *M*% of MMA as a function of the MMA monomer concentration.

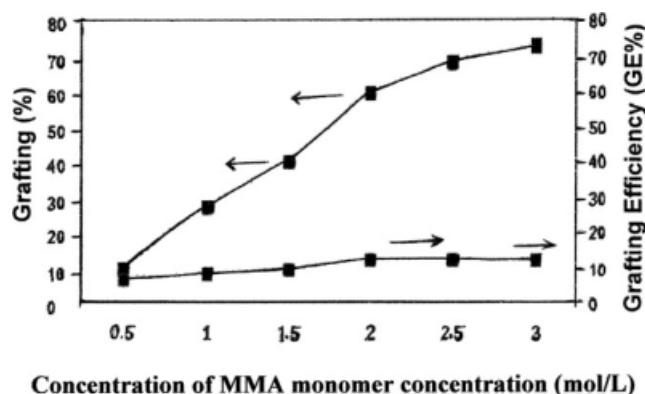


Figure 2 Effect of *G*% and *GE*% of MMA on PU-SR₁ as a function of the MMA monomer concentration.

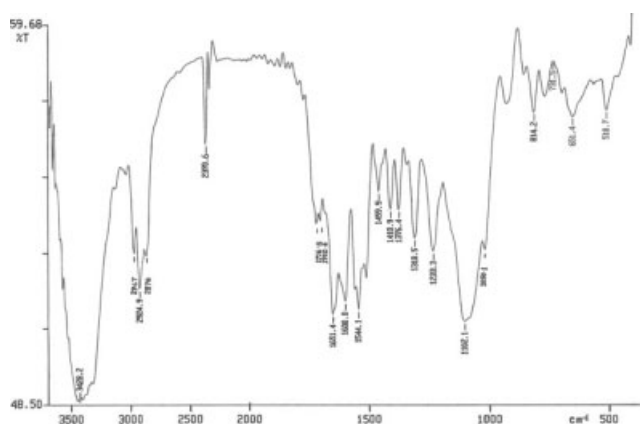


Figure 3 FTIR spectrum of PU-SR₁.

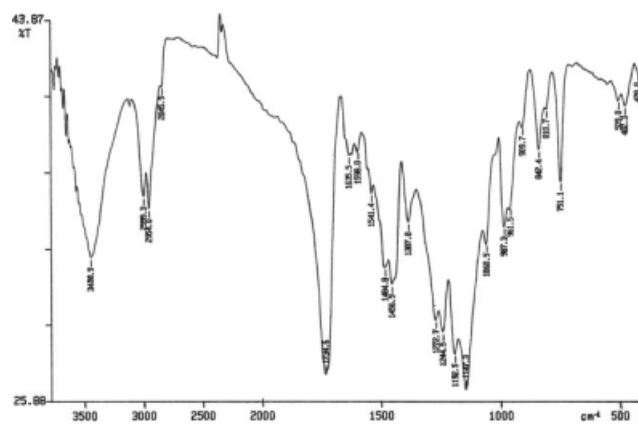


Figure 4 FTIR spectrum of the (PU-SR₁)-g-PMMA copolymer.

MMA (in various amount from 0.5085 to 2.5040 g) in DMSO was first purged with dry nitrogen. The reaction tubes were then sealed and photoirradiated in a Heber multilamp photochemical reactor at 254 nm for 6 h. The resulting polymers were isolated by precipitation in water. The graft copolymers were freed from the PMMA homopolymer by Soxhlet extraction with acetone.

The graft copolymers were characterized¹⁰ by monomer conversion (*M*%), grafting percentage (*G*%), and grafting efficiency (*GE*%), which were calculated as follows:

$$M\% = [F_1(g) - \text{PU-SR}_1(g)]/F_3(g) \times 100$$

$$G\% = [F_2(g) - \text{PU-SR}_1(g)]/F_2(g) \times 100$$

$$GE\% = [F_2(g) - \text{PU-SR}_1(g)]/[F_1(g) - \text{PU-SR}_1(g)] \times 100$$

where *F*₁ is the weight of the dry graft copolymer, *F*₂ is the weight of the dry graft copolymer after the removal of the homopolymer, and *F*₃ is the weight of the monomer (MMA) added.

RESULTS AND DISCUSSION

PU-SR₁ and polyurethane-*g*-PMMA were characterized by FTIR and ¹H-NMR spectroscopy. The polymers were further investigated by thermogravimetry, DSC, dilute solution viscometry, and SEM.

Effect of the monomer concentration

The effects of the change in monomer concentration on *M*%, *G*%, and *GE*% were investigated by the variation of the monomer (MMA) concentration. Figures 1 and 2 show the effects of *M*% of MMA, *G*%, and

GE% on PU-SR₁, respectively. The *M*% of MMA and *G*% increased with increasing monomer concentration. *GE*% also increased and finally attained a maximum value, at which it remained unaltered.

Spectroscopic analysis

The FTIR spectra of PU-SR₁ and the (PU-SR₁)-*g*-PMMA copolymer are shown in Figures 3 and 4, respectively. The absorption peak at 3430.9 cm⁻¹ was due to the N—H stretching of the urethane proton.¹¹ A broad peak appeared at 1734.6 cm⁻¹ and was due to the overlapping of C=O stretching from both the PMMA and urethane units in the polymer chain. The characteristic peak due to the —SC(S)N group¹² appeared at 1272.7 cm⁻¹. The C—O stretching peak for the O=C—OCH₃ of PMMA was observed at 1147.3 cm⁻¹ in the FTIR spectrum of (PU-SR₁)-*g*-PMMA. The absorption band appearing

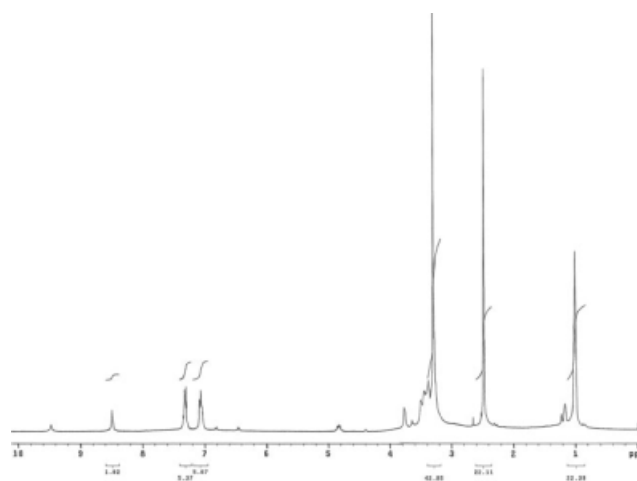


Figure 5 ¹H-NMR spectrum of PU-SR₁.

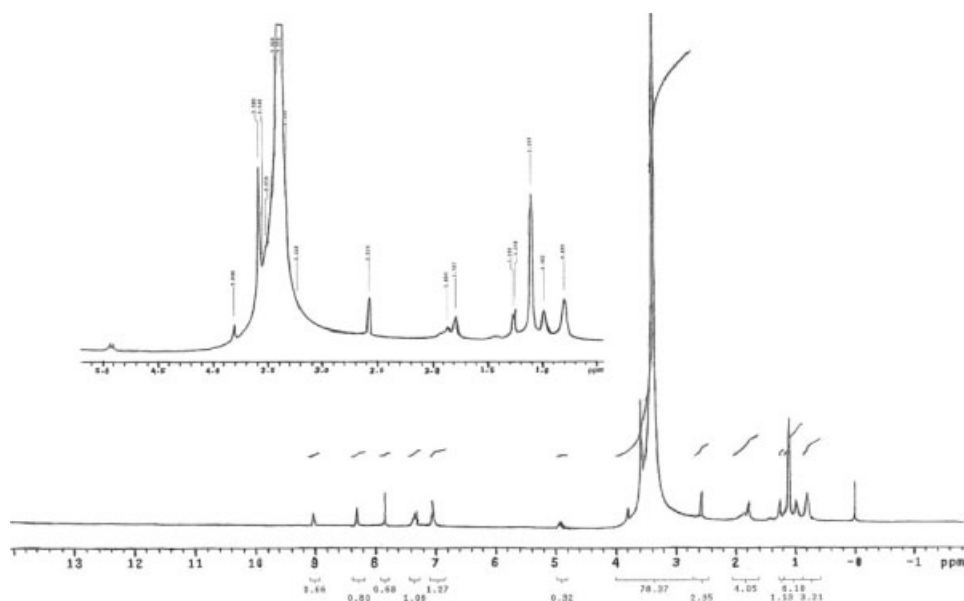


Figure 6 $^1\text{H-NMR}$ spectrum of the $(\text{PU-SR}_1)\text{-g-PMMA}$ copolymer.

at 1598 cm^{-1} was due to $\text{C}=\text{C}$ stretching from the aromatic rings.

The $^1\text{H-NMR}$ spectra of PU-SR_1 and $(\text{PU-SR}_1)\text{-g-PMMA}$ are shown in Figures 5 and 6, respectively. The peaks appearing at about $8.5\text{--}9.5\text{ ppm}$ in Figure 5 represented the N-H proton from the urethane units¹³ in the PU-SR_1 . The peaks appearing around $7.0\text{--}7.3\text{ ppm}$ were due to the aromatic protons from the MDI unit in the polymer chain. Peaks from the aliphatic protons ($-\text{OCH}_2$, $-\text{CH}_3$) of the PPG unit appeared around 3.5 and 1.0 ppm , respectively. The peak of the $-\text{OCH}_2$ protons adjacent to the urethane groups was observed around 3.8 ppm . The peaks of the $-\text{CH}_2$ and $-\text{CH}_3$ protons of the $\text{N-CH}_2\text{-CH}_3$ group of the DCPD unit appeared around 2.6 and 1.2 ppm , respectively. A broad peak appearing at

about 4.8 ppm was probably due to the CH protons of the PPG unit next to the urethane linkage.

Figure 6 shows the urethane N-H peaks around $8.3\text{--}9.0\text{ ppm}$. The peaks appearing in the range $7.0\text{--}7.4\text{ ppm}$ were due to the presence of aromatic protons from the polyurethane segments in the $(\text{PU-SR}_1)\text{-g-PMMA}$ copolymer. The resonance peak at 3.58 ppm was due to the $-\text{COOCH}_3$ protons from PMMA. The other peaks in $(\text{PU-SR}_1)\text{-g-PMMA}$ were same as those in PU-SR_1 .

TGA

TGA was carried out to determine the thermal stability of the graft copolymer with respect to that of PU-SR_1 . Figures 7 and 8 show the TGA

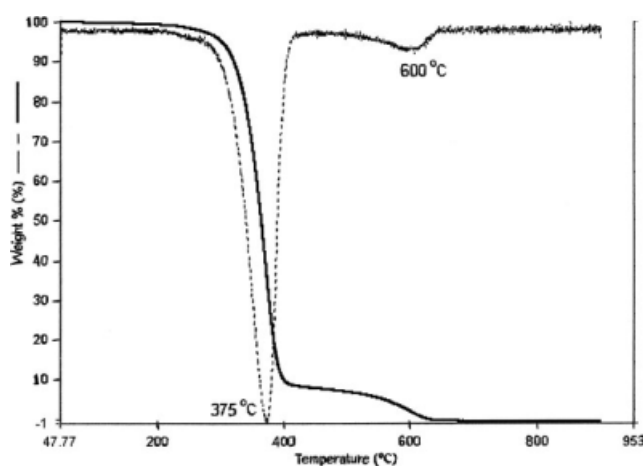


Figure 7 TGA thermogram of PU-SR_1 .

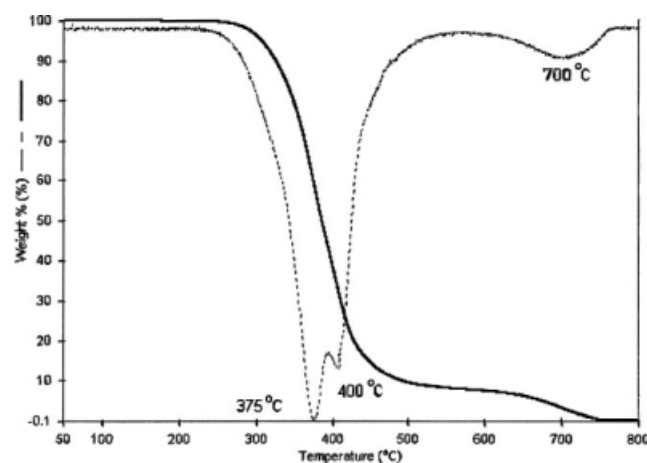


Figure 8 TGA thermogram of the $(\text{PU-SR}_1)\text{-g-PMMA}$ copolymer.

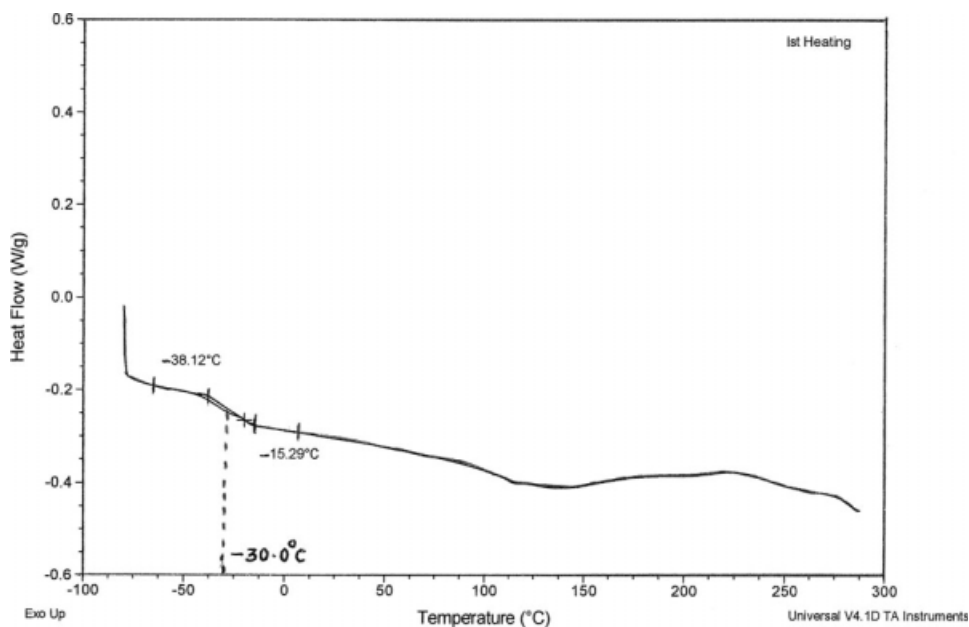


Figure 9 DSC thermogram of PU-SR₁ in the first heating cycle.

thermograms of PU-SR₁ and the corresponding graft copolymer (PU-SR₁)-g-PMMA, respectively. Although PU-SR₁ exhibited one-stage weight loss, the graft copolymer exhibited a two-stage weight loss process. The difference in the nature of the thermograms indicated a difference in their chemical composition, which was the result of the graft copolymerization of PMMA onto the polyurethane backbone. The macrophotoinitiator showed one-stage degradation at 375°C. On the other hand, the graft copolymer showed two-stage degradation at

375 and 400°C, respectively. Apparently, the thermal stability marginally increased as a result of graft copolymerization. The degradation at 400°C was probably due to the degradation of the grafted polyurethane segment.

DSC

DSC investigations were carried out to measure the glass-transition temperatures (T_g 's). Figures 9 and 10 show the DSC thermograms of the PU-SR₁ in the

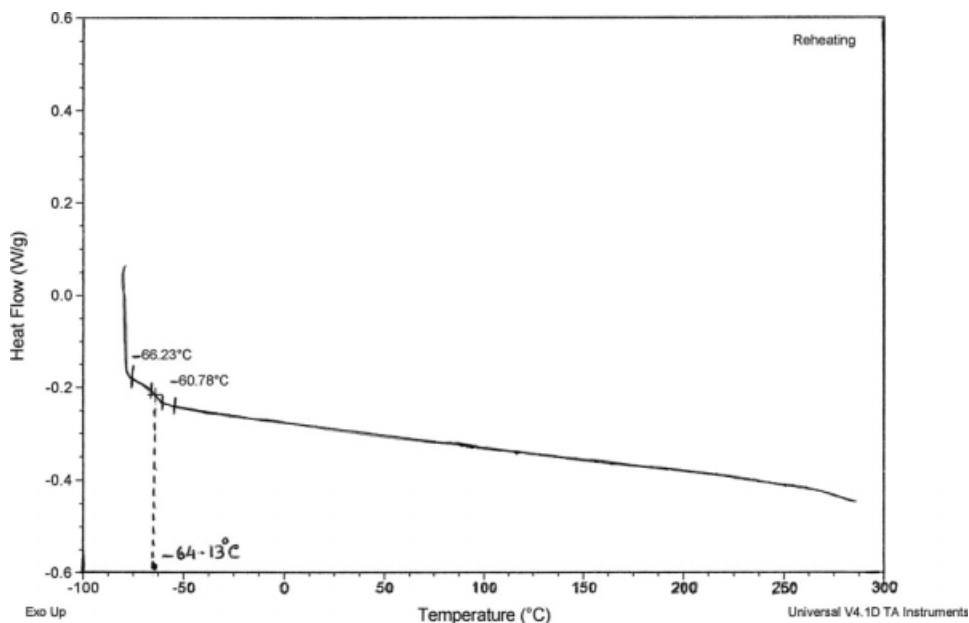


Figure 10 DSC thermogram of PU-SR₁ in the second heating cycle.

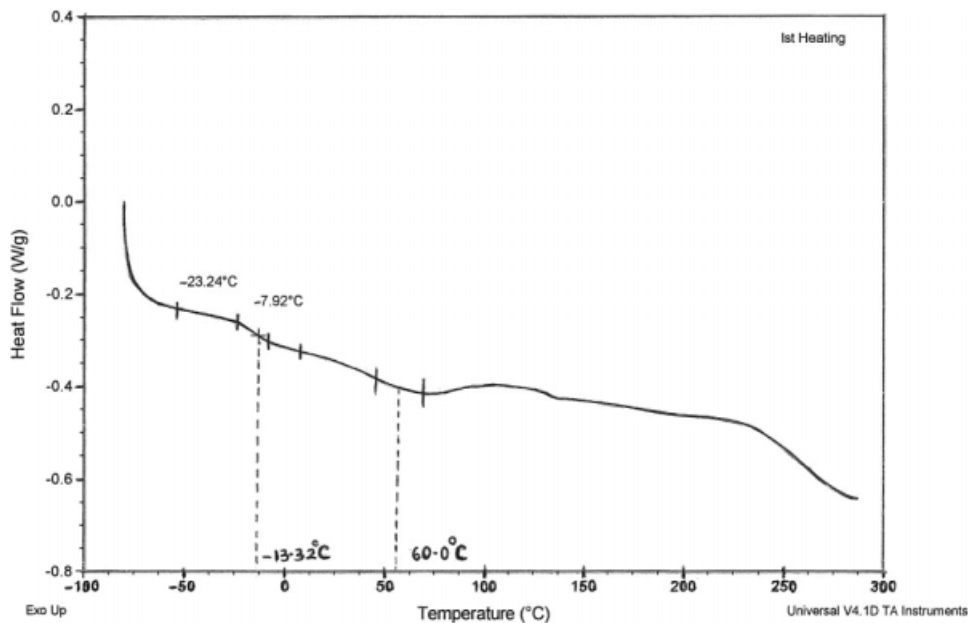


Figure 11 DSC thermogram of the (PU-SR₁)-g-PMMA copolymer.

first and second heating cycles, respectively, in the temperature range -100 to 300°C. The soft-segment T_g was observed at -30.0°C in the unquenched sample and at -64.13°C in the quenched sample (second heating cycle). The heating and quenching processes appeared to help the phase-segregation process, which resulted in a lower value of the soft-segment T_g . Figure 11 shows the DSC thermogram of the

(PU-SR₁)-g-PMMA copolymer measured in the temperature range -100 to 300°C. The soft-segment T_g of polyurethane segment was observed at -13.32°C. The T_g due to the PMMA segment was observed at 60.0°C, which was lower than the T_g of the homopolymer observed at 105°C. This was probably due to interactions between the polyurethane and PMMA segments.

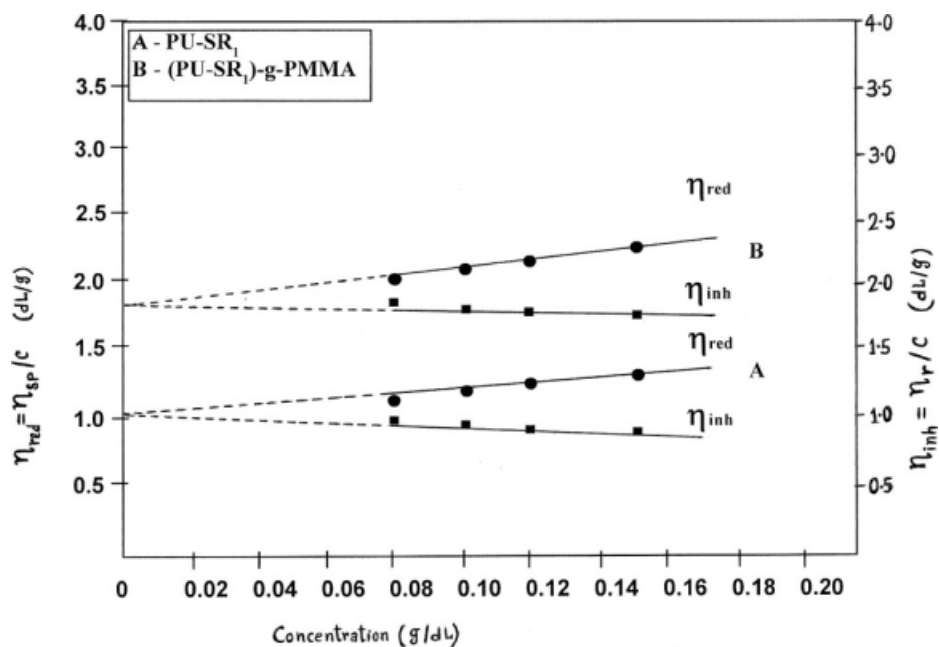


Figure 12 Plots of the reduced viscosity (η_{red}) and inherent viscosity (η_{inh}) of (A) PU-SR₁ and (B) (PU-SR₁)-g-PMMA as a function of concentration (c).

Dilute solution viscometry

A characteristic feature of a dilute polymer solution is that its viscosity is considerably higher than that of the pure solvent. The rise in viscosity generally reflects a rise in the molecular mass of the polymer. The dilute solution viscosity behavior of PU-SR₁ and the corresponding graft copolymer (PU-SR₁)-g-PMMA were investigated with an Ubbelohde viscometer (Borosil, India) in dimethylformamide at 25°C in a thermostated bath. The reduced viscosity and inherent viscosity behaviors are shown in Figure 12. The reduced viscosities in both cases decreased linearly with decreasing concentration. The inherent viscosity values were extrapolated to infinite dilution to investigate the limiting viscosity, that is, the intrinsic viscosity. The inherent viscosity increased linearly with decreasing polymer concentration.

The difference in the dilute solution viscosity behavior of PU-SR₁ and the corresponding graft copolymer (PU-SR₁)-g-PMMA was a reflection of the change of molecular architecture as a result of graft copolymerization. The intrinsic viscosity increased with increasing hydrodynamic volume. If the temperature and solvent were the same, the polymers presented different hydrodynamic volumes as a result of the higher molecular mass of the graft copolymer compared to PU-SR₁.

SEM

SEM investigations were carried out to study the surface morphology of the polymers. Electron microscopic investigations^{14–16} carried out on different types of polyurethanes revealed a two-phase morphology with a spherulitic or granular structure originating from a hard aromatic urethane microphase dispersed in the soft elastomeric phase of the polyether or polyester segment. Figure 13 shows the scanning electron micrograph of PU-SR₁, where

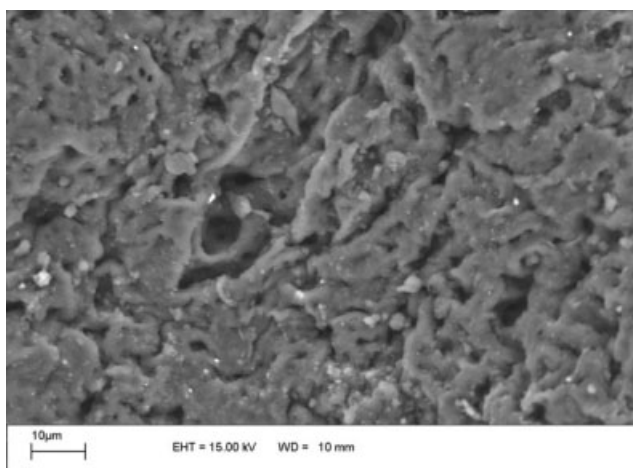


Figure 13 Scanning electron micrograph of PU-SR₁.

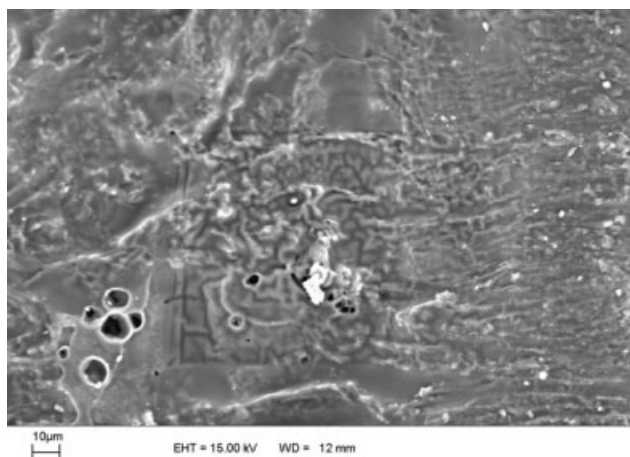


Figure 14 Scanning electron micrograph of the (PU-SR₁)-g-PMMA copolymer.

the chain-extender diol DCPD replaced 1,4-butane diol. The scanning electron micrograph shows a two-phase morphology, although the sizes of the hard-segment spherulites were observed to be smaller in size (0.87–2.61 μm). The scanning electron micrograph of (PU-SR₁)-g-PMMA (Fig. 14) shows a different morphology from that of the starting macrophotoinitiator (PU-SR₁). PMMA is an amorphous polymer. The nucleation process of the hard-segment spherulites in the polyurethane segment was influenced by the growing PMMA chain. The spherulite formation by the hard segment of polyurethane started earlier but undoubtedly incorporated some of the growing chains of PMMA into it. This resulted in the deformation of the spherulites, which led to increased coalescence and a resulting continuous morphology.

CONCLUSIONS

This study demonstrates the successful synthesis of a polyurethane-g-PMMA copolymer by a photograft copolymerization technique with a pendent photolabile group in the hard segment. The graft copolymers were characterized by FTIR and ¹H-NMR spectroscopy. The thermal behaviors of the copolymers and the dilute solution viscometry and SEM investigations together also indicated a successful graft copolymerization process. The results obtained from the study of the effect of monomer concentration on *M*% of MMA, *G*%, and *GE*% indicate that *M*% of MMA and *G*% increased with monomer concentration up to a limit. This means that PU-SR₁ efficiently initiated the polymerization. Furthermore, DSC showed that the graft copolymerization affected the *T*_g of the polyurethane segment. SEM revealed that the hard-soft domain segregation of PU-SR₁ was influenced as a result of the grafting of PMMA onto it.

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