

Synthesis of Poly(methyl methacrylate-*g*-glycidyl azide) Graft Copolymers Using *N, N*-Dithiocarbamate-Mediated Iniferters

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ABSTRACT: A glycidyl azide polymer with pendent *N, N*-diethyl dithiocarbamate groups (GAP-DDC) was prepared by the reaction of poly(epichlorohydrin) (PECH) with pendent *N, N*-diethyl dithiocarbamate groups (PECH-DDC) and sodium azide (NaN_3) in dimethylformamide (DMF). It was then used as a macro-photoinitiator for the graft polymerization of methyl methacrylate (MMA). Photopolymerization was carried out in a photochemical reactor at a wavelength greater than 300 nm. Conversion was determined gravimetrically and first-order time conversion plot for the polymerization system showed linear increase with the polymerization time indicating that polymerization pro-

ceeded in controlled fashion. The molecular weight distribution (M_w/M_n) was in the range of 1.4–1.6 during polymerization. The formation of poly(methyl methacrylate-*g*-glycidyl azide) (PMMA-*g*-GAP) graft copolymer was characterized by gel permeation chromatography, FT-IR spectroscopy, Thermogravimetric analysis, and differential scanning calorimetry. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 398–403, 2009

Key words: macrophotoinitiator; photopolymerization; graft copolymer; azide polymers; poly(methyl methacrylate-*g*-glycidyl azide)

INTRODUCTION

Insensitive munitions (IM) were developed to reduce the vulnerability of ammunitions during storage and transportation. The criteria for IMs comprise requirements such as high performance, low sensitivity, environmental acceptance, and reasonable costs.^{1,2} Polymeric materials are used as inert/energetic additives such as binders and plasticizers and are considered a practical solution in the development of new low sensitivity propellants.^{2,3} Glycidyl azide polymer (GAP) is an example of an energetic polymeric binder.⁴ Energetic thermoplastic elastomers based on GAP are usually prepared by a conventional urethane reaction with isocyanate monomers (condensation polymerization).^{1,4} The use of ceric ammonium nitrate to synthesize poly(methyl methacrylate-*b*-glycidyl azide) (PMMA-*b*-GAP) copolymer has been reported.⁵ The use of macro-azo-initiators based on the reaction of a GAP with 4, 4' azobis(4-cyanopentanoyl chloride) (ACPC) in the synthesis of poly(styrene-*b*-glycidyl azide) or poly(vinyl acetate-*b*-glycidyl azide) has also been reported.⁶

During the last 20 years, living/controlled radical polymerization has allowed researchers to success-

fully pursue one of the main goals in macromolecular development, namely the synthesis of new polymers with well-defined chemical structures, control of the molecular weight, and low polydispersity. Photopolymerization has some advantages over thermally initiated polymerization. This is evidenced in the rapid growth of radiation curing as an industrial process, which depends on the use of photoinitiators.⁷ Photoinitiators can be used in controlled radical reactions.^{8,9} The use of *N, N*-diethyl dithiocarbamate (DDC) derivatives as so-called photoiniferters during radical polymerization reactions has been reported.^{8–10} The term iniferter is used as first coined by Otsu, meaning substances that act as initiator, transfer agent and terminator in radical polymerization reactions.⁸

There is no previous report describing the utilization of controlled free radical polymerization for the preparation of azide polymers. This is possibly because azide polymers are unstable under conventional free radical polymerization conditions (i.e., the azide may decompose or even explode under thermal or UV conditions). In this article, the synthesis of macro-photoinitiators based on the grafting of *N, N* diethyl dithiocarbamate onto hydroxyl terminated GAP is reported. This macro-photoinitiator has the potential to initiate light induced free radical polymerization of different vinyl and acrylate monomers to yield different copolymers with GAP.

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EXPERIMENTAL

Materials

Epichlorohydrin (ECH), borontrifluoride etherate (BF_3 -etherate), 1, 4-butane diol, sodium *N, N*-diethyl dithiocarbamate, magnesium sulfate (MgSO_4), and sodium azide (NaN_3 ; purity > 98%) were obtained from Aldrich and used without further purification. Toluene and dichloromethane (DCM) were purified by standard procedures and dimethylformamide (DMF) (analytical grade) was used as received. All solvents were stored over molecular sieve. Methanol and ethanol (absolute) were used as received. The methyl methacrylate monomer was purified by vacuum distillation before use.

Characterization

The UV spectra were recorded on a GBC UV/visible 920 spectrometer. Concentrations of 1 mg/mL in dichloromethane were used. FT-IR spectra of polymers were recorded with a Perkin-Elmer spectrophotometer. Proton and carbon NMR spectra of polymers were recorded on a Varian VXR 300 spectrometer, using CDCl_3 as solvent and tetramethylsilane as an internal standard. The molecular weight of the polymers was determined by GPC (Waters). The GPC consisted of a Waters 717 Plus auto sampler, a Waters 600E system controller (run by Millennium32 V4 software), and a Waters 610 fluid unit. A Waters 410 differential refractometer was used as a detector. The flow rate used for the measurements was 1 mL/min, and typically 5 mg of sample was dissolved in 1 mL of solvent for analysis. The column oven was kept at 30°C and the injection volume was 100 μm . Two PLgel 5 μm Mixed-C columns and a precolumn (PLgel 5 μm Guard) were used. A set of narrow molecular weight polystyrene standard covering a molecular weight range of 350–3,500,000 g/mol was used as GPC standards. All molecular weights were reported as polystyrene equivalents. The DSC experiments were performed in a Perkin Elmer DSC-Q100 in the temperature range from 25 to 400°C, at a heating rate of 10°C/min, and under a nitrogen atmosphere. TGA analysis was carried out in a Perkin Elmer Thermogravimetric Analyzer Pyris TGA 7, at a heating rate of 10°C/min, and under a nitrogen atmosphere.

Experimental techniques

Preparation of poly(epichlorohydrin) and poly(epichlorohydrin) graft *N, N*-diethyl dithiocarbamate^{11,12}

The ring-opening polymerization of epichlorohydrin was carried out in the presence of 1,4-butane diol

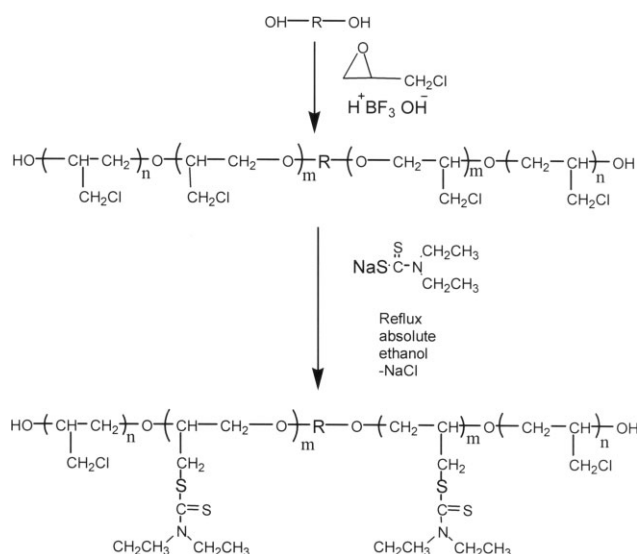
according to the procedure of Ivin and Sagusa.¹¹ Poly(epichlorohydrin) graft *N, N*-diethyl dithiocarbamate (PECH-DDC) was synthesized by refluxing hydroxyl terminated poly(epichlorohydrin) with sodium diethyl dithiocarbamate for 18 h in absolute ethanol according to the procedure of Alkaabi and Reenen.¹² Successful synthesis of PECH and PECH-DDC was confirmed by FTIR, UV, and NMR analysis. Preparation of PECH-diol and PECH-DDC is shown in (Scheme 1).

The yield of PECH was typically about 90% and analysis gave, for example: ^{13}C -NMR [CDCl_3] (ppm): $\delta = 26$ –26.5 [$-\text{CH}_2-$ of $-(\text{CH}_2)_4-$], $\delta = 43$ –46 [$-\text{CH}_2\text{Cl}$], $\delta = 69$ –71 [$-\text{O}-\text{CH}_2-$], $\delta = 79$ [$-\text{O}-\text{CH}-$]; FTIR (NaCl) (cm^{-1}): 3406 (s, $-\text{OH}$), 2906 (s), 2866 (s, CH_2CH), 1428 (s), 1292 (w), 1248 (w), 1108 (s, $-\text{C}-\text{O}-\text{C}-$), 838 (w), 744 (s, $-\text{CH}_2-\text{Cl}$), 704 (s); $\overline{M}_n = 830$ g/mol and $\overline{M}_w/\overline{M}_n = 1.2$.

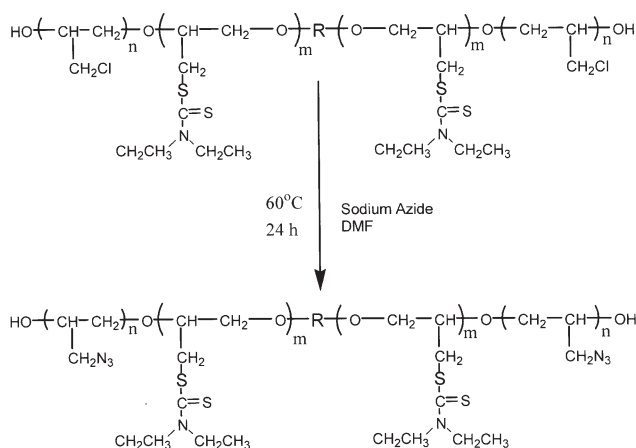
The yield was about 80% for the PECH-DDC and analysis gave, for example: ^{13}C -NMR [CDCl_3] (ppm): $\delta = 11.37$ [CH_3 of DDC], $\delta = 26.5$ [$-\text{CH}_2-$ of $-(\text{CH}_2)_4-$], $\delta = 34$ [CH_2 linked between PECH and DDC], $\delta = 38$ –46 [$-\text{CH}_2\text{Cl}$], $\delta = 48$ [CH_2 of DDC], $\delta = 68$ –72 [$-\text{O}-\text{CH}_2-$], $\delta = 79$ –80 [$-\text{O}-\text{CH}-$], $\delta = 195$ [$\text{C}=\text{S}$ of DDC]; FTIR (NaCl) (cm^{-1}): 3406 (s, $-\text{OH}$), 2906 (s, $-\text{CH}_2$), 2866 (s, $-\text{CH}$), 1640 (s, $\text{C}=\text{N}$), 1485 (w), 1420 (w, $-\text{SC}(=\text{S})\text{N}$), 1270 (w), 1108 (s, $-\text{O}-$), 908 (w), 830 (s), 744 (s, CH_2Cl) cm^{-1} ; $\overline{M}_n = 980$ g/mol and $\overline{M}_w/\overline{M}_n = 1.2$.

Preparation of GAP-*N, N*-diethyl dithiocarbamate

GAP graft *N, N*-diethyl dithiocarbamate (GAP-DDC) was synthesized by the azidation reaction of PECH-DDC in DMF as solvent (Scheme 2).



Scheme 1 Synthesis of poly(epichlorohydrin) and the reaction of poly(epichlorohydrin) with sodium diethyl dithiocarbamate ($\text{R} = 1,4$ -butane diol).



Scheme 2 Synthesis of GAP grafted diethyl dithiocarbamate ($R = 1, 4$ -butane diol).

Poly(epichlorohydrin) graft *N, N*-diethyl dithiocarbamate (2g) was charged into a two-necked flask with DMF (80 mL) and heated to 50°C for 2 h. Sodium azide (2 g) was slowly added and the reaction mixture stirred overnight at 60°C. On completion of the reaction the mixture was cooled to room temperature and diluted twice with dichloromethane. The un-reacted sodium azide and sodium chloride that formed was filtered off. The DMF was extracted with water in separation funnel. The product layer was dried over $MgSO_4$. The product was isolated by vacuum distillation and dried under reduced pressure. The yield was typically about 78% and product was characterized by UV, FT-IR, and NMR spectroscopy. 1H -NMR [$CDCl_3$] (ppm), $\delta = 1.2$, triplet [CH_3 of DDC], $\delta = 1.54$ [CH_2 of 1, 4-butane diol], $\delta = 3.37$ – 3.8 [CH_2N_3 and CH_2 of GAP], $\delta = 3.95$ [CH_2 of DDC]; $M_n = 1990$ g/mol and $M_w/M_n = 1.4$.

Photopolymerization

Photopolymerization reactions were carried out in toluene as solvent. A mixture of appropriate quantities of MMA and GAP-DDC were placed in a Pyrex tube and purged with nitrogen for about 15 min before irradiation. A photo-reactor equipped with 15 Philips 8 W/06 lamps emitting light nominally at $\lambda > 300$ nm, and a cooling system, was used for these reactions. The temperature of the photoreactor was maintained at 36°C. Conversions of the polymerization reactions were determined gravimetrically and the final yields obtained after precipitating the polymer and washing with excess amounts of methanol to remove of all unreacted GAP-DDC. All samples were dried under vacuum for overnight at room temperature.

RESULTS AND DISCUSSION

Synthesis of GAP-*N, N*-diethyl dithiocarbamate

The successful synthesis of the macro-initiators was confirmed by UV, FTIR, and NMR spectroscopy. UV spectrum of GAP-DDC is shown in Figure 1. The absorption peaks at λ_{max} 251 and 281 nm are attributed to the $-S-C=S$ and $S=C-N$ groups, respectively.^{13,14}

The FT-IR spectrum of GAP-*N, N*-diethyl dithiocarbamate shows the characteristic peak of the azide groups at about 2100 cm^{-1} , where absorptions at about 1664, 1207, and 980 cm^{-1} could be attributed to the $-S-C=S$ and $S=C-N$ groups.^{9,13} The GPC analysis of GAP-DDC shows that macro-initiator has number-average molecular weight of 1990 g/mol and the polydispersity based on polystyrene standard about 1.4.

The ^{13}C -NMR spectrum of PECH-DDC is shown in Figure 2. The spectrum displays the expected peaks for the methyl carbon of DDC (denoted 1), the methylene carbon of DDC (denoted 3), the methylene protons of azidomethane (denoted 4), the methylene carbon which links GAP to DDC (denoted 2), and the carbon disulfide of DDC (denoted 7). The rest of the assignments are indicated in the figure. The small peak at about 44–46 ppm could be attributed to un-reacted chloromethyl groups.^{15,16}

Synthesis of poly(methyl methacrylate-*g*-glycidyl azide) graft copolymer

Photo-irradiation of GAP-DDC in the presence of MMA monomer affords PMMA-*g*-GAP copolymer, according to the reaction depicted in (Scheme 3).

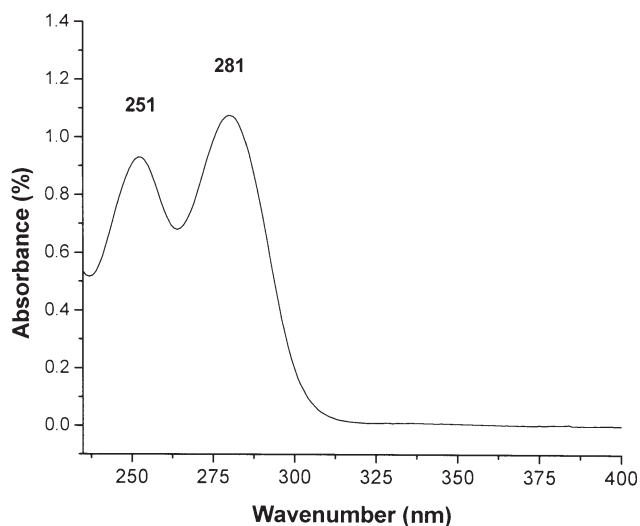


Figure 1 UV spectrum of GAP-DDC. (Solvent: dichloromethane; concentration 1 mg/5 ml).

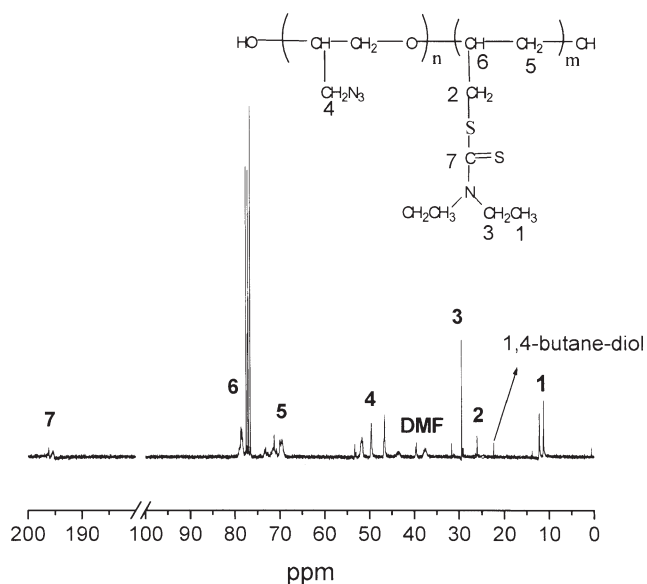
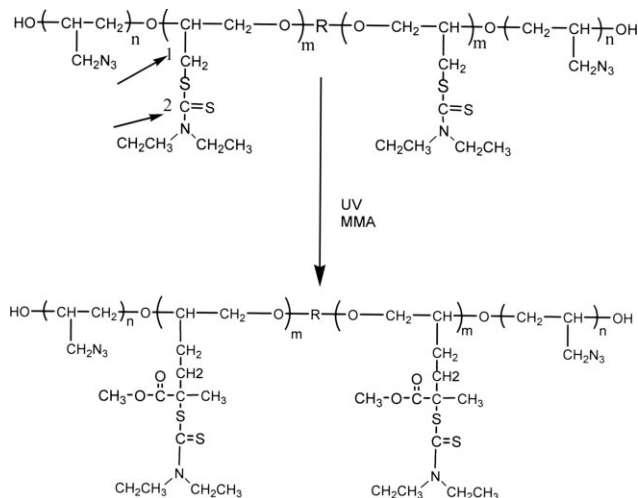


Figure 2 ^{13}C -NMR (CDCl_3) spectrum of GAP-DDC.

When a macro-photoinitiator with diethyl dithiocarbamate groups is subjected to UV radiation there are two possible mechanisms for the decomposition of the initiator: the first is homolytic scission of the C—S bond between the pendent methylene carbon (indicated by an arrow and marked 1 in Scheme 3) and the sulfur attached to it, and the second is scission of the bond between the sulfur and the carbon indicated by an arrow and marked 2 in Scheme 3. The decomposition of these groups depends on the bond length, bond energy, and bond order of the individually activated bonds. The first of these mechanisms is, however, the more generally accepted.¹⁷

The photopolymerization of MMA in toluene ($[\text{GAP-DDC}]/[\text{MMA}] = 0.014$) was carried out. Samples were taken at various UV irradiation times and



Scheme 3 Synthesis of poly(methyl methacrylate-g-glycidyl azide) graft copolymers ($\text{R} = 1, 4\text{-butane diol}$).

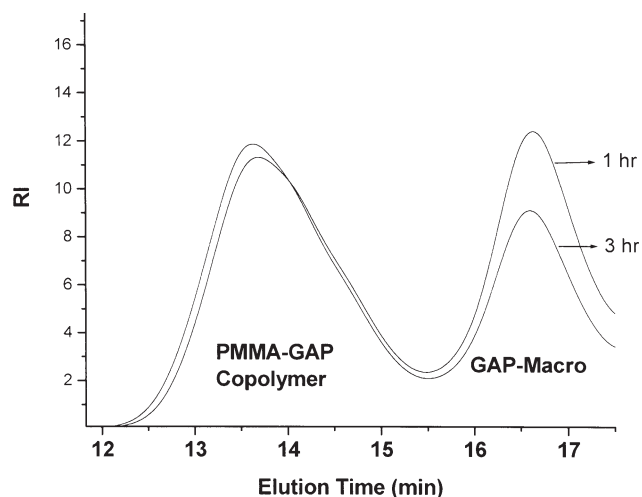


Figure 3 GPC profiles of photopolymerization of methyl methacrylate in toluene initiated by GAP-DDC ($[\text{GAP-DDC}]/[\text{MMA}] = 0.014$).

the effect of the reaction time was examined. Figure 3 illustrates the typical GPC profiles of these polymerization series. Samples were taken as the irradiation time increased and two peaks with good separation appear in the GPC profile. The first peak correspond to the GAP-DDC species (retention time at about 16.5 min) and the second peak correspond to the PMMA-g-GAP copolymer (retention time 13.5 min and less). All the GPC curves show a unimodal distribution and the elution peaks scarcely shifted to the high-molecular weight-side increasing with reaction time. GAP-macro-initiator peak disappeared after the polymerization solution was precipitated in methanol, providing proof of removal of un-reacted macro-initiator (GAP-DDC).^{12,18}

A first-order time conversion plot for this polymerization system is shown in Figure 4, where $[\text{M}]$ is the

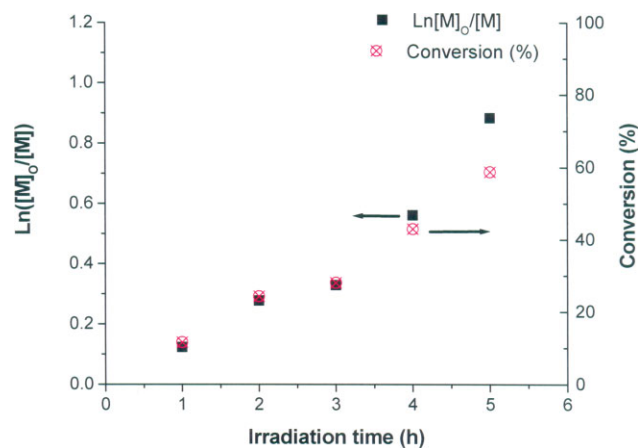


Figure 4 First-order time conversion plots for the photopolymerization of MMA in toluene initiated by GAP-DDC ($[\text{GAP-DDC}]/[\text{MMA}] = 0.014$), as a function of UV irradiation time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

monomer concentration and $[M]_0$ is the initial monomer concentration. The linear increase in the molecular weight of polymer with conversion gives an indication that the radical polymerization proceeded in a controlled fashion. Conversion was calculated by making use of gravimetric measurements. The conversion after 1 h of radiation was about 10%, and after running the reaction for another 4 h, there was only a 50% increase in the conversion. It appears, therefore, as if there is a deviation from linearity in the last stage of reaction. Possible explanations could be the following: (a) the formation of PMMA-g-GAP, which will increase the viscosity of mixture, leading to a decrease in reaction rate; (b) consumption of monomers; or (c) decomposition of diethyl dithiocarbamate in the initial period of the reaction. The latter should lead to an increase in polydispersity, which is, however, not evident (Fig. 5).

Figure 5 shows the plot of M_n or M_w/M_n against conversion. There is an increase in the molecular weight within the first period of the reaction compare to the last stage. The molecular weight did not change considerably as the polymerization proceeded. This is could be attributed to the reasons mentioned above. The polydispersity remained in the range of 1.4–1.6 (based on polystyrene standards). Therefore, it may be better to call this polymerization a “living” radical mechanism rather than a “controlled.” It is worth mentioning that running photopolymerization of MMA without using photoiniferter yielded only trace amounts of PMMA with high molecular weight and a polydispersity greater than 2.¹²

Characterization of poly(methyl methacrylate-glycidyl azide) graft copolymers

Figure 6 shows the FT-IR spectrum of the PMMA-g-GAP copolymer. The characteristic peak of the

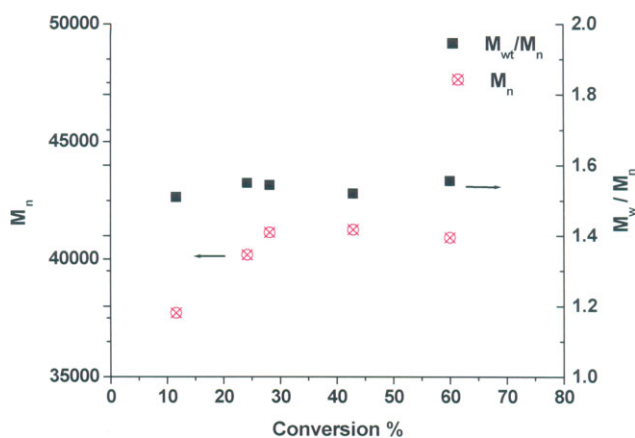


Figure 5 Plots of M_n or M_w/M_n against conversion for the photopolymerization of MMA in toluene initiated by GAP-DDC ($[GAP-DDC]/[MMA] = 0.014$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

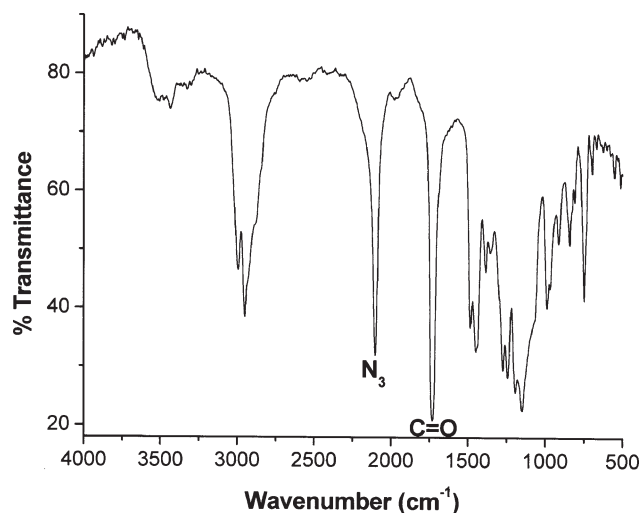


Figure 6 FT-IR spectrum of PMMA-g-GAP copolymer.

PMMA segment appears at about 1730 cm^{-1} , which corresponds to carbonyl groups. The characteristic peak of the GAP segment can be observed in the absorption at about 2100 cm^{-1} , which is attributed to the azide groups.

Thermal characterization of copolymer was investigated and Figure 7 shows the TGA thermogram of PMMA-g-GAP copolymer. The first decomposition starts at about 240°C , where about 40% of the copolymer was degraded due to exothermic decomposition of side N_3 groups.^{4,5} The second degradation step started above 321°C , which is attributed to the PMMA main chains, and about 50% weight loss occurred.¹⁹

Figure 8 shows the DSC analysis of PMMA-g-GAP copolymer. The DSC scan of PMMA-g-GAP shows an exothermic decomposition peak in the temperature range $160\text{--}295^\circ\text{C}$ with a maximum exothermic peak

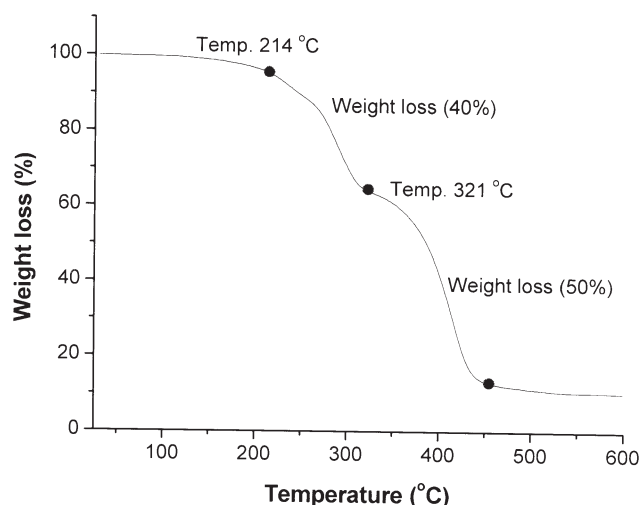


Figure 7 TGA analysis of PMMA-g-GAP copolymer. (Thermal analyses were carried out at heating rate $10^\circ\text{C}/\text{min}$ and under N_2 atmosphere.)

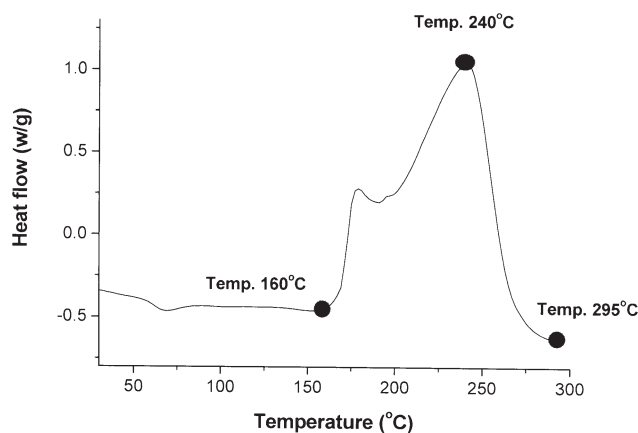


Figure 8 DSC trace of PMMA-g-GAP copolymer. (Thermal analyses were carried out at heating rate 10°C/min and under N₂ atmosphere.)

at about 240°C. The latter is attributed to the elimination of nitrogen by the scission of the azide groups. The graft copolymer shows a single glass transition temperature at about 75°C, which is between the T_g value of the corresponding homopolymers. The glass transition temperature of GAP and PMMA are -45 and 105°C, respectively.^{2,4,18} The presence of a single glass transition temperature is attributed to the miscibility of two different segments.^{20,6}

CONCLUSIONS

A macro-photoinitiator based on GAP and *N,N*-diethyl dithiocarbamate was successfully prepared. The photoinitiator was used for the grafting of PMMA to GAP through photopolymerization initiated by UV radiation ($\lambda > 300$ nm). The first-order time conversion plot for the polymerization system under UV irradiation and an increase in the molecular weight with only slight changes in the polydispersity confirmed that polymerization proceeded in a controlled manner. The presence of two different

segments was confirmed by spectroscopic and thermal analyses. The PMMA-g-GAP copolymer showed an exothermic decomposition at about 240°C due to exothermic decomposition of side N₃ groups and single glass transition temperature at about 75°C. PMMA-g-GAP copolymer is an energetic thermo-plastic elastomer and can be used for preparing composite materials for insensitive ammunition.

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