

Controlled Radical Polymerization of Poly(methyl methacrylate-*g*-epichlorohydrin) Using *N,N*-Dithiocarbamate-Mediated Iniferters

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ABSTRACT: Poly(epichlorohydrin) (PECH) with pendent *N,N*-diethyl dithiocarbamate groups (PECH-DDC) was prepared by reaction of PECH with sodium *N,N*-diethyl dithiocarbamate (DDC) in anhydrous ethanol, before being used as a macrophotoinitiator for the graft polymerization of methyl methacrylate. Photopolymerization was carried out in a photochemical reactor at a wavelength greater than 300 nm. Controlled radical polymerization was confirmed by the linear increase of the

molecular weight of polymers with conversion. The polydispersity remained at 1.4–1.6 during polymerization. The formation of PMMA-*g*-PECH copolymer was characterized by GPC, ¹H-NMR, FTIR spectroscopy, and DSC. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2528–2534, 2008

Key words: cationic polymerization; photopolymerization; graft copolymer; dithiocarbamate; methyl methacrylate

INTRODUCTION

Photopolymerization has some advantages over thermally initiated polymerization. This is evidenced in the rapid growth of radiation curing such as curing of coating on wood, metal, and paper, adhesives, printing inks, and photoresists, which depends on the use of photoinitiators.¹ The phenomenon of controlled radical polymerization allows for the synthesis of polymers with well-defined structures.² Photoinitiators can be used in controlled radical reactions, which is also of interest.^{2,3} Photoinitiators are defined as being substances that have the ability to convert physical energy of an incident light beam into chemical energy, by forming reactive radical intermediates. The use of *N,N*-diethyl dithiocarbamate (DDC) derivatives as so-called photoiniferters during radical polymerization reactions has been reported.^{2–5} The term iniferter is used as first coined by Otsu, meaning substances that act as initiator, transfer agent, and terminator in radical polymerization reactions.²

Photoiniferters such as DDCs and its derivatives can be used directly or as moieties attached to, *inter alia*, polymers. Polymeric photoiniferters have low volatility and do not suffer from initiator migration effects. Polymeric photoiniferters can also be used as precursors for block and graft polymerization reac-

tions. Several examples of the use of DDCs in this type of application have been recently reported.^{6–9} The use of a combination of living cationic polymerization and radical or controlled radical polymerization to prepare block copolymers has also been reported.^{10–18} Of some interest to us was the synthesis of a photoinitiator from 3-chloro-1,2-propanediol via the nucleophilic substitution of the chlorine atom by sodium diethyl dithiocarbamate and the reaction of high molecular weight poly(epichlorohydrin) (PECH) with sodium diethyl dithiocarbamate via the same process.^{6,19}

Recently, the combination of cationic polymerization and atom transfer radical polymerization (ATRP) for the synthesis of poly(methyl methacrylate-*g*-epichlorohydrin) (PMMA-*g*-PECH) and synthesis of block-graft copolymer [poly(epichlorohydrin-*b*-styrene)-*g*-poly(methyl methacrylate)] by combination of activated monomer polymerization, nitroxide-mediated polymerization, and ATRP were reported.^{20,21} Our interest lay in the possibility of synthesizing block or graft copolymers with PECH via photopolymerization.

In this article, we report on the synthesis of macrophotoinitiators based on the grafting of DDC onto hydroxyl-terminated PECH. This macrophotoinitiator has the potential to initiate light-induced free radical polymerization of different vinyl and acrylate monomers to yield different copolymers with PECH. If the PECH is produced by cationic ring-opening polymerization in the presence of low molecular weight diol then the resultant polymer will have

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hydroxyl terminal groups, which allow for further reaction.

EXPERIMENTAL

Materials

Epichlorohydrin (ECH), borontrifluoride etherate (BF₃-etherate), 1,4-butane diol, and sodium *N,N*-diethyl dithiocarbamate were obtained from Sigma Aldrich (Johannesburg, South Africa) and used without further purification. Toluene and dichloromethane were purified by standard procedures. Methanol and ethanol (anhydrous) were used as received. The methyl methacrylate (MMA) monomer was purified by vacuum distillation before use. All purified solvents and reagents were stored over molecular sieves.

Characterization

The UV spectra of polymers were recorded on a GBC UV/visible 920 spectrometer. FTIR 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 CDCl₃ 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 μL. 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 –40 to 130°C, at a heating rate of 10°C/min, and under a nitrogen atmosphere.

Experimental techniques

Ring-opening polymerization of ECH

The ring-opening polymerization of ECH was carried out according to the procedures of Ivin and Sagusa.²² Essentially BF₃-etherate was added to a stirred solution of the selected diol under nitrogen atmosphere, after which the ECH, dissolved in toluene, was added dropwise (Scheme 1). The reaction mixture was quenched after predetermined time by

adding 50 mL of distilled water with vigorous stirring. The resultant polymer was separated from solution and washed three times with water to remove all unreacted diol, monomer, and initiator. Finally, the polymer was isolated by drying under vacuum. The yield was typically about 90%. ¹³C-NMR [CDCl₃] (ppm): δ = 26–26.5 [–CH₂– of –(CH₂)₄–], δ = 43–46 [–CH₂Cl], δ = 69–71 [–O–CH₂–], δ = 79 [–O–CH–]; FTIR (NaCl) (cm^{–1}): 3406 (s, –OH), 2906 (s), 2866 (s, CH₂,CH), 1428 (s), 1292 (w), 1248 (w), 1108 (s, –C–O–C–), 838 (w), 744 (s, –CH₂–Cl), 704 (s); \overline{M}_n = 830 g/mol and polydispersity = 1.2.

Preparation of poly(epichlorohydrin)-*N,N*-diethyl dithiocarbamate diol

PECH-grafted *N,N*-diethyl dithiocarbamate diol was synthesized by refluxing PECH with sodium diethyl dithiocarbamate for about 18 h in anhydrous ethanol (Scheme 1). On completion of the reaction, the sodium chloride that was formed was filtered out, and the solvent removed under vacuum. The viscous product was dissolved in dichloromethane before being filtered and washed three times with water to remove all unreacted salts. The product was isolated by vacuum distillation and dried under vacuum. Products were characterized by UV, FTIR, and NMR spectroscopy, as well as by GPC.

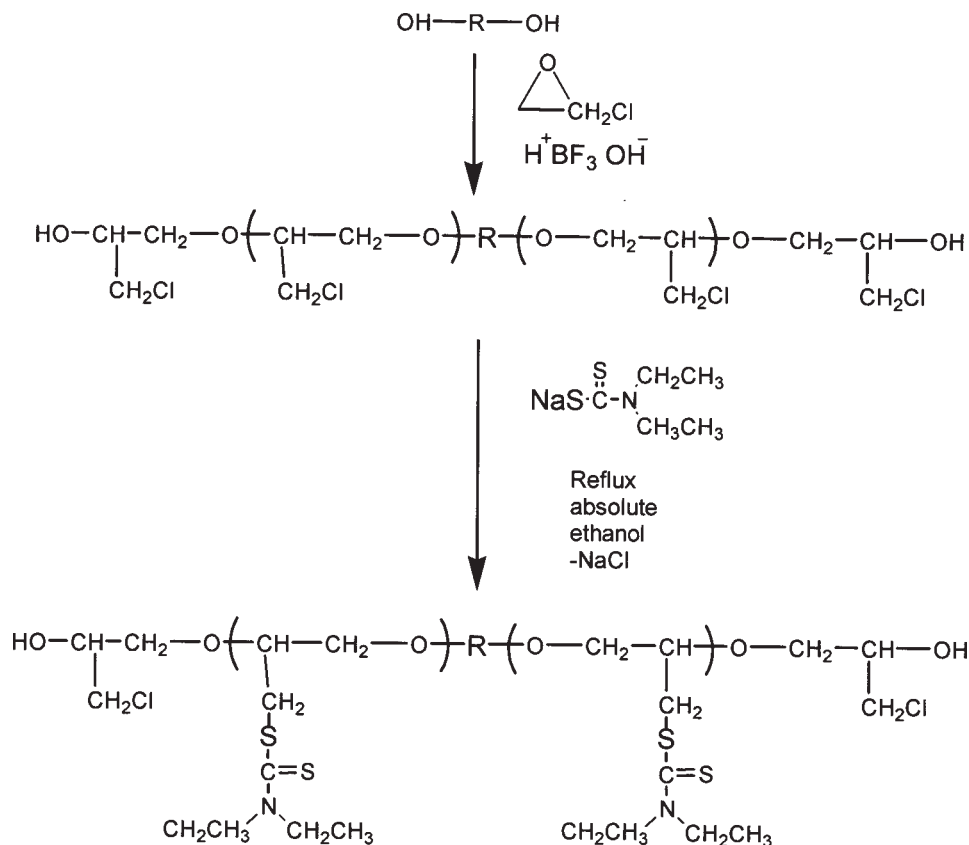
Photopolymerization

Photopolymerization reactions were carried out in toluene as solvent. A mixture of appropriate quantities of MMA and PECH-DDC were placed in a Pyrex tube and purged with nitrogen for about 15 min prior to irradiation. A photoreactor equipped with 15 Philips 8 W/06 lamps emitting light nominally at λ > 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 in order to get rid of all unreacted PECH-DDC. All samples were dried under vacuum at a room temperature over night.

RESULTS AND DISCUSSION

Ring-opening polymerization of ECH

Polymerization of PECH via the use of cationic ring-opening polymerization, by combination of BF₃-etherate (catalyst) and low molecular weight diol (initiator), is reported to yield polymers with an absence of cyclic oligomer formation.^{10,11,22,23} The use



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

of diols also affords the possibility for the production of linear telechelics when the polymerization is terminated with diols, alcohols, or water. In our case, polymerization proceeded to a high conversion (about 90%) and yielded materials with a narrow polydispersity. The PECH used for further reaction had a \overline{M}_n (GPC) of 830 g/mol and a polydispersity of 1.2 based on polystyrene standard. The FTIR spectra of PECH showed the expected peaks at 3450 cm^{-1} (OH end groups), 1190 cm^{-1} (polyether linkage), and 745 cm^{-1} (chloromethyl groups).

Synthesis of PECH-DDC

The successful synthesis of PECH-DDC was confirmed by FTIR, UV, and NMR analyses. The FTIR spectra of PECH and PECH with DDC pendent groups were compared and characteristic peaks due to the $-\text{SC}(=\text{S})\text{N}$ and $-\text{C}(=\text{S})-\text{N}$ groups appearing at 915 , 985 , 1415 cm^{-1} and 1205 , 1271 , 1480 , 1644 , and 3400 cm^{-1} could be assigned. While some of these peaks might overlap with some of the PECH homopolymer peaks, several are distinctive (e.g. at 1644 cm^{-1}).^{3,6,7,9,24,25}

The ultraviolet absorption (UV) spectra of PECH and PECH-DDC are shown in Figure 1. The UV

spectrum of PECH-DDC (B) shows absorption peaks at about 251 and 280 nm, which can be attributed to the $-\text{S}-\text{C}(=\text{S})-$ and $-\text{C}(=\text{S})-\text{N}$ groups, respectively.^{6,9} These absorption peaks were absent for the PECH.

The ^{13}C -NMR spectrum of PECH-DDC is shown in Figure 2. Assignments are indicated in the figure.

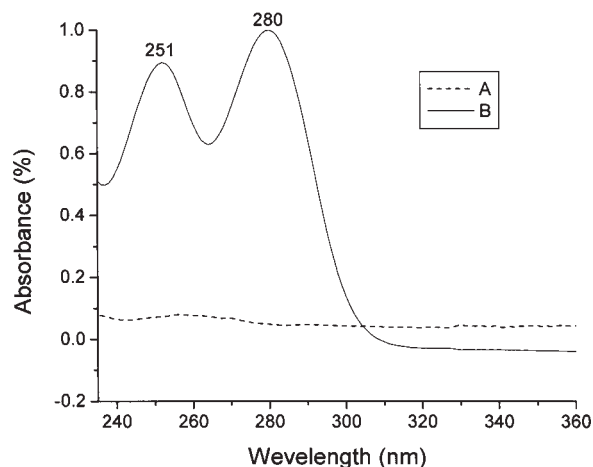


Figure 1 UV absorption spectra of (A) PECH and (B) PECH-DDC (solvent: dichloromethane; concentration 0.2 mg/mL).

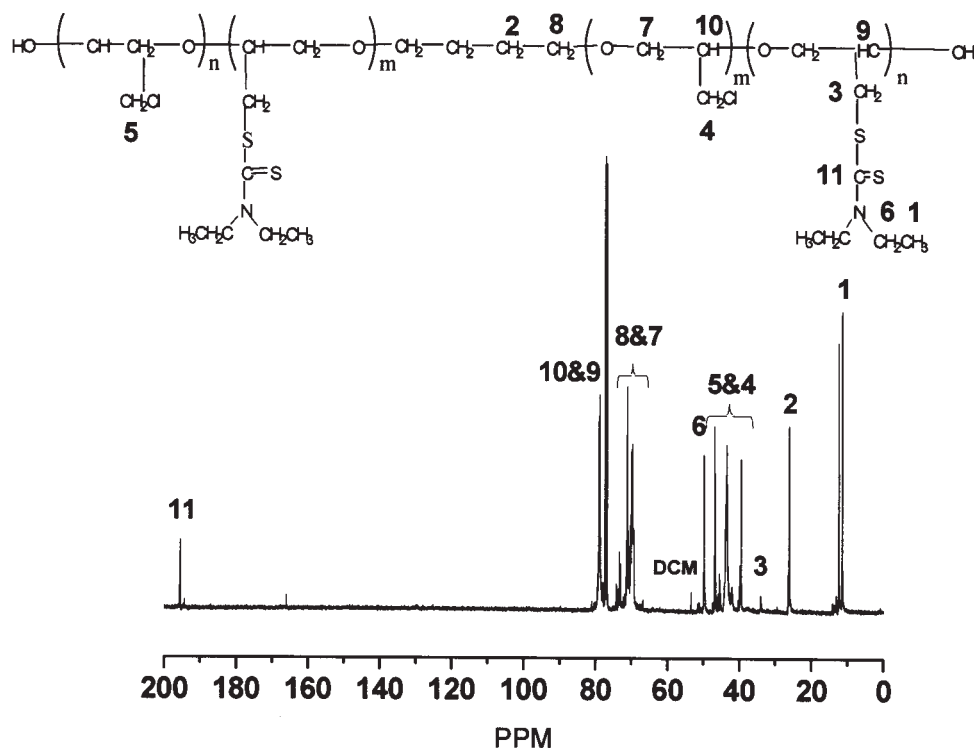


Figure 2 ^{13}C -NMR (CDCl_3) spectrum of PECH-DDC.

The spectrum displays the expected peaks for the methyl carbon of DDC (denoted 1), the methylene carbon of DDC (denoted 6), the methylene carbon which links PECH to DDC (3), and the carbon disulfide of DDC (11). The rest of assignments are indicated in the figure.

The GPC profiles of PECH before and after attachment of DDC indicate an increase in \overline{M}_n from 830 g/mol before the reaction to 980 g/mol after the reaction, while the polydispersity remains at about 1.2. The combination of UV, FTIR, NMR spectroscopy, and GPC results confirm the successful formation of PECH-DDC as macrophotoinitiator.

Synthesis of poly(methyl methacrylate)-grafted PECH

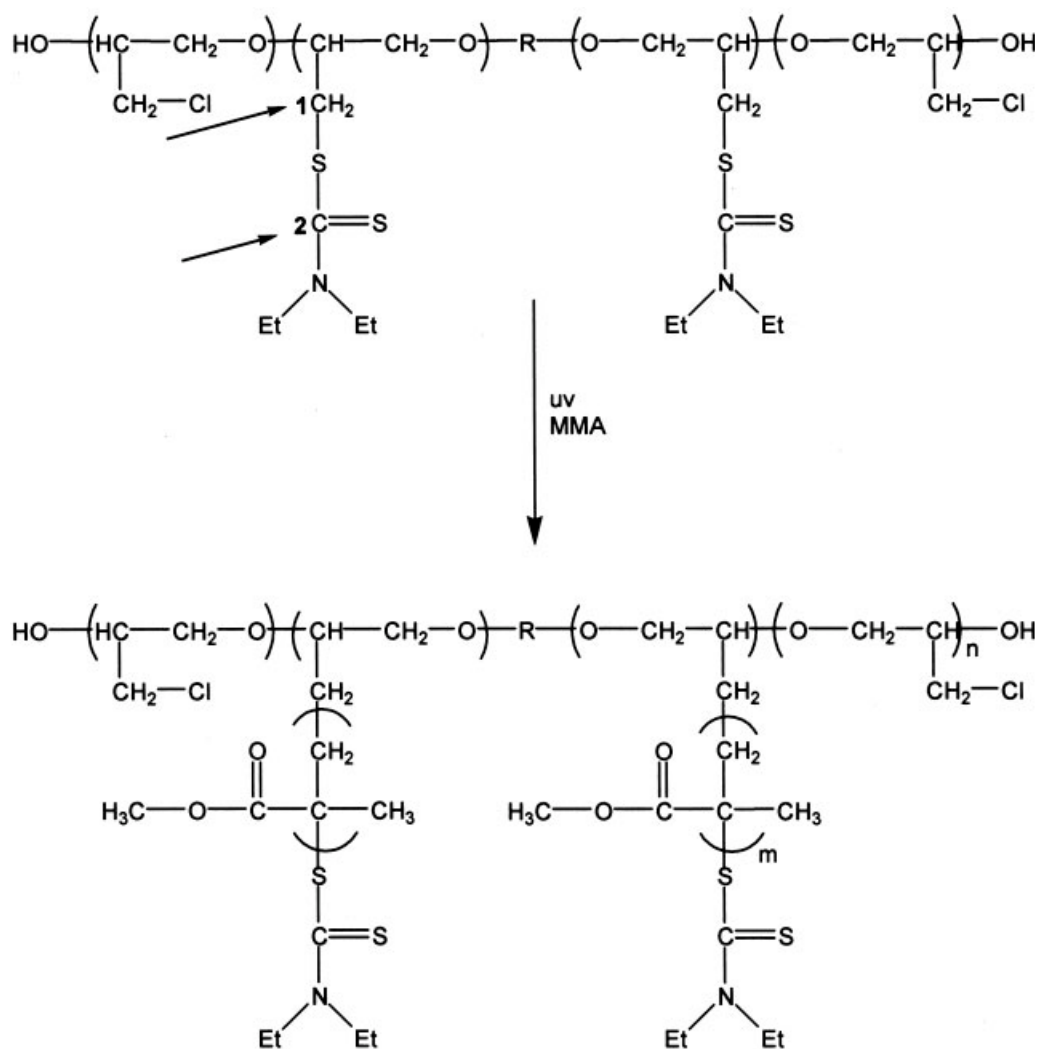
Photo-irradiation of PECH-DDC in the presence of MMA monomer affords PMMA-g-PECH copolymer, according to the reaction depicted in Scheme 2.

When macrophotoinitiator with DDC 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 2) 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 2. The decomposition of these groups depends on the bond length, bond energy, and bond order of the individually

activated bonds, but it appears as if the first of the above mechanisms is more generally accepted.²⁶ We therefore expected the formation of a polymer terminated by *N,N*-diethyl dithiocarbamyl (Et_2NCSS), applicable for further block copolymerization with other vinyl monomers.

The photopolymerization of MMA in toluene ($[\text{PECH-DDC}]/[\text{MMA}] = 0.0167$) was carried out and samples were taken at various UV irradiation times. As a reference, the thermally initiated polymerization of MMA in the absence of photoiniferter was also done. Figure 3 shows the UV spectra of two PMMA samples. Spectrum A is that of PMMA obtained from the thermal polymerization of MMA monomers without photoiniferter. Spectrum B is that of the PMMA obtained by photopolymerization of MMA monomers in the presence of PECH-DDC macrophotoinitiator. PMMA polymerized in the presence of macrophotoinitiator shows an absorption peak at 280 nm, which corresponds to the —S=C—N group, whereas this absorption peak was absent in the homo-PMMA obtained by the thermal polymerization reaction.

The effect of the reaction time was examined and Figure 4 illustrates the typical GPC profiles of these polymerization series. Two peaks with good separation appear in the GPC profile, the first one corresponding to the PECH-DDC species (retention time at about 18.4 min) and the second one corresponding to the PMMA-grafted PECH copolymer (retention



Scheme 2 Synthesis of poly(methyl methacrylate-g-epichlorohydrin) (R = 1,4-butane diol).

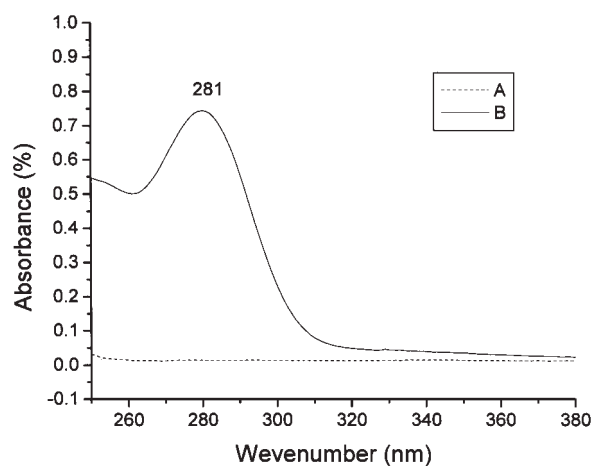


Figure 3 UV absorption spectra of (A) homo-poly(methyl methacrylate) obtained by thermal polymerization, and (B) poly(methyl methacrylate-g-epichlorohydrin) obtained by photopolymerization initiated by PECH-DDC (solvent: dichloromethane; concentration 0.2 mg/mL).

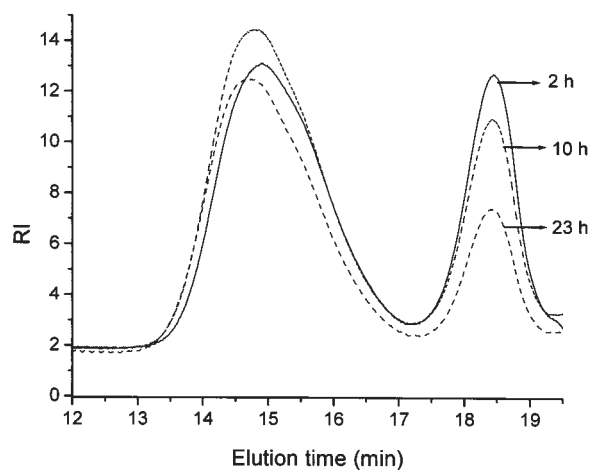


Figure 4 GPC profiles of photopolymerization of methyl methacrylate in toluene initiated by PECH-DDC ([PECH-DDC]/[MMA] = 0.0167) in THF as eluent, at 25°C. Samples were taken as the irradiation time increased.

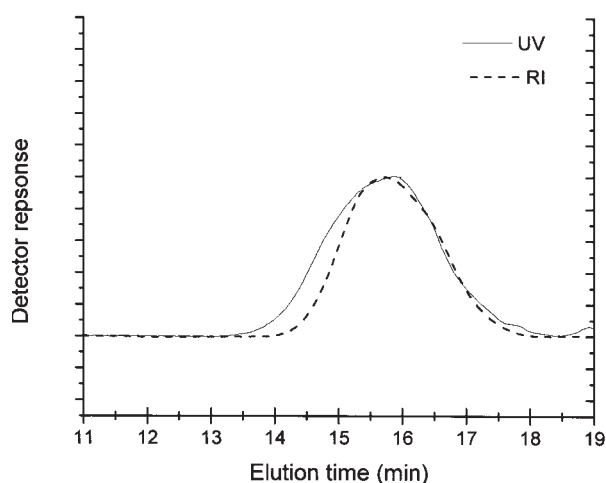


Figure 5 GPC traces of PMMA produced from the photopolymerization of MMA initiated by PECH-DDC ($[\text{PECH-DDC}]/[\text{MMA}] = 0.0167$) in THF as eluent, at 25°C, showing both UV and RI detector responses.

time 14.8 min and less). The shift to shorter retention time (higher molecular weight) with slight change in the polydispersity of the latter, as the reaction progresses, suggests that the polymerization proceeded via a controlled radical polymerization mechanism.

The GPC traces of PECH-g-PMMA using UV and refractive index (RI) detectors are shown in Figure 5. These chromatograms are of the final polymerization product, where polymer was precipitated and washed several times with methanol to extract all unreacted PECH-DDC, as confirmed by the successful removal of the first peak. The major overlap of the two peaks (UV and RI) indicates that material present is PMMA grafted onto the PECH (PECH-g-PMMA). Slight deviations in the shorter retention time could be due to high molecular weight homo-PMMA generated during polymerization.

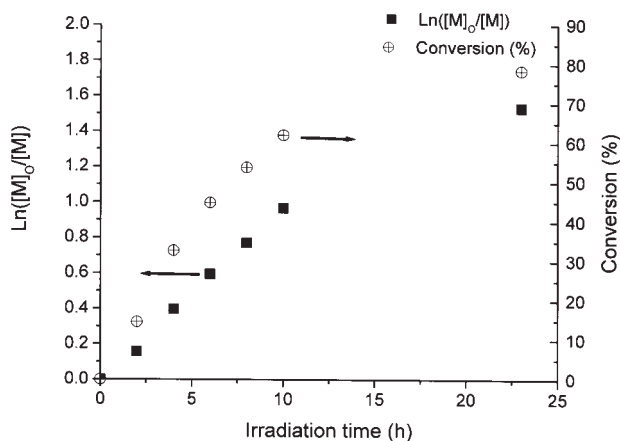


Figure 6 First-order time conversion plots for the photopolymerization of MMA in toluene initiated by PECH-DDC ($[\text{PECH-DDC}]/[\text{MMA}] = 0.0167$) as a function of UV irradiation time.

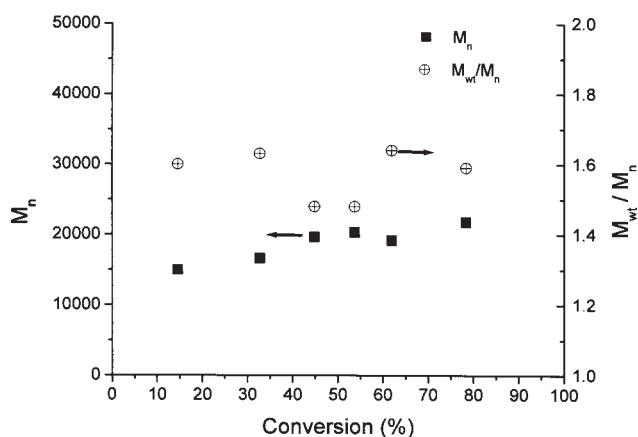


Figure 7 Plots of M_n or M_{wt}/M_n against conversion for the photopolymerization of MMA in toluene initiated by PECH-DDC ($[\text{PECH-DDC}]/[\text{MMA}] = 0.0167$) as a function of UV irradiation time.

A first-order time conversion plot is shown in Figure 6, where $[M]$ is the monomer concentration and $[M]_0$ is the initial monomer concentration. The conversion was estimated by gravimetric measurements. The conversion after 2 h of radiation was about 8%, and running the reaction for another 22 h conversion increased to about 75%. While we see an increase in molecular weight with an increase in conversion, there is a deviation from linearity regarding the rate of molecular weight increase as conversion increases. It appears, therefore, as if there is a decrease in reaction rate as the conversion increases. The reason is not clear, although possible explanations could be: (a) the synthesis of PMMA-g-PECH, which will increase the viscosity of mixture, leading to a decrease in reaction rate; (b) consumption of monomers; or (c) decomposition of DDC in the initial period of the reaction. The latter should lead to an

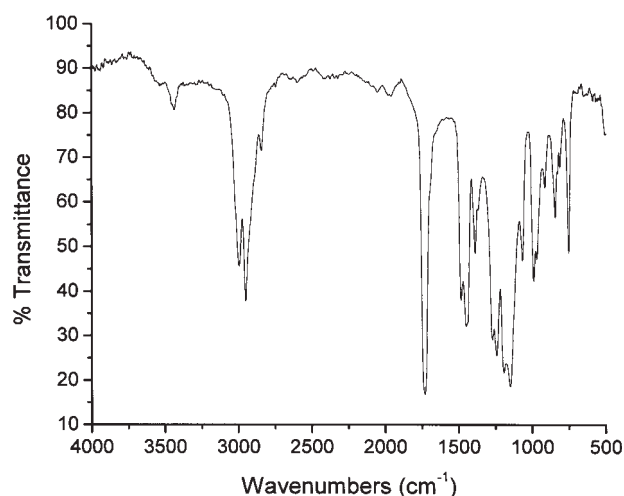


Figure 8 FTIR spectrum of PMMA-g-PECH copolymer.

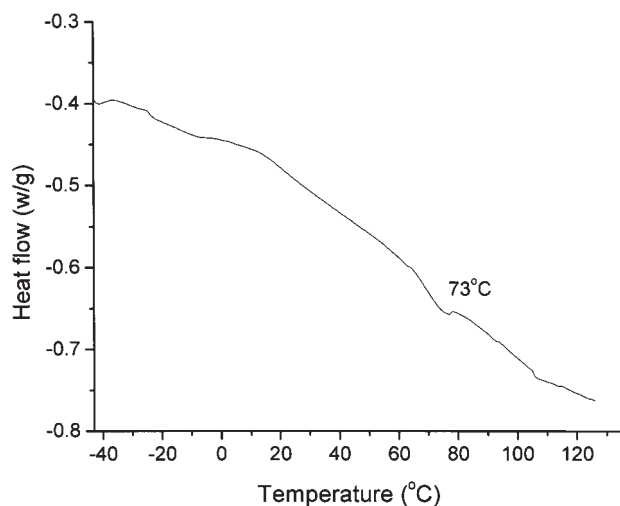


Figure 9 DSC thermogram of PMMA-g-PECH copolymer.

increase in polydispersity, which is not evident (Fig. 7).

The effect of the reaction time on the molecular weight and polydispersity of PMMA is demonstrated in Figure 7. There is an increase in the molecular weight with the reaction time. The polydispersity remained in the range 1.48–1.64. This indicates that polymerization proceeds in a reasonably controlled fashion. 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.

Figure 8 shows the FTIR spectrum of the PMMA-g-PECH copolymer. Characteristic peaks of PMMA at 1724 cm^{-1} (C=O) and of PECH at 745 cm^{-1} (CH_2Cl) can be seen. The structure of the grafted copolymer was analyzed by $^1\text{H-NMR}$, and the spectrum shows peaks at about 3.6, 2.0–1.5, and 1.1–0.7 ppm, which correspond to methoxy, methylene, and methyl protons, due to the PMMA segment. On the other hand, peaks at about 4 and 1.7 ppm are attributed to the chloromethyl group, and the methylene group of the PECH backbone.

The glass transition temperature (T_g) was measured to analyze the phase behavior of the graft copolymers. Figure 9 shows the DSC thermograms of PMMA-g-PECH copolymer. The grafted copolymer shows a single glass transition temperature at about 73°C , which is between the T_g of the corresponding homopolymers. The glass transition temperature of PECH and PMMA are -23 and 105°C , respectively.²⁰ The presence of a single glass transition temperature is attributed to the miscibility of two different segments.²⁷

CONCLUSIONS

Macrophotoinitiators based on PECH and DDC via nucleophilic substitution of chlorine atoms in PECH with the DDC group were successfully prepared. The photoinitiator was used for the grafting of PMMA to PECH through photopolymerization initiated with UV radiation ($\lambda > 300\text{ nm}$). The first-order time conversion plot for the polymerization system under UV irradiation and an increase in the molecular weight with slight changes in the polydispersity confirm that polymerization proceeded in a controlled manner. The terminal hydroxyl groups of the PECH remain available for further reaction.

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