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Synthesis of Triblock Copolymers via Photopolymerization of Styrene and Methyl Methacrylate Using Macrophotoinitiators Possessing Poly(ethylene glycol) Units

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Abstract

Macrophotoinitiators based on poly(ethylene glycol)s bearing benzyl tereftalmono amid moieties were synthesized by the reaction of poly(ethylene glycol) (PEG) terminated with terephtaloyl chloride and benzyl amine. The initiators possessing PEG with different molecular weights were used in the photoinduced radical polymerization of styrene (S) and methyl methacrylate (MMA) to yield poly(styrene-*b*-ethylene glycol-*b*-styrene) and poly(methyl methacrylate-ethylene glycol-*b*-methyl methacrylate) triblock copolymers. Characterization of macrophotoinitiators were performed by elemental anlysis, IR and ^{1}H-NMR spectrum. The elemental analysis results agreed with the theoretical values. The IR and ^{1}H-NMR spectra showed that the poly(ethylene glycol) units were reacting with the tereftloyl chloride and benzylamine. Characterization of the block copolymers was carried out by spectral measurements, GPC and fractional precipitation methods. The polydispersities of the block copolymers were observed between 1.2–2.32 for poly(methyl methacrylate-ethylene glycol-*b*-methyl methacrylate) and 1.25–1.90 for poly(styrene-*b*-ethylene glycol-*b*-styrene) from GPC measurements.

Introduction

Block copolymers have been extensively studied and have industrial applications in many fields. Among the various synthetic methods, polymeric photoinitiators have been used successfully for the synthesis of block copolymers via a radical mechanism [1–12]. The synthesis of block copolymers by photopolymerization exerts a number of technical and theoretical advantages over other methods. Because of the applicability at low temperatures, side reactions are minimized. A new poly(ethylene glycol) containing macrophotoinitiator has been prepared and used for the polymerization of styrene and methyl methacrylate by Cakmak [13]. Irradiation of this type of photoinitiator generates thyl and benzoyl radicals. The benzoyl radicals initiate the polymerization of a vinyl monomer and thyl radical mainly terminates the growing chain by primary radical initiation. The synthesis and use of several initiators have been reported in the literaure [14]. Most of the initiators undergo a Norrish Type I cleavage, giving rise to benzoyl radicals, which initiate the polymerization reaction. Some of the initiators include benzoin alkyl ethers and derivatives [15], acyl phosphine oxides [16], and *t*-butyl peresters [17, 18]. In addition, several sulphur containing-photoinitiators have also been reported in the literature [19–24]. These initiators identified as iniferters undergo predominantly β-cleavage rather than cleavage due to the presence of the relatively weak C–S bond, to give thyl radicals, which are poor initiators for polymerization. The iniferter concept was discovered by Otsu et al. [25]. Iniferters are basically organic sulphur compounds with low decomposition energy. Under suitable conditions, the compounds dissociated into reactive radicals and inert radicals, the latter serving as capping agents.

In the present work, a new macrophotoinitiator possessing a benzoyl and benzyl amine group was synthesized by the reaction of benzyl amine and PEG terminated with tereftaloyl chloride. Macrophotoinitiators prepared with various molecular weights of PEG were used for the polymerization of S and MMA to obtain ABA-type block copolymers.

Experimental

Materials

Poly(ethylene glycol)s (PEG) (Merck) with a molecular weight of 600, 1000 and 1500 were used as supplied. Methyl methacrylate, styrene, benzyl amine, tereftaloyl chloride and triethyl amine were either Merck or Fluka. Methyl methacrylate and styrene were purified by conventional procedures.

Preparation of Macrophotoinitiators (MPI)

A typical macrophotoinitiator (MPI) having a phenyl methylene benzamide group was prepared by the reaction of PEG, tereftlaoyl chloride and benzyl amine as follows:

Table 1. Synthesis and characterization of macrophotoinitiators

Code	PEG (mmol)	TFC (mmol)	TEA (mmol)	Mn (g/mol)	BA (mmol)	Elemental analysis					
						C		H		N	
						Calc.	Found	Calc.	Found	Calc.	Found
MPI-600	16.7	33.3	33.3	1328	66.8	63.27	59.26	7.23	6.89	2.62	1.78
MPI-1000	10.0	20.0	20.0	1803	40.0	60.75	59.35	7.44	7.56	1.90	1.89
MPI-1500	13.4	26.7	26.7	2091	53.6	59.17	56.52	8.09	8.11	1.42	0.81

Table 2. Photopolymerization of methyl methacrylate. Polymerization time: 45 min at ambient temperature

Initiator		MMA	Block copolymer			
Type	Amount (g)	(g)	Yield	M_n	M_w/M_n	γ (ml/ml)
MPI-600	0.40	2.0	0.17	14200	1.63	1.56
	0.60	2.0	0.24	34132	1.23	1.72
	0.70	2.0	0.23	29683	1.12	1.78
	0.30	2.5	0.12	22786	1.91	1.67
	0.30	3.0	0.16	28057	2.32	1.72
MPI-1000	0.30	2.0	0.16	35291	1.57	1.56
	0.40	2.0	0.24	37478	1.25	1.61
MPI-1500	0.90	6.0	0.40	59599	1.90	1.43

Table 3. Photopolymerization of styrene

Initiator		Time	Styrene	Block copolymer			
Type	Amount (g)	(min)	(g)	Yield	M_n	M_w/M_n	γ (ml/ml)
MPI-1000	0.60	240	6.0	0.15	10547	1.99	1.85
	0.90	240	6.0	0.19	11761	2.18	1.92
	0.75	180	6.0	0.16	9979	1.84	2.00
	0.75	360	6.0	0.34	13185	1.82	2.08

Into a flask equipped with a magnetic stirrer and addition funnel were placed 100 ml of benzene, 10.00 g (16.70 mmol) of PEG 600 and 3.37 g (33.30 mmol) triethyl amine. To this system 6.76 g (33.30 mmol) tereftaloyl chloride in 50 ml benzene were added over 1 h. The mixture stood overnight at ambient temperature. After the addition of 7.15 g (66.8 mmol) benzyl amine, the reaction mixture was stirred at 24 h. The evaporation of the solvent, flask content was precipitated into diethyl ether. The macrophotoinitiator was dried in a vacuum at room temperature. The synthesis results are gathered in Table 1.

Photopolymerization

Photopolymerization of MMA and S were carried out in a quartz tube at room temperature with a 400 w high pressure mercury lamp at 10 cm distance. After polymerization for a given time, the contents of the tube were poured into ten-fold excess of methanol to isolate the polymer. The yield of the polymer was determined gravimetrically. The results of the polymerization of MMA and S are shown in Tables 2 and 3 respectively.

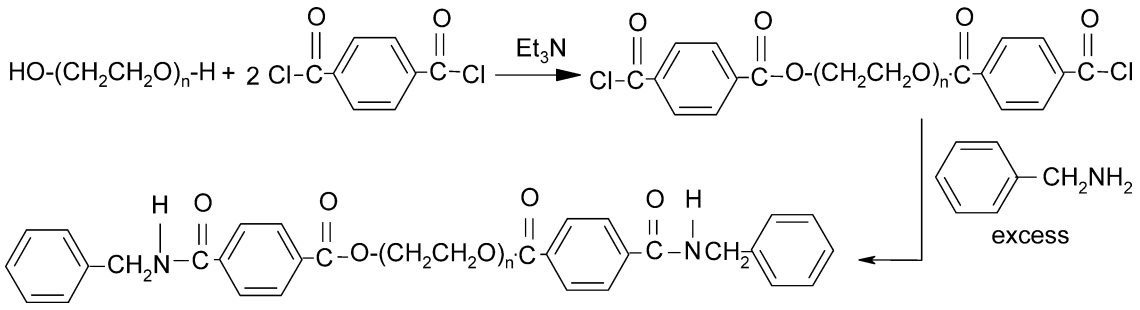
Characterization of the Products

Fractional precipitation distinguishes block copolymers form the homo polymers [14]. For this purpose block copolymer was dissolved in THF; and aliquot samples of the solution were taken for the precipitation by adding different volumes of petroleum ether (non-solvent). Homopolymer of MMA and S were separated at different volume ratios to solvents (γ) [γ: 0.50–0.55 for PMMA and γ: 2.5–3.2 for PS] [26]. IR spectra of the products were recorded with a Perkin Elmer spectrometer. The ^{1}H-NMR spectra of the products were obtained from $CDCl_3$ solutions on a 200 MHz Bruker spectrometer. GPC chromatograms were obtained using a Waters 510 instrument with THF as the solvent at a flow rate of 1 ml/min.

Results and Discussion

Synthesis of Macrophotoinitiators

In this study three different macrophotoinitiators (MPI) were synthesized from different molecular weight PEGs. They were first transformed into tereftaloyl chloride polymers using tereflaloyl chloride and triethyl amine. These were reacted with an excess amount of benzyl amine, providing



Scheme 1.

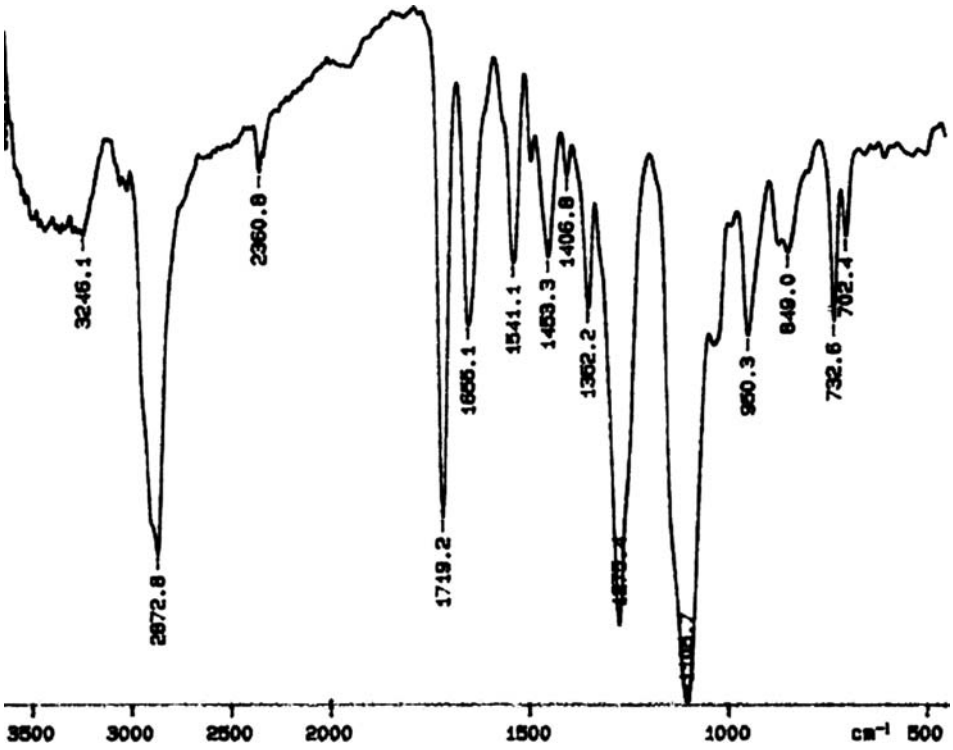


Figure 1. IR spectrum of MPI-600.

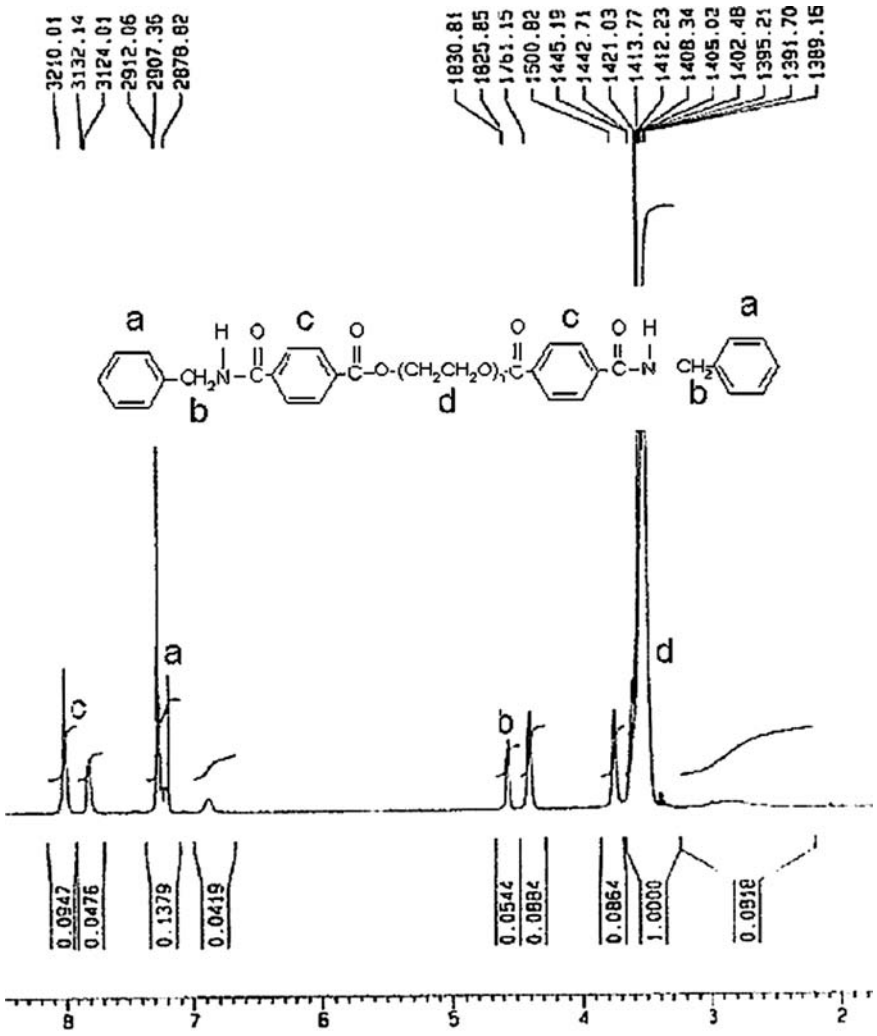
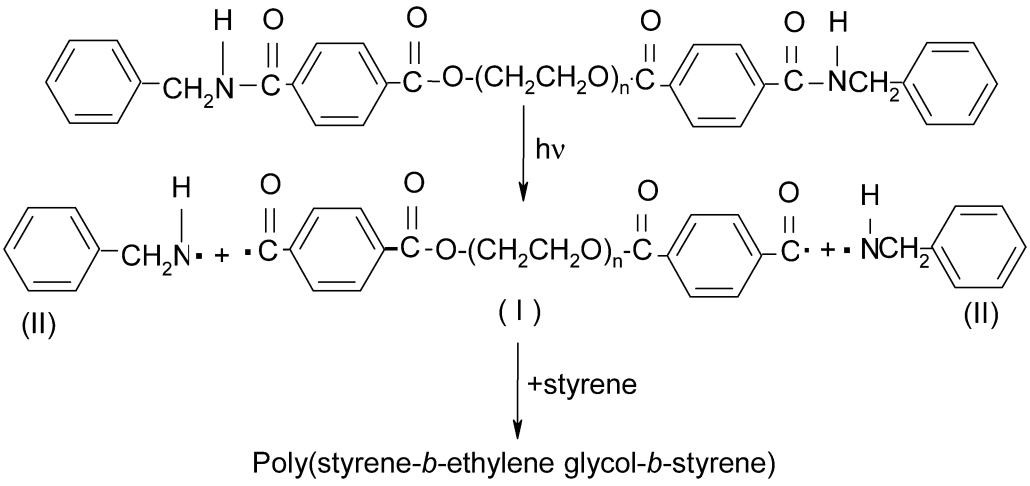


Figure 2. ^{1}H-NMR spectrum of MPI-600.



Scheme 2.

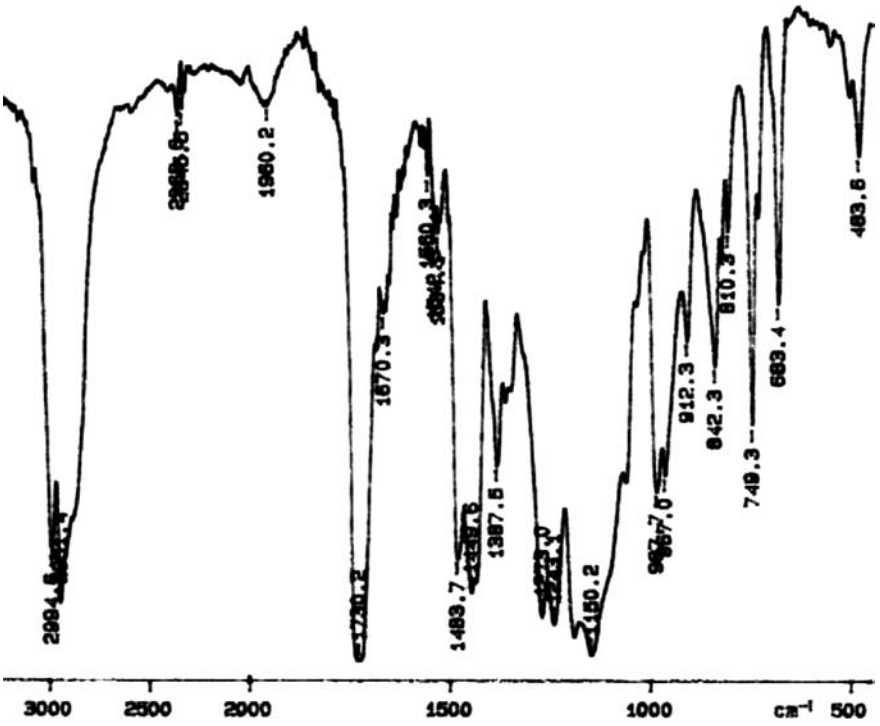


Figure 3. IR spectrum of poly(methyl methacrylate-*b*-ethylene glycol-*b*-methyl methacrylate) block copolymer.

primer amine end groups according to Scheme 1. The results of the synthesis of the macrophotoinitiators are summarized in Table 1. The results of the elemental analysis agreed with theoretical values. Macrophotoinitiators were characterized by IR and ^{1}H-NMR spectroscopy and elemental analysis. Figure 1 shows the IR spectrum of the macrophotoinitiator (MPI-600); 2873 cm^{-1} (aliphatic C–H), 2361 cm^{-1} (C–N), 1719 cm^{-1} (C=O), 1655 cm^{-1} (aromatic). The ^{1}H-NMR spectrum of MPI-600 in Figure 2 shows the 7.3–7.2 and 8.1–7.8 ppm for aromatic protons, 3.6 ppm for –OCH_2– protons, 4.6 ppm for –N–CH_2– protons of the macrophotoinitiator derived from PEG-600. Both IR and NMR spectra confirm the structure of the macrophotoinitiator (MPI-600). There was an increase in the molecular weights of the macrophotoinitiators of the original poly(ethylene glycol)s. It may be supposed that chain extension occurred during the end capping reaction since the observed molecular weights of the macrophotoinitiators were greater than the PEGs.

Photopolymerization

Photopolymerization of the styrene and methyl methacrylate were carried out in bulk. Dissociation of the macrophotoinitiator is expected to proceed according to the Scheme 2. (I) initiates the polymerization of styrene or methyl methacrylate and (II) terminates the growing chain by primary radical addition.

Characterization of the Products

The characterization of the block copolymer films, which are mostly transparent, can be summarized as follows. There was an increase in the molecular weights of the block

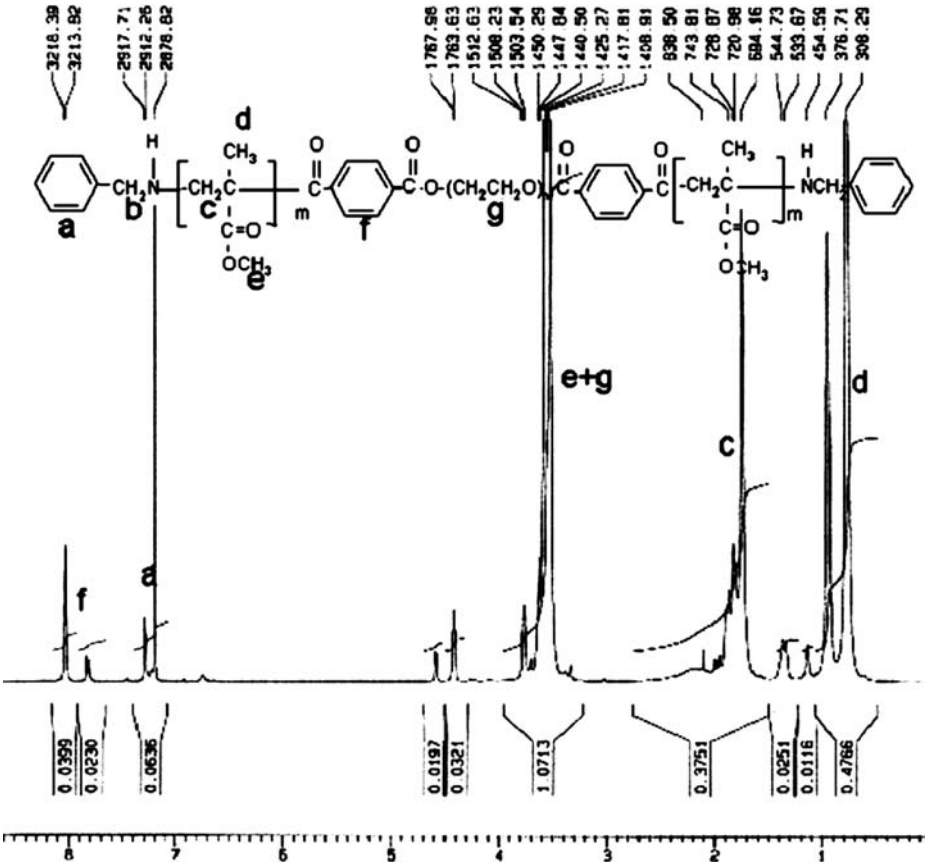


Figure 4. [1]H-NMR spectrum of pol(methyl methacrylate-*b*-ethylene glycol-*b*-methyl methacrylate) block copolymer.

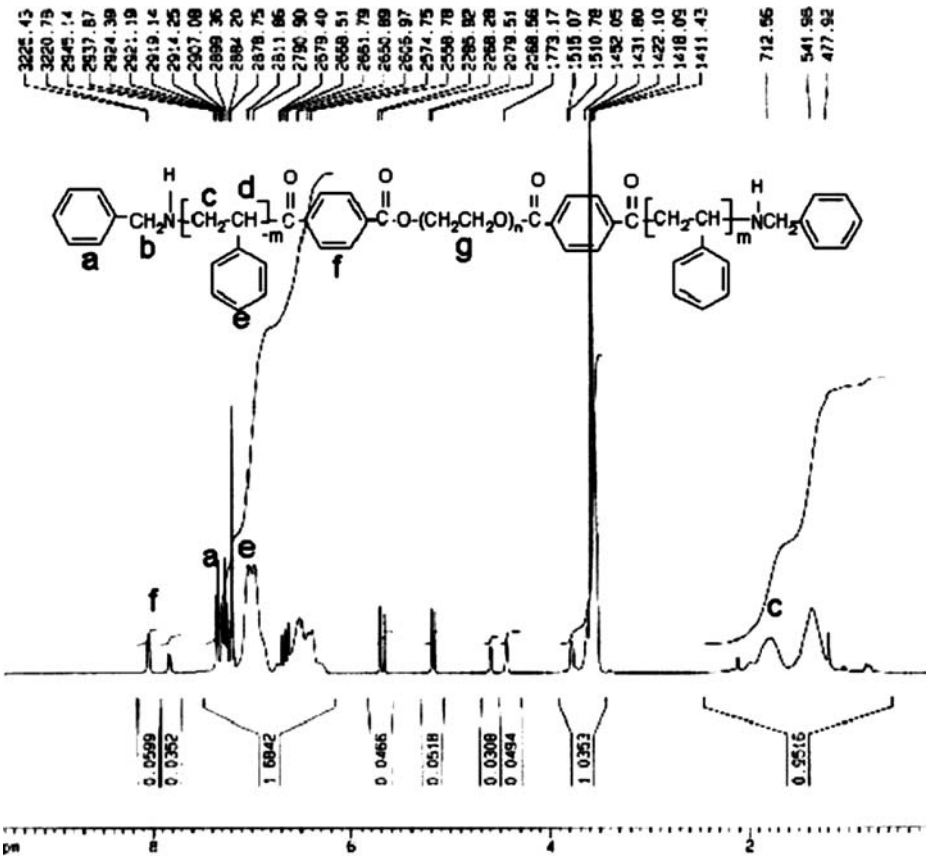


Figure 5. [1]H-NMR spectrum of poly(styrene-*b*-ethylene glycol-*b*-styrene) block copolymer.

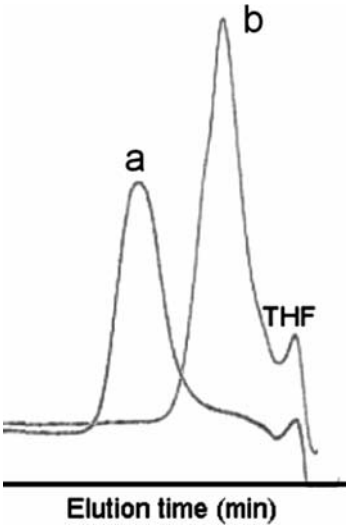


Figure 6. GPC curves of (a) block copolymer obtained after fractional precipitation (M_n: 13185 g/mol) and (b) macrophotoinitiator (M_n: 1803 g/mol).

copolymers of the original macrophotoinitiator. Increases in the molecular weights of the products when compared with the macrophotoinitiators confirm block copolymer formation. Fractional precipitation behavior gives one evidence for the formation of block copolymer. The γ values of the products lie between those of their related homo polymers, as shown in Tables 2 and 3. The IR spectrum of poly(methyl methacrylate-*b*-ethylene glycol-*b*-methyl methacrylate) block copolymer showed characteristic absorptions at 1730 cm^{-1}, due to the ester carbonyl group of the MMA, and at 1150 cm^{-1} for the C–O stretch of the PEG chain. The ^{1}H-NMR spectrum of a PMMA-PEG-PMMA block copolymer in Figure 4 shows the characteristic signals at 4.0–3.8 ppm for $–OCH_2$ and $–OCH_3$ protons, at 0.8–1.0 ppm for CH_3 protons of MMA block and 1.8 ppm $–CH_2$ protons of MMA. The formation of poly(styrene-*b*-ethylene glycol-*b*-styrene) block copolymer was also supported by ^{1}H-NMR. As can be seen from Figure 5, $–OCH_2$ protons appear in the 3.8–3.7 ppm region, in addition to peaks at 7.1 ppm for phenyl protons of the PS block. Block copolymer formation was demonstrated by gel permeation chromatography. Chromatograms recorded with an initial macrophotoinitiator and a poly(styrene-*b*-ethylene glycol-*b*-styrene) block copolymer obtained by fractional precipitation are shown in Figure 6. These chromatograms indicate a unimodal molecular weight distribution in both cases and an increase in the molecular weight as a result of block copolymerization.

Conclusion

The proposed procedures for the preparation of ABA type block copolymers by photopolymerization are simple and efficient. The initiators synthesized are less appropriate for styrene. The synthesis of block copolymer via macrophotoinitiators has numerous advantages over other methods. Because of applicability at low temperatures, side reactions which lead to homo polymer formation are minimized. Depending on the choice of monomer, a macrophotoinitiator tailor-made block copolymer can be obtained, e.g., hard–soft, amphilic, etc. The block length can be adjusted by varying the monomer and initiator concentrations.

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