Synthesis of PMMA-PTHF-PMMA and PMMA-PTHF-PST Linear and Star Block Copolymers

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ABSTRACT: Combination of cationic, redox free radical, and thermal free radical polymerizations was performed to obtain linear and star polytetramethylene oxide (poly-THF)-polymethyl methacrylate (PMMA)/polystyrene (PSt) multiblock copolymers. Cationic polymerization of THF was initiated by the mixture of $AgSbF_6$ and bis(4,4′ bromomethyl benzoyl) peroxide (BBP) or bis (3,5,3′,5′ dibromomethyl benzoyl) peroxide (BDBP) at 20°C to obtain linear and star poly-THF initiators with M_w varying from 7,500 to 59,000 Da. Poly-THF samples with hydroxyl ends were used in the methyl methacrylate (MMA) polymerization in the presence of Ce(IV) salt at 40°C to obtain poly(THF-*b*-MMA) block copolymers containing the peroxide group in the middle. Poly(MMA-*b*-THF) linear and star block copolymers having the peroxide group in the chain were used in the polymerization of methyl methacrylate (MMA) and styrene (St) at 80°C to obtain PMMA-*b*-PTHF-*b*-PMMA and PMMA-*b*-PTHF-*b*-PSt linear and star multiblock copolymers. Polymers obtained were characterized by GPC, FT-IR, DSC, TGA, ^{1}H-NMR, and ^{13}C-NMR techniques and the fractional precipitation method. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 219–226, 2004

Key words: star polymers; cationic polymerization; polystyrene; polyethers; redox polymers

INTRODUCTION

Poly-THF, obtained by cationic polymerization of THF with strong acids, Friedel Crafts catalyst,[1] and onium salt cationic photoinitiators,[2,3] is a very important synthetic biodegradable thermoplastic for industrial and environmental applications.

THF → Catalyst → Poly-(THF)
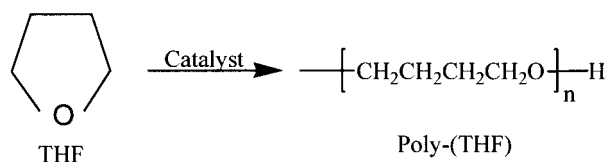
Carbocations can be generated from 4,4′-azo-*bis*-cyano-pentanoyl chloride in the presence of a silver salt, which initiates cationic polymerization of THF leading to poly-THF containing labile azo groups in the middle of the polymer chain.[3] In our laboratories, we have synthesized two types of bromomethyl benzoyl peroxides leading to linear[4] and star poly-THF[5] containing labile peroxide groups in the middle of the polymer chain in view of the star polymers also having some advantages from the corresponding linear polymers.[6] Polymers containing labile azo and/or 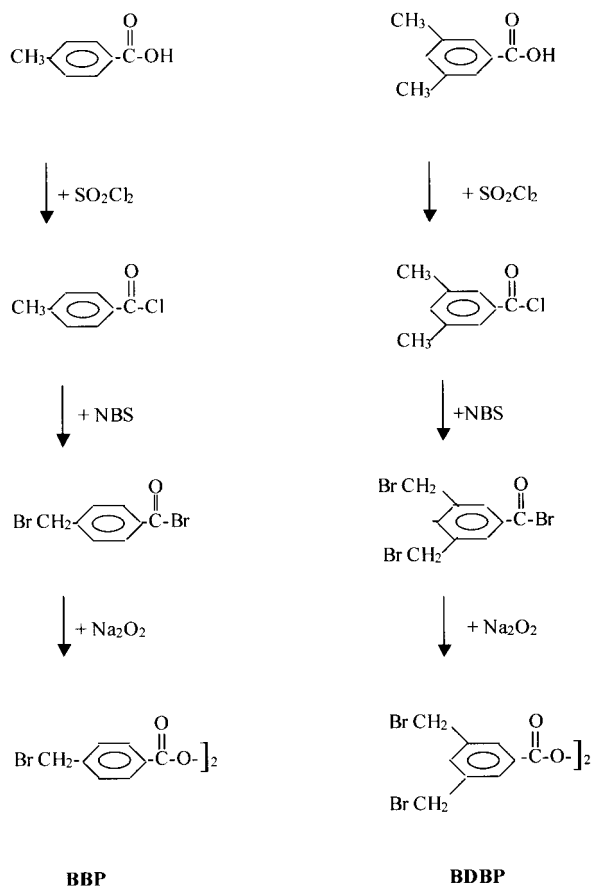peroxide groups can initiate vinyl polymerization to obtain block copolymers.[7] Polymethyl methacrylate (PMMA) is not biodegradable. It is very desirable to combine the biodegradability of the biodegradable polymers and the excellent application properties of PMMA. Several efforts have been made to copolymerize THF and MMA in our laboratories.[8,9] In one route, the cationic polymerization of THF was carried out by a mixture of bromomethyl benzoyl peroxide and $AgSbF_6$ to obtain a poly-THF macroinitiator; the poly-THF macroinitiator then can initiate MMA polymerization to give poly(THF-*b*-MMA) block copolymers.[9,10] In the other route, commercially available THF oligomers with hydroxyl end groups are used to initiate the redox polymerization of MMA in the presence of Ce(IV) salt to give poly(THF-*b*-MMA) block copolymers.[9] This work refers to combined cationic, redox, and thermal free radical polymerization methods in the preparation of linear and star poly(THF-*b*-MMA) and poly(THF-*b*-MMA and/or St) multiblock copolymers with four arms containing a peroxide group in the middle of the polymer chain. In this case, a combination of the three polymerization methods to obtain PSt and/or PMMA-poly-THF multiblock copolymer synthesis and star-branched multiblock copolymers with four arms are reported first.

EXPERIMENTAL

Materials

THF was refluxed and distilled over Na metal and benzophenone mixture after producing a purple color,

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Scheme 1 (left column)

CH₃–〈〉–C(=O)–OH

↓ + SO₂Cl₂

CH₃–〈〉–C(=O)–Cl

↓ + NBS

Br CH₂–〈〉–C(=O)–Br

↓ + Na₂O₂

Br CH₂–〈〉–C(=O)–O–]₂

BBP

(right column)

CH₃,CH₃–〈〉–C(=O)–OH

↓ + SO₂Cl₂

CH₃,CH₃–〈〉–C(=O)–Cl

↓ +NBS

Br CH₂, Br CH₂–〈〉–C(=O)–Br

↓ + Na₂O₂

Br CH₂, Br CH₂–〈〉–C(=O)–O–]₂

BDBP

Scheme 1 Reaction chart of the synthesis of BBP and BDBP.

just before use. MMA and St were freed from inhibitor by vacuum distilation over calcium hydride. AgSbF₆ was supplied from Aldrich and used as received. *N*-Bromo succinimide was supplied from Aldrich and used as received. Ceric ammonium nitrate, Ce(NH₄)₂(NO₃)₆, (CAN), was supplied by Fluka AG and used as received. All other chemicals were reagent grade and used as received.

Synthesis of bromomethyl benzoyl peroxide initiators: BBP and BDBP

Bis(4,4′ bromo-methyl benzoyl) peroxide (BBP) and bis (3,5,3′,5′ dibromomethyl benzoyl) peroxide (BDBP) were obtained from the reaction of the corresponding bromomethyl benzoyl bromides with sodium peroxide as described.[4,5] Scheme 1 contains the reaction chart used to obtain BBP and BDBP.

Cationic polymerization of THF

Poly-THF oligomers were synthesized at 20°C by the cationic polymerization of THF initiated by AgSbF₆ with BBP or BDBP initiator system, according to the described procedure.[4,5] Poly-THF was precipitated into cold water containing a small amount of a weak base such as an ammonia solution. Poly-THF was dried *in vacuo* at room temperature. The results and polymerization conditions are listed in Table I.

Copolymerization of MMA with poly-THF

The same polymerization procedure described in Arslan and Hazer[9] was applied to the preparation of

TABLE I
Results and Conditions of Cationic Polymerization of THF by Using the Catalyst System of AgSbF₆ with BDBP and BBP

Run no.	AgSbF₆ (mol/L) × 10²	BDBP (mol/L) × 10³	BBP × 10² (mol/L)	THF (g)	Temperature (°C)	Polymerization time (h)	Amount (g)	wt %	$M_n \times 10^{-4}$	MWD	[η] (dL/g)	$M_w \times 10^{-4}$
HM-1	1.72	4.29	—	32	20	19	2.56	8.0			0.924ᵃ	3.73
HM-2	1.72	4.29	—	32	30	19	4.19	13			0.92ᵇ	5.55
HM-3	2.40	6.00	—	31	20	22	7.80	25			—	—
HM-4	3.40	8.60	—	33	30	19	20.0	61			—	—
HM-5	2.00	5.00	—	30	20	13	9.70	32	5.16	1.46	—	—
HM-6	2.60	6.50	—	31	20	12	14.8	48	2.13	2.68	—	—
HM-8	1.50	3.75	—	30	25	5	0.90	3.0			0.332ᵇ	1.02
HM-9	2.00	5.00	—	32	25	5	1.30	4.1			0.402ᵇ	1.40
HM-11	1.50	3.84	—	29	25	19	1.91	6.6	4.07	1.68	—	—
HM-17	3.50	8.75	—	31	30	62	26.5	85	6.14	1.25	—	—
HM-18	3.00	7.50	—	51	30	24	16.0	32	3.41	1.93	—	—
HM-10	2.10	—	1.03	33	20	4	1.33	4.0	0.88	2.41	0.215ᵃ	0.58
HM-12	2.10	—	1.03	30	20	19	2.23	7.5	1.33	2.58	—	—
HM-13	2.00	—	1.00	30	30	19	1.71	5.8	1.91	2.25	—	—
HM-14	3.00	—	1.50	31	20	19	3.50	11	1.27	2.56	—	—
HM-16	2.70	—	1.36	32	30	38	19.5	61	5.9	1.36	—	—

ᵃ [η] = 25.1 × 10⁻⁵M⁰·⁷⁸ in toluene at 28°C. ᵇ[η] = 131 × 10⁻⁵M⁰·⁶⁰ in benzene at 30°C.

TABLE II
Results and Conditions of the Polymerization of MMA by Ce^{IV}/-diol Redox System at 40°C

| Run no. | Poly-THF used | | MMA (mL) | [HNO₃] (mol/L) | [Ce⁺⁴] | | Polymerization time (h) | Polymer yield (g) | $M_n \times 10^{-4}$ | MWD |
	Run no.	Amount (g)			(mol/L)	V (mL)				
B-2-10	HM-10	0.50	2.0	0.5	0.05	3	2	2.24	7.5	1.11
B-4-9	HM-9	1.20	3.5	0.5	0.05	3	5	4.95	7.6	1.10
B-2-16	HM-16	0.51	3.0	0.5	0.05	6	6	2.18	11.8	1.09
B-2-13	HM-13	0.50	3.0	0.5	0.05	6	6	1.92		
B-4-11	HM-11	0.51	3.0	0.5	0.05	6	6	1.91	5.4	1.23

poly(THF-*b*-MMA) block copolymers. An appropriate amount of hydroxyl-terminated THF polymer was put in a pyrex tube and then a CAN solution (initiator) and MMA (monomer) were added. Approximately 10 mg of tetrabutyl ammonium hydrogensulphate (TBAHS) was also added to increase the solubility of the diols. Nitrogen was introduced for 1 min though a needle into the homogenous mixture to expel the air. The tube was covered with a stopper and kept at 40°C for a given time with stirring during the polymerization. The product was precipitated into methanol, collected by filtration, and dried to a constant weight. The results and conditions of the block copolymer formation are collected in Table II.

Polymerization of MMA/St initiated by PMMA-b-PTHF copolymers

The polymerization of MMA/St initiated by PMMA-*b*-PTHF possessing in-chain peroxide groups was carried out under nitrogen at 80°C. After the desired time, block copolymer freed from homo-poly-THF was obtained by precipitation in excess methanol. The results and conditions of multiblock copolymer formation are given in Table III.

Characterization of the polymers obtained

Fractional precipitation

To separate block copolymers from unreacted homopolymers, the fractional precipitation method was carried out by measuring γ, the volume ratio of non-

solvent (methanol) to the solution of copolymers in chloroform, to separate pure block copolymers from the corresponding homopolymers.[10] For this purpose, a given amount of polymer was dissolved in a predetermined volume of $CHCl_3$; methanol was then gradually added to this solution until the polymer precipitated. The γ value of the polymer was calculated by taking the volume ratio of methanol used in $CHCl_3$ solution.

Molecular weight measurement

Molecular weights (M_n, M_w) and molecular weight distributions (MWD) were measured with a Knauer gel permeation chromatograph using ChromGate software, a WellChrom Interface Box, RI Detector K-2301, and WellChrom HPLC pump K-501. $CHCl_3$ was used as an eluent at a flow rate of 1 mL/min. A calibration curve was generated with six polystyrene standards: 2,500, 2,950, 5,050, 20,000, 52,000, and 96,400 Da, of low dispersity obtained from Polyscience.

Diluted solution viscosity measurements were also performed by using an Ubbelohde viscosimeter.

FT-IR spectrometry

FT-IR spectra were recorded of the block polymer films cast from $CHCl_3$ solutions, using a Jasco model 300E FT-IR spectrometer.
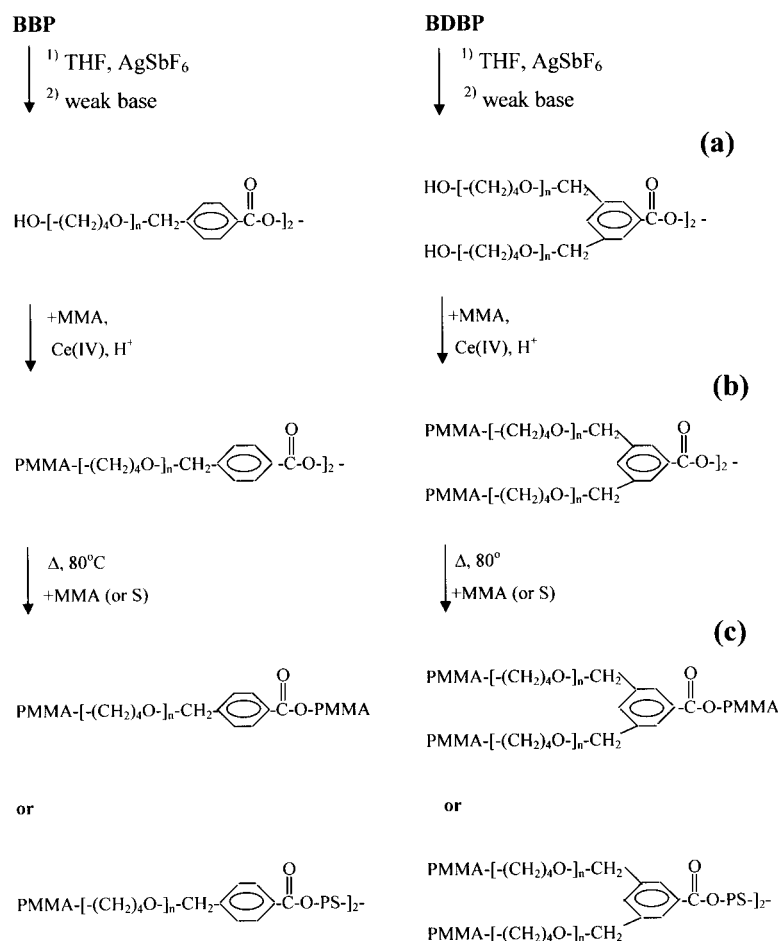
NMR

^{1}H-NMR and ^{13}C-NMR spectra of the products were recorded using a Bruker Avance-500 NMR spectrometer, in $CDCl_3$ solvent.

TABLE III
Results and Conditions of MMA and Styrene Polymerization Initiated by (PMMA-*b*-PTHF) Copolymers at 80°C for 8 h

| Run no. | Poly(THF-*b*-MMA) | | MMA (mL) | Styrene (mL) | Polymer yield (g) |
	Run no.	Amount (g)			
MB-2-131	B-2-13	0.41	3	—	0.75
MB-2-161	B-2-16	0.40	3	—	1.17
MB-4-92	B-4-9	0.39	—	3	0.58
MB-2-162	B-2-16	0.42	—	3	0.55

Thermal analysis

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were carried out under nitrogen by using a Perkin–Elmer/Pyris 1 DSC and Perkin–Elmer/Pyris1 TGA.

BBP
1) THF, AgSbF$_6$
2) weak base

BDBP
1) THF, AgSbF$_6$
2) weak base

(a)

HO-[-(CH$_2$)$_4$O-]$_n$-CH$_2$-⟨⟩-C(=O)-O-]$_2$ -

HO-[-(CH$_2$)$_4$O-]$_n$-CH$_2$ / HO-[-(CH$_2$)$_4$O-]$_n$-CH$_2$ ⟨⟩-C(=O)-O-]$_2$ -

+MMA, Ce(IV), H$^+$

+MMA, Ce(IV), H$^+$

(b)

PMMA-[-(CH$_2$)$_4$O-]$_n$-CH$_2$-⟨⟩-C(=O)-O-]$_2$ -

PMMA-[-(CH$_2$)$_4$O-]$_n$-CH$_2$ / PMMA-[-(CH$_2$)$_4$O-]$_n$-CH$_2$ ⟨⟩-C(=O)-O-]$_2$ -

Δ, 80°C
+MMA (or S)

Δ, 80°
+MMA (or S)

(c)

PMMA-[-(CH$_2$)$_4$O-]$_n$-CH$_2$-⟨⟩-C(=O)-O-PMMA

PMMA-[-(CH$_2$)$_4$O-]$_n$-CH$_2$ / PMMA-[-(CH$_2$)$_4$O-]$_n$-CH$_2$ ⟨⟩-C(=O)-O-PMMA

or

or

PMMA-[-(CH$_2$)$_4$O-]$_n$-CH$_2$-⟨⟩-C(=O)-O-PS-]$_2$-

PMMA-[-(CH$_2$)$_4$O-]$_n$-CH$_2$ / PMMA-[-(CH$_2$)$_4$O-]$_n$-CH$_2$ ⟨⟩-C(=O)-O-PS-]$_2$-

Scheme 2   Multiblock copolymer synthesis via combination of cationic, redox, and thermal polymerization.

RESULTS AND DISCUSSION

Cationic polymerization of THF

THF polymerization was performed using a catalyst mixture composed of the bromomethyl derivative of benzoyl peroxide and the AgSbF$_6$ at temperatures of 20, 25, and 30°C. Scheme 2(a) shows the reaction design of the poly-THF synthesis. BBP leads to the linear poly-THF while BDBP leads to the branched star poly-THF with four arms. Results and conditions of THF polymerization are listed in Table I. BBP has two bromomethyl groups and consumes 2 moles of the silver salt while BDBP consumes 4 moles of the silver salt. In this manner, BDBP yielded higher poly-THF than that of BBP. Molar masses of the poly-THF samples measured both GPC and viscosimetry. There was a good correlation of the molecular weights found by GPC and viscosity (see run no. 10 in Table I). Molar masses of poly-THF with hydroxyl ends and a peroxide group in the middle varied from 0.88 to 6.14 × 10^4. Higher catalyst concentration, higher temperature, and longer polymerization time give higher yields (compare HM-2 and HM-4, HM-1 and HM-2, and HM-8 and HM-11, respectively) and higher molecular mass of poly-THF (compare HM-10 and 14, 16), as expected in cationic polymerization.

Copolymerization of MMA with poly-THF

Poly-THF with hydroxyl ends and Ceric salts initiate the redox polymerization of MMA in aqueous media. Results and conditions of copolymerization of MMA with poly-THF were collected in Table II. In runs, B-2 refers to the block copolymers with two arms and B-4 refers to the block copolymers with four arms. Block copolymers were purified by using the fractional precipitation technique. There was no considerable amount of homo-PMMA determined by the fractional precipitation. When the solvent is chloroform and the nonsolvent is methanol, the gamma values of the block copolymers were approximately at 2.2 to 3.6 while the gamma values for PMMA was 2.2–2.7 and the gamma values for poly-THF was 7.0–7.5. The gamma values of the block copolymers were similar to that of homo PMMA but slightly shifted to the higher value because of poly-THF segments.

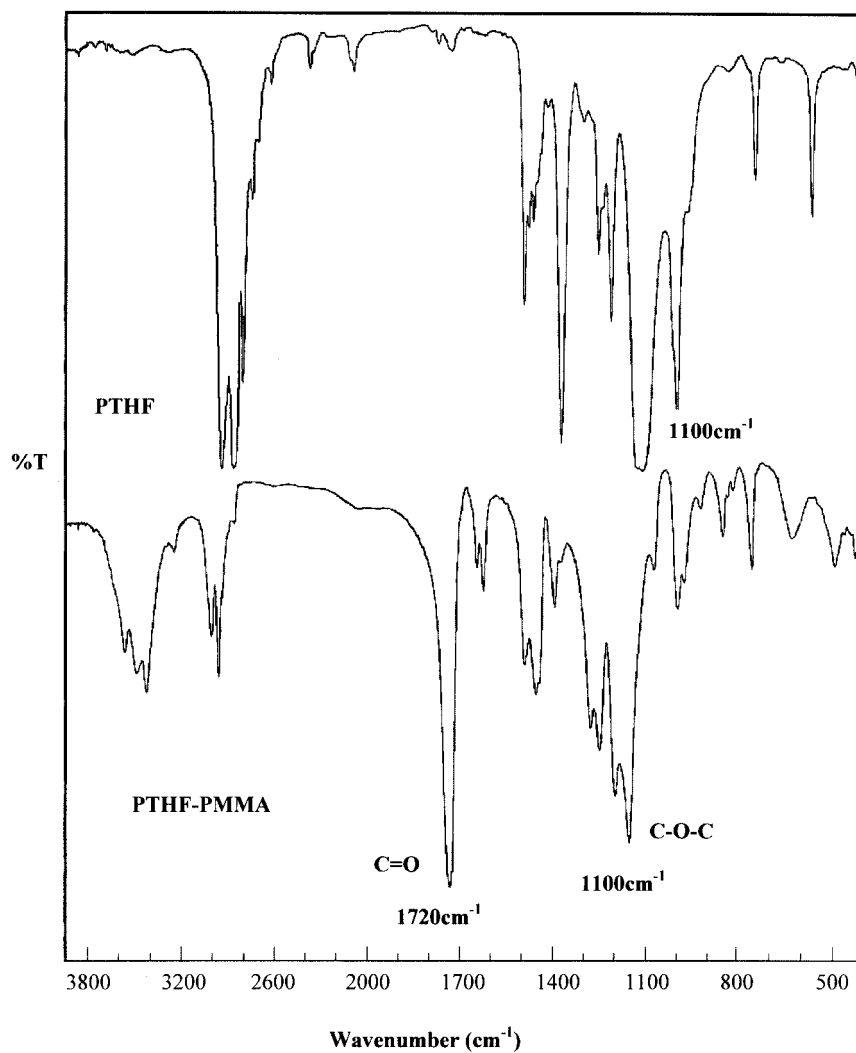The smaller molecular weight of poly-THF macroinitiator causes higher copolymer yield because of the

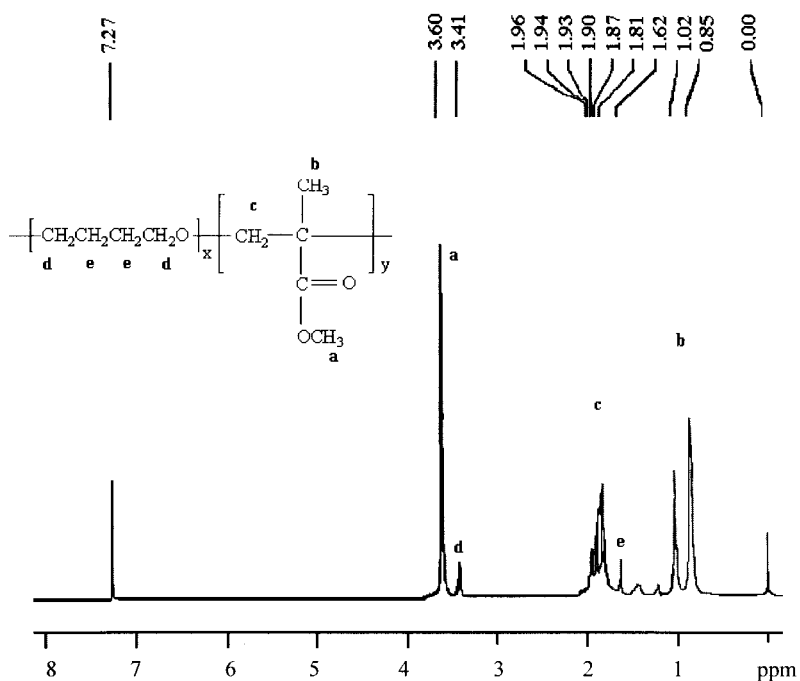**Figure 1** The FT-IR spectra of PTHF (HM-1) and PTHF-*b*-PMMA (B-4–9) block copolymer.

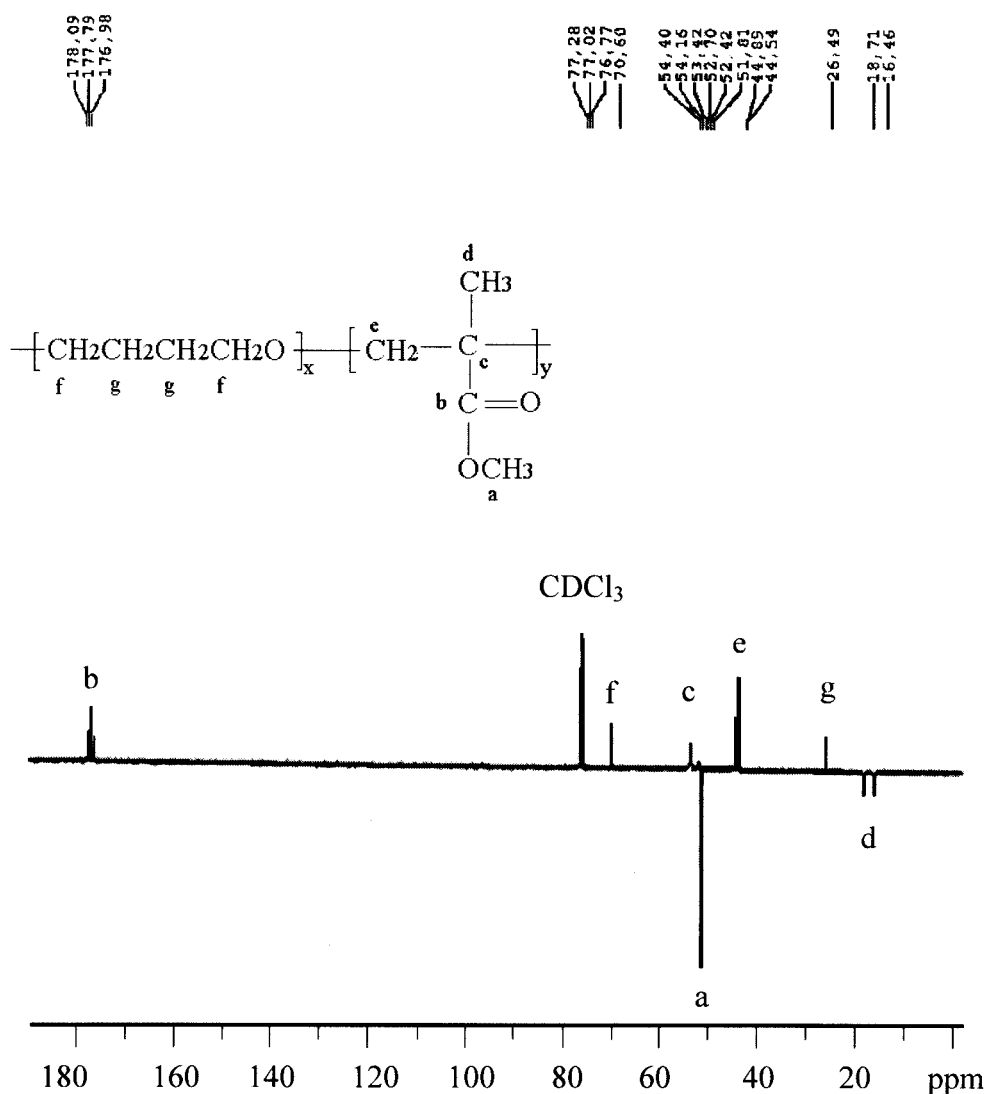**Figure 2** ^{1}H-NMR of PTHF-*b*-PMMA block copolymer (B-4–9).

Figure 3 ¹³C-NMR of PTHF-*b*-PMMA block copolymer (Sample no. B-4–11).

higher solubility of lower molecular mass poly-THF in water. Naturally, molar masses of poly-THF-*b*-PMMA block copolymers were higher than the corresponding poly-THF macroinitiator. For example, a block copolymer B-2–10 with M_n 74,500 Da was obtained from poly-THF with M_n 8,758. Block copolymers purified by fractional precipitation indicated very narrow MWD between 1.09 and 1.23 and unimodal GPC curves.

Characterization of block copolymers

Characterization of block copolymers was made by IR, TGA, DSC, ¹H-NMR, and ¹³C-NMR techniques. The IR spectrum of the PMMA-PTHF block copolymer showed characteristic absorptions at 1,720 cm⁻¹ due to the carbonyl group of the PMMA and at 1,100 cm⁻¹ due to the C—O—C stretching band of poly-THF.

Figure 1 shows FT-IR spectra of a block copolymer (B-4–11) and poly-THF (HM-1).

The ¹H-NMR spectra of block copolymers show the characteristic signals at δ (ppm) 0.85 for methyl protons, 3.60 for methoxy (—OCH₃) protons of PMMA, 3.41 for oxymethylene protons of poly-THF, and 1.62–1.96 for methylene protons of both units. Figure 2 gives the ¹H-NMR spectrum of block copolymer: B-4–9.

The ¹³C-NMR spectra of PMMA-*b*-PTHF block copolymers show the characteristic signals at δ (ppm) 16.46 for methyl carbon, 52.70 for methoxy (—OCH₃) carbon, 177.79 for carbonyl carbon, 70.60 for quarterner carbon, and 44.54 for methylene carbon of PMMA and 26.49 for methylene carbon and 54.16 for methylene carbon of poly-THF units. Figure 3 indicates the ¹³C-NMR spectrum of a PMMA-PTHF block copolymer sample: B-4–11.
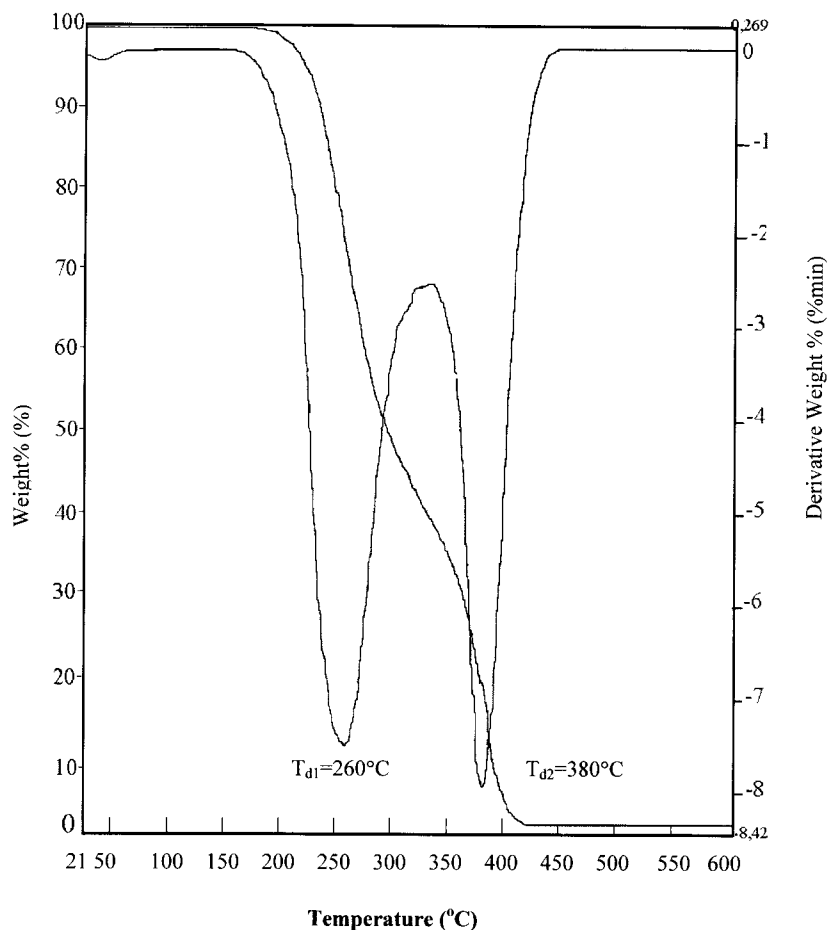
Figure 4 Thermogravimetric trace of block copolymer (B-4–11).

Thermal analysis of block copolymers was done by using TGA. As indicated in Figure 4, decomposition temperatures of the block copolymer sample B-4–11 at 260°C (for PTHF segment) and 380°C (for PMMA segment) were observed. By using the TGA curve, we can make an estimation of the poly-THF content as nearly 50 wt % in block copolymer sample B-4–11.

Block copolymers listed in Table II contain peroxide groups in the middle of the macromolecular chain; they can initiate polymerization of another vinyl monomer. Results and conditions of the multiblock copolymer synthesis were listed in Table III. Polymerization of MMA leads to the higher polymer yield than that of St as expected because peroxide decomposes faster in a benzene solution of MMA than in a similar solution of St.[11] In Table IV, compared to molecular weights, a smooth increase was observed. In the case of multiblock copolymers MB-4–91 and MB-4–92 obtained by the polymerization of MMA or St with B-4–9 macroperoxide block copolymer initiator, first, the peroxide bond in the middle of the PTHF-*b*-PMMA block copolymer (B-4–9) is breaking to produce radicals that initiate the MMA (or St) polymerization to give PMMA-*b*-PTHF-*b*-PMMA (MB-4–91), or PMMA-

b-PTF-PS (MB-4–92) multiblock copolymers. Similarly, according to the above conclusion, multiblock copolymers obtained by the MMA polymerization have higher molecular weights than that of block copolymer containing PS segments. The higher molecular weight of PS multiblock copolymers may be expected because of the combination termination of the polystyryl radicals; however, the very long macromolecular chain has only one peroxide unit in the middle.

In Scheme 2, we can estimate the microstructure of the block copolymers based on the BBP and BDBP initiators as ABBA, ABA, ABCBA, and $(AB)_4$ four branched, $(AB)_2A$ three branched, $(AB)_4C$ four branched, respectively. Where A: poly-THF, B: PMMA, and C: PS.

TABLE IV
Comparison of the Intrinsic Viscosities of the Polymers

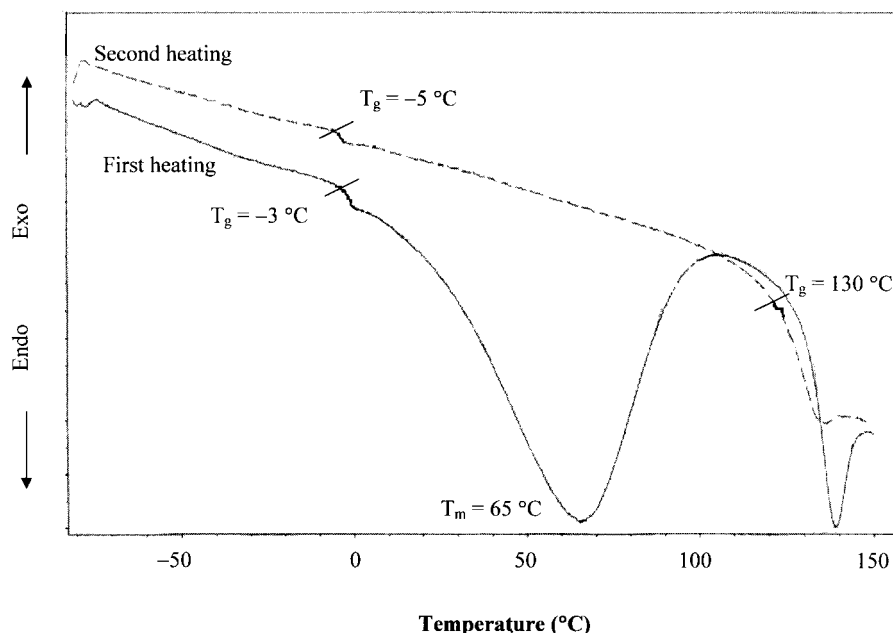| Polymer	Code	η (dl/g)
PTHF	HM-9	0.40
PTHF-b-PMMA	B-4-9	1.97
PMMA-*b*-PTHF-*b*-PMMA	MB-4-91	2.00
PS-*b*-PTHF-*b*-PMMA	MB-4-92	1.47

Figure 5 DSC trace of multiblock copolymer (MB-4–11).

Thermal analysis of the PMMA-*b*-PTHF-*b*-PMMA multiblock copolymer was performed by the DSC technique. Figure 5 indicates the DSC trace of a multiblock copolymer MB-4–11. Glass transition temperature (T_g) at around −3°C and melting transition temperature at around 65°C related to the poly-THF segments were observed in the first heating. Melting transition temperature (T_m) disappeared in the second heating, two T_gs at −5°C and 130°C related to the PTHF and PMMA segments, respectively. This higher T_g can be attributed to the tacticity of the PMMA blocks.[12]

CONCLUSION

A combination of free radical, redox, and cationic polymerization was used in the synthesis of linear and star multiblock copolymers. By using this method, the ABA type of block copolymers can be obtained, where A blocks are hard segments such as PMMA (or PS), and B block is a soft segment such as poly-THF. So it is also possible to produce biodegradable thermoplastic elastomers due to the biodegradability of the poly-THF blocks.

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