

Synthesis of Novel Macromonomeric Peroxy Initiators of Styrene with the Cationic Copolymerization and the Quantum Chemically Investigation of the Initiation System Effects

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ABSTRACT: Cationic polymerization of styrene (S) was performed with peroxy initiators synthesized from bis(4,4'-bromomethyl benzoyl peroxide) (BBP) or bromomethyl benzoyl *t*-butyl peroxy ester (*t*-BuBP) and AgSbF₆ or ZnCl₂ system at 0 and -10°C to obtain macromonomeric peroxy initiators (poly-S initiators). Kinetic studies were accomplished for poly-S initiators. Poly(styrene-*block*-methyl methacrylate) block copolymers [poly(S-*b*-MMA)] were synthesized by bulk polymerization of methyl methacrylate (MMA) with poly-S initiators. The quantum chemical calculations for the initiating systems of the cationic polymerization of S and poly(S-*b*-MMA) block copolymers were achieved using Hyperchem 7.5 program. The optimized geometries of the polymers were investigated with the quantum chemical calculations. Poly(S-*b*-MMA) block copolymers containing undecomposed peroxide groups were used

to initiate thermal copolymerization of acrylic acid (AA) to obtain crosslinked poly(S-*b*-MMA-*b*-AA) multicomponent copolymers. The crosslinked multicomponent copolymers were investigated by sol-gel analysis. Swelling ratio values of the crosslinked multicomponent copolymers in CHCl₃ were calculated. Poly-S initiators having undecomposed peroxygen groups were used for graft copolymerization of polybutadiene (PBd) to obtain crosslinked poly(S-*graft*-polybutadiene) graft copolymers [poly(S-*g*-PBd)]. The characterizations of the polymers were achieved by FTIR, ¹H-NMR, GPC, SEM, and DSC techniques. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 348–357, 2006

Key words: cationic polymerization; macroperoxy initiators; block and graft copolymers; multicomponent copolymers; quantum chemical calculations (MM2)

INTRODUCTION

Macro intermediates such as macroinitiators, macromonomers, and macrocrosslinkers are very important in polymer modification leading to block and graft copolymers.^{1–3} Macromonomeric initiators, which behave as a macromonomer, macroinitiator, or macrocrosslinker, have attracted a great interest because they lead to be synthesized crosslinked or branched block copolymers. Macroinitiators can be divided into two classes, according to the free radical initiator group: (1) macroazo initiators and (2) macroperoxy initiators. We have recently reported the synthesis of these two types of macroinitiators.^{4,5} Polytetrahydrofuran (poly-THF) peroxy initiators as macroperoxy initiators were previously synthesized by the reaction of poly-THF-diol, isophorandiisocyanate, 2,5-dimethyl-2,5-dihydroperoxy hexane, and isocyanatoethyl methacrylate.^{5,6} Moreover, we have de-

scribed the synthesis of poly-THF-peroxy initiators obtained from the cationic polymerization of THF with bromomethyl benzoyl *t*-butyl peroxy ester (*t*-BuBP) or bis(4,4'-bromomethyl benzoyl peroxide) (BBP) or bis(3,5-dibromomethyl benzoyl peroxide) (BDBP) in the presence of AgSbF₆⁷ or ZnCl₂.⁸ The initiators based on *t*-BuBP, BBP, and BDBP are important because they have undecomposed peroxygen groups. The peroxygen groups do not decompose during the cationic polymerization, because low reaction temperatures used for the cationic polymerization such as 0 or -10 °C is not enough to decompose them. Then, these peroxygen groups can lead to react with a monomer by using appropriate reaction conditions to obtain crosslinked block or graft copolymers. Although block and graft copolymers have many similar characteristics, graft copolymers have a branching chain structure attaching polymer units to another polymer backbone.⁹ Grafting onto a backbone structure such as commercially available natural polypropylene (PP) is important because these graft copolymers can have excellent mechanical properties.¹⁰

This article describes the synthesis of poly-S initiators obtained from the cationic polymerization of S

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with *t*-BuBP and BBP in the presence of AgSbF₆ or ZnCl₂. Poly-S initiators had decomposed peroxy groups and vinyl end groups, and so they could be polymerized with a monomer to obtain block, graft, or multicomponent copolymers. For this purpose, poly-S initiators were used to synthesize poly(*S*-*b*-MMA) block copolymers with methyl methacrylate (MMA). The copolymerization of acrylic acid (AA) with poly(*S*-*b*-MMA) at 90°C gave the crosslinked poly(*S*-*b*-MMA-*b*-AA) multicomponent copolymer. Then, we synthesized poly(*S*-*g*-PBd) graft copolymers by the copolymerization of poly-S initiators and PBd. Moreover, we investigated the effects of *t*-BuBP, BBP/AgSbF₆, ZnCl₂ initiating systems on the cationic copolymerization of S as quantum chemically by using Hyperchem 7.5 program.

Computational method

All calculations were performed using Hyperchem 7.5 program¹¹ on an IBM PC-Pentium-IV computer. The quantum chemical properties of *t*-BuBP/AgSbF₆, *t*-BuBP/ZnCl₂, BBP/AgSbF₆, BBP/ZnCl₂ initiating systems, poly-S initiator chains (degree of polymerization of polystyrene; *n* = 5), and the block copolymer chains (degree of polymerization of polystyrene; *n* = 5 and degree of polymerization of polymethyl methacrylate; *m* = 5) were calculated. The quantum chemical analyses of the initiating systems were performed using the Hyperchem 7.5 parameters for MM2. Full geometry optimization was carried out employing the Polak-Ribiere conjugate-gradient method until an RMS gradient was reached to 0.0001 kcal (Å mol)⁻¹. The optimized geometries of poly-S initiator chains (*n* = 5) and the block copolymer chains (*n* = 5 and *m* = 5) were performed by molecular mechanics MM2.¹²

EXPERIMENTAL

Materials

S and MMA (Aldrich, 99%) were washed with 5% aqueous NaOH solution five times and then with pure water until the aqueous phase became neutral. They were dried over anhydrous calcium chloride (CaCl₂, Aldrich) overnight and distilled under reduced pressure. Silver hexafluoroantimonate (AgSbF₆, Aldrich, 98%), zinc chloride (ZnCl₂, Aldrich, >99%), polybutadiene (PBd, Aldrich, 98% *cis*), and *N*-bromo succinimide (Aldrich, 99%) were used as received without any purification. Potassium salt of methacrylic acid was synthesized by the reaction of equimolar amounts of methacrylic acid (Aldrich, 99%) and saturated potassium hydroxide (KOH, Fluka, >86%) solution in methanol. It was purified by reprecipitation from methanol solution into excess acetone.¹³ Chloroform (CHCl₃, Technical) was distilled over anhydrous

CaCl₂ before using. Acrylic acid (AA, Aldrich, 99%) was distilled under reduced pressure and kept in cold.

Polymer characterization

The number-average molecular weights (*M_n*) and molecular weight distributions (MWD, *M_w*/*M_n*) of the polymers were measured at 35°C with a Shimadzu gel permeation chromatography instrument, including a CR-4A type computer and printer, a CTO-6A column furnace, a RID-6A detector, a LC-9A liquid pump, and a GPC 804 model column. THF was used as an eluent at a flow rate of 0.75 mL/min. A calibration curve was generated with polystyrene standards with various molecular weights (2500, 50,000, 90,000, and 200,000 g/mol) purchased from Polyscience.

FTIR spectra were taken with a Perkin-Elmer 1600 Series FTIR spectrometer. ¹H-NMR spectra of the polymers were recorded using a Varian/Mercury-200 NMR spectrometer in CDCl₃ as a solvent and tetramethylsilane as the internal standard. Differential scanning calorimetry (DSC) measurements were performed using a Setaram DSC-141 series thermal analysis system. The heating rate was 10°C/min.

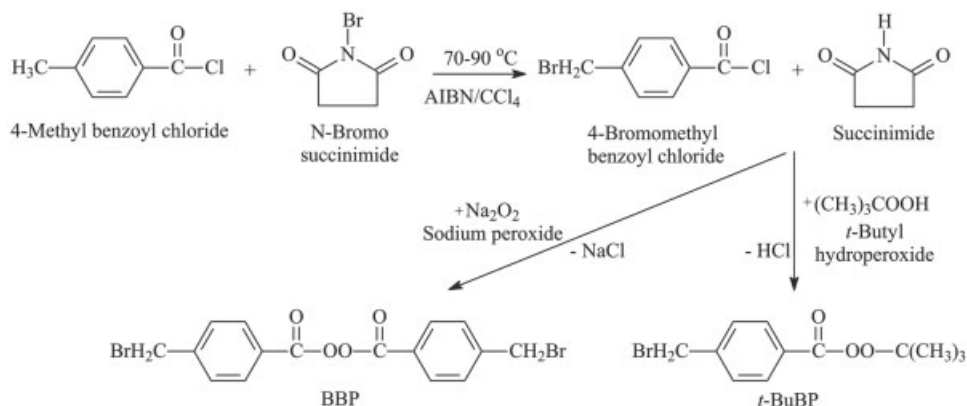
Scanning electron micrographs (SEM) were taken on a Jeol JXA-840A electron microscope. The specimens were frozen under liquid nitrogen, then fractured, mounted, and coated with gold (300 Å) on an Edwards S 150 B sputter coater. SEM measurements were operated at 10 kV. The electron images were recorded directly from the cathode ray tube onto a Polaroid film. The magnification employed was varied up to 6000×.

Synthesis of bromomethyl benzoyl peroxides (*t*-BuBP and BBP)

The mono functional bromomethyl benzoyl *t*-butyl peroxy ester (*t*-BuBP) and bis(4,4'-bromomethyl benzoyl peroxide) (BBP) were synthesized by the reaction of the corresponding bromomethyl benzoyl bromides with peroxides as in literature.^{14,15} Scheme 1 shows the reaction chart for *t*-BuBP and BBP.

Synthesis of poly-S initiators

Poly-S initiators were synthesized by the cationic polymerization of S (50 mL) initiated with *t*-BuBP or BBP and AgSbF₆ or ZnCl₂ initiating systems at 0 and -10°C, according to the described procedure.^{7,8} At the end of desired reaction time, potassium salt of methacrylic acid was added to the polymerization mixture to have methacrylic acid end groups. The solution was stirred for 3 h and filtered to remove precipitated AgBr or ZnBr₂ salts. Then, it was poured into 0.5 L of cold 0.1M NH₃ solution to purify poly-S initiator. Poly-S initiator was precipitated from diethyl



Scheme 1

ether:petroleum ether (1:1) solution at room temperature. Figure 1 shows the reaction mechanism of poly-S initiator with BBP ($n = 5$). The polymerization conditions and the results are listed in Table I.

Copolymerization of MMA with poly-S initiators

Kul et al.⁸ reported the same polymerization procedure to obtain block copolymers starting from *t*-BuBP and BBP. The required amount of poly-S initiator and MMA as monomer were put into a Pyrex tube and stirred until the solution became homogenous. Then, the solution was deoxygenated by bubbling N₂ for 10 min. The tube was covered with a stopper and placed into an oil bath at 80 °C. The polymerization continued

for 6, 12, and 24 h stirring during the polymerization. Subsequently, the reaction was terminated with excess methanol. Soluble and insoluble fractions of the block copolymers were separated by extracting with chloroform for purification. The conditions and the results are given in Table II.

Polymerization of AA with poly(S-*b*-MMA) block copolymers

Poly(S-*b*-MMA) block copolymers with various compositions were prepared in bulk polymerization at 90 °C. A typical procedure to synthesize the crosslinked poly(S-*b*-MMA-*b*-AA) multicomponent copolymer is as follows: 0.1 g of poly(S-*b*-MMA) block copolymer and 0.9 g of AA were put into a Pyrex tube and stirred until a homogenous solution. The solution was deoxygenated by bubbling N₂ for 10 min. Then, it was placed in an oil bath at 90 °C for 12 h. The reaction was terminated with excess methanol. The crosslinked multicomponent copolymer was separated from the soluble part soaking in CHCl₃. The purified copolymer network was dried under vacuum at 50 °C for a week. Table III shows the reaction conditions and the results of the crosslinked multicomponent copolymers.

Synthesis of poly(S-*g*-PBD) graft copolymers

As a typical procedure, 0.5 g of poly-S initiator, 0.5 g of PBD, and 30 mL of CHCl₃ as solvent were stirred for 24 h at room temperature. This solution was spread on a glass plate and dried in the air at room temperature for 2 days to obtain a polymer film. After drying, the polymer film was put into a Pyrex tube. Then, the polymerization was carried out in an oil bath at 90 °C under N₂ for 6 h. The graft copolymer mixture was extracted with CHCl₃ for 24 h, and so swollen graft copolymer was obtained. The swollen gels were filtered off and mixed with methanol to remove ho-

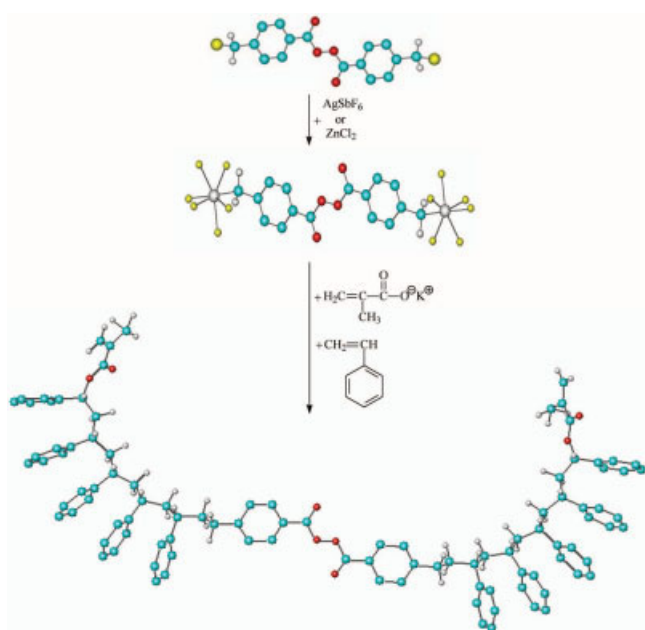


Figure 1 Reaction mechanism of poly-S initiators. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Cationic Polymerization of S with *t*-BuBP or BBP and AgSbF₆ or ZnCl₂ at 0 and -10°C

Initiating system	Run no	Polymerization temperature (°C)	Polymerization time (h)	Conversion (wt %)	M_n (g/mol)	MWD
$2 \times 10^{-2}M$ <i>t</i> -BuBP + $2 \times 10^{-2}M$ AgSbF ₆	1	0	6	6.2	2721	1.4
	2	0	12	9.4	2830	1.4
	3	0	24	17.0	4030	1.2
	4	-10	6	5.5	2560	1.4
	5	-10	12	12.6	3435	1.4
	6	-10	24	12.9	3950	1.2
$2 \times 10^{-2}M$ <i>t</i> -BuBP + $2 \times 10^{-2}M$ ZnCl ₂	7	0	6	0.54	726	1.5
	8	0	12	0.61	1210	1.5
	9	0	24	1.22	1969	1.4
	10	-10	6	0.55	723	1.5
	11	-10	12	0.57	1315	1.5
	12	-10	24	0.72	2528	1.3
$2 \times 10^{-2}M$ BBP + $4 \times 10^{-2}M$ AgSbF ₆	13	0	6	8.0	1230	1.4
	14	0	12	9.4	1447	1.4
	15	0	24	10.1	2620	1.2
	16	-10	6	8.8	2493	1.4
	17	-10	12	11.4	4204	1.1
	18	-10	24	14.1	4227	1.1
$2 \times 10^{-2}M$ BBP + $4 \times 10^{-2}M$ ZnCl ₂	19	0	6	0.65	3003	1.5
	20	0	12	1.15	3362	1.5
	21	0	24	1.38	3952	1.3
	22	-10	6	0.55	2968	1.5
	23	-10	12	1.13	4238	1.2
	24	-10	24	1.66	4962	1.4

mopolymers. Then, the resulting poly(S-g-PBd) graft copolymer was dried under vacuum at 50°C for a week. The results are listed in Table IV.

The calculations for the initiating systems

t-BuBP, BBP/AgSbF₆, ZnCl₂ initiating systems were investigated using molecular mechanic method (MM2). The distances between C—Sb atoms and

C—Cl atoms (r_{C-Sb} and r_{C-Cl}) and the strain energies (E_{str}) were calculated for the *t*-BuBP/AgSbF₆, BBP/AgSbF₆, *t*-BuBP/ZnCl₂, and BBP/ZnCl₂ initiating systems. The results obtained are given in Table V.

The calculations for the block copolymers

Poly-S initiators and the block copolymers with PMMA-PS-PMMA and PMMA-PS-PS-PMMA forms

TABLE II
Copolymerization of MMA with Poly-S Initiators at 80°C

Run no	Poly-S initiator		MMA (g)	Polym time (h)	Block copolymer yield	
	Run no in Table I	Amount (g)			(g)	(wt %)
25	3	0.104	0.9188	6	0.747	81.3
26	9	0.104	0.9138	6	0.756	82.7
27	18	0.106	0.9235	6	0.836	90.5
28	23	0.107	0.9270	6	0.839	90.5
29	3	0.097	0.9153	12	0.757	82.7
30	9	0.093	0.9246	12	0.775	83.8
31	18	0.094	0.9217	12	0.820	89.0
32	20	0.106	0.9177	12	0.845	92.0
33	3	0.092	0.9040	24	0.756	83.6
34	9	0.100	0.9002	24	0.763	84.8
35	15	0.099	0.9182	24	0.860	93.7
36	19	0.098	0.9276	24	0.879	94.8

TABLE III
The Copolymerization of AA with Poly(S-*b*-MMA) Block Copolymers at 90°C for 12 h

Run no	Run no in Table II	Poly(S- <i>b</i> -MMA) block copolymer (g)	Amount of AA (g)	Multi component copolym. yield (g)	Crosslinked multicomponent copolymer yield		q_v of the crosslinked multi component copolym. in CHCl ₃
					(g)	(wt%)	
37	33	0.1016	0.9165	0.3793	0.119	31.4	1.26
38	34	0.0923	0.9198	0.7303	0.100	13.6	1.48
39	28	0.1036	0.9250	0.1242	0.100	80.5	1.17
40	31	0.0972	0.9780	0.5567	0.113	20.3	1.58

were investigated using MM2 method. The internal rotation angle (φ) and the strain energy values (E_{str}) of poly-S initiators and the block copolymers were calculated by using MM2 method. The results obtained are given in Table VI. The optimized geometries of poly-S initiators and the block copolymers with PMMA-PS-PMMA and PMMA-PS-PS-PMMA forms are given in Figure 2.

RESULTS AND DISCUSSION

Synthesis of poly-S initiators

Mono- and di-functional peroxy esters^{7,8,14,15} were used for the synthesis of the living poly-THF initiators containing peroxgen groups (active poly-THF) in previous papers, which were terminated by the potassium salt of methacrylic acid to have vinyl end groups. In this study, the cationic polymerization of S was performed using a catalyst mixture composed of the bromomethyl derivatives of benzoyl peroxides and AgSbF₆ or ZnCl₂ at 0 and -10 °C (Fig. 1). The conditions and the results of the polymerization are listed in Table I. As a result of the cationic polymerization of *t*-BuBP and BBP with S, one- and two-armed poly-S initiators with vinyl end groups were obtained for *t*-BuBP and BBP, respectively. Thus, *t*-BuBP has one bromomethyl group and consumes 1 mol of silver or zinc salt, while BBP consumes 2 mol of silver or zinc salt. According to Table I, we see that the longer polymerization times gave higher molecular weights and yields as we expected. The number-average mo-

lecular weight (M_n) and the conversion (wt %) values of poly-S initiators with *t*-BuBP in the presence of AgSbF₆ are bigger than those in the presence of ZnCl₂. However, M_n values with BBP/AgSbF₆ initiating system are smaller than those with BBP/ZnCl₂ initiating system. It means that AgSbF₆ is more reactive in the cationic polymerization of *t*-BuBP and ZnCl₂ is more reactive for BBP. The reason may be steric effects between two-armed BBP and AgSbF₆ molecules. Moreover, molecular weight distribution (MWD, M_w/M_n) values of poly-S initiators in Table I are low (≤ 1.5). When MWD values of poly-S initiators were compared, it was seen that higher MWD values were obtained with ZnCl₂. These results are in a good agreement with the results obtained by Cai and Yan for the cationic polymerization of di-, tri-, and tetra-bromomethyl benzene.¹⁶

Kinetic studies were carried out to investigate controlled cationic polymerization of *t*-BuBP, BBP/AgSbF₆, ZnCl₂ initiating systems with styrene at 0 and -10°C. Figures 3(A) and 3(B) show the semi logarithmic kinetic plots for the polymerization of *t*-BuBP/AgSbF₆-BBP/AgSbF₆ initiating systems (run no 1, 2, 3, 13, 14, 15 in Table I) and *t*-BuBP/ZnCl₂-BBP/ZnCl₂ initiating systems (run no 7, 8, 9, 19, 20, 21 in Table I), respectively. M_n and MWD (M_w/M_n) results versus conversion (%) are shown in Figure 3(C) for *t*-BuBP/AgSbF₆-BBP/AgSbF₆ initiating systems (run no 1, 2, 3, 13, 14, 15 in Table I) and in Figure 3(D) for *t*-BuBP/ZnCl₂-BBP/ZnCl₂ initiating systems (run no 7, 8, 9, 19, 20, 21 in Table I). For all initiating systems, the

TABLE IV
The Copolymerization of PBd (~0.5 g) with Poly-S Initiators (~0.5 g) at 90°C for 6 h

Run no	Run no in Table I	wt % in the polymer mixture		Graft copolymer yield (wt %)	Crosslinked graft copolymer yield (wt %)	Content of homo PBd (wt %)	q_v of the crosslinked graft copolym in CHCl ₃
		PBd	Poly-S				
41	3	52	48	68.6	13.1	55.5	5.49
42	12	52	48	73.2	41.1	32.1	2.30
43	17	51	49	62.4	32.5	29.9	3.83
44	20	53	47	72.3	17.8	54.5	5.36

TABLE V
The Strain Energies and the Bond Lengths Between C—Sb and C—Cl Atoms ($r_{\text{C—Sb}}$ and $r_{\text{C—Cl}}$) of the Initiating Systems

Initiating system	MM2 E_{str} (kcal mol ⁻¹)	$r_{\text{C—Sb}}$ (Å)	$r_{\text{C—Cl}}$ (Å)
<i>t</i> -BuBP/AgSbF ₆	8.788	2.1754	—
<i>t</i> -BuBP/ZnCl ₂	8.001	—	1.7964
BBP/AgSbF ₆	9.914	2.1756	—
BBP/ZnCl ₂	7.556	—	1.7963

plots of $\ln([M_0]/[M_t])$ versus reaction time are linear, corresponding to first-order kinetics. Moreover, M_n and M_w/M_n -versus-conversion (%) plots demonstrate the good control of molecular weight as a function of conversion for all initiating systems.

The values of $r_{\text{C—Sb}}$ distance calculated quantum chemically for the *t*-BuBP/AgSbF₆ and BBP/AgSbF₆ initiating systems are 2.1754 and 2.1756 Å; the $r_{\text{C—Cl}}$ distances for *t*-BuBP/ZnCl₂ and BBP/ZnCl₂ initiating systems are 1.7964 and 1.7963 Å, respectively (Table V). C—Sb bond in SbF₆⁻C⁺ ion-pair is weaker and more unstable than C—Cl bond in Cl⁻C⁺ ion-pair. Since the $r_{\text{C—Sb}}$ distances in the *t*-BuBP/AgSbF₆ and BBP/AgSbF₆ initiating systems are bigger than $r_{\text{C—Cl}}$ distances in the *t*-BuBP/ZnCl₂ and BBP/ZnCl₂ initiating systems, it is easier to break $r_{\text{C—Sb}}$ bond than $r_{\text{C—Cl}}$ bond. In the same way, the addition of styrene molecules between Sb and C atoms of SbF₆⁻C⁺ ion-pair is easier than that between Cl and C atoms of Cl⁻C⁺ ion-pair. It was also found from the quantum mechanical calculations that the conversion (wt %) of the cationic polymerization of S with *t*-BuBP or BBP in the presence of AgSbF₆ is bigger than that in the presence of ZnCl₂.

The internal rotation angle (φ) and the strain energy (E_{str}) values of poly-S initiators and the block copolymers are given in Table VI. The internal rotation angles of poly-S initiators and the block copolymers are almost 180°. The strain energies were also calculated for poly-S initiators ($n = 5$) and the block copolymers ($n = 5$ and $m = 5$). According to Table VI, the strain energy increases with the variation of the conformational chain. For the sake of the dependability of the

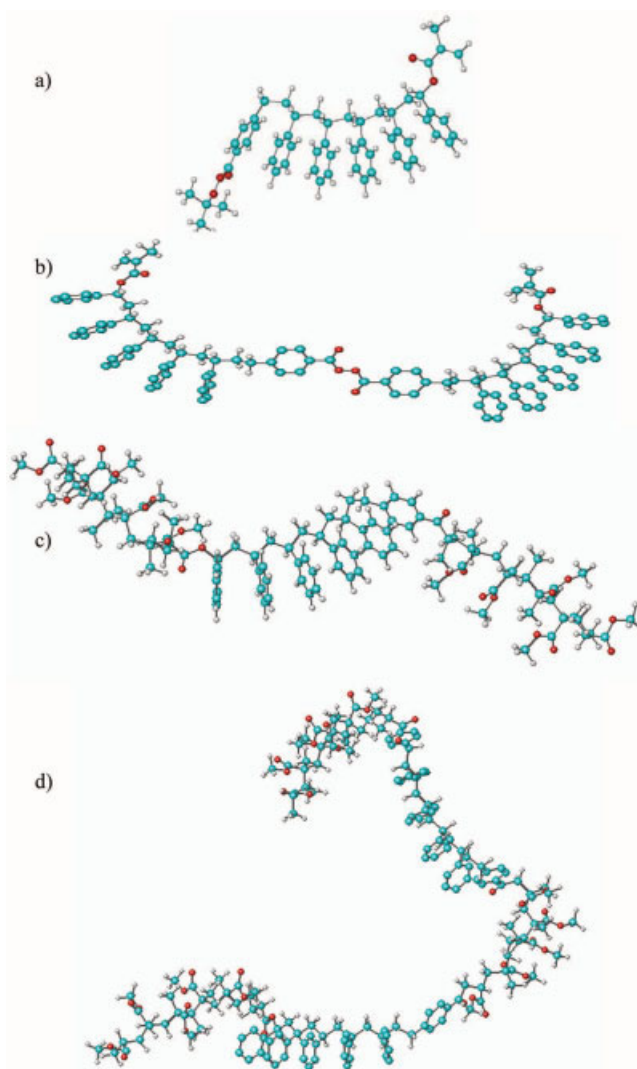


Figure 2 The optimized geometry of poly-S initiators and the block copolymers (a) poly-S (synthesized by the cationic polymerization of S with *t*-BuBP/AgSbF₆ initiating system) macroperoxy initiator; (b) poly-S (synthesized by the cationic polymerization of S with BBP/AgSbF₆ initiating system) macroperoxy initiator; (c) PMMA-PS-PMMA block copolymer; (d) PMMA-PS-PS-PMMA block copolymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE VI
The Strain Energies and the Internal Rotation Angles of Poly-S Initiators and the Block Copolymers According to MM2 Method

	Poly-S ¹	Poly-S ²	PMMA-PS-PMMA ($n = 5$ and $m = 5$)	PMMA-PS-PS-PMMA ($n = 5$ and $m = 5$)
E_{str} (kcal mol ⁻¹)	11.961	96.465	120.170	303.630
φ (°)	172.639	179.976	170.049	171.550

¹ Synthesized with the cationic polymerization of S with *t*-BuBP/AgSbF₆ initiating system.

² Synthesized with the cationic polymerization of S with BBP/AgSbF₆ initiating system.

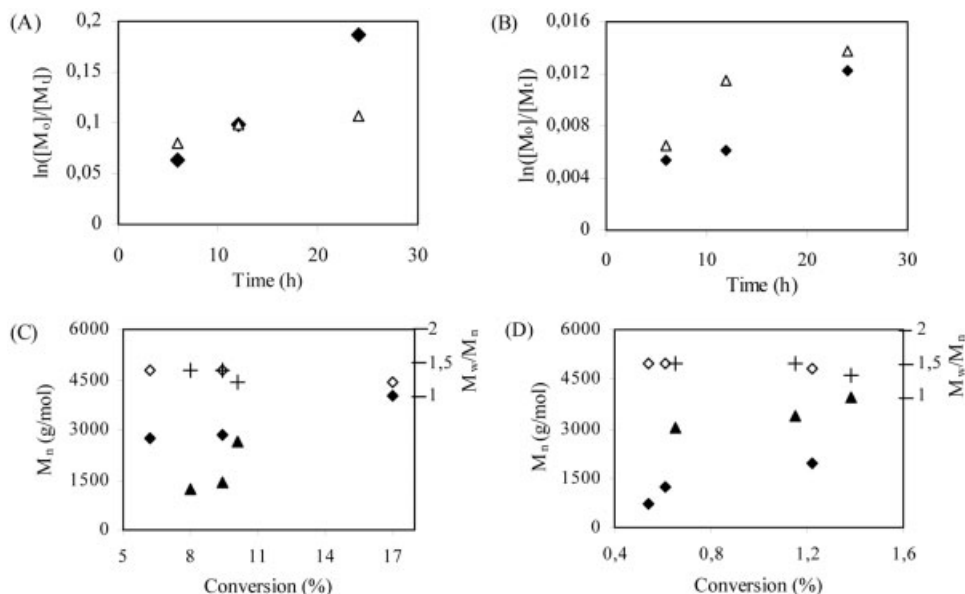


Figure 3 From the values in Table I, first-order plot for the cationic polymerization of (A) *t*-BuBP/AgSbF₆ (♦, run no 1, 2, 3) and BBP/AgSbF₆ (Δ, run no 13, 14, 15) initiating systems, (B) *t*-BuBP/ZnCl₂ (♦, run no 7, 8, 9) and BBP/ZnCl₂ (Δ, run no 19, 20, 21) initiating systems; (C) M_n (♦) and MWD (◇) values of poly-S initiator with *t*-BuBP/AgSbF₆ (run no 1, 2, 3), M_n (▲) and MWD (+) values of poly-S initiator with BBP/AgSbF₆ (run no 13, 14, 15); (D) M_n (♦) and MWD (◇) values of poly-S initiator with *t*-BuBP/ZnCl₂ (run no 7, 8, 9), M_n (▲) and MWD (+) values of poly-S initiator with BBP/ZnCl₂ (run no 19, 20, 21) as a function of conversion (%) by ¹H-NMR and GPC, respectively.

results obtained, conformational analysis of poly-S initiators ($n = 5$) and the block copolymers ($n = 5$ and $m = 5$) with different steric regularity were performed by the molecular mechanics. The optimized geometries of the structures are given in Figure 2.

Copolymerization of MMA with poly-S initiators

Copolymerization of MMA with poly-S initiators demonstrated that poly-S initiators showed the characteristic macroinitiator behavior,^{4,17,18} because block copolymers were obtained as a result of the copolymerization. The block copolymer yields obtained from MMA and poly-S initiators with *t*-BuBP/AgSbF₆ or ZnCl₂ initiating system were smaller than those from BBP/AgSbF₆ or ZnCl₂ initiating system (Table II). Thus, it is clear that BBP/AgSbF₆ or ZnCl₂ initiating system is more reactive to obtain block copolymers with MMA because poly-S initiators of BBP with two end groups have more vinyl and peroxy groups than poly-S initiators of *t*-BuBP with one end group.

Synthesis of the crosslinked poly(*S*-*b*-MMA-*b*-AA) multicomponent copolymers

We used poly(*S*-*b*-MMA) block copolymers as the initiator of the polymerization of AA to synthesize the crosslinked poly(*S*-*b*-MMA-*b*-AA) multicomponent copolymers. Table III gives the conditions and the results of the copolymerization of AA with poly(*S*-

MMA) block copolymers at 90°C. The swelling ratio (q_v) values of the crosslinked poly(*S*-*b*-MMA-*b*-AA) multicomponent copolymers in CHCl₃ are between 1.17 and 1.58. It was observed that the swelling ratio values increase for both *t*-BuBP (run no 37 and 38 in Table III) and BBP (run no 39 and 40 in Table III) when the crosslinking degree decreases.^{5,6}

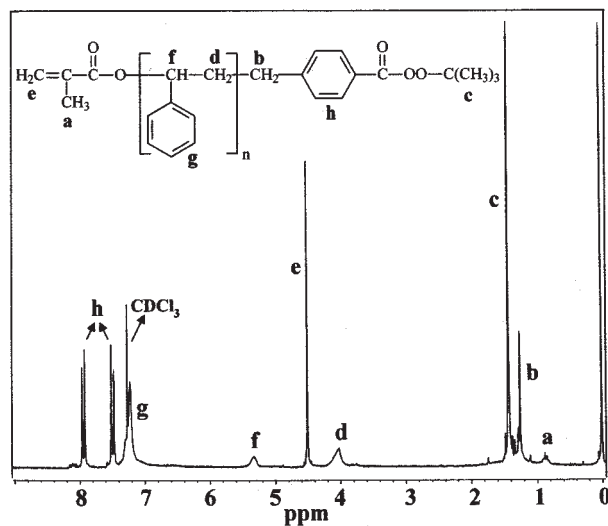


Figure 4 ¹H-NMR spectrum of poly-S initiator (run no 3 in Table I).

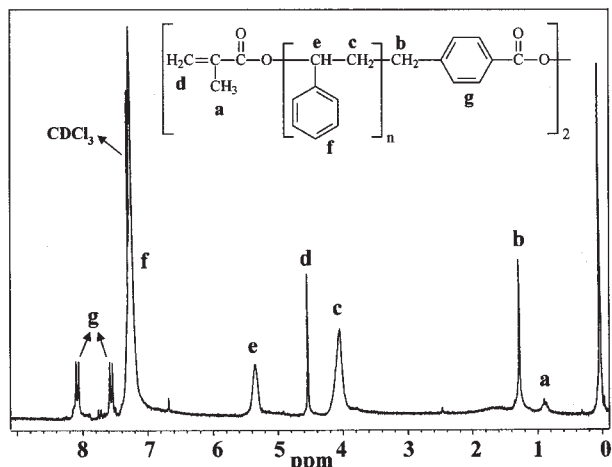


Figure 5 $^1\text{H-NMR}$ spectrum of poly-S initiator (run no 21 in Table I).

Synthesis of poly(S-g-PBd) graft copolymers

The graft copolymerization of poly-S initiators with polybutadien (PBd) could be synthesized at 90°C because poly-S initiators contain both vinyl and undecomposed peroxy groups. The conditions and the results of the copolymerization are given in Table IV. Poly(S-g-PBd) graft copolymer yields for the *t*-BuBP/ ZnCl_2 and BBP/ AgSbF_6 initiating systems at -10°C were bigger than those at 0°C . The swelling ratios of the crosslinked poly(S-g-PBd) graft copolymers decrease when the conversion (wt %) of the crosslinked graft copolymers increases.

Characterization of the polymers

The characterization of poly-S initiators and the block copolymers was achieved by FTIR, $^1\text{H-NMR}$, DSC,

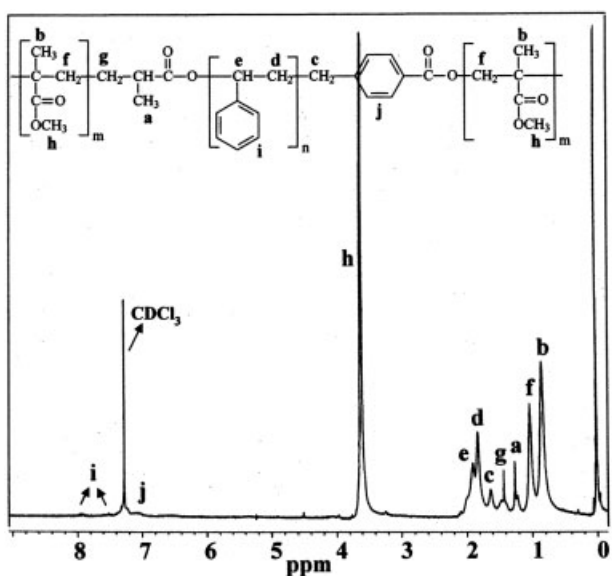


Figure 6 $^1\text{H-NMR}$ spectrum of poly(S-b-MMA) block copolymer (run no 31 in Table II).

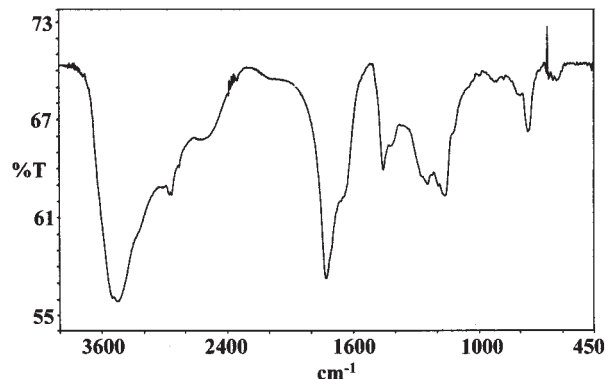


Figure 7 FTIR spectrum of the crosslinked poly(S-b-MMA-b-AA) multicomponent copolymer (run no 40 in Table III).

and GPC techniques. Figures 4 and 5 show $^1\text{H-NMR}$ spectrums of poly-S initiators for *t*-BuBP/ AgSbF_6 (run no 3 in Table I) and BBP/ ZnCl_2 (run no 21 in Table I) initiating systems. The most important difference between the spectrums is the characteristic peak of *t*-butyl groups at 1.5 ppm for the *t*-BuBP/ AgSbF_6 initiating system. Figure 6 shows $^1\text{H-NMR}$ spectrum of the block copolymer (run no 31 in Table II).

FTIR spectrum of the crosslinked poly(S-b-MMA-b-AA) multicomponent copolymer (run no 40 in Table III) in Figure 7 shows the characteristic peaks at $3000\text{--}3500\text{ cm}^{-1}$ for $=\text{CH}-$ groups of aromatic rings, at $2900\text{--}3000\text{ cm}^{-1}$ for $-\text{CH}_3$ groups, at 1730 cm^{-1} for $-\text{C}=\text{O}$ groups of methyl methacrylate and BBP, at 1453 cm^{-1} for $-\text{C}=\text{C}-$ groups, at 1240 cm^{-1} for $-\text{C}-\text{O}-$ groups of methyl methacrylate and BBP, and at $690\text{--}760\text{ cm}^{-1}$ for mono-substitution of polystyrene. FTIR spectrum of poly(S-g-PBd) graft copolymer (run no 42 in Table IV) in Figure 8 shows the characteristic peaks at $3000\text{--}3500\text{ cm}^{-1}$ for $=\text{CH}-$ groups of aromatic rings, at $2900\text{--}3000\text{ cm}^{-1}$ for $-\text{CH}_3$ groups, at 1720 cm^{-1} for $-\text{C}=\text{O}$ groups of *t*-BuBP, at 1270 cm^{-1} for $-\text{C}-\text{O}-$ groups of *t*-BuBP,

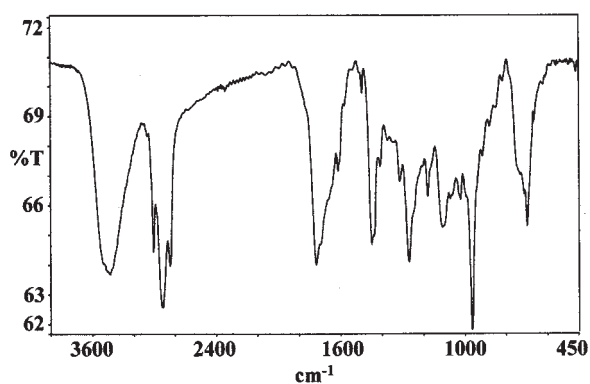


Figure 8 FTIR spectrum of poly(S-g-PBd) graft copolymer (run no 42 in Table IV).

and at $698\text{--}735\text{ cm}^{-1}$ for mono-substitution of polystyrene.

Thermal analysis of poly-S initiator, the block, graft, and multicomponent copolymers were carried out by taking DSC curves. All samples exhibited glass transition temperatures (T_g). The reported T_g values were obtained from the second heating curves. Figure 9 shows the second DSC curves of poly-S initiator, the block copolymer, the multicomponent copolymer, and the graft copolymer. Peroxygen decomposition of poly-S initiator (run no 4 in Table I) was around 140°C . T_g value of poly-S initiator was 39.23°C (run no 8 in Table I) in Figure 9(a). T_g value of poly(S-*b*-MMA) block copolymer was 37.84°C (run no 30 in Table II) in Figure 9(b) and of the crosslinked poly(S-*b*-MMA-*b*-AA) multicomponent copolymer was 53.48°C (run no 40 in Table III) in Figure 9(c). Poly(S-*g*-PBd) graft copolymer (run no 44 in Table IV) showed two glass transition temperatures: T_{g1} , 18.88°C and T_{g2} , 50.92°C in Figure 9(d). Only one glass transition temperature for poly-S initiators, the block copolymers, and the multicomponent copolymers shows the miscible nature of the related polymers. Two glass transition temperatures prove the immiscible nature of poly(S-*g*-PBd) graft copolymers.

Scanning electron microscopy (SEM) micrographs of the polymers were taken for the surface morphology characterization of the block, multicomponent, and graft copolymers. The polymers were coated with a thin layer of gold on their surfaces to provide electrical conductivity. The micrographs were photographed from different views. Figures 10(a) and 10(b) show the SEM micrographs of poly(S-*b*-MMA) block copolymers (run no 25 and 35 in Table II respectively). According to the SEM micrographs of the block copolymers, homogenization of the resulting block copoly-

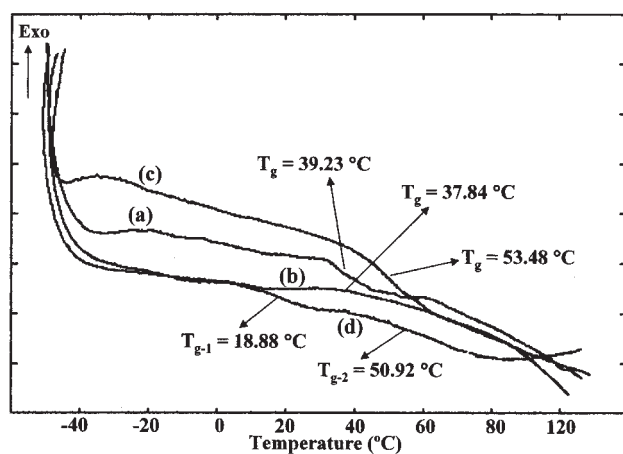


Figure 9 DSC curves of (a) poly-S initiator (run no 8 in Table I); (b) poly(S-*b*-MMA) block copolymer (run no 30 in Table II); (c) the crosslinked poly(S-*b*-MMA-*b*-AA) multicomponent copolymer (run no 40 in Table III); and (d) poly(S-*g*-PBd) graft copolymer (run no 44 in Table IV).

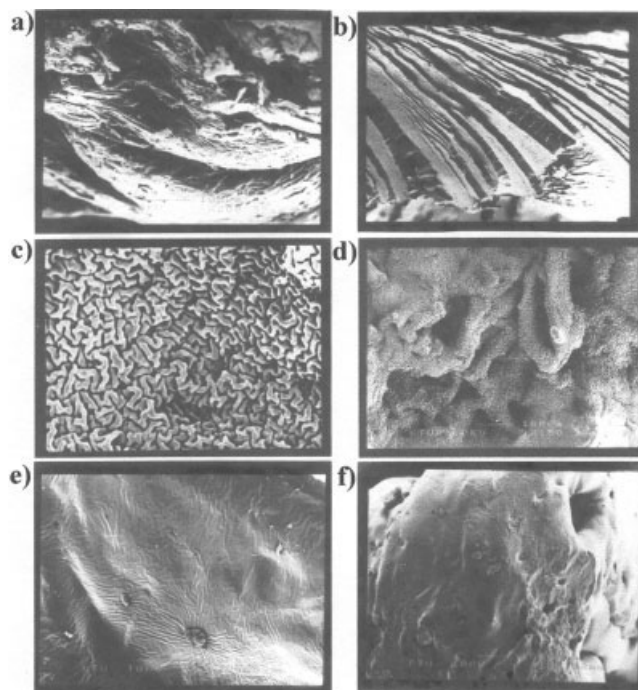


Figure 10 SEM micrographs of poly(S-*b*-MMA) block copolymers (a) run no 25 in Table II, (b) run no 35 in Table II; the crosslinked poly(S-*b*-MMA-*b*-AA) multicomponent copolymers (c) run no 39 in Table III, (d) run no 40 in Table III; poly(S-*g*-PBd) graft copolymers (e) run no 41 in Table IV, (f) run no 43 in Table IV.

mer was good. SEM micrographs of impact fracture surfaces of the block copolymer have a continuous poly-S matrix and a dispersed PMMA domain. The boundary between the phase domains of polystyrene and polymethyl methacrylate (PMMA) is clear and sharp. All poly(S-*b*-MMA) samples were characterized by a morphology consisting of gel sheets or platelets with irregular pores. The SEM micrograph of poly(S-*b*-MMA) block copolymer shows a smooth surface [Fig. 10(b)]. However, the micrographs of poly-S initiators and PMMA are shown in the structure of the separated phase and an excellent semi-IPN structure is formed. Figures 10(c) and 10(d) show the SEM micrographs of the crosslinked poly(S-*b*-MMA-*b*-AA) multicomponent copolymers (run no 39 and 40 in Table III respectively). The crosslinked poly(S-*b*-MMA-*b*-AA) multicomponent copolymer forms continuous gel structure with high connectivity where the gel is composed of polymer strings. Both pore system and gel network are continuous. Only the gel strands look more defined, i.e., the interfaces are sharper and the structure is more uniform, when the crosslinking amount increases. We attribute this with structural refinement to the lower molecular swellability of highly crosslinked gels, which makes the growing gel strands richer in the polymer. The rate of crosslinking increases with the increase of the crosslinker amount.

Thus, smaller pore sizes are expected with increase of the crosslinking. It can be seen from Figures 10(c) and 10(d) that the gel consists of a dense packing of rather large pores, separated by porous walls with channels. Figures 10(e) and 10(f) show the SEM micrographs of poly(S-g-PBd) graft copolymers (run no 41 and 43 in Table IV, respectively). The SEM micrograph of the graft copolymer shows a smooth surface [Fig. 10(e)]. The graft copolymer gels are made of poly-S macroperoxy initiator composed of small primary particles being continuously interconnected.

CONCLUSIONS

Poly-S macroperoxy initiators were obtained from the cationic polymerization of S with the *t*-BuBP, BBP/AgSbF₆ and *t*-BuBP, BBP/ZnCl₂ initiating systems. The resulting poly-S initiators did not lose their peroxygen groups after the cationic polymerization at 0 and -10°C. It was revealed that the reactivity of poly-S macroperoxy initiators was comparable with other common peroxide initiators. Poly(S-*b*-MMA) block copolymers and the crosslinked poly(S-*b*-MMA-*b*-AA) multicomponent copolymers could be prepared by using these macroperoxy initiators. The remaining peroxide groups of poly(S-*b*-MMA) block copolymers initiated the copolymerization of acrylic acid to form the crosslinked multicomponent copolymers. It was found from the quantum mechanical calculations that the initiator effect in the cationic polymerization of S with *t*-BuBP or BBP in the presence of AgSbF₆ was bigger than those in the presence of ZnCl₂. For poly-S

initiator, poly(S-*b*-MMA) block copolymer, and the crosslinked poly(S-*b*-MMA-*b*-AA) multicomponent, a single glass transition temperature was determined showing miscible character. However, poly-S initiator was immiscible with PBd, because two glass transition temperatures were observed for poly(S-g-PBd) graft copolymers.

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