

Synthesis of Asymmetric Star-Branched Block Copolymers Based on PS, PTHF, and PMMA by Combination of Cationic Ring Opening Polymerization and Redox Polymerization Methods

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ABSTRACT: Asymmetric star-branched block copolymers based on polystyrene (PS), polytetrahydrofuran (PTHF), and poly(methyl methacrylate) (PMMA) were synthesized by a combination of cationic ring opening polymerization and redox polymerization methods in two steps. At first, cationic ring opening polymerization of THF was initiated by using chain-end-multifunctionalized polystyrenes with 2, 4, and 8 benzyl bromide moieties as initiators in the presence of AgSbF_6 at 30°C to obtain 3-, 5-, and 9-arm AB_2 , AB_4 , and AB_8 type asymmetric star-branched polymers consisting of PS (A) and PTHF-OH (B) segments. Polymers obtained in this way were characterized by gel permeation chromatography, FTIR, ^1H NMR, and thermal analysis (DSC and TGA). At

second step, redox polymerization of methyl methacrylate was initiated by using these characterized asymmetric star-branched polymers as macroinitiators in the presence of Ce(IV) salt at 40°C to obtain PS-*s*-(PTHF-*b*-PMMA)_{*n*} (*n* = 2, 4, and 8) asymmetric star-branched block copolymers. PS-*s*-(PTHF-*b*-PMMA)_{*n*} (*n* = 2, 4, and 8) asymmetric star-branched block copolymers obtained were purified by fractional precipitation method before characterization. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 516–522, 2006

Key words: asymmetric star-branched block copolymers; cationic ring opening polymerization; redox polymerization; Ce (IV)

INTRODUCTION

Block copolymers are one of the most important polymeric materials in technological applications and theoretical research because of their exceptional properties due to the micro phase separation.^{1–4} A variety of synthetic methods for the preparation of block copolymers with various architectures such as linear diblock (AB), triblock (ABA or ABC), pentablock (ABABA), multiblock or segmented copolymers have been proposed.^{5–19}

Recent attention has focused on the synthesis of nonlinear polymers such as dendrimers,^{20–24} hyperbranched derivatives,²⁵ graft copolymers, and star(copoly)mers^{26–36} to get a better understanding of the relationship between their topology and their unique solution and bulk properties, as compared with linear polymers, and because of their unique novel physical, mechanical, chemical, and solution properties.

Dendrimers, the tree-like or star-shaped polymers that adopt generally a quasi-spherical shape, are a new class of polymeric materials that are highly branched and monodisperse macromolecules in the nanometer size range. The structure of these materials has a great impact on their physical and chemical properties. As a result of their unique behavior, dendrimers are suitable for a wide range of biomedical and industrial applications, such as adhesives and coatings, chemical sensors, medical diagnostics, drug-delivery systems, high-performance polymers, catalysts, building blocks of supermolecules, separation agents, and many more.^{37,38}

Star polymers are branched polymers that consist of more than three linear polymer chains linked together at one end of each chain by a central core or a single branch. Star polymers exhibit physical and mechanical properties quite different from linear analogues and are of interest because of their unique spatial shapes and lower viscosity when compared with those of linear polymers with similar molecular weight. There are essentially two methods to engineer star polymers: either by linking a given number of linear chains to central core (“arm-first” method) or by growing branches from an active core (“core-first” method) in

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TABLE I
Results and Conditions of Cationic Ring Opening Polymerization of THF Initiated by Chain-End-Multifunctionalized Polystyrenes with 2, 4, and 8 Benzyl Bromide Moieties [PS(BzBr)_n] as Initiators in the Presence of AgSbF₆ at 30°C

Run no.	PS(BzBr) ₂ (g)	PS(BzBr) ₄ (g)	PS(BzBr) ₈ (g)	THF (mL)	[AgSbF ₆] (10 ⁻³ mol/L)	Polm. time (h)	Yield (g)
AB ₂ -I	1.095	–	–	30	6.15	20	4.52
AB ₄ -I	–	0.577	–	30	6.15	20	8.69
AB ₂ -II	1.570	–	–	30	8.82	24	9.78
AB ₄ -II	–	0.824	–	30	8.82	20	18.05
AB ₈ -I	–	–	0.730	30	11.76	20	2.08

$M_n = 9650, 10,100,$ and $12,100$ for PS(BzBr)₂, PS(BzBr)₄, and PS(BzBr)₈ respectively.

AB₂, AB₄, and AB₈ type PS-*s*-(PTHF-OH)_x asymmetric star-branched polymers consist of PS (A) and PTHF-OH (B) segments.

the form of regular star-branched polymers, for instance, A₅ or asymmetric star-branched polymers whose arms differ in molecular weight and chemical composition, for instance AB₂C₂, A₂B₂.^{35,39}

The combination of controlled branching with block copolymerization provides additional opportunities to devise new molecular architectures. Inspired by this idea, in this work chain-end-multifunctionalized polystyrenes with 2, 4, and 8 benzyl bromide moieties synthesized and well characterized before⁴⁰ were used as a template to prepare asymmetric star-branched block copolymers based on polystyrene (PS), poly(tetrahydrofuran) (PTHF), and poly(methyl methacrylate) (PMMA) via cationic ring opening polymerization and free radical redox polymerization.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) was supplied by Merck (Germany) and refluxed and distilled over Na metal under nitrogen. Methyl methacrylate (MMA) was supplied by Fluka (Switzerland) A.G. and freed from inhibitor by vacuum distillation over calcium hydride. AgSbF₆ was supplied from Aldrich and used as received. Ceric ammonium nitrate, Ce(NH₄)₂(NO₃)₆, (CAN), was supplied by Fluka A.G. (USA) and used as received. Chain-end-multifunctionalized polystyrenes with 2, 4, and 8 benzyl bromide moieties [PS(BzBr)_n] were synthesized according to the procedure reported previously by Hirao and Haraguchi.⁴⁰ All other chemicals were of reagent grade and used as received.

Synthesis of asymmetric star-branched polymers

Cationic ring opening polymerization of THF to obtain PS-*s*-(PTHF-OH)_x asymmetric star-branched polymers

3-, 5-, and 9-Arm PS-*s*-(PTHF-OH)_x asymmetric star-branched polymers designed as AB₂, AB₄, and AB₈ (A is PS, B is PTHF-OH, and $x = 2, 4,$ and 8) were

synthesized via cationic ring opening polymerization of THF initiated by using chain-end-multifunctionalized polystyrenes with 2, 4, and 8 benzyl bromide moieties [PS(BzBr)_n] as initiators in the presence of AgSbF₆ at 30°C, according to the procedure described elsewhere.⁴¹ After a certain time, the reaction mixture was filtered to separate AgBr from the product, and then asymmetric star-branched polymers obtained in this way were precipitated in cold water containing a small amount of a weak base such as an ammonia solution and dried *in vacuo* at room temperature. The results and polymerization conditions are listed in Table I.

Synthesis of asymmetric star-branched block copolymers

Redox polymerization of MMA to obtain PS-*s*-(PTHF-*b*-PMMA)_n asymmetric star-branched block copolymers

PS-*s*-(PTHF-*b*-PMMA)_n ($n = 2, 4,$ and 8) asymmetric star-branched block copolymers were synthesized via redox polymerization of MMA initiated by using asymmetric star-branched polymers [PS-*s*-(PTHF-OH)_x] designed as AB₂, AB₄, and AB₈ (A is PS, B is PTHF-OH, and $x = 2, 4,$ and 8), which were obtained by cationic polymerization of THF at first step, as macroinitiators in the presence of Ce(IV) salt at 40°C. The general experimental procedure was as follows: An appropriate amount of one of AB₂, AB₄, or AB₈ type asymmetric star-branched polymers consisting of PS (A) and PTHF-OH (B) segments was put in a Pyrex tube, then a given amount of CAN solution and MMA were added to the tube. Approximately 10 mg of tetrabutyl ammonium hydrogen sulfate was also added to increase the solubility of MMA in the aqueous reaction media. Nitrogen was introduced for 1 min through a needle into the reaction mixture to expel the air. The tube was covered with a stopper and kept at 40°C for a given time under stirring during the polymerization. The reaction product was precipitated

TABLE II
Results and Conditions of Redox Polymerization of MMA Initiated by Asymmetric Star-branched Polymers [PS-*s*-(PTHF-OH)_{*x*}] as Macroinitiators in the Presence of Ce(IV) Salt at 40°C

Run no.	PS- <i>s</i> -(PTHF-OH) _{<i>x</i>}		Yield (g)	(PS- <i>s</i> -[PTHF- <i>b</i> -PMMA] _{<i>x</i>}) Star-Branched Block Copolymers Fractionation (wt %)			
	Type	g		$\gamma_{3.0-5.0}$	$\gamma_{5.2-6.7}$	$\gamma_{5.9-8.0}$	$\gamma >$
I	AB ₂ -I	0.25	1.89	71	–	–	29($\gamma > 6.5$)
II	AB ₄ -I	0.25	1.59	83	–	–	17($\gamma > 6.7$)
III	AB ₂ -II	0.25	1.75	89	1.0	–	10($\gamma > 6.2$)
IV	AB ₄ -II	0.25	0.21	–	60	6.0	34($\gamma > 8.0$)
IV-2 ^a	AB ₄ -II	0.25	0.22	–	–	–	–
V-1	AB ₈ -I	0.25	0.23	–	–	88	12($\gamma > 8.0$)
V-2 ^a	AB ₈ -I	0.25	0.24	–	–	–	–
V-3 ^b	AB ₈ -I	0.25	0.31	–	–	–	–

[MMA] = 4.65M (3 mL); [Ce(IV)] = 0.05M (3 mL); [HNO₃] = 0.5M; *t* (h) = 20.

γ is 0.4–0.9 for homo-PS, 3.0–3.9 for homo-PMMA, and $\gamma > 20$ for PTHF (soluble in methanol).

^a Polymerization time, 28 h 22 min.

^b 6 mL MMA.

in methanol, collected by filtration, and dried *in vacuo* at 30°C. The results and polymerization conditions are listed in Table II.

Purification of asymmetric star-branched block copolymers by fractional precipitation method

Pure block copolymers were isolated from unreacted macroinitiator via fractional precipitation method. This method was carried out by measuring γ value, the volume ratio of nonsolvent to solvent. For this purpose, a certain amount of polymer was dissolved in a predetermined volume of solvent (CHCl₃) to obtain polymer solution. Then the nonsolvent (methanol) was gradually added to this solution until the polymer precipitated. γ Values of block copolymers were calculated by taking the volume ratio of nonsolvent to solvent.

Characterization

The ¹H NMR spectra were recorded using Bruker AVANCE-500 spectrometer in CDCl₃.

The FTIR spectra were recorded using Jasco model 300E FTIR spectrometer.

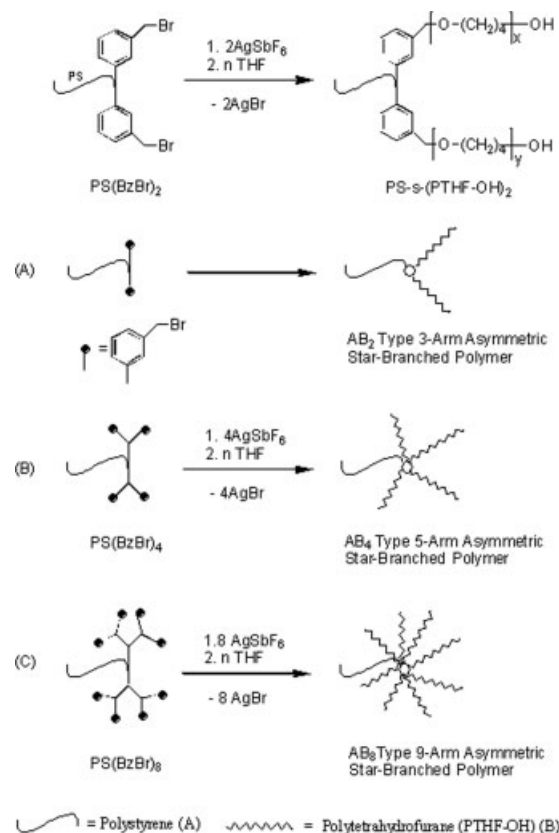
Gel permeation chromatography (GPC) experiments were conducted with a Knauer gel permeation chromatography in CHCl₃ solution at 35°C, at a flow rate of 1 mL/min using ChromGate software, a Well-Chrom Interface Box, RI Detector K-2301, and Well-Chrom HPLC pump K-501. Polystyrene standards with low dispersity obtained from Polyscience (Switzerland) were used to generate a calibration curve.

Differential scanning calorimetry (DSC) was carried out on a Setaram DSC 141 with a heating rate 10°C/

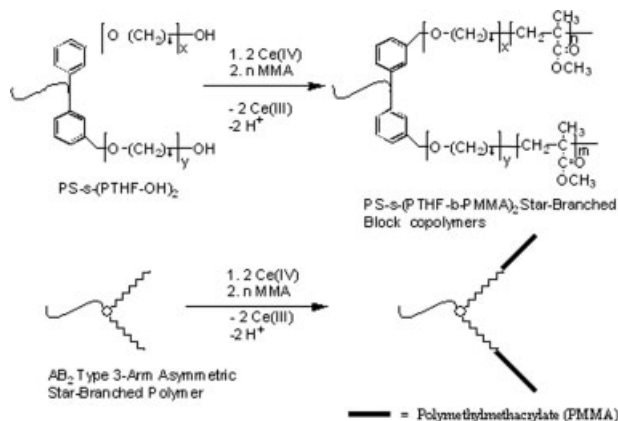
min under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed on PerkinElmer Pyris 1 a with scan rate of 10°C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

AB₂, AB₄, and AB₈ type 3-, 5-, and 9-arm asymmetric star-branched polymers consisting of PS (A) and PTHF-OH (B) segments were obtained via cationic ring opening polymerization of THF initiated by using chain-end-multifunctionalized polystyrenes with 2, 4, and 8 benzyl bromide moieties [PS(BzBr)_{*n*}] as initiators in the presence of AgSbF₆ at 30°C respectively (Scheme 1). Results and conditions of cationic ring opening polymerization of THF are given in Table I. Then, PS-*s*-(PTHF-*b*-PMMA)_{*n*} (*n* = 2, 4, and 8) asymmetric star-branched block copolymers were synthesized via redox polymerization of MMA initiated by using asymmetric star-branched polymers [PS-*s*-(PTHF-OH)_{*x*}] as macroinitiators in the presence of



Scheme 1 Cationic ring opening polymerization of THF initiated by using chain-end-multifunctionalized polystyrenes with 2, 4, and 8 benzyl bromide moieties [PS(BzBr)_{*n*}] as initiators in the presence of AgSbF₆ at 30°C. Schematic presentation of the synthesis of (a) AB₂ type 3-arm, (b) AB₄ type 5-arm, and (c) AB₈ type 9-arm asymmetric star-branched polymers.



Scheme 2 Free radical redox polymerization of MMA initiated by using asymmetric star-branched polymers [PS-*s*-(PTHF-OH)_{*x*}] as macroinitiators in the presence of Ce(IV) salt at 40°C.

Ce(IV) salt at 40°C (Scheme 2). Results and conditions of redox polymerization of MMA are given in Table II.

PS-*s*-(PTHF-*b*-PMMA)_{*n*} (*n* = 2, 4, and 8) asymmetric star-branched block copolymers were purified by fractional precipitation with chloroform as a solvent and methanol as a nonsolvent. The γ values of PS-*s*-(PTHF-*b*-PMMA)_{*n*} (*n* = 2 and 4) asymmetric star-branched block copolymers changed between 3.0 and 6.7, depending on PS, PTHF, and PMMA content and molecular weight of polymer, while γ values were 0.4–0.9 for homo-PS, 3.0–3.9 for homo-PMMA, and >20 for PTHF (soluble in methanol) (because of higher PMMA percent and lower PTHF percent, see Table III). γ Values of PS-*s*-(PTHF-*b*-PMMA)₈ asymmetric star-branched block copolymers were 5.9–8.0 because of higher PTHF percentages when compared with percentages of PS and PMMA in the structure (see Table III). Percentages of PS, PTHF, and PMMA in polymers were calculated from ¹H NMR spectra and the results are given in Table III. The first fractions of the copolymers were all used in the characterizations.

The molecular weights of the polymers were determined by GPC analysis and are listed in Table IV. The

TABLE III
Percentages of PS, PTHF, and PMMA Calculated from ¹H NMR Spectra in the Polymers

PS- <i>s</i> -(PTHF-OH) _{<i>x</i>}	% PS	% PTHF	% PMMA
AB ₂ -I	9	91	
AB ₄ -I	5	95	
AB ₂ -II	13	87	
AB ₈ -I	13	87	
PS- <i>s</i> -[PTHF- <i>b</i> -PMMA] ₂ (I)	3	12	85
PS- <i>s</i> -[PTHF- <i>b</i> -PMMA] ₄ (II)	7	22	71
PS- <i>s</i> -[PTHF- <i>b</i> -PMMA] ₂ (III)	3	11	86
PS- <i>s</i> -[PTHF- <i>b</i> -PMMA] ₈ (V-1)	13	80	7
PS- <i>s</i> -[PTHF- <i>b</i> -PMMA] ₈ (V-3)	4	77	19

TABLE IV
GPC Measurements of the Polymers

PS- <i>s</i> -(PTHF-OH) _{<i>x</i>}	<i>M_w</i> (10 ³)	<i>M_n</i> (10 ³)	MWD
AB ₂ -I	113.80	54.85	2.07
AB ₄ -I	590.15	241.25	2.45
AB ₂ -II	92.38	42.81	2.16
AB ₄ -II	250.53	130.18	1.92
AB ₈ -I	125.8	65.6	1.92
PS- <i>s</i> -[PTHF- <i>b</i> -PMMA] ₂ (I)	1312.59	869.66	1.51
PS- <i>s</i> -[PTHF- <i>b</i> -PMMA] ₄ (II)	1066.36	603.23	1.77
PS- <i>s</i> -[PTHF- <i>b</i> -PMMA] ₂ (III)	964.12	514.69	1.87
PS- <i>s</i> -[PTHF- <i>b</i> -PMMA] ₄ (IV)	782.94	355.22	2.2
PS- <i>s</i> -[PTHF- <i>b</i> -PMMA] ₈ (V-1)	132.15	71.19	1.86
PS- <i>s</i> -[PTHF- <i>b</i> -PMMA] ₈ (V-3)	153.39	73.61	2.08

systematic increase in the molecular weight of polymers, for example from 9250 for PS(BzBr)₂ to 54,850 for PS-*s*-(PTHF-OH)₂ (AB₂-I) and finally to 869,660 for PS-*s*-(PTHF-*b*-PMMA)₂ (I) (Table IV), demonstrated that the polymerizations proceeded successfully according to Schemes 1 and 2 respectively. Figure 1 showed GPC traces for PS-*s*-(PTHF-OH)₂ (AB₂-II) macroinitiator and PS-*s*-(PTHF-*b*-PMMA)₂(III) asymmetric star-branched block copolymers.

The spectroscopic characterization of the polymers was performed with FTIR and ¹H NMR analyses. In the FTIR spectrum of PS-*s*-(PTHF-OH)₂ (Run no. AB₂-I in Table I), a strong absorption peak was observed at 1110.80 cm⁻¹ due to the C—O—C stretching band of poly-THF blocks, and two peaks were observed at 700 and 1600 cm⁻¹ due to the phenyl groups of PS blocks [Fig. 2(a)]. In the FTIR spectrum of PS-*s*-[PTHF-*b*-PMMA]₂ (Run no. I in Table II), the observation of

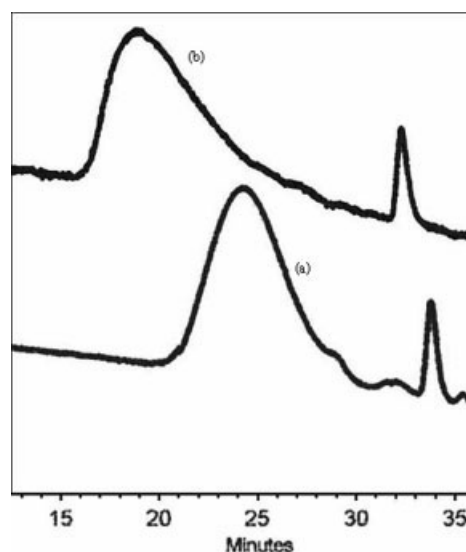


Figure 1 GPC traces of (a) PS-*s*-(PTHF-OH)₂ (AB₂-II in Table IV) asymmetric star-branched polymers and (b) PS-*s*-(PTHF-*b*-PMMA)₂ (III in Table IV) asymmetric star-branched block copolymers.

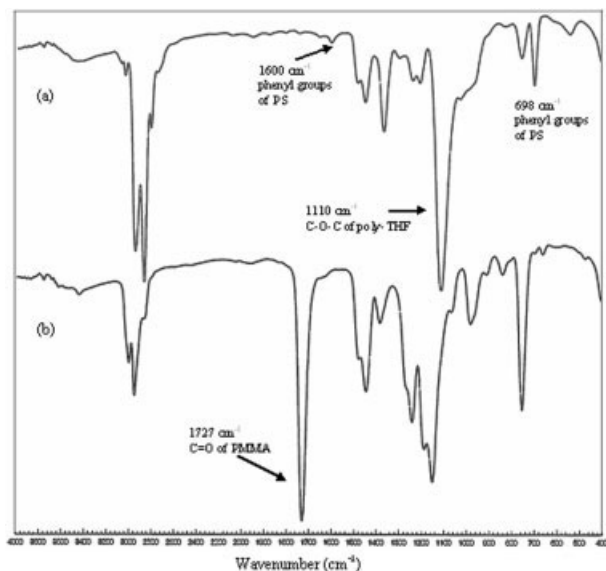


Figure 2 The FTIR spectra of (a) PS-*s*-(PTHF-OH)₂ (Run no. AB₂-I in Table I) asymmetric star-branched polymers and (b) PS-*s*-(PTHF-*b*-PMMA)₂ (Run no. I in Table II) asymmetric star-branched block copolymers.

absorption peak corresponding to carbonyl groups of PMMA blocks at 1727.91 cm⁻¹ in addition to characteristic absorption peaks of PS and PTHF blocks confirmed the formation of asymmetric star branched block copolymer structure according to Scheme 2 [Fig. 2(b)]. Figure 3 shows the ¹H NMR spectra of PS-*s*-(PTHF-OH)₄ (Run no. AB₄-I in Table I) and PS-*s*-(PTHF-*b*-PMMA)₄ (Run No. II in Table II). It shows all the peaks expected for the structures. In the ¹H NMR spectrum of PS-*s*-(PTHF-OH)₄ (Run no. AB₄-I in Table I), characteristic peaks for PS block at δ = 6.6–7.1 ppm due to aromatic protons, and characteristic peaks for PTHF blocks at 1.6 ppm due to methylene protons (–CH₂–) and at 3.4 ppm due to oxymethylene protons (–OCH₂–) were observed [Fig. 3(a)]. The ¹H NMR spectrum of PS-*s*-(PTHF-*b*-PMMA)₄ (Run no. II in Table II) revealed the characteristic peaks of PMMA blocks at δ = 1.0–0.8 ppm due to methyl protons (–CH₃), at 1.9–2.0 ppm due to methylene protons (–CH₂–), and at 3.6 ppm due to methoxy protons (–OCH₃), in addition to the ¹H NMR spectrum of PS-*s*-(PTHF-OH)₄ [Fig. 3(b)]. Figure 4 exhibits the ¹H NMR spectra of PS-*s*-(PTHF-OH)₈ (Run no. AB₈-I in

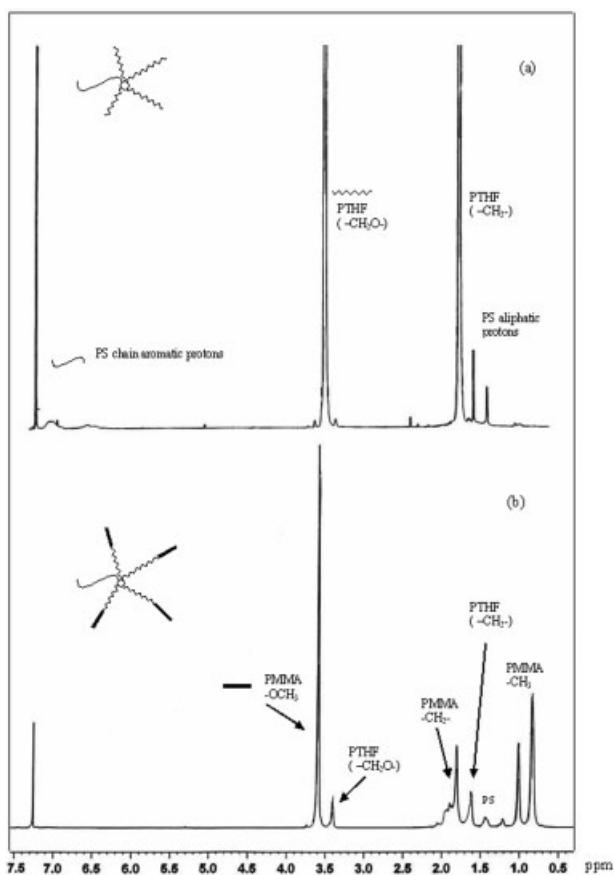


Figure 3 ¹H NMR spectra of (a) PS-*s*-(PTHF-OH)₄ (Run no. AB₄-I in Table I) asymmetric star-branched polymers and (b) PS-*s*-(PTHF-*b*-PMMA)₄ (Run no. II in Table II) asymmetric star-branched block copolymers.

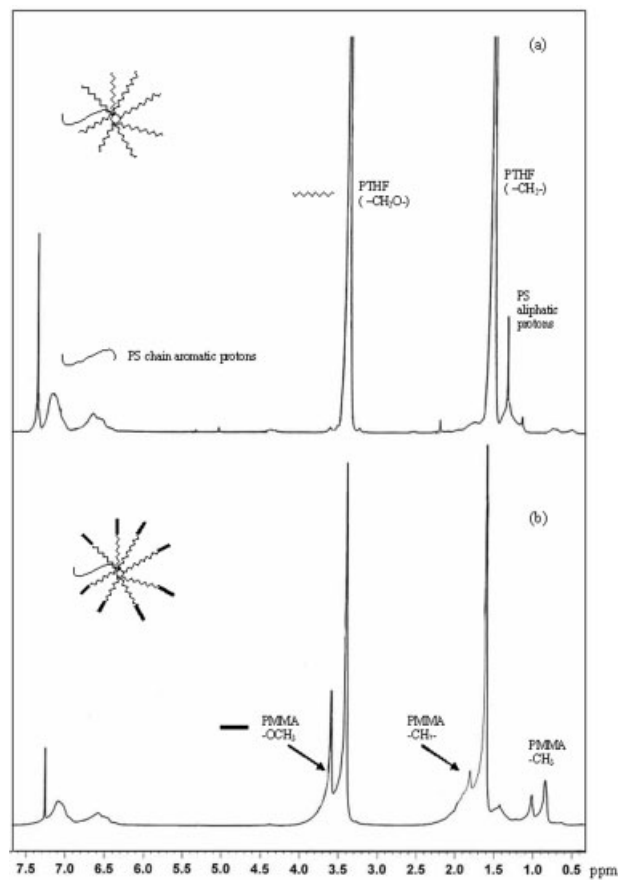


Figure 4 ¹H NMR spectra of (a) PS-*s*-(PTHF-OH)₈ (Run no. AB₈-I in Table I) asymmetric star-branched polymers and (b) PS-*s*-(PTHF-*b*-PMMA)₈ (Run no. V-3 in Table II) asymmetric star-branched block copolymers.

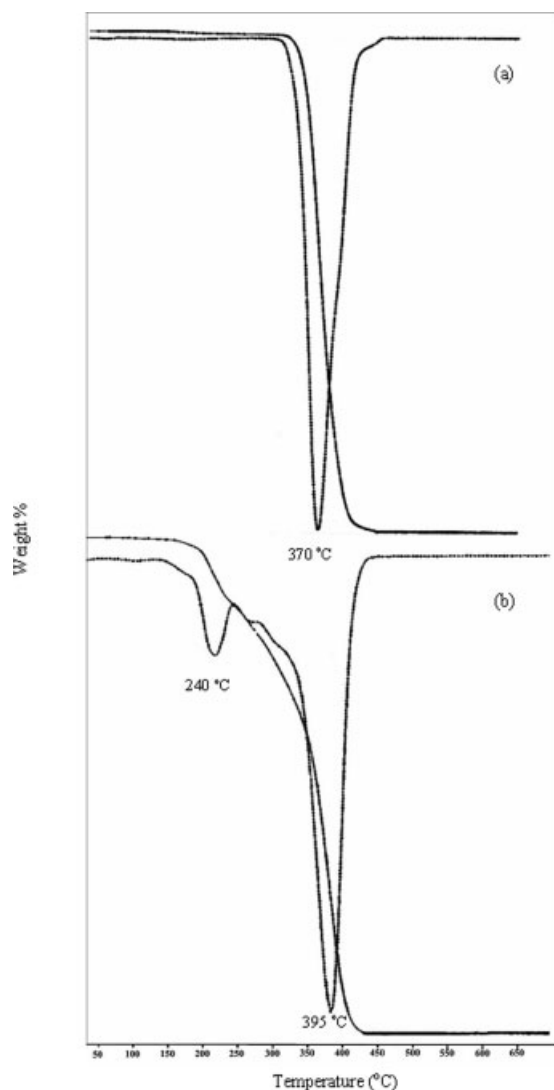


Figure 5 TGA thermograms of (a) PS-*s*-(PTHF-OH)₄ (Run no. AB₄-I in Table I) asymmetric star-branched polymers and (b) PS-*s*-(PTHF-*b*-PMMA)₄ (Run no. II in Table II) asymmetric star-branched block copolymers.

Table I) and of PS-*s*-[PTHF-*b*-PMMA]₈ (Run no. V-3 in Table II). Characteristic peaks for PS and PTHF were observed in ¹H NMR spectrum of PS-*s*-(PTHF-OH)₈ (Run no. AB₈-I in Table I) [Fig. 4(a)]. In addition to these peaks in the ¹H NMR spectrum of PS-*s*-[PTHF-*b*-PMMA]₈ (Run no. V-3 in Table II) was observed characteristic peaks for PMMA [Fig. 4(b)].

Thermal characterization of the polymers was done by using TGA and DSC techniques. TGA thermograms of AB₂, AB₄, and AB₈ type PS-*s*-(PTHF-OH)_{*x*} asymmetric star branched polymers exhibited only one decomposition temperature (*T_d*) at 370°C, while PTHF homopolymers have *T_d* at 230°C and PS homopolymers have *T_d* around 400°C. TGA thermograms of PS-*s*-(PTHF-*b*-PMMA)_{*x*} star-branched block copolymers exhibited two main decomposition temperatures (*T_d*'s), the first at 240°C and the second at

395°C. Figures 5(a) and 5(b) show the TGA curves of PS-*s*-(PTHF-OH)₄ asymmetric star branched polymers (Run no. AB₄-I in Table I) and PS-*s*-(PTHF-*b*-PMMA)₄ star-branched block copolymers (Run no. II in Table II) respectively. In the case of PS-*s*-(PTHF-*b*-PMMA)₄ star-branched block copolymers the observation of *T_d* at 240°C and shifting of second *T_d* from 370 to 395°C can be attributed to the insertion of the PMMA into the structure, because PMMA has two *T_d*'s, the first between 200 and 300°C for the decomposition of side chains of PMMA and the second around 430°C for the decomposition of the main chain of PMMA. DSC curves of PS-*s*-(PTHF-OH)_{*x*} asymmetric star branched polymers exhibited one sharp and strong melting transition at 47°C because of crystalline structure of PTHF [Fig. 6(a)]. In the DSC curves of PS-*s*-(PTHF-*b*-PMMA)_{*x*} star-branched block copolymers was observed one broad melting transition between 25 and 70°C (at around 50°C) because of insertion of PMMA into the PS-*s*-(PTHF-OH)_{*x*} structure and thus destruction of crystalline structure of PTHF [Fig. 6(b)].

CONCLUSIONS

Asymmetric star-branched block copolymers based on PS, PTHF, and PMMA were synthesized by a combination of cationic ring opening polymerization and redox polymerization methods. PS-*s*-(PTHF-*b*-PMMA)_{*n*} (*n* = 2, 4, and 8) asymmetric star-branched block copolymers obtained in this way were purified by fractional precipitation method before characteriza-

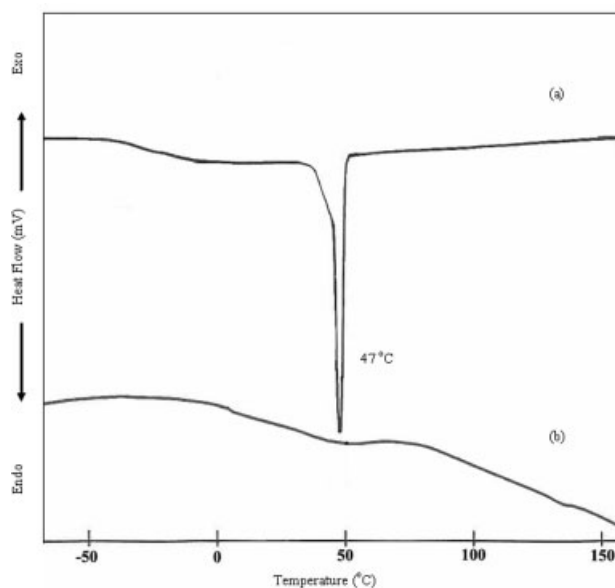


Figure 6 DSC curves of (a) PS-*s*-(PTHF-OH)₂ (Run no. AB₂-I in Table I) asymmetric star-branched polymers and (b) PS-*s*-(PTHF-*b*-PMMA)₂ (Run no. I in Table II) asymmetric star-branched block copolymers.

tion and characterized by GPC, FTIR, ^1H NMR, and thermal analyses (DSC and TGA).

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