

Nitroxide-Terminated Poly(Styrene-*co*-diethyl Fumarates) and Derived Block Copolymers

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ABSTRACT: Copolymerization of styrene (S) and diethyl fumarate (DEF) at 125°C in the presence of 2,2,6,6-tetramethylpiperidin-1-yloxy radical (TEMPO) and initiated with a thermal initiator, 2,2'-azobisisobutyronitrile (AIBN), was studied. The molar fraction of DEF in the feed, F_{DEF} , varied within 0.1–0.9. An azeotropic composition, $(F_{\text{DEF}})_A = 0.38$, was found for the copolymerization under study. At $F_{\text{DEF}} = 0.1$ –0.4, a quasi-living process was observed, transforming to a retarded conventional radical copolymerization at a higher content of DEF in the initial mixtures. The obtained TEMPO-terminated S-DEF copolymers were used to initiate polymerization of styrene. Poly(styrene-*co*-diethyl fumarate)-*block*-polystyrene copolymers were prepared with molecular weight distributions depending on the amount of inactive polymer chains in macroinitiators, as indicated by size-exclusion chromatography. A limited miscibility of the blocks in the synthesized block copolymers was revealed by using differential scanning calorimetry. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2432–2439, 2002

Key words: styrene-diethyl fumarate comonomers; nitroxide-terminated copolymers; quasi-living copolymerization; block copolymers

INTRODUCTION

Nitroxide-mediated controlled radical polymerization is one of modern synthetic routes for the preparation of well-defined polymers, which can serve also as precursors in chain-extension reactions.^{1–27} Two main characteristics are typical of this polymerization process: the fast initiation and reversible termination of the polymer radical with a nitroxide, such as 2,2,6,6-tetramethylpiperidin-1-yloxy radical (TEMPO). Bimolecular, irreversible termination reactions between polymer radicals, namely, recombination or disproportionation, proceeding in a conventional radical polymerization, are substantially suppressed by de-

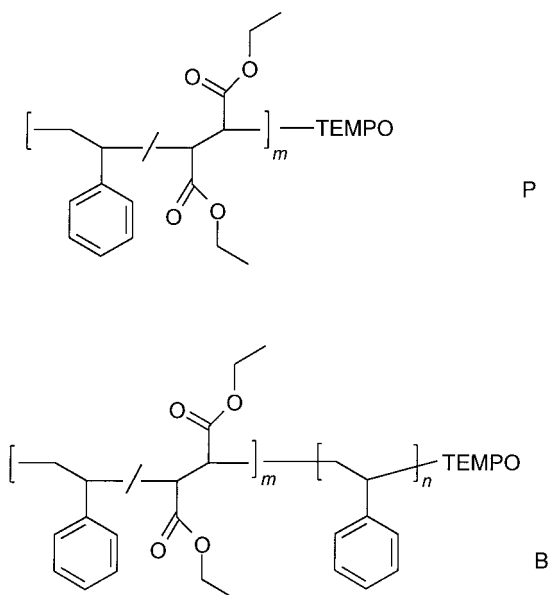
creasing the number of active polymer chains. Dissociation of the reversibly terminated polymer chains at temperatures above 100°C regenerates polymer radicals, which can repeatedly add monomer units before being trapped again by the nitroxide. Because of both fast formation of initiating centers and predominant reversible termination of polymer radicals, a quasi-living polymerization proceeds. As a result, molecular weights of the obtained polymers increase with increasing conversion and have a narrow distribution. The prepared polymers can be isolated, purified, and stored. They are potential macroinitiators in the synthesis of complex macromolecular architectures, such as block copolymers.

As convenient monomers for the quasi-living radical polymerization in the presence of TEMPO, a widely used stable nitroxyl radical proved to be styrene (S) and its derivatives. TEMPO-mediated polymerization of other vinyl monomers loses the

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Scheme 1 TEMPO-terminated poly(styrene-*co*-diethyl fumarates) (P) and poly(styrene-*co*-diethyl fumarate)-*block*-polystyrene copolymers (B).

quasi-living nature. However, vinyl monomers can copolymerize with S via quasi-living mechanism in systems containing an excess of the latter comonomer.^{10,28} By using the obtained TEMPO-capped copolymers as macroinitiators, a new group of block copolymers can be produced by the chain-extension method.

In most cases, the nitroxide-mediated radical copolymerization of S and monomers having 1- or 1,1-substituted polymerizable double bond was studied. Recently, we have reported the results concerning poly(*N*-butyl- or *N*-phenylmaleimide-*co*-styrenes) and derived block copolymers (i.e., polymers with incorporated heterocyclic derivatives of 1,2-dicarboxyethene), which were synthesized by using the nitroxide technique.^{29,30} Nitroxide-mediated polymerization leading to the copolymers of maleic anhydride was described by Hawker et al.^{26,31} The aim of our present work was to prepare TEMPO-terminated copolymers of S with another 1,2-substituted ethene, diethyl fumarate, and to employ them as macroinitiators in the synthesis of related poly(styrene-*co*-diethyl fumarate)-*block*-polystyrene copolymers (Scheme 1).

EXPERIMENTAL

Materials

Styrene (Kaučuk Group Co., Kralupy, Czech Republic) [boiling point (bp) 36°C/1.56 kPa] and di-

ethyl fumarate (Fluka) (bp 60–61°C/6.70 Pa) were distilled under reduced pressure prior to use. AIBN (Fluka) [melting point (mp) 105°C] was recrystallized from ethanol. The TEMPO radical (mp 36–39°C), a commercial product of Fluka, was used as received. The solvents were of analytical grade.

Synthesis of TEMPO-Terminated Styrene-Diethyl Fumarate Copolymers

A mixture of S and diethyl fumarate (DEF; 5×10^{-2} mol total), AIBN (1×10^{-4} mol), and TEMPO (1.5×10^{-4} mol) was heated in a sealed glass ampoule in an inert atmosphere at 125°C. The molar fractions of DEF in the feed, F_{DEF} , varied in the range of 0.1–0.9. After a predetermined time, the resulting TEMPO-terminated copolymer was precipitated from the reaction mixture and reprecipitated from chloroform solutions with hexane. It was dried under vacuum (6.7 Pa) at room temperature. The reaction conditions, conversions, compositions (molar fractions of DEF in the copolymers, f_{DEF}), molecular weights, their distributions (MWD), and the glass transition temperatures (T_g) for the copolymers P1–P9 are given in Table I. No homopolymerization of DEF (5×10^{-2} mol) was found to proceed in the presence of AIBN (1×10^{-4} mol) and TEMPO (1.5×10^{-4} mol) for 20 h.

Polymerization of S Using TEMPO-Terminated Styrene-Diethyl Fumarate Copolymer Macroinitiators

A solution containing 0.2 g of copolymer P1, P3, P5, or P6 (Table I) and 5 mL S was heated in a sealed glass ampoule in an inert atmosphere at 125°C for 1 h. Then, the reaction mixture was poured into a 10-fold excess of hexane. The obtained polymer was reprecipitated from a chloroform solution with hexane and dried under vacuum (6.7 Pa) at room temperature. Table II summarizes the yields and some characteristics of the synthesized polymers.

Measurements

The yields of copolymers were determined gravimetrically. The compositions were found from elemental analyses. The molecular weights and MWDs were evaluated by using SEC. Determination of the glass transition temperatures was based on the DSC measurements.

SEC Measurements

The SEC measurements for evaluation of number- and weight-average molecular weights (M_n

Table I Copolymerization of Styrene (S) and Diethyl Fumarate (DEF) in the Presence of TEMPO^a

Copolymer	F_{DEF}	Time (h)	Yield (%)	f_{DEF}	$M_n \times 10^{-3b}$	M_w/M_n	T_g^c (°C)
P1	0.1	6	29.0	0.16	10.3	1.23	74.0
P2	0.2	5.5	29.2	0.26	10.5	1.22	—
P3	0.3	4	17.0	0.34	8.4	1.20	72.6
P4	0.4	2	18.3	0.39	8.5	1.23	—
P4-1	0.4	1.5	10.1	—	5.3	1.22	—
P4-2	0.4	1	2.4	—	4.0	1.14	—
P5	0.5	7	17.8	0.43	7.4	1.31	65.6
P6	0.6	16	29.8	0.46	14.3	1.71	53.0
P7	0.7	24	38.0	0.47	17.2	2.14	52.6
P8	0.8	25	16.7	0.49	10.5	2.36	52.0
P9	0.9	25	6.9	0.53	8.3	2.02	49.4

F_{DEF} and f_{DEF} are molar fractions of DEF in the feed and in the copolymer, respectively.

^a 5×10^{-2} mol of comonomers, 1×10^{-4} mol of AIBN, 1.5×10^{-4} mol of TEMPO, 125°C.

^b Polystyrene-equivalent molecular weight of the copolymer determined by SEC.

^c Glass transition temperature determined by DSC from the second scan.

and M_w) were carried out on a PSS SDV 10000 column (8×600 mm, Polymer Standard Service, Germany), filled with $5 \mu\text{m}$ sorbent particles. Tetrahydrofuran, distilled and dried over molecular sieves (4 \AA), served as a mobile phase. Chromatographic data from refractometric and UV (254 nm) detectors were treated by using the Data-Monitor system (Watrex, Czech Republic). For the determination of molecular weights, a universal calibration equation calculated from the data on polystyrene standards (Merck, Germany) was used.

DSC Measurements

DSC was performed on a Perkin–Elmer DSC-7 apparatus. The measurements were carried out

in two or three scans in nitrogen atmosphere in the temperature interval from -10 to 130°C at a heating rate of $10^\circ\text{C}/\text{min}$. The sample weight was about 5 mg. The glass transition temperatures were determined from the obtained thermograms.

RESULTS AND DISCUSSION

TEMPO-Mediated Copolymerization of S and DEF

Table I presents the results on the S-DEF copolymerization initiated with AIBN in the presence of TEMPO radicals. The copolymerization process and properties of the obtained copolymers considerably depended on the molar fraction of DEF in

Table II Polymerization of Styrene Initiated with TEMPO-Terminated Poly(Styrene-co-diethyl Fumarate) Precursors^a

Product	Precursor ^b	Yield (g)	PS ^c (wt %)	$M_n \times 10^{-4}$ ^d	M_w/M_n	T_g^e (°C)
B1	P1	0.74	66.5	4.88	1.51	87.5
						99.1
						92.8 ^f
B3	P3	0.63	73.0	3.95	1.43	79.3
B5	P5	0.61	73.7	4.87	1.63	99.6
B6	P6	0.59	67.5	9.82	1.89	78.7
B9	P9	0.46	62.8	—	—	66.1
						94.3
B9-A ^g	—	—	—	26.03	1.36	—
B9-B ^g	—	—	—	1.32	1.92	—

^a 0.2 g of precursor, 5 mL of styrene, 1 h, 125°C.

^b See Table I.

^c Determined from elemental analysis.

^d Polystyrene-equivalent molecular weight of the copolymer determined by SEC.

^e Determined by DSC from the second scan.

^f From the third scan.

^g B9-A (78.3%) and B9-B (21.7%) are fractions of B9 as determined by SEC.

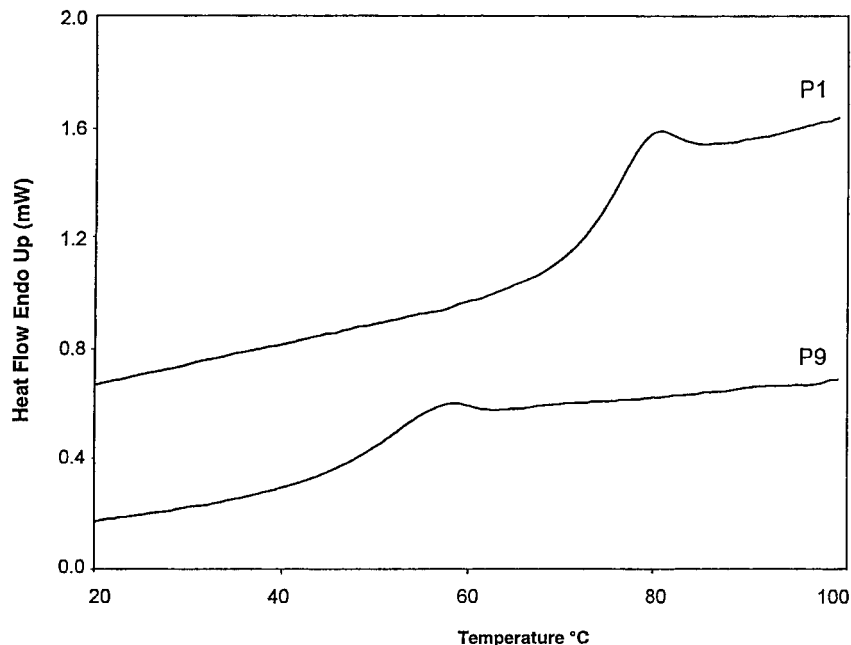


Figure 1 DSC thermograms for P1 and P9 (Table I).

the initial reaction mixture. At the same total amounts of the comonomers, the conversion was 18.3% after 2 h at $F_{\text{DEF}} = 0.4$, whereas the yield did not reach a similar value (17.8%) before 7 h at $F_{\text{DEF}} = 0.5$. In the mixtures with $F_{\text{DEF}} > 0.5$, the yields decreased with the increasing content of DEF in the feed, the conversion at $F_{\text{DEF}} = 0.9$ being only 6.9% after 25 h. Homopolymerization of DEF did not proceed. In this case, termination reactions between TEMPO and radical species from DEF probably take place, giving rather inactive products.

A large difference in the carbon content in the individual comonomers (92.26 and 55.81% in S and DEF, respectively) made it possible to determine easily the compositions of the copolymers from elemental analyses. The maximum amount of the incorporated DEF units was about 50 mol % ($f_{\text{DEF}} = 0.53$ at $F_{\text{DEF}} = 0.9$). The changes in the compositions were in accordance with the determined glass transition temperatures. As expected, the highest T_g (74.0°C) was found for copolymer P1 with the highest content of rigid S units. Increased DEF contents in the copolymers lowered T_g 's. However, T_g 's of P6 (53.0°C), P7 (52.6°C), P8 (52.0°C), and P9 (49.4°C) differed only slightly. For illustration, the DSC thermograms for P1 and P9 are depicted in Figure 1.

Figure 2 shows the dependence of the composition of the S-DEF copolymers prepared in the presence of TEMPO on the feed composition. Sim-

ilar to the conventional radical copolymerization of S and DEF, an azeotropic course was observed. According to the literature,³² in the absence of nitroxide, the monomer reactivity ratios (r) are 0.29 for S (r_S) and 0.02 for DEF (r_{DEF}). The calculated azeotropic composition, $(F_{\text{DEF}})_A = 1/[1 + (r_{\text{DEF}} - 1)/(r_S - 1)]$, equal to 0.42 for the con-

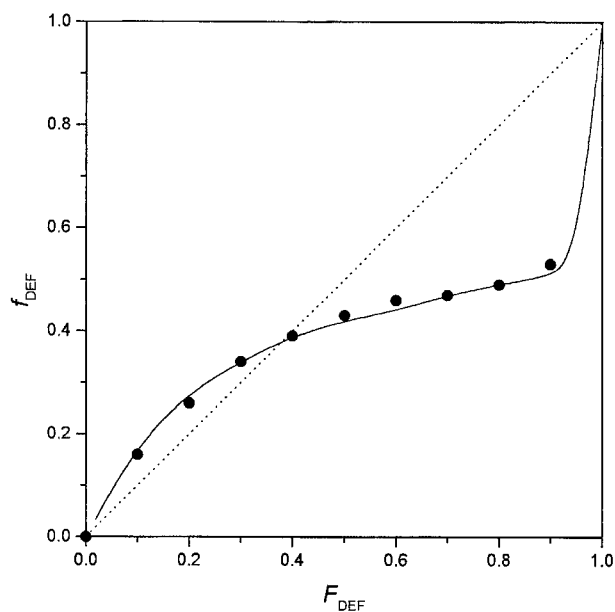


Figure 2 The dependence of the composition of S-DEF copolymers prepared in the presence of TEMPO (f_{DEF}) on the feed composition (F_{DEF}) (Table I).

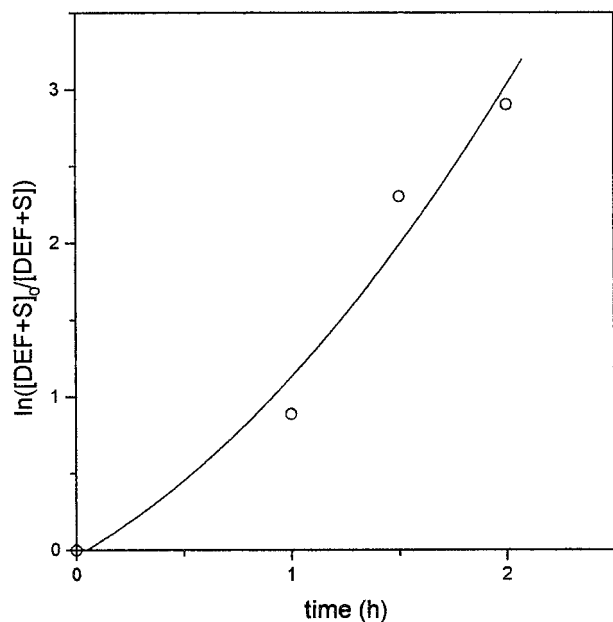


Figure 3 The semilogarithmic time-conversion plot for the S-DEF copolymerization at $F_{\text{DEF}} = 0.4$ (Table I). $[S + \text{DEF}]_0$ and $[S + \text{DEF}]_t$ are molar concentrations of the comonomers at the beginning and at a given time of the copolymerization, respectively.

ventional copolymerization, is close to that (0.38) determined experimentally for the S-DEF copolymerization in the presence of TEMPO.

The found molecular weights and their distributions gave further useful information about the copolymerization process. The P1–P4 copolymers showed fairly narrow MWDs, their M_w/M_n being lower than 1.25. In addition, in the S-DEF copolymerization at $F_{\text{DEF}} = 0.4$ (i.e., at the virtually azeotropic composition of the feed), the respective conversions and molecular weights increased from 2.4% and 4.0×10^3 (P4–P2) up to 18.3% and 8.5×10^3 (P4) within 1–2 h. Figure 3 presents the semilogarithmic time–conversion plot for this copolymerization. A slight initial increase is probably associated with an increase in the number of initiating centers due to the formation of *in situ* unimolecular initiators.¹² These initiators can be generated by trapping radicals from autopolymerization of the S-DEF mixture with TEMPO. The following linear course, however, demonstrates that, at the next stage, for the rate of copolymerization, R ,

$$R = -d[S + \text{DEF}]/dt = k_p[C^*][S + \text{DEF}] \quad (1)$$

where $[S + \text{DEF}]$ and $[C^*]$ are the molar concentrations of comonomers and initiating or poten-

tially initiating centers, respectively, at time t , and k_p is the rate constant of propagation; the $[C^*]$ is almost constant. The similar course was also observed in the TEMPO-mediated copolymerization of S and *N*-butylmaleimide.²⁹

The corresponding M_n -conversion dependence was also linear (Fig. 4). The shift of the line from the zero onset on the M_n axis could be due to the fact that the polystyrene-equivalent and rather low molecular weights were measured by SEC.

Both the above-mentioned dependences and narrow MWDs indicate a quasi-living nature of the copolymerizations at $F_{\text{DEF}} = 0.1$ – 0.4 under given conditions.

During the copolymerization at increasing F_{DEF} , the ratio between the adducts $P_{\text{DEF}}\text{-TEMPO}$ originating from macroradicals with terminal DEF units and $P_{\text{S}}\text{-TEMPO}$ from macroradicals with terminal S units increases. Considering the inability of DEF to homopolymerize in the presence of TEMPO, the $P_{\text{DEF}}\text{-TEMPO}$ is, in comparison with $P_{\text{S}}\text{-TEMPO}$, obviously unable to dissociate reversibly into the growing polymer radical. Another reason for deactivation of the polymer chains might be due to an irreversible disproportionation between macroradicals containing terminal DEF units and TEMPO, yielding an ω -unsaturated copolymer and a hydroxylamine derivative (Scheme 2). An analogous reaction occurring in the TEMPO-mediated polymerizations of acrylate or methacrylate monomers was described in detail recently.^{20–22}

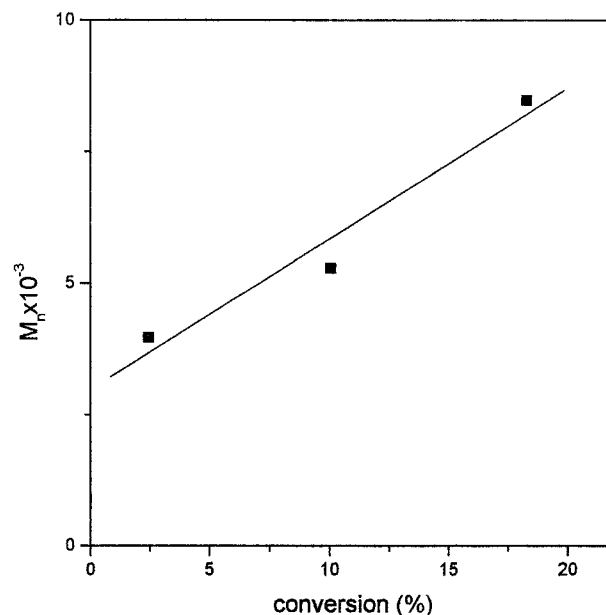
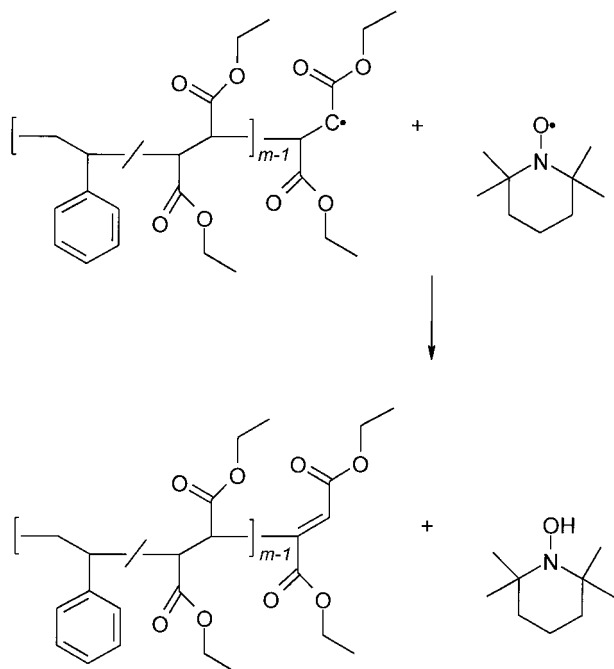


Figure 4 The M_n -conversion dependence for the S-DEF copolymerization at $F_{\text{DEF}} = 0.4$ (Table I).



Scheme 2 The disproportionation reaction between poly(styrene-*co*-diethyl fumarate) macroradical containing the terminal DEF unit and TEMPO.

Proportional to the extent of accumulation of dead polymer chains, the rate of the copolymerization decreases and copolymers having a broader MWD are formed. The M_w/M_n values for the copolymers P5 and P6 were found to be 1.31 and 1.71, respectively, and those for P7, P8, and P9 even exceeded the value of 2. The SEC curves for P5 and P9 are presented in Figure 5.

Evidently, it can be concluded that at $F_{\text{DEF}} > 0.5$, the copolymerization transforms from quasi-living to a retarded conventional radical copolymerization process.²⁸

Poly(styrene-*co*-diethyl Fumarate)-*block*-Polystyrene Copolymers

The TEMPO-terminated copolymers P1, P3, P5, P6, or P9 were used as macroinitiators in the polymerization of S at 125°C (Table II). The molecular weights of the resulting polymer products (B1, B3, B5, B6, and B9) were higher than those of the initial precursors, thus indicating the formation of poly(styrene-*co*-diethyl fumarate)-*block*-polystyrene copolymers. The amounts and lengths of the formed polystyrene blocks were dependent upon precursor characteristics, such as molecular weights and the number of active polymer chains. In comparison with B1 ($M_w/M_n = 1.51$) and B3 ($M_w/M_n = 1.43$), the copolymers

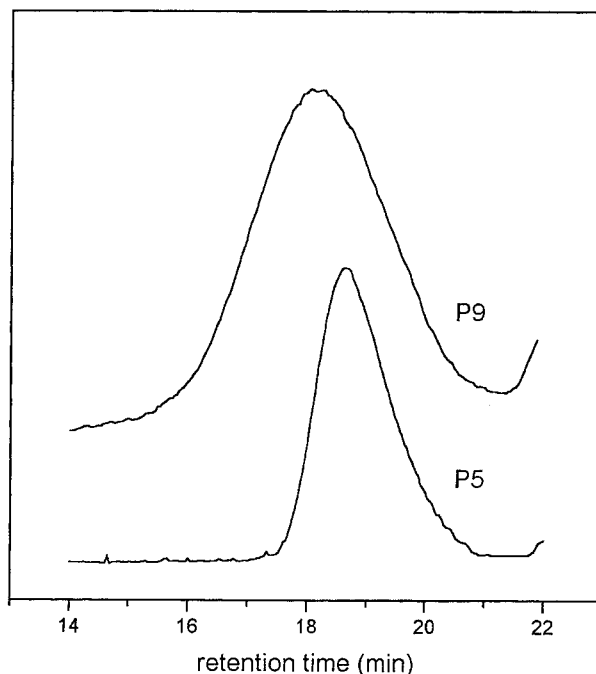


Figure 5 SEC curves for P5 and P9 (Table I).

B5 and B6 showed broader MWDs ($M_w/M_n = 1.63$ and 1.89, respectively). This is in accordance with the decreasing initiation efficiency of the P5 and P6 macroinitiators due to their higher content of

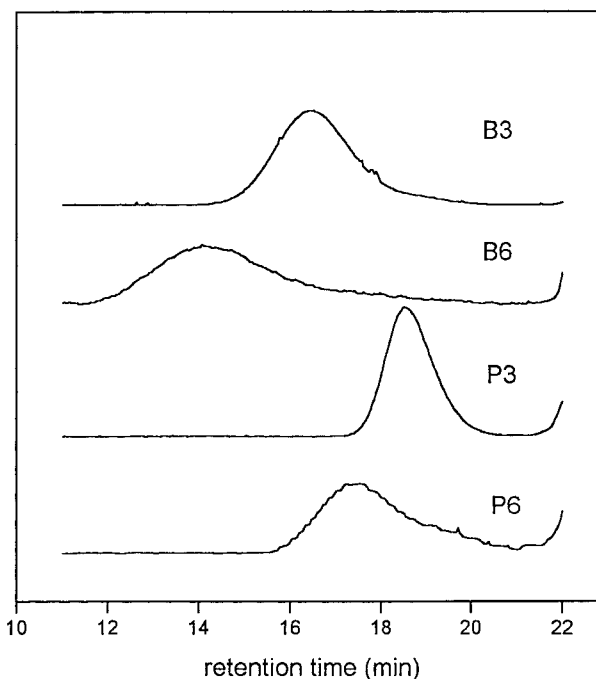


Figure 6 SEC curves for P3, P6 and B3, B6 (Tables I and II).

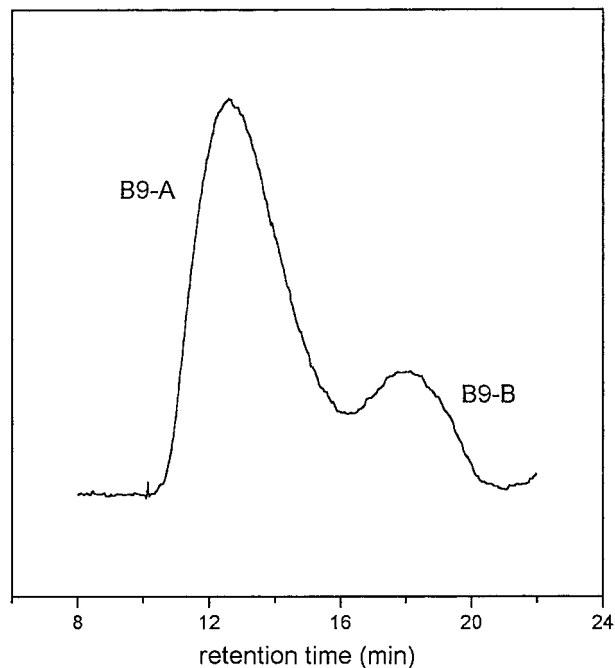


Figure 7 SEC curve for B9 (Table II).

inactive polymer chains (see the previous section). For illustration, Figure 6 presents the SEC curves for B3, B6, and for the corresponding precursors. A bimodal SEC curve was found for product B9, which was synthesized by using the P9 precursor with a broad MWD ($M_w/M_n = 2.02$) (Fig. 7). The SEC measurement revealed that B9

consists of two fractions, of B9-A containing largely a block copolymer and of B9-B with the unreacted P9 macroinitiator (about 22% of B9). A considerably high M_n of B9-A (about 2.6×10^5) is associated with a low number of reversibly dissociating polymer chains in P9.

The DSC measurements showed some details concerning the thermal behavior of the synthesized block copolymers. For B1 and B6, two T_g values were determined by DSC from the second scan; however, in the case of B1, the third scan afforded only one T_g (Fig. 8). One T_g value was found also for B3 and B5 (from the second scan). Apparently, miscibility of polymer blocks to some extent can be assumed in the prepared block copolymers. The T_g 's evidently depend on both the amount and the arrangement of incorporated comonomer units and reflect the limited compatibility of the blocks in the copolymers. Product B9 (i.e., a mixture of a block copolymer and an initial precursor) exhibited two T_g values.

CONCLUSION

The TEMPO-terminated copolymers were synthesized by copolymerization of S and DEF at 125°C, which was initiated with AIBN in the presence of TEMPO. The copolymerization was found to proceed in an azeotropic manner. The experimentally determined composition, $(F_{\text{DEF}})_A = 0.38$, did not

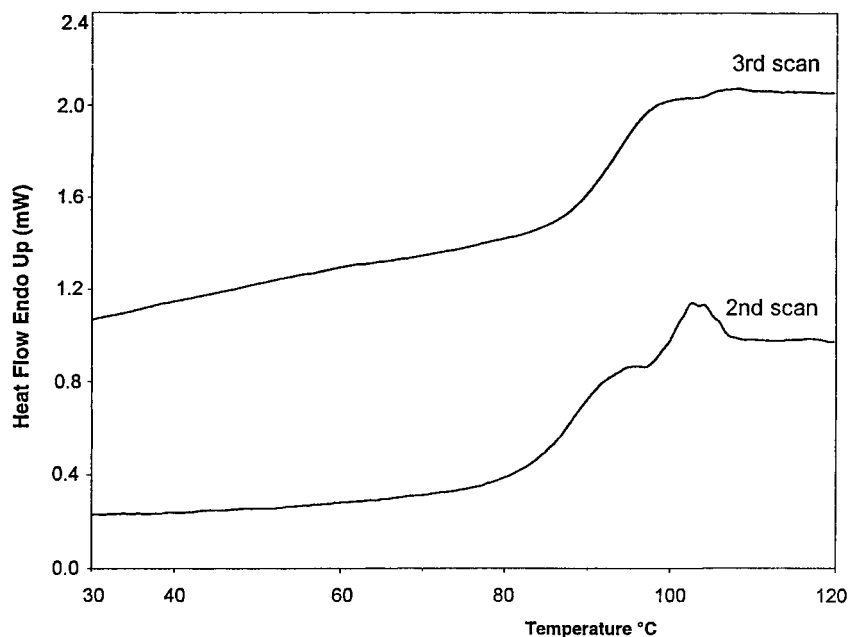


Figure 8 DSC thermograms for B1 (Table II).

differ substantially from that calculated for the conventional radical copolymerization of S and DEF (0.42). The narrow MWDs and linear semi-logarithmic time-conversion as well as M_n -conversion dependences indicate a quasi-living mechanism of the copolymerizations at $F_{\text{DEF}} = 0.1-0.4$, whereas at $F_{\text{DEF}} > 0.5$, the copolymerization lost the quasi-living nature. The prepared TEMPO-terminated poly(S-co-DEFs) readily initiated polymerization of S under formation of poly(S-co-DEF)-*block*-polyS copolymers. The MWDs of the block copolymers broadened with a higher content of inactive polymer chains in the macro-initiators. The DSC data showed that the polymer blocks are miscible to some extent.

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