Synthesis and Chain Extension of Nitroxide-Terminated Styrene–Maleimide Copolymers

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ABSTRACT: Thermal radical copolymerization of styrene (S) and maleimide (MI) at 125°C in diglyme in the presence of 2,2,6,6-tetramethylpiperidin-1-yloxyl radical (TEMPO) was studied. Mole fractions of maleimide in the feed, F_{MI}, varied in the range 0.1–0.9. A quasiliving reaction process proceeded yielding copolymers with a low polydispersity $(M_w/M_n = 1.17–1.41)$. The found azeotropic composition, $(F_{MI})_A = 0.46$, did not differ substantially from that (0.5) in the conventional radical S-MI copolymerization. At a higher conversion or MI content in the feed, deactivation of the copolymer chains occurred. The obtained TEMPO-terminated S-MI copolymers readily initiated polymerization of styrene; chain extension of the macroinitiators took place, giving poly(S-*co*-MI)-*block*-poly(S) diblock copolymers. The synthesized copolymers containing S and MI units were characterized by elemental analysis, NMR spectroscopy, size-exclusion chromatography, and differential scanning calorimetry. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1863–1868, 2004

Key words: styrene–maleimide copolymers; nitroxide-mediated radical copolymerization; chain extension reaction; diblock copolymers

INTRODUCTION

In recent years, the synthesis of polymers have achieved remarkable success due to new techniques such as nitroxide-mediated radical polymerization (NMRP).[1–22] In the presence of a nitroxide stable radical or *N*-alkoxyamine-based unimolecular initiator, a quasiliving radical polymerization proceeds at elevated temperatures (usually >100°C) in mixtures consisting of a thermal initiator [2,2′-azobis(isobutyronitrile), dibenzoyl peroxide] and monomer. Some monomers and comonomer couples (styrene and styrene-*N*-butyl- or *N*-phenylmaleimide) polymerize in the quasiliving manner even without any added initiator.[12,23,24] The mediating role of the nitroxide consists of reversible termination of growing polymer radicals under formation of thermally unstable *N*-alkoxyamine bond. Dissociation of the bonds regenerates the polymer radicals, which can add more monomer units before being trapped again with the nitroxide. The obtained nitroxide-terminated polymers have well-defined structure and properties. They can be employed in chain extension reactions for the synthesis of block copolymers.

Convenient monomers for the NMRP are styrene or its derivatives; the most widely used nitroxide is 2,2,6,6-tetramethylpiperidin-1-yloxyl radical (TEMPO). However, by using TEMPO, the structure and process control of polymerization are generally not achievable with monomer units containing functional groups. Nevertheless, the functional monomers can be introduced into polymer chains by the controlled copolymerization with excess styrene.[10,25]

In most cases, the nitroxide-mediated radical copolymerization of styrene and monomers having 1- or 1,1-substituted polymerizable double bond was studied. Recently, the copolymers with incorporated heterocyclic derivatives of maleic acid (maleic anhydride, *N*-substituted maleimides) were reported.[21,23,24,26] The present work is focused on the copolymerization of maleimide by using the nitroxide technique. Functional groups in maleimide molecule (i.e., NH and carbonyls) are favorable to supramolecular interactions based on triple hydrogen bonding.[27] This can be used in the formation of polymer blends,[28] liquid crystalline polymers,[29] and polymer networks.[30] Our aim was to prepare TEMPO-terminated copolymers of styrene with maleimide (C) and to synthesize related poly(styrene-*co*-maleimide)-*block*-polystyrene copolymers (BC) by the chain extension of C with styrene (Scheme 1). Investigation of the prepared maleimide copolymers as components of supramolecular aggregates is envisaged.

EXPERIMENTAL

Materials

Styrene (Kaučuk Group Co., Kralupy, Czech Republic) [boiling point (bp) 36°C/1.56 kPa] was distilled prior
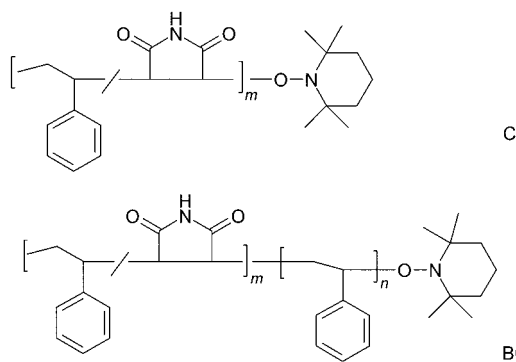
Scheme 1. TEMPO-terminated copolymers of styrene with maleimide (C) and poly(styrene-*co*-maleimide)-*block*-polystyrene copolymers (BC).

to use. Maleimide (Aldrich) [melting point (mp) 92–94°C] and TEMPO radical (Fluka; mp 36–39°C) were used as received. Bis(2-methoxyethyl) ether (diglyme; Fluka) and other solvents were of analytical grade.

Synthesis of TEMPO-terminated styrene–maleimide copolymers

A solution of styrene (S), maleimide (MI; 5×10^{-2} mol of comonomers), and TEMPO (1.5×10^{-4} mol) in diglyme (10 mL) was heated at 125°C in a sealed glass ampoule in nitrogen atmosphere. Mole fractions of MI, F_{MI}, varied in the range 0.1–0.7. After 2 h (at F_{MI} = 0.3 also after 1 or 1.5 h), the resulting TEMPO-terminated copolymer was precipitated from the reaction mixture with excess ethanol. It was dried under vacuum (6.6 Pa) at room temperature. The yields, compositions, molecular weights, molecular weight distributions (MWD) of the copolymers, and their

glass transition temperatures are given in Table I. At F_{MI} = 0.9, no copolymerization proceeded during 7-h heating of the reaction mixture at 125°C.

Chain extension of TEMPO-terminated styrene–maleimide copolymers with styrene

The TEMPO-terminated S-MI copolymer (0.2 g), styrene (5 mL), and diglyme (10 mL) in a glass ampoule were heated at 125°C in nitrogen atmosphere for 40 min (in the case of C4 also for 20 and 60 min). The reaction mixture was poured into a 10-fold amount of ethanol and the isolated diblock copolymer was dried under vacuum (6.6 Pa) at room temperature. Selective extraction of the copolymer (0.65 g) with cyclohexane (30 mL) for 48 h proved the absence of thermally generated polystyrene. Table II presents the yields and some characteristics of the obtained diblock copolymers.

Measurements

The yields of copolymers were determined gravimetrically; their compositions were determined from elemental analyses and ^{1}H-NMR measurements. The molecular weights and MWDs were evaluated by size-exclusion chromatography (SEC). Differential scanning calorimetry (DSC) was employed for the determination of glass transition temperatures.

Determination of molecular weights

The SEC measurements for evaluation of number- and weight-average molecular weights (M_n and M_w) were carried out on a Biosphere GM 1000 column (8 × 500 mm, Labio, Czech Republic) filled with 10-μm sorbent

TABLE I
Thermal Solution Copolymerization of Styrene (S) with Maleimide (MI) in the Presence of TEMPO

Copolymer	F_{MI}	Yield (%)	f_{MI}[a]	$M_n \times 10^{-4}$[b]	M_w/M_n	T_g[c] (°C)
C1	0.1	8.3	0.32, 0.26[d]	1.28	1.17	191
C2	0.2	15.4	0.37, 0.34[d]	1.52	1.27	217
C3	0.3	24.7	0.40, 0.39[d]	1.64	1.35	231
C31[e]	0.3	8.2	0.42	1.16	1.25	—
C32[f]	0.3	17.0	0.41	1.44	1.28	—
C4	0.4	31.2	0.43, 0.45[d]	1.72	1.41	231
C5	0.5	27.6	0.47	1.61	1.39	—
C7	0.7	8.1	0.53	1.18	1.36	—
C9[g]	0.9	0	—	—	—	—

F_{MI} and f_{MI} are mole fractions of MI in the feed and in the copolymer, respectively. The copolymerization was at 125°C for 2 h with 5×10^{-2} mol of comonomers and 1.5×10^{-4} mol of TEMPO in 10 mL of diglyme.
[a] From elemental analysis.
[b] Polystyrene-equivalent molecular weight determined by SEC.
[c] Glass transition temperature determined by DSC from the second scan.
[d] From ^{1}H-NMR.
[e] 1 h.
[f] 1.5 h.
[g] 7 h.

TABLE II
Polymerization of Styrene Initiated with TEMPO-Terminated Styrene–Maleimide Copolymers

Block copolymer	Precursor[a]	Yield (g)	Poly(S) blocks (wt %) [b]	[c]	$M_n \times 10^{-4}$[d]	M_w/M_n	T_{g1}[e] (°C)
BC1	C1	1.08	81.5	81.5	2.52	1.74	102
BC2	C2	1.05	81.0	81.9	2.94	1.72	102
BC3	C3	1.50	86.7	85.0	2.19	1.69	101
BC4	C4	1.23	83.7	86.3	2.73	1.78	103
BC41[f]	C4	0.78	76.9	78.8	2.56	1.76	—
BC42[g]	C4	1.51	86.8	89.3	2.90	1.76	—
BC7	C7	1.14	84.6	85.5	2.86	1.79	107

The polymerization was at 125°C for 40 min with 0.2 g of precursor and 5 mL of styrene in 10 mL of diglyme.
[a] See Table I.
[b] From gravimetry.
[c] From elemental analysis.
[d] Polystyrene-equivalent molecular weight determined by SEC.
[e] Glass transition temperature of polystyrene block.
[f] 20 min.
[g] 60 min.

particles. Distilled *N,N*-dimethylacetamide (Fluka) containing 0.5% of lithium bromide served as a mobile phase. The data from a refractive index detector were collected and treated by using CSW 1.7 software (Data Apex, Czech Republic). For the determination of molecular weights, a universal calibration equation calculated from the data on polystyrene standards (Merck, Germany) was used.

NMR measurements

^{1}H-NMR spectra (500.1 MHz) of 10% w/w copolymer solutions in deuterated dimethyl sulfoxide were measured at 300 K with a Bruker Avance 500 spectrometer and sodium 3-(trimethylsilyl)propane-1-sulfonate was used as an internal standard. Measurement conditions were as follows: 90° pulse width, 9.8 μs; acquisition time, 1.022 s; relaxation delay, 10 s; spectral width, 6 kHz, eight scans. The relative contents of MI and S units were found by comparing intensities of signals in the respective imide (NH) and phenyl groups.

DSC measurements

The DSC measurements were performed on a Perkin–Elmer Pyris 1 DSC apparatus. Samples (~ 10 mg) were examined on heating and cooling at a rate of ±10°C/min. The purge gas was helium. The glass transition temperatures were determined from the midpoints of the heat capacity change between the extrapolated glass and liquid lines in calorigrams corresponding to the second heating runs.

RESULTS AND DISCUSSION

TEMPO-terminated styrene–maleimide copolymers

According to the literature,[28,31] conventional solution radical copolymerization of S and MI initiated with 2,2′-azobis(isobutyronitrile) at 60°C proceeds with a strong tendency of the comonomers to the formation of alternating copolymers. The determined monomer reactivity ratios (r) corresponded to 0.1 for both styrene (r_S) and maleimide (r_{MI}) [i.e., the calculated azeotropic composition, $(F_{MI})_A = 1/[1 + (r_{MI} - 1)/(r_S - 1)]$, equaled 0.5]. The obtained S-MI copolymers showed rather broad MWDs ($M_w/M_n > 2$). Their polymer chains were irreversibly terminated, thus being excluded from chain extension reactions.

Table I presents the results of the S-MI copolymerization at 125°C in the presence of TEMPO without any added initiator. The thermal copolymerization is evidently induced by initiation centers originating from styrene (Scheme 2). As Mayo has found,[32] an unstable Diels–Alder adduct A is formed on heating of styrene. The adduct reacts with another S molecule giving radicals B* and S* derived from a tetrahydronaphthalene derivative and styrene, respectively. In the presence of TEMPO, the *in situ* generation of unimolecular *N*-alkoxyamine initiators S-TEMPO and B-TEMPO takes place.[12] They can participate in a quasiliving copolymerization process yielding copolymers with reversibly bonded TEMPO end groups. The found azeotropic composition, $(F_{MI})_A = 0.46$ (Fig. 1), is close to that determined for the conventional S-MI copolymerization (0.5). The obtained copolymers showed narrow MWDs ($M_w/M_n = 1.17$–1.41). In addition, molecular weights of copolymers C31, C32, and C3 increased with increasing conversion from 1.16 $\times$ 10^4 at 8.2% (C31) to 1.64 $\times$ 10^4 at 24.7% (C3).

A little higher M_w/M_n values (1.41 for C4 or 1.39 for C5) were observed when the conversion exceeded 25%; under these conditions, irreversible termination reactions occurred probably to a greater extent. At $F_{MI} = 0.7$, the yield (8.1%) and molecular weight (1.18
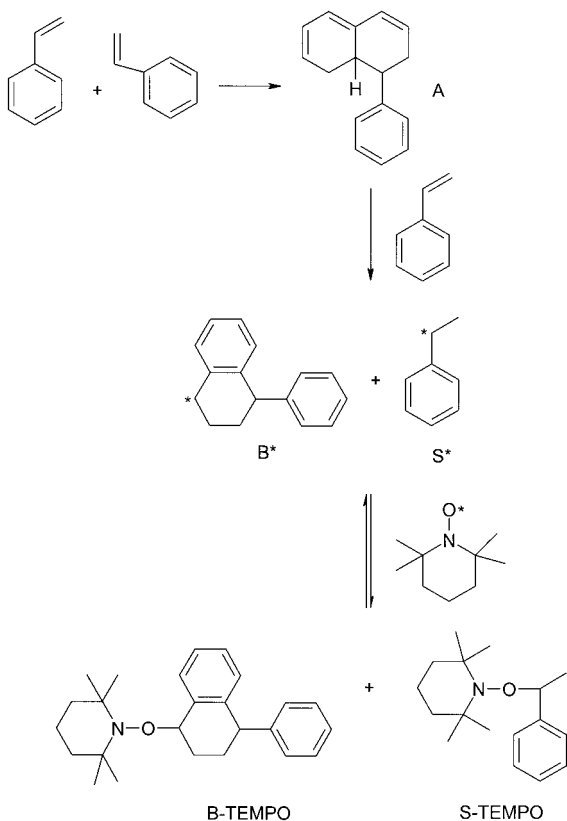
Scheme 2. *In situ* generation of unimolecular *N*-alkoxy-amine initiators S-TEMPO and B-TEMPO (ref. [12]).

$\times 10^4$) were lower than in the copolymerization of S and MI at F_{MI} ranging from 0.1 to 0.5. A mixture containing 90 mol % of MI even did not copolymerize.
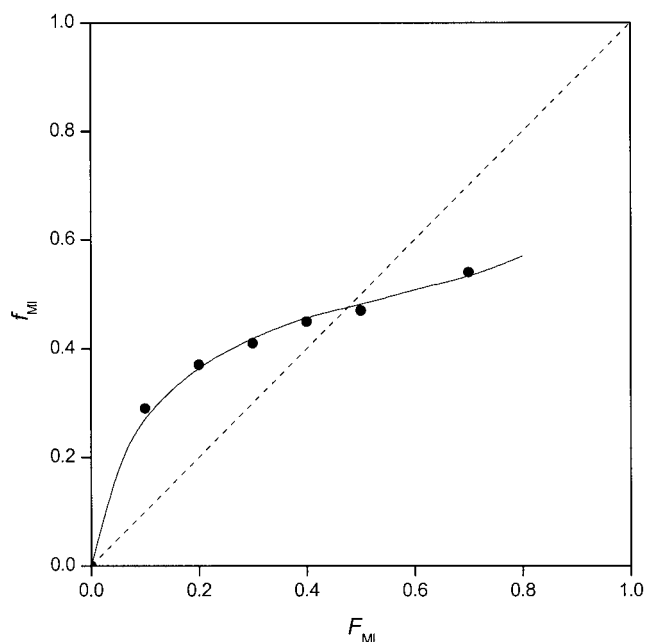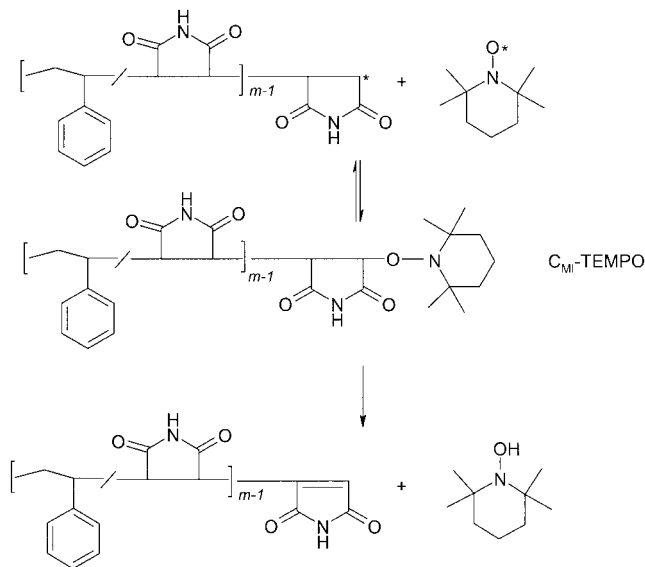

Figure 1 Dependence of the S-MI copolymer composition (f_{MI}) on the feed composition (F_{MI}).

Scheme 3. Deactivation of S-MI copolymer radicals or TEMPO-terminated S-MI copolymer chains.

This indicates that an increase in the MI content in the feed results in deactivation of some copolymer chains.[25] It can be expected that, in the course of the copolymerization, the ratio between the amounts of adducts C_{MI}-TEMPO originating from macroradicals with terminal MI units and of C_S-TEMPO from macroradicals with terminal S units increases. The C_{MI}-TEMPO is, in comparison with C_S-TEMPO, obviously unable to dissociate reversibly into the growing copolymer radical.

An irreversible disproportionation of TEMPO and macroradicals containing terminal MI units or thermal decomposition of the adduct C_{MI}-TEMPO might also take part in the deactivation process. As a result, an ω-unsaturated copolymer and a hydroxylamine derivative are formed (Scheme 3). Analogous reactions occurring in some TEMPO-mediated polymerizations were described recently.[17–19]

DSC measurements showed distinct glass transitions and rather high T_g values of the synthesized copolymers. The determined T_g's ranged from 197°C (C1) to 231°C (C3 or C4). The DSC curve of C2 in Figure 2 illustrates a typical thermal behavior of the S-MI copolymers. The high T_g values result from the rigidity of maleimide units and their ability to form hydrogen bonds.

Diblock copolymers comprising poly(styrene-*co*-maleimide) and polystyrene blocks

The prepared TEMPO-terminated S-MI copolymers C1, C2, C3, C4, and C7 were used as macroinitiators in polymerization of S at 125°C in a diglyme solution. The polymerization proceeded readily, giving poly-
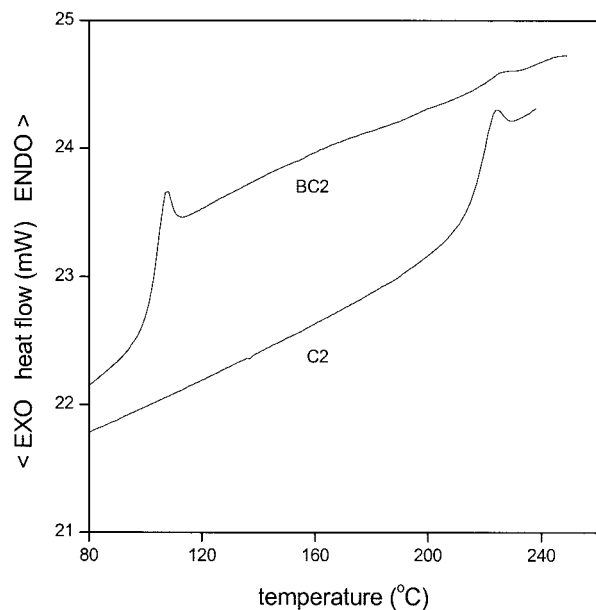
Figure 2 DSC curves (from the second scan) of the styrene–maleimide copolymer C2 and poly(styrene-*co*-maleimide)-*block*-polystyrene diblock copolymer BC2.

Figure 4 DSC curves (from the second scan) of the styrene–maleimide copolymer C2 and poly(styrene-*co*-maleimide)-*block*-polystyrene diblock copolymer BC2 (a detail).

Figure 3 SEC curves of the styrene–maleimide copolymer C2 and poly(styrene-*co*-maleimide)-*block*-polystyrene diblock copolymer BC2.

(styrene-*co*-maleimide)-*block*-polystyrene diblock copolymers. Their formation was confirmed by the yields, molecular weights (Table II), and unimodal SEC curves, indicating a complete consumption of the original TEMPO-terminated S-MI copolymer macroinitiator. As an example, Figure 3 depicts the SEC
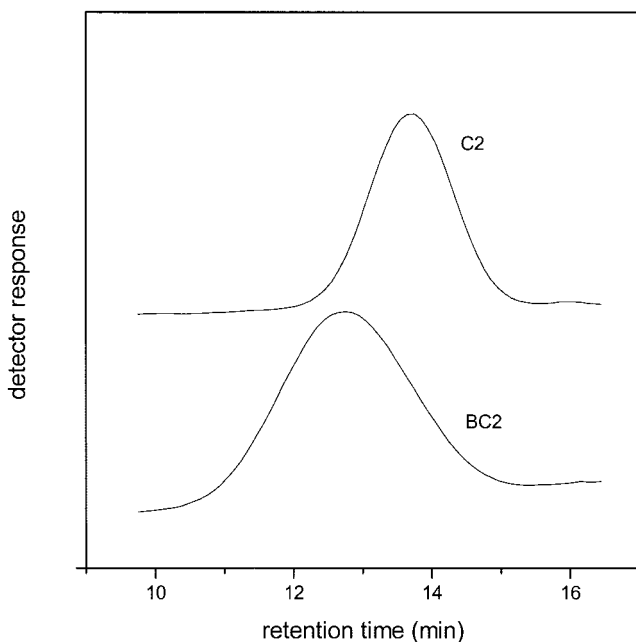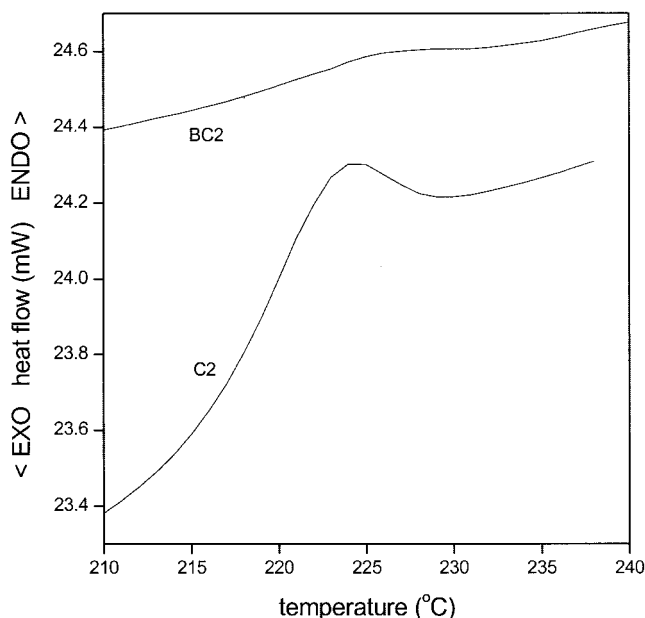
eluograms of diblock copolymer BC2 and corresponding macroinitiator C2.

The amounts of the formed polystyrene blocks were determined from the weight of the isolated product and from elemental analysis under the assumption that the macroinitiator was completely incorporated in chains of the resulting diblock copolymer. The values found by both methods were in a good agreement (Table II). A comparison of the content of poly(S) blocks in BC41, BC4, and BC42 reveals a favorable effect of comonomer units in macroinitiator C4 (or in other TEMPO-terminated S-MI copolymers) on the formation of diblock copolymers. The effect is apparent in initial fast addition of S units to the C4 copolymer radicals. After a 20-min polymerization, the amount of poly(S) blocks was 76.9–78.8 wt % (BC41). Further growth of the poly(S) blocks, however, proceeded more slowly. Their content reached 86.8–89.3 wt % in BC42 after the 60-min reaction. At the same time, polydispersity of the diblock copolymers derived from C4 practically did not change (M_w/M_n = 1.76–1.78).

Molecular weights of the obtained diblock copolymers were higher than those of the poly(S-*co*-MI) precursors and showed broader MWDs (M_w/M_n = 1.69–1.78). Evidently, in the course of the chain extension of the precursors with styrene, irreversible termination reactions with participation of thermally generated polystyrene radicals occurred.

DSC curves exhibited a very pronounced glass transition corresponding to the polystyrene block (T_{g1} = 101–107°C). However, the glass transition of the

poly(S-*co*-MI) block was hardly detectable. This is demonstrated in Figure 2 for diblock copolymer BC2. Therefore, a more detailed measurement was performed that made it possible to find the T_g of the second block in BC2 [viz. 217°C (Fig. 4)]. For comparison, Figure 4 also presents a part of the DSC curve of precursor C2. The described phenomenon might be associated with the nature of microphase separation in diblock copolymers under study. This is a subject for further investigation.

CONCLUSION

TEMPO-mediated thermal radical copolymerization of styrene and maleimide at 125°C in diglyme affords functional copolymers of narrow molecular weight distributions (M_w/M_n = 1.17–1.41). The copolymerization proceeds in a quasiliving azeotropic manner. The azeotropic composition, $(F_{MI})_A$ = 0.46, is close to that calculated from the published monomer reactivity ratios for the conventional radical S-MI copolymerization (0.5).

Chain extension of the synthesized TEMPO-terminated S-MI copolymers takes place by using them as macroinitiators in polymerization of styrene at 125°C in diglyme. In the chain extension, diblock copolymers comprising both macroinitiator and polystyrene blocks are formed.

References

1. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Macromolecules 1993, 26, 2987.
2. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Trends Polym Sci 1994, 2, 66.
3. Gaynor, S.; Greszta, D.; Mardare, D.; Teodorescu, M.; Matyjaszewski, K. J Macromol Sci, Pure Appl Chem 1994, 31, 1561.
4. Veregin, R. P. N.; Georges, M. K.; Hamer, G. K.; Kazmaier, P. M. Macromolecules 1995, 28, 4391.
5. Keoskerian, B.; Georges, M. K.; Boies-Boissier, D. Macromolecules 1995, 28, 6381.
6. Hawker, C. J.; Hedrick, J. L. Macromolecules 1995, 28, 2993.
7. Aoshima, K.; Ohumura, H.; Mouya, Y.; Suzuki, N.; Oshiba, Y. Polymer 1991, 32, 19.
8. Hawker, C. J.; Elce, E.; Dao, J.; Volksen, W.; Russell, T. P.; Barclay, G. G. Macromolecules 1996, 29, 2686.
9. Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Dewonport, W. Macromolecules 1996, 29, 5245.
10. Fukuda, T.; Terauchi, T.; Goto, A.; Tsujii, Y.; Miyamoto, T.; Shimizu, Y. Macromolecules 1996, 29, 3050.
11. Kazmaier, P. M.; Daimon, K.; Georges, M. K.; Hamer, G. K.; Veregin, R. P. N. Macromolecules 1997, 30, 2228.
12. Devonport, W.; Michalak, L.; Malmström, E.; Mate, M.; Kurdi, B.; Hawker, C. J.; Barclay, G. G.; Sinta, R. Macromolecules 1997, 30, 1929.
13. Ohno, K.; Tsujii, Y.; Miyamoto, T.; Fukuda, T.; Goto, M.; Kobayashi, K.; Akaike, T. Macromolecules 1998, 31, 1064.
14. Ohno, K.; Ejaz, M.; Fukuda, T.; Miyamoto, T.; Shimizu, Y. Macromol Chem Phys 1998, 199, 291.
15. Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. J Am Chem Soc 1999, 121, 3904.
16. Gabatson, L. I.; Furlong, S. A.; Jackson, R. A.; Armes, S. P. Polymer 1999, 40, 4505.
17. Goto, A.; Fukuda, T. Macromolecules 1999, 32, 618.
18. Burgiere, C.; Dourges, M.-A.; Charleux, B.; Vairon, J.-P. Macromolecules 1999, 32, 3883.
19. Fischer, A.; Brembilla, A.; Lochon, P. Macromolecules 1999, 32, 6069.
20. Chong, Y. K.; Ercole, F.; Moad, G.; Rizzardo, E.; Thang, S. H.; Anderson, A. G. Macromolecules 1999, 32, 6895.
21. Benoit, D.; Hawker, C. J.; Huang, E. E.; Lin, Z.; Russel, T. P. Macromolecules 2000, 33, 1505.
22. Lacroix-Desmazes, P.; Delair, T.; Pichot, C.; Boutevin, B. J. Polym Sci, Part A: Polym Chem 2000, 38, 3845.
23. Lokaj, J.; Vlček, P.; Kříž, J. J Appl Polym Sci 1998, 74, 2378.
24. Lokaj, J.; Holler, P.; Kříž, J. J Appl Polym Sci 2000, 76, 1093.
25. Zaremski, M. Yu.; Plutalova, A.; Lachinov, M. B.; Golubev, V. B. Macromolecules 2000, 33, 4365.
26. Harth, E.; Hawker, C. J.; Fan, W.; Waymonth, R. M Macromolecules 2001, 34, 3856.
27. Fouquey, C.; Lehn, J.-M.; Levelut, A.-M. Adv Mater 1990, 2, 254.
28. Lange, R. F. M.; Meijer, E. W. Macromolecules 1995, 28, 782.
29. Kato, T.; Kihara, H.; Uryu, T.; Fujishima, A.; Fréchet, J. M. J Macromolecules 1992, 25, 6836.
30. Hilger, C.; Dräger, M.; Stadler, R. Macromolecules 1992, 25, 2498.
31. van Paesschen, G.; Timmerman, D. Makromol Chem 1964, 78, 112.
32. Mayo, F. R. J Am Chem Soc 1968, 90, 1289.