Poly(styrene-*co*-*N*-butylmaleimide) Macroinitiators by Controlled Autopolymerization and Related Block Copolymers

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ABSTRACT: Autopolymerization of styrene-*N*-butylmaleimide mixtures at 125 or 140°C in the presence of a stable nitroxyl radical [2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO)] was found to proceed in a pseudoliving manner. Unimolecular initiators, which were originated by trapping self-generated radical species with TEMPO, took part in the process. Under the studied experimental conditions, the TEMPO-controlled autopolymerization with a varying comonomer ratio provided virtually alternating copolymers of narrow molecular weight distributions. The molecular weights of the copolymers increased with conversions. The obtained styrene-*N*-butylmaleimide copolymers containing TEMPO end groups were used to initiate the polymerization of styrene. The polymerization yielded poly(styrene-*co*-*N*-butylmaleimide)-polystyrene block copolymers with various polystyrene chain lengths and narrow molecular weight distributions. The compositions, molecular weights, and molecular weight distributions of the synthesized block copolymers and the initial poly(styrene-*co*-*N*-butylmaleimide) precursors were evaluated using nitrogen analysis, gel permeation chromatography, and ^{1}H- and ^{13}C-NMR spectroscopy. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2378–2385, 1999

Key words: controlled autopolymerization; stable nitroxyl radical; styrene-*N*-butylmaleimide copolymer; block copolymer

INTRODUCTION

In recent years initiating systems such as iniferters,[1–12] stable free radicals in the presence or absence of peroxides at elevated temperatures,[13–20] or organometallic complexes in association with stable radicals or peroxides[17,21] have become increasingly important in free-radical polymerization. Using these systems, reversibly terminated polymer chains are formed that impart a pseudoliving character to the radical polymerization process. Great attention has been paid to stable free-radical polymerization that offers the possibility of making polymer materials with a narrow molecular weight distribution (MWD), well-defined chain lengths, and complex architecture.[13–30] Stable radicals, such as 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO), mediate the reactivity of growing polymer chains by trapping the reactions under a formation of unstable alkoxyamine chain ends. After thermal dissociation, the radical chain ends regenerate; then they can repeatedly add monomer and be terminated with the released nitroxide until the monomer is consumed. The alkoxyamine-terminated poly-

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Table I Autopolymerization of Styrene (S)-*N*-Butylmaleimide (BuMI) Mixtures in Presence of TEMPO

Copolymer	F_{BuMI}	f_{BuMI}[a]	Conversion (%)	$M_n \times 10^{-4}$	M_w/M_n
P1	0.1	0.35	9.7	0.83	1.25
P2	0.2	0.40	38.8	1.93	1.29
P3	0.3	0.43; 0.43[b]	43.2	2.38	1.30
P4	0.4	0.47	12.3	1.13	1.27
P5	0.5	0.49	10.3	0.93	1.34
P5[c]	0.5	0.49	39.6	1.71	1.46
P6	0.6	0.50	6.6	0.76	1.28
P7	0.7	0.54	1.2	0.59	1.21

F_{BuMI} and f_{BuMI} are the molar fractions of BuMI in the feed and in the copolymer, respectively. The autopolymerization was at 125°C for 1 h with 5×10^{-2} mol total comonomers and 1.5×10^{-4} mol TEMPO.
[a] From nitrogen analysis.
[b] From NMR.
[c] 2.5 h.

mers are potential precursors for the chain-extension reactions and syntheses of block copolymers.

Two-component initiating systems, which usually consist of a thermal initiator of dibenzoyl peroxide and a stable nitroxyl radical[15] or unimolecular systems incorporating nitroxide and initiating groups in 1 : 1 stoichiometry,[22,23] are usually used for controlled stable free-radical polymerization. Nitroxide-mediated pseudoliving radical polymerization in the absence of added initiating systems also seems to be a promising method. Thus, for example, the self-generated (by autopolymerization) radicals of styrene (S), S derivatives, or S/(meth)acrylate comonomers react with nitroxide giving *in situ* unimolecular initiators, which take part in the controlled polymerization process.[26]

The aim of this study was to prepare copolymers of S with *N*-butylmaleimide (BuMI) by autopolymerization in the presence of TEMPO and to employ them as macroinitiators for the synthesis of poly(S-*co*-BuMI)-polystyrene block copolymers. Their compositions, molecular weights, and MWDs were evaluated for the characterization of the obtained products.

EXPERIMENTAL

Materials

The S (Fluka, bp 36°C/1.56 kPa) and BuMI (Fluka, bp 103°C/2.66 kPa) were distilled prior to use. TEMPO radical (mp 36–39°C) was a commercial product of Fluka.

Synthesis of Poly(S-*co*-BuMI) Macroinitiators

TEMPO-terminated poly(S-*co*-BuMI) macroinitiators were prepared by autopolymerization of S with BuMI in sealed glass ampoules in a nitrogen atmosphere at 125°C. The total amount of comonomers was 5×10^{-2} mol, the molar fraction of BuMI (F_{BuMI}) varied in the range of 0.1–0.7, and the amount of TEMPO was 1.5×10^{-4} mol. After 1 h or at $F_{BuMI} = 0.5$ after 1 and 2.5 h the resulting copolymers were precipitated from the reaction mixtures with methanol. In addition, in the case of $F_{BuMI} = 0.4$, the reaction times were also 40, 50, 70, and 80 min; using 1.5×10^{-4} and 3×10^{-4} mol of TEMPO, 1-h autopolymerizations were conducted at 140°C. The obtained copolymers were reprecipitated with methanol from chloroform solutions and dried in a vacuum at room temperature. The conversions, compositions, molecular weights, and MWDs of the copolymers are given in Tables I and II.

Synthesis of Poly(S-*co*-BuMI)-Polystyrene Block Copolymers

A solution of the TEMPO-terminated S-BuMI copolymer (0.2 or 0.3 g) in S (5 mL) was heated in a glass ampoule in an inert atmosphere at 125°C for 15, 30, 45, or 60 min. Then the ampoule was opened and the reaction mixture was poured into a 10-fold amount of ethanol. The isolated polymer products were reprecipitated with ethanol from chloroform solutions. The yields and characteristics of the block copolymers are summarized in Table III.

Table II Autopolymerization of Styrene (S)-*N*-Butylmaleimide (BuMI) Mixtures at F_{BuMI} = 0.4 in Presence of TEMPO

Copolymer	Reaction Time (min)	Conversion (%)	$M_n \times 10^{-4}$	M_w/M_n
P8	40	3.6	1.06	1.33
P9	50	8.6	0.82	1.35
P10	70	33.9	1.68	1.28
P11	80	39.1	2.03	1.32
P12[b]	60	55.1	2.02	1.63
P13[c]	60	47.8	1.06	1.70

F_{BuMI} is the molar fraction of BuMI in the feed. The autopolymerization was at 5×10^{-2} mol total comonomers and 1.5×10^{-4} mol TEMPO at 125°C.
[a] At 140°C.
[b] 140°C and 3.0×10^{-4} mol TEMPO.

Measurements

The yields of polymer products were determined gravimetrically. The compositions of poly(S-*co*-BuMI) macroinitiators were found from nitrogen analysis or ^{1}H- and ^{13}C-NMR measurements, whereas the composition of poly(S-*co*-BuMI)-polystyrene block copolymers was evaluated using ^{1}H- and ^{13}C-NMR spectroscopy. Gel permeation chromatography (GPC) was used to determine molecular weights of the copolymers.

Determination of Molecular Weights

The number- and weight-average molecular weights (M_n and M_w) of synthesized copolymers were evaluated by GPC with tetrahydrofuran (THF) as the eluent and toluene as the internal standard. The measurements were carried out on an apparatus (Labora, Czech Republic) equipped with refractometric and UV detectors. The separation system consisted of two 300 × 8 mm columns (PSS, Germany) filled with Styragel (porosities of 10^5 and 10^3 Å, respectively), and it was calibrated with poly(methyl methacrylate) standards. Eluograms were treated using the Mark–Houwink–Sakurada equation constants obtained for polystyrene/THF. The MWD curves were calculated from the corresponding refractometric responses.

NMR Measurements

^{1}H- and ^{13}C-NMR spectra of 10% (w/w) solutions of the copolymers in $CDCl_3$ were measured at 300.13 and 75.7 MHz, respectively, with a Bruker Avance DPX 300 spectrometer at 330 K. Hexamethyldisiloxane was used as the internal standard. In signal assignment, long-range 2-dimensional (2-D) and selective 1-D polarization transfer and J-modulated spin-echo techniques were

Table III Polymerization of Styrene Initiated by TEMPO-Terminated Styrene (S)-*N*-Butylmaleimide (BuMI) Copolymer P3

Polymer	Time (min)	Yield (g)	$M_n \times 10^{-4}$	M_w/M_n	S*/BuMI	f_{S*}	f_S	f_{BuMI}
B1	15	0.32	5.59	1.35	3.9	0.63	0.21	0.16
B2	30	0.45	6.37	1.35	5.6	0.71	0.17	0.12
B3	45	0.63	7.83	1.37	9.9	0.81	0.11	0.08
B4	60	0.76	8.51	1.37	11.7	0.83	0.10	0.07
B5[a]	60	0.78	5.38	1.27	5.8	0.72	0.16	0.12

S*/BuMI is the molar ratio and f_{S*}, f_S, and f_{BuMI} are the respective molar fractions of comonomers incorporated in B1–B5 (S* denoting a monomer unit in the polystyrene block) as determined by ^{1}H- and ^{13}C-NMR. There were 0.2 g of P3 and 5 mL of styrene at 125°C.
See Table I for the P3 data.
[a] Using 0.3 g of P2 (see Table I).

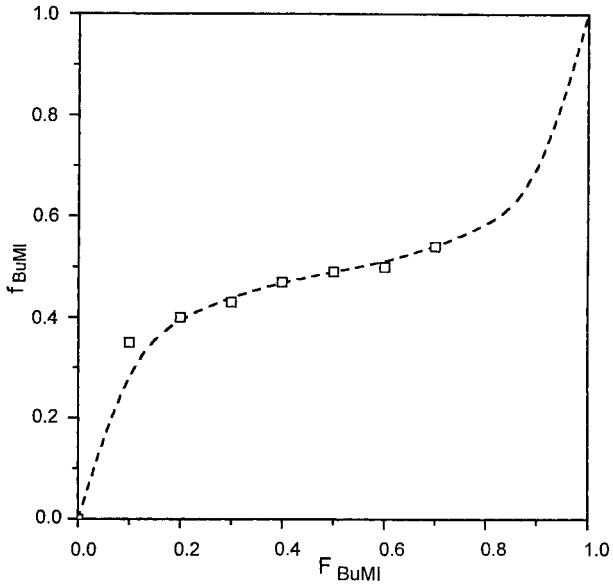


Figure 1 The dependence of the composition of the P1–P7 copolymers (f_{BuMI}, Table I) on the feed composition (F_{BuMI}) in the styrene (S)-*N*-butylmaleimide (BuMI) autopolymerization in the presence of stable nitroxyl radicals (TEMPO). F_{BuMI} and f_{BuMI} are the molar fractions of BuMI in the feed and in the copolymer, respectively.

used. In quantitative ^{13}C measurements, 1000 scans with 32 kilopoints were collected with inverse-gate decoupling and a repetition time of 10 s. Exponential weighting before the Fourier transform to 16 kilopoints (quadrature detection) with a line broadening of 1 Hz was used.

RESULTS AND DISCUSSION

TEMPO-Controlled Autopolymerization of S with BuMI

The S and BuMI are comonomers with a strong tendency toward radical alternating copolymerization. Using 2,2′-azobis(isobutyronitrile) (AIBN)[31] or the iniferter tetraethylthiuram disulfide (TDS)[12] to initiate the S-BuMI copolymerization, the monomer reactivity ratios (r) were found to be 0.025 ± 0.025 for S (r_S) and 0.06 ± 0.02 for BuMI (r_{BuMI}). As can be seen in Table I, the copolymerization without any added initiator (autopolymerization) in the presence of TEMPO is also of alternating nature. Almost all the experimentally determined molar fractions of BuMI in the copolymers fit in a curve in Figure 1; the curve illustrates the dependence of the copolymer composition (f_{BuMI}) on the feed composition (F_{BuMI}) and was calculated using monomer reactivity ratios of $r_S = 0.13$ and $r_{BuMI} = 0.10$. The latter values are a little higher than those found in the copolymerization initiated with AIBN or TDS, indicating some role of nitroxyl radicals in the transition state of the propagation step.

In the copolymerizations with a varying comonomer ratio in the feed (Table I, copolymers P1–P7), the highest conversions were reached at $F_{BuMI} = 0.2$ (38.8%, copolymer P2) and $F_{BuMI} = 0.3$ (43.2%, copolymer P3) at 125°C after 1 h. Then, as the content of BuMI in the initial mixture increased, the yields decreased, the conversion at $F_{BuMI} = 0.7$ being only about 1% (copolymer P7). The addition of nitroxyl radicals to BuMI probably provides rather inactive products under given conditions. The molecular weights followed conversions proportionally: at a higher conversion, a higher molecular weight was found. The conversion and molecular weight both depended on the reaction time. At a molar fraction in the feed of $F_{BuMI} = 0.5$, the found conversions and M_n values were, respectively, 10.3% and 0.93×10^4 after 1 h and 39.6% and 1.71×10^4 after 2.5 h. The composition of P5 copolymers did not change, because f_{BuMI} was close to F_{BuMI}.

An increase in the molecular weight along with the increasing conversion indicates the pseudoliving character of the polymerization process with participation of TEMPO radicals, which are reversibly bound to the polymer chains. The moderating role of TEMPO is evident from the narrow MWDs that were in the range of 1.21–1.34 in the 1-h autopolymerizations. A longer reaction time (2.5 h) brought about a slightly broader distribution (1.46). In this case, the irreversible termination of polymer chains obviously occurs to some extent. Figure 2 illustrates the MWD curves of copolymer P5 obtained in a 1-h and 2.5-h autopolymerization.

Table II summarizes the results of the autopolymerization of S-BuMI mixtures at $F_{BuMI} = 0.4$ in the presence of TEMPO (1.5×10^{-4} mol). Within the reaction times of 40–80 min at 125°C, the respective conversions and molecular weights increased from 3.6% and 1.06×10^4 up to 39.1% and 2.03×10^4. At the same time, the MWDs of the P8–P11 copolymers were about 1.3 (i.e., similar to those of the P1–P7 copolymers). As expected, a higher temperature (140°C) resulted in a higher conversion and molecular weight, as well as a broader MWD due to additional spontaneous thermal initiation (copolymer P12). Although the

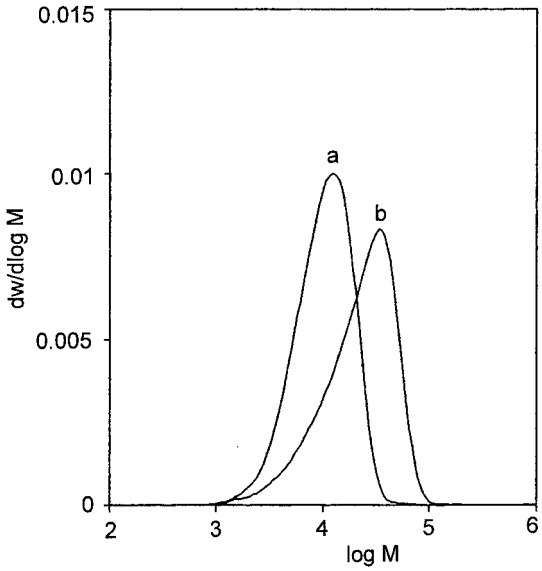


Figure 2 MWD curves of copolymer P5 (Table I) obtained in (a) 1-h and (b) 2.5-h autopolymerizations.

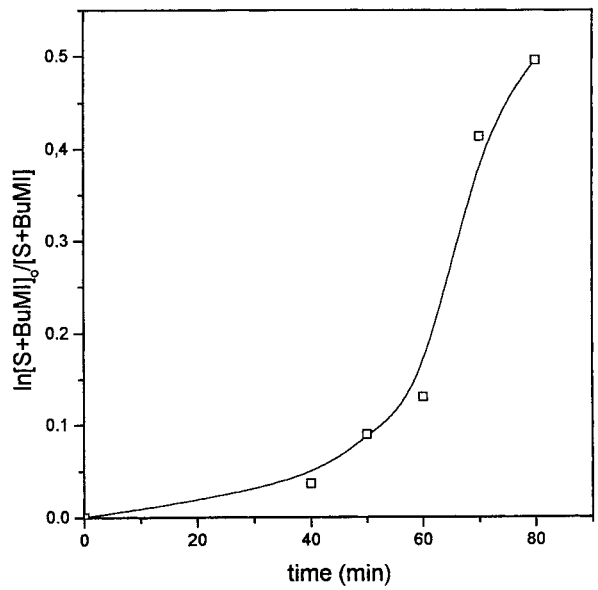


Figure 3 The semilogarithmic time-conversion dependence for the styrene (S)-*N*-butylmaleimide (BuMI) autopolymerization in the presence of stable nitroxyl radicals (TEMPO) at $F_{\mathrm{BuMI}} = 0.4$ (Tables I, II). F_{BuMI} is the molar fraction of BuMI in the feed and $[\mathrm{S} + \mathrm{BuMI}]_o$ and [S + BuMI] are the molar concentrations of the total comonomers at the beginning and at a given time of the autopolymerization, respectively.

addition of TEMPO caused a decrease in the conversion and molecular weight, the MWD was not narrower using 3×10^{-4} mol TEMPO(copolymer P13).

The semilogarithmic time-conversion plot for the copolymerization that yielded the P8, P9, P4, P10, and P11 copolymers (Tables I, II, Fig. 3) reveals some details of the process. The initial increase indicates that, similar to the case of S alone,[26] in the S-BuMI mixtures radical species are formed by thermal spontaneous initiation, which are captured by TEMPO to give *in situ* unimolecular initiators. The rates of initiation and propagation increase along with the increasing number of active (or potentially active) centers. The following linear course demonstrates the "livingness" of the process in accord with eqs. (1) and (2):

$$-\mathrm{d}[\mathrm{S} + \mathrm{BuMI}]/\mathrm{d}t = K_{\mathrm{app}}[\mathrm{S} + \mathrm{BuMI}] \quad (1)$$

$$K_{\mathrm{app}} = k_p[\mathrm{C}^*] \quad (2)$$

where [S + BuMI] and [C*] are the total molar concentrations of comonomers and active (or potentially active) centers, respectively, at time t, and k_p is the rate constant of propagation. Considering the observed linear dependence, the concentration of centers stemming from the unimolecular initiators is obviously approximately constant and predominant at this stage. After about 70 min of the copolymerization, a slight deviation from the linear course appears. However, the virtually unchanged narrow MWDs confirm that,

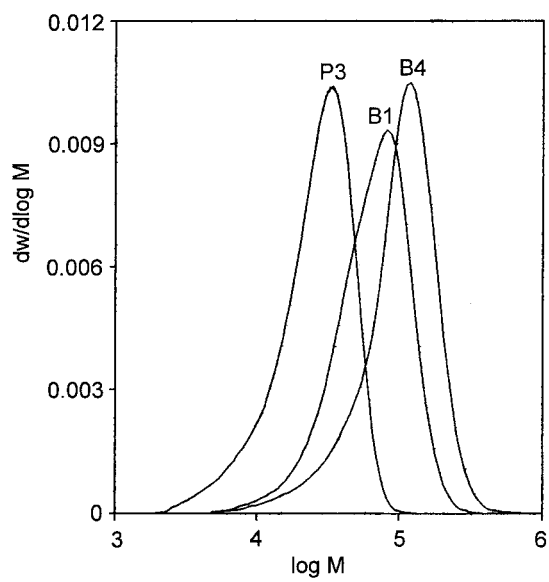


Figure 4 MWD curves of precursor P3 (Table I) and block copolymers B1 and B4 (Table III).

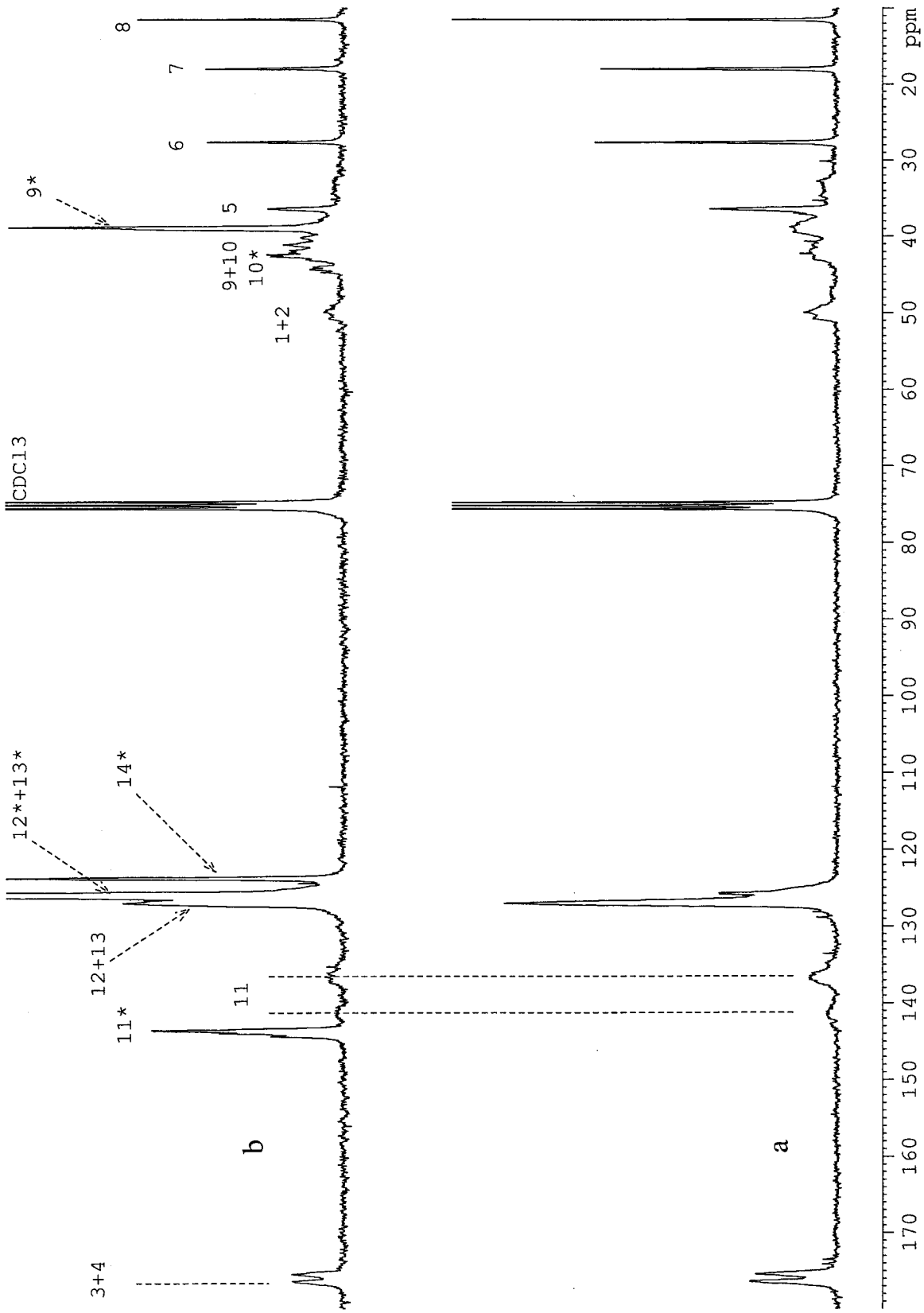
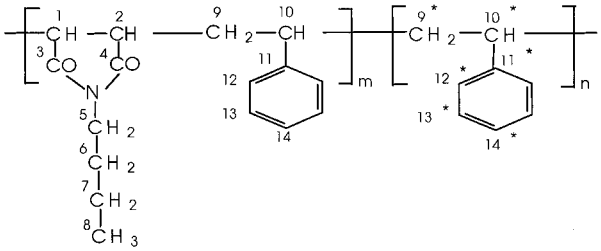


Figure 5 ^{13}C-NMR spectra of (a) precursor P3 (Table I) and (b) block copolymer B1 (Table III).

under given conditions, the TEMPO-controlled autopolymerization proceeds.

In comparison to the S-BuMI copolymerization initiated by the iniferter TDS,[12] the autopolymerization of the two comonomers in the presence of TEMPO affords more uniform polymer products. In contrast to thiyl fragments, TEMPO radicals do not initiate new chains and, consequently, TEMPO-terminated copolymers show a narrower MWD.



Scheme 1

Poly(S-*co*-BuMI)-Polystyrene Block Copolymers

The TEMPO-terminated S-BuMI copolymer P3 containing 43 mol % BuMI units (Table I) was used as the macroinitiator to initiate the polymerization of S at 125°C. The results on the polymerization are given in Table III. In 15 min, the GPC eluogram already indicated the absence of the free macroinitiator in the resulting product B1. No significant shoulder was detected at the elution position of P3 (Fig. 4). The molecular weight of B1 was more than double that of P3. With increasing reaction time, the yields and molecular weights of products B1–B4 increased; at the same time, the MWDs were fairly narrow and did not change significantly. These results demonstrate that the polymerization of S initiated by P3 can be regarded as a TEMPO-moderated process yielding block copolymers with polystyrene blocks and blocks of the S-BuMI copolymer. In addition to copolymer B4, copolymer B5 was also prepared in the 60-min polymerization using a higher amount of macroinitiator P2, which had approximately the same composition as P3. Compared to B4, the obtained copolymer B5 showed a lower molecular weight, which was evidently due to the fact that initiation and termination reactions occurred to a larger extent; the M_w/M_n ratio dropped to 1.27.

The evidence of both the polystyrene and initial macroinitiator blocks in products B1–B5 was corroborated by ^{13}C-NMR spectroscopy. Figure 5 presents the ^{13}C-NMR spectra of the approximately alternating copolymer precursor P3 and the corresponding block copolymer B1 with signal assignment according to Scheme 1.

As is clearly seen in Figure 5, the ^{13}C-NMR spectra of the approximately alternating S-BuMI copolymer and the polystyrene block significantly differ in their aromatic part. In the former copolymer the signals of quaternary carbons 11 are broadened and upfield shifted due to both long-range shielding and electron density perturbation by the proximate butylimide group. The observed splitting of signal 11 is probably due to a coexistence of two relatively stable chain conformations. The effect of the neighboring butylimide group on the magnetic shielding of the remaining phenyl carbons (12–14) is less pronounced but still detectable. In contrast, aromatic signals 12*–14* and in particular 11* are quite analogous to those of S homopolymer and can thus be assigned to a polystyrene block. Owing to their relative shifts, the intensities of signals 3 + 4, 11, and 11* can be used for the determination of S/BuMI and S*/BuMI molar ratios (S* denoting the monomer unit in a polystyrene block).

The found S*/BuMI molar ratios in B1–B4 distinctly increased with reaction time; molar fractions of S in the polystyrene blocks, (f_{S*}), increased in the range of 0.63–0.83 within 15–60 min. The remarkably high initial addition of S to the macroinitiator chains suggests that the alternating nature of the precursor is favorable to the polymerization process. The S/BuMI molar ratios in the incorporated precursor are similar (about 1.37) and complementarily confirm the block character of B1–B5.

CONCLUSIONS

Thermal radical copolymerization of S with BuMI at 125 or 140°C (autopolymerization) in the presence of stable nitroxyl radicals (TEMPO) yielded virtually alternating copolymers as found from nitrogen elemental analysis or ^{1}H- and ^{13}C-NMR measurements. At the initial stage, the spontaneously generated radicals in the S-BuMI mixtures were captured by TEMPO to give *in situ* unimolecular initiators. The copolymers showed fairly narrow MWDs due to the moderating role of TEMPO. The molecular weights of the copolymers increased with increasing conversions, thus indicating the pseudoliving character of the process.

The prepared TEMPO-terminated S-BuMI copolymers readily initiated the polymerization of S under the formation of poly(S-*co*-BuMI)-polystyrene block copolymers with a narrow MWD. The presence and compositions of the polymer blocks were determined using ^{1}H- and ^{13}C-NMR spectroscopy.

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