Synthesis and Characterization of Styrene–*N*-Butyl Maleimide Copolymers Using Iniferters Containing Thiyl End Groups

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ABSTRACT: The radical homopolymerization of styrene or copolymerization of styrene (S) with *N*-butyl maleimide (I) initiated by tetraethylthiuram disulfide was used to prepare macroinitiators having thiyl end groups. The S–I copolymers from the feeds containing 30–70 mol % I showed approximately alternating composition. The rate of copolymerization and molecular weights decreased with increasing maleimide derivative concentration in the feed; homopolymerization of I alone did not proceed. The macroinitiators served for synthesis of further S–I copolymers. Using polystyrene macroinitiator and the S–I copolymer with thiyl end groups in the polymerization of S–I mixture and styrene, respectively, the copolymers containing blocks of both polystyrene and alternating S–I copolymer were obtained. The copolymerization of S–I mixture initiated with the S–I copolymer bearing thiyl end groups led to the extension of macroinitiator chains by the blocks of alternating copolymer. The presence of the blocks in the polymer products was corroborated using elemental analysis, size exclusion chromatography, and differential scanning calorimetry. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 755–762, 1998

Key words: iniferter; thiyl groups; styrene–*N*-butyl maleimide copolymer; block copolymer

INTRODUCTION

Styrene and *N*-butyl maleimide represent a monomer pair with a strong tendency towards radical alternating copolymerization. The copolymerization of these monomers initiated by 2,2′-azobis-(isobutyronitrile) proceeds much faster than their homopolymerization, and the determined monomer reactivity ratios are close to zero ($r_S = 0.025 \pm 0.025$, $r_I = 0.06 \pm 0.02$).[1]

This study concerns the radical synthesis of styrene − *N*-butyl maleimide copolymers using compounds of an iniferter type. Iniferters rank among initiators, which are efficient transfer agents and are characterized by facile and reversible primary radical chain termination.[2] In radical polymerization initiated by the low-molecular-weight iniferters, monofunctional or α,ω-bifunctional polymers are formed. These can be used as macroinitiators to extend polymer chains or synthesize block copolymers. The homolytic thermal dissociation or photolysis of reversibly terminated polymers (macroinitiators) affords, in addition to the iniferter fragments, the polymer radicals, which can enter into a propagation reaction with the monomer present in a reaction mixture.

Functional end groups reversibly bound to polymer chains also include N,N-diethylthiocarbamoylthio, i.e., thiyl groups.[2-9]

The present work summarizes the findings on copolymerization reactions of the monomer pair styrene–N-butyl maleimide initiated by tetraethylthiuram disulfide or by polymers (polystyrene, styrene–N-butyl maleimide copolymer) containing thiyl end groups. The molecular weights and chemical composition of the copolymers obtained were determined, and their thermal properties were also investigated.

EXPERIMENTAL

Materials

Styrene (S) (Fluka) (bp 36°C/1.56 kPa) and 2,2'-azobis(isobutyronitrile) (AIBN) (Fluka) (mp 105°C) were purified by the procedure described in an earlier work.[10] N-Butyl maleimide (I) (bp 103°C/2.66 kPa) was a commercial product of Fluka. Tetraethylthiuram disulfide (TDS) (mp 71°C) was prepared by oxidation of diethylammonium salt of N,N-diethyldithiocarbamate.[11]

Polymerizations were carried out in sealed glass ampoules in an inert atmosphere at 60°C. The polymers were precipitated from reaction mixtures with methanol. After reprecipitation from benzene solutions with methanol, the polymers were dried in vacuum at room temperature.

Measurements

Determination of Molecular Weights

The molecular weights of polymers and their distribution were determined using the size exclusion chromatography (SEC) method. The measurements were carried out on a PSS SDV 10000 column (8×600 mm, Polymer Standard Service, Germany), filled with 5 μm sorbent particles. Tetrahydrofuran (Fluka), distilled and dried over molecular sieves (4 Å), was used as a mobile phase. The chromatographic data from refractometric and UV (254 nm) detectors in a series connection were evaluated using the integrative DataMonitor system (Waltrex, Czech Republic). For the determination of molecular weights, a general calibration equation calculated from the data on polystyrene standards (Merck, Germany) was used.
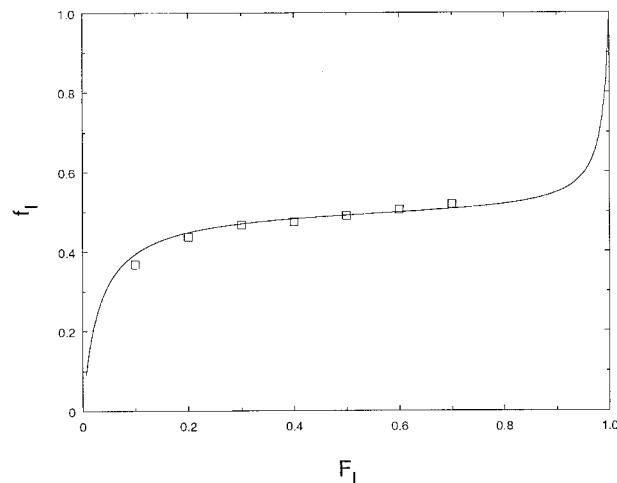

Figure 1 The dependence of composition of C1–C7 copolymers (f_I) (Table I) on the feed composition (F_I) in the styrene (S)–N-butyl maleimide (I) copolymerization initiated by tetraethylthiuram disulfide, where F_I and f_I are molar fractions of I in the feed and in the copolymer, respectively.

Thermal Analysis

The glass transition temperatures (T_g) and positions of relaxation maximum (T_r) were determined using a Perkin–Elmer DSC-2 calorimeter. The temperature and output scales were calibrated with indium and sapphire as standards. The measurements were carried out in two scans in the temperature interval 230–450 K. A heating or cooling rate was 10 K/min. The sample weights were about 5 mg. In the first scan, the initial sample was heated to 450 K, then was cooled to the initial temperature 230 K and heated again to 450 K. The glass transition temperature T_g was determined as an intercept of the average temperature dependence of polymer in the glass state (c_p^g) and in melt (c_p^i) with the experimental dependence $c_p = (c_p^g + c_p^i)/2$. The relaxation endotherm was characterized by the temperature of maximum T_r.

RESULTS AND DISCUSSION

Copolymerization of Styrene with N-Butyl Maleimide Initiated by Tetraethylthiuram Disulfide

The course of copolymerization is given in Table I and Figure 1. The total amounts of comonomers in initial reaction mixtures were 4×10^{-2} mol; that of tetraethylthiuram disulfide was 2.7×10^{-2}

Table I   Copolymerization of Styrene (S) with *N*-Butyl Maleimide (I) Initiated by Tetraethylthiuram Disulfide[a]

Copolymer	F_I	f_I	Conversion (%)	M_n	M_w	Polydispersity
C1	0.1	0.368	13.3	19200	29700	1.544
C2	0.2	0.437	17.1	17200	26400	1.531
C3	0.3	0.467	13.8	15100	22700	1.505
C4	0.4	0.475	14.3	14200	21300	1.495
C5	0.5	0.490	9.1	12200	17400	1.428
C6	0.6	0.506	6.2	12100	15900	1.311
C7	0.7	0.519	3.1	10100	12800	1.267
—	0.8		traces of polymer	—	—	—
—	0.9		0	—	—	—

F_I and f_I are molar fractions of *N*-butyl maleimide in the feed and in the copolymer, respectively. M_n and M_w are number-average and weight-average molecular weights, respectively.
[a] 4×10^{-2} mol of total comonomers, 2.7×10^{-4} mol TDS, 60°C, 5 h.

mol; and the concentration of *N*-butyl maleimide in the feed, which was expressed by its molar fraction (F_I), varied in the range of 0.1–0.9; reaction time was 5 h; temperature was 60°C.

The found molar fractions of *N*-butyl maleimide in the copolymers (f_I) show that, similar to the initiation by AIBN, the S–I copolymerization initiated by tetraethylthiuram disulfide (TDS) is of alternating nature.[1] Figure 1 illustrates the curve of the dependence of copolymer composition f_I on the feed composition F_I, which was calculated using the published monomer reactivity ratios[1] $r_I = 0.025$ and $r_S = 0.06$. The experimentally determined f_I values are in a good accordance with this dependence. Formation of copolymers having approximately alternating compositions is also confirmed by their similar glass transition temperatures from the second scan (Table II).

The rate of copolymerization significantly depended on the comonomer ratio in the feed. At a molar fraction of $F_I = 0.5$, the rate of copolymerization markedly dropped; at $F_I = 0.8$, only traces of polymer appeared, and no polymer was formed at $F_I = 0.9$ after 5 h. An increase in the content of *N*-butyl maleimide in the initial reaction mixture also caused a decrease in the number- and weight-average molecular weights of the copolymers and in their polydispersity (Table I). Not even heating *N*-butyl maleimide alone (5 mL) with TDS (2 $\times 10^{-2}$ mol L) or with equimolar amounts of TDS and AIBN (2×10^{-2} mol L) in an inert atmosphere at 60°C for 21 h led to the formation of the polymer. Whereas TDS initiates the homopolymerization of styrene under formation of polystyrene containing short chains, with thiyl groups reversibly terminated chains,[2] homopolymeriza-

Table II   The Glass Transition Temperature (T_g, T_{g0}) and Temperatures of Relaxation Maxima (T_r) for C1–C7 Copolymers[a]

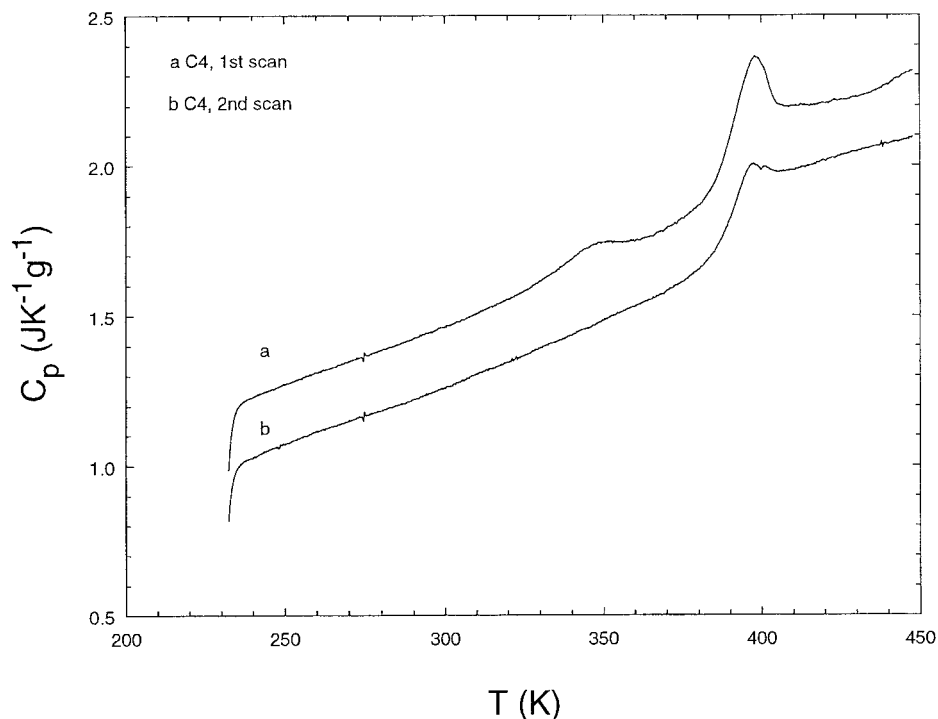| Copolymer	First Scan (K)			Second Scan [T_g (K)]
	T_g	T_{g0}	T_r	
C1	383.7	341.9	395.6	390.7
C2	386.2	340.6	398.9	391.7
C3	390.1	340.9	401.6	395.1
C4	386.4	338.5	397.9	392.7
C5	399.1	339.9	407.0	396.4
C6	396.1	341.9	404.0	395.8
C7	395.4	341.9	403.3	394.1

[a] Compare with Table I.

Figure 2 The temperature dependence of thermal capacity (c_p) for C4 copolymer.

tion of *N*-butyl maleimide in the presence of TDS does not proceed. The inability of TDS to initiate homopolymerization was also observed in the case of acrylonitrile (AN).[12] Both the monomers, *N*-butyl maleimide and acrylonitrile, are strongly polar compounds with a low electron density on their polymerizable double bond ($e_I = 3.70$, $e_{AN} = 1.20$).[13] Addition of thiyl radicals to these monomers probably affords products that act as termination agents and inhibit the polymerization process.

The thermograms of the prepared copolymers C1–C7 from the first scan showed a pronounced relaxation maximum T_r at about 400 K, associated with the glass transition temperature T_g (Table II). In addition, at about 340 K, a glass transition T_{g0} was observed (Figure 2), which is probably associated with the presence of short polymer chains. In the second scan, this transition did not appear.

Copolymerization of Styrene with *N*-Butyl Maleimide Initiated by Polystyrene Containing Thiyl End Groups

Polystyrene macroinitiator (PS) containing thiyl end groups was prepared according to the proce-

dure described earlier.[2] Its number- and weight-average molecular weights (M_n, M_w), were 23,400 and 53,000, respectively; polydispersity was 2.260. A mixture of macroinitiator (0.30 g), *N*-butyl maleimide (1.53 g, 1×10^{-2} mol), and styrene (1.04 g, 1×10^{-2} mol) was heated at 60°C in an inert atmosphere for 2 h. Then the polymer (0.45 g) was precipitated with methanol from a viscous reaction mixture; after drying, it was extracted with cyclohexane to remove the unreacted polystyrene macroinitiator.[8,9] The extracted polymer (P1), the weight of which decreased by about 50% as compared with that before extraction, contained 35.5 mol % *N*-butyl maleimide, according to the results of elemental analysis. In comparison with the original polystyrene macroinitiator, the obtained polymer showed higher both M_n and M_w (39,200 and 119,500, respectively) and a higher polydispersity (3.049) (Fig. 3, Table III). The determined values of molecular weight indicate formation of a block copolymer. A high polydispersity suggests that, in addition to the propagation reactions, which can proceed at one or at the two polymer chain ends, transfer reactions can also take place. Considering the equimolar amounts of both styrene and *N*-butyl maleimide, as well as a strong tendency of the two monomers to the alter-
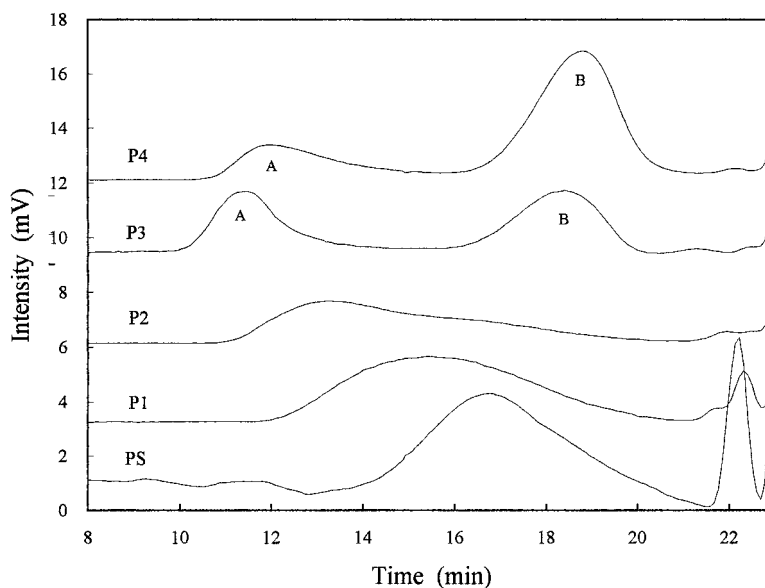
Figure 3   SEC chromatograms of PS, P1, P2, P3, and P4 polymers (Table III) prepared by using iniferters: (A) and (B) are polymer fractions.

nating copolymerization, the copolymer probably consists of blocks of both polystyrene (29 mol %) and alternating S–I copolymer (71 mol %).

The presence of the blocks of both polystyrene and alternating S–I copolymer was also corroborated by the differential scanning calorimetry (DSC) measurements. In the thermogram obtained from the second scan, the following two glass transition temperatures were found: T_{g1} = 372.9 K, corresponding to polystyrene; and T_{g2}

= 396.8, corresponding to the alternating styrene–N-butyl maleimide copolymer (Table III). Two pronounced relaxation maxima in the first scan and the glass transition temperatures corresponding to polystyrene and alternating S–I copolymer suggest that separation of the two polymer blocks occurs. A higher T_{g1} of the prepared P1 in comparison with that of the original PS indicates that the polystyrene block is bound to a polymer block exhibiting a higher glass transi-

Table III   The Number-Average and Weight-Average Molecular Weights (M_n, M_w), Glass Transition Temperatures (T_g, T_{g0}), and Temperatures of Relaxation Maxima (T_r) of Polystyrene Macroinitiator (PS) and of the Polymer Products (P1, P2, P3, P4) Prepared by Using Iniferters

			First Scan					Second Scan	
			T_{g1}	T_{g2}	T_{g0}	T_{r1}	T_{r2}	T_{g1}	T_{g2}
Polymer	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$			(K)			(K)	
PS	23.4	53.0	366.7	—	—	—	—	366.7	—
P1	39.2	119.5	a[b]	a	—	382.7	407.8	372.9	396.8
P2	91.6	261.4	a	a	—	383.0	402.3	375.9	396.5
P3 (A)[a]	708.9	791.5	—	—	—	—	—	—	—
—	—	—	—	398.8	329.7	—	413.0	—	404.8
(B)	14.2	19.4	—	—	—	—	—	—	—
P4 (A)	476.4	572.2	—	—	—	—	—	—	—
			a	a	329.3	387.7	409.0	375.6	398.4
(B)	11.4	15.8	—	—	—	—	—	—	—

[a] (A) and (B) are polymer fractions.
[b] a indicates "not evaluated".

tion temperature, i.e., to the alternating S–I copolymer.

The yield, composition of the block copolymer, and its further properties can be affected by the choice of reaction conditions. Thus, from a mixture of 0.30 g polystyrene macroinitiator, 3.06 g (2×10^{-2} mol) I, and 2.08 g (2×10^{-2} mol) S, after 5 h at 60°C, a block copolymer (P2, 2.15 g) was obtained. The latter contained 20.7 mol % polystyrene blocks and 79.3 mol % blocks of alternating S–I copolymer. The M_n and M_w of the copolymer were 91,600 and 261,400, respectively; polydispersity was 2.855. The found glass transition temperatures, $T_{g1} = 375.9$ K and $T_{g2} = 396.5$ K, confirmed the presence of the two polymer blocks in this case too.

Copolymerization of Styrene with *N*-Butyl Maleimide Initiated by the C3 Copolymer Containing Thiyl End Groups

The C3 copolymer ($f_I = 0.467$) was prepared by copolymerization of styrene with *N*-butyl maleimide ($F_I = 0.3$) initiated by TDS (Table I). A mixture of C3 (0.2 g), *N*-butyl maleimide (1.53 g, 1×10^{-2} mol) and styrene (1.04 g, 1×10^{-2} mol) was heated at 60°C for 5 h. A polymer product (P3) was precipitated with methanol from the reaction mixture and reprecipitated from a benzene solution; its composition (the C, H, and N contents) was almost the same as that of the original C3 copolymer. Using SEC, it was found that the product contains the high-molecular-weight fraction A (43%; $M_n = 708,900$; $M_w = 791,500$; polydispersity = 1.007), and the fraction B (57%), with molecular weights lower by one order of magnitude ($M_n = 14,200$; $M_w = 19,400$; polydispersity = 1.368) (Fig. 3). According to these results, the C3 copolymer functions as a macroinitiator and its polymer chains are extended due to the propagation reaction of styrene with *N*-butyl maleimide under formation of the A fraction; the B fraction probably corresponds to the unreacted macroinitiator.

In the thermogram (first scan) of the polymer product P3 with a bimodal distribution of molecular weights, only one relaxation endotherm was found (Fig. 4, Table III). The latter corresponds to the alternating copolymer and is shifted as far as beyond the distinct region of its glass transition. In general, relaxation endotherms can be used as indicators of demixing for two polymers showing similar glass transition temperatures.[14]

Hence, the observed shift T_{r2} as far as beyond the region of the glass transition T_{g2} can be due to the separation of the two main fractions of alternating copolymers in the mixture, which is a consequence of temperation at 100°C. A weak glass transition T_{g0} at about 330 K is probably associated with the presence of low-molecular-weight fractions in macroinitiator C3 (cf. Table II). On heating at 450 K, the homogenization of sample takes place, and the homogeneous structure is fixed by the following cooling, which manifests itself by the single glass transition temperature T_{g2} in the second scan (Fig. 4).

Polymerization of Styrene Initiated by the C4 Copolymer Containing Thiyl End Groups

The composition of the C4 copolymer ($f_I = 0.475$; Table I) was similar to that of C3 macroinitiator from the previous experiment ($f_I = 0.467$). The polymer product (P4), which was obtained on heating 0.2 g C4 and 5 mL styrene (5 h), contained, after extraction with cyclohexane, 31.8 mol % *N*-butyl maleimide and 68.2 mol % styrene structure units. Using the SEC method, two fractions with markedly different molecular weights were also found in this product (Fig. 3). The fraction A (23.5%) showed $M_n = 476,400$, $M_w = 572,200$, and polydispersity = 1.201; whereas the fraction B (76.5%) had $M_n = 11,400$, $M_w = 15,800$, and polydispersity = 1.389. In the course of this reaction, the chains of the C4 copolymer were extended by polystyrene blocks (A fraction); however, a substantial part of the used C4 did not participate in propagation reactions (B fraction).

DSC analysis does not allow to distinguish between the unreacted C4 and its chains with bound polystyrene blocks in the P4 product (Fig. 4). At about 330 K, a weak glass transition T_{g0} of a low-molecular-weight fraction in C4 was again observed (cf. Table II). The T_{g1} and T_{r1} are close to those for polystyrene blocks in the P1 and P2 copolymers (Table III); this indicates formation of a block copolymer upon the initiation of styrene polymerization by C4 macroinitiator.

Considering both a low initiation efficiency of the C4 macroinitiator and a difficult separation of the resulting P4 product, this procedure is not convenient for preparation of the block copolymer containing both polystyrene and alternating S–I copolymer blocks. The results obtained show that a more promising synthetic method consists in
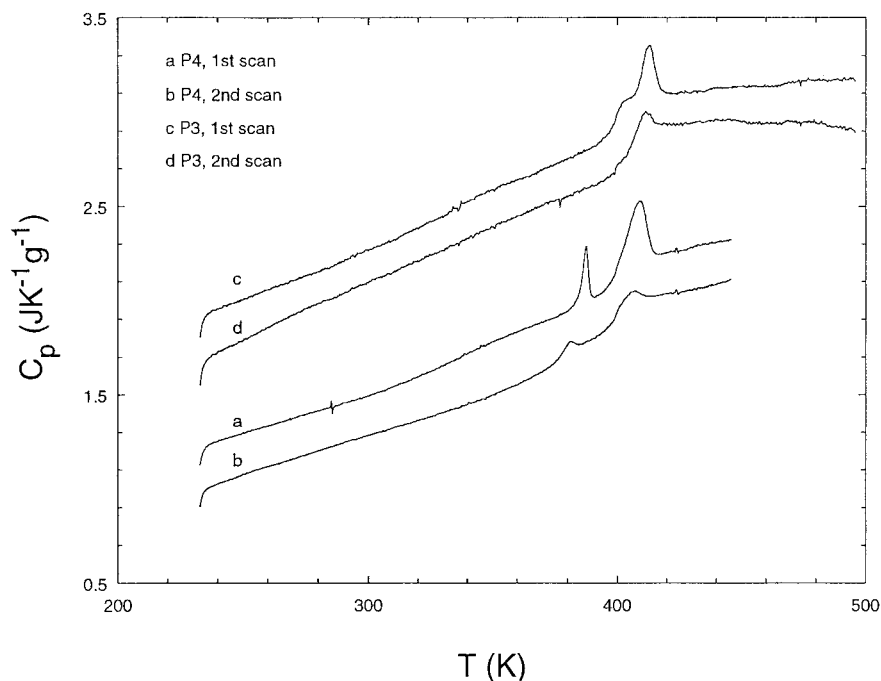
Figure 4   The temperature dependence of thermal capacity (c_p) for P3 and P4 polymers.

copolymerization of styrene with *N*-butyl malei-mide initiated by polystyrene macroinitiator having thiyl end groups. The yields of the block co-polymer are higher, and the unreacted or by thermal polymerization formed polystyrene can be easily removed by selective extraction of the pre-pared product with cyclohexane.

CONCLUSIONS

Tetraethylthiuram disulfide, a low-molecular-weight iniferter, initiates the radical copolymerization of styrene with *N*-butyl maleimide under formation of copolymers having approximately alternating composition at contents of 30–70 mol % imide in the feed. The yields and molecular weights of the copolymers decrease with increasing amounts of *N*-butyl maleimide in the initial reaction mixture.

Using the system polystyrene macroinitiator with thiyl end groups–styrene–*N*-butyl malei-mide, the block copolymer is formed, which con-tains both polystyrene and alternating S–I co-polymer blocks. The yields and properties of the block copolymer can be influenced by the choice of reaction conditions. It is possible to remove the unreacted polystyrene macroinitiator by the ex-traction with cyclohexane.

The S–I copolymer containing thiyl end groups functions in a similar manner as the polystyrene macroinitiator. The initiation of the S–I copoly-merization using this copolymer leads to the ex-tension of its chains by the alternating S–I copoly-mer blocks, the initiation of styrene polymeriza-tion brings about formation of a copolymer containing both polystyrene and alternating S–I copolymer blocks. The block copolymer is, how-ever, rather contaminated with the unreacted co-polymer macroinitiator.

Characterization of polymer products was based on the results of elemental analysis and of DSC and SEC measurements.

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