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Controlled polymerization of styrene in the presence of Blatter′s radicals

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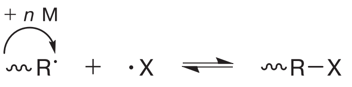
Controlled polymerization of styrene (both self-initiated and initiated with azobisisobutyronitrile) in the presence of Blatter′s radical at 125 °C was studied. When using the radical initiator, there is no induction period. On the basis of UV spectroscopy and MALDI mass-spectrometry studies, it was established that the Blatter radical is completely consumed at the initial stage of the polymerization, inserting into almost all macromolecules. The prepared polystyrene exhibits the ability to reinitialization in post-polymerization and the synthesis of block copolymers.

Key words: styrene, Blatter′s radical, controlled radical polymerization, reversible inhibition, macroinitiator, post-polymerization, block copolymer.

Controlled radical polymerization (CRP) considerably simplifies the problem of the structural control of formed polymers and makes it possible to obtain polymers with precisely controlled molecular structure. One of the CPR mechanisms is the mechanism with a reversible inhibition with participation of stable radicals, *viz.*, the stable free radical polymerization, SFRP. This type of CRP was discovered quite a long time ago,[1,2] but remains relevant today.[3—5] The SFRP process can be represented as shown in Scheme 1.

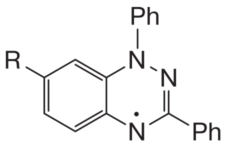
Scheme 1



R· is a chain propagation radical; ·X is a stable radical;
M is a monomer.

SFRP in the presence of a series of stable radicals such as triarylmethyl and related radicals,[6—8] phenoxyl,[9—12] nitroxyl,[13—16] and boroxyl radicals[3,4,17—20] or in the presence of their precursors is well studied. Stable radicals can be either introduced into the reaction mixture,[14,15,21] or generated *in* situ.[10—13,17—20] A wide variety of monomers can be used in this process.

Lately, a number of studies[21—25] devoted to Blatter′s radicals were reported. These radicals are interesting mainly because of their magnetic properties and ability to form semiconducting, pressure sensitive charge transfer complexes with tetracyanoquinodimethane. Only a few studies were devoted to polymerization in the presence of Blatter′s radicals.[21,26] The first of them[21] considered styrene polymerization in the presence of Blatter′s radicals bearing different substituents for the first time.



R = H, CF_3, I, Br, Cl, Ph, fur-2-yl-, 4-PhC_6H_4

It was shown that the formed polystyrene (PS) was characterized by a polydispersity index of 1.05—1.27, however the monomer conversion did not exceed 21.2%. Polymerization of styrene in the presence of two Blatter′s radicals (R = H, Ph) proceeds according to the SFRP mechanism (see scheme 1), however the GPC data indicate the presence in the system of a significant proportion of a dead polymer, which limits the practical value of such polymer products. In the second study,[26] it was suggested to increase the monomer conversion by using an iniferter, decomposition of which produces both initiating and inhibiting radicals. We believe that the use of a radical initiator in combination with Blatter′s radical can have

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an effect similar to the use of an iniferter since it should reduce the inhibiting effect of the stable radical and, therefore, significantly increase the monomer conversion.

This study is devoted to the investigation of the styrene polymerization initiated by azobisisobutyronitrile (AIBN) in the presence of Blatter′s radical (BR), *viz.*, 1,4-dihydro-1,3-diphenyl-1,2,4-benzotriazine-4-yl, as well as to an analysis of formed PS using GPC, UV spectroscopy, and MALDI-TOF mass spectrometry, to exploration of ability of formed PS to reinitialization, and to comparison of these results with those obtained for self-initiated styrene polymerization.

Experimental

Organic solvents were purified according to known procedures.[27] Styrene and methyl methacrylate (MMA) were washed from an inhibitor with a 10% alkali solution and, then, with distilled water to a neutral reaction, dried over anhydrous sodium sulfate, and distilled at 52—54 °C (at 4.3 kPa) in the case of styrene and at 25 °C (at 2.93 kPa) in the case of MMA.[28] Azobisisobutyronitrile (Reachem, RF) was recrystallized from diethyl ether and dried to constant weight.

Blatter′s radical was obtained according to Scheme 2. At the first step,[29] phenylhidrazine (0.049 mol) was dissolved in pyridine (39 mL), and benzoyl chloride (0.049 mol) was added. The reaction mixture was stirred at ~20 °C for 48 h. *N*′-phenyl benzohydrazide (**I**) (0.027 mol, 55%) was obtained in the form of colorless lamellar crystals. At the second step,[29] compound **I** (0.025 mol) and phosphorus pentachloride (0.0275 mol) were boiled in carbon tetrachloride (72 mL) under stirring for 3 h. Then, solution of phenol (0.13 mol) in carbon tetrachloride (36 mL) was added. The reaction mixture was stirred at 0 °C for 1 h. Colorless crystals of *N*′-phenyl benzohydrazonoyl chloride (**II**) (0.008 mol, 32%) were obtained. At the third step,[30] compound **II** (6 mmol) was dissolved in ethanol (3 mL), aniline (6.0 mmol) and a solution of triethylamine (7.1 mmol) in ethanol (1.5 mL) were added. The reaction mixture was boiled under stiring for 2 h. Pink crystals of *N,N*′-diphenyl benzohydrazone amide (**III**) (2.2 mmol, 36%) were obtained. At the last step,[26] compound **III** (1.1 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.11 mmol), and palladium on carbon (Pd/C, 0.017 mmol) were dissolved in methylene chloride (2.2 mL). The reaction mixture was stirred at 20 °C for 3 h. BR (0.9 mmol, 82%) was obtained in the form of air-stable black needle-shaped crystals. BR was characterized using MALDI-TOF mass spectrometry, UV, IR, and ESR spectroscopies.[31]

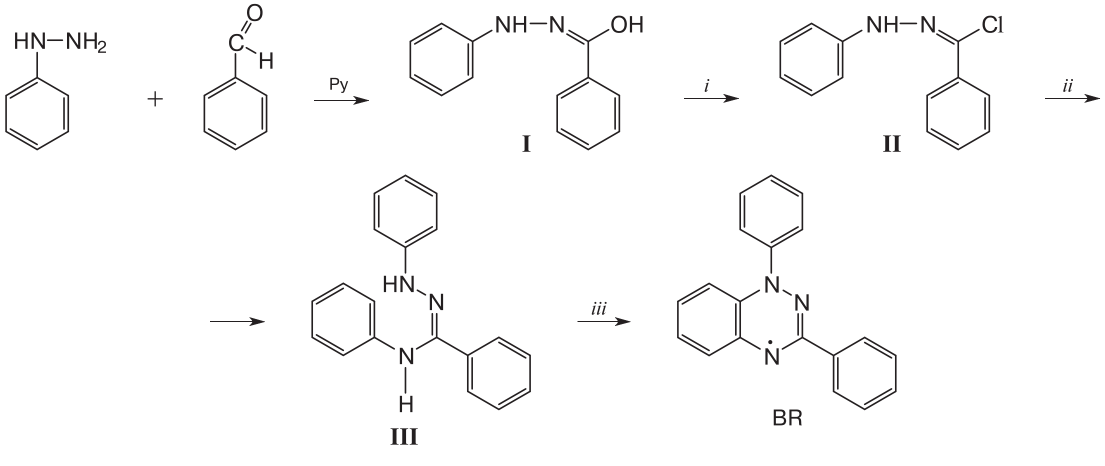
The purity of all used compounds was verified using NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using an Agilent DD2 400 NB spectrometer with operating frequencies of 400 and 101 MHz, respectively.

To carry out polymerization, a solution of BR (or BR and AIBN) in styrene was placed in an ampoule and degased three times using a freezing-thaw procedure at reduced pressure. The ampoule was sealed and placed in a thermostat heated to 125 °C. The styrene conversion was determined gravimetrically. Post-polymerization was carried out with PS obtained at conversions of 28—42%, which was twice re-precipitated from chloroform to isopropyl alcohol and dried. A 5% solution of polystyrene in styrene was used. Solutions of a macroinitiator (MI) in styrene were heated at 125 °C for 2 and 4 h. The synthesis of block copolymer of styrene and methyl methacrylate (PS-b-PMMA) was carried out analogously for 0.5 and 1 h.

Molecular weight distribution characteristics of obtained polymers were obtained using GPC in THF at 40 °C with the use of a Shimadzu liquid chromatograph equipped with columns filled with polystyrene gel with pore sizes of $1 \cdot 10^6$ and $1 \cdot 10^5$ Å. A differential refractometer was used as a detector. Chromatograms were processed using the LCsolution software. Narrowly dispersed PS standards were used for calibration.

UV spectra of solutions of BR and PS in chloroform were recorded using a Shimadzu UV-1800 spectrometer. MALDI-TOF mass spectra of polymers were obtained with the use of a Bruker Microflex LT mass spectrometer. Matrix substance for MALDI-MS was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile, a cationizing agent was silver acetate. The sample was prepared by mixing solutions of polymer, matrix, and cationizing agent (5 : 25 : 1) in THF and applying the resulting

Scheme 2



Reagents and conditions: *i.* 1) PCl_5, CCl_4; 2) PhOH, CCl_4; *ii.* $PhNH_2$, Et_3N, EtOH; *iii.* 0.1 eq. DBU, 1.6 mol.% Pd/C, CH_2Cl_2.

solutions to a stainless steel plate. Narrowly dispersed standards based on PS were used for calibration of the spectrometer.

Results and Discussion

Self-initiated styrene polymerization in the presence of 0.4 mol.% BRs of different composition was already considered in study[21] where the PS synthesis was carried out in a round bottom flask at 125 °C under the nitrogen atmosphere. Conversion was determined gravimetrically.[21] In the present study, the synthesis of polystyrene at 125 °C in the presence of 0.4 mol.% BR was performed in evacuated ampoules (Fig. 1, *a*, curve *1*). Note that a decrease in the BR concentration (see Fig. 1, *a*, curve *2*) reduces the polymerization rate and lengthens the induction period.

Styrene polymerization initiated by 0.1 mol.% AIBN is characterized by a higher rate (see Fig. 1, *b*, curve *4*) as compared to self-initiated polymerization (see Fig. 1, *a*, curve *3*). Introduction of BR together with AIBN (see Fig. 1, *b*, curves *1*—*3*) results in the disappearance of the inductive period and, in the presence of the 0.1 mol.% inhibitor, makes it possible to achieve high conversions (see Fig. 1, *b*, curve *3*). The styrene polymerization rate in the presence of 0.4 mol.% BR (see Fig. 1, *b*, curve *1*) is higher than in the presence of 0.25 mol.% BR (see Fig. 1, *b*, curve *2*) similarly to the case of self-initiated polymerization (see Fig. 1, *a*, curves *1* and *2*). It can be supposed that the use of a radical initiator increases the concentration of initiating radicals in comparison with the self-initiated polymerization, which reduces the inhibiting action of BR.

Thus, the changes in the polymerization kinetics due to variations in the BR and AIBN concentrations characterize BR as a weak inhibitor.

All PS samples prepared at different BR concentrations in the presence or absence of AIBN have number average molecular weights (M_n) lower (Figs. 2 and 3) than those

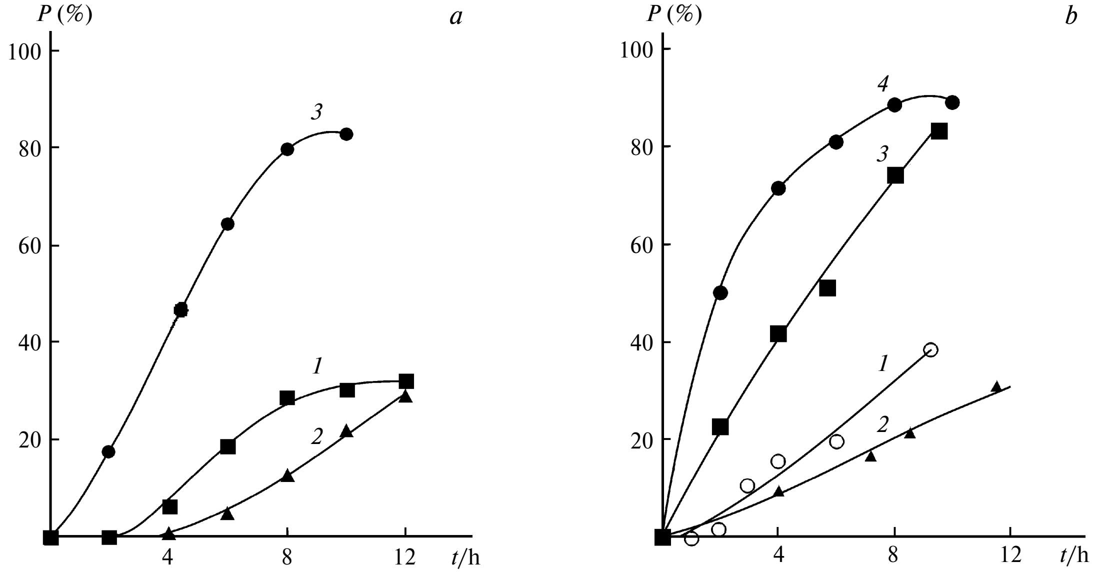


Fig. 1. Kinetics of styrene polymerization at 125 °C without initiator (*a*) in the presence of BR in concentrations of 0.4 (*1*), 0.25 mol.% (*2*), and without BR (*3*) and with 0.1 mol.% AIBN as an initiator (*b*) in the presence of BR in concentrations of 0.4 (*1*), 0.25 (*2*), 0.1 mol.% (*3*), and without BR (*4*).

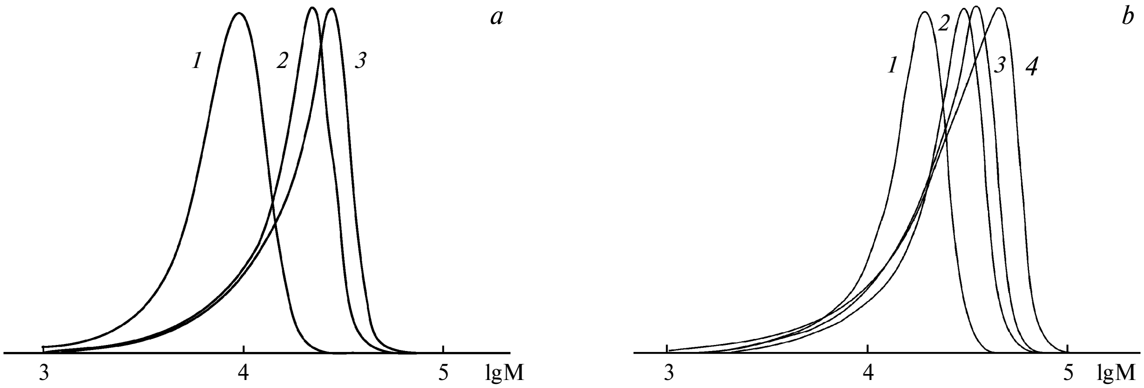


Fig. 2. Evolution of MMD for PS synthesized in the presence of 0.4 mol.% BR (*a*) at conversions of 6.3% (*1*), 18.7% (*2*), and 28.6% (*3*) and 0.25 mol.% BR (*b*) at conversions of 4.6% (*1*), 12.5% (*2*), 21.9% (*3*), and 28.8% (*4*).

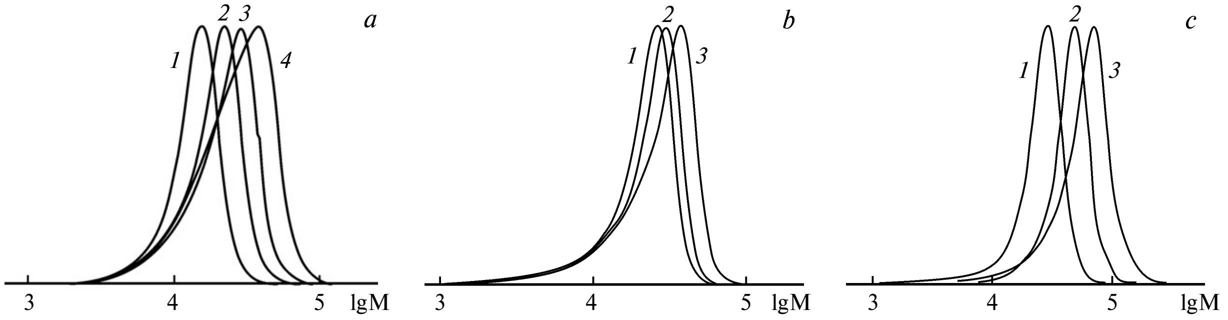
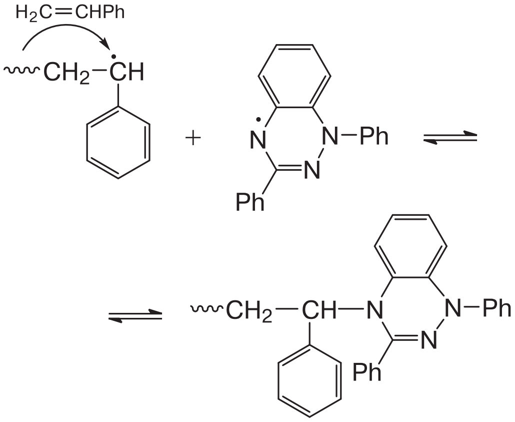


Fig. 3. Evolution of MMD for PS synthesized in the presence of 0.4 mol.% BR and 0.1 mol.% AIBN (*a*) at conversions of 10.3% (*1*), 15.5% (*2*), 19.8% (*3*), and 38.5% (*4*), in the presence of 0.25 mol.% BR and 0.1 mol.% AIBN (*b*) at conversions of 9.5% (*1*), 16.6% (*2*), and 31.1% (*3*), and in the presence of 0.1 mol.% BR and 0.1 mol.% AIBN (*c*) at conversions of 22.5% (*1*), 41.8% (*2*), and 74.2% (*3*).

of polymers prepared in the absence of the inhibitor. The number average molecular weights are 170000 in the case of self-initiated styrene polymerization and 70000 in the case of the AIBN initiated polymerization; the polydispersity index is in the range 1.1—1.5. There is a tendency to narrowing the dispersion of the M_n values.

The molecular mass distribution (MMD) curves shown in Figs. 2 and 3 correspond to regularities typical of the SFRP processes (Scheme 3), however, in all the cases, a low-molecular fraction is retained, which was attributed[21] to the presence of a certain fraction of dead polymer. Growth of M_n is proportional to the increase in the transformation depth (Fig. 4), which is typical of SFRP. However, this dependence does not pass through the origin of coordinates. This is due to the fact that the occurrence of CRP requires formation of an oligomeric adduct between radical propagating the chain and BR. This adduct plays a role of MI (see Scheme 3).

Scheme 3



In accordance with Scheme 3, the higher the concentration of starting BR, the higher the amount of MI formed. We believe that the increase in the BR concentration from 0.25 to 0.4 mol.% (see Fig. 1, curves *2* and *1*, respectively) favors formation of larger amount of MI and, therefore, the increase in the process rate.

The fact of embedding BR into the polymer chain was confirmed using UV spectroscopy (Fig. 5). The absorption bands at 271, 322, 372, 429, and 494 nm are present in the UV spectrum of free BR (see Fig. 5, curve *1*).[31] The UV spectrum of PS (see Fig. 5, curve *2*) prepared in the presence of BR has the same absorption bands, although, with considerably changed relative intensities. Thus, the electronic transitions determining the appearance of the bands at 322, 372, 429, and 494 nm remain unchanged for both free BR and BR included into the polymer chain. However, the extinction coefficients of these bands are determined by the probabilities of the corresponding electronic transitions, depending on the difference in polarizability of the ground and excited states. Therefore, the absorption band intensities should depend on the surroundings of the chromophore. Indeed, the relative intensities of these

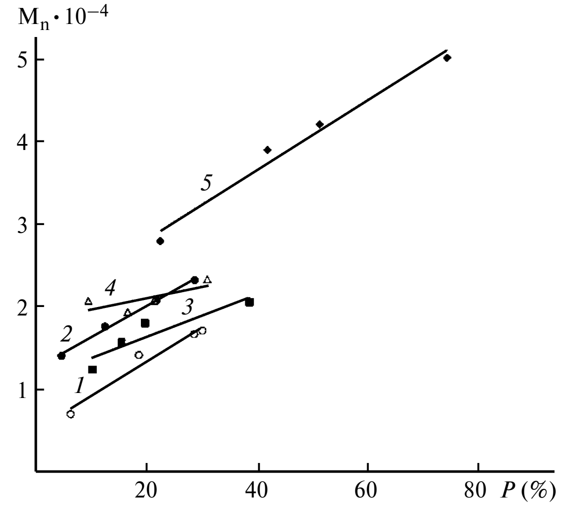


Fig. 4. Dependence of M_n on the conversion of PS samples prepared at 125 °C in the presence of BR in concentration of 0.4 (*1*) and 0.25 mol.% (*2*) and in the presence of 0.1 mol.% AIBN and BR in concentrations of 0.4 (*3*), 0.25 (*4*), and 0.1 mol.% (*5*).

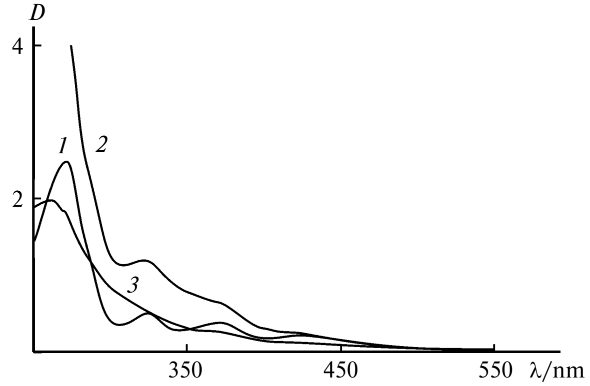
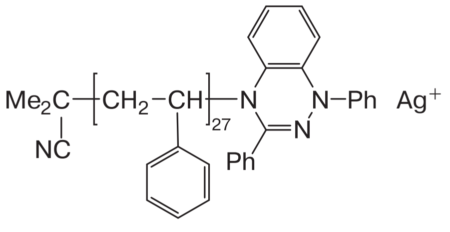


Fig. 5. UV spectra of chloroform solutions of BR (*1*), PS prepared by styrene polymerization in the presence of 0.25 mol.% BR at the 12.5% conversion (*2*), and mother liquor after precipitation of PS (*3*).

bands are different in the spectra of free and embedded BR, and this difference is stronger in the short-wavelength region because of the mentioned influence of the reaction center. The changes occurring with the band at 271 nm require a separate consideration. This band is the benzene fragment band (^1L_b according to the Platt notation), which is responsible for the transitions within the benzene ring. Substitution in the ring results in its bathochromic shift. The simultaneous presence of substituents of several types leads to the broadening of this band or to the appearance of a complex structure for it. The latter effect was observed in our case. The UV spectrum of the mother liquor after precipitation of the polymer (see Fig. 5, curve *3*) contains absorption bands in the region 250—280 nm, which belong to phenyl groups of oligomeric PS. Thus, all BR molecules are incorporated into the polymer chain already at the 10% conversion of the monomer.

Thus, all obtained experimental data indicate BR embedding into the polymer chain. However, the UV data do not answer the question if all chains contain BRs. To answer this question, a MALDI-TOF mass spectrometry study was carried out. A mass spectrum typical of all obtained polymers is shown in Fig. 6. Two main series of peaks differing by 104 Da, which corresponds to a styrene moiety, are seen in the spectrum. A peak at 3273.0 Da corresponds to a macrocation of a dormant chain, consisting of an AIBN residue, 27 links of styrene, BR, and silver cation (calculated value is 3272.3).



Macrocation

This observation of this peak confirms that the reversible inhibition due to addition of BR to growing chains takes place.

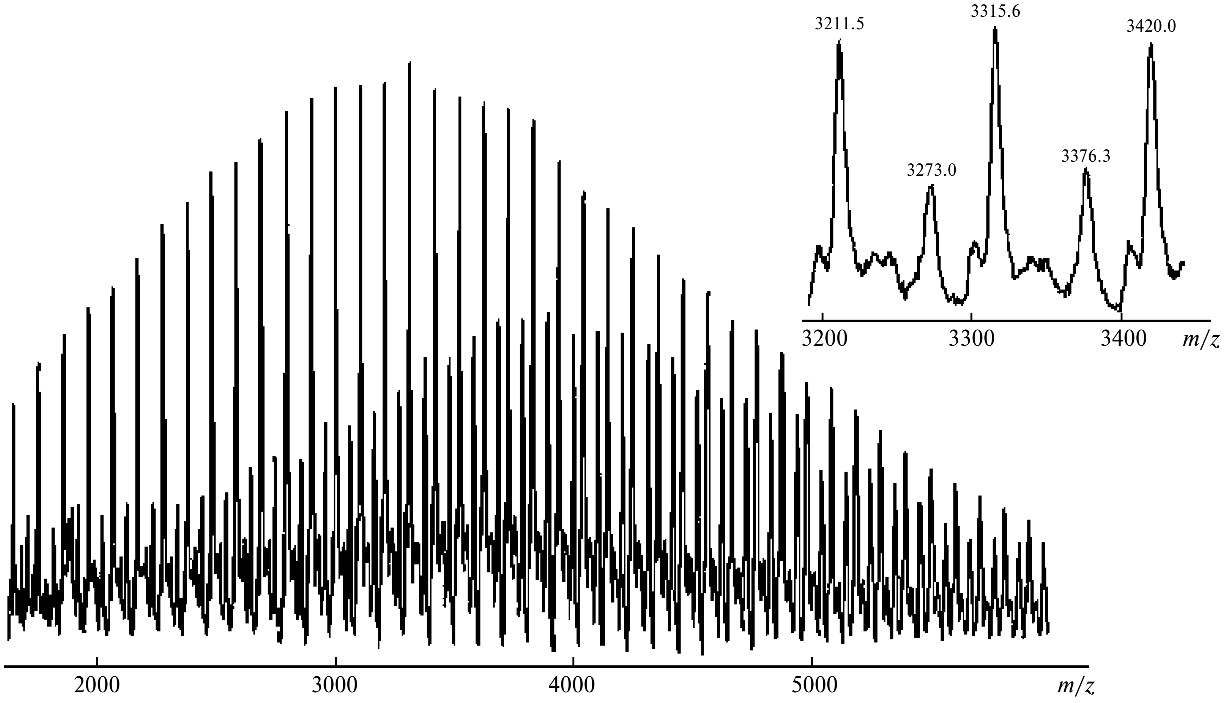
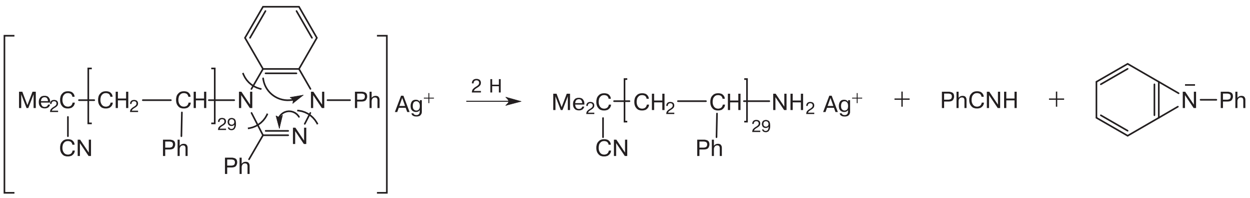


Fig. 6. MALDI-TOF MS of PS prepared at 125 °C in the presence of 0.1 mol.% AIBN and 0.25 mol.% BR; the inset shows an enlarged relevant part of the spectrum.

Table 1. Characteristics of MIs obtained by styrene polymerization at 125 °C in the presence of BR

MI	Initiator of the styrene polymerization	P (%)	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	M_w/M_n
I	BR (0.4 mol.%)	30.1	17	25	1.49
II	BR (0.25 mol.%)	28.8	23	34	1.46
III	AIBN (0.1 mol.%), BR (0.25 mol.%)	32.2	25	33	1.32
IV	AIBN (0.1 mol.%), BR (0.1 mol.%)	41.8	42	48	1.15

Scheme 4



The most intensive series of peaks in the mass spectrum (3211.5 and subsequent), apparently, corresponds to a product of fragmentation of BR moiety under the analysis conditions. Presumably, the fragmentation proceeds according to the pathway shown in Scheme 4 and results in the formation of macrocations containing an amino group at the end of the chain.

Similar fragmentation processes in mass spectrometry are well known for substituted imidazoles.[32] The calculated m/z value for the final cation consisting of an AIBN residue, 29 styrene links, an amino group, and silver cation is 3211.3, it well corresponds to the m/z value observed in the spectrum.

Thus, the conducted mass spectrometric study of the obtained samples showed that the predominant part of the formed polymer chains contain BR at their ends, while the proportion of dead polymer is insignificant.

One of the main characteristics of the controlled polymerization is the ability of the formed polymers to continue the process when a new portion of the monomer is added. Post-polymerization was carried out with PS samples whose characteristics and designations are given in Table 1.

All used MIs (see Table 1) exhibit the ability to reinitialization, which is evidenced by the increase in conversion and M_n (Table 2). The maxima on the MMD curves for the post-polymers are displaced to higher M_n values (Fig. 7, curves *2* and *3*) in comparison with those of the MMD curves for MIs (see Fig. 7, curve *1*).

Yields and M_n values tend to increase with the decrease in the BR concentration in MI (see Table 2). Polydispersity of post-polymers in comparison with MIs increases (see Table 2) due to incomplete consumption of the latter (see Fig. 7, curves *2* and *3*). However, MMD becomes narrower with the increase in the transformation depth except the case of MI **IV**. Probably, the fraction of dead polymer is high in the latter case, which can be related to the low content of BR in this MI.

The capability of PS obtained in the presence of BR to reinitialization was also studied in the synthesis of block copolymer PS-b-PMMA. In particular, MI **IV** (see Table 1) produces PS-b-PMMA as it follows from changes in M_n and MMD (Table 3, Fig. 8).

In the course of synthesis of PS-b-PMMA, MMD acquires a bimodal character (see Fig. 8, curves *2* and *3*). The low-molecular mode corresponds to MI **IV** (see Fig. 8, curve *1*), and the high-molecular one conforms with the block copolymer. With the increase in the transformation depth, the low-molecular mode decreases, while the high-molecular mode increases and becomes displaced to higher M_n. The obtained polymer cannot be a product of thermal polymerization of MMA since its M_n is an order of magnitude higher (see Fig. 8, curve *4*).

On the whole, we established that the self-initiated polymerization of styrene in the presence of BR proceeds according to the SFRP mechanism (see Scheme 3) and is accompanied by an induction period,[21] during which MI is formed. In the presence of AIBN, a radical initiator, there is no induction period, whereas the mechanism remains the same. In all the cases, BR is completely in-

Table 2. Data on post-polymerization of styrene at 125 °C in the presence of 5 wt.% MI (P_0 = 4.8%)

MI	t/h	P (%)	P/P_0	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	M_w/M_n
I	2	23.6	4.9	84	146	1.73
	4	43.0	9.0	109	183	1.68
II	2	19.1	4.0	92	209	2.27
	4	46.9	9.8	132	283	2.14
III	2.67	37.8	7.9	87	173	2.00
	4	44.5	9.3	110	220	2.00
IV	2	36.3	7.6	107	180	1.68
	4	47.4	9.9	122	250	2.05

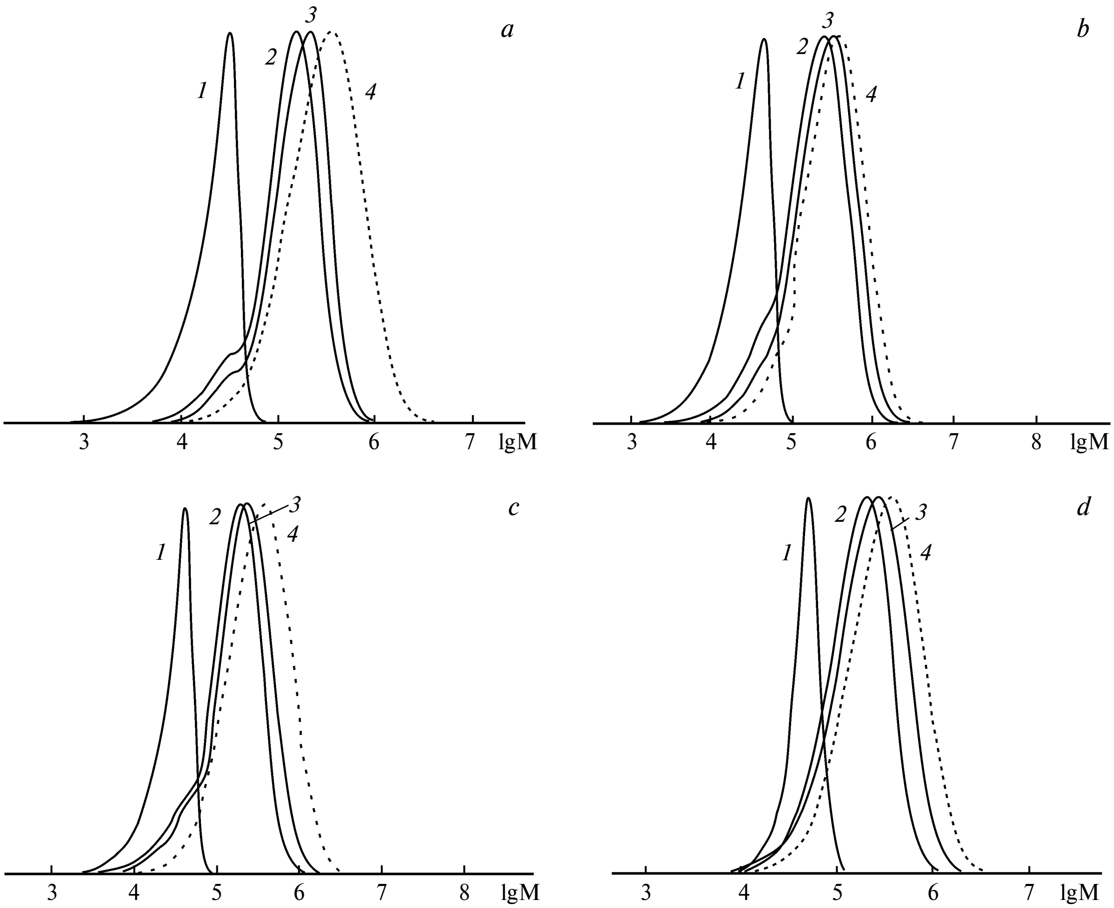


Fig. 7. MMD for MI **I** (*a*), MI **II** (*b*), MI **III** (*c*), and MI **IV** (*d*) (curves *1*) and post-polymers obtained for 2 (*2*) and 4 h (*3*), as well as of PS synthesized in the absence of MI (*4*).

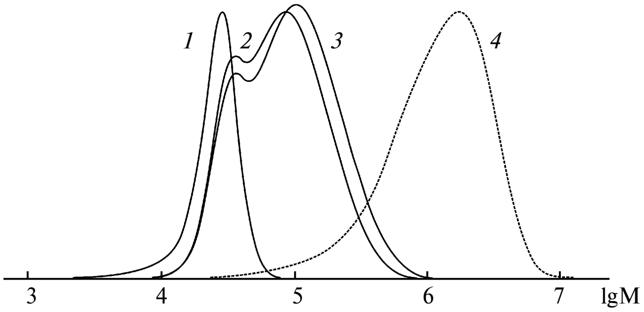


Fig. 8. MMD for MI **IV** (*1*) and PS-b-PMMA prepared for 0.5 (*2*) and 1 h (*3*), as well as for PMMA synthesized without addition of MI (*4*).

Table 3. Data on synthesis of PS-b-PMMA at 125 °C in the presence of 5 wt.% MI **IV** (P_0 = 4.8%)

t/h	*P* (%)	P/P_0	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	M_w/M_n
0.5	9.3	1.9	58	97	1.66
1.0	12.3	2.6	63	174	1.80

cluded in the polymer chain as it was confirmed by the UV data. At the same time, according to the MALDI-TOF mass spectrometry data, almost all polymer chains contain BR moieties at their ends. This indicates only an insignificant fraction of dead polymer. The obtained samples of PS actively participate in the processes of reinitialization, post-polymerization, and synthesis of block copolymers.

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