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MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Copolymerization of 1,3-Butadiene and Styrene in the Presence of an Initiating System Based on *n*-Butyllithium, Amine-containing Modifier, and 2,2'-Ditetrahydrofurylpropane

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Abstract—The kinetic parameters of copolymerization of 1,3-butadiene and styrene in hexane under the action of a ternary initiating system consisting of *n*-butyllithium, amine-containing alkali and alkaline earth metal alcoholates, and 2,2'-ditetrahydrofurylpropane were studied. The molecular mass characteristics and microstructure of the synthesized copolymer samples were examined. Physicomechanical tests of specimens of butadiene–styrene rubber prepared from solution and of vulcanized specimens based on them were performed.

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The development of environmentally friendly, so-called "green" tires has been given much attention in the past years. It involves improvement of the environmental and operation characteristics of tires, primarily reduction of the rolling loss to decrease the fuel consumption and harmful emissions and improvement of the traction characteristics and wear resistance of tires. One of the rubbers meeting the above requirements is functionalized solution butadiene–styrene rubber (s-BSR) with high content of 1,2-units [1, 2]. It is known from the literature [3, 4] that the presence of functional groups in the copolymer structure, e.g., of tin-, silicon-, and amine-containing groups, allows improvement of the distribution of reinforcing fillers in the rubber matrix, which, in turn, leads to reduction of hysteresis loss and improvement of the wear resistance and traction properties of protector rubbers. Therefore, studies in the field of preparation of s-BSR with functional groups and increased content of vinyl structures become more and more topical.

As found previously [5], a binary initiating system based on *n*-butyllithium (NBL) and a mixture of amine-containing alkali and alkaline-earth metal alcoholates (AMD) allows preparation of solution butadiene–styrene rubber with increased content of 1,2-units and random distribution of 1,3-butadiene and styrene units in the polymer chain. The modifier contains two secondary amino groups whose interaction with the *n*-butyllithium molecule is accompanied by the formation of lithium amide capable of initiating the copolymerization. This allows obtaining macromolecules containing functional fragments. Furthermore, the initial copolymerization rate increases in the presence of AMD. On the other hand, the observed increase in the reaction rate is insufficient, which is caused by low solvating ability of the amine-containing electron donor and low reactivity of lithium amide because of the covalent nature of the Li–N bond. Additional introduction of electron-donor compounds into the initiating system can be a possible solution of the problem.

This study was aimed at determining the kinetic parameters of the copolymerization of 1,3-butadiene and styrene in a hydrocarbon solvent under the action of a ternary initiating system consisting of *n*-butyllithium, amine-containing modifier, and 2,2'-ditetrahydrofurylpropane (DTHFP), the molecular mass characteristics of the synthesized s-BSR samples, and their microstructure. Physicomechanical tests of s-BSR specimens and of vulcanized specimens based on them were also performed.

EXPERIMENTAL

The monomers and solvent were pretreated by the procedures standard for anionic polymerization [6]. The copolymerization was initiated with *n*-butyllithium. We used as a modifier a mixture of amine-containing alkali and alkaline earth metal alcoholates (AMD) prepared by the reaction of *N,N*'-di(β-hydroxypropyl)ethylenediamine with barium hydroxide and sodium in accordance with [7]. The presumed structural formula of AMD is shown in Scheme 1.

The presence of barium alcoholates in the modifier ensures its increased solubility in hydrocarbon solvents (hexane, toluene, etc.). The synthesized modifier is characterized by the total alkalinity of 2.83 M and molar concentration of hydroxy groups of 0.0097 M. The molar concentrations of barium and sodium were 0.54 and 1.03 M, respectively.

As a polar additive we chose 2,2'-ditetrahydrofurylpropane. Its use allows the copolymerization rate and the content of 1,2-units in the butadiene moiety to be considerably increased [8]. In addition, DTHFP is characterized by low solubility in water and high boiling point (145°C), which allows the pollution of water bodies at synthetic rubber plants to be reduced and the polar additive to be recovered and reused in the production cycle.

The s-BSR synthesis was performed in hexane in a metal reactor equipped with a stirrer (200 rpm), a temperature-control jacket, and devices for introducing the initiator, modifier, and polar additive solutions and taking off the polymer solution. Copolymerization of 1,3-butadiene and styrene was performed at 50°C for 60 min. Ethanol was used for the initiator deactivation. Irganox 1520L was used as a copolymer stabilizer.

The monomer concentration in the solution was in the range 1.42–1.59 M. The weight ratio of 1,3-butadiene to styrene was 80 : 20. The concentrations of the modifier, polar additive, and initiator in the working hexane solutions used in the experiments were 0.25, 0.25, and 0.20 M, respectively. The monomer : NBL molar ratio was 1000 : 1. The AMD : NBL molar ratio in our experiments was 1 : 1, and the DTHFP : NBL molar ratio was varied from 0 : 1 to 5 : 1.

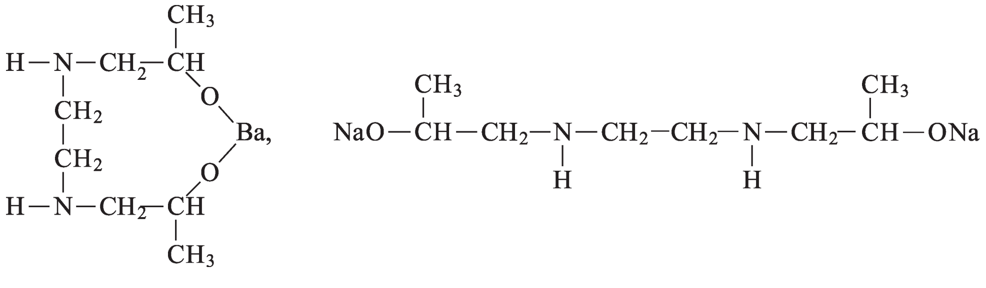
The concentration of the modifying additive was determined by measuring the total alkalinity. The method is based on the reaction of the modifying additive with water taken in excess to obtain alkali and alkaline earth metal hydroxides and amino alcohol, with the subsequent neutralization of the reaction products with an HCl solution in the presence of Bromothymol Blue indicator.

The weight fraction of 2,2'-ditetrahydrofurylpropane was measured by gas chromatography. The chromatograph was equipped with a capillary column, a flame ionization detector, an electron multiplier, and a computer with the software for device operation control and chromatographic data processing.

The molecular characteristics were determined by gel permeation chromatography using a Breeze liquid chromatograph (Waters) equipped with a refractometric detector. For this purpose, we used a set of high-resolution Styragel columns (Waters) with the separation range $50–4 \times 10^6$. Elution was performed with tetrahydrofuran at 40°C. The universal calibration was calculated using polystyrene reference samples (OOO Metrotsentr-SK) with the molecular masses in the range $890–4 \times 10^6$.

The copolymer microstructure and the weight fraction of bound styrene were determined by IR spectroscopy with a Perkin Elmer Spectrum GX 100 spectrometer in accordance with ISO 21561/2 standard. A small portion of the copolymer was placed on a crystal of the ATR (attenuated total reflection) attachment and pressed, and the IR spectrum in the range 1200–600 cm^{-1} was taken.

Scheme 1.



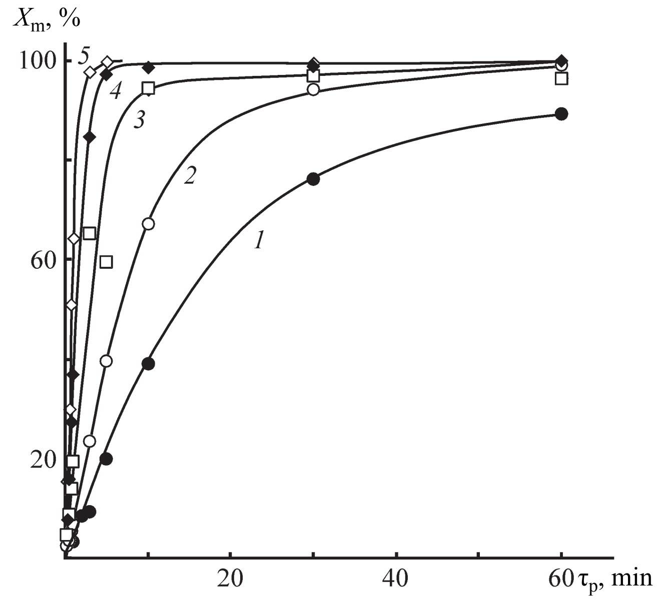


Fig. 1. Monomer conversion X_m as a function of copolymerization time τ_p at DTHFP to NBL molar ratios of (*1*) 0 : 1, (*2*) 0.1 : 1, (*3*) 0.5 : 1, (*4*) 1 : 1, and (*5*) 2 : 1.

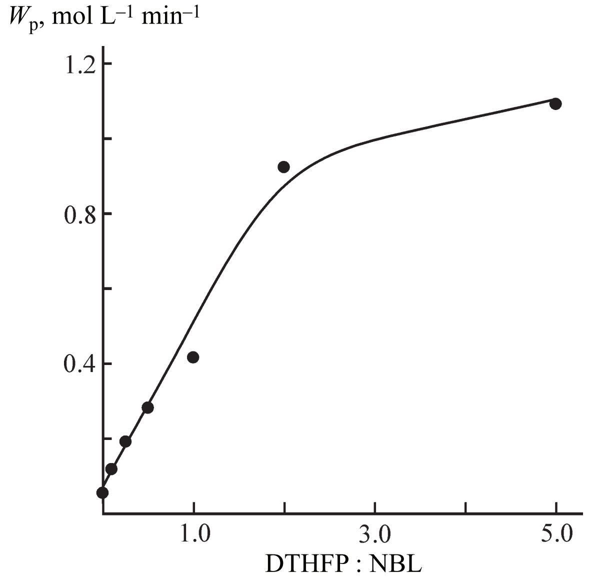


Fig. 2. Initial copolymerization rate W_p as a function of the DTHFP : NBL molar ratio.

Then, the optical densities at 699, 725, 755, 910, 967, 990, and 1200 cm^{-1} were measured. Using the equations given in the standard, we calculated the content of *cis*-1,4-, *trans*-1,4-, and 1,2-units and of bound styrene. To derive the equations, we used standards with 10 to 77% content of 1,2-units and 0 to 45% styrene content.

The kinetic parameters of the polymerization were calculated as described in [9].

To calculate the copolymerization constants, we used the Mayo–Lewis intersection method [10] and the Fineman–Ross sloping straight line method [11], both based on graphic solution of the differential equation of binary copolymerization.

Preparation and analysis of rubber stocks and physicomechanical tests of vulcanized s-BSR specimens were performed in accordance with the procedures described in [12]. Imported s-BSR of Nipol NS 616 grade was used as a reference sample.

The experimental data given in Fig. 1 show that introduction of even minor amounts of the polar additive into the reaction medium at the AMD : NBL molar ratio of 1 : 1 leads to a considerable increase in the monomer conversion. For example, at the DTHFP to NBL molar ratio of 0.5 : 1 the 95% monomer conversion is reached already in 10 min, whereas without this polar additive the monomer conversion is 89% in 60 min. On the whole, the polymerization activity of the initiating system increases as the DTHFP content of the reaction medium is increased. The results obtained are well consistent with the data of Halasa and Hsu [13], who noted positive synergistic effect from the joint use of sodium alkoxides and *N*,*N*,*N*',*N*'-tetramethylethylenediamine in anionic polymerization of 1,3-butadiene. Halasa and Hsu showed that the polymerization rate was high and demonstrated the possibility of preparing a high-vinyl elastomer.

The influence of the 2,2'-ditetrahydrofurylpropane concentration on the copolymerization is demonstrated more clearly in Fig. 2, which shows the dependence of the initial copolymerization rate W_p on the content of the polar additive in the system. As can be seen, the initial copolymerization rate increases on introducing DTHFP into the reaction medium. The increase in W_p is the most significant in the range of DTHFP to NBL molar ratios from 0.1 : 1 to 2 : 1, after which the curve tends to flatten out.

Within the framework of this study, we calculated the initiation, k_i, and propagation, k_p, rate constants. As seen from Table 1, copolymerization of 1,3-butadiene and styrene in the presence of individual n-butyllithium is characterized by the lowest values of k_i and k_p. It should be noted that the calculated initiation and propagation rate constants for the copolymerization of 1,3-butadiene with

Table 1. Characteristics of s-BSR samples and properties of rubber stocks and vulcanized rubbers based on them[a]

Parameter	Nipol NS-616	Laboratory s-BSA sample
Rubber characteristics		
M_t^r, arb. units	64	66
Content of styrene units, wt %	20.5	22.3
Microstructure of the butadiene moiety:		
1,2-units	60.5	61.3
cis-1,4-units	17.2	17.8
trans-1,4-units	22.3	20.9
Molecular mass characteristics:		
$M_n \times 10^{-3}$	168	209
$M_w \times 10^{-3}$	306	296
$M_z \times 10^{-3}$	597	384
M_w/M_n	1.82	1.41
Characteristics of rubber stocks		
M_t^{rs}, arb. units	90	81
M_L, dN m	2.4	2.4
M_H, dN m	20.8	19.5
t_{s1}, min	1.7	1.5
t_{50}, min	4.1	3.7
t_{90}, min	11.3	10.5
$\Delta G'$, kPa	180	206
Characteristics of vulcanized rubbers		
f_{100}, kPa	2.8	2.8
f_p, MPa	11.4	13.3
ε_p, %	230	290
H_A, arb. units	61	64
E, %	18	18
tan δ at 60°C	0.12	0.14

[a] M_t^r, Mooney viscosity of rubber, MB 1+4 (100°C); M_n, M_w, M_z, number-average, weight-average, and sedimentation-average molecular masses; M_t^{rs}, Mooney viscosity of rubber stock, MB 1+4 (100°C); M_L, M_H, minimal and maximal torque; t_{s1}, scorching onset time; t_{50}, t_{90}, time of reaching 50 and 90% degree of vulcanization, respectively; $\Delta G'$, difference between the elastic moduli G' at 1 and 50% shear amplitudes; f_{100}, nominal stress at 100% elongation; f_t, nominal tensile strength; ε_b, relative elongation at break; H_A, Shore hardness A; E, rebound elasticity at 23°C; tan δ at 60°C, mechanical loss tangent at 60°C, determined with an RPA 2000 device.

styrene in hexane, initiated by individual *n*-butyllithium, are in good agreement with the published data [9]. On introducing the amine-containing modifier into the reaction medium, k_i and k_p tend to appreciably increase. When the polar additive is introduced and the copolymerization is performed under the action of the ternary initiating system NBL–AMD–DTHFP, the rate constants increase considerably. It is interesting that k_i and k_p for the reaction performed under the action of the binary initiating system NBL–DTHFP are higher than those for the reaction performed with the NBL–AMD system.

It seems interesting to study how the polar additive influences the reactivity of the monomers in the presence of the chosen initiating system. It is known [14] that, in joint polymerization of 1,3-butadiene and styrene under the action of n-butyllithium in aliphatic, cycloaliphatic,

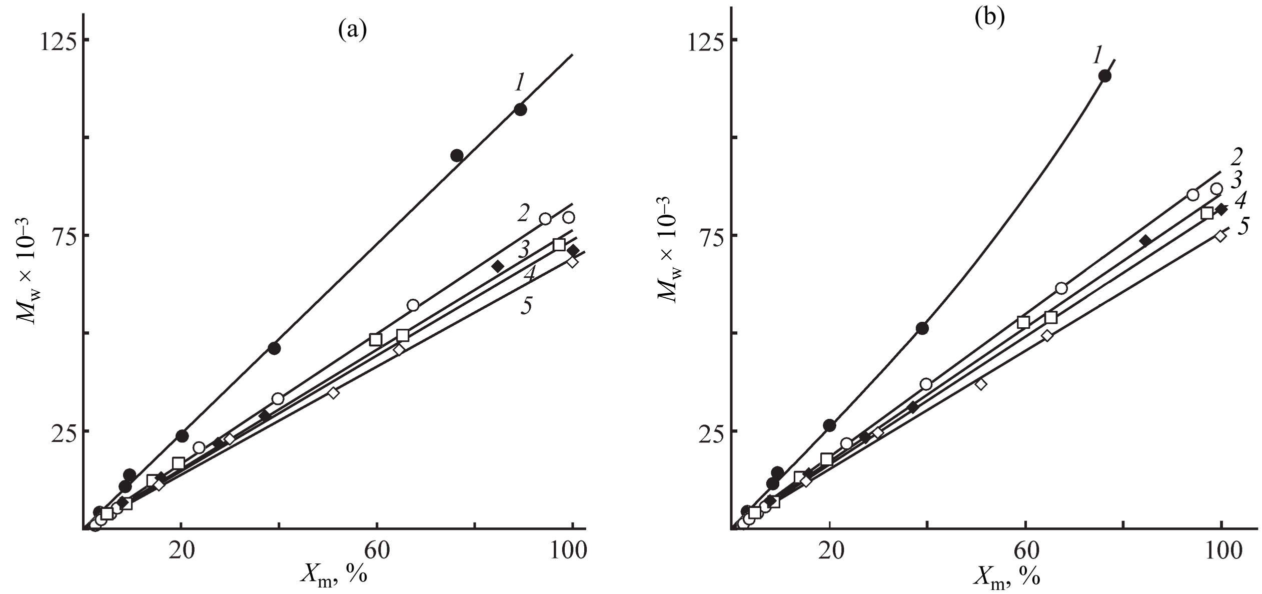


Fig. 3. (a) Number-average, M_n, and (b) weight-average, M_w, molecular masses as functions of the monomer conversion X_m at DTHFP to NBL molar ratios of (*1*) 0 : 1, (*2*) 0.1 : 1, (*3*) 0.5 : 1, (*4*) 1 : 1, and (*5*) 2 : 1.

and aromatic hydrocarbons, 1,3-butadiene polymerizes primarily. The vinylaromatic compound becomes involved in the reaction only after consumption of the major fraction of the conjugated diene. This is due to the fact that the copolymerization constant of 1,3-butadiene, r_1, is 10^2–10^3 times higher than the copolymerization constant of styrene, r_2. As shown previously [5], when using the amine-containing modifier, the reactivity of styrene increases to a greater extent than that of 1,3-butadiene, with r_1 and r_2 equal to 0.99 and 2.43, respectively.

In this study, we determined the copolymerization constants by the Mayo–Lewis and Fineman–Ross methods. We found that, on introducing the polar additive, the copolymerization constants of 1,3-butadiene and styrene in the process performed in the presence of the ternary initiating system NBL–AMD–DTHFP, r_1 and r_2, become still closer to each other and equal to 0.97 and 1.16, respectively.

Analysis of the molecular mass characteristics of the s-BSR samples shows that introduction of small amounts of 2,2′-ditetrahydrofurylpropane into the polymerization system leads to a considerable decrease in the number-average, M_n, and weight-average, M_w, molecular masses (Fig. 3). Apparently, on introducing DTHFP the concentration of the active sites increases owing to solvation of the positive counterion and to a decrease in the degree of association of NBL [15]. On the other hand, as the concentration of the polar additive is increased further in the range of DTHFP to NBL molar ratios from 0.1 : 1 to 2 : 1, the observed decrease in M_n and M_w is less significant. It should be noted that, irrespective of the content of the polar additive in the system, variation of the average molecular masses with the monomer conversion is described by a linear law, suggesting low probability of the chain termination and transfer reactions.

Figure 4 shows how the differential curve of the molecular mass distribution (MMD) of s-BSR synthesized in the presence of the ternary initiating system NBL–AMD–DTHFP varies depending on the monomer conversion. As can be seen, the samples obtained have narrow molecular mass distribution with the polydispersity index on the level of 1.1. Irrespective of the conversion, the MMD curves of the copolymer are bimodal. This fact suggests kinetic heterogeneity of the initiating system and the presence of at least two types of active polymerization sites. On the whole, an increase in the monomer conversion is accompanied by the shift of the molecular mass distribution toward higher molecular masses, with the shape of the differential curve remaining virtually unchanged.

A study of the microstructure of the s-BSR samples has shown that introduction of the polar additive into the reaction medium and increase in its concentration up to the DTHFP to NBL molar ratio of 0.5 : 1 is accompanied by an increase in the weight fraction of

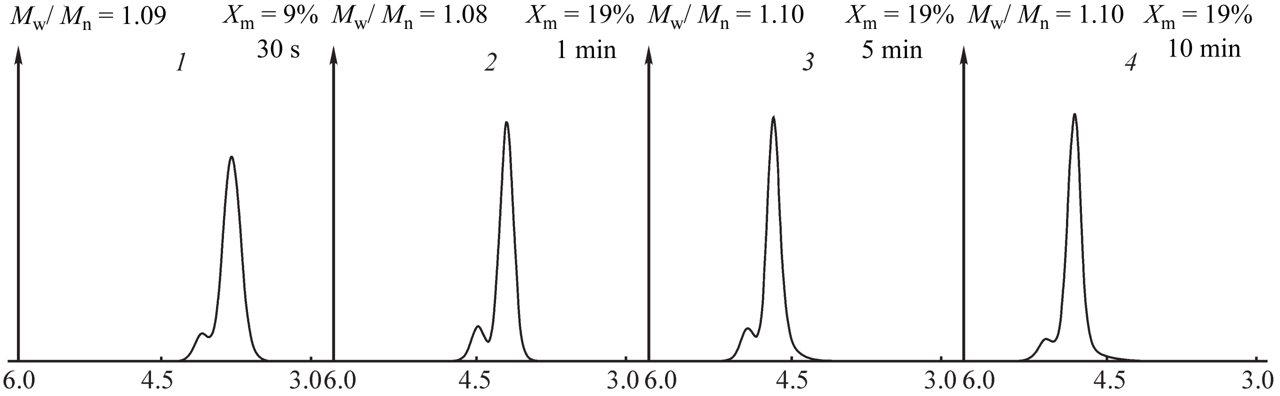


Fig. 4. Variation of the MMD curve of s-BSR prepared at the NBL to DTHFP molar ratio of 1 : 0.5 depending on the monomer conversion.

the 1,2-units from 58.3 to 64.5%, with the content of the 1,4-structures decreasing. A further increase in the 2,2'-ditetrahydrofurylpropane concentration in the system does not lead to significant changes in the copolymer microstructure. This fact is in good agreement with the data of Kozak and Matlengiewicz [8], who studied the 1,3-butadiene polymerization in the range of DTHFP to NBL molar ratios from 0.04 : 1 to 16.1 : 1 and reached the maximal content of vinyl structures of 67.5% (Fig. 5).

In the final step of the study, we synthesized an s-BSR sample under the action of the ternary initiating system at the NBL : AMD : DTHFP molar ratio of 1 : 1 : 0.5 and performed physicomechanical tests of the rubber obtained and of vulcanized rubbers based on it. For comparative evaluation of the final properties of the laboratory specimen, we used Nipol NS 616, a demanded grade of functionalized solution butadiene–styrene rubber (Zeon, Japan). As can be seen (Table 2), the vulcanization characteristics of rubber stocks based on the rubber samples studied are similar, whereas the characteristics of the vulcanized product (tensile strength and relative elongation) obtained from the laboratory s-BSR exceed those of the imported analog. The elastic hysteresis properties of the vulcanized rubbers prepared from the rubber samples under consideration are also comparable.

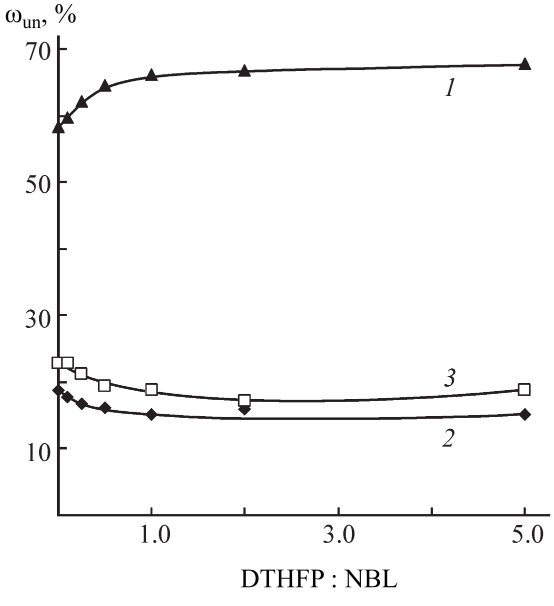


Fig. 5. Content of butadiene units of different configurations, ω_{un}, in the copolymer as a function of the DTHFP : NBL molar ratio. Units: (*1*) 1,2-, (*2*) *cis*-1,4-, and (*3*) *trans*-1,4-.

CONCLUSIONS

(1) Copolymerization of 1,3-butadiene and styrene in hexane under the action of a ternary initiating system consisting of *n*-butyllithium, a mixture of amine-containing alkali and alkaline earth metal alcoholates, and 2,2'-ditetrahydrofurylpropane was studied.

Table 2. Effect of AMD and DTHFP on the kinetic parameters of the 1,3-butadiene and styrene copolymerization under the action of *n*-butyllithium

AMD : NBL molar ratio	DTHFP : NBL molar ratio	Initiation rate constant k_i	Propagation rate constant k_p
mol : mol		L mol^{-1} min^{-1}	
0 : 1	0 : 1	0.23	7.50
1 : 1	0 : 1	0.62	41.83
0 : 1	0.5 : 1	1.81	101.79
1 : 1	0.5 : 1	2.63	150.00

(2) Introduction of 2,2'-ditetrahydrofurylpropane into the initiating system increases the copolymerization rate and makes the copolymerization constants of 1,3-butadiene and styrene closer to each other.

(3) The suggested initiating system allows synthesis of a copolymer with narrow molecular-mass distribution and high content of 1,2-units in the butadiene moiety.

(4) Physicomechanical tests of a laboratory s-BSR specimen were performed. The butadiene–styrene rubber prepared under the action of the suggested initiating system is similar to one of the most demanded imported analogs in the set of vulcanization, strength, and elastic hysteresis characteristics of vulcanized rubbers based on it.

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