



---

Soviet-era science, translated into English

# CHEMISTRY

L. S. BRESLER, Corresponding Member of the Academy of Sciences of the USSR, B. A. DOLGOPLOSK;

1963

SovietRxiv

---

View the original and related papers at <https://sovietrxiv.org/items/ru-196301.10979>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

## Abstract

## Full Text

CHEMISTRY

L. S. BRESLER, Corresponding Member of the Academy of Sciences of the USSR, B. A. DOLGOPLOSK;  
E. N. KROPACHEVA, K. V. NELSON, A. P. NIKITINA

# STUDY OF THE COPOLYMERIZATION PROCESS OF BUTADIENE-1,3 WITH 2,3-DIMETHYLBUTADIENE-1,3 IN THE PRESENCE OF VARIOUS IONIC-TYPE CATALYSTS

In the copolymerization of butadiene with isoprene by the cationic ( $\sim 1$ ) and anionic ( $\sim 2, \sim 3$ ) mechanisms, the relative activity of the monomers is determined by their polarity (the magnitude of the electron density on the double bonds, which can be estimated from the value of the Alfrey and Price  $Q - e$  scheme ( $\sim 4$ )). The copolymerization of butadiene and isoprene under the action of complex organometallic catalysts differs substantially from both typical anionic and cationic polymerization not only in the structure of the polymers formed, but also in the relative activities of the monomers ( $\sim 5$ ).

In the present work the relative activities of butadiene and 2,3-dimethylbutadiene in copolymerization under the influence of an anionic-type catalyst (the complex of butyllithium with tetrahydrofuran), a cationic-type catalyst (ethylchloroaluminum in the presence of hydrogen chloride), and complex organometallic catalysts—the systems  $\text{Al}(\textit{iso}\text{-C}_4\text{H}_9)_3 + \text{TiCl}_4$  and  $\text{Al}(\textit{iso}\text{-C}_4\text{H}_9)_2\text{Cl} +$  the complex  $\text{CoCl}_2$  with ethyl alcohol—were studied. The microstructure of the polymers obtained with the aid of the indicated systems was also investigated.

### Table 1

Dependence of the glass-transition temperature of copolymers of butadiene and 2,3-dimethylbutadiene, obtained under the action of the catalytic systems  $\text{Al}(\textit{iso}\text{-C}_4\text{H}_9)_3 + \text{TiCl}_4$  (I) and  $\text{Al}(\textit{iso}\text{-C}_4\text{H}_9)_2\text{Cl} + \text{CoCl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$  (II), on the composition of the copolymer

Content in the polymer, mol. %	Content in the polymer, mol. %	$T_g$ of copolymers obtained under the action of the system, °C	$T_g$ of copolymers obtained under the action of the system, °C
butadiene	2,3-dimethylbutadiene	I	II
0	100	-14 <sup>(6)</sup>	-4 <sup>(6)</sup>
30	70	-	-30
40	60	-50	-
60	40	-	-51
70	30	-76	-
80	20	-	-68
85	15	-85	-
100	0	-105 <sup>(9)</sup>	-110

For studying the composition of the copolymer, butadiene labeled with carbon C<sup>14</sup> was used. The procedure for preparing the catalysts, conducting the experiments, investigating the polymers, and calculating the copolymerization constants has been described previously (<sup>1</sup>, <sup>3</sup>, <sup>5</sup>). The microstructure of the polymers was investigated from the IR spectra of nonradioactive samples, recorded in a carbon disulfide solution on a UR-10 infrared spectrometer with a NaCl prism. The procedure made it possible to carry out a semi-quantitative estimate of the content in the copolymers of units of different configuration. The following were adopted as analytical bands: for butadiene-1,2 units, the band 909 cm<sup>-1</sup>; 1,4-cis, the band 740 cm<sup>-1</sup>; 1,4-trans, 967 cm<sup>-1</sup>; for 1,2-units of 2,3-dimethylbutadiene, 887 cm<sup>-1</sup>; for 1,4-units of dimethylbutadiene, the band 1200 cm<sup>-1</sup>.

It was established earlier, using butadiene and isoprene as an example, that the glass-transition temperature of a mixture of homopolymers is close to the glass-transition temperature of the homopolymer present in excess, whereas the glass-transition temperature of a copolymer changes monotonically as its

composition <sup>1</sup>. The glass-transition temperature of the polymerization product of mixtures of butadiene and 2,3-dimethylbutadiene under the action of catalytic systems I and II decreases monotonically as the butadiene content in it increases, which proves the formation under these conditions of true copolymers rather than mixtures of homopolymers (Table 1). A mixture of homopolymers obtained with the aid of catalytic system II has a glass-transition temperature close to the glass-transition temperature of the homopolymer present in excess (Table 2), in agreement with results obtained earlier <sup>2</sup>.

**Table 2**

<sup>1</sup>Reference marker as printed on the page.

<sup>2</sup>Reference marker as printed on the page.

**Glass-transition temperature of mixtures of polybutadiene and poly(2,3-dimethylbutadiene) obtained in the presence of**

$\text{Al}(\text{iso-C}_4\text{H}_9)_2\text{Cl} + \text{CoCl}_3 \cdot \text{C}_2\text{H}_5\text{OH}$

Content in the mixture, mol. %	Content in the mixture, mol. %	$T_g$ of mixture, °C
polybutadiene	polydimethylbutadiene	
0	100	-4 <sup>3</sup>
30	70	-12
70	30	-109
100	0	-110

Data on the dependence of the composition of the butadiene copolymer on the composition of the initial monomer mixture are presented in Fig. 1 and in Table 3.

In the cationic mechanism of polymerization (under the action of  $\text{C}_2\text{H}_5\text{AlCl}_2 + \text{HCl}$ ) the more active monomer is 2,3-dimethylbutadiene, which has the higher electron density on the double bonds ( $e = -1.88$ ); in anionic polymerization (under the action of  $\text{LiC}_4\text{H}_9$  in the presence of tetrahydrofuran) butadiene is more active (with a lower electron density on the double bonds,  $e = -1.05$ ).

**Fig. 1.** Dependence of the composition of the copolymer on the composition of the initial mixture of butadiene and 2,3-dimethylbutadiene in the presence of various catalysts.

1  $-\text{LiC}_4\text{H}_9$  (1 mol. % per monomer) + tetrahydrofuran (35 mol. % per monomer), at 20°; 2  $-\text{TiCl}_4$  (0.3 mol. % per monomer) +  $\text{Al}(\text{iso-C}_4\text{H}_9)_3$  (0.6 mol. % per monomer) at 30°, 1 M solution of monomers in benzene; 3  $-\text{CoCl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$  (0.01 mol. % per monomer) +  $\text{ClAl}(\text{iso-C}_4\text{H}_9)_2$  (1 mol. % per monomer), at 30°, 2 M solution of monomers in benzene; 4  $-\text{C}_2\text{H}_5\text{AlCl}_2$  (0.2 mol. % per monomer) +  $\text{HCl}$  (0.2 mol. % per monomer), at 12°, 1 M solution of monomers in benzene.

**Fig. 2.** IR absorption spectra of polymers obtained in the presence of  $\text{TiCl}_4 + \text{Al}(\text{iso-C}_4\text{H}_9)$ ;

a  $-\text{polybutadiene}$ , b  $-\text{copolymer of 65 mol. \% butadiene with 35 mol. \% dimethylbutadiene}$ , c  $-\text{copolymer of 85 mol. \% butadiene with 15 mol. \% dimethylbutadiene}$ .

The copolymer formed in the presence of complex catalysts (systems I and II) is somewhat enriched in butadiene compared with the initial monomer mixture. The relative activity of 2,3-dimethylbutadiene in addition to the active terminal butadiene unit of the growing chain, measured by the value  $1/r_1$ , is somewhat lower than in isoprene (the values of  $r_1$  in the copolymerization of butadiene with isoprene under the action of catalytic systems I and II are, respectively, 1.0

<sup>3</sup>Reference marker as printed on the page.

and 2.3; for dimethylbutadiene, 2.16 and 2.71). This phenomenon is probably associated with an increase in steric hindrance in

transition from isoprene to 2,3-dimethylbutadiene; it is known that steric factors have a great influence on the relative activity of monomers during polymerization under the action of complex organometallic catalysts (<sup>7</sup>, <sup>8</sup>).

Figs. 2 and 3 show infrared absorption spectra of copolymers obtained, respectively, in the presence of catalytic systems I and II.

**Table 3**

**Copolymerization constants of butadiene ( $r_1$ ) and 2,3-dimethylbutadiene ( $r_2$ ) in the presence of various catalysts**

Catalyst	$r_1$	$r_2$	Error in determining the constants, %
LiC <sub>4</sub> H <sub>9</sub> + (CH <sub>2</sub> ) <sub>4</sub> O	43.8	0.65	26
Al(iso-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> + TiCl <sub>4</sub>	2.16	0.392	9.2
Al(iso-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Cl + CoCl <sub>2</sub> (alcohol complex)	2.71	1.13	4.5
Al(C <sub>2</sub> H <sub>5</sub> )Cl <sub>2</sub> + HCl	0.053	4.24	9.7

Under the influence of catalytic system I, copolymers are formed whose structure does not differ from the structure of homopolymers obtained under the same conditions (the content of 1,2-units in the butadiene part of the copolymer chain, as in the homopolymer (<sup>9</sup>), does not exceed 4%; in the dimethylbutadiene part of the chain, as in the corresponding homopolymer (<sup>10</sup>), 1,2-units are not present). The same results were obtained in the copolymerization of isoprene and butadiene under the action of the indicated system (<sup>5</sup>).

In copolymerization under the action of the "cobalt" system, introduction of 2,3-dimethylbutadiene into the monomer mixture causes the formation of polymers with a high content of pendant vinyl groups (1,2-units of butadiene) and isopropenyl groups (1,2-units of dimethylbutadiene). Polybutadiene obtained in the presence of catalytic system II contains about 95% cis-1,4-units and only up to 5% 1,2-units (<sup>11</sup>); however, as dimethylbutadiene units are introduced into the copolymer, the content of 1,2-units in the butadiene part of the chain increases to 50% (at 15 mol.% dimethylbutadiene in the copolymer) and to 80% (at 70

Fig. 3. IR absorption spectra of polymers obtained in the presence of  $\text{CoCl}_2 \cdot \text{C}_2\text{H}_5\text{OH} + \text{Al}(\text{iso-C}_4\text{H}_9)_2\text{Cl}$ ; *a*—polybutadiene, —polydimethylbutadiene, —copolymer of 35 mol.% butadiene with 65 mol.% dimethylbutadiene, —copolymer of 60 mol.% butadiene with 40 mol.% dimethylbutadiene, —copolymer of 85 mol.% butadiene with 15 mol.% dimethylbutadiene

Figure 1: Fig. 3. IR absorption spectra of polymers obtained in the presence of  $\text{CoCl}_2 \cdot \text{C}_2\text{H}_5\text{OH} + \text{Al}(\text{iso-C}_4\text{H}_9)_2\text{Cl}$ ; *a*—polybutadiene, —polydimethylbutadiene, —copolymer of 35 mol.% butadiene with 65 mol.% dimethylbutadiene, —copolymer of 60 mol.% butadiene with 40 mol.% dimethylbutadiene, —copolymer of 85 mol.% butadiene with 15 mol.% dimethylbutadiene

mol.% dimethylbutadiene in the copolymer); conversely, an increase in the butadiene content in the copolymer leads to a decrease in the content of 1,2-units of dimethylbutadiene in the polymer (40% 1,2-units in polydimethylbutadiene and 25% of the same units at a content of 30% butadiene in the polymer).

The dependence of the microstructure on the composition of the copolymer obtained in the presence of the “cobalt” system was also observed for copolymers of butadiene with isoprene (<sup>5</sup>, <sup>12</sup>).

**Fig. 3.** IR absorption spectra of polymers obtained in the presence of  $\text{CoCl}_2 \cdot \text{C}_2\text{H}_5\text{OH} + \text{Al}(\text{iso-C}_4\text{H}_9)_2\text{Cl}$ ; *a*—polybutadiene, *b*—polydimethylbutadiene, *c*—copolymer of 35 mol.% butadiene with 65 mol.% dimethylbutadiene, *d*—copolymer of 60 mol.% butadiene with 40 mol.% dimethylbutadiene, *e*—copolymer of 85 mol.% butadiene with 15 mol.% dimethylbutadiene.

In the present investigation, using mixtures of butadiene and 2,3-dimethylbutadiene as an example, it has been shown that the principal regularities of the copolymerization process

in coordination-ionic systems have fundamental differences from the regularities characteristic of anionic and cationic systems.

Research Institute of Synthetic Rubber  
named after S. V. Lebedev

Received  
17 V 1963

## REFERENCES

1. L. S. Bresler, B. A. Dolgoplosk, E. N. Kropacheva, DAN, **149**, 595 (1963).
2. G. V. Rakova, A. A. Korotkov, DAN, **119**, 982 (1958).
3. L. S. Bresler, B. A. Dolgoplosk et al., DAN, **144**, 347 (1962).

4. L. J. Young, J. Polym. Sci., **54**, 411 (1961).
5. L. S. Bresler, B. A. Dolgoplosk et al., Vysokomolek. soed., **5**, 357 (1963).
6. A. I. Spasskova, Do Tszyan-bai, ZhPKh, **35**, 2786 (1962).
7. J. Natta, I. Paskuon, Kinetika i kataliz, **3**, 805 (1962).
8. F. Danusso, Chimica Industria, **44**, 611 (1962).
9. B. D. Babitskii, B. A. Dolgoplosk, V. A. Krol, Khim. nauka i prom., **2**, 393 (1957).
10. T. F. Yen, J. Polym. Sci., **35**, 533 (1959).
11. B. A. Dolgoplosk, E. N. Kropacheva et al., DAN, **135**, 847 (1960).
12. J. Pasquon, L. Porri et al., Chimica Industria, **43**, 509 (1961).

*Note: Figure translations are in progress. See original paper for figures.*

*Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.*