Chemistry

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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STUDY OF THE COPOLYMERIZATION PROCESS OF BUTADIENE WITH ISOPRENE IN THE PRESENCE OF VARIOUS IONIC-TYPE CATALYSTS

The mechanism of polymerization under the influence of Ziegler systems still appears insufficiently clear; however, it may be considered established that the process has an ionic character. Chain growth is thought to proceed along a polarized C—Me bond by an anionic type ([1]-[3]), or in ion pairs by a cationic type ([4]). It is known that the copolymerization constants, which characterize the relative reactivity of monomers, are in direct dependence on the nature of the active centers. For cationic and anionic mechanisms of chain growth, the dependence of the reactivity of monomers on their structure has an antibatic character. The copolymerization constants, as is known for organometallic compounds of alkali metals, are also to some extent dependent on the degree of polarization of the C—Me bond, which is determined by the nature of the metal and by the presence of electron-donor impurities that form complexes with the polymerization initiator, etc. ([5]).

Therefore, the study of copolymerization constants in a number of cases is very important for determining the nature of the process. In order to establish what place, among other types of ionic polymerization, is occupied by polymerization under the action of complex organometallic catalysts, we studied the copolymerization of butadiene with isoprene under the influence of anionic-type catalysts—complexes of butyllithium with tetrahydrofuran and triethylamine ([6]), of the cationic catalyst—ethylaluminum dichloride in the presence of hydrogen chloride, and of complex organometallic catalysts—the systems Al(iso-$C_4H_9)_3$ + $TiCl_4$ and Al(iso-$C_4H_9)_2$Cl + an alcohol complex of $CoCl_2$ ([7]).

Fig. 1. Dependence of the copolymer composition on the composition of the initial monomer mixture for the catalysts:
1 —LiC_4H_9 + $(CH_2)_4O$,
2 —LiC_4H_9 + $N(C_2H_5)_3$,
3 —Al(iso-$C_4H_9)_2$Cl + $CoCl_2$ (in benzene solution),
4 —Al(iso-$C_4H_9)_2$ + $TiCl_4$ (in benzene solution),

Fig. 2. Polymer yield with time during homopolymerization in benzene solutions of butadiene (1, 2) and isoprene (3, 4) under the action of: 1, 3 –Al(iso-C4H9)2Cl + CoCl2, 2, 4 –Al(iso-C4H9)3 + TiCl4.

Figure 2: Fig. 2. Polymer yield with time during homopolymerization in benzene solutions of butadiene (1, 2) and isoprene (3, 4) under the action of: 1, 3 –Al(iso-C4H9)2Cl + CoCl2, 2, 4 –Al(iso-C4H9)3 + TiCl4.

5 –$AlCl_2C_2H_5$ + HCl (polymerization conditions: monomers in benzene solution, 20 wt.%; $[AlCl_2C_2H_5]/[HCl] = 1$ (mol); temperature 12°, $[AlCl_2C_2H_5]/[\text{monomer}] = 1 : 400$ or $1 : 800$)

For studying the copolymer composition, butadiene labeled with C^{14} was used. The procedure for carrying out the experiments, studying the polymers, and calculating the copolymerization constants was given in previous communications ([6],[7]). The microstructure of homopolymers and copolymers of butadiene with isoprene was investigated by infrared spectroscopy ([8]) on nonradioactive— samples.* Experiments with nonradioactive monomer were carried out in a thermostated autoclave, with samples taken during the course of the process to determine the polymer yield as a function of time.

The dependence of the composition of the copolymer obtained under the action of various catalytic systems on the composition of the initial monomer mixture is presented in Fig. 1. Copolymers formed under the action of butyllithium complexes with electron-donor additives are enriched in butadiene as compared with the initial monomer mixture; copolymers obtained with the aid of a cationic-type catalyst are enriched in isoprene. In the presence of complex organometallic catalysts, copolymers are formed whose composition is close to that of the initial monomer mixture.

Fig. 2. Polymer yield with time during homopolymerization in benzene solutions of butadiene (1, 2) and isoprene (3, 4) under the action of:
1, 3 –$Al(iso\text{-}C_4H_9)_2Cl + CoCl_2$,
2, 4 –$Al(iso\text{-}C_4H_9)_3 + TiCl_4$.

From the data of Fig. 1, the copolymerization constants for butadiene with isoprene, given in Table 1, were calculated. Since the electron density at the double bonds in isoprene is higher than in butadiene (because of the presence of the methyl group), it could be expected that the reactivity of isoprene would be higher than that of butadiene in the case of cationic polymerization, and lower than that of butadiene in anionic polymerization. The data obtained by us agree with these concepts: $r_1 < r_2$ for the catalyst based on aluminum ethyl dichloride and $r_1 > r_2$ for catalysts containing butyllithium.

From the values of the copolymerization constants of butadiene with isoprene under the action of complex organometallic catalysts $Al(iso\text{-}C_4H_9)_3 + TiCl_4$ and $Al(iso\text{-}C_4H_9)_2Cl + CoCl_2$, it may be concluded that in this case the copolymerization process differs sharply both from the usual cationic process and from the anionic one. Judging from the overall rate of homopolymerization, it could have been expected that butadiene is a more active monomer than isoprene in the case of polymerization under the action of the "cobalt" catalyst, and somewhat less active than isoprene for the catalyst based on $TiCl_4$ (Fig. 2). However, the copolymerization constants are close to 1 ($r_1 \simeq r_2 \simeq 1$). It follows from this that the rates of addition of either of the two monomers to a given terminal unit are approximately equal to each other:

$$r_1 = 1 = k_{11}/k_{12}; \quad r_2 = 1 = k_{22}/k_{21}; \quad k_{11} = k_{12}; \quad k_{22} = k_{21}.$$

It may be assumed that identical values of the relative

Table 1

Copolymerization constants of butadiene (r_1) and isoprene (r_2) in the presence of various catalysts

Catalyst	r_1	r_2	Error in determination, %
LiC_4H_9 + $(CH_2)_4O$	4.5	0.13	15
LiC_4H_9 + $N(C_2H_5)_3$	3.6	0.11	17
Al(iso-C_4H_9)$_2$Cl+ $CoCl_2$ (alcohol complex)	2.3	1.15	4.3
Al(iso-C_4H_9)$_3$+ $TiCl_4$	1.0	1.0	5
$Al(C_2H_5)Cl_2$+ HCl	0.12	3.4	12

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* Studies of the microstructure of the polymers were carried out by K. V. Nelson and G. S. Solodovnikova, to whom the authors express their gratitude.

Table 2

Structure of the polymer chain during polymerization of butadiene and isoprene in the presence of ionic catalysts

Catalyst	Content in polymer, mol. % C_4H_6	Content in polymer, mol. % C_5H_8	Percent of total number of butadiene units 1,2	Percent of total number of butadiene units 1,4-trans	Percent of total number of butadiene units 1,4-cis	Percent of total number of isoprene units 1,2	Percent of total number of isoprene units 3,4	Percent of total number of isoprene units 1,4-units
$LiC_4H_9 + (CH_2)_4O$	100 [1]	–	80	10	10	–	–	–
$LiC_4H_9 + (CH_2)_4O$	50	50	many	few	–	–	many	–
$LiC_4H_9 + (CH_2)_4O$	–	100 [2]	–	–	–	31	69	–
Al(*iso*-$C_4H_9)_2Cl$ + $CoCl_2 \times C_2H_5OH$ [3]	100 [4]	–	4	4	92	–	–	–
Al(*iso*-$C_4H_9)_2Cl$ + $CoCl_2 \times C_2H_5OH$ [3]	79	21	17.5	7.5	75	–	5	95
Al(*iso*-$C_4H_9)_2Cl$ + $CoCl_2 \times C_2H_5OH$ [3]	60	40	39	3	58	–	15	85

Catalyst	Content in polymer, mol. % C_4H_6	Content in polymer, mol. % C_5H_8	Percent of total number of butadiene units 1,2	Percent of total number of butadiene units 1,4-trans	Percent of total number of butadiene units 1,4-cis	Percent of total number of isoprene units 1,2	Percent of total number of isoprene units 3,4	Percent of total number of isoprene units 1,4-units
Al(*iso*-$C_4H_9)_2Cl$ + $CoCl_2$ × C_2H_5OH 3	29	71	37	0	63	–	27	73
Al(*iso*-$C_4H_9)_2Cl$ + $CoCl_2$ × C_2H_5OH 3	–	100	–	–	–	3	31	66
Al(*iso*-$C_4H_9)_3$ + $TiCl_4$ 3	100 [5]	–	5	25	70	–	–	–
Al(*iso*-$C_4H_9)_3$ + $TiCl_4$ 3	75	25	3	23	74	–	3	97
Al(*iso*-$C_4H_9)_3$ + $TiCl_4$ 3	50	50	3	21	76	–	3.5	96.5
Al(*iso*-$C_4H_9)_3$ + $TiCl_4$ 3	25	75	3	28	69	–	2	98

Fig. 3. Absorption spectrum in the infrared region of copolymers obtained from an equimolar mixture of butadiene and isoprene: 1 –for the catalyst $AlCl_2C_2H_5$ + HCl, 2 –for the catalyst LiC_4H_9 + $(CH_2)_4O$

Figure 3: Fig. 3. Absorption spectrum in the infrared region of copolymers obtained from an equimolar mixture of butadiene and isoprene: 1 –for the catalyst $AlCl_2C_2H_5$ + HCl, 2 –for the catalyst LiC_4H_9 + $(CH_2)_4O$

Catalyst	Content in polymer, mol. % C_4H_6	Content in polymer, mol. % C_5H_8	Percent of total number of butadiene units 1,2	Percent of total number of butadiene units 1,4-trans	Percent of total number of butadiene units 1,4-cis	Percent of total number of isoprene units 1,2	Percent of total number of isoprene units 3,4	Percent of total number of isoprene units 1,4-units
Al(*iso*-$C_4H_9)_3$ + $TiCl_4$ [3]	–	100 [6]	–	–	–	–	2	98

[1] According to data of (10). [2] According to data of (11). [3] All 1,2-units in the copolymer are assigned to the butadiene part of the chain. [4] According to data of (15). [5] According to data of (17). [6] According to data of (13).

differences in the activity of butadiene and isoprene during copolymerization arise as a consequence of special conditions of chain growth on the active complex, when the rate of addition of a monomer molecule to the active chain end is determined mainly not by the nature of the monomer but by the nature of the active terminal unit of the chain. Thus, although addition to an isoprene and to a butadiene chain end apparently proceeds at different rates, in each case the rates of addition of isoprene and butadiene molecules to a terminal unit of a given type (for example, a butadiene one) are equal to one another. A similar explanation was previously proposed by Pasquon and co-workers, who obtained results analogous to ours in studying the copolymerization of butadiene with isoprene in toluene solution in the presence of cobalt diethylacetonate and aluminum diethyl chloride (9). The determining role of active terminal chain units is also manifested in their influence on the microstructure of the units during copolymerization on the "cobalt" system.

Fig. 3. Absorption spectrum in the infrared region of copolymers obtained from an equimolar mixture of butadiene and isoprene: 1 –for the catalyst $AlCl_2C_2H_5$

+ HCl, 2 –for the catalyst LiC_4H_9 + $(CH_2)_4O$.

The microstructure of the chain of homopolymers and copolymers depends on the nature of the catalyst used (Table 2, Fig. 3). As is known, in the presence of anionic catalysts butadiene polymerizes predominantly in the 1,2-position ([10]), and isoprene in the 3,4-position ([11]). In the infrared spectrum of the copolymer obtained by us with the aid of the catalytic com-

of the butyllithium complex with tetrahydrofuran, an absorption band is present at 1630 cm^{-1}, corresponding to external double bonds, and the band at 1650 cm^{-1} (internal double bonds) is absent.

Butadiene units of the 1,4-trans configuration are present only in an insignificant amount (weak absorption in the region of 967 cm^{-1}). Thus, in the copolymer of isoprene with butadiene obtained in the presence of an anionic catalyst, the monomer units have the same structure as in the corresponding homopolymers. The chain structure of the copolymer obtained in the presence of a cationic catalyst likewise corresponds to the structure of the homopolymers [12] (predominance of trans-1,4 units—absorption in the region of 965 cm^{-1}).

The complex organometallic catalysts selected by us are the most stereospecific for the preparation of cis-2,4 polymers: the catalytic system $Al(iso\text{-}C_4H_9)_3$ + $TiCl_4$ for preparing cis-1,4-polyisoprene [13,14], and the system $Al(iso\text{-}C_4H_9)_2Cl$ + $CoCl_2$ for preparing cis-1,4-polybutadiene [15,16].

Polymerization of butadiene under the action of $Al(iso\text{-}C_4H_9)_3$ + $TiCl_4$ leads to formation of a 1,4-polymer containing cis and trans units [17]. Polyisoprene obtained under the action of a $CoCl_2$-based catalyst contains 30% 3,4 units [7]. It should be noted that whereas the structure of the butadiene units in the copolymer and homopolymer obtained with the $TiCl_4$–$Al(iso\text{-}C_4H_9)_3$ system is the same, with the $CoCl_2$–$Al(iso\text{-}C_4H_9)_2Cl$ system the structure of the units in the copolymers differs substantially from the structure of the corresponding homopolymers (Table 2). As the isoprene content in the copolymer increases, the regularity of the structure of the butadiene portion of the chain decreases (the content of 1,2 units increases) and that of the isoprene portion of the chain decreases (the amount of 3,4 units increases). A similar phenomenon was also noted in the work of Pasquon et al. [9].

The change in the structure of the butadiene portion of the chain upon introduction of isoprene is apparently connected with the directing action of the preceding monomer unit.

The values of the copolymerization constants obtained by us and the data on the structure of the homopolymers and copolymers of butadiene with isoprene show that complex organometallic catalysts differ substantially from both typical anionic and cationic systems.

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