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Abstract

Full Text

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POLYMERIZATION OF CIS- AND TRANS-PIPERYLENE UNDER THE INFLUENCE OF COORDINATION CATALYTIC SYSTEMS

It was shown earlier that the copolymerization constants of butadiene with isoprene ([1,2]) and 2,3-dimethylbutadiene ([3]) under the influence of the complex catalyst R_2AlCl—$CoCl_2$ differ little from one another.

In the present investigation, piperylene was first used as the second monomer; according to chromatographic analysis it contained 65% trans isomer and 35% cis isomer. The procedure for carrying out the polymerization, for studying the copolymers formed, and for analyzing the composition of the copolymer obtained using butadiene labeled with C^{14} has been described in previous communications ([1–3]).

It was established preliminarily that the glass-transition temperature of copolymers of butadiene with piperylene decreases monotonically as the content of butadiene units increases, whereas the glass-transition temperature of a mixture of the corresponding homopolymers corresponds to the glass-transition temperature of the component present in excess (Table 1). Thus it was shown

Table 1

Glass-transition temperature of copolymers of butadiene with piperylene and of mixtures of homopolymers obtained in the presence of a "cobalt" catalyst

Content in copolymer, mol. %	Content in copolymer, mol. %	$-T_g$ of copolymer, °C	Content in mixture, mol. %	Content in mixture, mol. %	$-T_g$ of mixture, °C
butadiene	piperylene		polybutadiene	polypiperylene	
100	0	110	100	0	110
90	10	102	70	30	109
80	20	96	30	70	43
0	100	43	0	100	43

Table 2

Crystallinity at 30° of copolymers of butadiene with piperylene

Piperylene content in polymer, mol. %	Intrinsic viscosity in benzene at 25°	Crystallization rate, %/h	Crystallization time, min.	Depth of crystallization, %
0	1.85	13.8	9	2.3
3	1.93	1.3	110	1.8
5	2.04	0.1	1100	1.4
10	1.98	does not crystallize in 600 min.	does not crystallize in 600 min.	does not crystallize in 600 min.

the formation of true copolymers rather than mixtures of homopolymers. The formation of true copolymers is also indicated by the sharp decrease in crystallinity as compared with polybutadiene when piperylene units are introduced into the polymer (Table 2)*.

In studying the dependence of the copolymer composition on the composition of the monomer mixture, it was found that the copolymer is much more enriched in butadiene relative to the starting mixture than are the copolymers of butadiene with isoprene and 2,3-dimethylbutadiene. The indicated differences of piperylene from other dienes could be connected with the different activity of its geometric isomers in the polymerization process. To test this assumption, on the basis of the reaction of trans-piperylene with maleic anhydride ([4]), piperylene containing 85% cis isomer was prepared; by careful recti-

* The crystallinity study was carried out by A. I. Mareev and G. E. Novikova using a dilatometric method.

Table 3

Polymer yield in the polymerization of piperylene isomers and their mixtures with butadiene

Catalytic system	Monomer composition, mol. %: piperylene	Monomer composition, mol. %: butadiene	Piperylene composition, %: cis	Piperylene composition, %: trans	Polymerization time, h	Yield calculated per monomer taken, %: by piperylene	Yield calculated per monomer taken, %: by butadiene
Al(iso-$C_4H_9)_2Cl$ + $CoCl_2 \cdot C_2H_5OH$	0	100	–	–	24	–	100
Al(iso-$C_4H_9)_2Cl$ + $CoCl_2 \cdot C_2H_5OH$	100	0	85	15	24	10	–
Al(iso-$C_4H_9)_2Cl$ + $CoCl_2 \cdot C_2H_5OH$	100	0	97.5	2.5	24	2.5	–
Al(iso-$C_4H_9)_2Cl$ + $CoCl_2 \cdot C_2H_5OH$	100	0	6	94	24	95	–
Al(iso-$C_4H_9)_2Cl$ + $CoCl_2 \cdot C_2H_5OH$	50	50	85	15	0.75	15	81
Al(iso-$C_4H_9)_2Cl$ + $CoCl_2 \cdot C_2H_5OH$	100	–	97.5	2.5	24	4	–
Al(iso-$C_4H_9)_3$ + $TiCl_4$	100	–	6	94	24	92	–
Al(iso-$C_4H_9)_3$ + $TiCl_4$							

fractionation* a fraction containing 94% trans-piperylene was isolated, as well

as a fraction containing 97.5% cis-piperylene.

Homopolymerization of these piperylene samples, enriched in one of the isomers, showed that the maximum polymer yield does not exceed the content of the trans isomer (Table 3). In the polymerization of a mixture of equivalent amounts of labeled butadiene and piperylene of composition 85% cis isomer and 15% trans isomer, the polymer isolated after 45 min contained almost all of the butadiene introduced (81%) and only 15% of the piperylene taken. It follows from this that only trans-piperylene participates in the polymerization process. The copolymerization constants of trans-piperylene with butadiene are apparently close to the corresponding values for isoprene and 2,3-dimethylbutadiene, since from an equimolar mixture of all these monomers with butadiene, under the influence of the "cobalt" catalyst, copolymers are formed that contain equal amounts of butadiene (Table 4). The microstructure of the piperylene–butadiene copolymers differs from the microstructure of copolymers of butadiene with isoprene or 2,3-dimethylbutadiene. Introduction of isoprene or 2,3-dimethylbutadiene into the copolymer causes the appearance of 1,2 units in the butadiene part of the chain (1–3); conversely, in the butadiene part of the chains of copolymers with piperylene, 1,2 units are practically absent at any piperylene content.

Table 4

Composition of copolymers obtained from an equimolar mixture of butadiene with other dienes under the influence of the "cobalt"catalyst

Second monomer	Degree of polymerization, %	Butadiene in the copolymer, mol. %
Isoprene	10	61.7
2,3-Dimethylbutadiene	15	63
Trans-piperylene	19.5	60.1

In the presence of the catalytic system Al(iso-$C_4H_9)_3$ + $TiCl_4$ (at a molar ratio Al : Ti = 1.5), only trans-piperylene is likewise polymerized (Table 3).

A similar phenomenon was observed by Natta and co-workers in the polymerization of piperylene isomers under the influence of a coordination catalyst based on trialkylaluminum and a vanadium trichloride complex with tetrahydrofuran (5).

The inability of cis-piperylene to polymerize is apparently directly related to the specific features of the coordination polymerization process. If the first stage of the chain-growth reaction consists in the formation of a catalyst complex with the diene in the 1,4 position, then the methyl group—

* The mixture of cis- and trans-piperylene was distilled by V. G. Pines at the Efremov Synthetic Rubber Plant. Chromatographic analysis was carried out at VNIISK by B. I. Boguslavskaya.

schematic structures of complexes with trans- and cis-piperylene

Figure 1: schematic structures of complexes with trans- and cis-piperylene

of cis-piperylene in such a complex must be directed toward the catalyst, which creates greater steric hindrance. Thus, for the catalyst complex with the cis conformation of the monomer one may depict the following scheme (where all carbon atoms are in the plane of the drawing):

complex with trans-piperylene complex with cis-piperylene

All-Union Scientific Research Institute
of Synthetic Rubber
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Note: Figure translations are in progress. See original paper for figures.