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Abstract

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CHEMISTRY

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POLYMERIZATION OF HIGHER DIENE HYDROCARBONS

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In recent years, in the Soviet Union and the USA, polymers of isoprene have been synthesized which, in their set of properties, more closely approach natural rubber than other previously known synthetic rubbers ($^{1-5}$).

It was of interest to determine to what extent the high strength combined with high elasticity, characteristic of vulcanizates of natural rubber, is inherent in polymers of other diene hydrocarbons. For this purpose, polymers of 2-methylpentadiene-1,3, 2-ethylbutadiene-1,3, and 2-isopropylbutadiene-1,3 were synthesized.

2-Methylpentadiene-1,3 was obtained by contact conversion of a mixture of isopropyl alcohol and acetone over a modified S. V. Lebedev catalyst, according to the method of Yu. A. Gorin and A. A. Vasil' ev (^{6}). Its isolation from the mixture with other hydrocarbons was carried out by rectification on a laboratory column with an efficiency of 100 theoretical plates.

2-Ethylbutadiene-1,3 was obtained by the method with which Marvel and coworkers initially attempted to obtain this hydrocarbon (^{7})—with the difference that, for the dehydration of 2-ethyl-2-hydroxybutene-1, obtained as an intermediate product in this synthesis, not acidic potassium sulfate was used, but a catalyst prepared by impregnating pieces of coke with a solution of sodium dihydrogen phosphate, phosphoric acid, and butylamine phosphate (^{8}).

The yield of 2-ethylbutadiene-1,3 was 32.4% of the theoretical. 2-Isopropylbutadiene-1,3 was obtained by the method of Marvel (^{7,9}).

The monomers obtained were characterized by the following constants: 2-methylpentadiene-1,3, b.p. 75.5°/760 mm; n_D^{20} 1.4455, d_4^{20} 0.7179; 2-ethylbutadiene-1,3, b.p. 66.6°/760 mm; n_D^{20} 1.4328, d_4^{20} 0.7154; 2-isopropylbutadiene-1,3, b.p. 86–87°; n_D^{20} 1.4318, d_4^{20} 0.7252.

Table 1

Polymerization of alkylbutadienes

Monomer	Polymerization temp., °C	Polymerization method	Duration of process, h	Plasticity of polymer
2-Ethylbutadiene-1,3	50	Lithium	5	0.38
2-Ethylbutadiene-1,3	50	"	0.5	0.59
2-Ethylbutadiene-1,3	70	Butyl	0.08*	Indeterminate
2-Isopropylbutadiene-1,3	50	Lithium	4.5	0.37
2-Isopropylbutadiene-1,3	70	"	7	0.39
2-Methylpentadiene-1,3	50	"	16	0.66
2-Methylpentadiene-1,3	70	Butyl	7	0.62

* More precisely, 5 min.

In the polymerization of isoprene, in order to obtain a rubber analogous to natural rubber, other investigators used metallic lithium or a Ziegler catalyst as the initiator of the process (^{5}). In the polymerization of higher diene hydrocarbons we also used metallic lithium; in some experiments

Table 2

Properties of alkylbutadiene polymers

Polymer	Plasticity	T_g, °C	Strength, kg/cm^2	Relative elongation, %	Permanent elongation, %
Polyisoprene	0.35	−68	235	1180	14
Polyethylbutadiene	0.56	−76	200	1220	14
Polyisopropylbutadiene	0.36	−52	116	1080	16
Polymethylpentadiene	0.66	−28	200	620	14

Fig. 1. Rebound elasticity of vulcanizates of unfilled compounds. 1—2-ethylbutadiene-1,3, 2—2-isopropylbutadiene-1,3, 3—2-methylpentadiene-1,3

Figure 1: Fig. 1. Rebound elasticity of vulcanizates of unfilled compounds. 1—2-ethylbutadiene-1,3, 2—2-isopropylbutadiene-1,3, 3—2-methylpentadiene-1,3

butyllithium was used as the initiator. The polymerization was carried out in glass ampoules at temperatures from 50 to 100°. The degree of polymerization reached 98–100%.

As can be seen from the data presented in Table 1, the polymerization process of 2-ethylbutadiene-1,3 and 2-isopropylbutadiene-1,3 proceeds at a satisfactory rate.

The presence in the molecule of 2-methylpentadiene of a methyl group in the α-position to the double bond leads to a sharp slowing of the polymerization process. In polymerization in the presence of butyllithium, the process lasted 16 hours at 50° and 7 hours at 70°. The polymerization of 2-ethylbutadiene at 70° lasted 5 min.

The polymers obtained differ considerably from one another in glass-transition temperature (Table 2).

Fig. 1. Rebound elasticity of vulcanizates of unfilled compounds. 1—2-ethylbutadiene-1,3; 2—2-isopropylbutadiene-1,3; 3—2-methylpentadiene-1,3.

The polymer of methylpentadiene has a comparatively high glass-transition temperature; in it, for each unit added in the 1,4-position, there are two methyl groups. Polyisopropylbutadiene, which contains an isopropyl group in the unit, has a lower glass-transition temperature. Polyethylbutadiene has the lowest glass-transition temperature; it is even lower than the glass-transition temperature of natural rubber and polyisoprene.*

In terms of the strength of the vulcanizates of unfilled compounds, the polymers of ethylbutadiene and methylpentadiene differ little from polyisoprene. However, the polymers of methylpentadiene have low elasticity (Fig. 1). Polyethylbutadiene is not inferior to polyisoprene in elasticity either.

* As was previously shown by Marvel et al. (^{11}), the polymer of 2-ethylbutadiene-1,3 obtained by polymerization in emulsion also had a low glass-transition temperature (−70.5°).

These studies have shown that not only isoprene rubber but also polyethylbutadiene rubber possess high strength and high elasticity in the vulcanized state. In frost resistance, the latter somewhat surpasses isoprene rubber.

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