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Abstract

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Polymerization of 4-Phenylbutene-1 in the Presence of a Ziegler-Type Catalytic System

The present work, devoted to the study of the polymerization reaction of 4-phenylbutene-1 in the presence of a catalytic system consisting of triisobutylaluminum and titanium tetrachloride, is a continuation of our earlier published work on the polymerization of allylbenzene ([1]). The study of the polymerization of this monomer began comparatively recently. The first report on the polymerization of 4-phenylbutene-1 dates to 1942. Schmidt and Schoeller, in their work on obtaining lubricating oils by polymerization of a number of unsaturated compounds in the presence of aluminum chloride, obtained a liquid polymer of 4-phenylbutene-1. The degree of polymerization in this case was low and was only 3.1 ([2]). Recently, high-molecular-weight solid polymers of this monomer have been obtained and characterized ([3]-[5]).

[Figure 1 and Figure 2 graphs]

Fig. 1. Yield of poly-4-phenylbutene-1 as a function of temperature and of the ratio of catalyst components.
a –at 20°, *b* –at 70°

Fig. 2. Yield of liquid polymers of 4-phenylbutene-1 as a function of temperature and of the ratio of catalyst components.
a –at 20°, *b* –at 70°

4-Phenylbutene-1 was synthesized by the usual method from benzylmagnesium chloride and allyl bromide ([6]). The hydrocarbon yield was 65%. Its constants proved to be as follows: b.p. 65-70°/10-12 mm Hg, d_4^{20} 0.8895, n_D^{20} 1.5090. Molecular refraction: calculated 44.312; found 44.266.

The polymerization of 4-phenylbutene-1 was carried out in a glass reactor, in an atmosphere of dry nitrogen. The molar ratio of triisobutylaluminum to titanium tetrachloride was varied from 3 : 1 to 1 : 3. Most experiments were carried out at 20 and 70° and at normal pressure. A number of experiments were conducted at 60 and 90° with a ratio of triisobutylaluminum to titanium tetrachloride equal to 1 : 1. The duration of polymerization in all cases was 3 hours. Dry *n*-heptane was used as the solvent. After completion of the reaction, the polymer was precipitated with methanol. Triisobutylaluminum was used in the form of a prepared solution in *n*-heptane or in gasoline—kalosha. Its concentration was varied from 0.095 to 0.709 mol/l. The concentration of titanium tetrachloride, which was also used in the form of a heptane solution, was varied from 0.210 to 0.362 mol/l. Concentra-

the monomer concentration varied from 0.356 to 1.452 mol/l. The amount of solvent in all experiments was unchanged and was 100 ml.

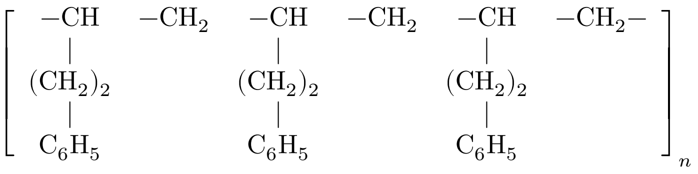
Figure 1 shows the dependence of the yield of solid polymer on the molar ratio of the catalyst components and on the temperature. If at 70° the character of this dependence remains the same as for allylbenzene (1), then at 20° the optimum shifts toward high ratios of triisobutylaluminum to titanium tetrachloride. As shown in Fig. 2, the yield of liquid polymers in both cases decreases as the ratio of triisobutylaluminum to titanium tetrachloride increases. The greatest monomer conversion takes place at low ratios of the catalyst components, although the bulk of the polymer then consists of a liquid low-molecular-weight product. Conversely, at high ratios of the catalyst components the monomer conversion is insignificant, but the product consists mainly of solid polymer.

Solid polymer of 4-phenylbutene-1 is a white powder with a softening temperature from 130 to 160°. Its solubility is considerably higher than that of polyallylbenzene. Thus, at room temperature it dissolves almost completely in benzene. Large amounts of it dissolve in acetone and ether.

Elemental analysis of the polymer gave the following results:

Found, %:	C 90.85; H 8.95
$(C_{10}H_{12})_n$. Calculated, %:	C 90.90; H 9.10

The average specific gravity of poly-4-phenylbutene-1, determined by the flotation method (7), was 1.025. The intrinsic viscosity of the crude polymer in benzene at 50° was found to be 1.39. X-ray analysis data showed that the polymer is an amorphous substance. Interpretation of the infrared spectrum of the polymer and comparison of it with the spectra of 2,3- and 2,4-dimethylalkanes showed that the linkage of the monomer units in the polymer chain is of the "head-to-tail" type*. We therefore believe that the structure of the polymer corresponds to the formula:



$$\left[\begin{array}{cccccc} -CH & -CH_2 & -CH & -CH_2 & -CH & -CH_2- \\ | & & | & & | & \\ (CH_2)_2 & & (CH_2)_2 & & (CH_2)_2 & \\ | & & | & & | & \\ C_6H_5 & & C_6H_5 & & C_6H_5 & \end{array}\right]_n$$

Individual samples and mixtures of samples of polymers obtained under various conditions were subjected to extraction fractionation with boiling solvents. This process was carried out in the same apparatus and by the same procedure as in the case of polyallylbenzene (1). In order to reveal the relationship between the fractional composition of the fractionated polymers and the temperature at which they were obtained, samples obtained, respectively, at 20, 70, and 90° were selected for fractionation. Unfortunately, because of the shortage of polymer obtained at 20° at a ratio of triisobutylaluminum to titanium tetrachloride equal to 1 : 1, for this fractionation it was necessary to select samples obtained at catalyst-component ratios of 2 : 1 and 3 : 1. The results of fractionation of these mixtures are given in Table 1.

Comparing the data of Table 1 and taking into account the fact that the acetone and ether fractions are relatively low-molecular-weight, it is easy to see that as the polymerization temperature increases there is a significant decrease in the content in the polymer of high-molecular-

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Table 1

Fractionation of a mixture of poly-4-phenylbutene-1 samples

Fraction no.	Fraction	Duration of fractionation, h	Weight of fraction, g	Relative amount of fraction, %	m.p., °C	Intrinsic viscosity *	Mol. weight **
Obtained at 20° and at various ratios of triisobutylaluminum to titanium tetrachloride							
1	Acetone	18	0.0628	9.30	38–56	–	–
2	Ether	18	0.0106	1.57	60–81	–	–
3	Benzene	18	0.6021	89.13	134–183	–	–

Fraction no.	Fraction	Duration of fractionation, h	Weight of fraction, g	Relative amount of fraction, %	m.p., °C	Intrinsic viscosity *	Mol. weight **
Obtained at 70° at a ratio of triisobutylaluminum to titanium tetrachloride of 1 : 1							
1	Acetone	18	0.2594	30.1	35–40	–	–
2	Ether	18	0.0507	5.9	75–90	–	–
3	Benzene	18	0.5359	62.2	139–145	–	–
4	Residue	–	0.0160	1.8	165–178	–	–
Obtained at 90° at a ratio of triisobutylaluminum to titanium tetrachloride of 1 : 1							
1	Acetone	20	2.50	48.1	58–68	0.0373	3,800
2	Ether	20	0.30	5.7	79–88	0.1310	27,000
3	Benzene	20	2.40	46.2	129–136	0.500	220,000

* In benzene at 50°.

** The molecular weight of the polymers was calculated by the Mark–Kuhn equation (see below).

molecular fractions. Thus, at 20° their proportion is about 90%, at 70° about 65%, and at 90° only about 50%. Accordingly, the proportion of low-molecular fractions increases with increasing temperature. Strictly speaking, such a comparison is valid only for data obtained at a ratio of triisobutylaluminum to titanium tetrachloride equal to 1 : 1. However, the general conclusion apparently does not contradict the regularity observed in polymerization. The absence of residue after fractionation of the polymer obtained at 20° with benzene is evidently also explained by the high ratios of triisobutylaluminum to titanium tetrachloride, since the highest-molecular products of polymerization are obtained at a catalyst-component ratio equal to 1 : 1.

In order to obtain a sufficient number of samples of poly-4-phenylbutene-1 fractions for determining the molecular weight and the coefficients of the Mark–Kuhn equation, we undertook fractionation of a mixture of individual samples of poly-4-phenylbutene-1 obtained under different conditions. The results of this fractionation are presented in Table 2.

Table 2

Fractionation of a mixture of poly-4-phenylbutene-1 samples

Fraction no.	Fraction	Duration of fractionation, h	Weight of fraction, g	Relative amount of fraction, %	m.p., °C	Intrinsic viscosity *	Mol. weight
1	Acetone	48	5.88	23.0	47–53	0.110	20,000
2	Ether	48	1.16	5.2	60–62	0.320	120,000
3	Benzene	120	15.17	68.4	145–150	1.14	720,000
4	Residue	–	0.77	3.4	165–180	–	–

* In benzene at 50°.

The molecular weights of the fractions were determined by the light-scattering method in benzene at 25° and at $\lambda = 546.1$ mμ*.

From the data in Table 2, coefficients were calculated for the Mark–Kuhn equation, which relates the intrinsic viscosity of a polymer to its molecular weight. These constants were found to be: $K = 1.91 \cdot 10^{-4}$ and $\alpha = 0.64$.

Thus, in the molecular-weight range from 20,000 to 720,000, the Mark–Kuhn equation for poly-4-phenylbutene-1 has the form:

$$[\eta] = 1.91 \cdot 10^{-4} \cdot M^{0.4}.$$

Using this equation, the molecular weights of the polymer fractions listed in Table 1 were calculated.

In addition to solid polymers, liquid polymers of 4-phenylbutene-1 were also obtained. They are viscous liquids ranging in color from yellow to brown, with a characteristic odor different from that of liquid polymers of allylbenzene. The molecular weight of the liquid products of 4-phenylbutene-1 polymerization ranged from 300 to 1400 (the molecular weight was determined cryoscopically in camphor by Rast' s method). The use of products of this type as lubricating oils has been described (^{5}).

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

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