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Abstract

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POLYMERIZATION OF ALLYLBENZENE IN THE PRESENCE OF A ZIEGLER-TYPE CATALYTIC SYSTEM

The aim of the present work was to obtain polymers of allylbenzene by means of a catalytic system consisting of titanium tetrachloride and triisobutylaluminum, and also to investigate certain properties of these polymers. Work with this monomer was of interest because polyallylbenzene is the second member of a polymer-homologous series: polystyrene, polyallylbenzene, poly-4-phenylbutene-1, and poly-5-phenylpentene-1, in which only polystyrene has been well studied.

The first attempt to polymerize allylbenzene in the presence of tin tetrachloride and thermally was undertaken by Staudinger in 1935 ([1]); it was not successful. In 1942 Schmidt and Scheller obtained an allylbenzene polymer in the presence of aluminum chloride with a degree of polymerization of about 6 ([2]). Other attempts to polymerize this monomer in the presence of various catalysts led to the preparation of low-molecular-weight products ([3],[4]). Only with the discovery of Ziegler–Natta type catalysts, consisting of aluminum alkyls and halides of transition metals, did it become possible to obtain high-molecular-weight products of the polymerization of allylbenzene ([5],[6]). These works give a brief characterization of the properties of this polymer.

The synthesis of the monomer was carried out by us according to the procedure of Gershberg ([7]), from phenylmagnesium bromide and allyl bromide. Allylbenzene obtained in this way in 80% yield had the following constants: d_4^{20} 0.8939, n_D^{20} 1.5129; b.p. 156–157°, 760 mm Hg.

Molecular refraction: calculated—39.694; found—39.69. For comparison we give the values obtained by Levina and Tsurikova ([8]): d_4^{20} 0.8924; n_D^{20} 1.5131; b.p. 156–157°, 751 mm Hg.

The polymerization of allylbenzene was carried out in a glass reactor, in an atmosphere of dry nitrogen, at various ratios of the catalyst components, at different temperatures, and with different reaction times. Dry *n*-heptane was used as solvent. After completion of the reaction, the polymer was precipitated with methanol. Triisobutylaluminum was used as a solution in "galosha" gasoline or in *n*-heptane. Its concentration was 0.0017–0.0033 mole/ml. Titanium tetrachloride was used as a solution in *n*-heptane. The concentration of titanium tetrachloride was 0.0020 mole/ml.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

In an experiment, 10 ml of monomer (0.076 mole), 100 ml of *n*-heptane, and 0.04 mole of triisobutylaluminum were taken. Since the ratio of triisobutylaluminum to titanium tetrachloride in the system was varied from 3 : 1 to 1 : 3, the amount of titanium tetrachloride taken ranged from 0.013 mole to 0.120 mole.

The influence of the molar ratio of the catalyst components and of the temperature at which the polymerization of allylbenzene was carried out is presented in Fig. 1. As is evident from this figure, the optimum ratio of triisobutylaluminum to titanium tetrachloride, both at 20° (*a*) and at 70° (*b*), is a ratio equal to 1 : 1. At all ratios of the catalyst components, the polymer yield increases with increasing temperature. At the optimum ratio of triisobutylaluminum to titanium tetrachloride, the yield of polyallylbenzene at temperatures of 20 and 70° was, respectively, 12.0 and 38.2%. A series of experiments at the optimum compo-

ratio of the catalyst components and at a temperature of 70° was carried out with the aim of determining the influence of the duration of polymerization on the polymer yield. Fig. 2 presents the results of these experiments at an Al : Ti ratio of 1 : 1. The yield of polyallylbenzene attained at a reaction time of 6 hr was taken as unity. Already 3 hr after the start of the reaction the polymer yield was 0.9 and thereafter changed only insignificantly.

Polyallylbenzene is a white powder with a softening temperature of about 192–210°. Only in one case—namely, at a ratio of triisobutylaluminum to titanium tetrachloride equal to 1 : 3 and at a temperature of 70°—was a low-melting polymer obtained (m.p. 77–107°). At room temperature polyallylbenzene is insoluble

Fig. 1

Fig. 2

in ordinary organic solvents. However, when the temperature is raised to 130–150° it dissolves in decalin, tetralin, α-bromonaphthalene, and cyclohexanone. In contrast, the low-melting polyallylbenzene dissolves in benzene already at room temperature.

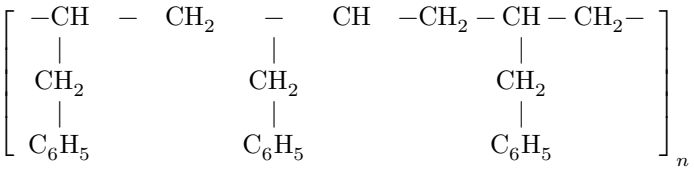
The mean specific gravity of polyallylbenzene, determined by the flotation method ([9]), was 1.055. Let us recall that for amorphous polystyrene this value is 1.040–1.065, for atactic polystyrene 1.050, and for isotactic polystyrene 1.085 ([10,11]).

Elemental analysis of polyallylbenzene gave the following results:

Found, %:	C 91.12; H 8.90
$(C_9H_{10})_n$. Calculated, %:	C 91.52; H 8.48

X-ray analysis data showed that the polymer obtained is an amorphous substance. However, upon recrystallization from decalin and toluene, the structure of the polymer reveals a certain degree of ordering.

The infrared spectra of a polyallylbenzene sample obtained at a ratio of triisobutylaluminum to titanium tetrachloride equal to 1 : 1 and a temperature of 70° indicate that the polymer chains are built in a "head-to-tail" fashion.* Therefore it may be considered that polyallylbenzene has the following structure:



Owing to the poor solubility of polyallylbenzene, its intrinsic viscosity was determined at a temperature of 150° in decalin, tetra-

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line and α-bromonaphthalene, and for the crude polymer it ranged from 0.238 (α-bromonaphthalene, 150°) to 0.340 (decalin, 150°).

For a more detailed clarification of the properties of the polymer, individual samples and mixtures of samples obtained in a series of experiments were subjected to extraction fractionation with boiling solvents. This process was carried out in a Soxhlet apparatus in the usual sequence adopted for stereoregular polymers (see, for example, (12)): low-molecular, oily products were extracted with acetone; with ether—products of higher molecular weight, appearing either as solid rubber-like or as powdery substances; and finally, with benzene—still higher-molecular products. After extraction with benzene, in most cases a residue remained. The duration of extraction with individual solvents ranged from 30 to 100 h.

Table 1

Results of fractionation of low-melting polyallylbenzene

No.	Fraction	Duration of fractionation, h	Fraction obtained, g	Content of fraction in polymer, %	Softening temperature, °C	Intrinsic viscosity	Molecular weight
1	Acetone	30	3.88	69.5	91–96	0.081	30 000
2	Ether	30	0.72	12.9	91–94	0.123	46 000
3	Benzene	30	0.98	17.5	91–104	0.137	50 000

Note: The intrinsic viscosity was determined in benzene at 50°; the molecular weight was determined by the light-scattering method in benzene solution for fractions 1 and 2 at 20° and for fraction 3 at 25°.

Table 1 gives the results of fractionation of low-melting polyallylbenzene obtained at a temperature of 70° and with a ratio of triisobutylaluminum to titanium tetrachloride equal to 1 : 3. The molecular weight of the polymer fractions was determined by the light-scattering method in benzene solution at 20–25° and at a light wavelength $\lambda_0 = 546$ μm. The values obtained for the molecular weight are given in Table 1*.

From the data in Table 1, the coefficients of the Mark–Kuhn–Houwink equation (13), $[\eta] = KM^{\alpha}$, were calculated. The following values were obtained: $K = 3.41 \cdot 10^{-6}$ and $\alpha = 0.977$.

The value of the coefficient α, close to 1, according to theoretical concepts (14), is consistent both with the relatively low molecular weight of the sample studied and with its good solubility in benzene. Thus, for polyallylbenzene in the molecular-weight range 30 000–50 000, the Mark–Kuhn–Houwink equation takes the following form:

$$[\eta] = 3.41 \cdot 10^{-6} M^{0.977}. \quad (1)$$

Table 2 gives the results of fractionation of a mixture of high-melting samples of polyallylbenzene. After extraction with benzene, a considerable residue is already obtained here (up to 58%) with a high softening temperature. The presence of this fraction apparently accounts for the high intrinsic viscosity of the crude polymer, as compared with low-melting polyallylbenzene. Unfortunately, because of the insolubility of the residue in benzene at 50°, it was not possible to determine its intrinsic viscosity.

* Measurements of the molecular weight by the light-scattering method were carried out by M. M. Kusakov, A. Yu. Koshevnikov, and E. A. Razumovskaya, to whom the authors express their gratitude.

impossible. For the remaining fractions, the intrinsic viscosities together with the molecular weights calculated by equation (1) are given in the same Table 2.

Comparing the results of fractionation of the high-molecular-weight and low-molecular-weight samples of polyallylbenzenes, we come to the conclusion that the low-molecular-weight product is formed in both cases; however, when the ratio of triisobutylaluminum to titanium tetrachloride is equal to

Table 2

Results of fractionation of a mixture of 24 samples of polyallylbenzene

No.	Fraction	Duration of fractionation, h	Fraction obtained, g	Fraction content in polymer, %	Softening temperature, °C	Intrinsic viscosity	Molecular weight (calc.)
1	Acetone	50	4.18	22.1	79–85	0.0938	35,000
2	Ether	50	0.31	1.6	105–112	0.0970	36,000
3	Benzene	100	3.53	18.6	153–155	0.1900	72,000
4	Residue	–	10.98	57.7	210–213	–	–

Note: The intrinsic viscosity was determined in benzene at 50°. The molecular weight was calculated by equation (1).

1 : 3, it constitutes the main mass of the reaction product; at a catalyst-component ratio equal to 1 : 1, a predominantly high-melting, high-molecular-weight residue is formed, insoluble in ordinary organic solvents.

In addition to solid powdery polymers, liquid reaction products were also isolated. They were more or less viscous opalescent liquids, with a characteristic odor and coloration ranging from yellow to brown-orange. The yields of liquid polymers and their molecular weights varied within very broad limits. The latter was determined cryoscopically in camphor by the Rast–Pirsch method and ranged from 200 to 800. Products with such a degree of polymerization, obtained in the presence of aluminum chloride, possessed the properties of lubricating oils (2).

High-molecular-weight samples of polyallylbenzene can be processed into films and fibers with a good set of physicochemical properties (5).

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