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Abstract

Full Text

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STUDIES IN THE FIELD OF BORON COMPOUNDS

OXIDATIVE POLYMERIZATION OF TRIALLYLBORON

The introduction of various heteroatoms into a polymeric hydrocarbon chain leads to the creation of polymers with new valuable properties. A large number of low-molecular-weight esters of boric acid, various polymers of thioboranes, aminoboranes, phosphinoboranes, polyorganoborosiloxanes, etc., are known. Gubo and Epple (^{1}), studying the thermal decomposition of trimethylboron at 400-600°, showed the formation, along with hydrogen and methane, of solid products of various colors—from light yellow to black—containing boron. When magnesium bromoacetylide is reacted with boron trifluoride etherate in benzene, the magnesium salt of tetraethynylboric acid is obtained, which, upon heating in vacuum, undergoes decomposition and polymerization (^{2}). Among the various pyrolysis products of $(CH_3)_2BCH_2CH_2B(CH_3)_2$, nonvolatile polymeric boron-containing compounds were obtained (^{3}). Kolesnikov and Fedorova (^{4}) showed that tributylboron in the presence of boron trifluoride etherate causes polymerization of acrylonitrile. It turned out that tributylboron is an active catalyst for the polymerization of styrene and methyl methacrylate.

The purpose of our investigation was to study polymers obtained on the basis of triallylboron (^{5}), and to test it as a catalyst for the polymerization of unsaturated hydrocarbon compounds.

Experimental Part

Under the conditions used for obtaining triallylboron in a stream of nitrogen insufficiently purified from oxygen, solid yellowish polymers are formed along with triallylboron. Elemental analysis confirmed the presence in them of boron and oxygen (Table 1). We carried out systematic experiments on the polymerization

Table 1

Polymers obtained by oxidation of triallylboron (elemental composition in percent)

Oxidation conditions	B	C	H	O	M.p., °C
With nitrogen not purified from O_2 (0.8%)	4.31	57.27	8.90	29.52	>250
In tert-butylbenzene at 130° ($N_2 + O_2$)	5.03	60.04	9.09	25.84	>250
In isopropylbenzene at 130° ($N_2 + O_2$)	4.38	61.55	9.19	24.88	>250
With benzoyl peroxide at 20° (1 : 1)	4.33	57.24	8.89	29.54	>250
With H_2O_2 at 20° (1 : 1)	4.26	56.02	9.24	30.48	>250

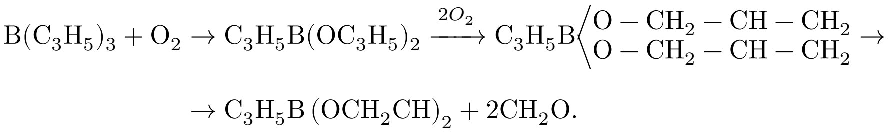
of triallylboron by atmospheric oxygen at room temperature, and also in solution in isopropylbenzene and tert-butylbenzene at 130° with a nitrogen–oxygen mixture. In these experiments polymers were obtained for which the elemental composition and melting temperature were determined.

When triallylboron was polymerized with the addition of 5 mol.% benzoyl peroxide in sealed ampoules, with air displaced from the gas phase by nitrogen at 100°, no polymer could be obtained. A polymer was obtained when benzoyl peroxide was added to triallylboron in a molar ratio of 1 : 1 or higher. The reaction proceeds very vigorously, with strong heating. Benzoyl peroxide decomposes according to the scheme

$$C_6H_5CO - O - O - COC_6H_5 \rightarrow (C_6H_5CO)_2O + O\cdot.$$

The reaction proceeds similarly with hydrogen peroxide.

Thus, triallylboron is a compound that is readily polymerized in the presence of oxygen. To clarify the mechanism of the polymerization reaction, triallylboron was oxidized with a nitrogen–oxygen mixture. The gas leaving the flask containing the oxidized sample, from the very first portions and then throughout the entire experiment, gives a strongly pronounced aldehyde reaction: when the sample is acidified with hydrochloric acid, fuchsin-sulfurous acid turns violet-blue. The following scheme of the polymerization process may be proposed:



$$B(C_3H_5)_3 + O_2 \rightarrow C_3H_5B(OC_3H_5)_2 \xrightarrow{2O_2} C_3H_5B\left\langle\begin{matrix} O - CH_2 - CH - CH_2 \\ O - CH_2 - CH - CH_2 \end{matrix}\right. \rightarrow$$

$$\rightarrow C_3H_5B\,(OCH_2CH)_2 + 2CH_2O.$$

The active units arising as a result of decomposition can bind by free valences both to one another and by addition at the site of the double bond to unoxidized triallylboron molecules, forming in both cases three-dimensional structures.

Table 2

Fractions of polymer obtained by oxidation of triallylboron (elemental composition in percent)

Experimental conditions	Fractions	B	C	H	O	Cl
Heating to 75° for 1.5 h in CCl_4	Insoluble	6.79	21.22	5.05	55.75	10.19
Heating to 75° for 1.5 h in CCl_4	Soluble	3.13	63.84	9.18	20.48	3.37
Heating to 65° for 1.5 h in tetrahydrofuran	Insoluble	11.71	23.90	5.01	59.38	–

Experimental conditions	Fractions	B	C	H	O	Cl
Heating to 65° for 1.5 h in tetrahydrofuran	Soluble	3.72	62.99	9.98	23.71	–
Standing at 20° for several days in 10% KOH	Insoluble	4.59	54.26	9.30	31.85	–
Standing at 20° for several days in 10% KOH	Soluble	5.49	58.98	9.39	26.15	–

The scheme of oxidative polymerization was proposed by Danilov and Kozmina (8), who, studying allylcellulose, came to the conclusion that this ether is capable of polymerizing through the allyl groups with the participation of oxygen.

The scheme proposed by these authors is fully confirmed by our investigations. As is known, three-dimensional polymers are insoluble, non-swelling, infusible products, and this is confirmed by the properties of the polymers we studied. They are poorly soluble in various solvents. Upon prolonged treatment of the polymer with 10%

With KOH, a soluble portion of the polymer and an insoluble portion are formed; the former was isolated from the alkaline solution by treating it with dilute hydrochloric or nitric acid. When the polymer was heated with carbon tetrachloride and tetrahydrofuran for 1.5 h at 65–75°, soluble and insoluble portions were formed. From the former, the solvent was removed by evaporation. In this way it is possible gradually to convert all the polymer soluble in CCl_4 into an insoluble one. The polymer behaves similarly with tetrahydrofuran. It is of interest to note that elemental analysis showed a considerably higher chlorine content in the polymer insoluble in CCl_4 (10.19%) than in the soluble polymer (3.37%), and a higher oxygen content in the polymer insoluble in tetrahydro-

Fig. 1. Dependence of the relative viscosity of polymethyl methacrylate on concentration

Figure 1: Fig. 1. Dependence of the relative viscosity of polymethyl methacrylate on concentration

furan and alkali than in the polymer soluble in them (Table 2). The melting points of the polymers studied are above 250°. It was not possible to determine the molecular weights of the polymers because of their poor solubility.

We also studied the ability of triallylboron to initiate or inhibit the polymerization reaction of a number of vinyl compounds. All experiments were carried out in sealed ampoules, with air displaced from the gas phase by nitrogen. The ampoules were kept at 100°; triallylboron was added in an amount of 5 mol.%.

Triallylboron proved to be an active catalyst for the polymerization of methyl methacrylate. The reaction proceeds with strong heating, and after only 1-1.5 h at room temperature methyl methacrylate had become a solid transparent block. The polymer yield was up to 86%. The absence of boron in determining the elemental composition (Table 3) indicates that triallylboron does not enter into copolymerization. The dependence of the viscosity of polymethyl methacrylate on concentration is shown in Fig. 1. Triallylboron has no appreciable effect on the polymerization of styrene. It slightly inhibits the polymerization process. Thus, ampoules with styrene, with and without the addition of triallylboron, were kept for 3, 6, and 9 h at 100°.

Fig. 1. Dependence of the relative viscosity of polymethyl methacrylate on concentration

Table 3

Substance	Experimental conditions	Polymer yield, %	Observed changes	Found, %	Found, %	Found, %
				B	C	H
Styrene	3 h, 100°	29.26	Transparent viscous liquid	–	92.21	7.79
Styrene + 5 mol.% $B(C_3H_5)_3$	3 h, 100°	23.36	Same	–	92.31	7.74
Styrene	6 h, 100°	51.23	Same	–	92.25	7.80
Styrene + 5 mol.% $B(C_3H_5)_3$	6 h, 100°	44.48	Same	–	92.20	7.80

Fig. 2

Figure 2: Fig. 2

Substance	Experimental conditions	Polymer yield, %	Observed changes	Found, %	Found, %	Found, %
Styrene	9 h, 100°	52.04	Transparent block	–	92.31	7.70
Styrene + 5 mol.% $B(C_3H_5)_3$	9 h, 100°	48.81	Same	–	92.35	7.67
Methyl methacrylate + 5 mol.% $B(C_4H_5)_3$	1-1.5 h, 20°	84.3	Same	–	60.70	8.25
Acrylonitrile + 5 mol.% $B(C_3H_5)_3$	70 h, 100°	–	Does not change	–		
Vinyl acetate + 5 mol.% $B(C_3H_5)_3$	50 h, 100°	–	Does not change	–		

The polymer yields are, respectively: without addition of $B(C_3H_5)_3$: 29.26; 51.23; 52.04%; with addition of 5 mol.% $B(C_3H_5)_3$: 23.36; 44.48; 48.81%. The dependence of the polymer yield is shown in Fig. 2. The viscosity of polystyrene obtained upon addition of triallylboron decreases significantly (Fig. 3).

Fig. 2. Kinetics of styrene polymerization in the presence of triallylboron at 100°: 1 –without $B(C_3H_5)_3$; 2 –with addition of 5 mol.% $B(C_3H_5)_3$.

Fig. 3. Dependence of the relative viscosity of polystyrene on concentration: 1 –without $B(C_3H_5)_3$; 2 –with addition of $B(C_3H_5)_3$.

We also studied the polymerization reaction of acrylonitrile and vinyl acetate

Fig. 3

Figure 3: Fig. 3

upon addition of 5 mol.% triallylboron. Triallylboron does not induce polymerization of these compounds even when the ampoule is kept for a long time at 100° (for 50-75 h). The data on the polymerization, studied by us, of a series of unsaturated compounds are summarized in Table 3.

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CITED LITERATURE

1. J. Goubeau, R. Apple, *Ber.*, **90**, 171 (1957).
2. U. Krüerke, *Zs. Naturforsch.*, **11b**, 364, 606 (1956).
3. G. Urry, J. Kerrigan et al., *J. Am. Chem. Soc.*, **76**, 3307 (1954).
4. G. S. Kolesnikov, L. S. Fedorova, *Izv. AN SSSR, OKhN*, 1957, 236; G. S. Kolesnikov, N. V. Klimentova, *Izv. AN SSSR, OKhN*, 1957, 652.
5. A. V. Topchiev, A. A. Prokhorova et al., *Izv. AN SSSR, OKhN*, 1958, 370.
6. S. N. Danilov, O. P. Kozmina, *ZhOKh*, **18**, 1823 (1948).

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