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## Abstract

## Full Text

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### CHEMISTRY

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# INITIATION OF LOW-TEMPERATURE POLYMERIZATION OF VINYL CHLORIDE BY TRIETHYLALUMINUM UNDER THE CO-CATALYTIC ACTION OF OXYGEN

One of the most important organometallic compounds used for the polymerization of various monomers are organoaluminum compounds and, first of all, triethylaluminum (TEA). The latter, with oxygen and certain oxygen-containing compounds, forms organoaluminum peroxides as intermediate products, capable of initiating the polymerization of vinyl monomers ([1],[2]). As for vinyl chloride, its polymerization initiated by aluminum alkyls under the cocatalytic action of oxygen has practically not been studied. In ([3]) it was noted that TEA (1.89 mole % relative to monomer) at 30° did not cause polymerization of vinyl chloride in sealed ampoules containing 10–30 mole % oxygen. Nevertheless, we succeeded in polymerizing vinyl chloride starting from triethylaluminum and oxygen, using a different experimental procedure (polymerization of the monomer in the course of continuous oxidation of TEA at −30°).

**Fig. 1.** Dependence of conversion–time for 10 wt.% $Al(C_2H_5)_3$ in benzene (1), chlorobenzene (3), dichloroethane (2). −30°; $C_2H_3Cl : Al(C_2H_5)_3 = 728 : 1$ mole/mole.

In Fig. 1 the dependence of conversion on time is presented for the polymerization of vinyl chloride in solutions of benzene, chlorobenzene, and dichloroethane. It is seen that the formation of polyvinyl chloride (PVC) begins after a certain time has elapsed from the moment of interaction of triethylaluminum with oxygen. Evidently, the induction period in the polymerization is in a definite way connected with the act of oxidation of TEA. In ($^4$) it was shown that the process of oxidation of triethylaluminum includes several stages proceeding through the formation and decomposition of organoaluminum peroxides.

$$\mathrm{Al(C_2H_5)_3} \xrightarrow{\mathrm{O_2}} \mathrm{Al(C_2H_5)_2OOC_2H_5} \qquad \text{(very fast)} \quad \mathrm{I}$$

$$\mathrm{Al(C_2H_5)_2OOC_2H_5} + \mathrm{Al(C_2H_5)_3} \rightarrow \mathrm{2Al(C_2H_5)_2OC_2H_5} \qquad \text{(very fast)}$$

$$\mathrm{Al(C_2H_5)_2OC_2H_5} \xrightarrow{\mathrm{O_2}} \mathrm{AlC_2H_5(OC_2H_5)OOC_2H_5} \qquad \text{(fast)} \quad \mathrm{II}$$

$$+\,\mathrm{Al(C_2H_5)_3} \qquad \text{(very fast)}$$

$$\begin{aligned}\mathrm{AlC_2H_5(OC_2H_5)OOC_2H_5} &\rightarrow \mathrm{Al(C_2H_5)_2OC_2H_5} + \mathrm{AlC_2H_5(OC_2H_5)_2}\\ &+\,\mathrm{Al(C_2H_5)_2OC_2H_5}\\ &\rightarrow \mathrm{2AlC_2H_5(OC_2H_5)_2} \qquad \text{(very fast)}\end{aligned}$$

$$\mathrm{AlC_2H_5(OC_2H_5)_2} \xrightarrow{\mathrm{O_2}} \mathrm{Al(OC_2H_5)_2OOC_2H_5} \qquad \text{(slow)} \quad \mathrm{III}$$

It could be assumed that the polymerization process should be initiated by reactions in which there is interaction of an organoaluminum peroxide with TEA or with aluminum alkylethoxy derivatives, dis—

since their interaction may be regarded as a kind of oxidation-reduction system, in which the Al—O—O—C grouping acts as an oxidizing agent for Al—C bonds.

According to the scheme of oxidation of triethylaluminum (4), such processes may occur in the case of reactions of triethylaluminum peroxide with TEA and of ethoxyaluminum peroxyethyl with TEA or diethoxyethylaluminum. In accordance with this, the relative contribution of each stage of TEA oxidation to the initiation of vinyl chloride polymerization was evaluated. For this purpose, the following model systems were used: triethylaluminum—oxygen, diethylaluminum ethoxide—oxygen, and diethoxyethylaluminum—oxygen. The results are given in Table 1.

**Table 1**

**Polymerization of vinyl chloride at different stages of oxidation of triethylaluminum1**

Figure 2

Figure 2: Figure 2

| Model system | PVC yield, % | Limiting viscosity number |
|---|---|---|
| $Al(C_2H_5)_3 \xrightarrow{O_2} Al(C_2H_5)_2OC_2H_5$(stage I) | 0 | – |
| $Al(C_2H_5)_2OC_2H_5 \xrightarrow{O_2}\rightarrow Al(C_2H_5)(OC_2H_5)_2$(stage II) | 3.6 | 0.27 |
| $AlC_2H_5(OC_2H_5)_2 \xrightarrow{O_2}\rightarrow Al(OC_2H_5)_2OC_2H_5$(stage III) | 0.44 | 0.21 |
| $Al(C_2H_5)_3 \xrightarrow{O_2}\rightarrow AlC_2H_5(OC_2H_5)_2$(stages I–III) | 3 | 0.2–0.26 |

1 Polymerization conditions: benzene, –30°, 4 h; air-flow rate 50 ml/min, VC : $Al(C_2H_5)_3$ = 7.28 : 1 mol/mol; VC : $Al(C_2H_5)_2OC_2H_5$ = 7.63 : 1 mol/mol; VC : $AlC_2H_5(OC_2H_5)_2$ = 7.50 : 1; 2 indicator method (5); 3 conductometric method (6); 4 iodometric analysis (2) in combination with the conductometric method of analysis.

As can be seen, the greatest polymerization activity is exhibited when the model system consisting of diethylaluminum ethoxide and oxygen is used (stage II). The systems triethylaluminum–oxygen (stage I) and diethoxyethylaluminum–oxygen (stage III) proved to be only slightly active in the polymerization reaction. At stage I the concentration of diethylaluminum peroxyethyl is very low owing to the extremely high reducing ability of triethylaluminum. At stage III, although high concentrations of diethoxyaluminum peroxyethyl can be reached (yield 40% and higher), the reducing ability of diethoxyethylaluminum is very small. Therefore the oxidation-reduction reaction does not occur. Additions of triethylaluminum and diethylaluminum ethoxide to diethoxyaluminum peroxyethyl led to decomposition of the peroxide, accompanied, in the presence of monomer, by its polymerization.

**Fig. 2.** Decomposition of diethoxyaluminum peroxyethyl by triethylaluminum and its derivatives (40 wt.%, peroxide : aluminum alkyl ratio = 1:1 mol/mol; –70°): 5 –diethylaluminum bromide, 4 –triethylaluminum, 3 –diethylaluminum ethoxide, 2 –ethylaluminum diethoxide, 1 –without additives.

The described results are in good agreement with the results of experiments on the decomposition of diethoxyaluminum peroxyethyl by aluminum alkyls of different reducing ability (Fig. 2). In addition, confirmation of these propositions should be seen in the results obtained by us in the polymerization of vinyl chloride during prolonged oxidation of TEA (for example, Fig. 1). In this

Fig. 3. Polymerization of vinyl chloride in the presence of donor additives

Figure 3: Fig. 3. Polymerization of vinyl chloride in the presence of donor additives

case, after a certain induction period the system contained appreciable amounts of both organoaluminum peroxides and reducing agents of high activity. The experimental data obtained make it easy to explain the negative results in the polymerization of vinyl chloride reported in work (3).

In all probability, the amount of oxygen present in the closed reaction volume was insufficient to obtain a system capable of initiating polymerization, and the process ended at the stage of the induction period. It is interesting to note that, as can be seen from Fig. 1, the yield of polyvinyl chloride depended on the nature of the solvent. In such solvents as dichloroethane and halobenzenes, which are good solvents for polyvinyl chloride, the polymer yield was 5 times greater than in polymerization in aliphatic and aromatic hydrocarbons, which do not dissolve it. Attention is drawn to the different behavior of nucleophilic solvents in the process under study. In oxygen-containing compounds (ethyl ether, tetrahydrofuran), a decrease in polymer yield was observed in comparison with polymerization in benzene, whereas in nitrogen-containing organic bases polymerization did not proceed at all. Interest in the polymerization of vinyl chloride in the presence of these additives was determined by the fact that the first elementary act in the oxidation of triethylaluminum should be considered the coordination of its molecule and an oxygen molecule, due to the donor properties of oxygen and the electronic unsaturation of the acceptor molecule. Donor agents present in the reaction medium form complexes with TEA and hinder nucleophilic attack at the aluminum atom. The results of experiments on the polymerization of vinyl chloride in benzene in the presence of donor additives when using catalytic systems triethyl-(triisobutyl)-aluminum—oxygen are given in Fig. 3. The inhibiting effect should be attributed to competition in complex formation between oxygen and the introduced donor with electrophilic TEA.

**Fig. 3.** Polymerization of vinyl chloride in the presence of donor additives of 10 wt.% $Al(C_2H_5)_3$ in benzene; −30°; 4 h, $C_2H_3Cl : Al(C_2H_5)_3 = 728 : 1$ mol/mol).
*a*—$(C_2H_5)_2O$ to $Al(C_2H_5)_3$; *b*—tetrahydrofuran to $Al(C_2H_5)_3$; *v*—$N(C_2H_5)_3$ to $Al(C_2H_5)_3$; *g*—$C_3H_5N$ to $Al(C_2H_5)_3$; *d*—$C_5H_5N$ to Al(iso-$C_4H_9)_3$; *e*—$(C_2H_5)_2O$ to Al(iso-$C_4H_9)_3$; *zh*—$N(C_2H_5)_3$ to Al(iso-$C_4H_9)_3$.

Oxygen is capable of displacing donor agents from donor-acceptor complexes, which was confirmed by special experiments in which, during the oxidation of complexes with ether, the latter was isolated in the free state by distillation. The difference in the course of the curves in the case of nitrogen- and oxygen-containing donor agents is probably due to two factors. Complexes involving nitrogen-containing donors are more stable than those with oxygen-containing donors, which lowers the rate of their displacement and, consequently, of the formation of active polymerization centers. This was confirmed by the fact that complexes of aluminum alkyls with ethers are readily titrated with triethylamine and pyridine. In addition, the organoaluminum peroxides formed give a new oxidation–reduction system with triethylamine (pyridine), destroying the peroxide.

In conclusion, we note that the PVC obtained differs in its properties both from ordinary atactic PVC and from the highly crystalline product obtained in the presence of TEA and titanium trichloride in benzene (heptane) medium with complex-forming additives ([7]). Thus, the glass-transition temperature of the synthesized samples, with practically the same molecular weight as in ([7]), was shifted toward higher temperatures (90° as against 75–80°), indicating an increase in the degree of syndiotacticity of the PVC macromolecules ([8]). The latter also follows from the elevated values of the ratios $D_{635}/D_{692}$ ([17–19]), calculated from the IR spectra and serving as a measure of the crystallinity of syndiotactic PVC ([9]). This value is close to the degree of syndiotacticity of polyvinyl chloride obtained by the ordinary free-radical polymerization method at analogous temperatures ([9]). Electron-diffraction study showed that, although the PVC is characterized by considerable structural ordering, it is not crystalline, since the electron diffraction patterns of its unoriented samples heated at 135° contained 6–8 reflections, as against 4 diffuse rings for the ordinary atactic product or 10 sharp reflections for crystalline polyvinyl chloride ([7]).

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