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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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INITIATION OF THE POLYMERIZATION OF VINYL CHLORIDE BY REACTIONS OF TRIETHYLALUMINUM WITH HALOGEN-CONTAINING ORGANIC COMPOUNDS

From the literature data ([1]) it is known that triethylaluminum (TEA) does not react with CCl_4 at 30°. Only after titanium tetrachloride was added to the reaction mixture was a vigorous reaction observed, accompanied by complete destruction of the aluminum alkyl. The authors believe that this reaction proceeds through the formation of a carbonium ion and is due to the interaction of ethylaluminum dichloride with CCl_4.

Later, a report appeared on the reaction of triisobutylaluminum with CCl_4, which stopped at the stage of formation of diisobutylaluminum chloride ([2]). The formation of dichlorocarbene is assumed. We have shown that the reaction of TEA with CCl_4, as well as with certain other halogen-containing organic compounds, initiates the polymerization of vinyl chloride.

Fig. 1. Dependence of the yield of PVC (*a*) and of the limiting viscosity number (*b*) on additions of benzene to the polymerization system (TEA $3.3 \cdot 10^{-3}$ mole, $TiCl_3$ $1 \cdot 10^{-3}$ mole, RCl 0.15 mole, monomer 0.15 mole, 20°, 10 hr).
1 and 1′—benzene + CCl_4; 2 and 2′—benzene + *iso*-C_4H_9Cl; 3 and 3′—benzene + C_2H_5Cl.

Table 1 presents data on the polymerization of vinyl chloride on the basis of TEA in the presence of certain chlorine-containing compounds (RCl) at a temperature of +20°. As RCl, alkyl (aryl) chlorides were used, as well as some di- and polychloro derivatives of saturated and unsaturated hydrocarbons. It is seen that, whereas in benzine, heptane, and benzene polymerization is absent, in the case of chloro derivatives the formation of polyvinyl chloride (PVC) was observed with yields from 4-5% to 80-85%, depending on the nature of RCl.

It is interesting to note that nonpolar hydrocarbons suppressed polymerization also when introduced as additives to RCl (Fig. 1). Even at a benzine : RCl ratio of 0.5-1 : 1, a decrease in the yield of poly-

Table 1

Polymerization of vinyl chloride based on (TEA–RCl–$TiCl_3$)* (TEA $3.3 \cdot 10^{-3}$ mol, $TiCl_3$ $1 \cdot 10^{-3}$ mol, RCl 0.15 mol, monomer = 0.15 mol, 20°, 10 h)

Chlorine-containing organic compound	Conversion, %	[η]	Cl, %
Benzine (benzene)	–	–	–
C_2H_5Cl	4–5 (0.2–0.3)	0.4–0.5	51.5–52.5
iso-C_3H_7Cl	24–26 (2.5)	0.35–0.4 (0.3)	–
iso-C_4H_9Cl	25–30 (2–4.5)	0.4–0.6 (0.3–0.4)	55.5–55.8
tert.-C_4H_9Cl	–	–	–
$CH_2Cl–CH_2Cl$	13–15 (0.5–0.7)	0.5–0.6	55.1–55.6
CH_2Cl_2	15–6 (1)	0.4–0.45	–
$CHCl_3$	27–30 (1–1.2)	0.14–0.16 (0.12)	–
CCl_4	80–85 (21–26)	0.12–0.2 (0.12)	55.3–55.5
$CHCl{=}CCl_2$	traces	–	–
$CCl_2{=}CCl_2$	traces	–	–
$C_6H_5–Cl$	5–6 (traces)	0.1–0.3	50.9–51.5
$C_6H_5CH_2Cl$	–	–	–
$CH_2{=}CH–CH_2Cl$	–	–	–

* In parentheses are given the conversion and the intrinsic viscosity for polymerization in the absence of $TiCl_3$.

by a factor of 2–4 with a simultaneous decrease in the intrinsic viscosity (the measurements were made from polymer solutions in cyclohexanone at 20°).

As for the chlorine derivatives themselves, compounds with a chemically inert chlorine atom (tri- and tetrachloroethylenes, chlorobenzene) do not initiate polymerization. An increase in the activity of chlorine on going to mono-, di-, and polychloro derivatives of saturated hydrocarbons (C_2H_5–Cl, *iso*-C_3H_7Cl, *iso*-C_4H_9Cl, $CH_2Cl–CH_2Cl$, CH_2Cl_2, $CHCl_3$, CCl_4) has a favorable effect on the polymerization of vinyl chloride. The fact that polymerization is absent in the case of tert-butyl chloride, benzyl chloride, and allyl chloride can probably be explained by the extremely high rate of interaction of the components. Their reaction with TEA proceeds explosively.

The experimental data obtained make it possible to propose that the initiation step is associated with the reaction between TEA and RCl, while titanium trichloride contributes to a considerable acceleration of this reaction and, as a consequence, to polymerization of the monomer (Table 1). Indeed, if the monomer and titanium chloride were added to a mixture of TEA and RCl, a polymerization reaction was observed every time. If, however, vinyl chloride was introduced into the reaction mixture after preliminary interaction of TEA, RCl, and $TiCl_3$, polymerization of the monomer was not observed. Polymer formation took place only upon addition of fresh TEA. It is appropriate to point out here that a catalytic system composed of an aluminum alkyl and titanium halide did not initiate polymerization of vinyl chloride under the experimental conditions.

Fig. 2. Conversion-time curves for the polymerization of vinyl chloride in the presence of: 1 –TEA + CCl_4 + $TiCl_3$; 2 –TEA + *iso*-C_4H_9Cl + $TiCl_3$; 3 –TEA + CCl_4; 4 –TEA + *iso*-C_4H_9Cl (TEA $3.3 \cdot 10^{-3}$ mol, $TiCl_3$ $1 \cdot 10^{-3}$ mol, RCl 0.15 mol, monomer 0.15 mol, 20°, 10 h)

The conversion-time curves for two catalytic systems, in which CCl_4 and *iso*-C_4H_9Cl were used as components, are presented in Fig. 2. The curves have a clearly pronounced S-shaped character. The influence of $TiCl_3$ on the rate of polymerization and the yield of PVC is clearly visible.

In the same vein, it was natural to expect that a change in the ratio of the components of the catalytic system, or a change in the reactivity of the aluminum alkyl (as well as of the chloro derivative), should be reflected in the course of the polymerization process.

Indeed, the dependence of monomer conversion on the TEA : RCl ratio (Fig. 3) has the form of a curve with a distinct maximum. Deterioration of the polymerizing properties of the catalytic system with increasing TEA content can be explained by a considerable acceleration of the reaction between TEA and RCl, leading to a decrease in the efficiency of initiation. A similar change in the value of the intrinsic viscosity number is noteworthy. Increasing, up to a certain limit ($0.02 \div 0.04$ mol/l), the amount of $TiCl_3$ introduced into the reaction mixture had practically no effect on the PVC yield. A decrease in the reactivity of TEA upon addition of donor agents (triethylamine) leads to a drop in monomer conversion. However, in the case of *tert*-C_4H_9Cl, which reacts very vigorously with TEA, a decrease in the activity of the latter (through use of the TEA complex with triethylamine) promoted polymerization, although it proceeded with low yields (1-3%). When TEA was replaced in the catalytic system studied by its derivatives (diethylaluminum chloride and diethylaluminum ethoxide), the polymerization reaction could still be observed, but with yields different from those obtained with TEA.

Fig. 3. Influence of the TEA/RCl ratio on PVC yield (*a*) and intrinsic viscosity number (*b*) ($TiCl_3$ $1 \cdot 10^{-3}$ mol, RCl = *iso*-C_4H_9Cl = 0.15 mol, monomer 0.15 mol, 20°, 10 h)

Fig. 3. Influence of the TEA/RCl ratio on PVC yield (a) and intrinsic viscosity number (b) ($TiCl_3$ $1 \cdot 10^{-3}$ mol, RCl = *iso*-C_4H_9Cl = 0.15 mol, monomer 0.15 mol, 20°, 10 h)

Figure 2: Fig. 3. Influence of the TEA/RCl ratio on PVC yield (a) and intrinsic viscosity number (b) ($TiCl_3$ $1 \cdot 10^{-3}$ mol, RCl = *iso*-C_4H_9Cl = 0.15 mol, monomer 0.15 mol, 20°, 10 h)

It should be noted that, using the catalytic system TEA—RCl—$TiCl_3$, polymerization can be carried out over a wide temperature range (from −50 to +50°); however, when the temperature was lowered, the polymer yield decreased.

In all cases the PVC obtained was characterized by a comparatively low molecular weight (intrinsic viscosity number from 0.1 to 0.6). The other properties of the polymer were at the level of the properties of PVC obtained by ordinary free-radical polymerization methods.

In an electron-microscopic study of the secondary structures of polyvinyl chloride dispersed by ultrasound, distinct globular formations of practically identical size were observed ($\simeq 0.1\ \mu$ in diameter).

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