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Chemistry

Corresponding Member of the Academy of Sciences of the USSR G. A. RAZUVAEV, K. S. MINSKER, Yu. A. SANGALOV

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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LOW-TEMPERATURE POLYMERIZATION OF VINYL CHLORIDE INITIATED BY THE REACTION OF ALUMINUM ALKYLS WITH HALOGENS

It was recently shown that the reaction of certain organoaluminum compounds with alkyl (aryl) halides can be used to initiate the polymerization of vinyl chloride (VC) (ˆ1). It was natural to expect that free halogens as well—in particular, chlorine or bromine—in combination with organoaluminum compounds would also be able to initiate polymerization. From the literature it is known that halides readily cleave most organometallic compounds (including organoaluminum compounds), giving alkyl or aryl halides (ˆ2), and, as indicated in a patent (ˆ3), the system $(C_2H_5)_3Al$—Cl_2 can polymerize VC at subzero temperatures.

Fig. 1. Effect of the polymerization temperature on the yield (1) and the characteristic viscosity of PVC (2) during polymerization of VC in the system $(C_2H_5)_3Al$—Cl_2 ($(C_2H_5)_3Al = 0.024$ mole, VC = 1.6 mole, 2.5 hr)

Experimental results show that the polymerization of VC is associated with the reaction of chlorine (bromine) with an aluminum alkyl. Indeed, when gaseous chlorine was continuously introduced into the reaction medium (a solution of triethylaluminum—1.5 mole % in liquid vinyl chloride—100 g) at a rate of 25–30 ml/min, the formation of polyvinyl chloride (PVC) was observed over a broad temperature range ($-15^\circ \div -70^\circ$) (Fig. 1).

An essential condition for the polymerization process is the introduction of chlorine into the reaction zone in moderate amounts. If a large amount of chlorine was introduced at once (for example, 3 moles of Cl_2 per mole of triethylaluminum), then in the temperature interval $+15^\circ \div +50^\circ$ the formation of polymeric products practically did not occur, while at subzero temperatures polymerization proceeded with small conversions.

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Figure 2

Figure 2: Figure 2

Polymerization of VC under the action of the organoaluminum compound–chlorine system proceeds without an induction period. PVC appears in the reaction system immediately after chlorine comes into contact with the aluminum alkyl (Fig. 2). In this case, as the components react with one another, a monotonic increase in the PVC yield is observed. The monomer conversion can be regulated by changing, at a constant triethylaluminum content, the amount of monomer introduced. Thus, it was observed that increasing the amount of VC in the reaction mixture from 1.6 mole to 3.2 mole (per 0.024 mole of $(C_2H_5)_3Al$) causes a 2.5-fold increase in conversion over the same polymerization time. However, a further increase in the VC charge (to 4.8 mole) no longer promoted an increase in conversion. The reaction of $(C_2H_5)_3Al$ with chlorine that occurs during polymerization proceeds through successive replacement of C_2H_5 groups by Cl atoms up to the complete exhaustion of all Me–C bonds: $(C_2H_5)_3Al \rightarrow AlCl_3$. In this connection, it was of interest

evaluate the catalytic activity of chloro derivatives of trialkylaluminum, as well as of some other of its derivatives, in the polymerization reaction. It was shown that neither $(C_2H_5)_3Al$ nor its chloro- or ethoxy derivatives, taken individually, caused polymerization of the monomer. The binary system $AlCl_3 + Cl_2$, which is an effective catalyst for Friedel–Crafts reactions, likewise did not polymerize VC to solid products. Consequently, the formation of the polymer is not associated with the appearance in the reacting system of ionic structures of the type $X^+(AlR_{nX_{4-n}})^-$. The polymerization process is initiated only when chlorine reacts with an organoaluminum compound containing at least one alkyl group. In this case, depending on the nature of the aluminum alkyl, the activity of the latter in polymerization changes (Table 1).

Fig. 2. Conversion–time dependence during polymerization of VC on the system $(C_2H_5)_3Al$—Cl_2 ($(C_2H_5)_3Al = 0.024$ mol, VC = 3.2 mol, -20°)

The highest yields of PVC were observed in the case of $(iso\text{-}C_4H_9)_3Al$ and $(C_2H_5)_3Al$. The successive introduction of chlorine into the molecule of $(C_2H_5)_3Al$ lowers the activity of the latter in the polymerization of VC. A decrease in conversion was also observed upon introduction of an ethoxy group into the molecule of triethylaluminum. Triphenylaluminum was inactive in polymerization. When diethylzinc was used instead of aluminum alkyls, PVC was also formed (diphenylzinc gave negative results). Polymerization of VC also could not be observed in reactions of halogens with organotin and organolead compounds. All this indicates that the nature of the organic groups and of the metal in organometallic compounds, which affects the course of their reaction with halogens ([2]), also determines the effectiveness of the polymerization process.

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Table 1

Polymerization of VC on the system: organometallic compound–chlorine*

Organometallic compound ($MeR_{nX_{m-n}}$)	PVC yield, %	η
$(C_2H_5)_3Al$	4.6–4.8	1.3–1.5
$(C_2H_5)_2AlCl$	1.4–1.6	0.14–0.15
$C_2H_5AlCl_2$	0.7	0.1
$AlCl_3$	–	–
$(C_2H_5)_2AlOC_2H_5$	2.7–2.9	0.9–1.0
$(iso\text{-}C_4H_9)_3Al$	5.7–6.0	0.7–0.8
$(C_6H_5)_3Al$**	–	–
$(C_2H_5)_2Sn$**	2–2.2	0.1
$(C_6H_5)_2Zn$**	–	–
$(C_2H_5)_4Sn$	–	–
$(C_2H_5)_4Pb$	–	–

* Polymerization conditions: $MeR_{nX_{m-n}} = 0.024$ mol, $C_2H_3Cl = 1.6$ mol, $-20°$, 2.5 h.
** The authors thank E. V. Mitrofanova and R. F. Galyulina for providing $(C_6H_5)_3Al$, $(C_2H_5)_2Zn$, and $(C_6H_5)_2Zn$.

Naturally, the nature of the halogen also had an effect on the polymerization of VC. If replacement of chlorine by bromine during polymerization in the presence of $(C_2H_5)_3Al$ was accompanied by a drop in conversion by 15–25% (the limiting viscosity number changed little), then in the case of iodine the formation of PVC under the experimental conditions could not be observed.

As regards the properties of the polymer obtained, they do not differ from those described in works ([1,4]), where reactions involving the interaction of organoaluminum compounds with oxygen or chloroalkyls were used to initiate polymerization.

In conclusion, we note that, by using reactions of halogens with aluminum alkyls, it proved possible to carry out low-temperature polymerization of other vinyl monomers as well, in particular vinyl acetate.

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REFERENCES

1. G. A. Razuvaev, K. S. Minsker, Yu. A. Sangalov, *DAN*, **158**, No. 1 (1964).

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2. Yu. Rokhov, D. Hurd, R. Lewis, *Chemistry of Organometallic Compounds*, Izd. IL, 1963, pp. 146, 203, 211.

3. Engl. patent No. 919198, 1963.

4. G. A. Razuvaev, K. S. Minsker et al., *DAN*, **151**, 110 (1963).

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