

COPOLYMERIZATION OF PROPYLENE WITH VINYL CHLORIDE BY A MODIFIED ZIEGLER-NATTA CATALYTIC SYSTEM

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Copolymerisation of propylene with vinyl chloride catalysed by the system titanium trichloride–equimolar complex of triethylaluminium and 2-hydroxyethylamine was studied in methylene chloride. It was found that both copolymerization parameters have the values considerably higher than 1. The dependence of the yield of copolymer on monomer mixture composition have a different course for each of both examined types of titanium trichloride. The results are interpreted so that in the mixtures rich in propylene, the copolymerisation proceeds *via* an ionic-coordination mechanism, while in the mixtures rich in vinyl chloride a radical mechanism is operative.

Vinyl chloride belongs to the class of polar monomers which are most frequently homo- and copolymerised by Ziegler–Natta catalytic systems. Some authors^{1–3} put forward the radical mechanism for these polymerisations, others call the attention to the possibility of a simultaneous operation of the radical and the ionic-coordination mechanisms during copolymerisation of vinyl chloride with propylene⁴ and they also stress a different mechanism of copolymerisation when even a slightly different catalytic systems are used⁵. Misono and coworkers^{6–9} when copolymerised vinyl chloride with ethylene by the catalytic system tetrabutyltitanium (or vanadium oxytrichloride)–alkylaluminium chlorides have observed the change of mechanism with the alteration of the catalyst components ratio or on addition of electron donors.

In the present study we would like to report on the observed change of polymerisation mechanism with monomer mixture composition. The catalytic system titanium trichloride–equimolar complex of triethylaluminium and 2-hydroxyethylamine, which is recommended in patent literature¹⁰ for this monomer couple, was used.

In the preliminary experiments the yield of copolymer was taken as a measure of the rate of polymerisation. Separate experiments have proved that the yield, at constant ratio of catalyst components, is roughly proportional to the concentration of titanium trichloride. A shallow minimum can be observed in the dependence of the copolymer yield *vs* monomer mixture composition (Fig. 1) for titanium trichloride type AA, in contrast to the same dependence for titanium trichloride type HA. In mixtures rich in propylene, type AA is more active as it is at the homopolymerisation of propylene catalysed by titanium trichloride–triethylaluminium (or diethylaluminium chloride) systems in hydrocarbon medium. On the other hand in mixtures rich in vinyl chloride, markedly more active is titanium trichloride type

HA. The composition of copolymers is depicted in Fig. 2, where curve 3 represents the theoretical dependence, assuming the validity of radical copolymerisation parameters¹¹ ($r_1 = 2.27$; $r_2 = 0.30$). The dependences (curves 1 and 2) determined experimentally can be formally interpreted as an azeotropic copolymerisation with both parameters higher than 1, even if the experiments so far performed do not allow us to calculate the exact values of r_1 and r_2 . Figure 2 indicates quite clearly that the curves 1 and 2 follow roughly the theoretical dependence only for mixtures rich in vinyl chloride. From this it can be judged that on this side of copolymerisation diagram the propagation proceeds *via* a radical mechanism, though we have no direct evidence for this assertion. The copolymerisation of mixtures rich in propylene proceeds most probably *via* an ionic-coordination mechanism as there is no known case of propylene polymerisation which would under the given conditions proceed by other mechanism.

It is also worth to note, that the minimum rate of polymerisation appears (Fig. 1) in the azeotropic region of the copolymerisation diagram, when titanium trichloride type AA is used. This similarity was not with certainty found for titanium trichloride type HA, even if the experiments made so far do not exclude it. The changes of chemical shifts of propylene units (from $8.2-9.2\tau$ towards the lower field up to 7.3τ) and the simultaneous changes of the intensity ratios and of the fine structure of these signals give evidence that it is a statistic copolymer of both monomers and not a mixture of homopolymers or a block copolymer.

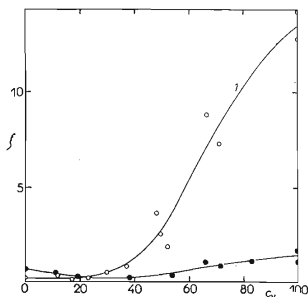


FIG. 1

Yield of Copolymer (ξ in mol.%) vs Vinyl Chloride Concentration in Monomer Mixture (c_v in mol.%)

Type of $TiCl_3$ in the catalyst: 1 HA, 2 AA.

EXPERIMENTAL

Chemicals. Titanium trichloride type HA (prepared by reduction of TiCl_4 with hydrogen and activated by subsequent grinding), triethylaluminium, propylene and purified nitrogen were specified earlier¹². Titanium trichloride type AA was prepared by grinding mixed crystals¹³ ($\text{TiCl}_3 \cdot 1/3 \text{AlCl}_3$). Vinyl chloride (CHZWP, Nováky, Czechoslovakia) was analysed by GLC for: acetylene (< 1 p.p.m.), methanol (< 20 p.p.m.) and higher chlorinated hydrocarbons (< 50 p.p.m.); the contents of water and oxygen were < 10 p.p.m. 2-Hydroxyethylamine (Merck, Darmstadt) was dried over molecular sieve 4 Å and freed from oxygen by the flow of nitrogen. Methylene chloride (Lachema, Brno) 99-96% by GLC was freed from water by distillation with phosphorus pentoxide. The complex $[\text{H}_2\text{NCH}_2\text{CH}_2\text{OH} \cdot \text{AlEt}_3]$ was prepared by adding dropwise the calculated amount of monoethanol amine to the heptane solution of triethylaluminium (15%) which was cooled by dry ice from outside; when the reaction was finished the crystals formed were dissolved in toluene (25% of toluene in the solution).

Apparatus and procedure. As a reaction vessel was used pressure dilatometer¹⁴ which was before use flushed with nitrogen at 100°C. After cooling the dilatometer was filled with methylene chloride, flushed with nitrogen at the temperature of the solvent boiling point and then the solution of the triethylaluminium-2-hydroxyethylamine complex and the heptane suspension of titanium trichloride were added by means of syringes. As the last components monomers were dosed from the cylinders in the following order: vinyl chloride, propylene. The total monomer concentration was around 100 g/l. The dilatometer was then heated up to 70°C and at this temperature kept 10 minutes (under continuous stirring). Unless it is stated otherwise, the concentration of titanium trichloride was 9 mmol/l and the ratio $[\text{Al}]/[\text{Ti}] = 7$. Polymerisation mixture was then poured into the excess of methanol to which hydrochloric acid was added; the polymer was filtered off, washed with pure methanol and dried under vacuum to a constant weight. The

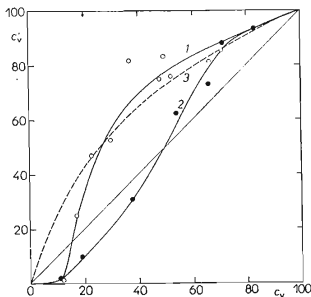


FIG. 2

Copolymer Composition (amount of vinyl chloride, c'_v , in mol.%) vs Vinyl Chloride Concentration in the Monomer Mixture

Type of TiCl_3 in the catalyst: 1 HA; 2 AA; 3 theoretical curve according to ref.¹¹.

composition of the copolymer was determined by NMR spectroscopy, using a Tesla BS 487 A apparatus at 80 MHz. *o*-Dichlorobenzene served as a solvent (polymer was dissolved at 130°C). The measurements were carried out at 160°C and the polymer concentration was 100–200 mg per 1 ml of the solution. Hexamethyldisiloxane was used as a standard.

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