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Abstract

Full Text

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COPOLYMERIZATION OF VINYL CHLO- RIDE WITH OLEFINS ON ZIEGLER SYS- TEMS

The processes of homopolymerization of vinyl chloride and olefins under the action of Ziegler catalysts—aluminum alkyl chlorides of transition metals—proceed in a distinctive manner and differ from one another. Whereas, for example, ethylene and propylene are polymerized effectively in the presence of trialkylaluminum or dialkylaluminum halide in combination with titanium chloride, vinyl chloride is not capable under these conditions of forming solid polymeric products.

It was found that the polymerization of vinyl chloride can be carried out by using, as the homogeneous component of the Ziegler catalyst, alkoxy derivatives of organoaluminum compounds ($\hat{1}$). It proved that under these same conditions the polymerization of ethylene and propylene also proceeds at a sufficiently high rate ($\hat{2}$, $\hat{3}$). Subsequently, an attempt was made to carry out the joint polymerization of olefinic hydrocarbons with vinyl chloride.

As in ordinary heterogeneous polymerization proceeding under the influence of Ziegler catalysts, individual aluminum alkyls or chlorides of metals of variable valence proved inactive. The polymerization process was observed only in the presence of a mixture of both components. Of the three aluminum alkyls studied, $(C_2H_5)_3Al$, $(C_2H_5)_2AlOC_2H_5$, and $C_2H_5Al(OC_2H_5)_2$, diethylaluminum ethoxide was active in the copolymerization reaction.

Use of the catalytic system $(C_2H_5)_2AlOC_2H_5 + TiCl_4$, $(C_2H_5)_2AlOC_2H_5 + C_2H_5Al(OC_2H_5)Br + TiCl_4$ made it possible reproducibly to obtain (60°; olefin pressure 10 atm; 300 g VC; reactor volume 4 l) copolymeric products with a chlorine content of 42-53% (Table 1).

The yield of the copolymeric product depended on the concentration of the catalyst in the reaction mixture.

Copolymerization of vinyl chloride with ethylene proceeded successfully also when diisobutylaluminum isobutoxide was used as cocatalyst. However, the activity of the catalyst in comparison with diethylaluminum ethoxide (under comparable conditions) was much lower (Table 1).

As can be seen, the yield and composition of the copolymer, as in the case of the

ethyl derivative of aluminum, depended on the concentration of diisobutylaluminum isobutoxide in the reaction volume. An increase in the yield of copolymer could be achieved by adding bromine to diisobutylaluminum isobutoxide before mixing it with titanium tetrachloride.

It was discovered that a mixture of titanium tetrachloride, diethylaluminum ethoxide, and ethylaluminum ethoxybromide also catalyzed the copolymerization of vinyl chloride with propylene.

A copolymeric product containing 40–48% chlorine was obtained in good yield (Table 1). It is evident that the yield of copolymer depended on the ratio of the components of the catalytic system. The molar ratio of diethylaluminum ethoxide to ethylaluminum ethoxybromide in the mixture $(C_2H_5)_2AlOC_2H_5 +$

$+C_2H_5Al(OC_2H_5)Br + TiCl_4$ was varied over very wide limits, taking as limiting cases mixtures of $(C_2H_5)_2AlOC_2H_5 + TiCl_4$ (Al : Ti = 16 : 1) and $C_2H_5Al(OC_2H_5)Br + TiCl_4$ (Al : Ti = 16 : 1). In contrast to the yield, the composition of the copolymerization product changed little.

Further experiments showed the possibility of simple control of the copolymerization process of vinyl chloride with olefins. This is quite clearly seen in the example of the copolymerization of vinyl chloride with ethylene.

It was noted that the composition of the copolymer product obtained in the presence of $(C_2H_5)_2AlOC_2H_5 + C_2H_5Al(OC_2H_5)Br + TiCl_4$ or $(C_2H_5)_2AlOC_2H_5 + TiCl_4$ is strongly affected by the addition of unoxidized triethylaluminum. Introduction of the electrophilic aluminum trialkyl reduced the ac-

Table 1

Copolymerization of vinyl chloride with olefins. Vinyl chloride 300 g; olefin 10 atm (constant make-up to 10 atm); reactor volume 4 l; liquid-mixture volume 0.5 l; solvent—benzene; 60°C; 20 h

No.	TiCl ₄ , mol	Aluminum compound	Molar ratio of catalyst components, Al : T	Yield, g	Chlorine content in copolymer, wt. %
Copolymerization of vinyl chloride with ethylene					
1	0.015	$(C_2H_5)_2AlOC_2H_5 + C_2H_5Al(OC_2H_5)Br$	16 : 1	33.6	42

No.	TiCl ₄ , mol	Aluminum compound	Molar ratio of catalyst components, Al : T	Yield, g	Chlorine content in copolymer, wt. %
Oxidized (to monoxide) mixture					
2	0.015	(C ₂ H ₅) ₃ Al + (C ₂ H ₅) ₂ AlBr	10 : 6 : 1	300	45
3	0.015	Same	8.5 : 5 : 1	200	49
4	0.01	Same	8.5 : 5 : 1	130	—
5	0.01	(C ₂ H ₅)AlOC ₂ H ₅	10 : 1	120	48
6	0.015	(iso-C ₄ H ₉) ₂ AlOC ₂ H ₅	10 : 1	15	31
7	0.015	Same	10 : 1	30	10
8	0.015	Same	15 : 1	38	2
9	0.015	(iso-C ₄ H ₉) ₂ AlOC ₂ H ₅ + Br ₂	1 : 130 (0.7)		6
Copolymerization of vinyl chloride with propylene					
10	0.015	(C ₂ H ₅) ₂ AlOC ₂ H ₅	6 : 1	167	48
11	0.015	(C ₂ H ₅)AlOC ₂ H ₅ + (C ₂ H ₅) ₂ AlOC ₂ H ₅ + Br ₂	10 : 1	190	41.6
12	0.015	Same	10 : 6 : 1	190	42.3
13	0.015	Same	8 : 8 : 1	228	41.4
14	0.015	Same	4 : 12 : 1	59	44
15	0.015	C ₂ H ₅ AlOC ₂ H ₅ + Br ₂	6 : 1	Sol. high-mol. polymer, oil	Sol. high-mol. polymer, oil

tivity of vinyl chloride in copolymerization, while at the same time increasing the rate of the ethylene-chain growth reaction. Thus, at the ratio (C₂H₅)₃Al : (C₂H₅)₂AlOC₂H₅ = 1 : 10 (60°), the copolymerization constants of ethylene and vinyl chloride were related as $r_1 : r_2 = 41.3$ (0.691 : 0.0167). Introduction of an excess of unoxidized triethylaluminum up to the amount determined by the

Figure 1 and Figure 2 plots

Figure 1: Figure 1 and Figure 2 plots

ratio $(C_2H_5)_3Al : (C_2H_5)_2AlOC_2H_5 = 4 : 10$ led to an increase in the difference between the constants by an order of magnitude, $r_1 : r_2 = 403.6 (22.2 : 0.055)$. This made it very easy to regulate the composition of the copolymer product obtained by changing the ratio between the oxidized and unoxidized forms of the aluminum alkyl in the catalyst, while leaving the initial concentrations of the monomers practically unchanged.

Figure 1 presents a dependence characterizing the copolymerization process as a function of the change in catalyst concentration while maintaining the molar ratio $(C_2H_5)_2AlOC_2H_5 : C_2H_5AlOC_2H_5Br : TiCl_4 = 10 : 3 : 1$. In the range of concentrations studied, there occurred (curves 1 and 2) an increase in the yield of polymer product almost proportional to the increase in the concentration of the catalyst used (the usual dependence for Ziegler polymerization). At the same time, the content

chlorine in the copolymer product remained practically constant (curve 3).

Figure 2 shows the dependence of the yield and composition of the copolymer product on the duration of the reaction. It is seen that in the course of the process the crude product of copolymerization becomes enriched in vinyl chloride units. This may be a consequence of enrichment of the reaction mass with vinyl chloride due to a change in the ratio of the monomer concentrations in the reaction zone (the pressure in the reactor was maintained constant by feeding ethylene).

Fig. 1. Effect of changing the catalyst concentration on the copolymerization of vinyl chloride with ethylene. $(C_2H_5)_2AlOC_2H_5 : C_2H_5AlOC_2H_5Br : TiCl_4 = 10 : 3 : 1$; vinyl chloride 300 g; ethylene to $P_{total} = 10$ atm; 60° ; 2 hours. 1 –copolymer yield; 2 –yield per unit of catalyst; 3 –chlorine content in the copolymer.

Fig. 2. Dependence of the composition of the copolymer and of the product yield on the reaction time. $(C_2H_5)_2AlOC_2H_5$ 0.18; $C_2H_5Al(OC_2H_5)Br$ 0.054; $TiCl_4$ 0.018 mole; vinyl chloride 300 g; ethylene –to $P_{total} = 10$ atm. 1, 3 – copolymer yield; 2, 4 –chlorine content in the product. 1, 2 –without addition of vinyl chloride; 3, 4 –with addition of vinyl chloride.

In those cases where the concentrations of monomers in the reaction zone were kept constant by simultaneous feeding of both monomers into the reactor, the composition of the copolymerization product practically did not change during the course of the process (Fig. 2, curve 4).

On the basis of the results given above, one could expect a dependence of the product composition on the ratio of vinyl chloride to ethylene present in the reaction zone. Indeed, such a dependence was found (Fig. 3). Up to a vinyl

Figure 3 plot

Figure 2: Figure 3 plot

chloride : ethylene ratio equal to 3 : 1, preferential polymerization of ethylene took place (vinyl chloride units were contained in the copolymerization product in small amounts). With an increase in this ratio it was possible to regulate the composition of the copolymer within wide limits.

Fig. 3. Dependence of the chlorine content in the copolymer on the molar ratio vinyl chloride : ethylene. TiCl_4 0.018; $(\text{C}_2\text{H}_5)_2\text{AlOC}_2\text{H}_5$ 0.18; $\text{C}_2\text{H}_5\text{AlOC}_2\text{H}_5\text{Br}$ 0.054; ethylene —to $P_{\text{total}} = 10$ atm; 60° ; 2 hours. 1 —copolymer yield; 2 — chlorine content in the copolymer.

The copolymerization products were white powders of very fine structure for the vinyl chloride-ethylene pair and slightly granular powders for the vinyl chloride-propylene pair.

Depending on the chlorine content in the copolymer product, its physical, physicochemical, and thermomechanical properties changed substantially. The copolymerization products possessed increased solubility, compared with the homopolymers, in dichloroethane, cyclohexanone, nitrobenzene, chloroform, chlorobenzene, and xylene. It should be noted that upon repeated reprecipitation, for example from nitrobenzene, the composition of the copolymer products—

products (90–95% of the residue after the first reprecipitation) did not change. The limiting viscosity number was within the range $[\eta] = 0.1\text{—}0.5$ (nitrobenzene, 20°).

The glass-transition temperature of the samples (T_c) was lower than the T_c of ordinary polyvinyl chloride, but higher than the T_c of the homopolymers of the olefins used. The flow temperature (from thermomechanical curves) of the copolymers of vinyl chloride with propylene lay in the range $60\text{—}90^\circ$, and that of vinyl chloride with ethylene in the range $90\text{—}128^\circ$. The thermostability varied within 3–40 min (with a change in the Cl content of the product from 50 to 1%). The decomposition temperature changed analogously. The increased solubility of the copolymer products in various solvents, as compared with polyvinyl chloride, polyethylene, and polypropylene, together with other characteristics and properties, permits the assumption that the copolymer products obtained from vinyl chloride with ethylene and from vinyl chloride with propylene are copolymers of regular structure.

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