Chemistry

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1964

SovietRxiv

Abstract

Full Text

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POLYMERIZATION OF PENTENE-1 IN THE PRESENCE OF ISOPRENE ON A COMPLEX CATALYST

The copolymerization of olefins with dienes by Ziegler catalysts has to date been studied comparatively little: the copolymerization of propylene with isoprene has been investigated, and a number of patents describe the joint polymerization of butadiene-1,3 and isoprene with alpha-olefins (^{2}). These literature data do not make it possible to draw an unambiguous conclusion about the formation of true copolymers in the presence of the catalyst $TiCl_4$—Al (iso-Bu)$_3$.

Table 1

Separate polymerization of isoprene and pentene-1 on the complex catalyst $TiCl_4$—Al (iso-C_4H_9)$_3$.
TiCl concentration, mol. 1.0%, relative to the monomer, solvent—hexane, $t = 20^\circ \pm 1.0$; experiment duration 30 min.

Molar ratio Al:Ti	1.0:1.0	1.2:1.0	1.4:1.0	1.6:1.0	1.8:1.0	2.0:1.0
Monomer—isoprene (4.15 mol/l)						
Polymer yield, %	89	94	33—40	24—32	8—11	1.5
Intrinsic viscosity	1.6	3.4	2.0	1.85	1.1	0.1
Monomer—pentene-1 (3.3 mol/l)						

Molar ratio Al:Ti	1.0:1.0	1.2:1.0	1.4:1.0	1.6:1.0	1.8:1.0	2.0:1.0
Polymer yield, %	5.5—6.0	8.5—9.0	8.5	11.5	10.0	9.0
Intrinsic viscosity	1.05	1.9	1.4	2.1	1.5	1.9

In the present communication the results are presented of a study of the polymerization of isoprene, pentene-1, and their mixtures under comparative conditions in the presence of a catalyst obtained by the interaction of $TiCl_4$ with Al (iso-Bu).

In the separate polymerization of isoprene, an optimum is observed in the ratio of the catalyst components Al : Ti from 1.0 : 1.0 to 1.2 : 1.0, corresponding to the greatest yield of high-molecular-weight cis-1,4-polyisoprene (3,4) (see Table 1).

In the case of pentene-1, the polymer yield depends little on the ratio of the catalyst components within the limits investigated by us (see Table 1). The activity of pentene-1 is substantially lower than that for isoprene at Al : Ti ratios close to 1.0 : 1.0, and higher at 2.0 : 1.0, when isoprene practically does not polymerize.

In the polymerization of a mixture of isoprene and pentene-1 at a ratio Al : Ti = 1.0 : 1.0, a polymer is formed containing 83% isoprene units, but the yield and intrinsic viscosity are lower than in the separate polymerization of isoprene (see experiments 1 and 2 of Table 2).

The results of fractionation of this polymer show that under the experimental conditions a mixture of homopolymers is formed (see Table 3).

Table 2

Polymerization of a mixture of isoprene and pentene-1 on the complex catalyst $TiCl_4$—Al(iso-C_4H_9)$_3$.
Isoprene concentration 4.0 mol/l, pentene 3.7 mol/l, $TiCl_4$—1.0% relative to isoprene, solvent—hexane, $t = 20^\circ \pm 1$

No.	Molar ratio Al:Ti	Polymer composition n_D^{20}	Polymer composition, isoprene content, %	Yield, g	Intrinsic viscosity	Entered into polymerization: isoprene, g	Entered into polymerization: isoprene, % of initial	Entered into polymerization: pentene-1, g	Entered into polymerization: pentene-1, % of initial
1	1.0:1.0	1.5154	83.5	2.55	0.28	2.13	63	0.42	13
2	1.0:1.0	1.5154	83.5	2.15	–	1.80	53	0.35	11
3	1.2:1	1.5215	100	3.05	2.7	3.05	89	0	0
4	1.2:1	1.5213	100	2.84	–	2.84	85	0	0
5	1.4:1	1.5180	90.5	0.16	0.32	0.145	4.3	0.015	0.4
6	1.4:1	1.5182	91	0.15	–	0.135	4.0	0.015	0.4
7	1.6:1	1.5170	88	0.12	0.30	0.106	3.0	0.014	0.4
8	1.6:1	1.5160	85	0.1	–	0.085	2.5	0.015	0.4
9	1.8:1	1.5148	81	0.06	–	0.05	1.5	0.01	0.3

Thus, on the catalyst obtained by the interaction of $TiCl_4$ with $Al(iso\text{-}C_4H_9)_3$, taken in a ratio of 1:1, there are at least two types of active centers, one of which is specific for the polymerization of isoprene, the other only for pentene-1. At higher Al:Ti ratios, the active centers of the second type, nonspecific for the polymerization of isoprene, are evidently completely destroyed, and those of the first type only partially (see Table 1).

Table 3

Fractionation of the polymers from experiments Nos. 1 and 2 (see Table 2).

Polymer	Weight, g	n_D^{20}	Intrinsic viscosity	Isoprene, %	Pentene, %
Initial	1.31	1.5154	0.28	83.5	16.5
Fraction 1	0.53	1.5215	0.30	100	0
Fraction 2	0.39	1.5220	0.17	100	0
Fraction 3	0.21	1.5215	–	100	0
Fraction 4	0.22	1.4810	0.025	2	98

At the same time, active centers of a third type appear, again specific for the polymerization of pentene-1, but, owing to the strong adsorption of isoprene, they are practically completely blocked and therefore are incapable of carrying out the polymerization of pentene-1 even at Al:Ti ratios of 1.8:1 and 2:1, when

Fig. 1

Figure 1: Fig. 1

pure isoprene does not polymerize. This observation agrees with the data obtained in work (^{1}) on the effect of increasing additions of isoprene on the yield of polypropylene with the catalyst $TiCl_4$—$Al(C_2H_5)_3$. At the same time, the presence of pentene-1 promotes the chain-termination reaction of isoprene only at Al:Ti ratios higher than 1.2:1.0.

The conclusion that different catalytic centers are present in the system we studied agrees with data on the presence of catalytic complexes of different stereospecificity in the $TiCl_4$—RMgHal system (^{5}) and in the $TiCl_4$—AlR_3 system (^{6}).

Experimental Part

Starting materials. Technical isoprene was purified by the usual method, subjected to rectification, and dried over calcium hydride; immediately before use it was distilled from butyllithium at 0°. Pentene-1 was obtained by the previously described procedure (^{7}); before use it was distilled from butyllithium.

A technical 50-60% solution of triisobutylaluminum in heptane was distilled under vacuum at a temperature not above 40° into sealed graduated ampoules. Titanium tetrachloride was purified by distillation over copper turnings into sealed ampoules. A solution of the desired concentration of the catalyst components was prepared by breaking the ampoule in a nitrogen tube, into which a measured amount of hexane had first been distilled from butyllithium.

Fig. 1

Polymerization was carried out in carefully dried ampoules; the catalyst components were dosed from nitrogen tubes, and the catalyst was aged for 20 min at 20°; then, under vacuum at $-70°$, isoprene and pentene-1 were introduced. The polymer obtained was dissolved in benzene and precipitated with methanol.

Fractional fractionation of the polymer was carried out from a 0.8% solution by precipitation with methanol. The refraction of the polymers was determined on an IRF-22 refractometer. A solution of the polymer in benzene was repeatedly applied to the prism of the refractometer and, after complete removal of the solvent, the refractive index of the film formed was determined. The composition of the polymer was determined on the assumption of additivity of the refractive index for copolymers and mixtures of homopolymers (Fig. 1).

For polyisoprene, $n_D^{20} = 1.5218$ was found; for polypentene, $n_D^{20} = 1.4800$.

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Received
20 IX 1963

REFERENCES CITED

1. N. S. Volkova, G. V. Khutareva et al., *Vysokomolek. soed.*, **1**, 12, 1758 (1959).

2. N. Gaylord, T. Mark, *Linear and Stereoregular Polymers. Polymerization with Controlled Chain Growth*, IL, 1962, p. 400.

3. W. M. Saltman, W. E. Gibbs, J. Lal, *J. Am. Chem. Soc.*, **80**, 21, 5615 (1958).

4. H. E. Adams, R. S. Stearns et al., *Ind. and Eng. Chem.*, **50**, 1507 (1958).

5. B. A. Dolgoplosk, L. M. Romanov et al., *DAN*, **115**, No. 4 (1957).

6. G. Natta, L. Porri et al., *Chim. e ind.*, **41**, 398 (1959).

7. I. S. Lishanskii, A. A. Korotkov et al., *ZhPKh*, **32**, 2344 (1959).

Note: Figure translations are in progress. See original paper for figures.