

NOTES

Polymerization of Propylene Oxide with Ziegler-Natta Catalysts

Many catalyst systems for polymerizing propylene oxide (PO) have been reported.¹⁻³ Aluminum trialkyls are effective catalysts and binary systems with water,⁴ chelating agents,⁵ metal chelates,⁶ and metallic soaps⁷ were found to increase the catalytic activity to give the high molecular weight crystalline poly(propylene oxide). However, no detailed investigation of the polymerization of PO with the catalyst systems consisting of aluminum alkyls and transition metal halides, so-called Ziegler-Natta catalyst, has been reported.

The present paper describes the results of the polymerization of PO catalyzed by systems of aluminum alkyls, i.e., $\text{Al}(\text{C}_2\text{H}_5)_3$, $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, and $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$, and transition metal halides (TiCl_3 , TiCl_4 , VCl_3 , and VCl_4).

Results and Discussion

The results of the polymerization of PO are summarized in Table I. It was found that the system $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_3$ was the most effective in producing a polymer of high yield, reduced viscosity, and crystallinity. The catalytic activity was markedly affected

TABLE I
Polymerization of PO Catalyzed by Systems of Aluminum
Alkyls and Transition Metal Halides in *n*-Heptane at 80°C.^a

Catalyst system	Al/Ti (or Al/V)	Time, hr.	Polymer				Appearance
			Yield, %	η_{sp}/c , dl./g. ^b	Crystallinity %		
$\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_3$	1	24	14.4	0.05	—	Viscous liquid	
$\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_2$	2	24	72.9	0.31	30.6	Waxy	
$\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_3$	4	5	78.8	0.59	40.6	Waxy	
$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl-TiCl}_3$	2	24	60.0	0.02	—	Viscous liquid	
$\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2\text{-TiCl}_3$	2	24	54.0	0.02	—	"	
$\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_4$	2	24	81.7	0.03	3.6	"	
$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl-TiCl}_4$	2	24	82.0	0.03	Trace	"	
$\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2\text{-TiCl}_4$	2	24	61.5	0.05	6.7	"	
$\text{Al}(\text{C}_2\text{H}_5)_3\text{-VCl}_3$	2	36	52.0	0.08	—	"	
$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl-VCl}_3$	2	36	51.8	0.05	—	"	
$\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2\text{-VCl}_3$	2	36	5.5	—	—	Liquid	
$\text{Al}(\text{C}_2\text{H}_5)_3\text{-VCl}_4$	2	24	27.7	0.02	—	Viscous liquid	
$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl-VCl}_4$	2	24	3.4	—	—	Liquid	
$\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2\text{-VCl}_4$	2	24	8.8	—	—	"	
$\text{Al}(\text{C}_2\text{H}_5)_3$	2	24	46.7	0.21	19.7	Waxy	

^a $[\text{PO}] = 7.4$ mole/l., $[\text{TiCl}_n \text{ or } \text{VCl}_n] = 0.074$ mole/l.,

^b Determined in 0.5% solution in benzene at 30°C.

^c Estimated from the solubility in acetone at 0°C.

by the type of aluminum alkyl and transition metal components in the catalyst systems used, and decreased in the following order: $\text{Al}(\text{C}_2\text{H}_5)_3 > \text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} > \text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$; $\text{TiCl}_3 > \text{TiCl}_4$; $\text{VCl}_3 > \text{VCl}_4$; $\text{TiCl}_3 > \text{VCl}_3$, as the ratio Al/Ti or V was 2. These results suggest that the increased cationic nature of the catalyst systems decreased the catalytic activity for the PO polymerization. It was also found that the activity of the system $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_3$ was increased as a function of the Al/Ti ratio, supporting the above consideration.

TABLE II
Polymerization of Epoxides with $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_3^a$

Epoxide	Yield, %	η_{sp}/c , dl./g.	Acetone- insolubles, %
Epichlorohydrin	74.7	0.07	13.7
1,2-Butene oxide	68.7	0.17	26.3
Styrene oxide	81.5	0.03	8.7
Phenyl glycidyl ether	74.7	0.11	18.4
Allyl glycidyl ether	23.8	0.10	10.8

^a [Epoxide] = 7.4 mole/l., $[\text{TiCl}_3] = 0.074$ mole/l., $[\text{Al}]/[\text{Ti}] = 4$.

The copolymerization of PO with epichlorohydrin (ECH) catalyzed by the system $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_3$ (Al/Ti = 4) was attempted. The composition of the resulting copolymers was almost identical to that of the monomer feed mixtures. This result was quite different from that obtained by using the cationic catalyst system $\text{Al}(\text{C}_2\text{H}_5)_3\text{-H}_2\text{O}$ ($r_{(\text{PO})} = 4.65$, and $r_{(\text{ECH})} = 0.09$).⁸

Table II shows the results of the polymerization of the other epoxides with the system $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_3$ (Al/Ti = 4). It was found that these epoxides could readily polymerize as well as PO and all the resulting polymers contained some acetone-insoluble fractions.

Experimental

Monomers and the other reagents were purified by ordinary methods. Aluminum alkyls and transition metal halides, which were the same as used in the previous paper,⁹ were used without further purification. Polymerization or copolymerization was carried out in a sealed glass tube at 80°C. Each binary catalyst system was prepared in *n*-heptane and aged for 1 hr. at room temperature before use. After polymerization for a given time, the tube was opened and the contents poured into isopropanol containing hydrochloric acid. The reaction mixture was then diluted with methylene chloride, and the catalyst residue was removed by dissolving with dilute hydrochloric acid, followed by repeated washing with distilled water. The resulting polymer was isolated by distilling off the volatile materials under reduced pressure, and then dried at about 50°C. *in vacuo*.

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