A New Catalyst System for the Polymerization of Tetrahydrofuran

By Iwao YAMASHITA, Minoru SERIZAWA and Takaharu MIYAKAWA

(Received August 21, 1963)

The ring-opening polymerization of tetrahydrofuran (THF) by the use of metal halides or triethyl aluminum as a catalyst has recently been reported by several authors.[1] In such cases, a cocatalyst or comonomer, such as alkyl halides, ortho acid esters, hydrogen halides, alkylene oxides, oxethanes, diketene, β-propiolactone, and phenyl isocyanate, have been used together with the catalyst.

We have now examined the polymerization of THF by the use of organometallic compounds (Et_3Al, Et_2AlCl, Et_2Zn) or metal halides ($BF_3 \cdot Et_2O$, $AlCl_3$, $FeCl_3$) in the presence of phosphorus pentaoxide (P_2O_5) and have found that Et_3Al was the most effective of the substances examined.

Bulk polymerization was carried out in a nitrogen atmosphere in a sealed test tube. The polymeric product was isolated by pouring the reaction mixture into a large quantity of water containing hydrochloric acid. The crude polymer was washed with methanol and then dissolved in THF at room temperature by leaving it standing for 24 hr. The THF-soluble fraction was recovered by again pouring the solution into a large excess of water and then drying it in vacuo. The THF-insoluble fraction was washed with THF and dried in vacuo.

Several results of the polymerization of THF by the use of the P_2O_5-Et_3Al system are shown in Table I and Figs. 1 and 2. The effect of P_2O_5 is obvious. Both the THF-soluble and the THF-insoluble fraction contain a small amount phosphorus.*

When the THF-soluble fraction was compared with polytetrahydrofuran prepared by the method of Muetterlies[3] (catalyst: PF_5), considerable differences in the thermal properties were noticed, whereas the X-ray diffraction patterns and infrared spectra of the two polymers were similar. On the other hand, an apparent difference was found between those of the THF-soluble fraction and those of the

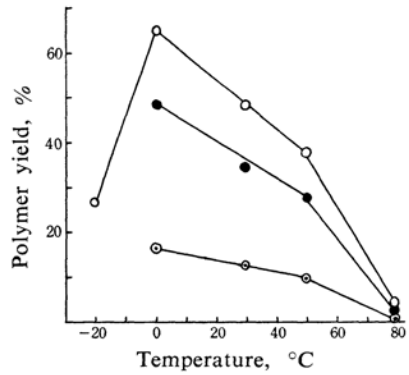

Fig. 1. The yield of polymer vs. polymerization temperature.
Catalyst, $1/2P_2O_5$ (2 mol. %)-Et_3Al (2 mol. %)
Polymerization time, 24 hr.
○: Total yield
●: Yield of THF-insoluble fraction
⊙: Yield of THF-soluble fraction

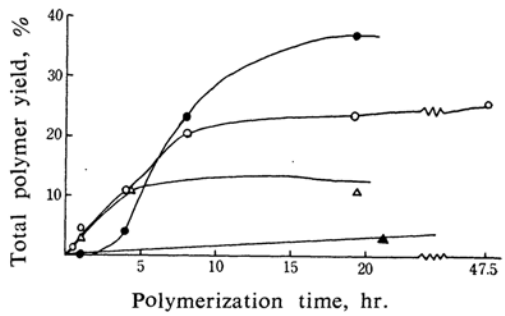

Fig. 2. The total polymer yield vs. polymerization time.
Catalyst, $1/2P_2O_5$ (2 mol. %)-Et_3Al (1 mol. %)
●: 0°C, ○: 30°C, △: 50°C, ▲: 80°C

1) See, for example, H. Meerwein, *Angew. Chem.*, **72**, 927 (1960); T. Saegusa et al., presented at the Meeting of the Society of Polymer Science, Osaka, November, 1962.

* The quantitative analysis of the phosphorus in the polymer was carried out by the Nakamura's method.[2]

2) M. Nakamura, *J. Agr. Chem. Soc. Japan* (*Nogei Kagaku Zasshi*), **24**, 1 (1950).

3) E. L. Muetterties, U. S. Pat. 2856370 (1958).

TABLE I. POLYMERIZATION OF THF BY Et_3Al-P_2O_5 SYSTEM
EFFECT OF AMOUNT OF P_2O_5
THF : 0.05 mol., Et_3Al : 0.001 mol. (2 mol. %), Polymerization at 30°C for 24 hr.

$1/2P_2O_5$ / Et_3Al	Total yield %	THF-sol. fraction			THF-insol. fraction	
		Yield %	η_{sp}/c*	P Content %	Yield %	P Content %
0	0	—	—	—	—	—
0.2	5.7	5.6	—	—	0.1	0.92
0.6	22.6	6.1	2.28	—	16.5	0.83
1.0	48.5	13.5	1.75	0.17	35.0	0.90
1.6	34.2	9.2	2.58	—	25.0	1.92
2.0	43.0	12.7	2.79	—	30.3	1.19

* Measured on a solution of 0.2 g. polymer in 100 ml. benzene at 30°C.

THF-insoluble fraction. These differences seem to have some relation to their phosphorus contents.

Further details of the reaction mechanism of such a catalyst system and such properties of polymers will be published elsewere.

Government Industrial Research Institute, Osaka
Oyodo-ku, Osaka