Iron(III) Chloride-Triphenyl Phosphite as a New Catalyst for the Polymerization of Tetrahydrofuran

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The polymerization of tetrahydrofuran by the use of Friedel-Crafts catalysts with co-catalysts, such as alkylene oxides, active halogen compounds and so on, was first examined by Meerwein.[1] Subsequently Muetterties[2] reported the use of phosphorus pentafluoride to give a polymer. Recently Saegusa et al.,[3] Weissermel and Nölken[4] and the present authors[5] have reported that triethyl aluminum is a effective catalyst when used with co-catalysts. In this communication, it will be reported that iron(III) chloride-triphenyl phosphite is an interesting new catalyst system for the polymerization of tetrahydrofuran.

Bulk polymerization was carried out in a nitrogen atmosphere in a sealed glass ampoule. The polymerization mixture was allowed to stand at a desired temperature. The polymeric product was isolated by pouring the reaction mixture into a large amount of diluted hydro chloric acid (0.001～0.005 N). The crude polymer was washed with methanol and then dissolved in tetrahydrofuran. The purified polymer was recovered by again pouring the solution into a large excess of water and then dried in vacuo at room temperature.

The effects of the amount of iron(III) chloride and the polymerization temperature on the yield and the reduced viscosity of the polymer are shown in Figs. 1, 2A and 2B.

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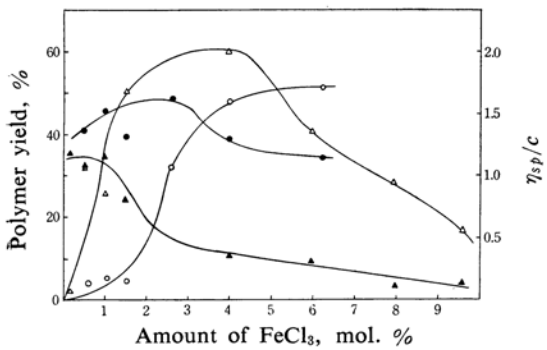

Fig. 1. The yield and the reduced viscosity of polymer vs. the amount of $FeCl_3$.
THF 0.05 mol., $(PhO)_3P$ 0.05 mol. % to monomer
Polymerization time 24 hr.
-△- Yield of polymer at 30°C
-○- Yield of polymer at 0°C
-▲- η_{sp}/c of polymer at 30°C
-●- η_{sp}/c of polymer at 0°C
(η_{sp}/c was measured on a solution of 0.2 g. polymer in 100 ml, of benzene at 30°C)

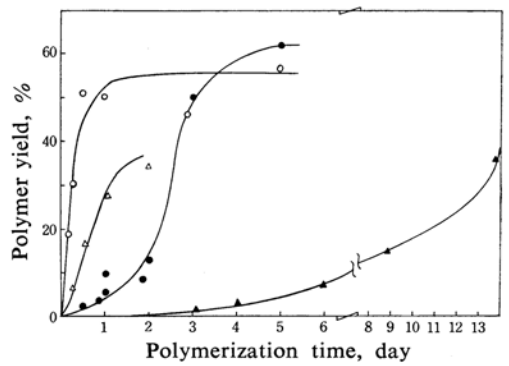

Fig. 2-A. The yield of polymer vs. polymerization time.
THF: 0.05 mol., $FeCl_3$: 1.5 mol. %, $(PhO)_3P$: 0.5 mol. %
-○- at 30°C
-△- at 15°C
-●- at 0°C
-▲- at −20°C

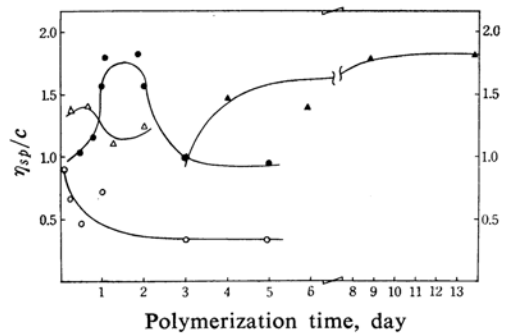

Fig. 2-B. The reduced viscosity of polymer vs. polymerization time.

1) H. Meerwein, *Angew. Chem.*, **72**, 927 (1960).
2) E. L. Muetterties, U. S. Pat. 2856370 (1958).
3) T. Saegusa, H. Imai and J. Furukawa, *Makromol. Chem.*, **65**, 60 (1963).
4) K. Weissermel and E. Nölken, ibid., **68**, 140 (1963).
5) I. Yamashita, M. Serizawa and T. Miyakawa, This Bulletin, **36**, 1368 (1963).

chloride, boron fluoride etherate, titanium chloride and zinc chloride) was used in place of iron(III) chloride, together with triphenyl phosphite, these catalyst systems gave no polymer under the polymerization conditions examined. Moreover, none of the polymerizations occurred when triphenyl phosphite was used alone or when iron(III) chloride itself was used as a catalyst.

The infrared spectra, the solubilities and the thermal properties of the polymer were very similar to those of the polytetrahydrofuran prepared by the use of the other catalysts (phosphorous pentafluoride[2] and triethyl aluminum-epichlorohydrin[3]).

Further details on such polymerization results and on the role of triphenyl phosphite in such a catalyst system will soon be published.

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