

## SHORT COMMUNICATIONS

## The Polymerization of Tetrahydrofuran Catalyzed by Tungsten(VI) Chloride

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Tetrahydrofuran (THF) has been known to be polymerized by such catalysts as Lewis acid-cocatalyst systems,<sup>1,2</sup> triethyl aluminum-cocatalyst systems,<sup>3-5</sup> the triethyl aluminum-water(1:1)-cocatalyst,<sup>3</sup> ferric chloride-triphenyl phosphite,<sup>6</sup> phosphorous(V) fluoride,<sup>7</sup> and antimony(V) chloride.<sup>7</sup> Of these catalysts, phosphorous(V) fluoride and antimony(V) chloride appear highly active. We will now report on the utility of tungsten(VI) chloride, whose activity nearly corresponds with those of the above two catalysts.

Tetrahydrofuran was dried over sodium and distilled immediately before use. Polymerization was carried out in a sealed tube which had been allowed to stand at a desired temperature while being occasionally shaken. The initiation of the polymerization was shown by a change in the color of the polymerization mixture from a black suspension to a reddish brown solution. The mixture was washed with acetone-water (20:1), and the crude polymer was isolated by cooling. The polymer was then purified by pouring a THF solution of the crude polymer into a large amount of water, followed by washing it with methanol and drying it in vacuo at room temperature.

In all the experiments presented, 0.5 g. of tungsten(VI) chloride was used for 20 ml. of THF. This catalyst level of 0.5 mol. % was found to be the optimum. A further increase

in the amount of the catalyst resulted in a decrease in the yield of the polymer.

A summary of the results is presented in Table I. The first six runs indicate that the yield and the reduced viscosity maxima occur at 0°C. At 20–40°C, the color of the polymerization mixture turns blue after about 3 hr. It appears that in the blue-colored mixture no polymerization but, rather, a rather slow

TABLE I. THE YIELD AND THE REDUCED VISCOSITY OF THE POLYMER

Time hr.	Temp. °C	Yield %	$\eta_{sp}^*$
8	-20	1.5	—
8	-10	54.5	0.80
8	0	81.1	1.15
8	10	74.4	0.75
8	20	41.4	0.55
8	30	6.2	0.20
2	0	29.8	0.80
4	0	64.0	1.30
24	0	79.8	0.75
48	0	85.5	0.60

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

depolymerization occurs. At 0°C, the yield of the polymer is 80% at a reaction time of 8 hr. and is slightly affected by a further increase in the reaction time.

The infrared spectra of the polymer are very similar to that of polytetrahydrofuran prepared by the use of the other catalyst.<sup>3</sup>

A further investigation of this polymerization is in progress and will be reported on later.

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