The Polymerization of Trioxane Catalyzed by Rhenium Pentachloride and Molybdenum Pentachloride

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It is well known that the polymerization of trioxane is catalyzed by such Lewis acids as boron fluoride, tin(IV) chloride and antimony-(V) chloride.1) Also, it has been recently found2) that rhenium pentachloride and molybdenum pentachloride act as Lewis acids and are effective catalyst for alkylation and carbonylation. Therefore, the present authors have tried to polymerize trioxane by using these catalysts. Three types of polymerization, that is, solid state polymerization by the simultaneous sublimation of monomer and catalyst,3)

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1) S. Okamura, T. Higashimura and M. Fugawa, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 712 (1962); S. Okamura, T. Higashimura and K. Takeda, *Makromol. Chem.*, **51**, 217 (1962).

2) J. Tsuji and M. Morikawa, Private Communication.

3) H. Miyama and M. Kamachi, *J. Polymer Sci.*, **B 1**, 465 (1963).

solution polymerization, and bulk polymerization, were performed.

In the solid state polymerization by simultaneous sublimation, commercial trioxane (American Celanese Co.) was purified by repeated sublimation at a high vacuum and then introduced, at the pressure $10^{-4} \sim 10^{-5}$ mmHg, into an ampoule cooled by liquid nitrogen. At the same time, the desired quantity of rhenium pentachloride or molybdenum pentachloride, which had also been purified by repeated vacuum sublimation, was introduced into the ampoule. After it had been sealed off, the ampoule was placed in a thermostat of a definite temperature for a definite time and then opened. In this reaction, as soon as the polymerization occurred, the color of the reaction system changed from yellow to blue-violet in the case of rhenium pentachloride, and from light yellow to dark yellow in the case of molybdenum pentachloride. The polymer obtained was washed completely with benzene, methyl alcohol, and water to remove any unreacted monomers and catalyst. The inherent viscosity of the polymer was measured in a *p*-chlorophenol solution (0.1 g./100 ml.) containing 2% of α-pinene by using a Ostwald viscometer at 60°C. The results obtained are shown in Table I.

TABLE I

Catalyst	Concn. of catalst wt. %	Polymn. time min.	Polymn. temp. °C	Yield %	η_{inh}
$ReCl_5$	0.6	60	62	90.5	2.60
			65	84.5	2.81
			43	81.4	2.77
			−10	25.0	3.11
$MoCl_5$	0.6	30	62	93.3	1.36
			50	82.7	0.71
			30	63.1	1.43
			21	64.3	1.47
			0	23.9	2.14
			−10	20.7	1.77
			−20	20.1	1.82

In the solution polymerization, 0.1 g. of the catalyst was dissolved or suspended in 50 cc. of benzene or another solvent. This solution was then mixed with a solution consisting of 20 cc. of benzene and 10 g. of trioxane. The mixture was made to react in the stream of nitrogen. The color of the system changed as soon as the polymerization occurred. For example, when rhenium pentachloride was used in a benzen-ethyl chloroacetate solution, the color changed from green to gray-green. The results are shown in Table II where "solvent" means the reagent used for dissolving of dispersing the catalyst.

In the bulk polymerization, 2 g. of trioxane and 0.01 g. of the catalyst were dispersed into 10 cc. of petroleum ether. After moisture and air had been removed by evacuation at the temperature of liquid nitrogen, the petroleum ether was evaporated; the reaction vessel was then sealed off and kept at 80°C for one hour. Results are shown in Table III.

In the solid state polymerization of trioxane by the simultaneous sublimation of monomer

TABLE II

Catalyst	Solvent	Polymn. time hr.	Polymn. temp. °C	Yield %	η_{inh}
$ReCl_5$	Benzene	4	60	88	0.63
	Benzene	2	40	34	0.63
	Benzene	4	40	46	0.80
	Ethylene dichloride	2/3	40	91	0.37
	Cyclohexane	1	40	48	0.85
	Acetone	1	40	62	0.64
	Methyl ethyl ketone	1	40	54	0.81
	Tetrahydrofrane	1	40	18	0.59
	Ethyl chloroacetate	2/3	40	93	0.65
	Ethyl chloroacetate	1	25	90	0.76
$MoCl_5$	Benzene	4	60	54	0.65
	Benzene	4	55	52	0.71
	Benzene	3	40	47	0.64
	Cyclohexane	3	55	69	0.88
	Cyclohexane	5.5	40	66	0.78
	Acetone	3	40	74	0.66
	Acetone	3	25	52	0.73
	Ethyl chloroacetate	3	40	91	0.75
	Ethyl chloroacetate	3	25	87	0.68

TABLE III

Catalyst	Yield, %	η_{inh}
$ReCl_5$	90	1.6
$MoCl_5$	70	1.4

and iodine,[3] it was once suggested by the present authors that the initiation of radical polymerization takes place in association with the crystal dislocations caused by the simultaneous sublimation and that polymerization occurs in the temperature range between 0°C and 15°C. However, the situation is very different for the present case because the polymerization occurs even at the temperature of -20°C and also in solution and in bulk. Moreover the color of the polymerization system changes as soon as the polymerization occurs, and the coexistence of a polar solvent increases the polymer yield markedly. On the basis of these findings, it is considered that rhenium pentachloride and molydenum pentachloride catalyze the ionic polymerization of trioxane by forming a complex with trioxane.

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