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Polymerization Catalyst of the Triethylaluminum-Chloral Hydrate System. II. Copolymerization of Acetaldehyde with Chloral

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It has been found that the $AlEt_3$-chloral hydrate system induces the random copolymerization of acetaldehyde with chloral. The homogeneity of the product polymer was confirmed by a study of the infrared spectra and by turbidimetric titration. The thermal stability of the copolymer was much better than that of homopolyacetaldehyde. The copolymer was soluble in chloroform, and films were cast from chloroform solutions.

In our previous paper,[1] we reported the reaction of $AlEt_3$ with chloral hydrate and the cationic polymerizations of several monomers using the reactions mixture as the catalyst. In the present paper, we wish to report on the characteristic catalyst behavior of the $AlEt_3$-chloral hydrate system in the copolymerization of acetaldehyde with chloral.

The copolymerization between acetaldehyde and chloral was once performed using $AlEt_3$ as the catalyst; the product polymer was always 1 : 1 alternating copolymer.[2] Several aluminum alkoxides, such as $Et_2AlOC_4H_9$-*s*, $Et_2AlOCH_2CCl_3$, $Et_2AlOCH(Et)CCl_3$, and some aluminum trialkoxides have been applied to the polymerization system of an acetaldehyde-chloral mixture. None of these aluminum alkoxides, however, caused any copolymerization; they gave only acetaldehyde homopolymers with low molecular weights.[2] The difference in catalytic behavior between $AlEt_3$ and aluminum alkoxides has been explained in terms of the mechanism of coordinate anionic polymerization.

The $AlEt_3$-chloral hydrate system of the present study is distinguished by its catalyst activity inducing random copolymerization between acetaldehyde and chloral.

Experimental

Reagents. *Acetaldehyde.* Acetaldehyde was prepared and purified by a method similar to that of the previous paper.[2]

The other reagents were purified by a method similar to that of another preceding paper.[1]

Preparation of Catalyst System. Catalytic systems were prepared similarly as has already been described in the preceding paper.[1]

Copolymerization. The monomer mixture and the solvent were placed in a glass tube under a nitrogen atmosphere and cooled to −78°C. After a catalyst solution had been added, drop by drop, to this cold mixture, the polymerization mixture was kept standing at −78°C for a definite reaction time. Then the polymerization was stopped by adding methanol. The copolymers were fractionated to methanol-soluble and chloroform-soluble (methanol-insoluble) fractions. The compositions of the copolymers were calculated from the

TABLE 1. COPOLYMERIZATION OF ACETALDEHYDE WITH CHLORAL. EFFECT OF SOLVENT

$AlEt_3$-$Cl_3CCHO \cdot H_2O$ (2/1): 2 mmol; Cl_3CCHO: 0.1 mol; CH_3CHO: 0.1 mol; polymn.: at −78°C

Solvent	(m*l*)	Polymn. time (day)	Polymer (%)		
			Total yield	Methanol-soluble part[a)]	Chloroform-soluble part[a)]
Ether	(40)	16	22	6(27)	16(73)
Toluene	(45)	3	17	12(69)	5(31)
Toluene	(40)	11	18	8(43)	10(57)[b)]
Methylene chloride	(45)	3	16	10(64)	6(36)
Dioxane	(45)	5	18	16(87)	2(13)

a) The values in parentheses indicate the relative percentages to total yield.
b) $[\eta]=1.55$ in chloroform at 30.0°C.

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1) Part I: T. Saegusa, H. Fujii, T. Ueshima and K. Tanaka, This Bulletin, **41**, 1188 (1968).

2) T. Iwata, T. Saegusa, H. Fujii and J. Furukawa, *Makromol. Chem.*, **97**, 49 (1966).

chlorine and carbon contents determined by elemental analyses.

Turbidimetric Titration. Turbidimetric titration was carried out using a photo-electric turbidimeter of the Shimadzu Co. (Kyoto, Japan). The copolymer sample was a chloroform-soluble (methanol-insoluble) fraction composed of CH_3CHO and Cl_3CCHO units in the ratio of 72/28; this fraction had been prepared using the $AlEt_3$-chloral hydrate (2/1) system. In 100 m*l* of chloroform, 20 mg or 40 mg of the sample were dissolved, and methanol was added to the mixture at a rate of 1.6 m*l*/min at 16°C. The light scattered was measured at an angle of 90°.

TABLE 2. COPOLYMERIZATION OF ACETALDEHYDE WITH CHLORAL, EFFECT OF MONOMER RATIO

$AlEt_3$-$Cl_3CCHO \cdot H_2O$ (2/1): 2mmol;
total monomer: 0.2mol; Polymn.: 3days;
at −78°C

CH_3CHO/Cl_3CCHO (mmol) (mmol)	Polymer yield (%)	CH_3CHO unit in copolymer (mol%)
160 / 40	13	73
100 / 100	16	65
40 / 160	6	56

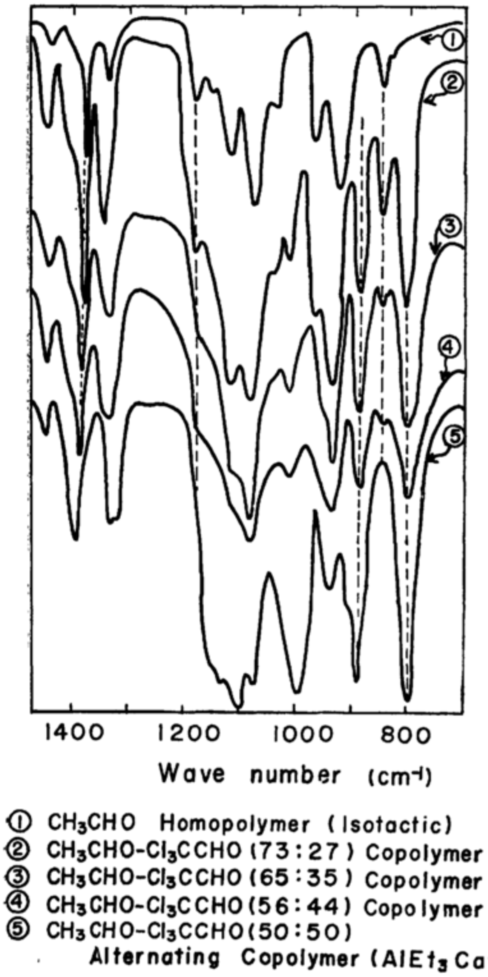

Fig. 1. Infrared spectra of the copolymer by $AlEt_3$-$Cl_3CCHO \cdot H_2O$ system compared with those of other aldehyde.

Results and Discussion

Copolymerization of Acetaldehyde with Chloral. In the copolymerization between acetaldehyde and chloral, the 1 : 1 alternating copolymerization by the $AlEt_3$ catalyst[2)] was the sole example up to the present study. Several aluminum alkoxides have brought about the formation of the acetaldehyde homopolymer.

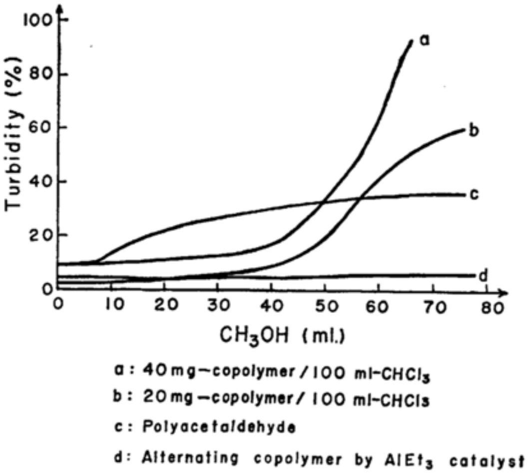

Fig. 2. Turbidimetric titration of the copolymer of acetaldehyde with chloral.

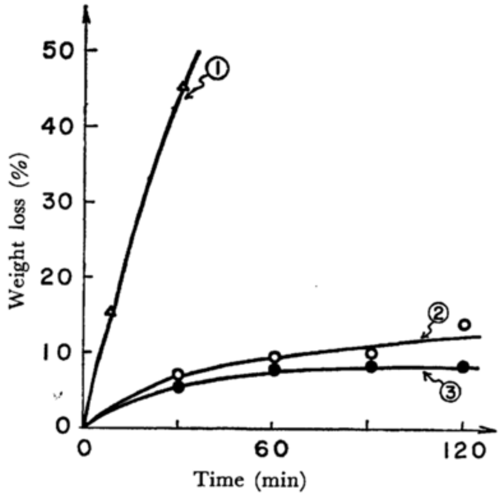

Fig. 3. Thermal decompositions of polyaldehydes at 105°C under nitrogen atmosphere.

①△: Polyacetaldehyde
②○: CH_3CHO-Cl_3CCHO (63 : 37) Copolymer ($AlEt_3$-$Cl_3CCHO \cdot H_2O$ catalyst)
③●: Alternating copolymer ($AlEt_3$ catalyst)

The results of the copolymerization by the $AlEt_3$-chloral hydrate system are illustrated in Tables 1 and 2.

As shown in Table 1, the product polymers can be fractionated into methanol-soluble and chloroform-soluble (methanol-insoluble) fractions. However, no difference was observed in the infrared spectra of these two fractions; only the difference in the molecular weights of the copolymers induced the fractionation.

The infrared spectra of the product copolymers of various compositions in Table 2 are shown in Fig. 1, where they are compared with those of the acetaldehyde homopolymer and the alternating copolymer prepared by the $AlEt_3$ catalyst. As shown in Fig. 1, the spectra of the copolymers gradually vary with the change in composition. The absorption bands at 1187, 973, and 845 cm^{-1} observed in homopolyacetaldehyde decrease with the increase of chloral units in the copolymer and vanish in the alternating copolymer, whereas the bands at 995 and 895 cm^{-1}, which are not observed in homopolyacetaldehyde, appear and gradually increase in the copolymers. These observations suggest that the copolymer produced by the $AlEt_3$-chloral hydrate system is a real random copolymer and not a mixture of homopolyacetaldehyde and the 1 : 1 alternating copolymer.

The homogeneity of the product copolymer was supported by turbidimetric titration. The results are shown in Fig. 2. It is there shown that the product copolymer is fairly homogeneous and does not contain homopolyacetaldehyde or the 1 : 1 alternating copolymer.

It is worthy of mention that copolymers prepared using the $AlEt_3$-chloral hydrate system are of fairly high molecular weights, as indicated by their intrinsic viscosity values in chloroform (*cf.* Table 1). The alternating copolymerization by $AlEt_3$ catalysts always gave polymers with lower intrinsic viscosities.[2]

The thermal stability of the copolymer is much better than that of homopolyacetaldehyde (Fig. 3).

The copolymer is soluble in chloroform, and films can be cast from the chloroform solution. The copolymer, however, decomposes at 180±5°C without melting.