Intramolecular-Intermolecular Polymerization of Glutaraldehyde[1]

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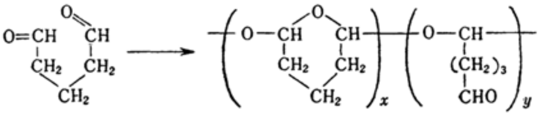
Recently, many studies were reported on the intramolecular-intermolecular polymerization of nonconjugated diolefins[2]. This reaction process was extended to the addition polymerization of glutaraldehyde (I). It was reported that certain dialdehydes yielded glassy materials without catalyst, but their structures were not described[3].

I was polymerized to the white, powdery polymer with an organometallic catalyst such as triethylaluminum or partially hydrolyzed one. Boron trifluoride-ether complex and other cationic catalysts were also effective. These polymers cantained a few residual aldehyde groups by infrared analysis. This suggests that the ring formation was occurred during the propagation process.

Some results of the polymerization with triethylaluminum-water catalyst are shown in Table I. The soluble fraction (II) of considerably high viscosity and low residual aldehyde content, melted at about 75~85°C, and was depolymerized quantitatively to I by pyrolysis in vacuo. II has the strong infrared absorption bands at 1150~950 cm^{-1}, which are assigned to ether bond. The sharp absorption bands are also observed at 805 and 855 cm^{-1}. A sample of 2-ethoxycyclooxahexane prepared for comparison shows the corresponding bands at 811 and 872 cm^{-1}.

Therefore, it would seem reasonable to believe that II posessed the six-membered cyclic ether units and the linear nature evidenced by solubility and fusibility.

It was presumed from these results that the polymerization proceeded mainly by intramolecular-intermolecular mechanism and the polymer thus obtained had the ring structure as shown below:



where the ratio of x to y was nearly equal to ten.

The soluble tetramer or pentamer obtained from I after being kept at room temperature without catalyst, contained about one aldehyde group per one molecule, and showed the similar infrared spectrum to that of II. The polymers obtained with the cationic catalysts, on the other hand, were less soluble and showed the different infrared spectrum from II.

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TABLE I. EXAMPLES OF POLYMERIZATION OF GLUTARALDEHYDE WITH $Al(C_2H_5)_3$-H_2O (1 : 1) IN TOLUENE AT −76°C (CATALYST CONCENTRATION 5.0 mol.% TO MONOMER)

Monomer g./ml.	Time hr.	Conversion %	Soluble[a] fraction %	Soluble fraction	
				$[\eta]$[b] dl./g.	Residual[c] aldehyde, %
0.050	1.5	27.4	17.9	0.26	6.4
0.058	2.7	51.4	27.6[d]	0.24	8.7

a) Soluble fraction of polyglutaraldehyde in cold benzene.
b) Intrinsic viscosity of benzene solution at 30°C.
c) Determined by infrared absorption at 1730 cm^{-1}.
d) Analysis: Found: C, 59.20; H, 8.16. Calcd. for $(C_5H_8O_2)_n$: C, 59.98; H, 8.05%.

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[1] Presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

[2] G. B. Butler and R. J. Angelo, *J. Am. Chem. Soc.*, **79**, 3128 (1957); C. S. Marvel and R. D. Vest, ibid., **79**, 5771 (1957); C. Aso, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 363 (1960); and etc.

[3] C. Harries and L. Tank, *Ber.*, **41**, 1701 (1908); and etc.