Studies on the Polymerization of Bifunctional Monomers. IV.[*1] *The Intramolecular-Intermolecular Polymerization of 3-Substituted Glutaraldehydes*[*2]

By Chuji Aso and Yuzo Aito

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Previously, the present authors found that the concept of intramolecular-intermolecular polymerization, which had been proposed in the polymerization of non-conjugated divinyl compounds,[1] might be applied to the addition polymerization of glutaraldehyde.[2,3]

The polymerization of glutaraldehyde[*3] was also studied by Overberger et al.,[4] Meyersen et al.,[5] and Moyer et al.[6] at almost the same time as by the present authors. These workers, as well as the authors, came to the conclusion that the polymer contained a tetrahydropyran ring as a main structure, although there were a few differences in the polymerization conditions, etc.

Meyersen et al. also described how 3-methylglutaraldehyde and 3-phenylglutaraldehyde were polymerized without a catalyst.[5] However, the catalytic polymerization of these dialdehydes was not reported. The present authors, independently, studied the polymerization of these 3-substituted glutaraldehydes in the absence of a catalyst. Moreover, 3-methyl- and 3-phenylglutaraldehyde were polymerized with a catalytic system of triethylaluminum-water, in order to clarify whether these dialdehydes would yield polymers containing a ring structure similar to that of poly(glutaraldehyde). The influences of substituents and of several additives to the reaction rate were also investigated.

Experimental

3-Methylglutaraldehyde and 3-phenylglutaraldehyde were prepared by hydrolysis of the corresponding 4-substituted 2-ethoxy-3, 4-dihydropyrans.[8] 3-Methylglutaraldehyde: b. p. 87.0 ~ 88.0°C/21.0 mmHg, n_{D}^{25}, 1.4365. Found: C, 62.51; H, 8.84. Calcd. for $C_6H_{10}O_2$: C, 63.13; H, 8.83%. 3-Phenylglutaraldehyde: b. p. 129.0~131.5°C/4.5 mmHg, n_{D}^{14}, 1.5355. Found: C, 74.48; H, 7.19. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87%.

The catalyst, solvents and polymerization procedures have been previously described.[3] The viscosities of the soluble polymers were determined in benzene at 30°C, using a modified Ubbelohde viscometer. Molecular weights were measured by Rast's method (solvent: camphene), and the infrared spectra, with a Nippon Koken model 301 spectrophotometer.

The pendant aldehyde content in the polymers was determined by the aid of infrared spectroscopy at the 1730 cm^{-1} band, which is characteristic of the carbonyl group.[3]

Results and Discussion

3-Substituted glutaraldehyde was polymerized at a low temperature to a white solid by using a triethylaluminum-water system as the catalyst. Some of these results are listed in Table I. Polymers in general consist of soluble as well as of insoluble fractions in benzene. The properties of the soluble polymers are shown in Table II.

The infrared spectra of the soluble and the insoluble fractions of poly(3-substituted glutaraldehydes) were quite similar. The infrared spectra of the soluble fraction of 3-methyl- and 3-phenylglutaraldehyde polymers are shown in Figs. 1 and 2 respectively. A very weak band was still observed at 1730 cm^{-1} (C=O band). However, quantitative comparison of the carbonyl bands of these soluble polymers with those of monomers and some monoaldehydes suggests that the pendant aldehyde content of the polymers is very low. Moreover, the absorption bands of these polymers in the

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[*1] Contribution No. 51 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka, Japan.

[*2] Partly presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

1) 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); etc.

2) C. Aso and Y. Aito, This Bulletin, **35**, 1426 (1962).

3) C. Aso and Y. Aito, *Makromol. Chem.*, **58**, 195 (1962).

[*3] Recently, Yokota et al. reported the polymerization of glutaraldehyde and 3-methylglutaraldehyde through the Tischenko reaction by using the aluminum alkoxide as a catalyst.[7]

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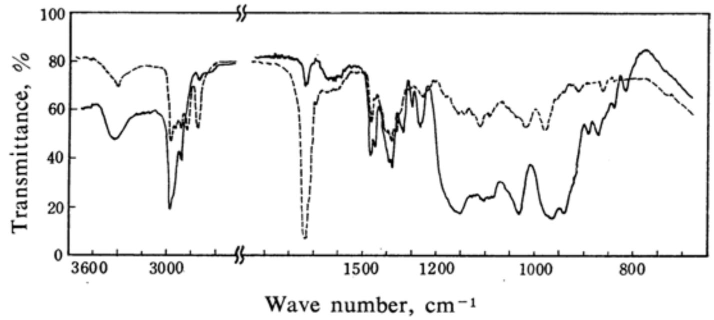
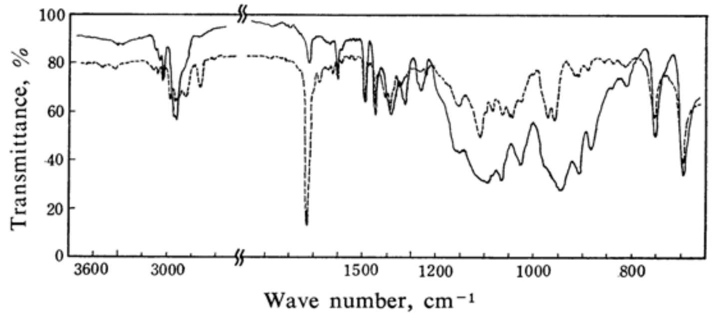


Fig. 1. Infrared spectra of 3-methylglutaraldehyde (in liquid film ; - - -) and poly(3-methylglutaraldehyde) (in KBr disk ; ——).



Fig, 2. Infrared spectra of 3-phenylglutaraldehyde (in liquid film ; - - -) and poly(3-phenylglutaraldehyde) (in KBr disk ; ——).

TABLE I. POLYMERIZATION OF 3-METHYLGLUTARALDEHYDE AND 3-PHENYLGLUTARALDEHYDE WITH TRIETHYLALUMINUM-WATER CATALYST (−78°C, IN TOLUENE)

No.[a]	Monomer concn. g./ml.	Catalyst concn. mol.% to monomer	Time hr.	Total conversion %	Soluble fraction[b] %
M-1	0.050	5.60	44.0	9.2	30.5
M-2	0.083	5.87	39.5	14.9	29.6
M-24	0.100	5.02	26.0	13.3	32.2
Ph-12	0.100	5.03	21.0	54.5	80.0
Ph-13	0.050	4.95	25.0	40.2	99.0

a) M : Poly(3-methylglutaraldehyde) Ph : Poly(3-phenylglutaraldehyde)
b) Fraction of the polymer, soluble in benzene.

TABLE II. PROPERTIES OF SOLUBLE POLYMERS OBTAINED BY CATALYST SYSTEM OF TRIETHYLALUMINUM-WATER

No.	M. p. °C	η_{sp}/C[a]	[CHO][b] %	Molecular weight
M-1a	35∼ 44	—	11.0	1900∼2500
M-2a	35∼ 40	—	15.8	1000∼1200
M-24a	115∼120	0.18	18.3	—
Ph-12a	93∼ 97	0.07	6.1	—
Ph-13a	87∼ 96	0.06	23.3	—

a) η_{sp}/C (C=0.150 g./dl. in benzene, 30°C)
b) Pendant aldehyde content determined by the infrared spectroscopy.

1000∼800 cm^{-1} region resemble those of the 4-substituted 2-ethoxytetrahydropyrans chosen as model compounds. These facts suggest that the polymer formed by the triethylaluminum-water catalyst consists also of recurring tetrahydropyran rings, as Meyersen et al. indicated in the case of spontaneous polymerization.[5)]

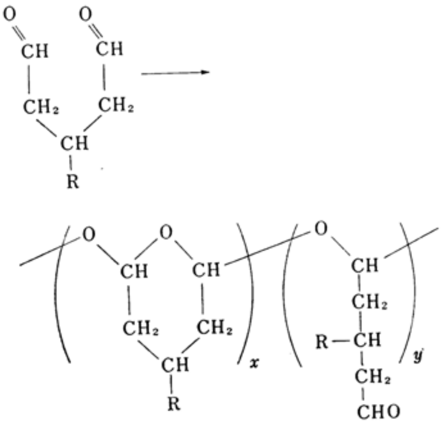
3-Substituted glutaraldehydes changed spontaneously to glassy materials at room temperature or in an ice-box. After repeated reprecipitations, white, solid polymers were obtained. Some properties of these polymers are shown in Table III.

TABLE III. SOME PROPERTIES OF SPONTANEOUS POLYMERS OF 3-METHYLGLUTARALDEHYDE AND 3-PHENYLGLUTARALDEHYDE

No.	M. p. °C	[η] dl./g.	[CHO] %	Molecular weight
M-4	56∼67	—	8.7	700∼800
M-5	62∼67	0.03	8.1	—
Ph-2	83∼86	—	16.3	∼700
Ph-3	79∼82	0.03	17.6	—

Since the infrared spectra of the polymers obtained spontaneously are almost in accordance with those of the polymers obtained with a catalyst, the structure of the former is considered to be substantially the same as that of the latter.

As mentioned above, the solubility, the fusibility, the low pendant aldehyde group content and the resemblance of the infrared spectrum of the polymer to those of the model compounds suggest that the ring formation occurs in the course of the polymerization of 3-substituted glutaraldehyde and that the polymer mainly consists of the tetrahydropyran ring. Therefore, polyglutaraldehydes obtained by the polymerization, with or without a catalyst, are probably polyethers with the following structures:



where R is H, CH_3, or C_6H_5. As the content of the ring unit in the polymer is high, the polymerization is considered to proceed mainly through alternative intramolecular cyclization and intermolecular propagation reactions. Succinaldehyde seems also to polymerize through this mechanism.[9]

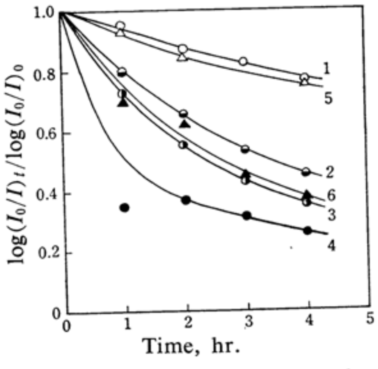


Fig. 3. Influence of additives in polymerization system.
1 : Glutaraldehyde (non-additives)
2 : Glutaraldehyde (5% of phenol was added)
3 : Glutaraldehyde (5% of benzyl alcohol was added)
4 : Glutaraldehyde (10% of water was added)
5 : 3-Methylglutaraldehyde (non-additives)
6 : 3-Methylglutaraldehyde (5% of ethanol was added)

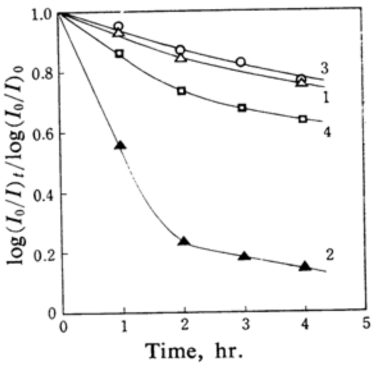


Fig. 4. Influence of polymerization temperature and substituents.
1 : 3-Methylglutaraldehyde, at 25°C
2 : 3-Methylglutaraldehyde, at 59°C
3 : Glutaraldehyde, at 25°C
4 : 3-Phenylglutaraldehyde, at 25°C

The infrared absorption intensity due to the carbonyl group of aldehyde was measured during the spontaneous polymerization under given conditions. The ratio of the intensity at time t to that at $t=0$ was plotted against the time.

The rate of consumption of the aldehyde group was markedly accelerated by the addition of a small quantity of water, ethanol or benzyl alcohol, as shown in Fig. 3. The infrared spectrum of the polymer formed spontaneously in the presence of benzyl alcohol shows the presence of a benzyl group in the polymer chain. Thus, these added substances seem to influence the initiation of the polymerization. The polymerization temperature and the substituent at the β-position to the aldehyde group also influenced the rate of aldehyde consumption (Fig. 4). The polymerization mechanism, however, is now being investigated; the details will be reported in the future.

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Department of Organic Synthesis
Faculty of Engineering
Kyushu University
Fukuoka

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[9] C. Aso, Y. Aito and A. Furuta, presented at the 12th Annual Meeting of the High Polymer Chemical Society of Japan, Tokyo, May, 1963.