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Stereospecific Polymerization of *o*-Phthalaldehyde

Recently, Aso *et al.*[1-4] reported the cyclopolymerization of *o*-phthalaldehyde by ionic catalysts to give poly(*o*-phthalaldehyde) the *trans*-oxyphthalan ring content of which varied widely from 15 to 88% depending on the nature of catalyst, including $[R_2AlOCR'NPh]_2$-type catalyst. We found that water or peracetic acid was an indispensable cocatalyst in the stereospecific polymerization of acetaldehyde catalyzed by $[R_2AlOCR'NPh]_2$[5-7] or R_2AlOR'.[8] This paper describes the essential role of water as a cocatalyst for the stereospecific polymerization of *o*-phthalaldehyde and the preparation of the crystalline poly(*o*-phthalaldehyde).

Practically no polymer was obtained when *o*-phthalaldehyde purified by repeated distillation was used as monomer, crystalline $[Me_2AlOCMeNPh]_2$ (**1**) as catalyst and tetrahydrofuran dried throughly over Na-K alloy as solvent. In contrast to this result, the polymerization proceeded smoothly at −78° in a homogeneous state throughout the polymerization in the presence of an appropriate amount of water (Figure 1). The optimum amount of added water for obtaining a maximum yield of the polymer was about 1/20th mol/mol of **1**. This optimum amount is the same order of magnitude as that observed in the stereospecific polymerization of acetaldehyde catalyzed by $[R_2AlOCR'NPh]_2$[5,6] or by R_2AlOR'.[8]

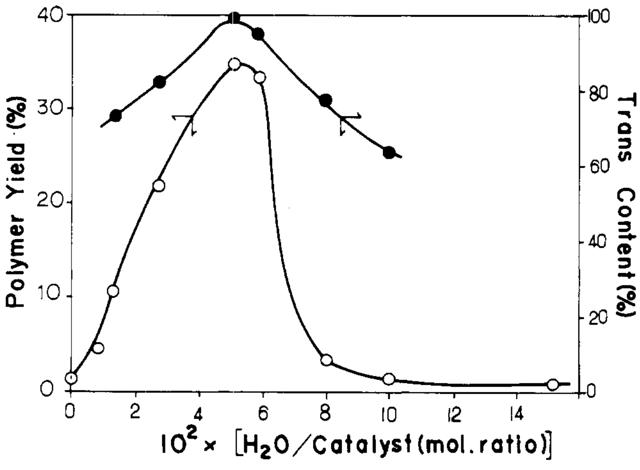
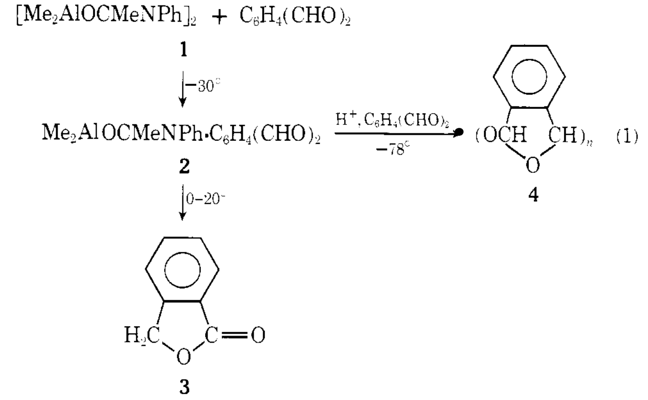


Figure 1. Cocatalytic action of added water in the polymerization of *o*-phthalaldehyde catalyzed by **1**. Catalyst concentration, 1 mol % of monomer. Solvent, toluene (40 ml/g of monomer). Polymerization, −78° for 70 hr.

The polymerization carried out in the presence of an optimum amount of added water gave a fibrous, crystalline polyether whose ir spectrum had no free C=O absorption, while that in the presence of a larger or a smaller amount of added water gave a low-crystalline, powdery polymer. The content of *trans*-oxyphthalan unit was determined by chemical shifts and peak areas of methine proton signals in the nmr spectrum, according to the method developed by Aso *et al.*[3] The nmr spectrum of the polymer (Figure 2) obtained by the catalyst **1** in the presence of an optimum amount of water showed only one sharp methine peak at δ 6.9 ppm in tetrahydrofuran, while that obtained by $BF_3\cdot OEt_2$ showed a complicated spectrum containing seven peaks and that obtained by Ph_3COK catalyst showed two single peaks in a ratio of 1:1 at δ 6.90 and 6.52 ppm assignable to trans and cis methine protons, respectively. Therefore, the content of *trans*-oxyphthalan unit in the crystalline polymer obtained by **1** is nearly 100%. The trans content decreased and the cis content increased when the amount of added water was larger or smaller (Figure 1).

The 1:1 monomer–catalyst complex **2** was obtained as colorless crystals by mixing **1** with *o*-phthalaldehyde in an equimolar ratio at a temperature slightly higher than the ceiling temperature of polymerization (−40°). The complex **2** is stable only in a narrow temperature range, because it transformed gradually to give phthalide (**3**) quantitatively at 10° and converted to poly(*o*-phthalaldehyde) **4** at below −40° (eq 1). These reactions proceeded also in the presence of excess of *o*-phthalaldehyde.



The composition and structure of **2** were determined by spectroscopic methods. In the nmr spectrum (60 MHz) recorded in toluene-d_8 solution at −10°, the peak area ratio of signals assigned to methyl protons attached to aluminum atom, to those in the OCMeNPh grouping, and the phenyl protons of the *o*-phthalaldehyde moiety corresponded to the formula of **2**. The ir spectrum gave valuable information on the structure of **2**. On forming **2**, the carbonyl absorption of *o*-phthalaldehyde shifted from 1699 to 1679 cm^{-1} and the absorption band assigned to the O–C–N grouping of **1** shifted from 1568 to 1572 cm^{-1}. The latter shift (from 1568 to 1572 cm^{-1}) is equal to that observed in the formation of the benzaldehyde complex $Me_2AlOCMeNPh\cdot PhCHO$.[9] It is reasonable to conclude

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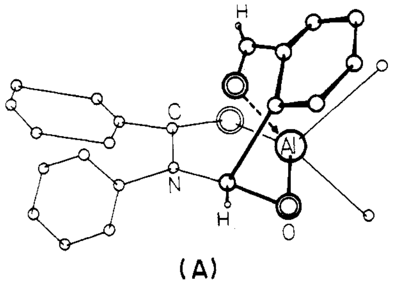
that one aldehyde group of *o*-phthalaldehyde is inserted between aluminum and nitrogen atoms in **1**, similarly to that of acetaldehyde in $Me_2AlOCPhNPh\cdot MeCHO$,[7] while another is simply coordinated to the aluminum atom. The examination of molecular models based on the three-dimensional structure of $[Me_2AlOCPhNPh\cdot MeCHO]_2$[7] leads to structure A, in which two hydrogen atoms of the aldehyde groups of the *o*-phthalaldehyde moiety are located so as to favor the formation of a *trans*-oxyphthalan ring in the polymerization process.



(A)

The polymer obtained in maximum yield in the presence of an optimum amount of added water is the fibrous, crystalline polymer composed exclusively of *trans*-oxyphthalan rings. This fact parallels the result that a highly isotactic, crystalline poly(acetaldehyde) is obtained in a nearly quantitative yield in the presence of an optimum amount of added water in the polymerization of acetaldehyde. In addition, the optimum amounts of added water in polymerizations carried out with the identical catalyst **1** are nearly equal in both cases. These facts suggest that stereospecific polymerization of these two monomers proceeds by an identical mechanism.

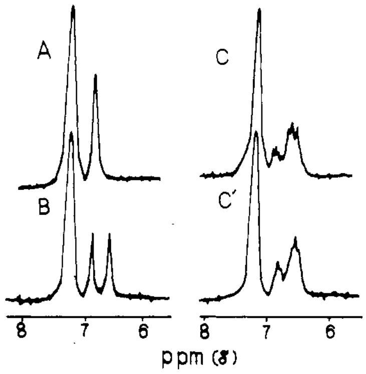


Figure 2. Nmr spectra of poly(*o*-phthalaldehyde) prepared by 1 (A), Ph_3COK (B) and $SnCl_4$ (C) (solvent, H_4furan) and by $SnCl_4$ (C′) (solvent, Me_2SO).

By referring to the coordinate cationic mechanism proposed for the stereospecific polymerization of acetaldehyde,[5,6] examination of molecular models with respect to the mode of attack of the initiating proton to A favors the isotactic structure for the crystalline polyether having a *trans*-oxyphthalan ring, but a definite conclusion must await the X-ray structure analysis. Thus, the coordination of the monomer to the catalyst and the presence of a trace amount of water are decisive factors for obtaining the fibrous, crystalline polymer exclusively composed of *trans*-oxyphthalan ring.

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