Polymerization of Aromatic Aldehydes. III. The Cyclopolymerization of Phthalaldehyde and the Structure of the Polymer[1]

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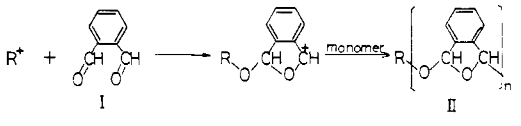
ABSTRACT: The polymerizations of phthalaldehyde were carried out with anionic (*t*-BuOLi, etc.) and coordination catalysts ($AlEt_3$–transition metal compounds, etc.) at −78°. All polymers were composed only of cyclized units (1,3-dialkoxyphthalan ring). The stereochemical structure (*cis* and *trans*) of the ether ring in the polymer was inferred from the comparison of the nmr spectra of the polymer with those of the isomeric 1,3-dialkoxyphthalans. Coordination catalysts gave high contents of the *trans* configuration. The amount of *cis* structure decreased in the following order: γ-ray irradiation > cationic catalysts ≥ anionic catalysts > coordination catalysts. Cyclopolymers of phthalaldehyde obtained by cationic polymerization had high *cis* content. The mechanism of this arrangement is discussed in more detail.

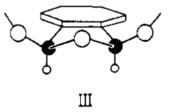
Aliphatic aldehydes polymerize comparatively easily with various types of catalysts,[2] but the homopolymerization of aromatic aldehydes is difficult. Recently, however, it has been shown that phthalaldehyde I could be polymerized with cationic catalysts or by γ-ray irradiation. A cyclopolymer II was obtained which is composed of the dioxyphthalan unit, as shown in eq 1.[3] In the preceding paper[4] we described the equilibrium polymerization of phthalaldehyde with cationic catalysts. The enhanced polymerizability of this monomer was explained in terms of the intermediate type or, preferably, concerted propagation scheme.



(1)

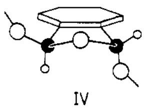
I II

It was expected that phthalaldehyde might give similar cyclopolymers with other kinds of catalyst. The aim of this investigation was to study the polymerization with anionic (*t*-BuOLi, etc.) and coordination catalysts ($AlEt_3$–transition metal compounds, etc.), and to elucidate the configurations of these polymers. *cis*- and *trans*-1,3-dialkoxyphthalans (III and IV) were selected to serve as models of the cyclic units in the polymer. Nmr spectra of the polymers were compared with those of the model compounds.



III

cis configuration
(ee ⇄ aa)



IV

trans configuration
(ea ⇄ ae)

○, oxygen; ●, carbon; o, hydrogen

Results

1. Stereoisomers of 1,3-Dialkoxyphthalan. 1,3-Dimethoxyphthalan purified by repeated distillations showed four nmr peaks at 7.17 ppm (phenyl protons), at 6.05 and 5.81 ppm (methine protons), and at 3.25 ppm (methyl protons) in carbon tetrachloride at room temperature. The area ratios of these protons were 4.0:2.0:6.4, corresponding to the theoretical values of 4:2:6. The two peaks of methine protons cannot be due to the spin–spin coupling, but rather suggest the presence of two stereoisomers. The splitting of the methyl signal into two in benzene also indicates the existence of two isomers (Table I). We previously determined the configuration of 2,5-dialkoxytetrahydrofurans[5] and 2,5-dialkoxydihydrofurans[6] by nmr spectroscopy. These compounds had been selected as models for the cyclic units of polysuccinaldehyde and polymalealdehyde, respectively. A similar argument can be applied to the determination of the configurations of 1,3-dialkoxyphthalan isomers.

Table I
Chemical Shifts of 1,3-Dimethoxyphthalan[a]

Assignment	Solvent CCl_4	Solvent C_6H_6	Confign of isomer
Methyl protons	3.25	3.27	*trans*
	3.25	3.31	*cis*
Methine protons	5.81	6.01	*cis*
	6.05	6.28	*trans*

[a] Chemical shifts (δ values) are given in parts per million. All the values[1] presented at the Sept 1967 meeting of the American Chemical Society were corrected with TMS standard.

Since the ether ring of phthalan is fused to the phenyl ring, it probably exists in the envelope form as shown by III or IV. We believe that the *cis* isomer has the two

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(1) Parts of this paper were read at the 154th American Chemical Society Meeting, Chicago, Ill., Sept 1967; *Polym. Preprints*, **8** [2], 906 (1967).

(2) (a) O. Vogl, *J. Macromol. Sci., A*, **1**, 201 (1967); (b) J. Furukawa and T. Saegusa, "Polymer Review," Vol. 3, Interscience Publishers, New York, N. Y., 1963, p 43.

(3) C. Aso and S. Tagami, *J. Polym. Sci., Part B*, **5**, 217 (1967).

(4) (a) C. Aso, S. Tagami, and T. Kunitake, paper presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, 1968; (b) C. Aso, S. Tagami, and T. Kunitake, *J. Polym. Sci.*, in press.

(5) Y. Aito, T. Matsuo, and C. Aso, *Bull. Chem. Soc. Jap.*, **40**, 130 (1967).

(6) (a) C. Aso, T. Kunitake, M. Miura, and S. Tagami, paper presented at the International Symposium on Macromolecular Chemistry, Kyoto: *Preprints*, **1**, 201 (1966); (b) C. Aso, T. Kunitake, and K. Koyama, *Makromol. Chem.*, **117**, 153 (1968).

TABLE II
CHEMICAL SHIFTS OF METHINE PROTONS OF 1,3-DIALKOXYPHTHALANS AND POLYPHTHALALDEHYDE[a]

Compd		Solvent			
		CCl_4	C_6H_6	DMSO	THF
1,3-Dimethoxyphthalan	*cis*	5.81	6.01	6.05	
	trans	6.05	6.28	6.32	
1,3-Diethoxyphthalan	*cis*	6.00	6.11	6.08	6.04
	trans	6.24	6.37	6.33	6.27
Polyphthalaldehyde	*cis*			6.3–6.7 (max 6.59)	6.4–6.8 (max 6.70)
	trans			6.75–7.0 (max 6.90)	6.8–7.1 (max 6.98)

[a] See Table I, footnote *a*.

alkoxy groups in the equatorial position, *i.e.*, ee conformation. The *trans* isomer will rapidly convert between the two conformations: ea $\rightleftarrows$ ae. Thus the methine peak of the *cis* isomer may be expected to appear at a higher magnetic field due to the magnetic anisotropy of the phenyl ring. The peaks of 1,3-dimethoxyphthalan at 5.81 and 6.05 ppm are, therefore, assigned to the methine protons of the *cis* and *trans* isomers, respectively, though the isomers could not be isolated.

The high-boiling fraction of 1,3-diethoxyphthalan crystallized and showed one methine peak at 6.24 ppm in the nmr spectrum. The low-boiling fraction consisting of two compounds according to gas chromatogram gave also two methine peaks (intensity ratio 3:1) at 6.00 and 6.24 ppm in the nmr spectrum. We concluded that the crystalline compound was the pure *trans* isomer and the low-boiling fraction a 3:1 mixture of the *cis* and *trans* isomers.

Nmr chemical shift of the methine protons of 1,3-dialkoxyphthalans varied slightly, depending on the solvent used, as seen in Table II. The signal of the *cis* isomer always appeared at a higher field than that of the *trans* isomer.

The ir spectra of *trans*- and *cis*-1,3-diethoxyphthalans were very similar except for the 900-cm^{-1} region. The *trans* isomer showed a sharp peak at 885 cm^{-1} and a shoulder at 900 cm^{-1}. The *cis* isomer has a sharp peak at 900 cm^{-1} and no absorption band at 885 cm^{-1}.

2. Nmr Spectra of Polyphthalaldehyde. Figure 1 shows the nmr spectra of three polymers (obtained by γ-ray irradiation and with BF_3OEt_2 and $AlEt_3/TiCl_4$ catalysts) in dimethyl sulfoxide. Peak C at 7.43 ppm may be assigned to the phenyl proton and peak A (max 6.59 ppm) and B (max 6.90 ppm) to the methine proton. The area ratio C/(A + B) was 3.92/2 (in Figure 1a), in good agreement with the theoretical value of 4/2. When the polymer spectrum was taken in tetrahydrofuran, peaks A, B, and C appeared at 6.70, 6.98, and 7.43 ppm, respectively, but the over-all shape of the spectrum was almost the same as that in dimethyl sulfoxide.

As the ratio A/B varied with the polymerization condition, as is clear from Figure 1, it seemed to show the difference in the configuration. The distance between peak A and B, about 0.3 ppm, is relatively close to the distance between the methine peaks of two isomers of the model compounds (Table II). Thus, we believe that A and B correspond to the methine protons of the *cis* and *trans* cyclic units, respectively. Maxima of both peaks of the polymer shifted somewhat to a lower magnetic field as compared with methine peaks of the model compounds. This difference may be due to the deshielding effect of the neighboring aromatic rings along the polymer chain. Thus the *cis* content of the polymer repeat unit can be estimated by the value of A/(A + B).

3. Polymerization Results. Phthalaldehyde could be polymerized readily with anionic or coordination catalysts used in this investigation, as well as with cationic catalysts. The results are listed in Tables III, IV, and V. The molecular weights of these polymers were not very high. All polymers were soluble in tetrahydrofuran and dimethyl sulfoxide and were identified as cyclopolymers from the ir and nmr spectra. A comparison of the *cis* contents of polymers obtained with cationic catalysts and by γ-ray irradiation is shown in Table VI.

Cationically initiated polymerization gave a *cis*-rich polymer, while the coordination catalyzed polymer was *trans* rich. The amount of *cis* structure decreased in

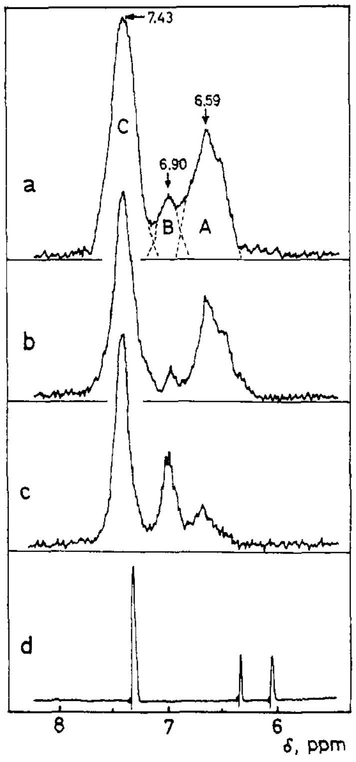

Figure 1. Nmr spectra in DMSO: (a) polymer (catalyst BF_3OEt_2); (b) polymer (γ-ray irradiation); (c) polymer (catalyst $AlEt_3$–$TiCl_4$); (d) 1,3-diethoxyphthalan (the mixture of *cis* and *trans* isomers).

TABLE III
RESULTS OF POLYMERIZATION OF PHTHALALDEHYDE WITH COORDINATED CATALYSTS AT −78°
(MONOMER 1.0 G)

Catalyst	Molar ratio	Al, mol %	Solvent (ml)	Time, hr	Convn,[a] %	Sp,[i] °C	*cis* content, mol %
$AlEt_3/TiCl_4$	2/1	4	$C_6H_5CH_3$ (54)	70	28	152–154	37
	2/1	4	$C_6H_5CH_3$ (60)	43	Sol 11[d]		70
					Ins 14[e]		17
	2/1	4	$C_6H_5CH_3$ (60)	41	Sol 17	132–134	43
					Ins 11	126–128	
	3/1	3	$C_6H_5CH_3$ (54)	70	37		38
$AlEt_3/TiCl_4/I_2$	2/1/1	4	$C_6H_5CH_3$ (60)	40	Sol 28[f]	136–138	36
$AlEt_3$ $TiCl_3$	1/1	4	$C_6H_5CH_3$ (60)	42	Ins 26	139–140	16
$AlEt_3/Cp_2TiCl_2$[b]	1/1	3	$C_6H_5CH_3$ (65)	70	22[g]	139–141	40
$AlEt_3/VCl_4$	2/1	4	$C_6H_5CH_3$ (60)	40	Sol 17	130–132	40
					Ins 4	143–146	23
$AlEt_3/VOCl_3$	2/1	4	$C_6H_5CH_3$ (60)	40	Sol 30	137–138	44
					Ins 4	147–149	23
$AlEt_2Cl/VOCl_3$	2/1	4	$C_6H_5CH_3$ (60)	43	23	139–140	58
$AlEt_2Cl/Cr(acac)_3$[c]	3.5/1	4	$C_6H_5CH_3$ (60)	70	14	143–145	17
$AlEt_3/CoCl_2$	1/2	6	$C_6H_5CH_3$ (60)	43	Sol 21	137–138	66
					Ins 11	159–161	30
$AlEt_3$/*i*-PrOH	1/1	4	$C_6H_5CH_3$ (60)	43	Sol 20	138–140	27
					Ins 2		21
$AlEt_3/PhNHCOCH_3$	1/1	4	THF (10)	62	31[h]	164–165	34
	1/1	4	CH_2Cl_2 (10)	62	11	161–162	18

[a] Sol, soluble in benzene; ins, insoluble in benzene. [b] Biscyclopentadienyltitanium dichloride. [c] Chromium acetylacetonate. [d] $(\eta) = 0.14$ in THF at 30°. [e] $(\eta) = 0.10$ in THF at 30°. [f] $\overline{M}_n = 5400$. [g] $\overline{M}_n = 2000$. [h] $\overline{M}_n = 3110$. [i] Softening point.

TABLE IV
RESULTS OF POLYMERIZATION OF PHTHALALDEHYDE BY ALUMINUM COMPOUNDS AT −78°
(MONOMER 1.0 G, CONCENTRATION OF CATALYST 4 MOL %)

				Polymer		
Catalyst	Solvent (ml)	Time, hr	Convn, %	$\overline{M}_n \times 10^{-3}$	Sp,[a] °C	*cis* content, mol %
$AlEt_3$	CH_2Cl_2 (10)	20	9		114–117	51
	$C_6H_5CH_3$ (54)	20	5			
$AlEt_2Cl$	CH_2Cl_2 (10)	20	81		129–130	80
	$C_6H_5CH_3$ (60)	5	20		146–148	44
$AlEt_2Cl/AlCl_3$	CH_2Cl_2 (10)	20	77	5.18	126–128	67
	$C_6H_5CH_3$ (60)	20	38	7.37	137–138	77
$AlCl_3$	CH_2Cl_2 (10)	20	69		121–125	79
	$C_6H_5CH_3$ (80)	40	8			

[a] Softening point.

the following order: γ-ray irradiation > cationic catalysts ≥ anionic catalysts > coordination catalysts. Polymers obtained with some coordination catalysts contained a benzene-insoluble fraction, which was shown to have high *trans* content. Cationic and anionic catalysts gave only benzene–soluble polymers. The solubility in benzene reflects the stereochemical structure of the polymer (Table III).

Discussion

The fact that 1,3-dialkoxyphthalans are obtained in good yields by reacting phthalaldehyde with various alcohols[7,8] suggests the inherent ability of this monomer to cyclize. Since the two aldehyde groups of phthalaldehyde are fixed at the *ortho* position, the ready intramolecular reaction is certainly to be expected from the steric reason, as in the case of malealdehyde[9] and *cis*-1-methylcyclohexene-4,5-dicarboxyaldehyde.[10] Furthermore, we believe that the cyclopolymerization of a monomer with two functional groups is facilitated by the interaction between two groups. The importance of the electronic interaction between two C=C double bonds in the cyclopolymerization of divinyl compounds has been reported by Butler.[11] On the other hand, the dipole–dipole interaction, the presence of which was pointed by Schnider and Bernstein in the case of formal-

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(7) E. Schmitz, *Chem. Ber.*, **91**, 410 (1958).

(8) M. R. Powell and D. R. Rexford, *J. Org. Chem.*, **18**, 810 (1953).

(9) (a) C. Aso and M. Miura, *J. Polym. Sci., Part B*, **4**, 171 (1966); (b) C. Aso and M. Miura, *Kobunshi Kagaku*, **24**, 178 (1967).

(10) C. Aso, T. Kunitake, and K. Koyama, paper presented at the 17th Annual Meeting of the Society of Polymer Science, Japan, Tokyo, 1968.

(11) (a) G. B. Butler, *J. Polym. Sci.*, **48**, 279 (1960); (b) G. B. Butler, paper presented at the 153rd Meeting of the American Chemical Society, Miami Beach, Fla., April 1967; *Polym. Preprints*, 8 (1), 35 (1967).

TABLE V
RESULTS OF ANIONIC POLYMERIZATION OF PHTHALALDEHYDE AT −78° (MONOMER 1.0 G)

					Polymer			
Catalyst	Concn of catalyst, mol %	Solvent (ml)	Time, hr	Convn, %	$\bar{M}_n \times 10^{-3}$	(η), dl/g	Sp,[a] °C	*cis* content, mol %
t-BuOLi	1.6	THF (10)	22	24	5.62	0.13	117–119	56
t-BuOLi	5.0	$C_6H_5CH_3$ (20)	12	44	1.28		98–100	53
Na naphthalene	3.7	THF (10)	21	80	5.62	0.13	113–116	60
Na benzophenone	7.7	THF (10)	21	34	2.04	0.07		

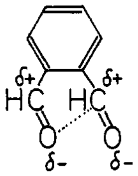
[a] Softening point.

TABLE VI
RESULTS OF CATIONIC POLYMERIZATION OF PHTHALALDEHYDE AT −78° (MONOMER 1.0 G)

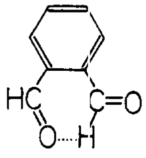
					Polymer			
Catalyst	Conc of catalyst, mol %	Solvent (ml)	Time, hr	Convn, %	$\bar{M}_n \times 10^{-3}$	(η), dl/g	Sp,[b] °C	*cis* content, mol %
BF_3OEt_2	1.0	CH_2Cl_2 (10)	12	87	11.7	0.31		66
BF_3OEt_2	5.0	$C_6H_5CH_3$ (60)	16.5	95			108–109	68
Ph_3CBF_4	0.5	CH_2Cl_2 (10)	24	87	8.6	0.17	125–127	77
$SnCl_4$	1.0	CH_2Cl_2 (10)	24	88			110–127	64
Et_3OBF_4	0.03	CH_2Cl_2 (10)	2	91	19.1	0.28	137–139	66
γ-ray[a]		CH_2Cl_2 (10)	115	24	2.0	0.06	130–132	87

[a] Dose rate 8.6 × 10^4 R/hr. [b] Softening point.

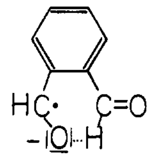
dehyde,[12] between two aldehyde groups seems to play an important role in the cyclopolymerization of aliphatic dialdehydes,[9,13] as illustrated by V. Recently, Lumbroso and coworkers reported the existence of intramolecular hydrogen bond as shown by VI.[14]



V



VI

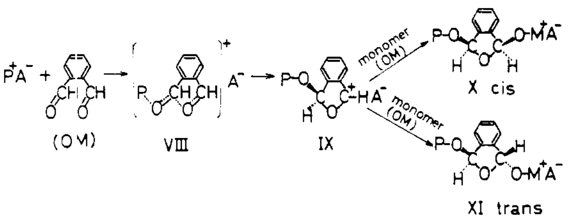


VII

Accordingly, in the polymerization of phthalaldehyde, the intramolecular cyclization process can be promoted by the steric effect and by the interaction shown by V or VI. These considerations are consistent with the intermediate or concerted scheme of propagation proposed from the thermodynamic data in the cationic polymerization.[4]

cis-Rich polymers were usually obtained in the cationic polymerization as given in Table VI. This phenomenon may be also supported by the result that the *cis*-rich 1,3-diethoxyphthalan (*cis* 60%) was obtained in 70% yields by reacting phthalaldehyde with excess Et_3OBF_4 and then by adding an ethanol solution of C_2H_5ONa.[15]

In the cationic polymerization of phthalaldehyde, the formation of the cyclic cation IX will be shown as in the following equation. Since a five-membered ring ether oxygen is nearly planar and the carbonium ion in IX is placed between an ether oxygen and a phenyl ring, the cation IX seems to be stabilized as a sp^2 type or a quite shallow pyramidal type. Accordingly, it is clear that the direction of approach of the new monomer to the cyclic cation IX will determine the configuration of the ring of the polymer, *cis* or *trans*.



The preferred formation of the *cis* structure in the cationic polymerization may be explained in two different ways. One of the explanations is based on the mechanism of the isotactic propagation, which was proposed previously by our research group for the cationic polymerization of vinyl compounds.[16] In the case of polymerization of phthalaldehyde, the counteranion A^- is assumed to be present at the lower side of the carbonium ion (below the plane of this paper) in IX, so as to avoid the steric repulsion with the penaltimate unit. Then the monomer molecule reacts with the cyclic cation IX from the upper side (remote from the counteranion), forming the *cis* structure preferentially.

Another explanation makes use of the difference in the stability of the cyclic unit. The free energy of propagation of phthalaldehyde was found to be −0.82 kcal/mol at 195°K.[4] Since the free energy is small, it is conceivable that the difference in the stability of the phthalan ring formed is reflected in the transition state. That is, the transition state of propagation leading to

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(12) W. G. Schneider and H. G. Bernstein, *Trans. Faraday Soc.*, **52**, 13 (1956).

(13) C. Aso, *Kogyo Kagaku Zasshi*, **70**, 1920 (1967).

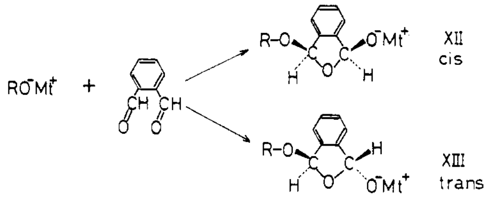
(14) H. Lumbroso, D. M. Bertin, M. Robba, and B. Roques, *C. R. Acad. Sci., Paris*, **262**, 36 (1966).

(15) C. Aso and S. Tagami, unpublished results.

(16) C. Aso and T. Kunitake, paper presented at the 17th Discussion Meeting of the Society of Polymer Science, Japan, 1967, p 37.

the *cis* ring unit would be more stable than that leading to the *trans* ring unit, the *cis* structure being formed preferentially.

The ring formation in the anionic polymerization of phthalaldehyde will follow the scheme.



Stone and Maki reported that the most stable conformation of phthalaldehyde anion was the *meso* type VII through the stabilization by the formation of cyclic hydrogen bond.[17] Although it is not yet clear whether reaction of the two aldehyde groups in the anionic polymerization is a concerted or a stepwise process, the possibility of cyclization through the formation of hydrogen bond similar to VII cannot be eliminated. It should be pointed out that the stereochemical structure (*cis* or *trans*) of the cyclic unit is determined during the intramolecular cyclization. The anionic catalysts used in this work gave polymers possessing comparable amounts of the *cis* and *trans* structures, as shown in Table V.

It is interesting that $AlEt_2Cl$ gave quite different polymers, depending on the solvent used, as shown in Table IV. This is indicative of the different catalytic action of $AlEt_2Cl$ with solvents.

Coordination catalysts used in this investigation gave *trans*-rich polymers. Some catalysts, such as $AlEt_3$–$TiCl_4$, gave the polymer consisted of the benzene-soluble and insoluble fractions (Table III). The former had smaller *trans* contents than the latter. This is best accounted for by assuming the presence of more than one catalytic species, since, as for example, $AlEt_2Cl$ and/or $AlEtCl_2$ are produced as by-products during preparation of Ziegler catalyst. The cationic species formed probably produced a fraction of a smaller *trans* content. This is also supported by the fact that the $AlEt_3$–$TiCl_3$ system which does not form cationic catalytic species gave only a benzene-insoluble polymer (*trans* 84%).

Experimental Section

Phthalaldehyde (mp 54.5–55.0°) was prepared according to the method of Bill and Tarbell.[18]

1,3-Dimethoxyphthalan was prepared by the reaction of phthalaldehyde and methanol according to Schmitz.[7] The product purified by repeated distillations, bp 116–118° (11 mm), was 95% pure by nmr spectroscopy and gas chromatography. The by-product was the tetraacetal of phthalaldehyde (nmr spectrum). The tetraacetal was obtained in greater amounts from the high-boiling fraction. 1,3-Dimethoxyphthalan obtained was found to be a mixture of the stereoisomers (60% *cis* and 40% *trans*) from its nmr spectrum.

1,3-Diethoxyphthalan was prepared from phthalaldehyde and ethanol according to the method of Powell and Rexford:[8] yield 88%; bp 101–104° (5 mm) [lit.[8] 120–129° (25 mm)]. *Anal.* Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.10; H, 7.97. The gas chromatogram of 1,3-diethoxyphthalan consisted of two peaks, and they were the stereoisomers according to the nmr spectrum. Fractional distillation using a spinning-band column gave a low-boiling fraction, bp 142.0–142.1° (11 mm), consisting of 75% *cis* and 25% *trans* isomers, confirmed by gas chromatography. The high-boiling fraction, bp 144° (11 mm), crystallized and gave colorless crystals, mp 45–46°, of pure *trans* isomer after recrystallization from hexane (−25°). *Anal.* Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.92; H, 7.96.

The polymerization of phthalaldehyde were carried out in glass-stoppered ampoules under nitrogen. Cationic polymerizations were terminated by adding pyridine and pouring the reaction mixture into methanol or ethyl ether; white powdery polymer was thus obtained. Anionic polymerizations were terminated by adding a THF solution of acetic anhydride. The polymer was recovered by pouring the reaction mixture into methanol. Coordination polymerizations were terminated by pouring the reaction mixture into methanol.

Solvents. Methylene chloride was washed with dilute alkali, dried over calcium chloride, refluxed over phosphorus pentoxide, and distilled over calcium hydride. Toluene was washed with concentrated sulfuric acid and dilute alkali, dried over calcium chloride, refluxed over metalic sodium, and distilled. Tetrahydrofuran was refluxed over potassium hydroxide and distilled over metallic sodium.

Anionic Catalysts. *t*-BuOLi was prepared by reaction of dry *t*-butyl alcohol with lithium in benzene under nitrogen. The reaction mixture was filtered and the benzene was evaporated. Sodium naphthalene and sodium benzophenone complex were prepared by reaction of sodium with naphthalene and benzophenone in tetrahydrofuran under nitrogen. This reaction mixture was used as a catalyst solution after filtration.

Ziegler-Type Catalysts. $AlEt_3$ or $AlEt_2Cl$ was allowed to react with transition metal compounds in toluene. The reaction mixture was aged at room temperature or at 40° for 10–30 min while stirring. After cooling to −78°, the catalyst solution was added to a toluene solution of a monomer at −78°.

$AlEt_3$–*i*-PrOH Catalyst. According to Furukawa's method,[19] $AlEt_3$ was mixed in toluene with the equimolar amount of isopropyl alcohol. The reaction mixture was kept for 30 min at room temperature, and used as a catalyst solution.

$AlEt_3$–$PhNHCOCH_3$ Catalyst. According to the method of Tani, *et al.*,[20] $AlEt_3$ was allowed to react in toluene with the equimolar amount of acetanilide at 20°, until evolution of ethane ceased. This reaction mixture was used as a catalyst solution.

Other Catalysts. BF_3OEt_2 was purified by distillation under nitrogen, and $SnCl_4$ was treated with tin foil and then distilled over phosphorus pentoxide. $TiCl_4$ was heated at 100° with copper powder and distilled. Et_3OBF_4 and Ph_3CBF_4 were prepared according to Meerwein's[21] and Dauben's[22] method, respectively. $AlEt_3$ (Ethyl Corp., U. S. A.) and $AlEt_2Cl$ (Mitsui Petrochemical Co.) were used without

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further purification. $AlCl_3$ was purified by repeated sublimation under HCl. $AlEt_2Cl/AlCl_3$ was prepared by reaction of $AlEt_2Cl$ with the equimolar amount of $AlCl_3$ in toluene.

Measurements. Nmr spectra were taken with a Varian Model A-60 spectrometer (60 Mc). All the polymer and the dialkoxyphthalans spectra were obtained as solution of approximately 1 mol (per unit) per liter at about 40° against TMS standard in a capillary. Molecular weights were measured with a vapor pressure osmometer (Mechrolab Model 301 A) in benzene at 37°. Viscosity determinations were carried out at 30° in benzene by using an Ubbelohde dilution-type viscometer.

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Polymers with Chelated Polyquinoxaline Segments

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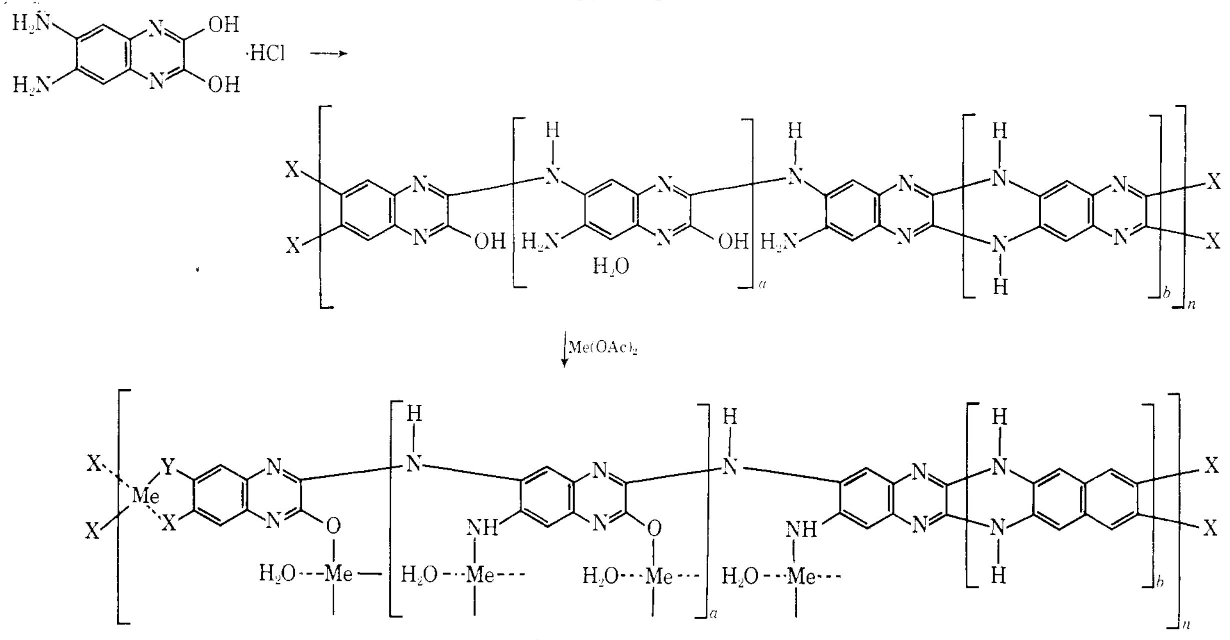
ABSTRACT: Polymeric chelates between polyquinoxaline prepolymers and copper, nickel, and cadmium acetates have been synthesized. The copper chelate showed better high-temperature stability than the high molecular weight polytetraazaanthracene. The ac and dc conductivities of the chelates increased with the increasingly covalent nature of the organic ligand–metal bond. Esr studies on the monomers and prepolymers showed the presence of free radicals and from their fine structure spectra an assignment to the appropriate anion radicals was made.

There are two major methods available for building chelate polymers with metal ions. One of the methods involves the use of polyfunctional monomers which on reaction with a metal ion or salt produce the polymer. The other involves first the synthesis of a polymer which has repeating units that can react with a metal ion to then form the polymeric chelate. One can visualize also a third approach which combines the above two and was the goal of this work in the preparation of polymeric chelates containing the basic polyquinoxaline segment as a part of the polymer chain. This was accomplished by first synthesizing polyquinoxaline "prepolymers" of low enough molecular weight so that they were completely soluble in organic solvents, and then follow by the polychelation reaction with copper, nickel, and cadmium acetates. The type of structures obtained are illustrated in Scheme I. Spectroscopic (ir, uv, and esr) studies were conducted on the chelated materials and they were evaluated for thermal and conductivity properties.

SCHEME I



a = number of repeat units in one segment
b = number of repeat units in the other segment
X, Y = end groups, not determined

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