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Cyclopolycondensations. VIII. New Thermally Stable Aromatic Polybenzoxazinones by Solution Polymerization in Polyphosphoric Acid*

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Summary

High molecular weight polybenzoxazinones have been prepared by cyclopolycondensation reaction of 4,4'-diamino-3,3'-biphenyldicarboxylic acid with a variety of aromatic carbonyl compounds using a solution polymerization technique in polyphosphoric acid. From the model reactions of anthranilic acid, and 4,4'-diamino-3,3'-biphenyldicarboxylic acid with benzoyl chloride in polyphosphoric acid, it is established that the cyclopolycondensation proceeds through the formation of an open-chain tractable precursor, polyamic acid of high molecular weight ($\eta_{inh} = 2.66$) in the first step, which subsequently undergoes thermal or chemical cyclodehydration along the polymer chain, to yield, in the second step, a fully aromatic polybenzoxazinone. Polybenzoxazinones thus obtained have excellent thermal stability both in nitrogen and in air.

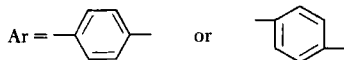
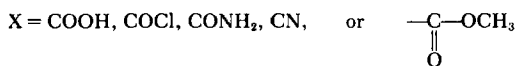
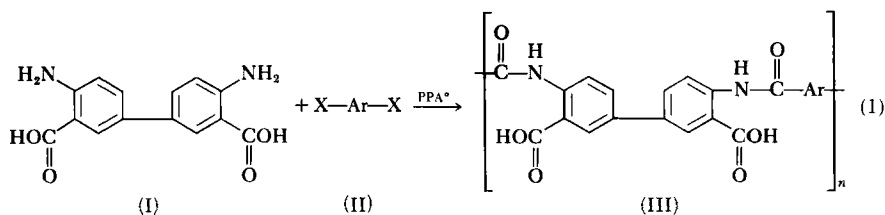
The optimum polymerization conditions for obtaining polyamic acid of high molecular weight are determined by the study of reaction variables such as polymerization temperatures, monomer concentrations, and reaction time as well as the effect of P_2O_5 concentrations in polyphosphoric acid.

Recent reports (1–8) from this laboratory have described a facile and efficient method of preparation of thermally stable polymers containing quinazolinedione (1–3) or benzoxazinone ring systems (4–8). In the course of study of cyclopolycondensation reactions, new aromatic polybenzoxazinones were prepared by the cyclopolycondensation of 4,4'-diamino-3,3'-biphenyldicarboxylic acid

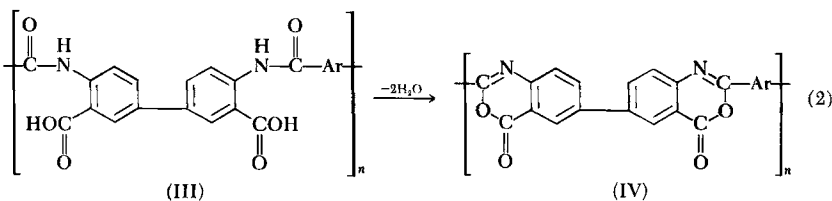
* Part VII of this series: Tohyama, Kurihara, and Yoda (1).

(BDC) with a variety of aromatic carbonyl compounds using a solution polymerization technique in polyphosphoric acid. Polyphosphoric acid has been extensively used in recent years (9,10) on the polymerization medium and dehydrating agent of cyclopolycondensation reactions.

In the present paper we wish to report the first successful preparation of fully aromatic polybenzoxazinones using a polyphosphoric acid solution polymerization technique. The aromatic polyamic acids of high molecular weight are obtained in



The polyamic acid, an open-chain tractable precursor, undergoes thermal or chemical cyclodehydration along the polymer chain



to yield fully aromatic polybenzoxazinones with excellent thermal stability. The detailed account of polymerization conditions in polyphosphoric acid is described.

° PPA, polyphosphoric acid.

EXPERIMENTAL

Instrument

All the melting points were taken on a Büchi melting point apparatus and were uncorrected. Microanalyses were carried out by the Microanalytical Section of this laboratory. Infrared spectra were recorded with Perkin-Elmer Model 125 and Hitachi Model EPI-S recording spectrophotometers in potassium bromide disk or film. Differential thermal analysis was made with the Shimadzu DT-10 instrument using 50 mg of sample at the rate of 6°C/min. Thermal gravimetric analyses (TGA) in nitrogen and air were obtained with the Shimadzu RT-3 using 100 mg of sample at the rate of 6°C/min.

Materials

4,4'-Diamino-3,3'-biphenyldicarboxyl Acid (BDC) (11,12) and Its Dihydrochloride Dihydrate (BDC·2HCl·2H₂O)(1)(7). This was prepared in 92% yield from *o*-nitrobenzoic acid by the method of alkaline reduction with zinc and sodium hydroxide, followed by benzidine rearrangement with hydrochloric acid to obtain free BDC as crystals m.p. 300°C (dec.), and its dihydrochloride dihydrate as colorless needles m.p. 300°C (dec.).

Analysis: Free BDC: Found: C, 61.53; H, 4.53; N, 10.12; calcd. for C₁₄H₁₂O₄N₂: C, 61.76; H, 4.44; N, 10.29

Analysis: BDC·2HCl·2H₂O: Found: C, 44.22; H, 4.88; N, 7.28; Cl, 18.27; calcd. for C₁₄H₁₈O₆N₂Cl₂: C, 44.13; H, 4.76; N, 7.35; Cl, 18.60

Polyphosphoric Acid (PPA). Chemically available c.p. grade PPA (P₂O₅ content: 84%) of Nippon Kagaku Kogyo Ltd., Yoneyama Kagaku Ltd., was used. Highly purified PPA was synthesized by the method of Pearson and Stone (13). A mixture of phosphoric acid and phosphorus pentoxide is referred to as PPA.

Syntheses of Model Compounds

Model compounds are prepared according to the procedure described in the previous papers (7,8,14), and the physical properties, elemental analyses, and infrared characteristic absorption bands of model compounds are summarized in Table I.

TABLE I
Infrared Spectra of Benzoxazinone Model Compounds

Compounds	Structure	Absorption band, cm^{-1}	Melting point, $^{\circ}\text{C}$	Elemental analyses					
				Calcd., %			Found, %		
				C	H	N	C	H	N
V	N-Benzoylanthranilic acid	1670 1644	180-183	69.70	4.59	5.80	69.49	4.85	5.30
VI	2-Phenyl-4H-3,1-benzoxazine-4-one	1760 1260	121	75.32	4.06	6.28	75.15	4.03	6.21
VII ^b	N,N'-Dibenzoyl-3,3'-benzidine-dicarboxylic acid	1690 1670	360	69.99	4.20	5.83	69.67	4.26	5.91
VIII ^b	2,2'-Diphenyl-[6,6'-bi-4H-3,1-benzoxazine]-4,4'-dione	1760 1620 1260	> 360	75.67	3.63	6.30	75.83	3.75	6.28
IX ^b	2,2'-Di- <i>p</i> -tolyl-[6,6'-bi-4H-benzoxazin]-4,4'-dione	1660 1760 1650 1258	> 360	76.26	4.27	5.93	75.91	4.46	6.20
X	2-Methyl-4H-3,1-benzoxazine-4-one	1064 1757 1647	80-81	67.07	4.38	8.09	67.15	4.45	8.20
XI	2,2'-Dimethyl-[6,6'-bi-4H-3,1-benzoxazine]-4,4'-dione	1268 1054 1750 1650 1263 1058	304-306	67.50	3.78	8.75	67.37	3.89	8.51

^a KBr dish.

^b New compounds.

Polymerizations

Typical Preparation of a Polyamic Acid (III). The polyphosphoric acid solution polymerization was carried out by the reaction of 4,4'-diamino-3,3'-biphenyldicarboxylic acid or its dihydrochloride dihydrate with aromatic dicarboxylic acid derivatives. In a three-necked flask equipped with nitrogen inlet and outlet tube, a stirrer, and an apparatus to introduce the reagent under inert atmosphere, 200 g of 84% PPA (P_2O_5 content) was added and it was heated at 60°C. Then a 2.03-g portion of terephthaloyl chloride was added into the flask under a thin stream of nitrogen and heated at 80–100°C. When the compound was completely dissolved, the powder of a 273-g portion of 4,4'-diamino-3,3'-biphenyldicarboxylic acid was added gradually. The reaction mixture was heated under nitrogen at 140–160°C. Usually, after 4.0–5.0 hr of heating, the reaction mixture became very viscous. The polymer was isolated by pouring the hot reaction mixture into distilled water and the solution was centrifuged or filtered. The precipitate was washed thoroughly with distilled water. The solid product was then dipped in 5% aqueous sodium carbonate solution and allowed to stand overnight at room temperature. Finally, the polymer was washed with dilute hydrochloric acid and water, methanol, and then dried under vacuum at 80°C. The yield of polymer was nearly quantitative (4.4 g) and the inherent viscosity was 2.66 in concentrated sulfuric acid (0.5% concn., 25°C). The polyamic acid (III) thus obtained was dissolved in N-methylpyrrolidone containing 5% lithium chloride, and polymer solution was poured onto a glass plate and dried at 120°C for 30 min, to afford transparent tough film. The infrared spectrum of polyamic acid film shows an amide carbonyl band at 1670 cm^{-1} , and an NH-stretching band appears at 3400 cm^{-1} . The polyamic acid is soluble in dimethylacetamide, N-methyl-2-pyrrolidone, N,N-dimethylformamide, and dimethylsulfoxide containing lithium chloride or amine. It is soluble in concentrated sulfuric acid.

Analysis: Found: C, 63.33; H, 3.69; N, 6.44; calcd. for $C_{22}H_{14}O_6N_2$: C, 65.67; H, 3.51; N, 6.96

The experimental results are summarized in Tables 2, 3, 4, and 5.

Conversion to Polybenzoxazinone. Three types of dehydration processes, (a), (b), and (c), are employed for the ring closure. The infra-

TABLE 2
 Polymerization of Polyamic Acid (III) in Polyphosphoric Acid

Expt.	Monomer		Diacid derivative, ^c g	Solvent PPA ^a g	Monomer concn., %	Inorganic salt LiCl, g	Polymerization condition		η_{inh}^e
	BDC, ^a g	BDC-2HCl-2H ₂ O, ^b g					°C	hr	
1	2.73	—	TPCI	2.03	200 ¹	—	135	1.0	0.90
2	1.36	—	TPCI	1.03	44 ²	—	130-150	2.0	0.95
3	2.62	—	TPCI	1.95	183 ³	—	140-150	0.5	0.85
4	2.76	—	TPCI	2.10	44 ²	—	180-185	5.0	0.13
5	3.70	—	IsPCI	2.43	230 ¹	—	150	17.0	0.15
6	1.36	—	TPA	0.83	42 ²	—	130-150	3.5	0.57
7	2.04	—	TPN	0.91	60 ²	—	200	0.5	0.40
8	1.36	—	DMT	0.97	91 ²	—	200	5.0	0.20
9	1.36	—	TPDA	0.83	60 ²	—	180	2.0	1.07
10	1.36	—	IsDA	0.83	44 ²	—	150-160	5.0	0.28
11	—	1.72	TPCI	1.12	100 ³	—	140-150	7.0	1.84
12	—	3.44	TPCI	2.24	200 ³	0.20	145-150	8.5	2.66
13	—	1.72	TPA	0.83	100 ³	—	144	6.5	1.95
14	—	0.86	DMT	0.53	50 ³	—	155-162	7.5	0.41

^a 4,4'-Diamino-3,3'-biphenyldicarboxylic acid.

^b 4,4'-Diamino-3,3'-biphenyldicarboxylic acid dihydrochloride dihydrate.

^c TPCI, terephthalic chloride; IsPC, isophthalic chloride; TPA, terephthalic acid; TPN, terephthalonitrile; DMT, dimethylterephthalate; TPDA, terephthalic diamide; IsDA, isophthalic diamide.

^a 1. 84% PPA synthesized by the method of Pearson and Stone (13) is used.

2. Commercially available 84% PPA (Yoneyama Kagaku Ltd.).

3. Commercially available 84% (Nippon Kagaku Kogyo Ltd.).

^e 25.0°C, 0.5% concn. in H₂SO₄.

TABLE 3
Effect of Polymerization Temperature on the Extent of Polymerization

Expt.	Monomer		Monomer ratio BDC:2HCl:2H ₂ O/ TPCl	Solvent PPA, ^c g	Monomer concn., %	Polymerization condition		η_{inh}^d
	BDC:2HCl:2H ₂ O, ^a g	TPCl, ^b g				°C	hr	
1	0.86	0.56	1	50	2.8	130	16.0	1.36
2	0.86	0.56	1	50	2.8	146-150	7.0	1.84
3	0.86	0.56	1	50	2.8	160	9.5	1.80
4	0.86	0.56	1	50	2.8	190	9.5	0.65
5	0.86	0.56	1	50	2.8	210	16.0	0.33

^a 4,4'-Diamino-3,3'-biphenyldicarboxylic acid dihydrochloride dihydrate.

^b Terephthaloyl chloride.

^c Commercially available 84% PPA (Nippon Kagaku Kogyo Ltd.).

^d Concn. H₂SO₄, 25°C, 0.5%.

TABLE 4
Effect of Monomer Concentration on the Extent of Polymerization

Expt.	BDC·2HCl·2H ₂ O, ^a g	TPCl, ^b g	Monomer ratio	Solvent PPA, ^c g	Monomer concn., %	Polymerization condition		
						°C	hr	η_{inh}^d
1	0.86	0.56	1	80	1.8	140	21.0	0.29
2	0.86	0.56	1	50	2.8	140	12.0	0.59
3	0.86	0.56	1	38	3.8	140	9.5	1.50
4	0.86	0.56	1	35	4.0	140	4.2	1.87
5	0.86	0.56	1	25	5.7	140	4.5	0.50

^a 4,4'-Diamino-3,3'-biphenyldicarboxylic acid dihydrochloride dihydrate.

^b TPCl, terephthalic chloride.

^c Commercially available 84% PPA (Nippon Kagaku Kogyo Ltd.).

^d 25.0°C, 0.5% concn. in H₂SO₄.

red spectra of these dehydration products are compared in Fig. 1.

(a) The polyamic acid film was heated on a frame in an oven at 180–360°C under vacuum (1 mm Hg). The dehydration was initiated at 200°C as evidenced by the differential thermal analysis in Fig. 2. And followed by cyclization a benzoxazinone (IV) of high molecular weight was obtained.

Analysis: Found: C, 71.05; H, 2.81; N, 7.51; calcd. for (C₂₂H₁₀-O₄N₂)_n C, 72.13; H, 2.75; N, 7.65

(b) The dehydration was also effected by treating polyamic acid film with a solvent pair of acetic anhydride and pyridine (1:1), followed by heating the film at 130–180°C under vacuum for 20 min.

(c) The polyamic acid was heated in PPA at 200–250°C for 1–3 hr. The formation of a benzoxazinone ring by the intramolecular thermal dehydration of polyamic acid was confirmed by the comparison of infrared spectra of model compounds. The appearance of new characteristic absorption bands for the benzoxazinone ring at 1760 cm⁻¹, 1260 cm⁻¹, and 1060 cm⁻¹ supports the formation of the benzoxazinone ring along the polymer chain.

RESULTS AND DISCUSSION

Model Reactions in Polyphosphoric Acid

To study the structural correlations between model compounds and the resulting polymers, the model reactions in PPA were studied and the influence of experimental conditions on the structure of reaction products was determined. The reactions are described in Eqs. (3) and (4).

TABLE 5
Effect of the P₂O₅ % of PPA on the Extent of Polymerization

Expt.	BDC·2HCl·2H ₂ O, ^a g	TPCl ^b g	Monomer ratio	Solvent PPA, ^c g	P ₂ O ₅ content, %	Monomer concn., %	Polymerization condition		η_{inh}^d
							°C	hr	
1	1.74	1.12	1	100	70.0	2.86	140	26.0	0.036
2	1.74	1.12	1	100	75.0	2.86	140	23.0	0.040
3	1.74	1.12	1	100	80.0	2.86	140	21.0	0.074
4	1.74	1.12	1	100	83.5	2.86	140	19.0	0.23
5	1.74	1.12	1	100	84.0	2.86	140	15.0	1.45
6	1.74	1.12	1	100	85.0	2.86	140	16.0	0.32
7	1.74	1.12	1	100	86.5	2.86	140	19.0	0.28
8	1.74	1.12	1	100	87.0	2.86	140	20.0	0.12

^a 4,4'-Diamino-3,3'-biphenyldicarboxylic acid dihydrochloride dihydrate.

^b Terephthalic chloride.

^c 87.0% PPA synthesized by the method of Pearson and Stone (13) and water are used.

^d 25.0°C, 0.5% concn. in H₂SO₄.

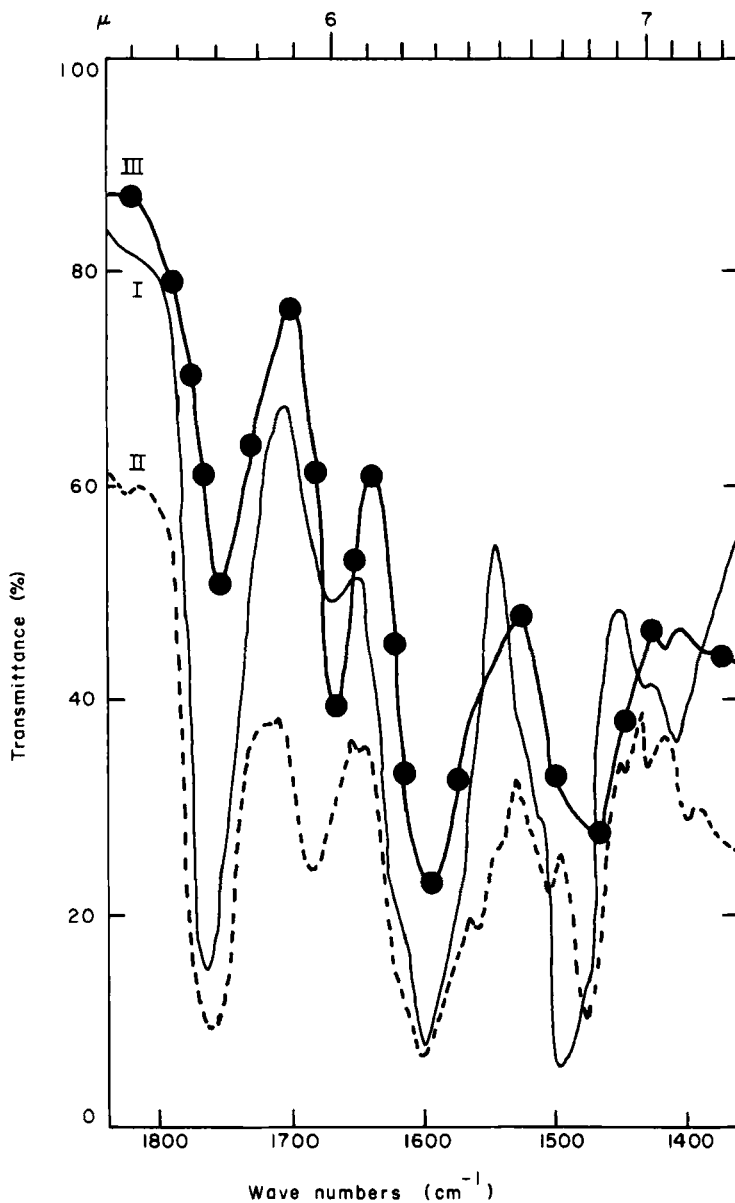


FIG. 1. Conversion to polybenzoxazinone by thermal dehydration (I, solid line) and chemical dehydration (II, acetic anhydride/pyridine, 1 week at 25.0°C, dotted line; III, 86% PPA, 250°C/2 hr, —●—●—).

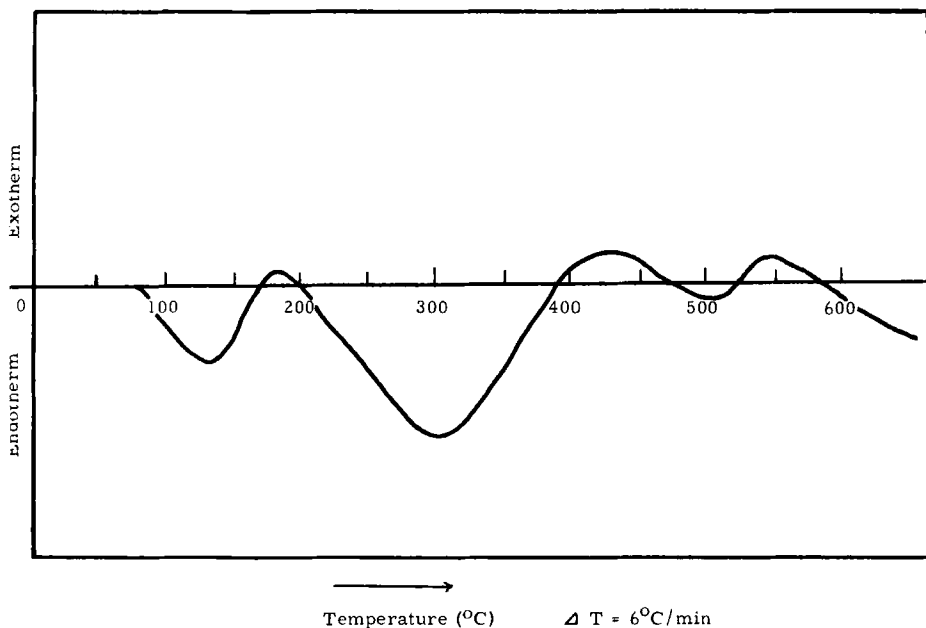
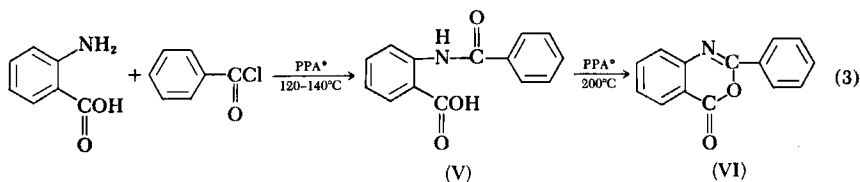
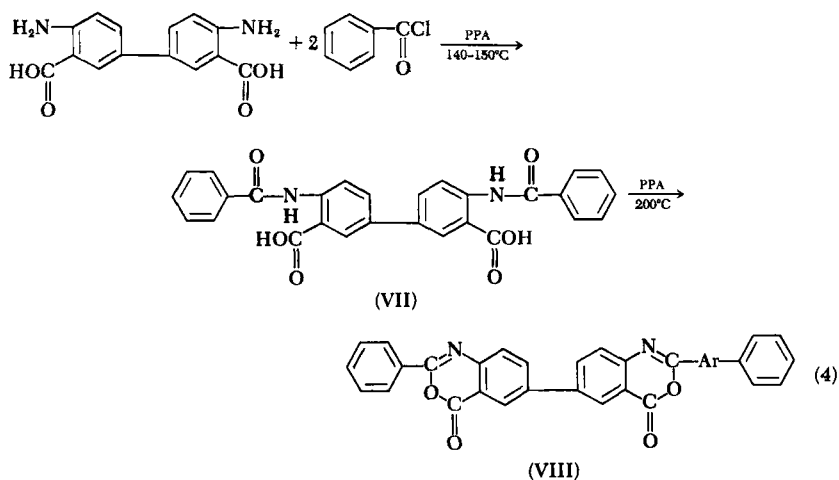


FIG. 2. Differential thermogram of polyamic acid (III) in nitrogen.

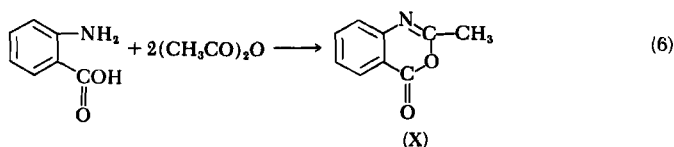
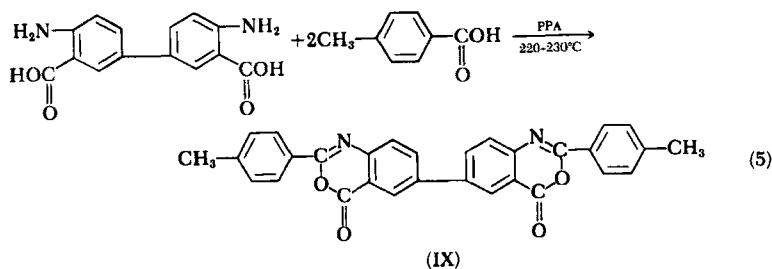


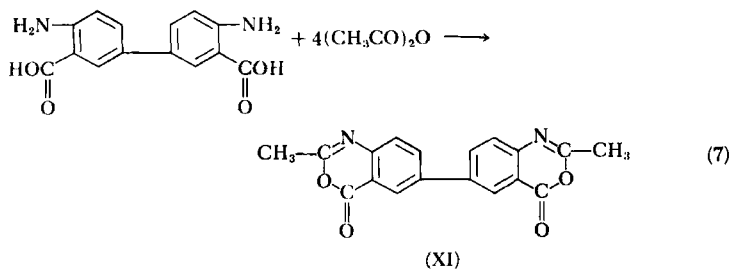
The reaction of benzoyl chloride with anthranilic acid in PPA affords N-benzoyl anthranilic acid (V) quantitatively at 120–140°C, and it can be isolated as a stable crystalline product. When N-benzoyl anthranilic acid (V) is treated with PPA at a higher temperature than 195–200°C, the intramolecular cyclodehydration takes place to afford 2-phenyl-4H-3,1-benzoxazine-4-one (VI) in quantitative yield as shown in Eq. (3). It shows that the reactions involve two stages in PPA, and it suggests the possibility of two-stage cyclopolycondensation reactions of polybenzoxazine by a PPA solution polymerization technique. Similarly, it is established that the bifunctional derivatives such as N,N'-dibenzoyl-3,3'-benzidinedi-
 ° PPA, polyphosphoric acid.

carboxylic acid (VII) are successfully prepared by the reaction of 4,4'-diamino-3,3'-biphenyldicarboxylic acid with benzoyl chloride at 140–150°C in PPA, which is converted to the 2,2'-diphenyl-[6,6'-bi-4H-3,1-benzoxazine]-4,4'-dione (VIII) at 220–230°C in PPA as shown by



The structures were confirmed by both the infrared spectra and the elemental analyses as described in the experimental section, and several model compounds containing a benzoxazinone ring system were prepared as described in Eq. (5), and also by the cyclocondensation reaction of anthranilic acid or BDC with acetic anhydride as shown in Eqs. (6) and (7).





As described in Table 1, uncyclized amide acid derivative (VII, solid line) shows strong carbonyl stretching bands of a carboxyl group at 1690 cm^{-1} and an amide group at 1670 cm^{-1} , whereas the cyclized benzoxazinone derivative has a sharp ester carbonyl absorption band of benzoxazinone at 1760 cm^{-1} and also the new characteristic absorption bands of the benzoxazinone ring system appear at 1260 and 1060 cm^{-1} . It is clearly demonstrated by the model reactions, therefore, that in PPA the open-chain polyamic acid precursor is obtained in quantitative yield at moderate reaction temperatures (in PPA at $120\text{--}150^\circ\text{C}$). The aromatic amic acid is converted to the described benzoxazinone derivative by the treatment in PPA at $200\text{--}230^\circ\text{C}$.

Solution Polymerizations in Polyphosphoric Acid

Although it has not been possible so far to isolate an open-chain polyamide precursor by means of the solution polymerization in PPA, it is reasonably presumed from the investigation with model reactions that the two-stage polymerization technique might be applied to the preparation of polybenzoxazinones, and the tractable open-chain precursor may well be obtained in the cyclopolycondensation (4,5,8) of 4,4'-diamino-3,3'-biphenyldicarboxylic acid with aromatic dicarboxylic acid derivatives in polyphosphoric acid at $140\text{--}150^\circ\text{C}$. Thus we extended the reaction to cyclopolycondensation of bifunctional aromatic compounds by a solution polymerization technique in polyphosphoric acid. The authors found that the high molecular weight polyamic acid (III) was obtained by the solution polymerization in PPA. The experimental details using BDC and a variety of carbonyl compounds and dinitrile as monomers are summarized in Table 2. As shown in Table 2, polyamic acids (III) of high molecular weight are prepared when carboxylic

acid chlorides and diamides are employed. It suggests the initial formation of phosphorylated reaction species as polymerization intermediates, and the carbonyl groups of acid chloride or amide are attacked by the nucleophilic reagent such as PPA to produce activated reaction intermediates. It subsequently undergoes polycondensation reactions with amino groups of BDC to afford polyamic acid of high molecular weight. When aromatic esters and nitriles such as dimethyl terephthalate and terephthalonitrile are employed as acid components, the more drastic polymerization conditions in PPA are necessary to prepare polyamic acid of high molecular weight, mainly because they are more resistant to phosphorylation in PPA than carboxylic acid chloride or amide. The polymerization mechanism and the experimental evidence for the phosphorylation reaction will be reported in a separate article (18). The polyamic acids of inherent viscosity above 0.4 have the film-forming property and the transparent tough film is obtained by film casting.

Table 1 shows the effect of inorganic salts in the solution polymerization of BDC-dihydrochloride-dihydrate in PPA. It is demonstrated that the dihydrochloride of BDC is an effective monomer to produce polyamic acid of high molecular weight. The increased solubility of both monomers and polymers in the presence of lithium chloride in PPA is the major factor in obtaining polymers of higher molecular weight, and the liberation of hydrogen chloride in the PPA polymerization system also assists the diffusion of monomer into the polymerization media of PPA in the propagation step to increase the rate of polymerization as well.

Optimum Polymerization Conditions for Polyphosphoric Acid Solution Polymerization

To prepare a linear tractable polyamic acid (III) of high molecular weight, the optimum polymerization conditions were determined by the reaction of 4,4'-diamino-3,3'-biphenyldicarboxylic acid dihydrochloride dihydrate with terephthalic acid chloride for the preparation of polyamic acid (III) by measuring variation in the extent of polymerization with reaction variables. The results are summarized in Tables 3, 4, 5 and Fig. 3. The data in Table 3 show that the optimum polymerization temperature is found to be

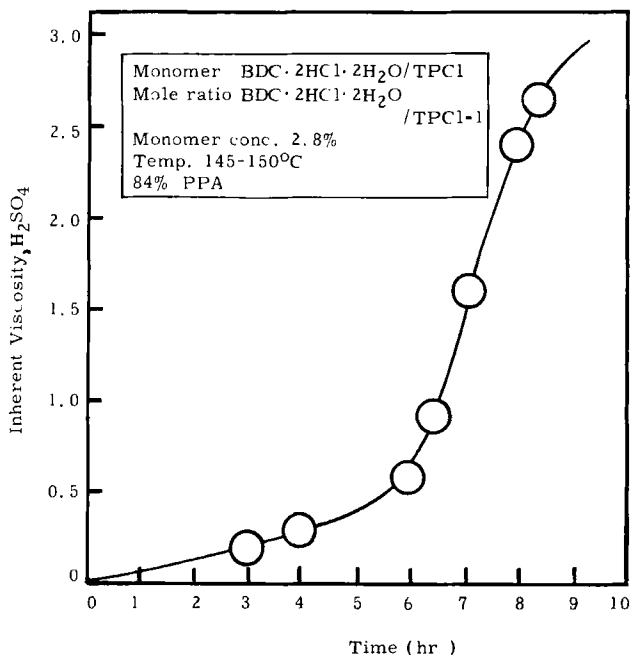


FIG. 3. Rate of polymerization of BDC·2HCl·2H₂O with TPCL at 145–150°C.

in the range 140–160°C, where the maximum inherent viscosity is observed. In Table 4 the effect of monomer concentration on the inherent viscosity was studied, and total monomer concentration of 3–4 wt. % in PPA was found to be optimum in the polymerization. The highest inherent viscosity $\eta_{inh} = 1.86$ was attained when a monomer concentration of 4 wt. % was employed. The plots in Fig. 3 show that the polymerization period should be less than 8 hr at 150–160°C in 84% PPA to obtain the tractable open-chain precursor, because the longer heating results in the formation of infusible polymer by the cyclodehydration and cross-linking after gelation. Therefore, it is necessary to stop the reaction before gelation sets in. Since the polymerization proceeds through the dehydration or dehydrochlorination reactions, the P₂O₅ content in PPA is quite sensitive to the molecular weight of the resulting polymer. A variety of polyphosphoric acids of different P₂O₅ concentrations are employed for the polymerization media at 140°C, and the data are given in Table 5. It is clearly shown that 84% PPA is the most

effective for the preparation of the polyamic acid of the highest molecular weight. It is found that a trace of moisture in the polymerization system affects seriously the decrease of molecular weight of the resulting polyamic acid.

Thermal Stability of Polyamic Acid and Polybenzoxazinone

The polyamic acid (III) are soluble in dimethylacetamide, N-methylpyrrolidone, dimethylformamide, and dimethylsulfoxide

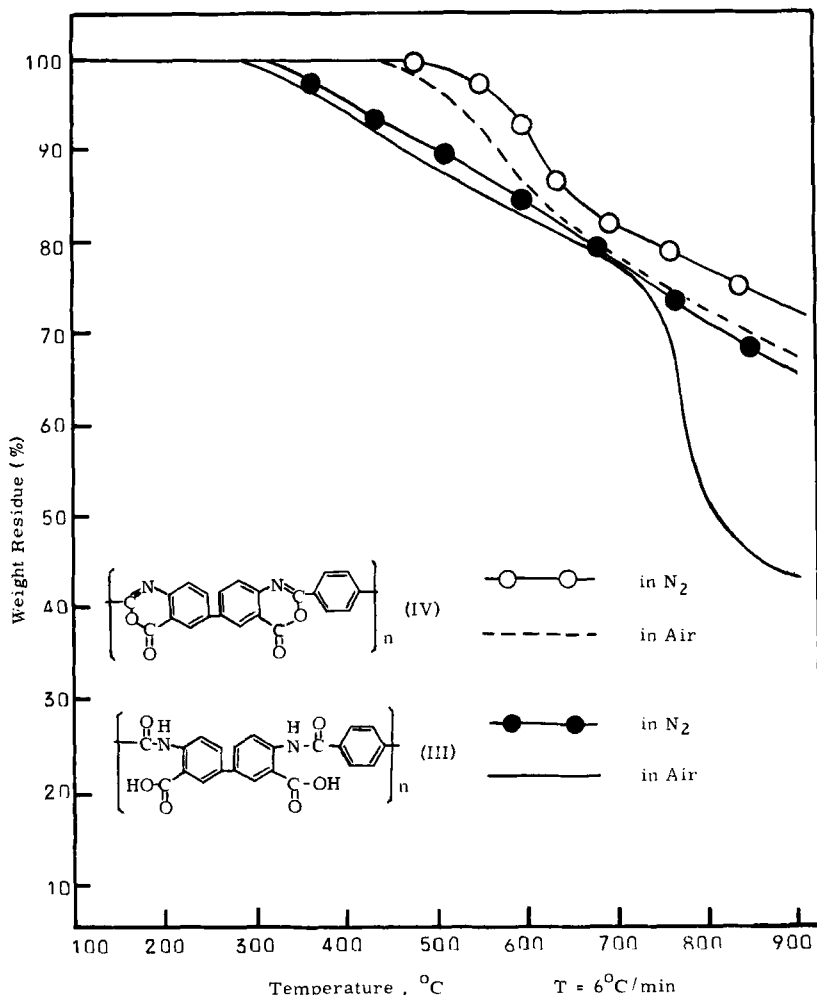


FIG. 4. Thermogravimetric analysis of polyamic acid (III) and polybenzoxazinone (IV) in nitrogen and in air.

containing lithium chloride. They are also soluble in concentrated sulfuric acid. The polybenzoxazinone (IV) is insoluble in most organic solvents; it is soluble in fuming nitric acid and concentrated sulfuric acid. The differential thermal analysis of polyamic acid shows an endotherm inflection at 200°C as shown in Fig. 2. It is fully confirmed that the intramolecular cyclodehydration takes place at 200°C to form polybenzoxazinone, which is evidenced by the observation of a carbonyl absorption band at 1760 cm^{-1} in the infrared spectrum in Fig. 1. The thermal stability of polyamic acid (III) and the resulting fully aromatic polybenzoxazinone (IV) were measured either in nitrogen or in air by the thermogravimetric method, as shown in Fig. 4. These benzoxazinone polymers have excellent thermal stabilities and the decomposition starts at about 550°C in nitrogen.

A detailed account of polymerization mechanism in polyphosphoric acid, including analytical, IR, and NMR data, will be reported in a forthcoming article (18).

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Zusammenfassung

Hochmolekulare Polybenzoxazinone wurden durch Kondensation von 4,4'-Diamino-3,3'-biphenyldicarbonsäure mit einer Reihe von aromatischen Carbonylverbindungen dargestellt unter den Bedingungen der Lösungs-polymerisation in Polyphosphorsäure. Aus der Modellreaktion der Anthranilsäure und 4,4'-Diamino-3,3'-biphenyldicarboxylsäure mit Benzoylchlorid in Polyphosphorsäure ergab sich, dass die Cyclopolymerisation über die Bildung eines offenkettigen Vorproduktes verläuft, in erster Stufe über hochmolekulare Polyaminsäuren ($\eta_{inh} = 2.66$), welche weiterhin thermisch oder chemisch in einer zweiten Stufe entlang der Kette cyclodehydriert werden um ein vollaromatisches Polybenzoxazinon zu ergeben. Die so dargestellten Polybenzoxazinone zeigen ausgezeichnete thermische Stabilität in Stickstoff als auch in Luft.

Die optimalen Polymerisationsbedingungen für Darstellung hochmolekularer Polyaminsäure wurden festgelegt, indem die Reaktionsvariablen wie Polymerisationstemperatur, Monomerenkonzentration, Reaktionszeit und auch der Einfluss der P_2O_5 Konzentrationen in Polyphosphorsäure untersucht wurden.

Résumé

Préparation des polybenzoxazinones à masse moléculaire élevée par la réaction de cyclopolycondensation de l'acide diamino-4,4'-biphenyl-3,3'-dicarboxylique avec des différents composés aromatiques carbonylés, utilisant la technique de polymérisation en solution dans l'acide polyphosphorique. On a établi à l'aide de la réaction modèle de l'acide anthranilique et de l'acide diamino-4,4'-biphenyl-3,3'-dicarboxylique avec le chlorure de benzoyl dans l'acide polyphosphorique, que le premier stade de la cyclopolycondensation procède avec formation d'un précurseur, à chaîne

ouverte et traitable, l'acide polyamique à poids moléculaire élevé ($\eta_{inh} = 2.66$). Dans le deuxième stade ce composé subit une cyclodeshydratation thermique ou chimique le long de la chaîne, et donne une polybenzoxazinone complètement aromatique. Les polybenzoxazinones ainsi obtenues sont douées des stabilités thermiques excellentes à la fois en atmosphère d'azote et dans l'air.

On a déterminé les conditions optima pour la préparation de l'acide polyamique de poids moléculaire élevé par l'étude des variables de la réaction tels que les températures de la réaction, concentration en monomères et durée de réaction, ainsi que l'effet des concentrations du P_2O_5 dans l'acide polyphosphorique.

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