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Study of the Mechanism for Poly(*p*-phenylene)benzoxazole Polymerization—A Remarkable Reaction Pathway To Make Rigid-Rod Polymers

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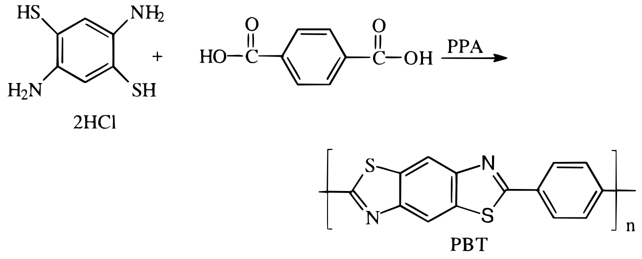
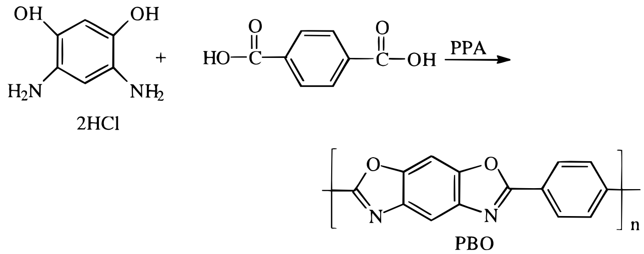
ABSTRACT: The mechanism of poly(*p*-phenylenebenzoxazole) formation from terephthalic acid (TA) and diaminodihydroxybenzene dihydrochloride (DADHB) in polyphosphoric acid (PPA) was studied. The solubility of TA in PPA with 86% P_2O_5 content was determined to be 0.02% at 100 °C and 0.06% at 140 °C. Dissolved TA existed as three species, TA, α-(4-carboxybenzoyl)-*ω*-hydroxypoly(oxyphosphinico), and α,α′-[1,4-phenylenebis(carbonyl)]bis[*ω*-hydroxypoly(oxyphosphinico)]. DADHB also reacts with PPA, and DADHB, α-(2,4-diamino-5-hydroxyphenyl)-*ω*-hydroxypoly(oxyphosphinico), and α,α′-(4,6-diamino-1,3-phenylene)bis[(*ω*-hydroxypoly(oxyphosphinico)] were found. During the course of polymerization, conversion of DADHB was higher than that of TA. NMR, IR, and mass spectroscopy characterization of PBO oligomer and its product with benzoic-*carboxy*-^{13}C acid suggested both chain ends were capped with DADHB, which is different from oligomers of conventional AA plus BB step-growth polymers. An unprecedented polymerization mechanism is proposed to account for this unusual oligomer structure and the remarkable fact that high molecular weight PBO was obtained even when 5% excess of one of the monomers, TA, was used. The reactivities of the two functional groups in DADHB toward carboxylic acid to form benzoxazole in PPA were different.

Introduction

Poly(*p*-phenylenebenzothiazole) (PBT) and poly(*p*-phenylenebenzoxazole) (PBO) are rodlike polymers with extended chain conformation. These polymers have excellent thermal and oxidative stability and good hydrolytic and solvent resistance. Fibers prepared from these polymers have superior tensile strength and modulus, cut and abrasion resistance, and flame retardance. PBO fiber is used in high-performance composites and comfortable protective garments.[1] The synthesis, processing, and characterization of these materials have been actively pursued.[2−5]

PBT and PBO are prepared by the reaction of 1,4-diamino-2,5-dithiobenzene dihydrochloride and 1,3-diamino-4,6-dihydroxybenzene dihydrochloride (DADHB) with terephthalic acid (TA) or TA derivatives in poly(phosphoric acid) (PPA). The final P_2O_5 content of PPA must be carefully adjusted to prepare polymers of high molecular weight.[2] Low molecular weight rigid-rod polymers were made when the final P_2O_5 content was below 82.5%. The viscosity of the polymerization solution increased dramatically when the final P_2O_5 content was above 84.5%.





Model compounds, benzoic acid and *o*-aminophenol, were used to study the mechanism of benzoxazole formation. In PPA, benzoic acid forms α-(benzoyl)-*ω*-hydroxypoly(oxyphosphinico) (mixed anhydride), and for *o*-aminophenol, the amino group is protonated with the hydroxyl group partially converted to phosphate ester. The free hydroxyl portion reacts with the mixed anhydride to generate an ester, 2-aminophenyl benzoate, which undergoes rapid acyl migration to form (2-hydroxyphenyl)benzanilide. The ring closure step is acid-catalyzed. The reaction pathway of benzoic acid

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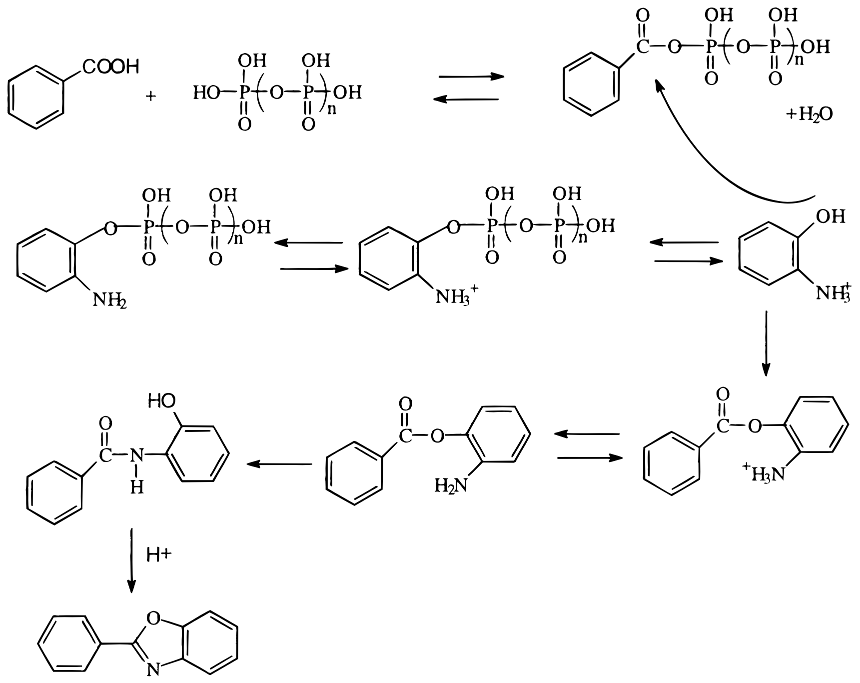
Scheme 1



and *o*-aminophenol in PPA to generate 2-phenylbenzoxazole is shown in Scheme 1.[6]

In this article, we report the extension of study with model compounds to the polymerization mechanism of PBO from TA and DADHB in PPA. The fate of the two monomers in PPA was studied.

Even micronized TA has an extremely low solubility in the reaction medium, PPA. The solubility limit of this monomer, however, does not prohibit the formation of high molecular weight polymer. The solubility of micronized TA in PPA was determined to understand the role of TA in PBO polymerization.

For AA plus BB step-growth polymerization with equal reactivity of functional groups, three varieties of molecules may be formed in the polymeric mixture:[7]

•if x, the total number of reactant molecules combined in the polymer molecule, is an even integer

$$\frac{x}{2}\mathrm{AA} + \frac{x}{2}\mathrm{BB} \rightarrow \mathrm{AA(BBAA)}_{(x-2)/2}\ \mathrm{BB}$$

•if x is odd, either

$$\left(\frac{x+1}{2}\right)\mathrm{AA} + \left(\frac{x-1}{2}\right)\mathrm{BB} \rightarrow \mathrm{AA(BBAA)}_{(x-3)/2}\mathrm{BBAA}$$

or

$$\frac{x-1}{2}\mathrm{AA} + \frac{x+1}{2}\mathrm{BB} \rightarrow \mathrm{BBAA(BBAA)}_{(x-3)/2}\mathrm{BB}$$

Oligomers were isolated in PBO polymerization and, surprisingly, only structures end-capped with DADHB were detected. A unique polymerization mechanism was proposed to explain this unprecedented oligomer structure.

For the polymerization of bifunctional monomers AA plus BB (e.g., diol plus diacid or diamine plus diacid), one must precisely adjust the stoichiometric balance of the bifunctional monomers. The number average degree of polymerization $\bar{X}_n$ with stoichiometric unbalanced r at complete conversion is

$$\bar{X}_{\mathrm{n}} = \frac{(1+r)}{(1-r)}$$

With 5% excess of one monomer, the maximum number average degree of polymerization is about 20. Surprisingly, high molecular weight PBO was obtained even with 5% excess of TA.[8] The proposed polymerization mechanism can also be used to rationalize this phenomenon.

Results and Discussion

I. Solubility of TA in PPA. Solubility of TA in PPA was determined to assess its role in the polymerization reaction. NMR spectroscopy was chosen because this technique detects dissolved species only and therefore is capable of dealing with opaque solutions containing excess solids. ^{1}H NMR spectroscopy was chosen for its sensitivity, and the PPA was made with D_2O in order to reduce the dynamic range of signals. The deuterio-PPA was prepared by combining 85 wt % P_2O_5 with 15 wt % D_2O. This corresponds to an 86 to 14 wt ratio of PPA and H_2O (86 wt % PPA). Methanesulfonic acid (MSA) was used as the internal standard. The MSA contained 1.006 OH per CH_3 and a trace amount ($<1\%$) of anhydride by NMR analysis.

The NMR signal of the TA ring protons was a single line at a chemical shift of 8.23 ppm with internal MSA set at 3.16 ppm (Figure 1A,B). Although only one kind of TA moiety was apparent, the resolution of these scans was not sufficient to determine whether TA existed as the diacid, α-(4-carboxybenzoyl)-*ω*-hydroxypoly(oxyphosphinico) (a monoacid−monoanhydride), or α,α′-[1,4-phenylenebis(carbonyl)]bis(*ω*-hydroxypoly(oxyphosphinico) (a dianhydride). The broad background signals, which intensified at 140 °C to multiple resolved lines, apparently arose from construction materials in the NMR probe. They were aliphatic in nature and behaved like a polymeric material that softened upon heating (Figure 1B).

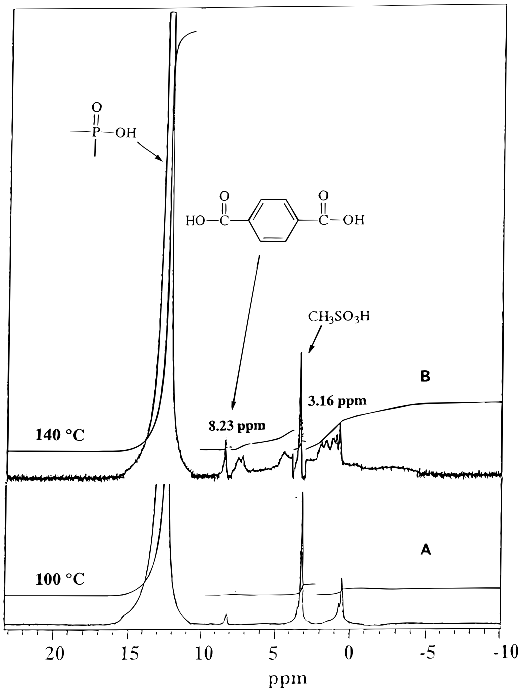


Figure 1. ^{1}H NMR spectrum of TA in PPA with MSA as the internal standard at 100 and 140 °C.

Table 1. Solubility of Terephthalic Acid in Polyphosphoric Acid

temp, °C	time at temp,h	integral TA/OH	integral MSA/OH	μg of TA/g of PPA
		Process 1		
100	0.9	7.57	84.3	172
100	2.4	7.96	86.26	181
100	0.9	26.56	75.71	605
140	1.8	24.24	71.26	552
140	3.1	28.23	79.85	643
140	0.3	15.35	82.58	350[a]
100	0.8	13.66	82.21	311[a]
100	2.1	9.12	86.08	208
		Process 2		
100	0.9	8.81	86.13	189
100	2.4	8.12	87.42	174
100	0.9	27.65	71.25	593
140	1.8	25.77	78.02	552
140	3.1	27.42	79.37	588
140	0.3	16.85	92.42	361
100	0.8	14.54	88.84	312
100	2.1	10.05	93.39	215

[a] Not used in calculation.

The P_2O_5 content of the PPA was 86 wt %, and the TA in the sample exceeded its solubility limit. The sample was held at 100 °C for 3 h, raised to 140 °C for 3 h, and then returned to 100 °C for 3 h. Spectra were scanned and integrated at intervals. Quantitative analysis was performed by comparing the integrals for TA with those for MSA. The integrations were performed two times (processes 1 and 2), using the same set of raw data, and the results are shown in Table 1. The solubilities of TA in 1 g of PPA with 86 wt % P_2O_5 at 100 and 140 °C are 190 ± 20 and 590 ± 60 μg, respectively.[9]

Figure 2 compares the time dependence of TA solubility with temperature. It shows that dissolution occurred within 30 min after raising the sample to a temperature to 100 °C, and reprecipitation upon cooling required 3 h or more. The longer reprecipitation time upon cooling may arise, in part, from the finite lifetime of the mixed anhydrides, which are expected to be soluble in PPA.

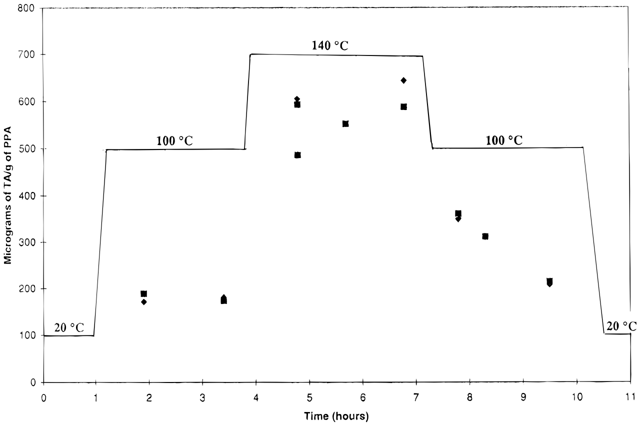


Figure 2. Time dependence of TA solubility in 86% P_2O_5 content PPA with temperature: (◆) process 1; (■) process 2.

II. Formation of TA–PPA Mixed Anhydride. Studies with both ^{13}C and ^{31}P NMR spectroscopy demonstrated that benzoic acid in PPA is partially converted to benzoic–phosphoric mixed anhydride. Peaks in the ^{13}C NMR spectrum of benzoic acid in PPA were distinctively assigned to carboxylic acid (173.2 ppm) and mixed anhydride (160.9 ppm). The ratio of mixed anhydride to benzoic acid increased dramatically as the P_2O_5 content of PPA increased. Benzoic acid, mixed anhydride, and PPA were in dynamic equilibrium.[6]

The ^{13}C NMR spectrum of a slurry of micronized TA in PPA did not show any signal. The solubility of TA in PPA was too low to permit direct detection using natural abundance ^{13}C NMR spectroscopy. TA with ^{13}C-labeled carboxylic acid groups was used to enhance NMR sensitivity 100-fold, thereby producing measurable signals. A sample of 0.26 wt % α,α′-di-^{13}C-terephthalic acid in PPA with 85% P_2O_5 was examined. Only dissolved species were detected. There was excess solid TA because TA solubility is 0.02% at 100 °C and 0.06% at 140 °C. ^{13}C NMR spectra were scanned at 100 °C and at 140 °C. Only ^{13}C-labeled carboxylic carbons were detected. They existed as free –COOH (two lines at 172.8 and 172.2 ppm) and as mixed anhydride (one broader line at 159.4 ppm). The line at 172.8 ppm was stronger than that at 172.2 ppm at both temperatures (Figure 3). The acid lines logically may be assigned to diacid and to monoacid–monoanhydride.

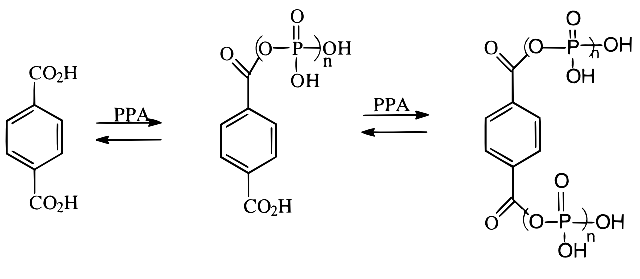


Table 2 gives the mole proportions of acid and anhydride, based on NMR integrals. The acid-to-anhydride ratios were 110/90 at 140 °C and 120/80 at 100 °C. The ratios of the diacid to the monoacid were approximately 59/51 at 140 °C and 71/50 at 100 °C. The mole percents of diacid, monoacid–monoanhydride, and

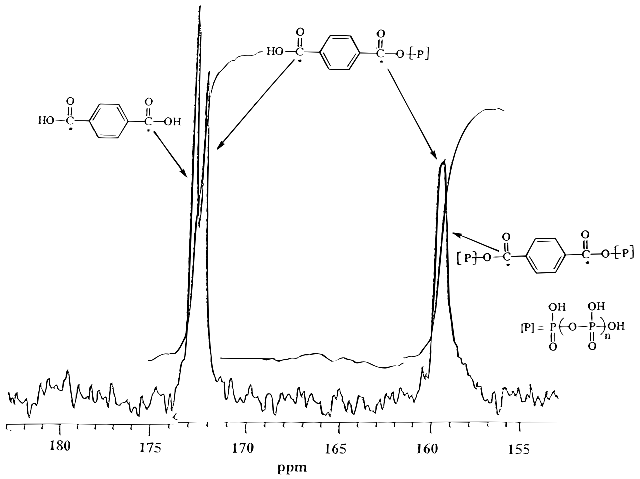


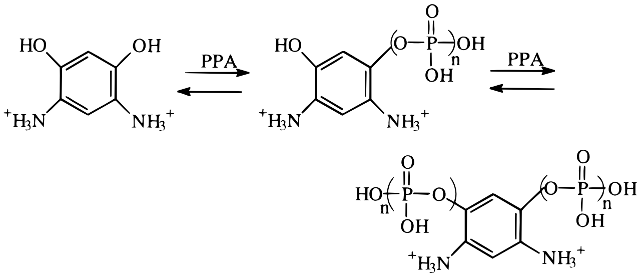
Figure 3. Carbonyl region of the ^{13}C NMR spectrum of α,α′-di-^{13}C-terephthalic acid in PPA with 85% P_2O_5 at 140 °C.

Table 2. Distribution of Acid and Anhydride Terminations for Terephthalic Acid in 85% P_2O_5 Content PPA

mol/100 mol of dissolved TA	100 °C	140 °C
acid ends, −C(O)OH	120 ± 6	110 ± 4
anhydride ends, −C(O)O[P]	80 ± 6	90 ± 4
ratio of diacid to monoacid	71/50	59/51
diacid	∼35	∼30
monoacid−monoanhydride	∼50	∼50
dianhydride	∼15	∼20

dianhydride at 100 °C were 35, 50, and 15, respectively. At 140 °C, the numbers were 30, 50, and 20.[10]

III. Diaminodihydroxybenzene (DADHB) in PPA. The ^{31}P NMR spectrum of DADHB in PPA was very similar to the spectra of phenol and *o*-aminophenol in PPA.[6] Phosphate esters were observed. Figure 4 is the ^{13}C NMR spectrum of a sample prepared from DADHB and PPA with 83.7% initial P_2O_5 content. Peaks were assigned to protonated DADHB, α-(2,4-diamino-5-hydroxyphenyl)-*ω*-hydroxypoly(oxyphosphinico), and α,α′-(4,6-diamino-1,3-phenylene)bis[*ω*-hydroxypoly(oxyphosphinico)].



IV. Unusual Structure of PBO Oligomer. Components in the PBO oligomerization reaction were isolated and characterized. Samples were removed from a PBO polymerization reaction at 5.0, 7.1, 8.7, 10.3, and 14 h after the reaction started. Unreacted DADHB was extracted with hydrochloric acid, and TA was isolated by DMSO extraction. PBO oligomer was washed thoroughly with water and then dried to constant weight.

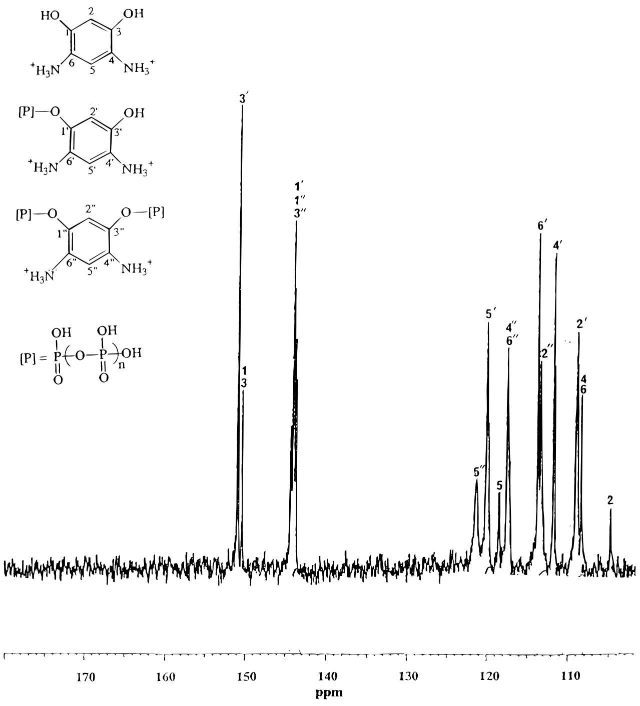


Figure 4. ^{13}C NMR spectrum of diaminodihydroxybenzene in PPA.

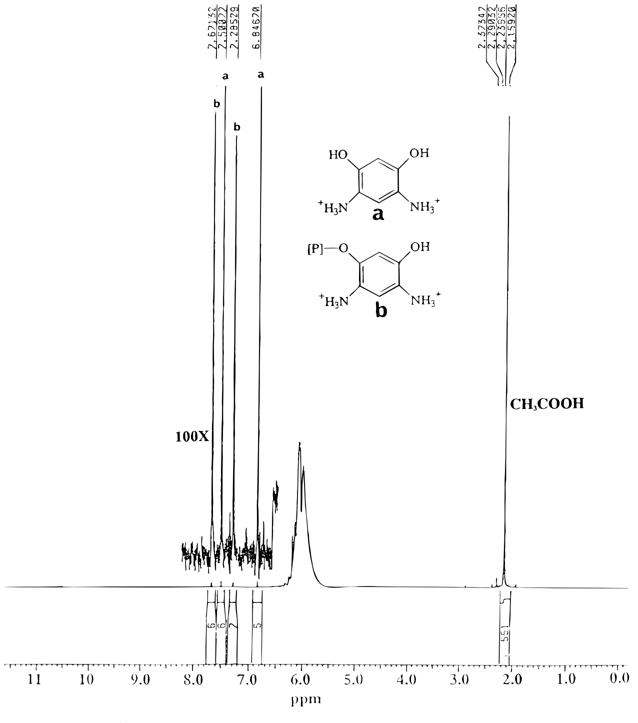


Figure 5. ^{1}H NMR spectrum of hydrochloric acid extraction from PBO polymerization solution.

The ^{1}H NMR spectrum of hydrochloric acid extraction showed peaks at 7.67, 7.50, 7.29, and 6.85 ppm (Figure 5). Signals at 7.50 and 6.85 ppm were attributed to DADHB. The intensity of these peaks gradually increased while peaks at 7.67 and 7.29 ppm became smaller and finally disappeared. Absorption peaks at 7.67 and 7.29 ppm were attributed to α-(2,4-diamino-5-hydroxyphenyl)-*ω*-hydroxypoly(oxyphosphinico) (a DADHB−PPA monoester), which was hydrolyzed to DADHB. DADHB content was determined by NMR integration of DADHB peaks and DADHB−PPA ester peaks, with sodium acetate as the internal standard. Extraction of the residue with DMSO yielded TA with 95−100% purity.

Table 3 lists recovered DADHB, DADHB conversion, recovered TA, TA conversion, isolated PBO oligomer,

Table 3. Analytical Results of PBO Polymerization Solution as the Reaction Progressed[a]

dope, g	recovered DADHB, g (wt %)	DADHB conversion	recovered TA, g (wt %)	TA conversion	wt of oligomer, g	P in oligomer, %
	(8.35)		(10.1)			
21.69	0.6 (2.77)	0.67	1.10 (5.07)	0.50	2.07	6.4
20.04	0.43 (2.15)	0.74	0.78 (3.89)	0.61	2.24	5.8
18.81	0.28 (1.49)	0.82	0.64 (3.4)	0.66	2.38	3.4
21.94	0.17 (0.79)	0.90	0.47 (2.14)	0.79	2.75	3.0
16.03	<0.1	~1	0.07 (0.70)	0.93	2.73	1.2

[a] Samples were removed from the reactor at 5.0, 7.1, 8.7, 10, and 14 h after TA and DADHB were added. The reactor initially contained 10.1 wt % TA and 8.35 wt % DADHB.

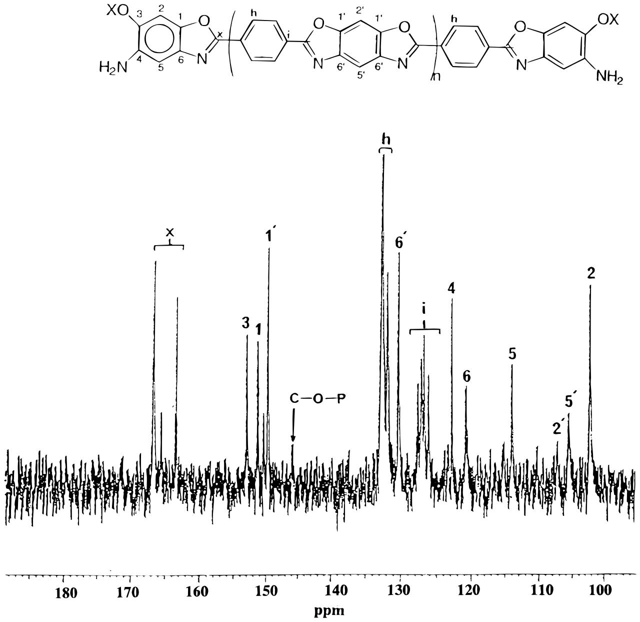


Figure 6. ^{13}C NMR spectrum (in MSA) of PBO oligomer isolated 5 h after the reaction started.

and the phosphorus content in the oligomer after thorough wash with water as the polymerization reaction progressed. Conversion of DADHB was always higher than that of TA. A significant amount of phosphorus was found in PBO oligomer even after repeated water washings. The amount of residual phosphorus decreased as the conversion of reactants increased. The oligomers were partially soluble in dilute NaOH solution to give a deep orange-brown color, which is characteristic for phenoxides.

The IR spectra of the PBO oligomer showed the absence of carboxylic acid, ester, or amide. Peaks at 1630 and 1620 cm^{-1} were assigned to benzoxazole and $-NH_2$ bending, respectively. A broad absorption extending over the region 3700−1750 cm^{-1} was observed, which could be due to the presence of both NH_2 and OH groups. ^{13}C NMR spectra of oligomer in MSA from the five samples were similar, and only the spectrum from the sample removed at 5.0 h is shown (Figure 6). The carbon for −COOH, which would be expected at around 174 ppm, was not detected. Peaks at 120.6 and 151.2 ppm were tentatively assigned to $C-NH_2$ and C−OH, respectively. ^{31}P NMR spectra of oligomer samples showed H_3PO_4 at 2.6 ppm. The absorption peak at −7.91 ppm and a very weak peak at −9.21 ppm were assigned to α-carbonyl-ω-hydroxypoly(oxyphosphinico) at the chain ends. The pH values of the PBO oligomer slurry in water ranged from 2.5 to 4.0. Analysis of the oligomer by mass spectroscopy was attempted, but no components came out of the probe.

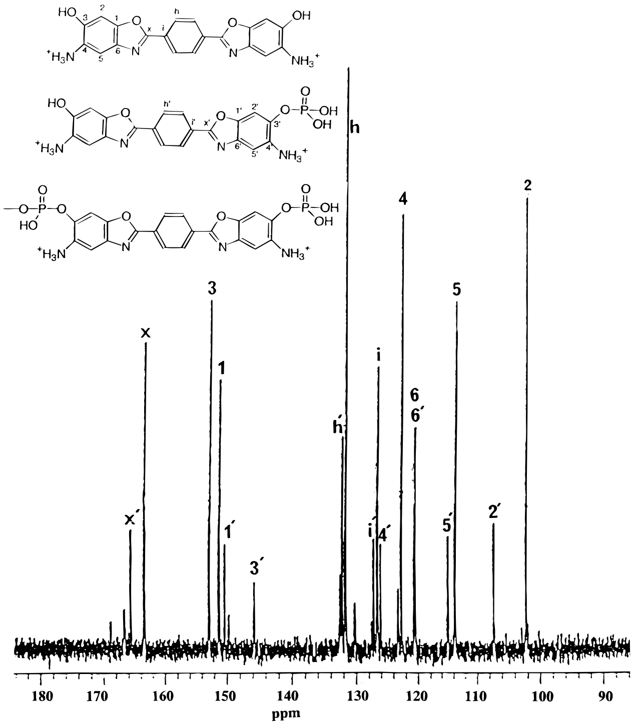
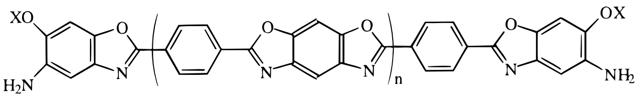


Figure 7. Initial ^{13}C NMR spectrum of 2,2′-(1,4-phenylene)bis(5-amino-6-benzoxazolol) (**1**) in MSA.

The uncommon structure of the PBO oligomer shown below was suggested by consistently higher conversion of DADHB over TA in the course of polymerization, the fact that −COOH in oligomer samples was not detected by IR and ^{13}C NMR spectroscopy, and high phosphorus contents in oligomer that decreased as the polymerization reaction progressed.[11] The proposed nature of phosphorus in the oligomer was based on the study of model compounds with ^{31}P NMR spectroscopy.



X = H or -P[(O)(OH)]$_n$OH

Because an oligomer end-capped with only one type of functional group has never been reported for any AA plus BB step-growth polymerization, several experiments were carefully carried out to confirm this unusual structure.

A PBO model compound, 2,2′-(1,4-phenylene)bis(5-amino-6-benzoxazolol) (**1**), with DADHB at both ends, was made by the reaction of TA with excess DADHB in PPA. Compound **1** was isolated with NaOH extraction followed by neutralization with HCl. The isolated compound was dissolved in MSA, and the initial ^{13}C

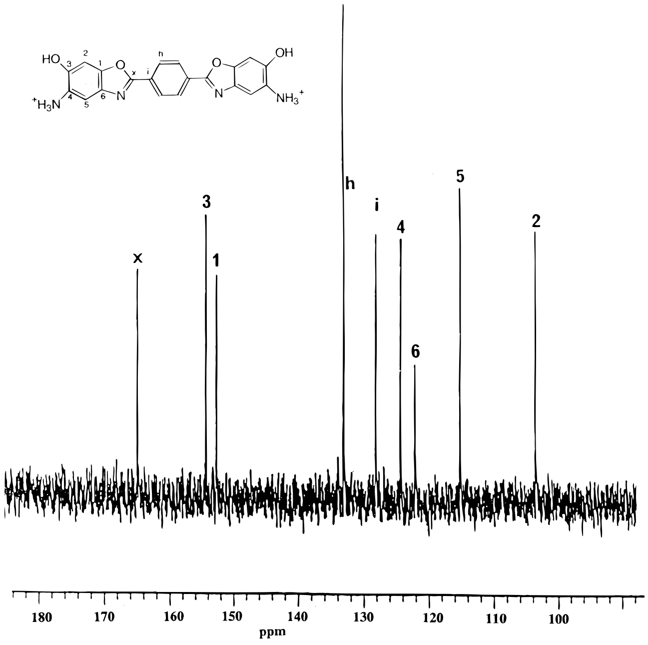


Figure 8. ^{13}C NMR spectrum of 2,2′-(1,4-phenylene)bis(5-amino-6-benzoxazolol) (**1**) 50 h after water was added to the MSA solution.

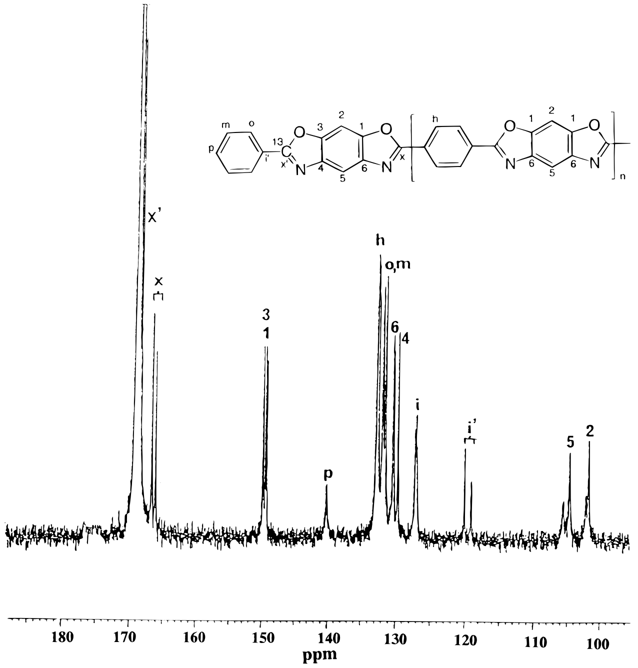
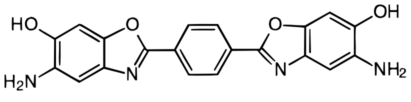


Figure 9. ^{13}C NMR spectrum of the product from isolated PBO oligomer and benzoic-*carboxy*-^{13}C acid.

NMR spectrum was very complex (Figure 7). ^{31}P NMR spectroscopy showed H_3PO_4 and phosphate ester. A drop of water was then added to the NMR sample. Fifty hours after adding the water, the ^{13}C and ^{1}H NMR spectra corresponded to the proposed DADHB−TA−DADHB structure with the amino groups protonated (Figure 8). For the hydrolyzed product, no phosphate ester was detected by ^{31}P NMR spectroscopy. The complexity of the initial sample was due to the presence of phosphate esters, which hydrolyzed to give a single component with only *o*-aminophenol functional groups at the ends.



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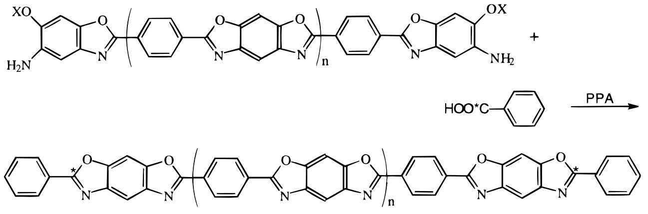
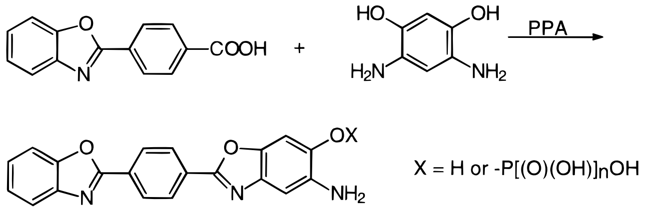
The ^{13}C NMR spectrum of PBO oligomer (Figure 6) is very similar to that of the model compound **1** (Figure 7). With reference to the assignments for the model compound, we were able to assign most of the peaks in the ^{13}C NMR spectrum of the oligomer.

Oligomer isolated from the sample removed at 5 h was redissolved in PPA and reacted with benzoic-*carboxy*-^{13}C acid. The ^{13}C NMR spectrum of the product showed very strong absorption for benzoxazole carbon, which was consistent with reaction of chain-end DADHB with benzoic acid (Figure 9). The most convincing evidence was the MS of the product. The only products detected by MS were benzoic-*carboxy*-^{13}C acid end-capped PBO compounds of up to five TA molecules plus six DADHB molecules (Figure 10).



V. Nature of Phosphorus in PBO Oligomer. The nature of phosphorus in DADHB end-capped benzoxazole compounds was further studied with 2-[4-(2-benzoxazolyl)phenyl](5-amino-6-benzoxazolol) (**2**), which was made by the reaction of 4-(2-benzoxazolyl)benzoic acid with a large excess of DADHB in PPA. The product was isolated by coagulation and washed with water. The compound was studied in detail because its chemistry and spectroscopy were expected to be close to that of PBO.



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The isolated product dissolved readily in MSA. Its ^{31}P NMR spectrum showed the strongest line at 2.7 ppm, which was assigned to H_3PO_4. A small line at −12.95 ppm was assigned to $CH_3S(O)_2OP(O)(OH)_2$. The second strongest signal was a single line at −7.96 ppm, and there was a much smaller signal at −9.36 ppm. These signals were attributed to aromatic phosphate esters, $O{-}P(O)(OH)_2$ and $O{-}[P(O)(OH)]_nOP(O)(OH)_2$, respectively.

The distribution of ^{31}P species in this MSA solution changed over a period of hours. Sixteen hours after the sample was prepared, the −12.95 ppm signal disappeared but the phosphate ester signals remained. A drop of water was added to the NMR tube at 17 h, and the spectrum was run again within 0.5 h, showing no measurable change. The sample was monitored by ^{31}P NMR spectroscopy daily, which showed that the H_3PO_4

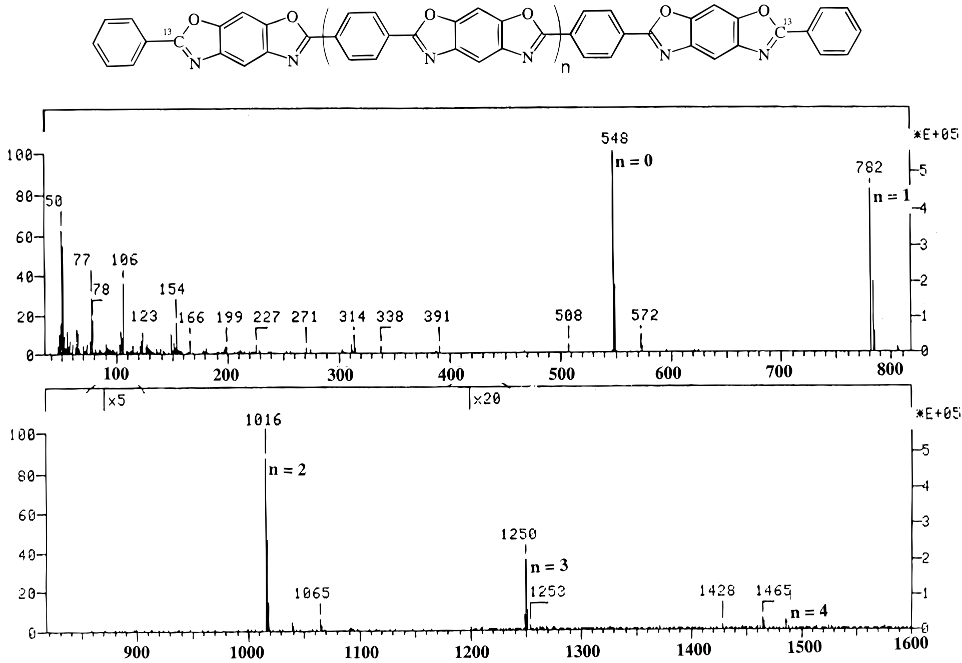
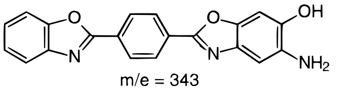


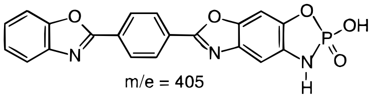
Figure 10. MS of the product from isolated PBO oligomer and benzoic-*carboxy*-^{13}C acid.

peak grew at the expense of the phosphate ester peaks. After 14 days, all phosphorus had been converted to H_3PO_4. The initial ^{13}C NMR spectrum in MSA was complicated and showed phosphate ester. After 2 weeks of hydrolysis, the ^{13}C NMR spectrum became less complex and all absorption peaks were assigned (Figure 11). The structure was consistent with 2-[4-(2-benzoxazolyl)phenyl](5-amino-6-benzoxazolol).

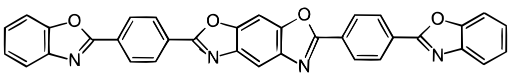
The MS of isolated compound **2** showed *m*/*e* of 343 (60%), 371 (30%), 405 (100%), 546 (50%), and 712 (90%). The proposed structures of the ions are shown below. The compound with *m*/*e* of 371 was unidentified.



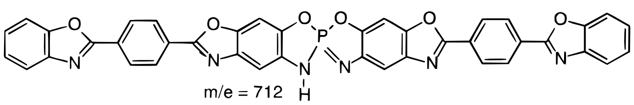
m/e = 343



m/e = 405



m/e = 546



m/e = 712

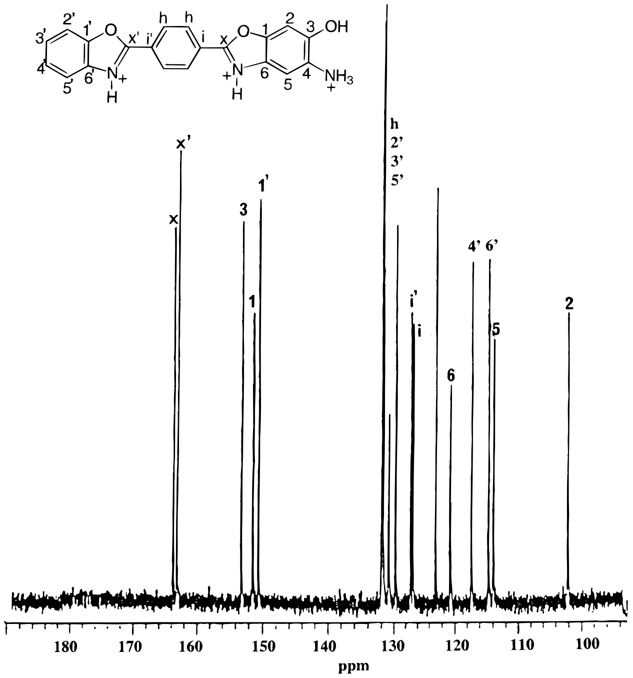
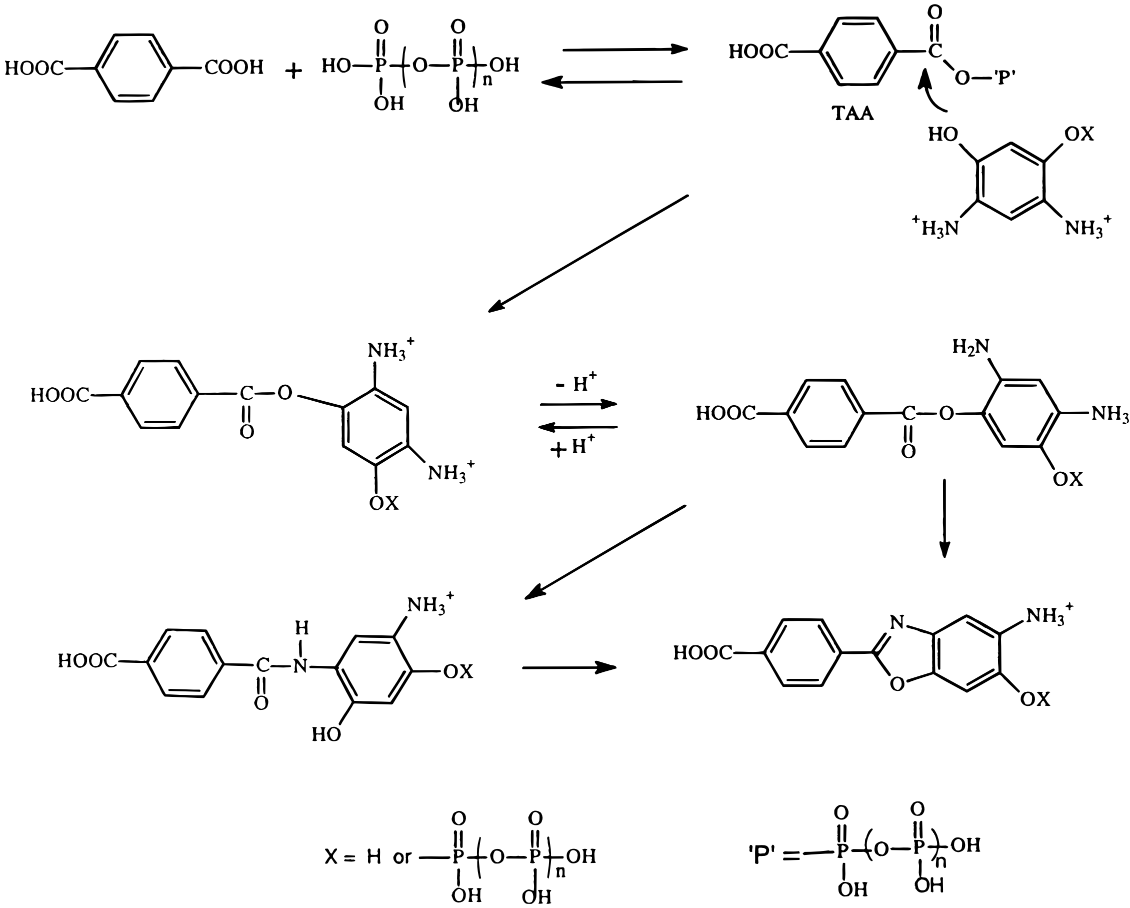


Figure 11. ^{13}C NMR spectrum of 2-[4-(2-benzoxazolyl)phenyl]-(5-amino-6-benzoxazolol) in MSA.

The ^{31}P and ^{13}C NMR studies of the two model compounds, compounds **1** and **2**, and PBO oligomer suggested that part of the chain-end DADHB existed as a phosphate ester, which hydrolyzed slowly in aqueous acid.[12] The phosphate ester in compound **2**, which is expected to mimic PBO, has a longer half-life than that of compound **1**. This stable phosphate ester bond was attributed to the high phosphorus content in the PBO oligomer samples.

VI. PBO Polymerization Mechanism. Based on the NMR data of TA and DADHB in PPA and the reaction mechanism of benzoic acid and *o*-aminophenol in PPA, the early stage reactions between TA and DADHB in PPA are described in Scheme 2. The carbonyl group in TA is activated through the formation of a carboxylic–phosphoric mixed anhydride. The hydroxyl group attacks the mixed anhydride to form an ester. Although the first product from the reaction of benzoic acid and *o*-aminophenol in PPA, 2-aminophenyl benzoate, undergoes an acyl migration to form the amide before ring closure (Scheme 1), in the case of TA and DADHB, the ester may produce the benzoxazole ring directly without going through an acyl migration. When the polymer chain starts to grow, acyl migration of a large group is expected to become difficult.

Scheme 2



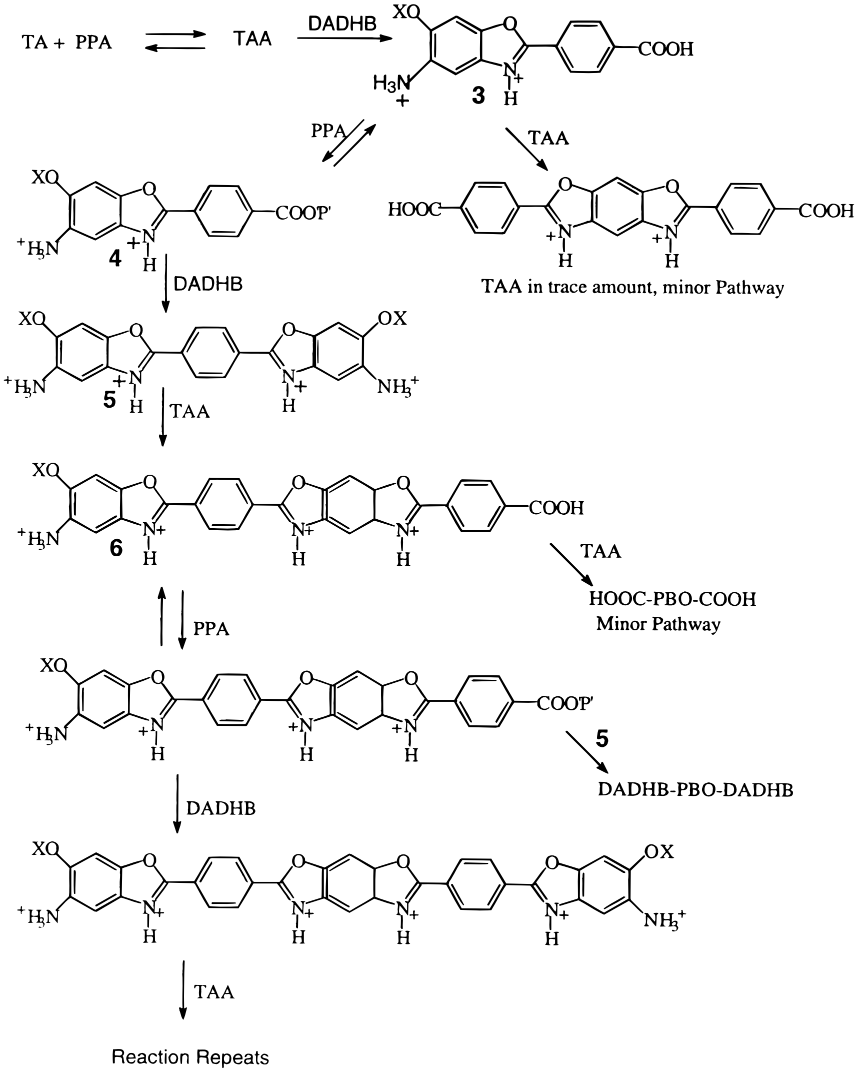
The unusual structure of the PBO oligomer and the very low solubility of TA in PPA suggest the mechanism for PBO polymerization as shown in Scheme 3. TA and DADHB form the dimer, 4-[2-(5-amino-6-benzoxazolol)]-benzoic acid (**3**). The chance for the *o*-aminophenol end of **3** to find a TA anhydride (TAA) to react is very low due to the extremely low concentration of TAA in PPA. The carboxylic acid end of **3** can readily react with the solvent, PPA, to form the anhydride, **4**, which then reacts with DADHB to generate the trimer, 2,2′-(1,4-phenylene)bis(5-amino-6-benzoxazolol) (**5**). Compound **5** must encounter a TAA to produce the tetramer, **6**. Compound **6** has the same fate as **3**. The probability that compound **6** will form an anhydride with PPA and then react with DADHB or an oligomer end-capped with DADHB is much higher than its probability of encountering a TAA. The proposed mechanism explains why PBO oligomers are end-capped with DADHB. Because IR and NMR spectra of isolated oligomer did not show any ester, amide, or their hydrolysis products, benzoxazole ring closure in PPA is fast.

Unlike conventional AA plus BB step-growth polymerization reactions, high molecular weight PBO was obtained even when TA was in excess. This unusual phenomenon is explained by the extremely low solubility of TA in the reaction medium, PPA. Only TA species that dissolve in PPA participate in PBO polymerization at a given time. As polymerization progressed, dissolved TA is consumed and solid TA gradually dissolves to maintain the TA solubility level at the reaction temperature. TA is “spoon-fed” in the reaction until practically all DADHB functional groups are converted. Excess solid TA did not participate in the reaction and therefore high molecular weight PBO is obtained at high DADHB conversion. On the other hand, low molecular weight PBO was generated when excess DADHB was used. Like conventional AA plus BB step-growth polymerization with stoichiometry imbalance, the number average degree of polymerization is limited by the conversion of DADHB at complete TA conversion.

VII. Change in Reactivity of DADHB and TA on Reaction. The change in reactivity of one functional group upon reaction of the other has been noted. This behavior usually occurs with monomers having two functional groups in close proximity and where polymerization involved a significant change in the electron-donating or electron-withdrawing ability of the functional group.[13] Reactivity of the two functional groups in DADHB was compared. One mole each of DADHB and benzoic acid were reacted in PPA. When all the benzoic acid was consumed, 1 mol of benzoic *carboxyl*-^{13}C acid was added to complete the reaction of DADHB. Reaction products were isolated. Analysis by MS with calibration of natural ^{13}C showed that the ratio of mass 312 ($^{12}C-^{12}C$) to 313 ($^{12}C-^{13}C$) to 314 ($^{13}C-^{13}C$) equaled 40.6 to 26.5 to 32.9. If the two sides of DADHB had equal reactivity, the ratio of the products should be 25 to 50 to 25. The relative reactivity of the two functional groups of DADHB toward benzoic acid in PPA is $(26.5/50)/(40.6/25) = 1/3$. Conversion of the first functional group in DADHB to benzoxazole makes the second functional group more reactive toward carboxylic acid.

The study of the relative reactivity of the two carboxylic acid groups in TA is hindered by the very low solubility of TA in PPA. The reactivity of the first carboxylic acid group in TA is determined by the

Scheme 3



conversion of solid TA into PPA-soluble TA species. The adduct of TA and DADHB, 4-(2-benzoxazolyl)benzoic acid, is expected to be soluble in PPA. The comparison of the reactivity between a species that is soluble in the reaction medium to TA, which is mostly in the solid state in PPA, is meaningless.

Conclusion

In PBO polymerization, one of the two monomers, TA, has extremely low solubility in the reaction medium, PPA. Dissolved TA existed in three forms, TA, α-(4-carboxybenzoyl)-ω-hydroxypoly(oxyphosphinico), and α,α′-[1,4-phenylenebis(carbonyl)]bis[ω-hydroxypoly(oxyphosphinico)]. DADHB also reacted with PPA to form α-(2,4-diamino-5-hydroxyphenyl)-ω-hydroxypoly(oxyphosphinico), α,α′-(4,6-diamino-1,3-phenylene)bis(ω-hydroxypoly(oxyphosphinico). Consumption of the monomers was monitored. The conversion of DADHB was higher than that of TA. Only PBO oligomer with both chain ends capped with DADHB was found. Part of the −OH groups in the PBO oligomer chain ends existed as phosphate esters. The unusual structure of PBO oligomer was carefully characterized by conversion of the chain-end o-$(NH)_2(OH)$ group to benzoxazole and comparison of NMR spectra of two model compounds. An unprecedented polymerization mechanism is proposed to account for the remarkable oligomer structure, different conversion of the two monomers, and the fact that high molecular weight PBO was generated even in excess TA. The reactivities of the two functional groups in DADHB are different. Conversion of the first functional group to benzoxazole makes the second functional group more reactive toward carboxylic acid.

PPA plays several roles in PBO polymerization. It activates the carbonyl groups of TA by formation of mixed anhydrides, protects DADHB by protonation of the amino groups and formation of phosphate esters, picks up water liberated from condensation, catalyzes closure of the benzoxazole ring, and protonates the nitrogens in the polymer to keep it soluble.

Experimental Section

Materials. PPA and MSA were purchased from Fisher Scientific Co. MSA was distilled over P_2O_5. TA from Amoco Co. was micronized with Jet Pulverizing Micro-Master jet mill equipment (Napp Chemical Inc.). α,α′-Di-^{13}C-terephthalic acid was from Merck Sharp & Dohme/Isotopes. DADHB was made with 1,2,3-trichlorobenzene as the starting material.[16]

Preparation of NMR Samples. PPA was placed in a 250-mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and an adaptor connected to a gas trap. DADHB was added, and the contents in the flask was heated with stirring at 70 °C until no HCl evolution was detected. The flask was placed in a nitrogen-purged glovebag. The warm PPA solution was transferred into a 10-mm-diameter

NMR tube. TA was stirred in PPA at 100 °C for 1 h before the warm solution was transferred into a 10-mm-diameter NMR tube.

Measurements. Mass spectral analysis was conducted with a Finnigan MAT TSQ-70 mass spectrometer. Infrared spectra were measured using a Nicolet Magna-IR FTIR/550 spectrometer. Instrumentation, experimental conditions, chemical shift references, and assignment of ^1H, ^{13}C, and ^{31}P NMR spectra were previously described unless specified.[6]

Determination of TA Solubility in PPA. The deuterio-PPA was prepared by combining 85 parts P_2O_5 with 15 parts D_2O, by weight. This corresponded to a P_2O_5 to H_2O weight ratio of 86 to 14. The MSA contained 1.006 OH per CH_3 and less than 1% of MSA anhydride by NMR analysis. The sample was made by mixing 200 mg of TA, 61.6 mg MSA, and 50 g of deuterio-PPA.

^1H NMR spectra (600 MHz) were scanned on a GE Omega 600 spectrometer with variable temperature accessory, using a proton coil of a 10-mm, broad-band probe. Spectral lines were broad due to high solution viscosity.

The temperature of the sample was held at 100 °C for 3 h, raised to 140 °C for 3 h, and then returned to 100 °C for 3 h. Spectra (Figure 1) were scanned and integrated at intervals. Quantitative analysis was performed by comparing the integrals for TA with those for MSA as follows:

$$\text{micrograms of TA per gram of PPA} = C(A/B)$$

where A is the signal of aromatic protons in TA to OH integration ratio, B is the signal of methyl groups in MSA to OH integration ratio, and

$$C = (\text{mol wt of TA}/4)(3/\text{mol wt of MSA}) \times (61.8\ \text{mg of MSA}/50\ \text{g of PPA})(1000\ \text{g/mg})$$

This approach was taken because the measurement of MSA methyl integration at 140 °C suffered serious interference from the background "polymer" signal. The OH signal, on the other hand, suffers no interference, and the amount of OH present does not vary with temperature.

Study of α,α-Di-^{13}C-terephthalic Acid in PPA by NMR Spectroscopy. A sample was prepared from 100 mg of α,α-di-^{13}C-terephthalic acid and 35 g of PPA with 85% P_2O_5 content. ^{13}C NMR (75 MHz) spectra were scanned at 100 and 140 °C using a Nicolet NT-300 spectrometer and pulse-FT technique. The chemical shift reference was the ^{13}C NMR signal of a separate sample of ethylene glycol scanned at the same magnetic field and placed at 64.0 ppm vs TMS.

The spectrum at 140 °C was acquired over a period of 3 h, starting approximately 2 h after reaching the temperature. The spectrum at 100 °C was acquired over a period of 11 h, starting a few minutes after cooling from 14 to 20 °C then raising to 100 °C. Figure 3 shows the carbonyl region of α,α′-di-^{13}C-TA in PPA at 140 °C: δ (ppm) = 172.8, (COOH)$_2$, 172.3 (COOH)(COOP), 159.4 [COOP, (COOP)$_2$]. The acid-to-anhydride ratios were 110/90 at 140 °C and 120/80 at 100 °C. The ratios of the two acid types were approximately 59/51 at 140 °C and 71/50 at 100 °C. Although the proportions are within estimated experimental error of one another, the overall conclusion was that the ratio of the 172.8 ppm line to the 172.2 ppm line definitely was greater at 100 °C than at 140 °C.

DADHB in PPA at 100 °C. DADHB (4.6 wt %) was dissolved in PPA with 83.7% P_2O_5 content, and a portion of the sample was transferred into a 10-mm-diameter NMR tube. The ^{13}C NMR spectrum (Figure 4) was obtained with a Bruker WM-360 at 90 MHz. The reference was TMS in the sample: δ (ppm) = 150.84, 150.31 (C−OH, 10.11), 144.33, 144.01, 143.73 (C−O−phosphate, 14.80), 121.24, 119.98 (16.96), 118.49, 117.46 (11.30), 113.66, 113.37 (14.43), 111.58 (8.15), 108.85, 108.30 (10.99), 104.73 (1.21). The same instrument with resonance frequency at 145 MHz was used for the ^{31}P NMR spectrum: δ (ppm) = 0.289 (H_3PO_4), −6.526 (PhOP(O)(OH)$_2$, −13.942, −14.183 (chain-end phosphorus), −20.438, −20.954, −21.225 (PhOP(O)(OH)[OP(O)(OH)]$_n$OH), −27.559, −28.505, −28.897, −29.284, −29.644, −30.613 (midchain phosphorus).

Polymerization. PBO polymer was produced at The Dow Chemical Co. The following was the procedure for mixing, dehydrochlorination, oligomerization, and molecular weight buildup.[15] A 91.68 lb quantity of PPA containing 85.4 wt % P_2O_5 and 18.97 lb of P_2O_5 was added to a 25-gal reactor with agitation by a helical dual ribbon impeller. At 60 °C under a nitrogen atmosphere, 13.71 lb of micronized TA and 17.24 lb of DADHB were added. Mixing was continued for 3 h at 60 °C, 7 h at 120 °C, and 4 h at 140 °C. At this time, a viscosity of about 300 Poise was reached.

Separation of Components in Polymerization Solutions. Samples were collected at 5.0, 7.1, 8.7, 10, and 14 h after the addition of DADHB and were coagulated with 250 mL of 2 N HCl. One gram of $SnCl_2$ was used to minimize the oxidation of DADHB. The slurry was filtered, and the orange solid was washed with another 50 mL of 2N HCl. The amount of unreacted DADHB and its phosphate ester was determined by ^1H NMR spectroscopy with sodium acetate trihydrate as the internal standard. The orange solid was washed four times with 400 mL of water to remove PPA and then stirred in 250 mL of dimethyl sulfoxide (DMSO) at 25 °C for 3 h. The residue was filtered and washed with another 100 mL of DMSO. The DMSO solutions were combined.

Analysis of DADHB from HCl Extractions in Polymerization Solution by ^{1}H NMR Spectroscopy. The concentrated HCl extraction (3.0 mL) was combined with a known amount of sodium acetate trihydrate (0.041 48 g for the sample removed at 5.0 h) and diluted with 3 mL of D_2O to dissolve all contents. A 0.5-mL portion was transferred to a 5-mm NMR tube, and the 300 MHz proton NMR spectrum was scanned with an IBM AF-300 spectrometer. Solvent suppression was employed to reduce the OH signal intensity. The primary chemical shift reference was tetramethylammonium bromide set at 3.25 ppm vs TMS (Figure 5): δ (ppm) = 7.67 (s), 7.50 (s), 7.26 (s), 6.85 (s). The signals at 7.67 and 7.26 ppm diminished and the peaks at 7.50 and 6.85 ppm grew over a period of hours to days. The DADHB equivalent of the two species was determined by the integral of the four ring proton lines versus the acetate methyl group integral:

$$\text{wt \% of DADHB equivalence} = (A/2)(3/B)(\text{mol wt of DADHB/mol wt of } CH_3COONa{\cdot}3H_2O)(C/D)(E)100$$

where A is the summed integrals of the four ring proton lines, B is the acetate CH_3 integral, C is the volume extract per weight of the polymer sample, D is the volume extract used, and E is the weight of sodium acetate trihydrate.

Isolation of TA from Polymerization Solution. DMSO was removed from the extracts by heating under vacuum. Water was added to the residue. The solid was collected with a sintered glass filter, washed thoroughly with water, and dried. ^1H NMR (DMSO-d_6): δ (ppm) 13.5 (broad s, 2H), 8.10 (s, 4H). ^{13}C NMR (DMSO-d_6): δ (ppm) 166.66, 134.39, 129.41. MS: $m/e = 166$. IR (KBr): 3500−2500, 1685 cm^{-1}.

PBO Oligomer. PBO oligomer isolated from the five samples had very similar spectroscopic data. The results from the first sample are described below: ^{13}C NMR in MSA (Figure 6): δ (ppm) = 166.55, 165.48, 163.46, 163.22, 152.92, 151.24, 150.37, 149.69, 132.51, 131.73, 130.15, 127.55, 127.03, 126.63, 126.03, 122.65, 120.53, 114.99, 113.61, 107.14, 113.61, 107.14, 105.43, 102.08. IR (cm^{-1}): 3700−2700 (broad), 1630 (benzoxazole), 1620 (−NH_2 bending).

Reaction Product of PBO Oligomer and Benzoic-*carboxy*-^{13}C Acid in PPA. Isolated PBO oligomer from the 5 h sample (173 mg), benzoic-*carboxy*-^{13}C acid (200 mg, excess), and PPA (50 g) were heated with stirring at 70 °C for 24 h. The temperature was increased to 90 °C and maintained for 24 h before it was set at 120 °C for 4 h, 150 °C for 4 h, and 170 °C for 16 h. The reactor was cooled to room temperature, and water was added to coagulate the product. The product was washed thoroughly with water and then with ethyl acetate to remove any unreacted benzoic acid. The yield of product was 150 mg and, unlike the starting material, it was insoluble in 0.1 N NaOH solution. ^{13}C NMR in MSA (Figure 9): δ (ppm) = 169.82, 166.59, 166.02, 149.73, 149.38, 149.17, 140.04, 132.61, 131.78, 131.41, 130.30, 130.18, 129.56, 126.91, 119.94, 118.97, 105.44, 104.56, 101.63. MS, *m*/*e*: 548 (100%), 782, 1016, 1250, 1484. IR (KBr): 1627 cm^{-1} (benzoxazole). ^{31}P NMR spectroscopy did not show phosphorus.

2,2′-(1,4-Phenylene)bis(5-amino-6-benzoxazolol) (1) and 4-(2-Benzoxazolyl)benzoic Acid. The synthesis and characterization of these two compounds have been reported.[14]

2-[4-(2-Benzoxazolyl)phenyl](5-amino-6-benzoxazolol). DADHB (7.5 g, 35 mmol) was stirred in 100 g of PPA at 80 °C in a resin kettle equipped with a mechanical stirrer, a nitrogen inlet, and a gas trap. 4-(2-Benzoxazolyl)benzoic acid (0.33 g, 1.4 mmol) was added in portions. The reaction mixture was heated at 120 °C for 4 h and 150 °C for 8 h. The product was isolated by the addition of water. Yield of a black solid after washing with water and drying to constant weight was 0.43 g. The ^{13}C NMR spectrum of a freshly prepared sample in MSA was very complicated: δ (ppm) = 163.5, 162.7, 152.8, 151.1, 150.3, 145.5, 132.1, 131.6, 130.7, 130.2, 129.4, 126.9, 126.4, 122.7, 120.5, 117.0, 114.9, 114.5, 113.7, 102.1. After 2 weeks of hydrolysis, some peaks disappeared (Figure 11): δ (ppm) = 163.5, 162.7, 152.8, 151.1, 150.3, 132.1, 131.6, 130.7, 129.3, 126.9, 126.4, 122.7, 120.5, 117.0, 114.2, 114.0, 102.1. ^{31}P NMR of the freshly prepared sample: δ (ppm) = 2.7, −7.96, −9.36, −12.95. MS, *m*/*e*: 343 (60%), 371 (30%), 405 (100%), 546 (50%), 712 (90%); IR (KBr): 3700−1780, 1630, 1620 cm^{-1}.

Change in Relative Reactivity of DADHB on Reaction. DADHB (1.0024 g, 0.0047 mol), benzoic acid (0.5744 g, 0.0047 mol), and PPA (50 g) were stirred at 70 °C for 2 h. P_2O_5 (4 g) was added, and the temperature was increased to 90 °C and maintained at that temperature for 48 h. An aliquot was worked up, and IR did not show any carboxylic acid. The temperature was lowered to 70 °C, and benzoic *carboxy*-^{13}C acid (0.585 g, 0.0047 mol) was added. The temperature was maintained at 70 °C for 24 h to avoid sublimation of benzoic acid before reaction. The reaction was completed with the following profile: 90 °C (8 h), 120 °C (16 h), 140 °C (3 h), 150 °C (6 h), 170 °C (16 h). The product, which was isolated by addition of water, weighed 1.339 g (91%). The ratio of 1,4-(bis-2-benzoxazole)benzene with $^{12}C-^{12}C$, $^{12}C-^{13}C$, and $^{13}C-^{13}C$ as determined by mass spectroscopy was 40.6 to 26.5 to 32.9 after calibration of natural ^{13}C.

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