Macromolecules **1995,** *28,* 7289−7290

A Mechanistic Study of Polybenzoxazole Formation with Model Compounds

Ying-Hung So,* Jerry P. Heeschen, and Cheryl L. Murlick

Central Research & Development, Material Science & Development, 1712 Building, The Dow Chemical Company, Midland, Michigan 48640

Received March 14, 1995

Revised Manuscript Received June 23, 1995

Introduction

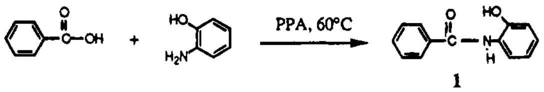
Poly(*p*-phenylenebenzobisoxazole) (PBO) and poly(*p*-phenylenebenzothiazole) (PBT) are rodlike polymers with extended-chain conformations. These polymers have excellent thermal and oxidative stability and good hydrolytic and solvent resistance. PBO and PBT fibers have extremely high tensile strength and tensile modulus. The synthesis, processing, and mechanical properties of these polymers have been actively investigated.[1−4]

PBO and PBT are prepared by the reaction of terephthalic acid (TA) in poly(phosphoric acid) (PPA) with 1,3-diamino-4,6-dihydroxybenzene (DADHB) or 1,4-diamino-3,6-dithiohydroxybenzene (DADTB), respectively. To minimize the decomposition of DADHB or DADTB, the monomers are reacted at temperatures below 120 °C for several hours to form oligomers before buildup of molecular weight at higher temperatures.[5,6] Very little has been reported on the reaction mechanism. The previously proposed mechanism involves the formation of a benzoyl−polyphospate mixed anhydride from TA and PPA. The amino groups in DADHB or DADTB react with the activated carbonyl group to form 2-hydroxybenzanilide which then cyclizes to benzoxazole or benzothiazole.[7,8] The cyclization reaction is acid catalyzed.[9] Scheme 1 shows the proposed reaction mechanism for TA and DHDAB in PPA.

The reaction mechanism of TA and DADHB in PPA was studied by means of model compounds, benzoic acid and *o*-aminophenol. We report herein that the ester, 2-aminophenyl benzoate, is formed first from benzoic acid and *o*-aminophenol in PPA. The amide, 2-hydroxybenzanilide (**1**), is the acyl migration product of the ester.

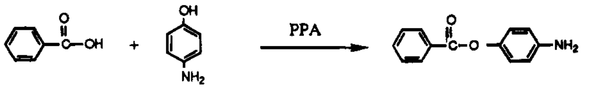
Results and Discussion

An equimolar mixture of benzoic acid and *o*-aminophenol was stirred in PPA at 60 °C for 2 h. The mixture was quenched with ice water and then extracted with ethyl acetate. Product analysis by liquid chromatography showed **1** as almost the only product with less than 3% of 2-phenylbenzoxazole (**2**).



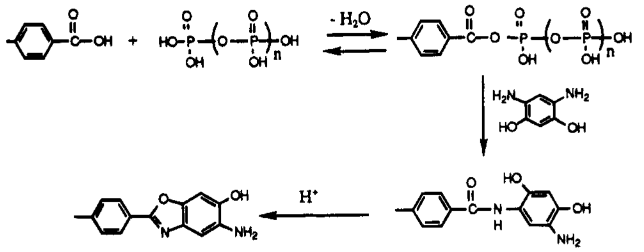
1

Benzoic acid and *p*-aminophenol, however, reacted in PPA to produce 4-aminophenyl benzoate (**3**) as the only product at 60 or 90 °C.

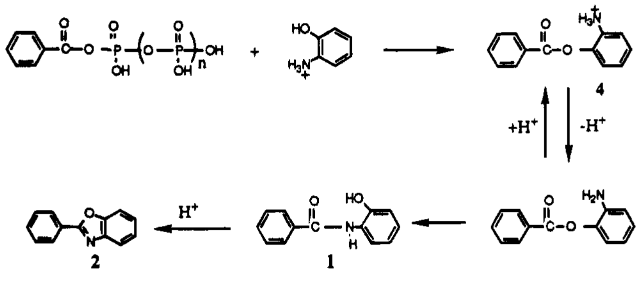


3

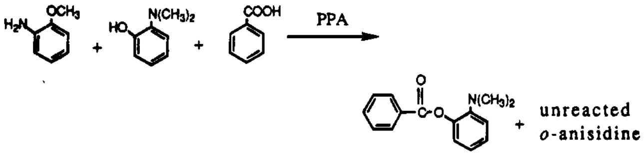
Scheme 1



Scheme 2



When *o*-anisidine and *o*-(*N*,*N*-dimethylamino)phenol competed for benzoic acid at 60 or 90 °C in PPA, *o*-(*N*,*N*-dimethylamino)phenyl benzoate was the only reaction product, and unreacted *o*-anisidine was quantitatively recovered.

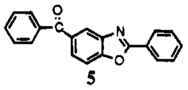


Benzoic acid reacted with *o*-anisidine in PPA to produce 2-methoxybenzanilide only at temperatures above 140 °C. When the mixture was further heated at 190 °C for 5 h, 2-methoxybenzanilide was converted into **2**. Several unidentified products were also generated.

The above experiments clearly demonstrate that *o*-aminophenol and benzoic acid in PPA first produce the ester, (2-aminophenyl) benzoate (**4**), which then undergoes rapid acyl migration to form the amide, **1**, as shown in Scheme 2.[10]

For **3**, acyl migration is impossible, and the ester was isolated. The fact that, in PPA, benzoic acid reacted with *o*-anisidine only at above 140 °C to generate 2-methoxybenzanilide whereas **1** was produced from *o*-aminophenol at 60 °C suggests that the amine group is essentially converted to the ammonium salt, thereby reducing its nucleophilicity and enhancing the preferential reaction of benzoic acid with the phenol group. In basic solvents such as NMP or DMAc, the amino group reacts much faster with anhydride or acid chloride functions, thus favoring the formation of hydroxyamides.

When benzoic acid and *o*-aminophenol were heated in PPA at 60 °C for 2 h and then at 120 °C for another 2 h, **2** and a byproduct, 2-phenyl-5-benzoylbenzoxazole (**5**), were obtained.[11] However, **1** isolated from PPA did not totally convert to **2** after 8 h at 200 °C. This was consistent with Hodd's previous report that benzoxazole ring formation was acid catalyzed.[9]



5

0024-9297/95/2228-7289$09.00/0

These results suggest that, in PBO formation, benzoyl–phosphate mixed anhydride reacts with DADHB to form an ester as the first reaction intermediate. Amide is formed by acyl migration followed by acid-catalyzed benzoxazole ring closure.

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR300. Chemical shifts are reported in δ (ppm), and coupling constants are given in hertz. Mass spectra and IR spectra were measured on a Finnigan 4600 quadruple GC/MS system in the EI mode and a Perkin-Elmer 598 infrared spectrometer, respectively. GLC analysis was performed on a HP5840A chromatograph with a 30-m J&W fused-silica capillary column. Benzophenone was the internal standard. The liquid chromatograph used consisted of a Perkin-Elmer Model ISS-200 autosampler with a Zorbax-SB phenyl column (4.6 × 150 mm, 5-μm packing). TLC detection was fluorescence under UV light of 250 nm.

Materials. Benzoic acid, *o*-aminophenol, *o*-anisidine, 4-benzoylbenzoic acid, 3-benzoylbenzoic acid, and PPA were purchased from Aldrich Chemical Co. 2-Phenylbenzoxazole was from TCI. *o*-(*N*,*N*-Dimethylamino)phenol was prepared with a literature procedure.[12] 2-Methoxybenzanilide was made from *o*-anisidine and benzoyl chloride.

2-Hydroxybenzanilide (1). Benzoic acid (1.22 g, 10 mM) and *o*-aminophenol (1.09 g, 10 mM) were stirred in PPA (40 g) at 60 °C for 2 h. The PPA solution was poured into a mixture of ice and water. Organic materials were extracted with ethyl acetate which was dried with anhydrous sodium sulfate. Compound **1** (1.8 g, 92% yield) was obtained with silica gel column chromatography: mp 166 °C; IR (Nujol) 3400, 1640, 1549 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 3.30 (b, 1H, exchange with water, OH), 6.88 (m, 1H, para to OH), 7.00 (m, 1H, ortho to OH), 7.07 (m, 1H, meta to OH), 7.53 (m, 1H, meta to carbonyl), 7.60 (m, 1H, para to carbonyl), 7.84 (m, 1H, ortho to NH), 8.03 (m, 1H, ortho to carbonyl), 9.46 (s, b, NH); ^{13}C NMR δ 167.04 (s), 149.26 (s), 135.10 (t), 132.73 (d), 129.45 (d), 128.27 (d), 127.53 (m), 126.46 (d), 123.15 (d), 120.61 (d), 117.93 (d); MS *m/z* (relative intensity) 213 (M^+, 18), 105 (100), 77 (47). Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.24; H, 5.16; N, 6.57. Found: C, 73.29; H, 5.14; N, 6.59.

2-Phenylbenzoxazole (2). Benzoic acid (1.22 g, 10 mM) and *o*-aminophenol (1.09 g, 10 mM) were stirred in PPA (40 g) at 60 °C for 2 h and then at 120 °C for 2 h. The PPA solution was poured into a mixture of ice and water. Organic materials were extracted with ethyl acetate which was dried with anhydrous sodium sulfate. Compound **2** (1.76 g, 90% yield) was obtained with silica gel column chromatography.

2-Phenyl-5-benzoylbenzoxazole (5) was also isolated (35 mg): IR (KBr) 1645, 1626 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30–8.20 (m, 3H), 7.86–7.81 (m, 3H), 7.69–7.47 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.90, 163.61, 152.49, 141.08, 136.89, 133.70, 131.49, 131.13, 129.13, 128.13, 127.44, 127.13, 126.94, 126.69, 125.75, 121.83, 109.70. ^{1}H and ^{13}C NMR spectra were different from those of [[4-(2-benzoxazolyl)phenyl]phenyl]methanone or [[3-(2-benzoxazolyl)phenyl]phenyl]methanone prepared from *o*-aminophenol and 4-benzoylbenzoic acid or 3-benzoylbenzoic acid; MS *m/z* (relative intensity) 299 (M^+, 20), 194 (42), 105 (100). Anal. Calcd for $C_{20}H_{13}NO_2$: C, 80.26; H, 4.35; N, 4.68. Found: C, 80.20; H, 4.37; N, 4.70. The spectroscopic data could not distinguish between **5** and its isomer, 2-phenyl-6-benzoylbenzoxazole.

4-Aminophenyl Benzoate (3). The same procedure for the preparation of **1** was used. A 1 N NaOH solution was used to convert the ammonium salt to amine: IR (KBr) 3440, 3360, 1710, 1270, 1190 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (d, J = 8.0 Hz, 2H), 7.63–7.45 (m, 3H), 6.83 (ABq, J = 8.8 Hz, Δ = 98.4 Hz, 4H), 3.75 (b, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.89, 144.51, 143.18, 133.53, 130.22, 130.00, 128.65, 122.39, 115.84; MS *m/z* (relative intensity) 213 (M^+, 20), 105 (100). Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.24; H, 5.16; N, 6.57. Found: C, 73.20; H, 5.21; N, 6.61. In another experiment, to PPA at 120 °C was added a mixture of 4-aminophenol and benzoic acid. The mixture was stirred for 45 min. Yield of **3** was 90%.

***o*-(*N*,*N*-Dimethylamino)phenol**:[12] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08–6.74 (m, 4H), 2.85 (s, 6H), 1.6 (b, 1H).

***o*-(*N*,*N*-Dimethylamino)phenyl Benzoate**. Benzoic acid (1.22 g, 0.01 M), *o*-anisidine (1.23 g, 0.01 M), and *o*-(*N*,*N*-dimethylamino)phenol (1.37 g, 0.01 M) were stirred in 60 g of PPA at 60 °C for 3 h. The PPA solution was poured with stirring into ice water which was then neutralized with a 1 N NaOH solution. The organic materials were extracted with ethyl acetate. GC yield of *o*-(*N*,*N*-dimethylamino)phenyl benzoate and recovered *o*-anisidine were 97% and 95%, respectively. *o*-(*N*,*N*-Dimethylamino)phenyl benzoate was isolated by preparative TLC: mp 149–151 °C; IR (KBr) 1732, 1516, 1269, 1209, 1064 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, J = 8.2 Hz, 2H), 7.62–7.48 (m, 3H), 7.11–7.07 (m, 2H), 6.78–6.74 (m, 2H), 2.96 (s, 6H); ^{13}C NMR (75 MHz, acetone-d_6) δ 166.00, 149.75, 142.95, 134.29, 134.44, 130.99, 130.95, 130.60, 129.56, 122.81, 113.90, 41.06; MS *m/z* (relative intensity) 241 (56), 136 (86), 105 (100). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.69; H, 6.22; N, 5.81. Found: C, 74.72; H, 6.24; N, 5.76. The experiment was repeated by adding benzoic acid, *o*-anisidine, and *o*-(*N*,*N*- dimethylamino)phenol to PPA at 90 °C followed by stirring for 1 h. GC yield of *o*-(*N*,*N*-dimethylamino)phenyl benzoate was 90%.

2-Methoxybenzanilide. To 70 g of PPA were added *o*-anisidine (1.23 g, 0.01 mol) and benzoic acid (1.22 g, 0.01 mol). Progress of the reaction was checked by removal of samples from the reaction quenching with ice water, neutralization, extraction with ethyl acetate, and monitoring by GC. Retention times and GC/MS were used to identify the products. 2-Methoxybenzanilide was not detected until the temperature had risen to 140 °C. After 10 h at 140 °C, GC peak area integration showed *o*-anisidine (2.6%), benzoic acid (0.8%), **2** (15%), 2-methoxybenzanilide (77%), and an unidentified compound (4.6%). When the mixture was further heated at 190 °C for 5 h, GC showed the complete conversion of 2-methoxybenzanilide to **2** and several unidentified products.

Acknowledgment. We thank Drs. Nelson Rondan and Don McLemore of The Dow Chemical Co. for helpful discussion.

References and Notes

(1) Wolfe, J. F. In *Encyclopedia of Polymer Science and Technology*, 2nd ed.; Mark, H. F., Kroschmitz, J. I., Eds.; Wiley: New York, 1988; Vol. 11, pp 601–635.

(2) *The Materials Science and Engineering of Rigid-Rod Polymers*; Adams, W. W., Edy, R. K., McLemore, D. E., Eds.; Symposium Proceedings, Vol. 134, Materials Research Society, Pittsburgh, PA, 1989.

(3) Yang, H. H. *Aromatic High-Strength Fibers*; Wiley-Interscience: New York, 1989; Chapter 2.

(4) Rosenberg, S.; Quarderer, G. J., Jr.; Sen, A.; Nakagawa, M.; Faley, T. L.; Serrano, M.; Teramoto, Y.; Chau, C. C. U.S. Patent 5,294,390, 1994.

(5) Wolfe, J. F.; Sybert, P. D. U.S. Patent 4,703,103, Oct 1987.

(6) Gregory, T.; Hurtig, C. W.; Ledbetter, H. D.; Quackenbush, K. J.; Rosenberg, S.; So, Y. H. U. S. Patent 5,194,568, March 1993.

(7) Choe, E. W.; Kim, S. N. *Macromolecules* **1981**, *14*, 920–924.

(8) Wolfe, J. F.; Sybert, P. D. AFWAL-TR-82–4191, Jan 1983.

(9) (a) Hodd, K. A. Thermal Analysis. *Proc. 4th ICTA, Budapest* **1974**, *2*, 91–103. (b) Ghaffari, F.; Hodd, K. A. *Thermochim. Acta* **1980**, *41*, 213–224.

(10) Raiford, L. C.; Couture, J. R. *J. Am. Chem. Soc.*, **1924**, *46*, 2305–2318.

(11) Lleda, M.; Sugita, H.; Sato, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 1010–1026.

(12) Boyland, E.; Manson, D.; Sims, P. *J. Chem. Soc.* **1953**, 3623–3628.

MA950334M