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A Study of Poly(benzo[1,2-*d*:5,4-*d*′]bisoxazole-2,6-diyl-1,4-phenylene) Reactions at Elevated Temperatures

Ying-Hung So,[*,†] Stephen W. Froelicher,[‡] Britton Kaliszewski,[†] and Richard DeCaire[†]

Central Research and Development, 1712 Building, and Analytical Sciences Laboratory, 1896 Building, The Dow Chemical Company, Midland, Michigan 48674

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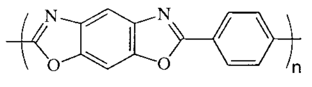
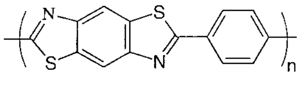
ABSTRACT: The reaction mechanism of poly(benzo[1,2-*d*:5,4-*d*′]bisoxazole-2,6-diyl-1,4-phenylene) (PBO) at elevated temperatures was studied by means of model compounds and a ^{13}C-labeled PBO polymer. Products from model compound thermal degradation suggest that the dominating reactions are homolytic scission of a single bond and decomposition of a heterocyclic ring to produce an aromatic nitrile. The major volatile products from PBO high-temperature degradation were CO_2, benzonitrile, and dicyanobenzene. Benzene was also a product. Correlation of ^{13}C in the polymer and the volatile products suggests that benzonitrile and dicyanobenzene result from decomposition of the heterocyclic ring(s) but not from substitution of cyano radicals onto aromatic rings. Scrambling of carbons was not an important reaction in the PBO pyrolysis. A reaction mechanism for PBO at elevated temperatures is proposed.

Introduction

Poly(benzo[1,2-*d*:5,4-*d*′]bisoxazole-2,6-diyl-1,4-phenylene) (PBO) and poly(benzo[1,2-*d*:4,5-*d*′]bisthiazole-2,6-diyl-1,4-phenylene) (PBT) have unique extended rigid-rodlike configurations. The synthesis, processing, and properties of these polymers have been actively pursued at Wright-Patterson Air Force Base, SRI International, The Dow Chemical Co., Toyobo Co. in Japan, and other research institutions.[1−3] Zylon is a trademark of Toyobo for PBO fiber.


PBO


PBT

PBO fiber has superior tensile strength and modulus compared to *p*-aramid fibers. It has outstanding flame and chemical resistance and hydrolytic and thermal stability compared to other organic fibers.[4−8] PBO fiber also shows excellent performance in such properties as creep, cut/abrasion resistance, and high-temperature abrasion resistance. Applications of PBO fiber include high-performance fiber composites and comfortable protective garments.[9]

Spun PBO fiber drawn under tension through an oven at 525−650 °C shows high tenacity and extremely high modulus.[10] The excellent thermal stability and high flame resistance of PBO make it the material of choice for high-temperature applications. Therefore, it is important to understand the reactions of PBO when the polymer is exposed to elevated temperatures.

The thermal properties of PBO have been reported. The study was carried out with thermogravimetric analysis (TGA), isothermal aging, and thermogravimetric-mass spectral analysis (TGA/MS).[6,7] It was suggested that thermal decomposition of one of the heterocyclic rings begins at 600 °C and reaches a maximum at 660 °C as indicated by the concurrent loss of CO_2, CO, and HCN. Water and ammonia were observed in small amounts, with benzene and benzonitrile only in trace amounts.

The study of polymer degradation reactions is obstructed by the difficulty in identifying macromolecular products, which, in most cases, are almost impossible to characterize by any analytical method. In this article, we report the study of PBO thermal degradation by means of model compounds. Structures of fragments from heating PBO model compounds under helium were determined. Identification of reaction products was used to further understand the thermal degradation mechanism of PBO. The effect of chain-end functional groups, *o*-aminophenol, and carboxylic acid on PBO under pyrolytic conditions was also studied.

A ^{13}C-labeled PBO sample from reacting 22 mol % of α,α′-di-^{13}C-terephthalic acid and 78 mol % of unlabeled terephthalic acid (TA) with diaminodihydroxybenzene dihydrochloride (DADHB·2HCl) was used to elucidate the thermal degradation process. Pyrolysis of this labeled PBO was studied by TGA/MS and TGA/GC/MS. A PBO thermal degradation mechanism is proposed based on fragmentation patterns of PBO model compounds and correlation of ^{13}C percentage in PBO polymer to that of the pyrolysis products.

Experimental Section

Synthesis of Model Compounds and Polymer. The synthesis and purification of 2,2′-(1,4-phenylene)bis(6-phenylbenzo[1,2-*d*:5,4-*d*′]bisoxazole (**1**), 2,6-bis[4-(2-benzoxazolyl)-phenyl]benzo[1,2-*d*:5,4-*d*′]bisoxazole (**2**), 2,2′-(1,4-phenylene)-bis(5-amino-6-benzoxazolol) and its phosphate esters (**3**), and 2,2′-(1,4-phenylene)bis(5-amino-6-benzoxazolol) (**4**) were previously reported.[11] The phosphorus contents as determined by elemental analysis of **3** and **4** were 5.24% and 8.63%, respectively. 2,6-(4-Carboxyphenyl)benzobisoxazole (**5**) was prepared by reacting excess TA with DADHB in a large volume of polyphosphoric acid (PPA) followed by extraction with NaOH solution. Preparation of PBO was previously described.[12] α,α′-di-^{13}C-terephthalic acid was purchased from Merck Sharp & Dohme/Isotopes and used as received. Micronized/unlabeled TA with mean particle size of 5.2 μm was used.[13] The intrinsic viscosity of the polymer was 22 dL/g.

[†] Central Research and Development.

[‡] Analytical Sciences Laboratory.

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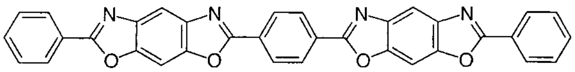

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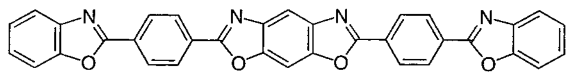

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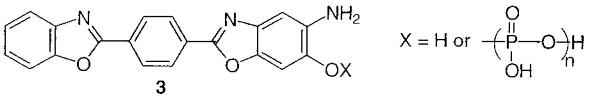

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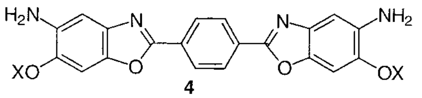

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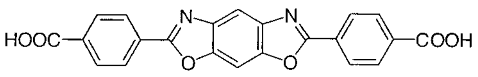

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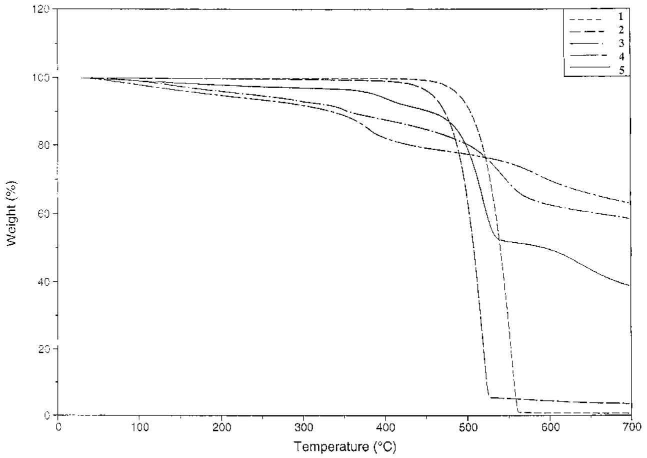


Figure 1. Thermogravimetric analysis of PBO model compounds: 2,2′-(1,4-phenylene)bis(6-phenylbenzo[1,2-*d*:5,4-*d*′]-bisoxazole (**1**), 2,6-bis[4-(2-benzoxazolyl)phenyl]benzo[1,2-*d*:5,4-*d*′]bisoxazole (**2**), 2,2′-(1,4-phenylene)bis(5-amino-6-benzoxazolol) and its phosphate esters (**3**), 2,2′-(1,4-phenylene)bis(5-amino-6-benzoxazolol) (**4**), and 2,6-(4-carboxyphenyl)benzobisoxazole (**5**).

2,6-(4-Carboxyphenyl)benzobisoxazole. TA (20.1 g, 0.121 mol), DADHB·2HCl (2.01 g, 0.00944 mol), and 650 g of PPA were heated under nitrogen in a 1000 mL resin kettle equipped with a mechanical stirrer at 90 °C (24 h), 100 °C (4 h), 120 °C (16 h), and 150 °C (24 h). The PPA slurry was quenched with water. Solid was collected in a sintered glass filter and washed thoroughly with water, dimethyl sulfoxide (DMSO), water, and then a 1 N NaOH solution. The filtrate of the NaOH solution was neutralized with 1 N HCl solution. The precipitated product was collected and dried. Yield was 0.9 g (24% based on DADHB·2HCl). No melting point was observed up to 400 °C by differential scanning calorimetry (DSC). IR (KBr): 1690, 1610 cm^{-1}. ^1H NMR (300 MHz, methanesulfonic-d_6 acid (MSA-d_6): δ 10.3 (b, 2H), 8.43 (s, 1H), 8.23 (s, 1H), 8.13 (ABq, $J = 8$ Hz, $\Delta\nu = 24$ Hz, 8H) ppm. ^{13}C NMR (75 MHz, MSA): δ 164.5, 161.8, 143.8, 132.0, 127.3, 126.1, 124.3, 118.2, 99.4, 96.2 ppm. HRMS (FAB): calcd for $C_{22}H_{12}N_2O_6$, 400.0692, found, 400.0700.

Analysis. Evolved gas analysis was performed on the sample using the simultaneous techniques of TGA/MS and TGA/GC/MS. The TGA unit was a tube furnace equipped with a Mettler ME21 microbalance. A TGA experiment was performed on a sample of known weight. As the sample was exposed to a controlled temperature environment, helium purge gas (100−120 cm^3/min) was continuously swept past the sample pan. Approximately 45 cm^3/min of purge gas (containing evolved gases) was directed from the TGA furnace region to the ion source of a Finnigan 4500 GC/MS via a molecular jet separator for real-time mass spectral analysis of the evolved gases. During the TGA/MS experiment, a portion of the evolved gas stream was directed to a cryogenically cooled trap, where the gases were condensed into a sample plug for subsequent GC/MS analysis. The remaining purge gas flow was vented. The real-time data permitted determination of the temperature(s) at which a particular component evolved from the sample. The GC/MS data permitted identification of the components evolved.

Loading the TGA sample boat with PBO fiber required winding the fiber onto tweezers, followed by placement of the spooled fiber into the sample boat. Loose strands of fiber had to be trimmed to allow the sample pan to rest freely in the vertical TGA tube. The furnace region was purged for 15 min to remove air, prior to the start of the experiment.

For the simultaneous TGA/MS and TGA/GC/MS experiments, the Finnigan 4500 GC/MS was operated in the electron impact (EI) ionization configuration (electron energy = −70 eV; electron multiplier = −1100 V; mass range = 15−600 amu; scanning rate = 1, 2, or 5 s/scan). The GC separations were carried out on a 15-m, J&W DB-5 megabore capillary column. The GC temperature program used was as follows: (1) warm from −140 °C (cryogenic trap temperature) to room temperature for 2 min and (2) heat from 15 to 300 °C at 15 °C/min.

Results and Discussion

Thermogravimetric Analysis and Real Time Mass Spectra of Model Compounds. PBO model compounds were studied by TGA, and the results are shown in Figure 1. PBO model compounds without chain-end functional groups had very good thermal stability. Compound **1** lost about 1% of its weight up to 420 °C. Catastrophic weight loss occurred in the narrow range between 470 and 570 °C. Since **1** sublimed at high temperature and low pressure, weight loss in TGA might not be completely due to sample decomposition. The TGA of **2** was similar to that of **1** except the temperature shifted to about 20 °C lower.

TGA of **3** and **4**, model compounds with *o*-aminophenol and its phosphate esters at the chain end(s), showed a gradual weight loss from about 70 to 370 °C. The rate of weight loss increased at about 370 °C. TGA/MS indicated that water evolved at two temperature ranges. The first peak of water evolution was from about 70 to 170 °C, which could be from absorbed moisture. Water of the second peak, which started at about 190 °C and peaked at 320 °C, could be from dehydration of chain-end phosphate esters.[14] Benzonitrile, dicyanobenzene, and 2-phenylbenzoxazole (in the case of **3)** started to evolve at about 440 °C.

For **5**, a PBO model compound with a carboxylic acid group at both ends, weight loss up to 300 °C was due to absorbed water as indicated by TGA/MS. CO_2 started to evolve at 350 °C. TGA/MS began to detect benzoic acid and cyanobenzoic acid at 370 °C. 2,6-(Diphenyl)-benzobisoxazole (**6**) was not detected until 470 °C.

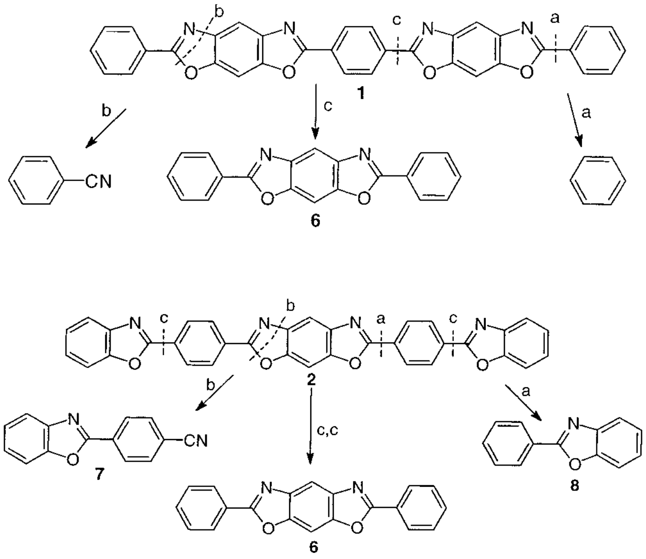
Products from Pyrolysis of PBO Model Compounds. Table 1 shows the normalized peak area percentage of pyrolytic products from **1** to **5** based on TGA/GC/MS multiple ion chromatograms. MS fragmentation patterns were compared with those of authentic standards to confirm the identities. For **1** and **2**, about 80% of the peak area was due to **6**, which could be formed from homolytic bond breaking followed by hydrogen abstraction. Benzonitrile and 2-(4-cyanophenyl)benzoxazole (**7**) were also important products from

Table 1. Normalized Peak Area Percentage of Pyrolytic Products from PBO Model Compounds 1−5 Based on TGA/GC/MS Multiple Ion Chromatograms[a]**.**

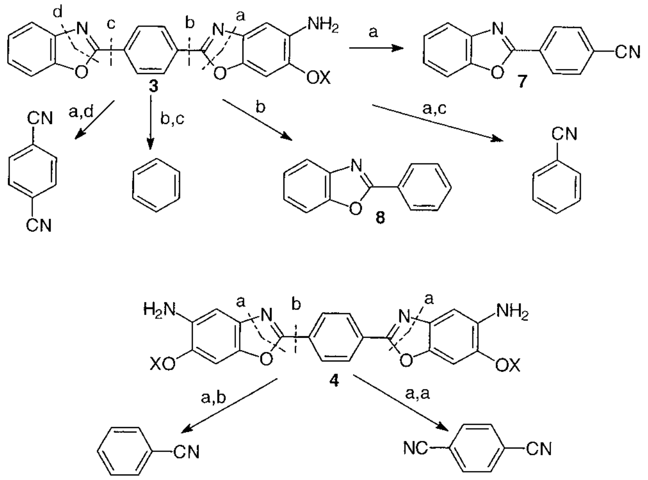
	CO_2	HCN	benzene	aniline	benzonitrile	dicyanobenzene	benzoic acid	cyanobenzoic acid	**6**	**7**	**8**
1	2.5	trace	1.0		7.5				89		
2	3	trace							79	15	3
3	0.2	trace	5.2	trace	10.6	5.0				69	10
4	0.2	trace	1.7	trace	34	64					
5	11	trace	6		6		6	30	41		

[a] Compounds **6**, **7**, and **8** are 2,6-(diphenyl)benzobisoxazole, 2-(4-cyanophenyl)benzoxazole, and 2-phenylbenzoxazole, respectively

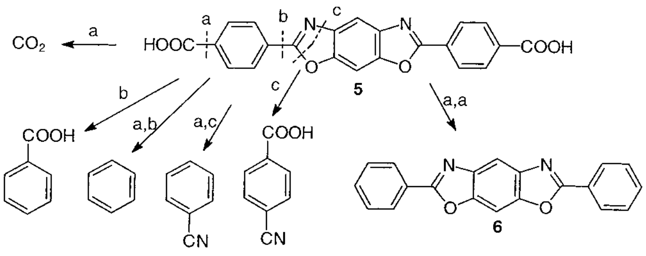
Scheme 1. Reaction Pathways for Thermal Decomposition of PBO Model Compounds without Chain-End Functional Groups



Scheme 2. Reaction Pathways for Thermal Decomposition of PBO Model Compounds with *o*-Aminophenyl at Chain-End(s)



Scheme 3. Reaction Pathways for Thermal Decomposition of PBO Model Compounds with Carboxylic Acid End Groups



1 and **2**, respectively. Both nitriles were products from decomposition of a heterocyclic ring. Thermal reaction pathways of **1** and **2** are shown in Scheme 1.

The major products from pyrolysis of **3** and **4**, PBO model compounds with a DADHB unit at chain end(s), were nitriles from benzoxazole ring decomposition. Compound **7** and dicyanobenzene were the most important products from **3** and **4**, respectively. Benzonitrile, which was formed from benzoxazole ring decomposition and homolytic breakage of the phenyl−benzoxazole bond, was also an important product from **4**. It appeared that chain-end DADHB was readily converted into a nitrile. Small amounts of aniline and ammonia were detected in TGA/GC/MS of **3** and **4**. Scheme 2 shows the thermal reaction pathways of **3** and **4**. The major products from **5** were CO_2, cyanobenzoic acid, and **6**. Benzene, benzonitrile, and benzoic acid were also formed. Decarboxylation was an important reaction for **5**. The thermal reaction pathways of **5** are shown in Scheme 3.

CO_2 was observed, but CO_2 that evolved at below 500 °C might not be from PBO as demonstrated in the pyrolysis of a ^{13}C-labeled PBO. The source of CO_2 evolved at low temperature was not clear. A previous study found that HCN was a major product in PBO thermal degradation.[6] However, only small amounts of HCN were observed in our study. The reasons for the discrepancy are unknown.

^{13}C-Labeled PBO. A ^{13}C-labeled PBO sample was prepared by reacting DADHB·2HCl with 22 mol % α,α′-di-^{13}C-terephthalic acid and 78 mol % unlabeled TA. The sample was studied to determine the labeled degradation products in order to understand the thermal degradation mechanism. A TGA temperature program from 30 to 770 °C at 20 °C/min in a helium atmosphere was used. The TGA was similar to that reported by Wolfe and Arnold.[6] Figure 2 illustrates the TGA/MS single ion profiles of $m/z = 18$ (H_2O), 44 (CO_2), 45 ($^{13}CO_2$), 78 (benzene), 103 (benzonitrile), 104 (benzonitrile containing one ^{13}C atom), 128 (dicyanobenzene), 129 (dicyanobenzene containing one ^{13}C atom), and 130 (dicyanobenzene containing two ^{13}C atoms). The data illustrate that H_2O evolved mainly above about 590 °C. A small amount of H_2O evolved below 590 °C. CO_2 and $^{13}CO_2$ co-evolved above 510 °C with peak evolution rates observed between 670 and 705 °C. A very small amount of CO_2, but no $^{13}CO_2$, was observed to evolve between 185 and 510 °C. The data also illustrate that benzene and benzonitrile evolution preceded dicyanobenzene evolution by about 5−10 °C. The ion intensity levels of $m/z = 103$ and 128, the ^{12}C molecular ions of benzonitrile and dicyanobenzene, were similar in the TGA/MS data. Benzonitrile and ^{13}C-enriched benzonitrile co-evolved between 660 and 750 °C with peak evolution at about 705 °C. Dicyanobenzene, dicyanobenzene with one ^{13}C atom, and dicyanobenzene enriched with two ^{13}C atoms co-evolved between 670 and 770 °C with peak evolution at 710−715 °C. TGA/GC/MS obtained from

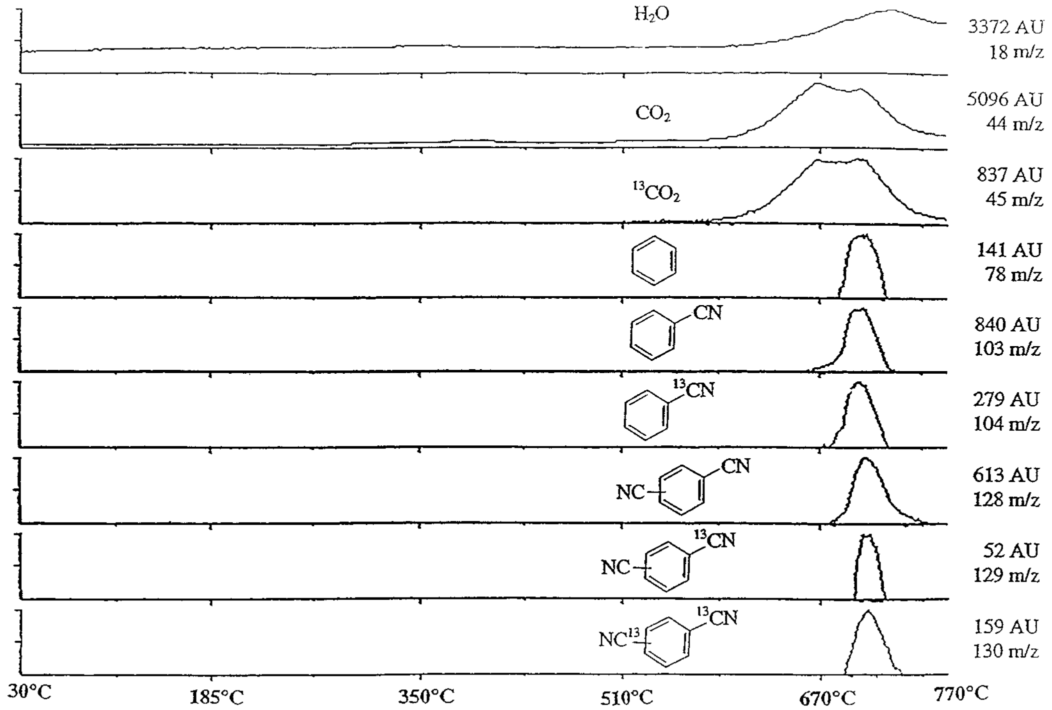


Figure 2. Thermogravimetric-mass spectroscopic single ion profiles of *m/z* 18 (H_2O), 44 (CO_2), 45 ($^{13}CO_2$), 78 (benzene), 103 (benzonitrile), 104 (benzonitrile containing one ^{13}C atom), 128 (dicyanobenzene), 129 (dicyanobenzene containing one ^{13}C atom), and 130 (dicyanobenzene containing two ^{13}C atoms).

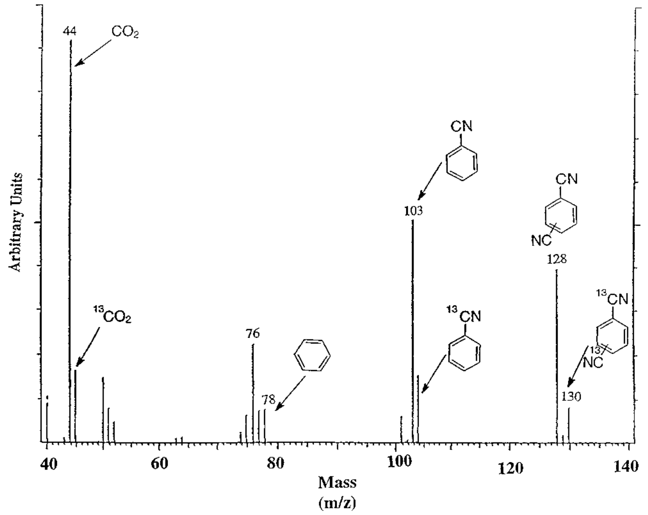
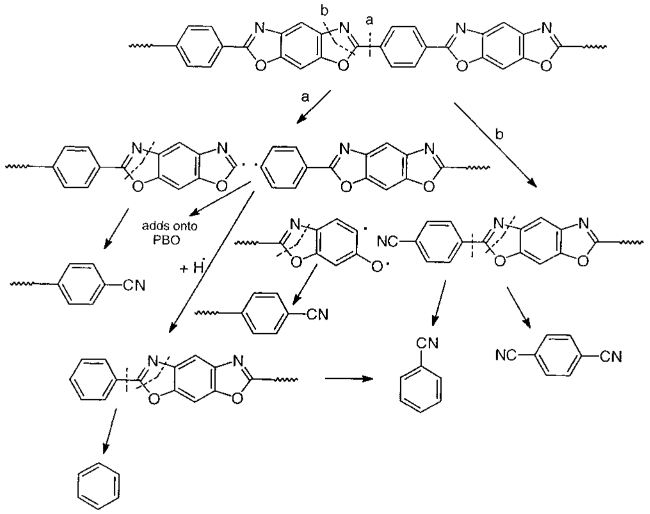


Figure 3. Composite mass spectrum of all gases evolved from a ^{13}C-labeled PBO fiber between about 600 and 770 °C.

Scheme 4. Thermal Degradation Pathways of PBO



gases cryogenically trapped during the TGA experiment showed CO_2, benzonitrile, dicyanobenzene, and a small amount of benzene. Figure 3 is the composite mass spectrum of all gases evolved from the polymer between 600 and 700 °C from the TGA/MS data.

The major components evolved from TGA/GC/MS were CO_2, benzonitrile, and dicyanobenzene. Mass spectra of each component indicated a significant ^{13}C-enriched molecular ion. The observed abundance of $^{13}CO_2$, benzonitrile with one ^{13}C atom, and dicyanobenzene with two ^{13}C atoms, after correction for natural abundance, were 15.7, 27.7, and 17.1%, respectively. The percentage of dicyanobenzene with one ^{13}C atom was the same as expected from natural abundance, which suggested that benzonitrile and dicyanobenzene were formed from decomposition of the heterocyclic ring(s) but not from addition of cyano radicals onto aromatic rings. Benzene, which was not ^{13}C-enriched, was also observed in the chromatograph. The result suggests that scrambling of carbons was not an important reaction in the PBO pyrolysis. Scheme 4 shows the proposed thermal degradation pathways for PBO polymer.[15] Upon heating, PBO undergoes homolytic bond scission to generate a benzoxazole radical and a phenyl radical (pathway a in Scheme 4). The benzoxazole radical is unstable under the experimental conditions and fragments to produce an aromatic nitrile along with possibly HCN, CO_2, H_2O and other carbon compounds. The phenyl radical grafts onto another PBO molecule or abstracts hydrogen to generate phenylbenzobisoxazole, which produces benzonitrile and benzene. The other mode of PBO thermal degradation is decomposition of a heterocyclic ring to give a nitrile, which generates benzonitrile, dicyanobenzene, and an unstable diradical (pathway b in Scheme 4). The diradical fragments produce an aromatic nitrile along with possibly HCN, CO_2, H_2O, and other carbon compounds. These proposed PBO thermal degradation pathways can also be used to account for the products identified in pyrolysis of PBO model compounds.

Conclusion. Thermal degradation products from PBO model compounds suggest that homolytic scission of a single bond and decomposition of a heterocyclic ring are the most important reactions when PBO is exposed to elevated temperatures. The major volatile components from PBO high-temperature degradation were CO_2, benzonitrile, and dicyanonitrile. Benzene was also a product. Benzonitrile and dicyanobenzene resulted from decomposition of the heterocyclic ring(s) but not from addition of cyano radicals onto aromatic rings. Scrambling of carbon was not an important reaction in PBO pyrolysis. Upon heating, PBO undergoes homolytic bond scission to generate a benzoxazole radical and a phenyl radical. The benzoxazole radical is unstable and fragments to produce an aromatic nitrile along with possibly HCN, CO_2, H_2O, and other carbon compounds. The phenyl radical grafts onto another PBO molecule or abstracts a hydrogen to generate phenylbenzobisoxazole, which produces benzonitrile and benzene. The other mode of PBO thermal degradation is decomposition of a heterocyclic ring to give a nitrile and an unstable diradical. The diradical fragment produces an aromatic nitrile, which generates benzonitrile and dicyanobenzene, along with possibly HCN, CO_2, H_2O, and other carbon compounds.

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References and Notes

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