# Aromatic Polyamides and Polyimides with Benzoxazole or Benzothiazole Pendent Groups Prepared from 5-(2-Benzoxazole)- or 5-(2-Benzothiazole)-1,3-phenylenediamine

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ABSTRACT: A series of polyamides and polyimides containing pendent benzoxazole or benzothiazole pendent groups were prepared from two new monomers, 5-(2-benzoxazole)- or 5-(2-benzothiazole)-1,3-phenylenediamine. In addition, model compounds were synthesized and characterized by elemental analyses, FT-IR, and $^1$H-NMR. Characterization of polymers was accomplished by inherent viscosity measurements, FT-IR, X-ray, DTA, TGA, and isothermal gravimetric analysis. Water absorption studies were also carried out for the polyamides. The properties of the modified polymers were correlated with those of the corresponding unmodified ones. The solubilities of modified polyamides in common organic solvents as well as their hydrophilicities were enhanced compared to these of the corresponding unmodified polyamides. The synthesized polyamides softened between 200 and 300 °C, but no softening was observed for the polyimides. The modified polyamides and polyimides suffered less weight loss under TGA and isothermal gravimetric analysis than the parent structures. Their initial decomposition temperatures in $N_2$ or air and the anaerobic char yields at 800 °C were, respectively, 24–68 °C and 5–9% higher than those of the unmodified polymers.

## Introduction

Aromatic polyamides and polyimides are thermally stable and widely used polymers.[1] However, their high softening temperatures and/or insoluble nature in most organic solvents make them difficult to process. Therefore, the interest of the investigators was focused on the development of structurally modified aromatic polyamides and polyimides having increased solubility in order to improve their processability with retention of their thermal stability. A synthetic approach to achieve the above goals is the incorporation of bulky substituents as pendent groups along the polymer backbone.

Various polymers, such as poly(terephthalamides),[2] poly(terephthalates),[3] polyimides,[4] and other polyheterocycles,[5] have been modified by polycondensation of monomers containing bulky pendent groups. Recently, certain aromatic polyamides with benzoxazole[6] or benzothiazole[7] side groups have been synthesized.

The present investigation deals with the synthesis and characterization of a new class of modified polyamides and polyimides bearing benzoxazole or benzothiazole pendent groups. The incorporation of these voluminous side groups along the polymer backbone is expected to affect their properties and enhance the solubility in organic solvents. In addition, the modified polyamides and polyimides are expected to exhibit less weight loss under thermal testing than the corresponding unsubstituted polymers, because benzoxazole and benzothiazole are among the most heat-resistant structures. The present work is a continuation of our previous publications on the preparation of modified poly(isophthalamides) by incorporating *N*-benzylidene,[8] phthalimide,[9] or furamido[10] pendent groups.

## Experimental Section

**Instrumentation.** Melting temperatures were determined on a Thomas-Hoover electrothermal melting point apparatus IA6304 and are uncorrected. IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer with KBr pellets. $^1$H-NMR spectra were obtained using a Varian T-60A spectrometer at 60 MHz. Chemical shifts ($\delta$ values) are given in ppm with tetramethylsilane as an internal standard. DTA and TGA were performed on a DuPont 990 thermal analyzer system. Ground polymer samples of about 10 mg each were examined by TGA and isothermal gravimetric analysis (IGA), and the weight loss comparisons were made between comparable specimens. DTA measurements were made using a high-temperature (1200 °C) cell at a heating rate of 20 °C/min in $N_2$ atmosphere at a flow rate of 60 cm$^3$/min and with a $\Delta T$ sensitivity of 0.5 °C/in. Dynamic TGA measurements were made at a heating rate of 20 °C/min in atmospheres of $N_2$ or air at a flow rate of 60 cm$^3$/min. The inherent viscosities of polyamides were determined for solutions of 0.5 g/100 mL in *N*,*N*-dimethylformamide (DMF) at 30 °C using an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett-Packard Model 185 analyzer. The wide-angle X-ray diffraction patterns were obtained for powder specimens on an X-ray PW-1840 Philips diffractometer.

To determine the equilibrium water absorption, powder samples of polymers were previously conditioned at 120 °C in an oven for 12 h. They were subsequently placed in a desiccator, where 65% r.h. (relative humidity) was maintained by means of a supersaturated aqueous solution of $NaNO_2$ at 20 °C, and were periodically weighed.

**Reagents and Solvents.** 3,5-Dinitrobenzoyl chloride and terephthaloyl dichloride were recrystallized from *n*-hexane. Pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride. 2-Aminophenol was recrystallized from distilled water. 2-Aminothiophenol was distilled under reduced pressure (bp 125–127 °C/6 mm). Benzoyl chloride and triethylamine were purified by distillation. Phthalic anhydride was sublimed under reduced pressure. Dimethylacetamide (DMAc) was dried by refluxing over, and fractionally distilled from, $CaH_2$. Nitrobenzene and hydrazine hydrate were used as supplied.

**Preparation of Starting Materials (Scheme 1). 5-(2-Benzoxazole)-1,3-phenylenediamine ($3_o$).** A flask equipped with a dropping funnel and magnetic stirrer was charged with a solution of 2-aminophenol (5.2411 g, 48.0 mmol) in DMAc (30 mL). Triethylamine (4.8571 g, 48.0 mmol) was added to the solution. 3,5-Dinitrobenzoyl chloride (11.0669 g, 48.0 mmol) dissolved in DMAc (30 mL) was added dropwise to the stirred solution at 0 °C under $N_2$. Next, the mixture was

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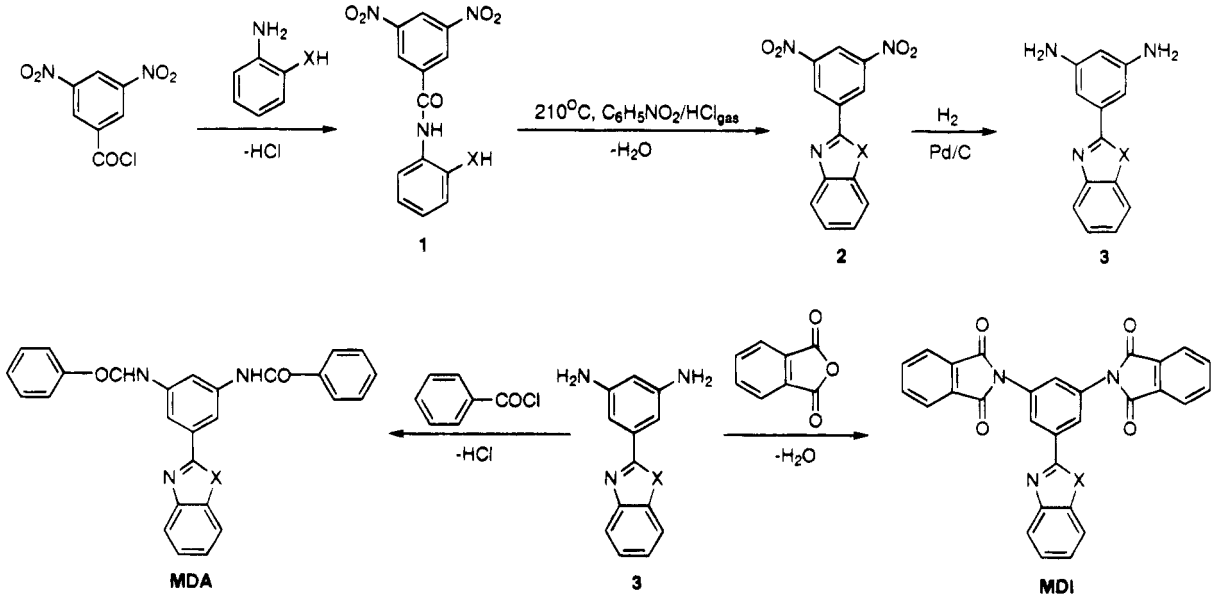
**Scheme 1**




heated at 60 °C overnight in a stream of $N_2$. It was poured into ice/water, and the pale brown solid obtained was filtered off, washed with water, and dried to afford $\mathbf{1_o}$ (9.75 g, yield 67%). A purified sample obtained by recrystallization from a mixture of $CH_3CN$/water (1:1, v/v) had mp 241–244 °C. Anal. Calcd for $C_{13}H_9N_3O_6$: C, 51.48; H, 2.99; N, 13.86. Found: C, 51.25; H, 3.08; N, 13.74. IR (KBr, $cm^{-1}$): 3394–3106 (N–H and O–H stretching), 1658 (C=O), 1596 (aromatic), 1542, 1342 ($NO_2$), 1286 (C–OH stretching). $^1$H-NMR (DMSO-$d_6$): $\delta$ 9.00–8.83 (m, 2H, OH, NHCO; 3H, aromatic of 3,5-dinitrobenzoic acid ring), 7.40–6.67 (m, 4H, other aromatic).

A flask equipped with a magnetic stirrer and gas trap was charged with a mixture of $\mathbf{1_o}$ (9.6500 g, 31.8 mmol) and nitrobenzene (70 mL). Dry HCl was bubbled through the stirred mixture as a catalyst, and it was refluxed for 4 h. The solvent and volatile components were stripped off by distillation under reduced pressure. The residue was washed thoroughly with ether and dried to afford $\mathbf{2_o}$ as a brown solid (8.54 g, yield 94%). It was recrystallized from a mixture of 1,4-dioxane/water (2:1, v/v) and had mp 204–207 °C. Anal. Calcd for $C_{13}H_7N_3O_5$: C, 54.73; H, 2.48; N, 14.74. Found: C, 54.52; H, 2.50; N, 14.68. IR (KBr, $cm^{-1}$): 1610 (C=N), 1594 (aromatic), 1534, 1346 ($NO_2$). $^1$H-NMR (DMSO-$d_6$): $\delta$ 8.70–8.52 (m, 3H, aromatic of 3,5-dinitrobenzoic acid ring), 7.38–7.10 (m, 4H, other aromatic).

A flask equipped with a dropping funnel and magnetic stirrer was charged with a mixture of $\mathbf{2_o}$ (8.5400 g, 30.0 mmol), ethanol 95% (70 mL), and a catalytic amount of 10% palladium on activated carbon. Hydrazine hydrate (15 mL) diluted with ethanol (20 mL) was added dropwise to the stirred mixture at about 60 °C, and then it was refluxed overnight. During this period the solid gradually dissolved. The mixture was filtered, and approximately two-thirds of the solvent was removed by distillation under reduced pressure. The residue was diluted with water, and the brown–red solid obtained was filtered off, washed with water, and dried to afford $\mathbf{3_o}$ (4.40 g, yield 65%). A purified sample obtained by recrystallization from a mixture of DMF/water (1:2, v/v) had mp 228–231 °C. Anal. Calcd for $C_{13}H_{11}N_3O$: C, 69.32; H, 4.92; N, 18.65. Found: C, 68.96; H, 4.87; N, 18.73. IR (KBr, $cm^{-1}$): 3404–3330 (N–H stretching), 1626 (N–H deformation), 1610 (C=N), 1244 (C–N stretching). $^1$H-NMR (DMSO-$d_6$): $\delta$ 7.50, 7.16 (m, 4H, aromatic of benzoxazole segment), 6.57 (m, 2H, aromatic of 4 and 6 positions of 1,3-phenylenediamine ring), 5.90 (m, 1H, aromatic of 2 position of 1,3-phenylenediamine ring), 4.90 (br, 4H, $NH_2$).

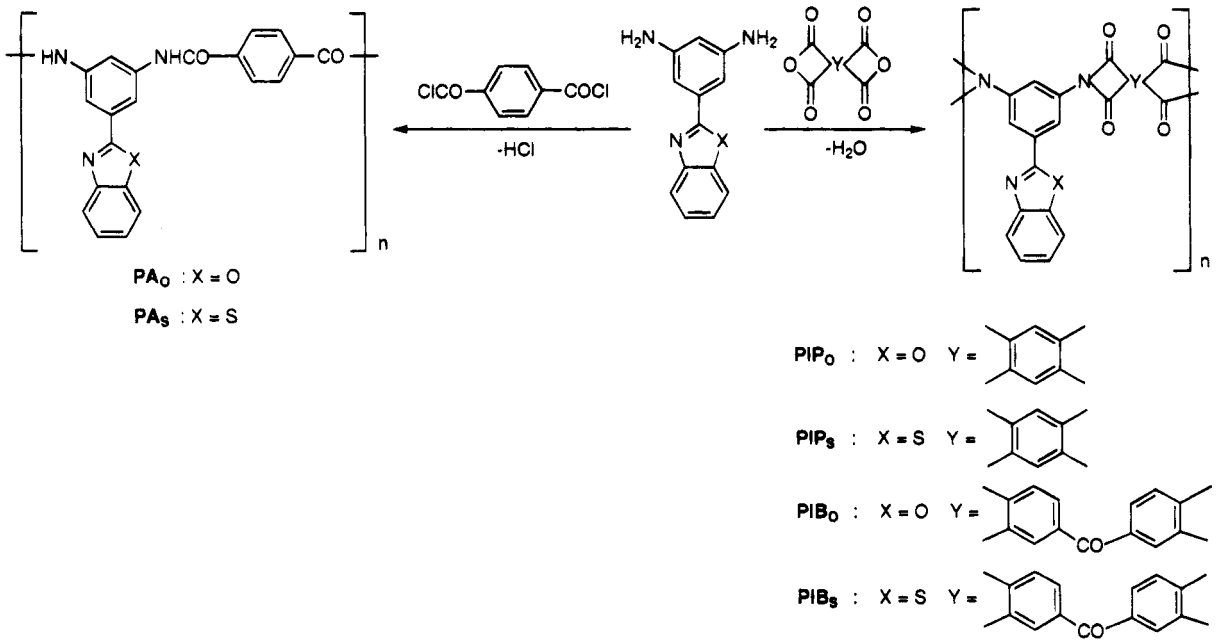
**5-(2-Benzothiazole)-1,3-phenylenediamine ($\mathbf{3_s}$).** Compound $\mathbf{1_s}$ was prepared as a brown–yellow solid in 85% yield by reacting 2-aminothiophenol with 3,5-dinitrobenzoyl chloride in the presence of triethylamine according to the procedure described for $\mathbf{1_o}$. It was recrystallized from a mixture of acetone/water (1:1, v/v) and had mp 163–166 °C. Anal. Calcd for $C_{13}H_9N_3O_5S$: C, 48.90; H, 2.84; N, 13.17. Found: C, 48.63; H, 2.89; N, 13.12. IR (KBr, $cm^{-1}$): 3364–3088 (N–H stretching), 2600–2550 (S–H stretching), 1684 (C=O), 1580 (aromatic), 1538, 1344 ($NO_2$). $^1$H-NMR (DMSO-$d_6$): $\delta$ 9.02–8.82 (m, 1H, NHCO and 3H, aromatic of 3,5-dinitrobenzoic acid ring), 7.16–6.47 (m, 4H, other aromatic), 3.68 (s, 1H, SH).

Compound $\mathbf{2_s}$ was prepared as a brown solid in 87% yield from the cyclodehydration of $\mathbf{1_s}$ according to the procedure described for $\mathbf{2_o}$. It was recrystallized from DMSO. Mp: 214–218 °C. Anal. Calcd for $C_{13}H_7N_3O_4S$: C, 51.82; H, 2.34; N, 13.96. Found: C, 51.14; H, 2.30; N, 13.87. IR (KB, $cm^{-1}$): 1627 (C=N), 1596 (aromatic), 1540, 1344 ($NO_2$). $^1$H-NMR (DMSO-$d_6$): $\delta$ 8.72–8.53 (m, 3H, aromatic of 3,5-dinitrobenzoic acid ring), 7.90–7.03 (m, 4H, other aromatic).

Compound $\mathbf{3_s}$ was prepared as a brown solid in 58% yield from the hydrogenation of $\mathbf{2_s}$ according to the procedure described for $\mathbf{3_o}$. It was recrystallized from a mixture of DMF/water (1:3, v/v) and had mp 169–176 °C. Anal. Calcd for $C_{13}H_{11}N_3S$: C, 64.71; H, 4.60; N, 17.43. Found: C, 64.12; H, 4.63; N, 17.56. IR (KBr, $cm^{-1}$): 3398–3330 (N–H stretching), 1616 (N–H deformation), 1608 (C=N), 1198 (C–N stretching). $^1$H-NMR (DMSO-$d_6$): $\delta$ 7.77, 7.35 (m, 4H, aromatic of benzothiazole segment), 6.57 (m, 2H, aromatic of 4 and 6 positions of 1,3-phenylenediamine ring), 5.97 (m, 1H, aromatic of 2 position of 1,3-phenylenediamine ring), 4.70 (br, 4H, $NH_2$).

**Preparation of Model Compounds (Scheme 1). Model Diamides MDAo and MDAs.** A flask equipped with a dropping funnel was charged with a solution of $\mathbf{3_o}$ (0.6756 g, mmol) in DMAc (10 mL). Triethylamine (0.6071 g, 6.0 mmol) was added to the solution. Benzoyl chloride (0.8434 g, 6.0 mmol) diluted with DMAc (10 mL) was added dropwise to the stirred solution at 0 °C under $N_2$. Next, the mixture was stirred at ambient temperature for 4 h in a stream of $N_2$. It was poured into ice water, and the light brown solid obtained was filtered off, washed with water, and dried to afford $\mathbf{MDA_o}$ (1.13 g, yield 87%). A purified sample obtained by recrystallization from a mixture of 1,4-dioxane/water (1:1, v/v) had mp 260–263 °C. Anal. Calcd for $C_{27}H_{19}N_3O_3$: C, 74.80; H, 4.42; N, 9.70. Found: C, 74.43; H, 4.60; N, 9.63. IR (KBr, $cm^{-1}$): 3280 (N–H stretching), 1650 (C=O), 1600 (C=N and aromatic), 1538 (N–H deformation), 1284 (C–N stretching). $^1$H-NMR (DMSO-$d_6$): $\delta$ 7.78 (m, 2H, NHCO and 4H, aromatic ortho to C=O), 6.25 (m, 10H, other aromatic).

**Scheme 2**




**$MDA_s$** was similarly prepared as a brown solid in 89% yield by reacting **$3_s$** with benzoyl chloride in the presence of triethylamine. It was recrystallized from a mixture of DMF/water (1:2, v/v) and had mp 258–261 °C. Anal. Calcd for $C_{27}N_{19}N_3O_2S$: C, 72.14; H, 4.26; N, 9.35. Found: C, 71.86; H, 4.32; N, 9.21. IR (KBr, $cm^{-1}$): 3280 (N–H stretching), 1654 (C=O), 1602 (C=N and aromatic), 1546 (N–H deformation), 1282 (C–N stretching). $^1$H-NMR (DMSO-$d_6$): $\delta$ 7.77 (m, 2H, NHCO and 4H, aromatic ortho to C=O), 6.23 (m, 10H, other aromatic).

**Model Diimides $MDI_o$ and $MDI_s$.** A flask was charged with a solution of **$3_o$** (0.6756 g, 3.0 mmol) in DMF (15 mL). Phthalic anhydride (0.8887 g, 6.0 mmol) was added to the stirred solution at 0 °C under $N_2$. Stirring of the mixture was continued for 3 h in a stream of $N_2$. Acetic anhydride (5 mL) and fused sodium acetate (0.2 g) were added to the mixture, and it was heated at 70 °C overnight. Next it was poured into water, and the brown solid obtained was filtered off, washed with water, and dried to afford **$MDI_o$** (0.92 g, yield 63%). It was recrystallized from a mixture of $CH_3CN$/water (1:1, v/v) and had mp 135–139 °C. Anal. Calcd for $C_{29}H_{15}N_3O_5$: C, 71.74; H, 3.12; N, 8.66. Found: C, 71.16; H, 3.18; N, 8.73. IR (KBr, $cm^{-1}$): 1776, 1722 (C=O), 1602 (C=N and aromatic), 1238 (C–N stretching). $^1$H-NMR (DMSO-$d_6$): $\delta$ 7.67 (m, 8H, aroamtic of phthalimide segment and 4H, aromatic of benzoxazole segment), 7.25 (m, 3H, aromatic of 1,3-phenylenediamine ring).

**$MDI_s$** was similarly prepared as a brown solid in 68% yield by reacting **$3_s$** with phthalic anhydride. It was recrystallized from acetonitrile and had mp 144–148 °C. Anal. Calcd for $C_{29}H_{15}N_3O_4S$: C, 69.45; H, 3.02; N, 8.38. Found: C, 69.04; H, 3.06; N, 8.41. IR (KBr, $cm^{-1}$): 1780, 1722 (C=O), 1604 (C=N and aromatic), 1234 (C–N stretching). $^1$H-NMR (DMSO-$d_6$): $\delta$ 7.65 (m, 8H, aromatic of phthalimide segment and 4H, aromatic of benzothiazole segment), 7.27 (m, 3H, aromatic of 1,3-phenylenediamine ring).

**Preparation of Polymers (Scheme 2). Polyamides $PA_o$ and $PA_s$.** A flask equipped with a dropping funnel and magnetic stirrer was charged with a solution of **$3_o$** (0.6756 g, 3.0 mmol) in DMAc (10 mL). Triethylamine (0.6071 g, 6.0 mmol) was added to the solution. Terephthaloyl dichloride (0.6091 g, 3.0 mmol) dissolved in DMAc (10 mL) was added dropwise to the stirred solution at 0 °C under $N_2$. The mixture was subsequently stirred at ambient temperature for 4 h in a stream of $N_2$. It was poured into water, and the brown solid precipitate was filtered off, washed with water, and dried in a vacuum oven at about 150 °C to afford **$PA_o$** [0.87 g, yield 82%, inherent viscosity ($\eta_{inh}$) 0.31 dL/g in DMF]. Anal. Calcd for $(C_{21}H_{13}N_3O_3)_n$: C, 70.98; H, 3.69; N, 11.82. Found: C, 69.65; H, 3.74; N, 11.60.

**$PA_s$** was similarly prepared as a light green solid in 91% yield by reacting **$3_s$** with terephthaloyl dichloride in the presence of triethylamine. It had $\eta_{inh}$ 0.29 dl/g in DMF. Anal. Calcd for $(C_{21}H_{13}N_3O_2S)_n$: C, 67.91; H, 3.53; N, 11.31%. Found: C, 66.73%; H, 3.57%; N, 11.14%.

**Polyimides $PIP_o$, $PIP_s$ and $PIB_o$, $PIB_s$.** PMDA (0.6544 g, 3.0 mmol) was added to a stirred solution of **$3_o$** (0.6756 g, 3.0 mmol) in DMF (40 mL) at 0 °C. The solution became very viscous, and stirring was continued at ambient temperature for 3 h under $N_2$. Acetic anhydride (5 mL) and fused sodium acetate (0.2 g) were added to the solution, and it was heated at 90 °C overnight. It was subsequently poured into water, and the brown solid obtained was chopped in a home blender, filtered, and dried in a vacuum oven at approximately 150 °C to afford **$PIP_o$** (1.12 g, yield 92%). Anal. Calcd for $(C_{23}H_9N_3O_5)_n$: C, 67.82; H, 2.23; N, 10.32. Found: C, 66.93; H, 2.26; N, 10.15. The intermediate poly(amic acid) had $\eta_{inh}$ 0.53 dL/g in DMF.

**$PIP_s$** was similarly prepared as a brown solid in 91% yield by reacting **$3_s$** with PMDA. Anal. Calcd for $(C_{23}H_9N_3O_4S)_n$: C, 62.25; H, 2.14; N, 9.92. Found: C, 61.20; H, 2.16; N, 9.75. The intermediate poly(amic acid) had $\eta_{inh}$ 0.48 dL/g in DMF.

**$PIB_o$** was similarly prepared as a brown solid in 90% yield by reacting **$3_o$** with BTDA. Anal. Calcd for $(C_{30}H_{13}N_3O_6)_n$: C, 70.45; H, 2.56; N, 8.22. Found: C, 69.27; H, 2.60; N, 8.06. The intermediate poly(amic acid) had $\eta_{inh}$ 0.46 dL/g in a DMF solution.

**$PIB_s$** was similarly prepared as a brown solid in 94% yield from the reaction of **$3_s$** with BTDA. Anal. Calcd for $(C_{30}H_{13}N_3O_5S)_n$: C, 68.21; H, 2.48; N, 7.97. Found: C, 67.42; H, 2.53; N, 7.83. The intermediate poly(amic acid) had $\eta_{inh}$ 0.43 dL/g in DMF.

## Results and Discussion

Two new aromatic diamines bearing pendent benzoxazole or benzothiazole moieties were synthesized according to the synthetic route depicted in Scheme 1. More particularly, 3,5-dinitrobenzoyl chloride reacted with 2-aminophenol or 2-aminothiophenol in the presence of triethylamine to afford compounds **$1_o$** or **$1_s$**, respectively. The reaction took place in DMAc, and the mixture was slightly heated due to the deactivation cuased by the strongly electron-withdrawing nitro groups

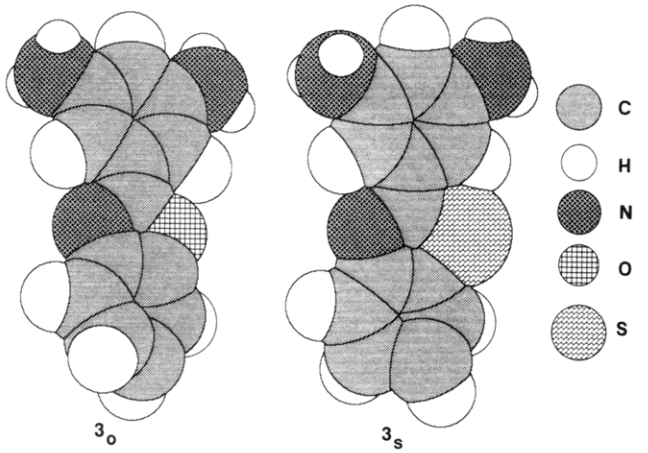



**Figure 1.** Optimized geometries of compounds $\mathbf{3_o}$ and $\mathbf{3_s}$ (ChemDraw 3D PlusΣ Molecular Modeling System, Version 3.1.1, 1993; Cambridge Scientific Computing, Inc.).

of 3,5-dinitrobenzoyl chloride. Compounds $\mathbf{1_o}$ and $\mathbf{1_s}$ were cyclodehydrated to the benzoxazole or benzothiazole derivative by gradual heating to ca. 200 °C of a suspension of these compounds in nitrobenzene using anhydrous HCl as catalyst. The catalytic action of HCl was caused by the increasing electrophilic reactivity of the carbon atom to the protonated carbonyl group.[11] Compounds **2** were catalytically hydrogenated by means of hydrazine hydrate to afford the corresponding diamines **3**.

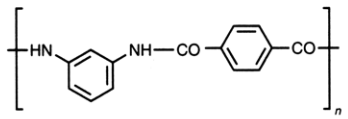
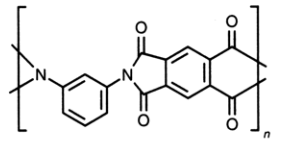
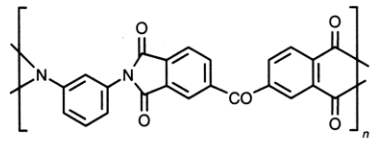
An attempt was made to estimate the structural characteristics of the synthesized new diamines $\mathbf{3_o}$ and $\mathbf{3_s}$. The presence of the bulky benzoxazole or benzothiazole pendent group could influence their reactivities toward dicarboxylic acids to a some extent because of steric hindrance. Figure 1 presents the geometries of $\mathbf{3_o}$ and $\mathbf{3_s}$, as calculated by means of CSC Chem 3D PlusΣ Molecular Modeling System (Version 3.1.1, 1993). It is seen that their structures do not seem to cause a considerable steric hindrance on the amino groups. The ring of 1,3-phenylenediamine and that of benzoxazole or benzothiazole do not deviate significantly from the planar conformation. An analogous behaviour has been observed in 5-(2-benzoxazole) or 5-(2-benzothiazole) isophthaloyl chlorides[6,7] utilized for the preparation of aromatic polyamides.

To obtain fundamental information about the structure of polymers, certain model compounds were synthesized (Scheme 1). Specifically, model diamides **MDA** and diimides **MDI** were prepared from the reactions of **3** with benzoyl chloride or phthalic anhydride, respectively.

A series of modified poly(terephthalamides) were prepared from the reactions of diamines **3** with terephthaloyl dichloride by the solution polycondensation method at low temperature in DMAc (Scheme 2). In addition, modified polyimides were prepared from the reactions of **3** with PMDA or BTDA and subsequent cyclodehydration of the intermediate poly(amic acids). Finally, the corresponding unmodified polymers were prepared for comparative purposes under the same experimental conditions utilizing 1,3-phenylenediamine instead of **3**. Table 1 presents their chemical structures, the $\eta_{inh}$ values, and designations.

The modified polymers were obtained in 82–94% yields. Polyamides $\mathbf{PA_o}$ and $\mathbf{PA_s}$ had $\eta_{inh}$ 0.31 and 0.29 dL/g, respectively, in DMF. Since the modified polyimides were partially soluble in polar aprotic solvents,

**Table 1. Structures and Designations of Unmodified Polymers**

| structure | designation |
|---|---|
|  | **PA**[a] |
|  | **PIP**[b] |
|  | **PIB**[b] |

[a] Polyamide **PA** was prepared in a DMAc solution containing 5 wt % LiCl. It had an inherent viscosity ($\eta_{inh}$) 0.51 dL/g in DMF. [b] The $\eta_{inh}$ of polyimides **PIP** and **PIB** could not be determined due to the limited solubility of these polyimides in polar aprotic solvents. The $\eta_{inh}$ of the intermediate poly(amic acids) were determined by taking an aliquot from their solutions in DMF and diluting before making the measurements. The poly(amic acids) of polyimides **PIP** and **PIB** had $\eta_{inh}$ 0.53 and 0.48 dL/g, respectively.

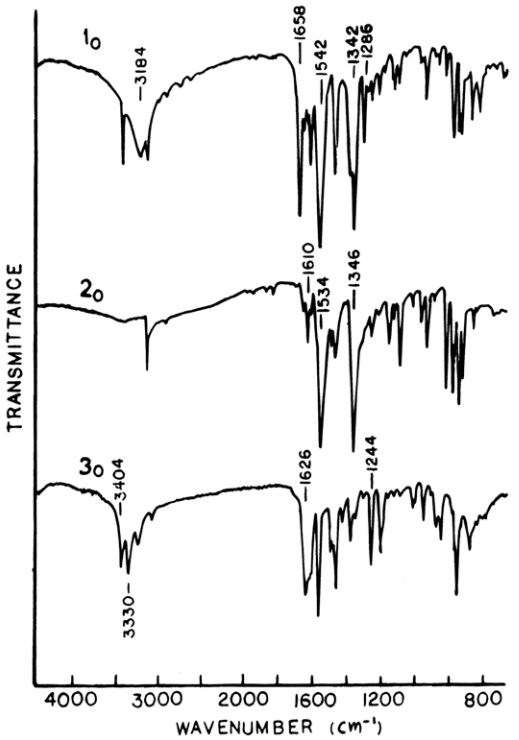



**Figure 2.** FT-IR spectra of compounds $\mathbf{1_o}$, $\mathbf{2_o}$, and $\mathbf{3_o}$.

their $\eta_{inh}$ could not be determined. The $\eta_{inh}$ of the intermediate poly(amic acids) were determined by taking an aliquot from their solutions in DMF and diluting before making the measurements. The $\eta_{inh}$ of the poly(amic acids) ranged from 0.43 to 0.53 dL/g (see the Experimental Section).

All monomers were characterized by elemental analyses as well as IR and $^1$H-NMR spectroscopy. Figure 2 shows the FT-IR spectra of $\mathbf{1_o}$, $\mathbf{2_o}$, and $\mathbf{3_o}$. It is seen that the cyclodehydration reaction could be monitored by IR spectroscopy, because $\mathbf{2_o}$ lacked the absorption bands of $\mathbf{1_o}$ at 3184 (N–H and O–H stretching), 1658 (C=O), and 1286 cm$^{-1}$ (C–OH stretching). In addition,

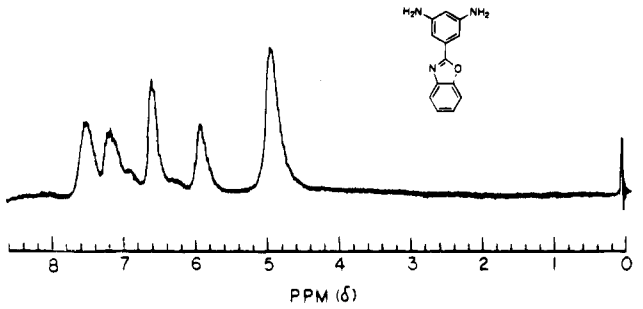



**Figure 3.** $^1$H-NMR spectrum of compound $\mathbf{3_o}$ in a DMSO-$d_6$ solution.

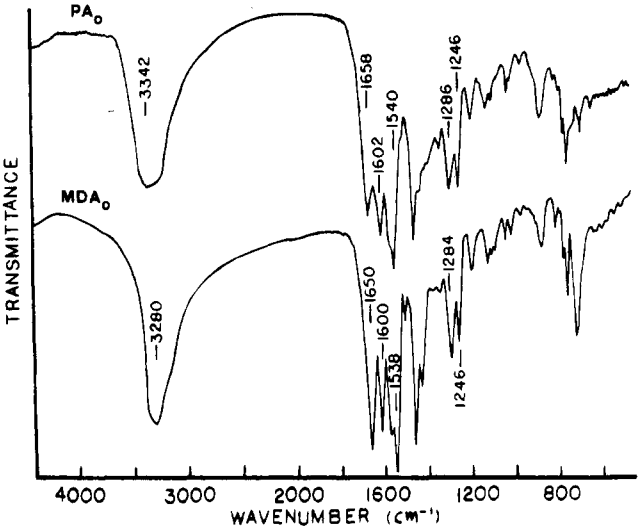



**Figure 4.** FT-IR spectra of model diamide $\mathbf{MDA_o}$ and polyamide $\mathbf{PA_o}$.

it displayed a new absorption at 1610 cm$^{-1}$ (C=N). On the other hand, $\mathbf{3_o}$ lacked the absorptions of $\mathbf{1_o}$ and $\mathbf{2_o}$ near 1530 and 1340 cm$^{-1}$ associated with the nitro groups, thus supporting their complete reduction.

The $^1$H-NMR spectrum of $\mathbf{3_o}$ (Figure 3) showed a broad peak at 4.90 ppm ($NH_2$) and multiplets at 5.90 (proton of 2 position of 1,3-phenylenediamine ring), 6.57 (protons of 4 and 6 positions of 1,3-phenylenediamine ring), and 7.16, 7.50 ppm (protons of benzoxazole segment). The protons of amino groups were exchangeable with $D_2O$.

The IR spectra of model compounds were in agreement with those of the corresponding polymers. Figure 4 presents the FT-IR spectra of model diamide $\mathbf{MDA_o}$ and polyamide $\mathbf{PA_o}$. The latter displayed characteristic absorptions at 3342 (N−H stretching), 1658 (C=O), 1602 (C=N and aromatic), 1540 (N−H deformation), and 1286, 1246 cm$^{-1}$ (C−N stretching and N−H bending). The broadening of the absorption at 3342 cm$^{-1}$ was ascribed to the terminal amino and carboxy groups.

Figure 5 presents the FT-IR spectra of model diimide $\mathbf{MDI_o}$ and polyimide $\mathbf{PIB_o}$. Both spectra showed the characteristic absorptions of the imide structure. In the case of $\mathbf{PIB_o}$, they appeared at 1782, 1726 (imide-I), 1354 (imide-II), 1094 (imide-III), and 716 cm$^{-1}$ (imide-IV). The imide-I band was attributed to the stretching vibrations of the two carbonyls, whereas the imide-II, -III, and -IV bands were assigned to axial, transverse, and out-of-plane vibrations of the cyclic imide structure, respectively.

One of the aims of the present investigation was the enhancement of the polymer solubility by introducing voluminous pendent groups along the polymer back-

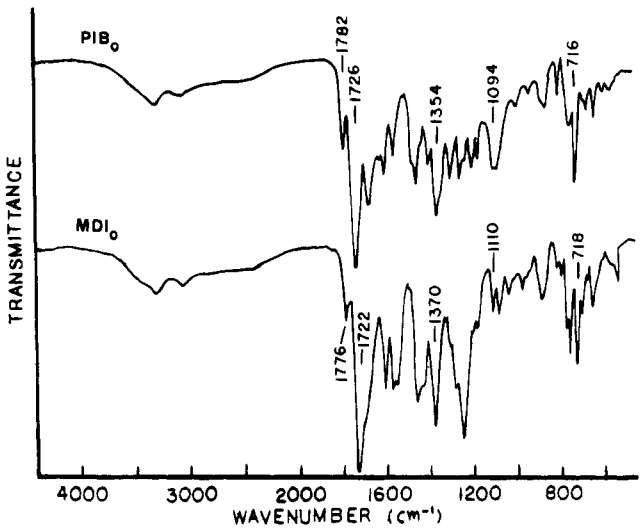



**Figure 5.** FT-IR spectra of model diimide $\mathbf{MDI_o}$ and polyimide $\mathbf{PIB_o}$.

bone. Table 2 presents the solubility behavior of $\mathbf{PA_o}$ and **PA**. The modified polyamide $\mathbf{PA_o}$ was readily soluble in polar aprotic solvents (DMF, *N*-methylpyrrolidone, DMSO) and concentrated $H_2SO_4$. It also dissolved upon heating in trichloroacetic acid and *m*-cresol, while it was partially soluble in 1,4-dioxane, acetonitrile, and cyclohexanone. Polyamide $\mathbf{PA_s}$ compared to $\mathbf{PA_o}$ displayed almost the same solubility in these solvents. In contrast, the reference polyamide **PA** dissolved at ambient temperature only in concentrated $H_2SO_4$ and upon heating in polar aprotic solvents and trichloroacetic acid. In addition, it was completely insoluble in less efficient solvents such as 1,4-dioxane, acetonitrile, cyclohexanone, and *m*-cresol. The better solubility of modified polyamides $\mathbf{PA_o}$ and $\mathbf{PA_s}$ was attributed to the disruption of a dense chain packing caused by the bulky benzoxazole or benzothiazole side groups. Furthermore, the presence of the latter directly affected the ability of polyamides to establish intermolecular hydrogen bonds. Noticeable improvements have been observed also for the solubilities of polyamides derived from 5-(2-benzoxazole) or 5-(2-benzothiazole) isophthaloyl chlorides.[6,7]

The solubility of the synthesized polyimides was also compared with that of the corresponding reference polyimides. Table 2 presents the results for a typical pair of polyimides $\mathbf{PIP_o}$ and **PIP**. They showed identical solubility and were dissolved only in concentrated $H_2SO_4$ upon heating. The stiff and rigid imide structure counteracted the effect of the bulky side groups, so that the solubility remained unchanged in this case.

The modified polyamides as well as the intermediate poly(amic acids) of the modified polyimides gave brittle films from DMF or DMAc solutions undoubtedly due to their relatively low degree of polymerization.

A first approach for structural characterization was made by X-ray methods with "as-prepared powders". Figure 6 shows the wide-angle X-ray diffractograms of all modified polymers. They displayed weak diffraction peaks which indicate the presence of a small fraction of crystalline or mesomorphic material.

The water absorption of polyamides was measured and related to the proportion of amide groups in each polymer. It has been reported that moisture absorption is proportional to the frequency of amide groups in polymer.[12] The isothermal moisture absorption of polyamides $\mathbf{PA_o}$, $\mathbf{PA_s}$, and **PA** is shown in Figure 7. The

**Table 2. Solubilities[a] of Polymers**

| sample | solvent[b] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | DMF | NMP | DMSO | $H_2SO_4$ | $CCl_3COOH$ | *m*-cresol | 1,4-dioxane | $CH_3CN$ | CH |
| $PA_0$ | ++ | ++ | ++ | ++ | + | + | +− | +− | +− |
| PA | + | + | + | ++ | + | − | − | − | − |
| $PIP_0$ | +− | +− | +− | + | +− | − | − | − | − |
| PIP | +− | +− | +− | + | +− | − | − | − | − |

[a] Solubility: ++, soluble at room temperature; + soluble in hot solvent; +−, partially soluble; −, insoluble. [b] DMF = *N*,*N*-dimethylformamide; NMP = *N*-methylpyrrolidone; DMSO = dimethyl sulfoxide; CH = cyclohexanone.

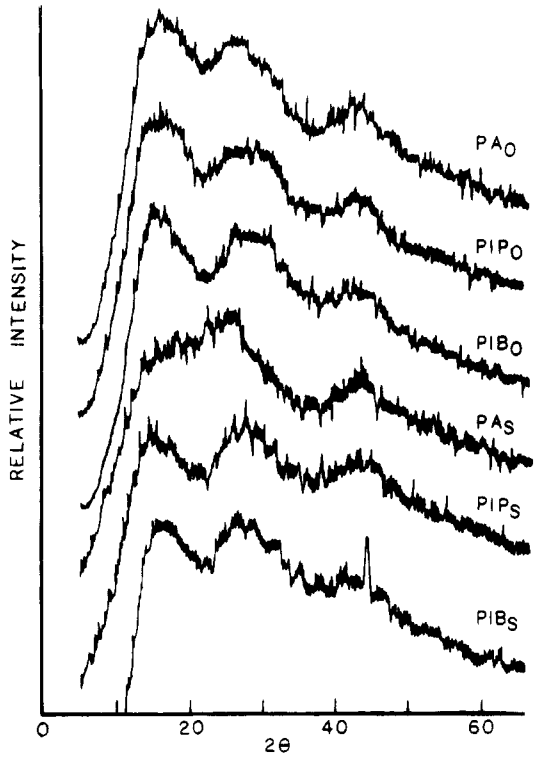



**Figure 6.** Wide-angle X-ray scattering curves for the modified polymers.

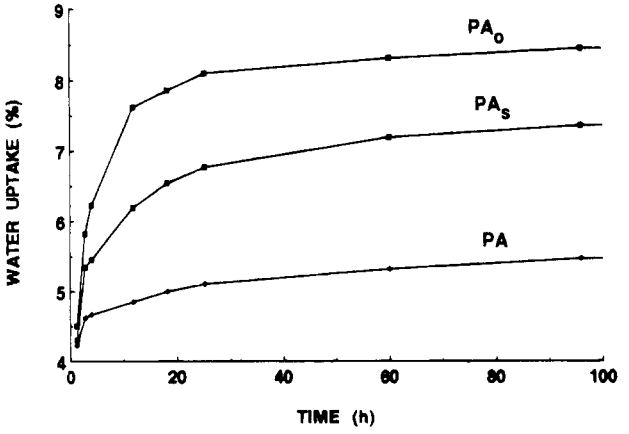



**Figure 7.** Water absorption (%) versus time for polyamides $PA_o$, $PA_s$, and **PA**.

number of moles of absorbed water per amide equivalent weight was 0.83, 0.76, and 0.36, respectively, after exposure for 100 h. The significantly higher hydrophilicity of modified polyamides was ascribed to the less dense packing of the chains that increased the water accessibility. In the case of $PA_o$, additional hydrogen bonding could take place due to the presence of the benzoxazole oxygen.

The thermal behavior of polymers was investigated by DTA in $N_2$ (Figure 8). Polyamides $PA_o$ and $PA_s$

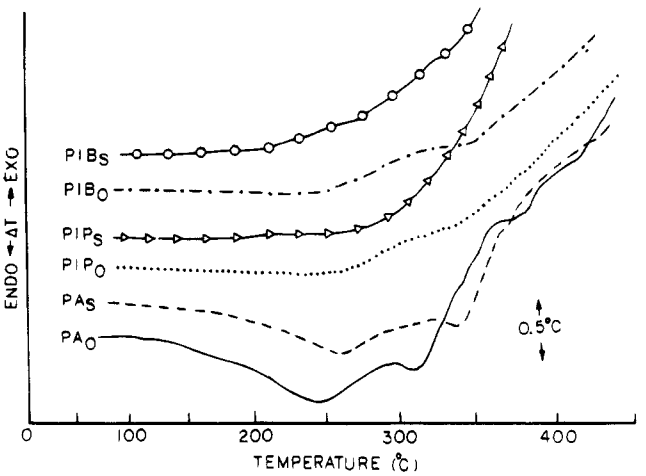



**Figure 8.** DTA traces of modified polymers. Conditions: $N_2$ flow, 60 $cm^3$/min; heating rate, 20 °C/min.

**Table 3. Thermal Stabilities of Polymers**

| sample | $N_2$ | | | | air | | | |
|---|---|---|---|---|---|---|---|---|
| | IDT[a] (°C) | PDT[b] (°C) | $PDT_{max}$[c] (°C) | $Y_c$[d] (%) | IDT (°C) | PDT (°C) | $PDT_{max}$ (°C) | wt loss[e] (%) |
| $PA_0$ | 370 | 498 | 523 | 63 | 368 | 471 | 493 | 22.0 |
| $PA_s$ | 368 | 508 | 519 | 64 | 367 | 486 | 523 | 24.7 |
| PA | 344 | 463 | 528 | 56 | 341 | 433 | 471 | 42.0 |
| $PIP_0$ | 411 | 574 | 616 | 62 | 408 | 527 | 552 | 8.7 |
| $PIP_s$ | 407 | 545 | 582 | 63 | 404 | 482 | 508 | 12.5 |
| PIP | 367 | 501 | 551 | 57 | 366 | 489 | 527 | 19.0 |
| $PIB_0$ | 441 | 582 | 623 | 62 | 438 | 510 | 545 | 2.5 |
| $PIB_s$ | 437 | 567 | 604 | 65 | 432 | 519 | 556 | 3.3 |
| PIB | 374 | 533 | 589 | 56 | 370 | 474 | 501 | 5.8 |

[a] Initial decomposition temperature. [b] Polymer decomposition temperature. [c] Maximum polymer decomposition temperature. [d] Char yield at 800 °C. [e] Weight loss after 20 h of isothermal aging at 320 °C in static air.

displayed broad endotherms between 200 and 300 °C attributable to their softening. They also softened at this temperature region upon gradual heating in a conventional melting point apparatus. No endotherms associated with softening were observed in the DTA traces of polyimides. All polymers showed exotherms above 300 °C assigned to their thermal degradation.

The thermal stability of both modified and unmodified polymers was evaluated by TGA in $N_2$ and air atmospheres as well as isothermal gravimetric analysis (IGA). The initial decomposition temperature (IDT), the polymer decomposition temperature (PDT), the maximum polymer decomposition temperature ($PDT_{max}$) in both $N_2$ and air as well as the anaerobic char yield ($Y_c$) at 800 °C for all polymers are listed in Table 3. The IDT and PDT were determined for a temperature at which 0.5 and 10% weight loss was observed, respectively. $PDT_{max}$ corresponds to the temperature at which the maximum rate of weight loss occurred. Figure 9 presents typical TGA curves in $N_2$ and air of polymers $PA_o$, $PIP_o$, and $PIB_o$.

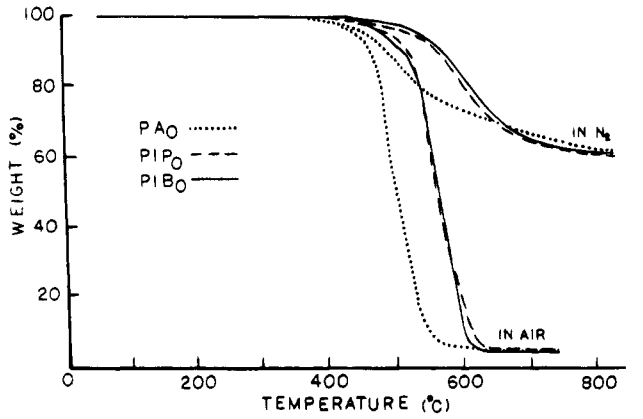



**Figure 9.** Typical TGA thermograms of polymers $\mathbf{PA_o}$, $\mathbf{PIP_o}$, and $\mathbf{PIB_o}$ in $N_2$ and air. Conditions: gas flow, 60 $cm^3$/min; heating rate, 20 °C/min.

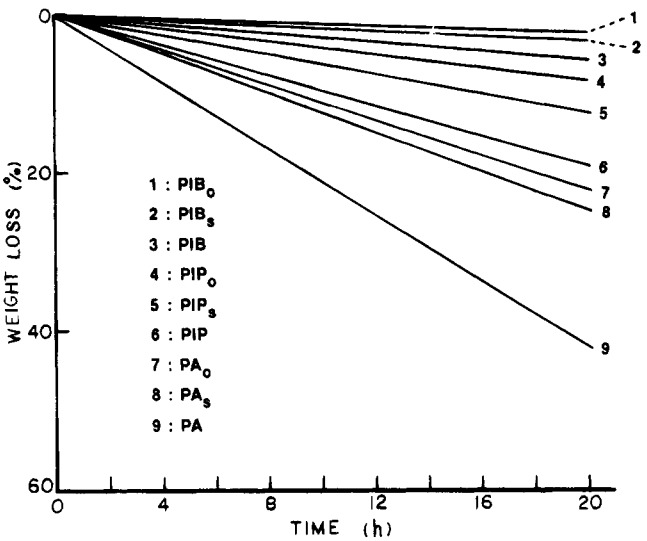



**Figure 10.** IGA traces in static air at 320 °C of both modified and unmodified polymers.

The modified polymers started to lose weight at higher temperatures than the corresponding unmodified ones, since their IDT values were higher by 24–68 °C. In addition, the modification of polymers increased their anaerobic $Y_c$ at 800 °C by 5–9%. The heat–resistant benzoxazole or benzothiazole structure incorporated as pendent groups to the polymer backbone was responsible for this behavior. Upon comparing the chemical structures of the pendent groups, it is seen that benzoxazole was somewhat more thermally stable than benzothiazole. It has been reported that polyamides bearing pendent benzoxazole[6] or benzothiazole[7] groups displayed better thermal stability than the unmodified ones.

Figure 10 presents the IGA traces of both modified and unmodified polymers at 320 °C in static air. The weight losses obtained after 20 h of isothermal aging are listed in Table 3. The results showed that all modified polymers suffered less weight loss than the corresponding unmodified ones. The remaining weights determined from the IGA traces were of the following order:

$$\mathbf{PIB_o > PIB_s > PIB > PIP_O > PIP_s > PIP > PA_o > PA_s > PA}$$

## Conclusions

1. 5-(2-Benzoxazole)- or 5-(2-benzothiazole)-1,3-phenylenediamine was used as starting material for the preparation of modified polyamides and polyimides containing benzoxazole or benzothiazole pendent groups.
2. The geometries of the above diamines, as calculated by a molecular modeling system, revealed that their structures do not cause a significant steric hindrance on the amino groups.
3. The FT-IR spectra of model compounds were in agreement with those of the corresponding polymers.
4. The modification of polyamides and polyimides increased the solubility in common organic solvents of the former but did not influence that of the latter.
5. The modified polyamides showed higher hydrophobicity than the unmodified ones.
6. The modified polyamides softened between 200 and 300 °C. No softening was observed for the modified polyimides.
7. All modified polymers suffered less weight loss under TGA and IGA testing than the parent polymers. They were stable up to 367–441 °C in $N_2$ or air and afforded anaerobic char yields of 63–65% at 800 °C.

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