Aromatic polyamides with pendent heterocycles: 2. Benzoxazole groups*

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A series of polyisophthalamides (PIPAs) containing pendent benzoxazole groups was prepared from six aromatic diamines and a new monomer, 5-(2-benzoxazole)isophthaloyl chloride. These polymers, having moderate to high inherent viscosity values, were synthesized by the low temperature polycondensation method in high yields. A striking feature of these polymers is that their solubility and thermal properties were enhanced compared to the corresponding unmodified PIPAs. Thus, all of the polymers were soluble in aprotic polar solvents and glass transition and decomposition temperatures were, respectively, 15–40°C and 25–35°C higher than for the reference PIPAs. The tensile strengths were somewhat lower than those for the unmodified PIPAs.

(Keywords: monomer synthesis; pendent groups; benzoxazole)

INTRODUCTION

Aromatic polyisophthalamides (PIPAs) are polymers with relatively high molecular rigidity, although they show lower stiffness than typical rod-like polymers. Still, they are not soluble in common solvents; for instance, a representative member of the family, poly(*m*-phenyleneisophthalamide) (MPD-I), is soluble only in strong acids and in highly polar solvents containing dissolved salts. Chain stiffness is only one of the properties affecting solubility. In aromatic polyamides, a major parameter that contributes to insolubility is the intermolecular bonding energy developed through hydrogen bridges and through dipole–dipole interactions. Regular aromatic polyamides, i.e. from symmetrical monomers, can develop high degrees of crystallinity, a factor that works against solubility and processability. Thus, our synthetic research efforts have been directed towards structural modifications designed to promote solubility and processability. An attractive synthetic approach to achieve the above goals is the incorporation of bulky substituents as pendent groups along the polymer backbone. If the pendent groups are carefully chosen, it is possible to promote solubility without impairing thermal and mechanical properties to any great extent. In fact, many polymers, such as polyterephthalamides[1], polyterephthalates[2], polyimides[3] and other polyheterocycles[4], have been chemically modified by polycondensation or co-condensation of monomers bearing bulky pendent groups.

In previous work, we have reported the synthesis and characterization of modified PIPAs with better solubility than conventional PIPAs[5–8]. We always followed the same general approach, consisting of the synthesis and polycondensation of 5-substituted derivatives of isophthaloyl chloride. When phthalimide[7] or 2-benzothiazole[8] rings were used as pendent groups, beneficial effects were observed, not only in the solubility but also in the thermal properties. These results prompted us to prepare a new condensation monomer, 5-(2-benzoxazole)isophthaloyl chloride, and to study the properties of the polyamides obtained by polycondensation of it with aromatic diamines.

It is important to note that polybenzoxazoles and polybenzothiazoles are recognized as a class of heterocyclic polymers with superior mechanical and thermal properties. Therefore, it can be expected that PIPAs with benzoxazole pendent groups can provide a good balance of useful properties. Here we report on the evaluation of the properties of the new polymers and compare these properties with those of unsubstituted polyisophthalamides.

EXPERIMENTAL

Solvents and reagents were commercially available and were used as received unless otherwise indicated. *N,N*-Dimethylacetamide (DMA) was distilled at reduced pressure twice – the first time over phosphorus pentoxide and the second time over calcium hydride. The DMA was then stored in a sealed, dark flask over molecular sieves. Lithium chloride was dried at 325°C for 12 h. The diamines were purified by sublimation over silica gel just before use.

2-(3,5-Dimethylphenyl)benzoxazole **1** was prepared by the reaction of equimolar amounts of 3,5-dimethylbenzoic

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acid and 2-aminophenol in a mixture of phosphorus pentoxide and methanesulfonic acid (1:5) at 120°C, blanketed by dry nitrogen, over 24 h. The dark red solution was poured into water, and the resulting precipitate was filtered off and treated with a 0.1 N solution of NaOH up to a pH of 3. The solid was separated by suction and thoroughly washed with water. Once dried, it was recrystallized from ethanol. The average yield of several operations was 89%. The pure solid had a melting point of 125–126°C.

5-(2-Benzoxazole)isophthalic acid **2** was synthesized by oxidizing **1** with $KMnO_4$ in a mixture of pyridine and water. A 10-fold molar excess of $KMnO_4$ was used to oxidize fully the dimethyl intermediate and the reaction was carried out at 90°C for 24 h. By-product MnO_2 (black powder) was eliminated by filtration and the diacid was precipitated from the clear solution with 2 N HCl to a pH of approximately 3. The product was dissolved in 1 N NaOH and reprecipitated by acidification with a 0.1 N solution of HCl up to a pH of 3. The white precipitate was filtered off, washed with water until a neutral reaction was obtained and dried in a vacuum oven at 110°C overnight. The yield was 80%, and the melting point of the solid was 360°C (with decomposition) (recrystallized from a 3:2 mixture of dimethylformamide (DMF) and water).

5-(2-Benzoxazole)isophthaloyl chloride **3** was prepared by refluxing **2** with a five-fold molar excess of thionyl chloride and some drops of DMF for 5 h. The excess of thionyl chloride was distilled off and toluene was added to dissolve the solid residue. Next, the solution was concentrated to dryness and the diacid chloride was purified by recrystallization from a mixture of chloroform and hexane (1:4), followed by vacuum sublimation. The yield was 75%, and the melting point of the solid was 165–166°C. The analysis for $C_{15}H_7Cl_2NO_3$ (320.13) was as follows: (calculated) C 56.28%, H 2.20%, N 4.38%, Cl 22.15%; (found) C 56.01%, H 2.21%, N 4.45%, Cl 21.94%.

Polymer synthesis

The general procedure consisted of adding portionwise 20.0 mmol of **3** to a stirred solution of 20.0 mmol of diamine in 40 ml of DMA at 0°C. The mixture was allowed to react under a blanket of nitrogen for 2 h, then the temperature was raised to 20°C and the reaction was allowed to proceed for 2 h more. The solution was then cooled to 0°C and a small excess of **3** (0.2 mmol) was added, then the cooling bath was removed and the reaction was kept at room temperature for 2 h. The viscous polymer solution was poured into distilled water and the polymer was filtered off, washed with water several times, extracted with acetone in a Soxhlet for 24 h, and finally dried in a vacuum oven at 100°C overnight. Yields of over 95% were obtained.

Measurements

Microanalyses were carried out by the analysis service of the Centro Nacional de Química Organica, Madrid. ^1H and ^{13}C n.m.r. spectra were recorded on a Varian Unity spectrometer tuned at 499.84 and 125.697 MHz, respectively, using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent and tetramethylsilane (TMS) as reference at 60°C. Proton spectra were obtained using the following conditions: pulse angle, 90°; acquisition time, 6 s; sweep width, 4000 Hz; data size, 64K. Proton-decoupled ^{13}C n.m.r. spectra were obtained with WALTZ decoupling using the following conditions: pulse angle, 53°; acquisition time, 1.3 s; sweep width, 25 000 Hz; data size, 64K. Heteronuclear 2D shift-correlated spectra were performed using the following conditions: $^1J(C–H) = 150$ Hz; spectral width in ^{13}C dimension, 3750 Hz; spectral width in ^1H dimension, 1050 Hz; relaxation delay, 2 s; number of experiments, 256; and 512 × 1024 points for the data table.

Viscosities were measured on 0.5% *N*-methyl-2-pyrrolidone (NMP) solutions at 30 ± 0.1°C in an automatic Ubbelohde viscometer.

Differential scanning calorimetry (d.s.c.) measurements and thermogravimetric analysis (t.g.a.) studies were performed on Perkin-Elmer models DSC-7 and TGA-7, respectively. All samples were tested under nitrogen at a heating rate of 10°C min^{-1}.

Wide-angle X-ray diffraction (WAXD) patterns were obtained from polymer films at room temperature by using a Philips Geiger X-ray diffractometer, operating in the 2θ range between 3 and 32° at a rate of 2° min^{-1} and using Ni-filtered CuKα radiation.

For the measurement of mechanical properties, strips 5 mm wide and 80 mm long were cut from polymer films and tested on an Instron 1122 dynamometer at 20°C. Pneumatic clamps were used, and an extension rate of 2 mm min^{-1} was applied with a gauge length of 10 mm.

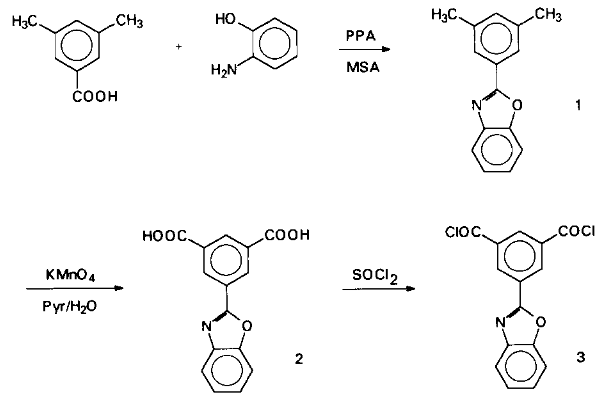
RESULTS AND DISCUSSION

Monomer and polymer syntheses

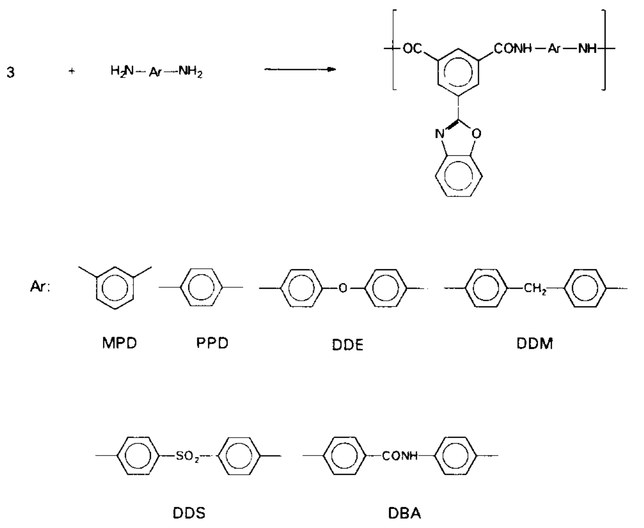
The synthesis of the new monomer, 5-(2-benzoxazole)-isophthaloyl chloride **3**, was carried out by the synthetic route depicted in *Scheme 1*.

In previous work we described the convenience of using polyphosphoric acid (PPA) as a condensation medium to prepare benzazole derivatives[8]. Thus, the preparation of intermediate **1** was performed using 3,5-dimethylbenzoic acid and 2-aminophenol in PPA/methanesulfonic acid in about 90% yield, which means that the three-step synthetic route adopted for the preparation of monomer **3** is a convenient, high-yield method. A similar method has been mentioned previously by Tsai and Arnold for the preparation of benzazole terephthalic acids[4].

The polycondensation of **3** with aromatic diamines was carried out in DMA by the traditional low-temperature solution method (*Scheme 2*). The results of the polycondensation reactions are shown in *Table 1*.



Scheme 1 Synthesis of 5-(2-benzoxazole)isophthaloyl chloride



Scheme 2 Structures of the modified polyisophthalamides

Table 1 Solution properties of aromatic polyamides with benzoxazole pendent groups

Polymer	η_{inh}[a] (dl g^{-1})	Solubility[b] DMF	Solubility[b] *m*-Cresol
MPD-BOI	0.49	+ (+)	+ + (−)
PPD-BOI	0.38	+ (−)	+ − (−)
DDE-BOI	0.74	+ + (+ +)	+ + (−)
DDM-BOI	0.66	+ + (+ +)	+ + (−)
DDS-BOI	0.58	+ +(+ +)	+ (+ −)
DBA-BOI	0.91	+ + (+ +)	+ − (−)

[a] Measured on solutions of 0.5 g dl^{-1} in NMP at 30°C

[b] The indications for solubility are: + +, soluble at room temperature; +, soluble in hot solvent; + −, partially soluble or swollen; −, insoluble. The solubilities of the corresponding unsubstituted polyisophthalamides are shown in parentheses

High yields (97–100%) were obtained in every case; inherent viscosities in the range 0.38–0.91 dl g^{-1} were measured.

Although the values of the viscosities are not comparable, further attempts to optimize the reaction and to improve the viscosities were not made. Nevertheless, the current polyisophthalamides formed tough, transparent films when cast from solutions in DMA, except for polymer PPD-BOI, which showed an inherent viscosity of only 0.38 dl g^{-1} and therefore was of too low a molecular weight for good film formation.

Theoretical calculations

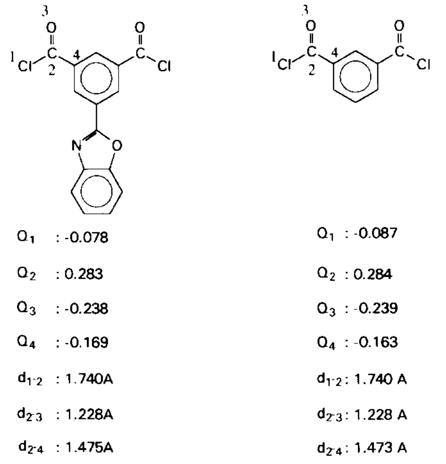
On using a new condensation monomer, it is interesting to investigate its reactivity compared with known, well-documented monomers. This propery can be estimated by modern quantum mechanical methods that allow theoretical calculations of the reactivity of functional groups based on molecular parameters, such as molecular geometry, charge distribution, and orbital energies.

Thus, a study was made of the influence of the molecular geometry on the accessibility of nucleophiles to the functional groups of **3** involved in the polyamidation reaction. The charge distribution was also calculated to determine whether a sigificant deviation of the electronic charge on the carbonyl carbons with respect to those of isophthaloyl chloride would account for an enhancement or a lowering of monomer reactivity. For this purpose, AM1[9] molecular orbital calculations were carried out, using the MOPAC[10] program with the Precise option for improving the convergence. The method yielded the results shown in *Scheme 3*. These results predict a similar reactivity for **3** and isophthaloyl chloride. The electronic charges on the carbonyl carbons of each monomer are almost identical, which means that monomer **3** should theoretically behave towards diamines in a similar manner to isophthaloyl chloride, provided that steric effects do not negatively influence the reactivity.

Because of the presence of a bulky substituent on the 5 position of monomer **3**, it might be thought that this could affect the reactivity of the carbonyl groups. However, the rigid structure of monomer **3** does not cause any significant steric hindrance towards the carbonyl groups. A value of 0° was estimated for the dihedral angle formed by the planes of the isophthaloyl ring and the benzoxazole ring, showing that there is no interaction that makes the benzoxazole ring deviate from the all-planar conformation. Thus, concerning reactivity as an acid chloride, monomer **3** should be as suitable a monomer as isophthaloyl chloride for polycondensation reactions, and it could provide high-molecular-weight polymers under standard conditions.

N.m.r. characterization

The polymers were characterized by n.m.r. spectroscopy. As an example, the ^{1}H n.m.r. spectrum of polymer DDS-BOI is shown in *Figure 1*. All of the signals could



Scheme 3 Bond distances and atomic charges of isophthaloyl chloride and monomer **3** calculated using AM1

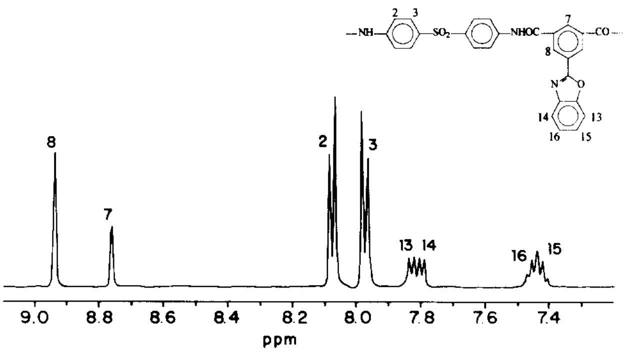


Figure 1 ^{1}H n.m.r. spectrum of polymer DDS-BOI

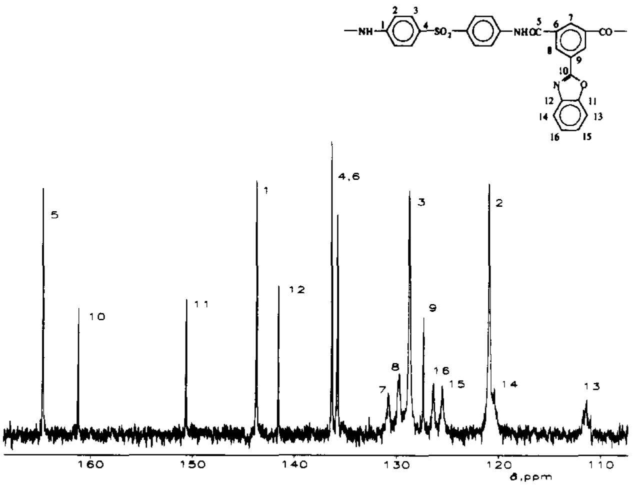


Figure 2 ^{13}C n.m.r. spectrum of polymer DDS-BOI

be easily assigned, except for the systems formed by protons 13–14 and 15–16, whose assignments can be interchanged. The strong electron-withdrawing effect of the benzoxazole group can be clearly observed from the chemical shifts of protons 7 and 8. A comparison with the spectrum of the polymer DDS-I, without pendent groups, showed downfield shifts of 0.22 and 0.75 ppm for protons 7 and 8, respectively. This effect is slightly greater than that observed for benzothiazole pendent groups.

The ^{13}C n.m.r. spectrum of the same polymer (*Figure 2*) was quite complex but it could be assigned according to previous data[11]. The peaks that appeared in the region 120–130 ppm were broadened with respect to the other peaks in the spectrum. A heteronuclear ^{1}H–^{13}C correlation showed that the broadened peaks correspond only to the protonated carbons. This broadening effect, which appeared also in PIPAs containing benzothiazole pendent groups[8] and in the unmodified polyisophthalamides, was attributed to the low mobility of the polymer chain. However, a more thorough n.m.r. study is required to make clear this abnormal behaviour.

The presence, in the aromatic diamine, of a bulky hinge group that hinders the rotation of both aromatic rings also causes broadening of the signals from the protonated carbons. This effect can be observed in the spectrum of DDS-BOI (*Figure 2*) if we compare the intensities of the signals from carbons 2 and 3 with the intensities of the signals from carbons 1 and 4.

Polymer properties

Solubility. While films of all the polymers were found to be essentially amorphous, irrespective of the diamine employed in the synthesis, the solubilities of the various polymers depended mainly on the diamine monomer from which they were prepared. PIPAs derived from wholly aromatic diamines, such as MPD-BOI and PPD-BOI, were soluble in sulfuric acid and trifluoroacetic acid, but they were only partially soluble in amide-type solvents like DMA or DMF. However, they could be synthesized in DMA, and they gave clear solutions in this solvent at the end of the polycondensations, without needing the addition of inorganic salts. Apparently, they developed some ordering upon precipitation into water because, although no crystallinity could be measured by WAXS, incipient crystallinity or some type of molecular ordering must be responsible for the observed insolubilization effect.

Diamines with two phenylene rings linked by a hinge group produced polymers that showed good solubility in DMA and DMF (over 5% w/v at room temperature). All polymers, except PPD-BOI and DBA-BOI, were soluble in *m*-cresol at ambient temperature as well.

Regarding the effect of pendent group, it is interesting that, as a rule, incorporation of a benzoxazole ring as a pendent substituent enhances the solubility of PIPAs. The unsubstituted parent PIPAs showed limited solubility in DMF and very poor solubility in *m*-cresol. In particular, the solubilities in *m*-cresol were highly improved compared with the homologous parent PIPAs. The improvement can be attributed in part to the fact that certain polybenzoxazoles are soluble in *m*-cresol[12], but for the most part the improvement should be attributed to the interchain steric repulsion caused by the bulky pendent hetero ring. The chain separation effect accounts for a weakening of the strong interactions through hydrogen bonding and the steric factor must be dominant because the other effects, such as dipole attraction or chain rigidity enhancement, should work against good solubility.

D.s.c. evaluations. The thermal behaviour of these new polymers was evaluated by differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.). Neither crystallization exotherms nor melting endotherms were observed by d.s.c. in the range 50–450°C and only the inflection associated with the glass transition could be detected. The values of T_g listed in *Table 2* show that the introduction of pendent benzoxazole rings caused an increase of between 15 and 40°C in the T_g values compared with the unmodified PIPAs. This result is very similar to that found in the thermal characterization of polyisophthalamides with benzothiazole pendent groups[8]. This agrees with a similar volume and polarity for both types of hetero rings, and it suggests that the structural rigidities introduced by them are very similar in terms of T_g enhancement.

T.g.a. evaluations. The t.g.a. results are also summarized in *Table 2*. Because of the polar character of amide groups, polyamides absorb significant amounts of moisture. Thus, the elimination of water accounts for the weight loss observed in the thermograms in the range 60–160°C. For the current PIPAs, water desorption in that temperature interval varied between 2 and 3%, i.e. similar to the

Table 2 Thermal and tensile properties of aromatic polyamides with benzoxazole pendent groups[a]

Polymer	T_g (°C)	T_d (°C	E^b (MPa)	ΔL^c (%)	M^d (GPa)
MPD-BOI	315 (276)	475 (450)	73.2 (122.5)	13	1.76
PPD-BOI	329 (295)	500 (470)	–[e] (117.0)	–	–
DDE-BOI	293 (267)	475 (445)	84.9 (112.0)	18	1.64
DDM-BOI	281 (264)	465 (430)	79.3 (107)	14	1.53
DDS-BOI	336 (315)	475 (440)	83.1 (–)	21	1.82
DBA-BOI	308 (–)	465 (–)	91.4 (–)	28	1.93

[a] The properties of the corresponding unsubstituted polyisophthalamides are shown in parentheses
[b] Tensile strength
[c] Elongation to break
[d] Tensile modulus
[e] The casting of the DMA solution gave a brittle film

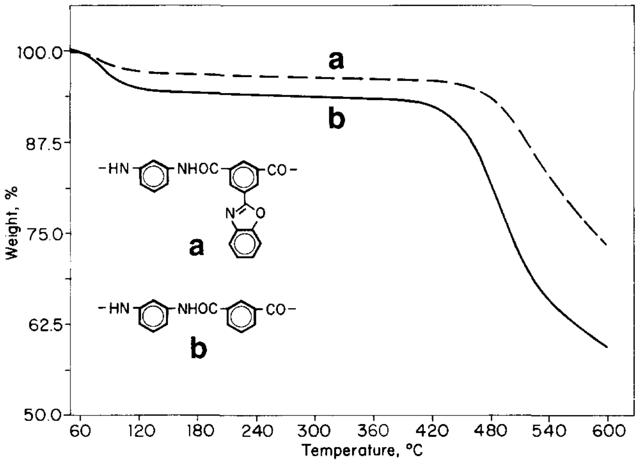


Figure 3 T.g.a. curves of polymers MPD-BOI (a) and MPD-I (b)

unmodified PIPAs. The decomposition temperature T_{d} (N_2, $10^{\circ}\mathrm{C\,min}^{-1}$) was taken at the onset of the t.g.a. curve. Values of T_{d} between 465 and 500°C were measured for the set of polymers. These values of the thermal decomposition temperature are slightly higher (25–35°C) than the values of T_{d} for the parent polyamides. Interestingly, only one weight loss onset was observed in the t.g.a. curves (*Figure 3*). This means that, unlike other pendent groups, the benzoxazole group did not separate from the polymer before the thermal rupture of the main chain occurred at temperatures of over 460°C.

Tensile evaluations. The current PIPAs could be cast from their DMA solutions to give yellowish, transparent films except for PPD-BOI, which gave a brittle film undoubtedly due to its relatively low molecular weight. The values of tensile strength, elongation to break and initial modulus are shown in *Table 2*. Although the figures for tensile strength are somewhat lower than those for the reference PIPAs, the measured values of the mechanical properties compare well with other experimental aromatic polymers. These differences should be considered only as approximate because of the higher viscosities (probably indicating higher molecular weights) of the unmodified PIPAs used in the comparison[5].

Removing all traces of solvent from the films was extremely difficult. Even after heating to 160°C in vacuum for some hours residues of solvent could be detected by t.g.a. (1–3%). Additionally, water absorption while performing mechanical tests could not be excluded. Both effects should account to some degree for the comparatively high values of elongation found for these PIPAs.

CONCLUSIONS

It has been shown that PIPAs having bulky benzoxazole pendent groups can be obtained in high molecular weights (as evidenced by high inherent viscosities) from the reaction of 5-(2-benzoxazole)isophthaloyl chloride with several aromatic diamines.

The presence of the benzoxazole rings greatly affects the spectroscopic characteristics and the general properties of these polymers compared to the unmodified PIPAs. Enhanced solubility, higher T_{g} values and increased thermal resistance were found for the modified polymers. The tensile properties were poorer than those of the unmodified PIPAs.

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