Aromatic polyamides with benzothiazole pendent groups: synthesis, nuclear magnetic resonance structural study and evaluation of properties*

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(Received 27 January 1993; revised 21 June 1993)

A new family of aromatic polyamides were prepared from six aromatic diamines and a new monomer derived from isophthalic acid: 5-(2-benzothiazolyl)isophthaloyl chloride. Theoretical calculations of the reactivity of the new monomer were made by semiempirical methods. The polymers were synthesized by the solution polycondensation method at low temperature, in high yields and moderate to high inherent viscosities. The presence of pendent benzothiazole rings brought about remarkable changes in the spectral (nuclear magnetic resonance) characteristics, compared with those of the homologous unmodified polyisophthalamides. Noticeable improvements were observed also for the solubility and for the glass transition temperatures, which rose 20–30°C relative to those of the conventional polyisophthalamides. Thermogravimetric analyses showed that the new polymers have better thermal stability than the unmodified ones.

(Keywords: synthesis; benzothiazole pendent groups; aromatic polyamides)

INTRODUCTION

In previous work, we reported the synthesis and characterization of polyisophthalamides (PIPAs) with bulky pendent groups, including imide pendent groups[1–5]. The incorporation of phthalimide groups as pendent substituents of PIPAs on the 5 position of the phthaloyl moieties caused remarkable changes both in the solubility and in the thermal behaviour of polyisophthalamides[4,5]. Noticeable changes in the properties of aromatic polyimides have also been described in the early work of Korshak *et al.*[6,7]. As is known from early studies on the thermal resistance of polyheterocycles, aromatic imides are among the heterocycles that provide better heat stability, but benzimidazoles, benzothiazoles and benzoxazoles are even more thermally stable[8]. Thus, one can expect that the incorporation of side benzazole hetero rings will improve the performance of previously reported polyisophthalamides and modified polyisophthalamides. In fact, thermally stable polyamides and polyheteroarylenes with various pendent hetero rings have previously been reported[9,10].

Consequently, the aim of the present work was the preparation and evaluation of a series of new PIPAs with benzothiazole pendent groups. Although the incorporation of benzothiazole units within the main chain of polyaromatic systems is an approach often reported[11–13], there are few examples of polymers modified by benzothiazole pendent groups[9,10]. The combination of a semirigid main chain of aromatic polyamide with a side 2-benzothiazole substituent per repeat unit will give rise to polymers that should exhibit a favourable balance of properties. The presence of the bulky pendent groups will enhance the solubility in organic solvents because the dense packing of the polymer chains will be hindered. Moreover, the thermal resistance will not be impaired, as polybenzothiazoles are recognized to have very good thermal and oxidative stability[9,10].

EXPERIMENTAL

All materials and solvents were commercially available and they were used as received unless otherwise indicated. *N,N*-Dimethylacetamide (DMA) was distilled twice, the first time over phosphorus pentoxide and the second time over calcium hydride. It was stored in a sealed dark flask over molecular sieves. The diamines were first recrystallized from suitable solvents under N_2, except *m*-phenylenediamine, which was vacuum distilled from zinc powder. Then they were purified by sublimation just before use.

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* Presented in part at the Meeting of the American Chemical Society, August 1992

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0032-3861/94/04/0872–06

2-(3,5-Dimethylphenyl)benzothiazole (1)

This was prepared by the reaction of 0.1 mol of 3,5-dimethylbenzoic acid and 0.1 mol of 2-aminothiophenol in 300 g of polyphosphoric acid (PPA) at 200°C blanketed by nitrogen for 24 h. The dark PPA solution was poured into water, the precipitate was filtered off and treated twice with 0.1 N Na_2CO_3, and finally thoroughly washed with water. Once it was dried, it was recrystallized from ethanol. Yield was 92%; m.p. 76–77°C. Anal. calcd for $C_{15}H_{13}SN$ (239.30): C, 75.28; H, 5.47; N, 5.85; S, 13.40. Found: C, 75.04; H, 5.83; N, 5.75; S, 13.16.

5-(2-Benzothiazolyl)isophthalic acid (2)

This was synthesized by oxidizing 0.1 mol of **1** with 1 mol of $KMnO_4$ in 700 ml of a mixture of pyridine/water (1/1). A 10:1 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. The by-product MnO_2 black powder was eliminated by filtration under reduced pressure, and the diacid was precipitated from the clear solution by acidification with 2 N HCl to a pH of approximately 3. The product was dissolved in 1 N NaOH and reprecipitated by acidification with a solution of 1 N HCl up to a pH of approximately 3. The white precipitate was filtered off, washed with water until a neutral reaction was obtained on the washing water, and dried in a vacuum oven at 80°C overnight. Recrystallized from DMA/water (2/1) it gave a m.p. of 365°C (d). Yield was 85%. Anal. calcd for $C_{15}H_9SNO_4$ (299.30): C, 60.30; H, 3.03; N, 4.68; S, 10.71. Found: C, 60.21; H, 3.15; N, 4.72; S, 10.45.

5-(2-Benzothiazolyl)isophthaloyl chloride (3)

This was prepared by refluxing **2** with a 10-fold molar excess of thionyl chloride for 5 h. Once the excess of thionyl chloride was distilled off, toluene was added until the solid residue was dissolved. Then, the solution was concentrated at low pressure to dryness. The diacid chloride was purified by recrystallization from chloroform, followed by sublimation. The m.p. was 172–173°C. Anal. calcd for $C_{15}H_7SNO_2Cl_2$: C, 53.59; H, 2.10; N, 4.17; S, 9.54; Cl, 21.09. Found: C, 53.47; H, 2.14; N, 4.32; S, 9.41; Cl, 20.89.

Polymer synthesis

The general procedure consisted of adding portionwise 20 mmol of **3** into a stirred solution of 20 mmol of diamine in 40 ml DMA at 0°C. The mixture was allowed to react under nitrogen for 1 h, and then the temperature was raised to 20°C, the reaction proceeding for 2 h. Then the solution was cooled to 0°C and a small excess of **3** (0.2 mmol) was added, cooling was discontinued and the reaction was stopped after 2 h at room temperature. The polymer solution was poured into distilled water and the polymer was washed with water and acetone several times and finally dried in a vacuum oven at 100°C overnight. Yields over 97% were obtained.

Measurements

Microanalyses were carried out by the Analysis Service of the Centro Nacional de Química Orgánica, Madrid.

^1H and ^{13}C n.m.r. spectra were recorded on a Varian Unity 500 spectrometer at 499.843 and 125.697 MHz respectively, using deuterated dimethylsulfoxide (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, 2366.4 Hz; and data size, 64 000. 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; and data size, 64 000. Heteronuclear two-dimensional (2D) shift correlated spectra were performed with the following conditions: $^1J(C\text{–}H) = 150$ Hz; spectral width in ^{13}C dimension, 3750 Hz; spectral width in ^1H dimension ± 525 Hz; number of experiments 256; and 512×1024 points for the data table.

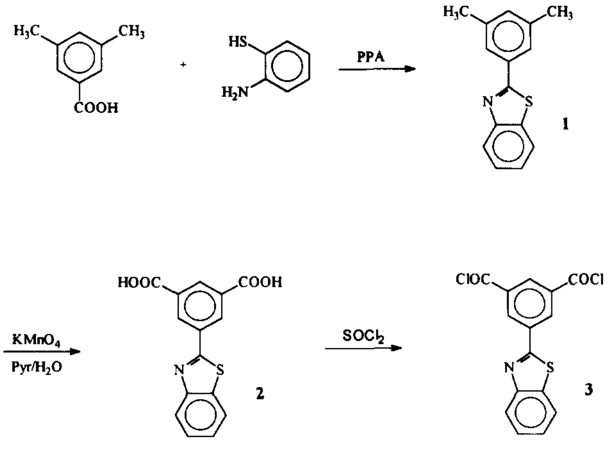
Viscosities were measured on 0.5% *N*-methyl-2-pyrrolidone solutions at 30 ± 0.1°C in an Ubbelohde viscometer. Differential scanning calorimetry (d.s.c.) and thermogravimetric analyses (t.g.a.) were made with Perkin–Elmer analysers DSC-7 and TGA-7, respectively. All the samples were tested under nitrogen at a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

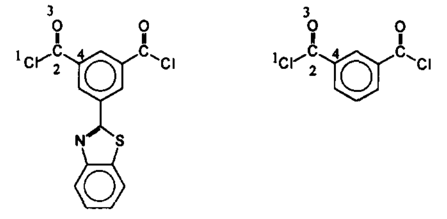
The monomer for the synthesis of benzothiazole-containing PIPAs was synthesized from 2-aminophenol and 3,5-dimethylbenzoic acid according to the synthetic route depicted in *Scheme 1*. The three steps of the monomer synthesis are high-yield reactions, so that **3** could be prepared in considerable amounts. The method is a variation of the route described by Tsai and Arnold for the synthesis of benzothiazolylterephthalic acid[10].

Parallel to the synthesis and purification of the monomer, we made an estimate of its structural characteristics. We were mainly interested in the reactivity of the functional groups, and in the influence of the molecular geometry on the accessibility of the nucleophiles to the functional groups of **3** involved in the polyamidation reaction. For this purpose, AM1[14] molecular-orbital calculations were carried out using the MOPAC[15] program. The method yielded the results shown in *Figure 1*.

From the data of AM1 calculations, it could be confirmed that the electronic charge on carbonyl carbons is very close to the charges of isophthaloyl chloride. This means that electronic effects are favourable, and that the monomer **3** will behave, in principle, as reactive against diamines as isophthaloyl chloride is, provided steric effects do not negatively influence the reactivity.

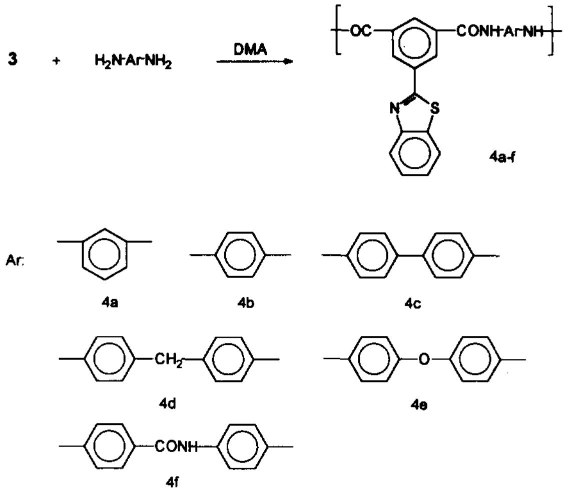


Scheme 1 Synthesis of 5-(2-benzothiazolyl)isophthaloyl chloride (3)



Q_1 : -0.079	Q_1 : -0.087
Q_2 : 0.283	Q_2 : 0.284
Q_3 : -0.239	Q_3 : -0.239
Q_4 : -0.164	Q_4 : -0.163
$d_{1\text{-}2}$: 1.738 Å	$d_{1\text{-}2}$: 1.740 Å
$d_{2\text{-}3}$: 1.228 Å	$d_{2\text{-}3}$: 1.228 Å
$d_{2\text{-}4}$: 1.475 Å	$d_{2\text{-}4}$: 1.473 Å

Figure 1 Bond distances and atomic charges of isophthaloyl chloride (right) and compound 3 (left), calculated by AM1



Scheme 2 Structure of the series of modified polyisophthalamides

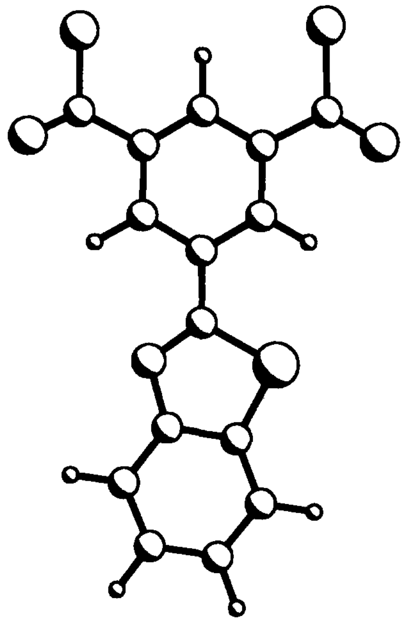


Figure 2 Optimized (AM1) geometry of 5-(2-benzothiazolyl)isophthaloyl chloride

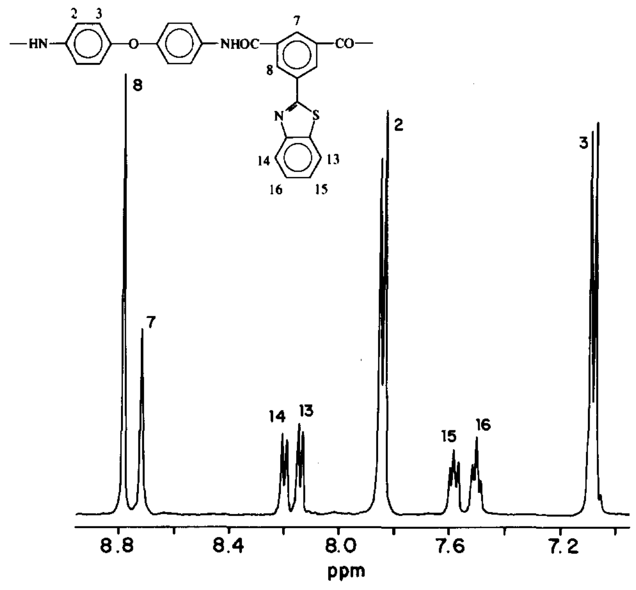


Figure 3 ^{1}H n.m.r. spectrum of polymer **4e**

The presence of a voluminous pendent group could affect the reactivity to some extent because of steric hindrance. A lowering of the reactivity of 5-substituted isophthaloyl chloride, compared to isophthaloyl chloride, has been observed for the case of phenylsulfonyl pendent groups[16]. However, here, the rigid-rod structure of compound 3 does not seem to cause a significant steric hindrance on the carbonyl groups. In fact, a value of 6° was calculated for the dihedral angle formed by the planes of the isophthaloyl ring and the benzothiazole ring, indicating that there is no interaction that makes the benzothiazole ring deviate significantly from the planar conformation (see *Figure 2*).

A series of modified PIPAs were prepared from monomer 3 and six aromatic diamines by the solution polycondensation method at low temperature in *N*,*N*-dimethylacetamide (DMA) (*Scheme 2*). Yields and inherent viscosities are listed in *Table 1* along with elemental analyses. High yields were obtained in every case, and inherent viscosities in the range 0.42–1.12 dl g^{-1} were measured. Although very high viscosities were not obtained for all of them, the polymers always formed tough transparent films when cast from solutions in DMA. These results confirmed that the presence of the benzothiazole groups, strongly electron-withdrawing, in the 5 position of the isophthaloyl moiety, does not impair the reactivity of the chlorocarbonyl groups towards aromatic diamines.

A first characterization of the chemical structure was made by n.m.r. spectroscopy. The ^{1}H spectrum of polymer **4e** is shown in *Figure 3*. The spectrum could be assigned easily except for the systems formed by the protons 13–14 and 15–16 whose assignments can be interchanged.

According to spectroscopic tables[17], the peak at 8.14 ppm should correspond to proton 13 while that at 8.20 ppm should correspond to proton 14. However, this assignment is contradictory with that reported by Hedrick[18]. From the coupling constants, it could be deduced that the proton that appeared at 7.50 ppm was near that appearing at 8.20 ppm, while the one appearing

Table 1 Synthesis of modified polyisophthalamides

Polymer	Yield (%)	η_{inh} (dl g^{-1})	Repeat unit M_w		Analysis (%) C	H	N	S
4a	Quant.	0.44	371.41	Calc.	67.91	3.53	11.31	8.63
				Found	67.73	3.55	11.18	8.11
4b	98	0.53	371.41	Calc.	67.91	3.53	11.31	8.63
				Found	67.11	3.72	11.23	8.37
4c	97	0.42	447.51	Calc.	72.47	3.83	9.39	7.16
				Found	70.89	3.88	9.42	7.17
4d	98	0.52	461.54	Calc.	72.87	4.15	9.10	6.95
				Found	72.17	4.08	9.32	6.67
4e	98	0.68	463.51	Calc.	69.97	3.70	9.07	6.92
				Found	68.81	3.75	9.27	6.52
4f	Quant.	1.12	490.54	Calc.	68.56	3.70	11.42	6.54
				Found	67.94	3.75	11.40	6.29

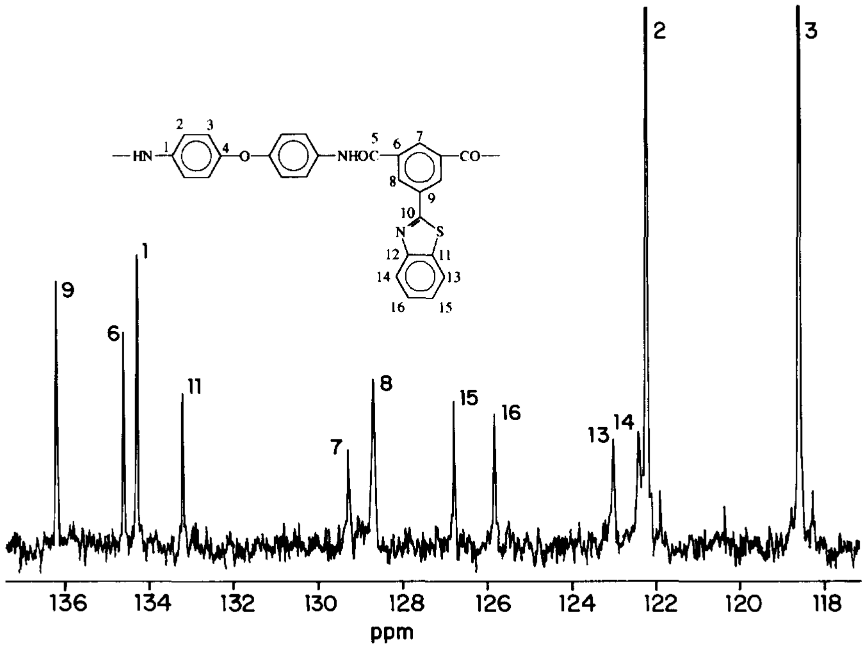


Figure 4 ^{13}C n.m.r. spectrum of polymer **4e**

at 7.58 was coupled with that of 8.14 ppm. The strong electron-withdrawing effect of the benzothiazole group could be clearly observed from the chemical shift of protons 7, and still more noticeably from protons 8. A comparison with the spectrum of the polymer IPADDE*, without pendent groups, showed a downfield shift of 0.65 ppm for protons 8, and of 0.20 ppm for protons 7. The ^{13}C spectrum of the same polymer (*Figure 4*) is complicated, with 16 different peaks, some of which could not be directly assigned. In addition, the peaks that appeared in the region 122–130 ppm were clearly broadened with respect to the other peaks of the spectrum.

From a heteronuclear correlation ^{1}H–^{13}C (*Figure 5*), the carbons with broadened signals, in the region 122–130 ppm, could be assigned as protonated carbons. Again, there is contradictory information regarding these carbons[19,20] and the assignments of 13–14 and 15–16 can be reversed. However, a tentative assignment could be made, which is shown in *Figure 4*. The peaks in the region 133–136 ppm had to be assigned to carbons 1, 6, 9 and 11. Although a tentative assignment could be made again (see *Figure 4*), the small chemical-shift differences

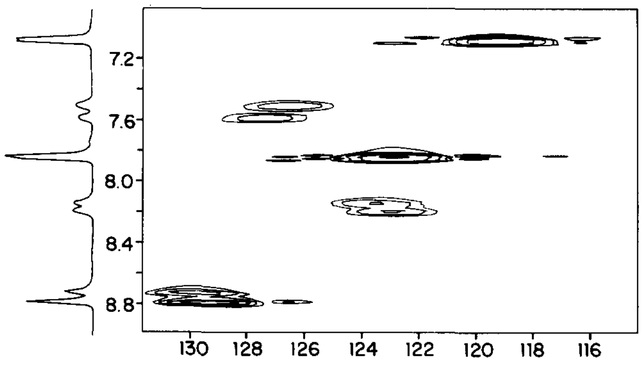


Figure 5 Heteronuclear correlation (^{1}H–^{13}C) spectrum of polymer **4e**

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* IPADDE = poly(4,4′-oxydiphenyleneisophthalamide)

and the fact that all of them are quaternary carbons did not allow a certain assignment.

The broadening that was observed in all the protonated carbons of the diacid moiety did not appear in the spectrum of the 5-(2-benzothiazolyl)isophthalic acid. Therefore, we consider that it should be attributed to the low mobility of the polymer chain. This is consistent with the fact that the protonated carbons in the isophthalic moiety of the reference unmodified polymer also appeared broadened. The electron-withdrawing effect of the benzothiazolyl group also can be observed in the chemical shift of carbon 9, where a strong deshielding (9.2 ppm) is observed with respect to the reference unmodified polymer.

The chain separation effect attributable to the bulky pendent groups accounted for the enhanced solubility developed by the modified PIPAs relative to the solubility of the unmodified counterparts. Indeed, remarkable improvements of solubility in solvents such as *m*-cresol and dimethylformamide (DMF) could be observed (*Table 2*). So, it seems that the presence of the pendent benzoxazole groups does provide a lowering in the density of the interchain secondary bonds, which brings about an enhancement of the solubility.

The thermal properties were investigated by d.s.c. and t.g.a. By d.s.c., a wide endotherm appeared between 100 and 200°C in the first run in every case. This is due to the loss of water associated with PIPAs, and, therefore, two runs were needed to obtain neat d.s.c. traces, as shown in the example of *Figure 6* for polymer **4b**. Neither crystallization exotherms nor melting endotherms were detected between 50 and 400°C. The values of T_g listed in *Table 2* confirm that the introduction of pendent benzothiazole rings caused an average increase of about 25°C in T_g compared to that of the parent PIPAs, which supports the preliminary assumption regarding the beneficial effect of the pendent heterocycles on the thermal transitions of aromatic polyamides. Also the nature of the diamine moiety played a significant role on the T_g values. These went down in the series **4c** > **4b** > **4f** > **4a** > **4e** > **4d**. The same trend or similar one has been observed previously by us and other authors[1,16,21].

Table 2 Properties of polyisophthalamides[a]

Polymer	Solubility[b]		T_g (°C)	T_d[c] (°C)
	DMF	*m*-Cresol		
4a	+ (+)	+ + (−)	306 (276)	480 (450)
4b	+ (−)	+ − (−)	322 (295)	480 (470)
4c	+ + (−)	+ − (−)	336 (303)	485 (460)
4d	+ + (+ +)	+ + (−)	284 (264)	445 (430)
4e	+ + (+ +)	+ + (−)	292 (267)	475 (445)
4f	+ + (+ +)	+ − (−)	312	460

[a] Figures in parentheses are the values of the reference unmodified PIPAs

[b] + +, Soluble at room temperature; +, soluble in hot; + −, partially soluble or swollen; −, insoluble

[c] T_d = Onset of initial weight loss

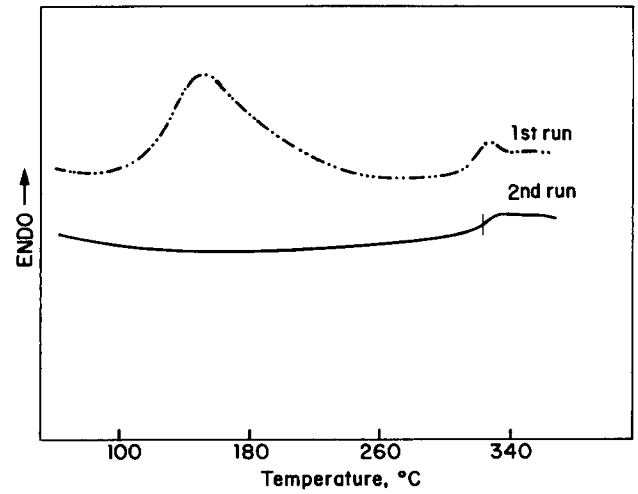

Figure 6 D.s.c. thermograms of polymer **4b**

The enhancement of the thermal behaviour was also evident when the thermal resistance was evaluated by t.g.a. As was observed for T_g values, the initial decomposition temperatures (T_d) of the new PIPAs in a nitrogen atmosphere were higher than the T_d values of the homologous reference polymers. Differences of 20–25°C could be measured (*Table 2*).

It had been previously reported that, if the pendent groups did not have thermal stability equal to or greater than that of the aromatic amide groups, homolytic scission processes lead to the loss of the pendent substituents at temperatures below the T_d of reference PIPAs[1,22]. Thus, the current results allow us to state that the thermal stability of the pendent groups, and particularly the dissociation energy of the C_{Ar}–C_{Ar} bond that holds the hetero ring joined to the isophthaloyl moiety, is very high; in any case it is equal to or higher than the bonds involved in the main-chain amide linkages. The measured improvement of the T_d values is, however, difficult to explain if only bond dissociation energies are considered, as the bond strength of the main-chain linkages are expected not to be modified by the presence of the side hetero rings. Nevertheless, these results agree with early results published on the thermal resistance of PIPAs with phthalimide pendent groups[4].

CONCLUSION

By a favourable high-yield synthetic route, a new polycondensation monomer, 5-(2-benzothiazolyl)isophthaloyl chloride (**3**), has been synthesized, and its reactivity against nucleophiles has been calculated by semiempirical methods. These results have confirmed that monomer **3** is as good a polycondensation monomer as isophthaloyl chloride. Experimentally it has been proved that high-molecular-weight (high-inherent-viscosity) PIPAs with benzothiazole pendent groups can be obtained by the polycondensation of **3** with aromatic diamines.

The presence of the pendent bulky hetero rings greatly affected the spectroscopic characteristics and the general properties of these polymers, compared to those of the unmodified PIPAs. Better solubilities and higher T_g values were measured for the modified polymers. The gain of 20–25°C in the T_g values qualifies the current modified PIPAs among the aromatic polyamides based on isophthalic acid with highest T_g described so far. Moreover, the thermal resistance as measured by t.g.a. is also better than that of the reference PIPAs.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support provided by the CICYT (Mat. 198/92). A. E. L. is indebted to the Spanish Science and Education Ministry for providing a post-doctoral grant. J. P. is indebted to DARPA for support of a portion of the work, which was administered by the Office of Naval Research under Contract N0014-88-C-0672. We wish to thank also Dr M. L. Jimeno for her help in executing heteronuclear 2D n.m.r. spectra.

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