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Synthesis and characterization of random poly(amide-sulfonamide)s: 3. Copolymers from two diamino monomers

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Four new series of poly(amide-sulfonamide)s (PASAs), having different ratios of two different diamino monomer moieties in the polymer backbone, were obtained by low-temperature solution polycondensation of the respective diamines with terephthaloyl chloride/isophthaloyl chloride. With the exception of the most highly symmetric polymer series, all of the other polymers were readily soluble in aprotic polar solvents such as *N*,*N*-dimethylacetamide, dimethylformamide and dimethyl sulfoxide. The three series of soluble polymers had intrinsic viscosities in the ranges 0.51–0.72, 0.33–0.49 and 0.70–0.92 dl g^{-1}. Differential scanning calorimetry showed these PASAs to have glass transition temperatures greater than 250°C. Thermogravimetric analysis of the polymers showed moderate thermal stabilities, with 10% weight losses being recorded over the range 382–408°C. X-ray diffraction studies indicated that some of these polymers possess a certain degree of crystallinity.

(Keywords: poly(amide-sulfonamide)s; membrane materials, random polymers)

INTRODUCTION

Membrane technology represents one of the most effective and energy-saving ways to a wide range of separation processes, including reverse osmosis (RO)[1]. Although many areas of membrane technology have achieved commercial success, as reviewed by the US Department of Energy in ref. 2, the demand for the development of solvent and/or chemical resistant selective membranes for a variety of applications is still of high priority. In the search for new polymeric materials from membrane applications, we have focused on the molecular design and synthesis of poly(amide-sulfonamide)s (PASAs). Since polyamides and polysulfonamides are both film-forming materials, PASAs containing both amide and sulfonamide linkages in their molecular backbones should have good potential for membrane applications. However, to date PASAs have not been extensively studied[3,4]. Recently, we have reported the facile preparation of the series of new diamine monomers **1a**–**1g** shown in *Figure 1*[5]. Film-forming PASAs were subsequently obtained by polymerization reactions with terephthaloyl or isophthaloyl chloride. Preliminary studies revealed that some of these polymers have good RO properties[5]. In order to achieve some insight into the relationship between chemical structure and RO properties, i.e. salt rejection and water flux, we have carried out a programme to synthesize and characterize various series of copolymers deriving from the diamino monomers **1a**, **1b**, and **1c**. By systematically controlling the relative amounts of the two different diamino monomers in the polymerization reaction with terephthaloyl or isophthaloyl chloride, several new series of structurally similar PASAs were prepared. These materials provided an ideal opportunity to study the relationship between the polymer structures and their RO behaviour, as well as various other properties. These findings could in turn give opportunities for the chemical design of viable RO membrane materials. The objective of this present work was the synthesis and characterization of four new structurally similar PASA copolymer series.

EXPERIMENTAL

Diamino monomers

The syntheses of the diamino monomers **1a**–**1g** (*Figure 1*) have been described elsewhere[5]. Gram quantities of these monomers can be obtained via a two-step synthetic procedure starting from *p*-acetamidobenzenesulfonyl chloride[4].

Polymer syntheses

The following experimental procedure is representative of the general method used for the preparation of the PASAs.

In a 50 ml round-bottomed flask equipped with a drying tube, 0.3657 g (0.95 mmol) of monomer **1c** and

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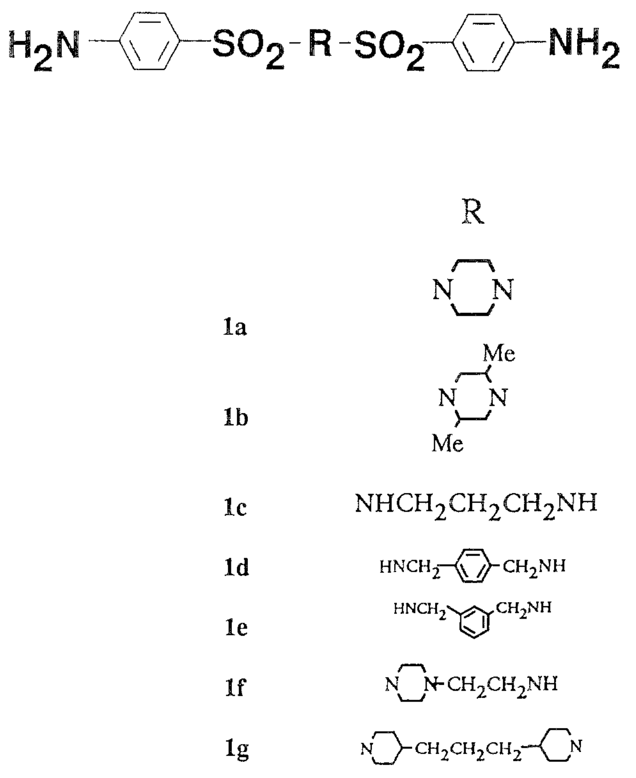

Figure 1 Structure of the series of diamino monomers **1a**–**1g**

3.6343 g (3.81 mmol) of monomer **1b** were dissolved in 80 ml of dry *N*,*N*-dimethylacetamide (DMAc). The mixture was then cooled down to −17°C by the use of a bath containing a mixture of acetone and liquid nitrogen, and 1.9336 g (9.52 mmol) of solid terephthaloyl chloride was added to the solution while stirring at low temperature. After all of the terephthaloyl chloride had dissolved, the mixture was stirred at room temperature for 45 min. Then 1.5067 g (19.05 mmol) of pyridine was added to the solution in order to neutralize the acid produced, and the mixture was stirred for a further 2 h. The resulting polymer was separated by pouring the reaction mixture into 1 l of cold water and was then collected by filtration. The product was washed with water and methanol, and finally dried in a vacuum oven. In this particular case, after drying, 5.11 g of polymer **4b** was obtained as a white solid (yield = 97.5%). other copolymers were prepared under similar conditions using different ratios of the various diamino monomers with terephthaloyl or isophthaloyl chloride.

General characterization

Infra-red (i.r.) spectra were recorded on a Hitachi 270-30 spectrophotometer. ^1H n.m.r. spectra were measured in DMSO-d_6 with a Joel JNM-EX270 spectrometer (270 MHz for ^1H). Differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.) were carried out by using a Shimadzu differential scanning calorimeter DSC-50 equipped with an LTC-50 cooling unit, and a TGA-40 thermal gravimetric analyzer, respectively. Wide-angle X-ray diffraction patterns were obtained at room temperature on a Rigaku D-MAX apparatus using nickel-filtered CuKα radiation (40 kV, 40 mA). Viscosity measurements were carried out using an Ubbelohde-type capillary viscometer.

Polymer characterization

Spectroscopic studies. Each of the new polymers was characterized by i.r. and high-field ^1H n.m.r. spectroscopic methods.

Solubilities. The solubilities of the polymers (0.1 g) were determined at room temperature (20°C) in a wide variety of common organic solvents (5 ml). The solutions were shaken vigorously and if the polymers failed to dissolve the mixtures were then warmed in a hot-water bath in order to achieve complete dissolution.

Viscosities. The viscosities of the polymers in DMAc or concentrated sulfuric acid were measured in an Ubbelodhe-type capillary viscometer. For a good solvent, the following equation, derived from the Huggins and Kraemer equation, was used to calculate the intrinsic viscosities [η]s of the polymers[6]:

$$[\eta] = \frac{1}{c}\sqrt{2(\eta_{sp} - \ln \eta_r)}$$

where c is the concentration and η_{sp} and η_r are the specific viscosity and relative viscosity, respectively.

Thermal characterization. Approximately 3 mg of each of the PASAs (in the form of amorphous powders) were subjected to d.s.c., at a heating rate of 10°C min^{-1}, over the temperature range from −50° to 300°C. The thermal stabilities of the polymers were examined by t.g.a., with experiments being carried out on ~ 8 mg of sample at a heating rate of 10°C min^{-1}, up to a temperature of 600°C.

Crystallinities. Wide-angle X-ray diffraction (WAXD) data were obtained on polymer thin films which had been prepared from dilute DMAc solutions of the polymers.

RESULTS AND DISCUSSION

Polymer synthesis

By using the low-temperature solution polymerization technique, four series of polymers (i.e. **2**–**5**), containing a total of 20 PASAs, were obtained in excellent yields (> 95%). In contrast to our previous investigations[4], the purities of the diamino monomers have been greatly improved by using a reprecipitation technique[5]. As a result, and without too much effort involved in optimizing the polymerization conditions, polymers of good strength were obtained by reacting equal mole ratios of the various diamino monomers with terephthaloyl and isophthaloyl chlorides in DMAc (*Table 1*).

Polymer characterization

I.r. and ^1H n.m.r. spectroscopy. I.r. spectra of the polymer samples were measured using polymer films. For all of the PASA films, the characteristic peaks for the amide carbonyl, and the symmetric and asymmetric sulfonamide stretching modes, were observed at 1666, 1154 and 1322 cm^{-1}, respectively. As expected, the i.r. spectra of the polymers within a specific copolymer series were very similar, exhibiting the same number of peaks but with slight differences in intensity. For those polymers which are soluble in dimethyl sulfoxide (DMSO)

Table 1 Synthesis of poly(amide-sulfonamide)s

Polymer	Diamino monomers (ratio)	Chloride[a]	Yield (%)	$[\eta]_{\text{intrinsic}}$[b] ($\text{dl g}^{-1}$)
2a	**1a**:**1c** (1:0)	A	98.2	1.04
2b	**1a**:**1c** (9:1)	A	98.2	0.51
2c	**1a**:**1c** (8:2)	A	99.0	0.52
2d	**1a**:**1c** (7:3)	A	98.7	0.61
2e	**1a**:**1c** (6:4)	A	99.2	0.56
2f	**1a**:**1c** (5:5)	A	99.1	0.72
3a	**1a**:**1c** (1:0)	B	95.0	0.24[c]
3b	**1a**:**1c** (9:1)	B	95.1	0.072[c]
3c	**1a**:**1c** (8:2)	B	96.2	0.104[c]
3d	**1a**:**1c** (7:3)	B	95.5	0.194[c]
3e	**1a**:**1c** (6:4)	B	98.3	0.122[c]
3f	**1a**:**1c** (5:5)	B	97.1	0.150[c]
4a	**1b**:**1c** (1:0)	A	98.5	1.07
4b	**1b**:**1c** (9:1)	A	97.3	0.44
4c	**1b**:**1c** (8:2)	A	98.1	0.36
4d	**1b**:**1c** (7:3)	A	98.5	0.48
4e	**1b**:**1c** (6:4)	A	99.2	0.49
4f	**1b**:**1c** (5:5)	A	99.3	0.33
5a	**1b**:**1c** (1:0)	B	97.8	0.89
5b	**1b**:**1c** (9:1)	B	97.5	0.91
5c	**1b**:**1c** (8:2)	B	98.5	0.79
5d	**1b**:**1c** (7:3)	B	99.0	0.92
5e	**1b**:**1c** (6:4)	B	99.0	0.70
5f	**1b**:**1c** (5:5)	B	99.5	0.75

[a] A = terephthaloyl chloride; B = isophthaloyl chloride

[b] Intrinsic viscosity in DMAc solution at 25.00 ± 0.05°C

[c] Intrinsic viscosity in concentrated sulfuric acid at 25.00 ± 0.05°C

(i.e. series **2**, **4** and **5**) the materials were adequately characterized by using ^{1}H n.m.r. spectroscopy. Typical spectra of the polymers together with selected signal assignments, are shown in *Figure 2*. The compositions of the various copolymers, with respect to the relative amounts of the two different monomer units, could be estimated from the relative intensities of the selected signals of the two diamino subunits. Within the accuracy of the spectroscopic method, the composition of selected polymer samples was found to be close to the respective feed compositions (*Table 2*). Therefore, it is reasonable to assume that the reactivities of the different diamino monomers in these polymerization reactions are similar. Furthermore, we would expect random copolymers to be produced in these experiments.

Solubilities. As found for the parent polymers, all of the copolymers produced in this work, with the exception of those of series **3**, were very soluble in polar aprotic solvents such as dimethylformamide (DMF), DMAc and DMSO (*Table 3*). Polymer films and membranes could be conveniently made from DMAc solutions of the polymers. Members of the copolymer series **3** are insoluble in all of the common aprotic polar solvents. Introduction of the diamino monomer **1c** into the backbone of the highly symmetrical polymer **3a** did not alter the close packing of the polymer chain in such a way that solubility was improved. On the other hand, all of the PASAs are soluble in concentrated sulfuric acid. However, the viscosities of sulfuric acid solutions of the polymers gradually decreased on standing, indicating that decomposition of the polymers occurred under the influence of a strong acidic medium.

Viscosities. Based on ^{1}H n.m.r. spectroscopic data and solubility studies of the polymers, it is reasonable to assume that the polymers had very similar molecular weights. Using this assumption, the viscosities of the various PASAs correlate well with their chemical structures. In general, copolymers which consist of more symmetric moieties, such as the terephthaloyl and piperazine groups, have higher viscosities. It is not a surprise therefore to observe that the viscosities of members of copolymer series **5** are greater than those of series **2**, which are in turn greater than those of series **4**. Because of the insolubility of the series **3** copolymer in DMAc, direct comparison of their viscosities with the other copolymers is not possible. Within the same copolymer series, the viscosities are comparable. Polymer series **2**, **4** and **5** have intrinsic viscosities of 0.51–0.72, 0.33–0.49 and 0.70–0.92 dl g^{-1}, respectively. We were also pleased to find that most of them are tough enough (i.e. $[\eta]_{\text{intrinsic}} > 0.4$) for the fabrication of polymer membranes.

Thermal characterization. The thermal behaviour of the PASAs was evaluated by means of differential scanning calorimetry and thermogravimetric analysis. Particular attention was paid to the behaviour variation within each of the copolymer series. For comparison purpose, the d.s.c. thermograms, over the temperature range from −50 to 300°C, obtained for the polymers **4b**–**4f** and **5b**–**5f** are displayed in *Figure 3*. The thermograms all show an exothermic peak, extending from 30 to 120°C, due to loss of water (including both absorbed and weakly bonded species). Close examination of the thermograms indicated that the glass transition temperatures (T_gs) of

Table 2 Estimation of copolymer composition from the corresponding ^{1}H n.m.r. spectroscopic data

Copolymer	Intensity of selected signals			Polymer composition	Feed composition
	$\delta = 0.83$(d)	$\delta = 1.55$(t)	$\delta = 10.88$(s)	**1a** or **1b**:**1c**	**1a** or **1b**:**1c**
2d	0.247	–	0.632	7.7:3	7:3
4b	2.00	0.070	–	9.5:1	9:1
4c	2.00	0.162	–	8.2:2	8:2
4d	2.00	0.264	–	7.5:3	7:3
4e	2.00	0.414	–	6.4:4	6:4
4f	2.00	0.618	–	5.3:5	5:5
5d	2.00	0.280	–	7.2:3	7:3

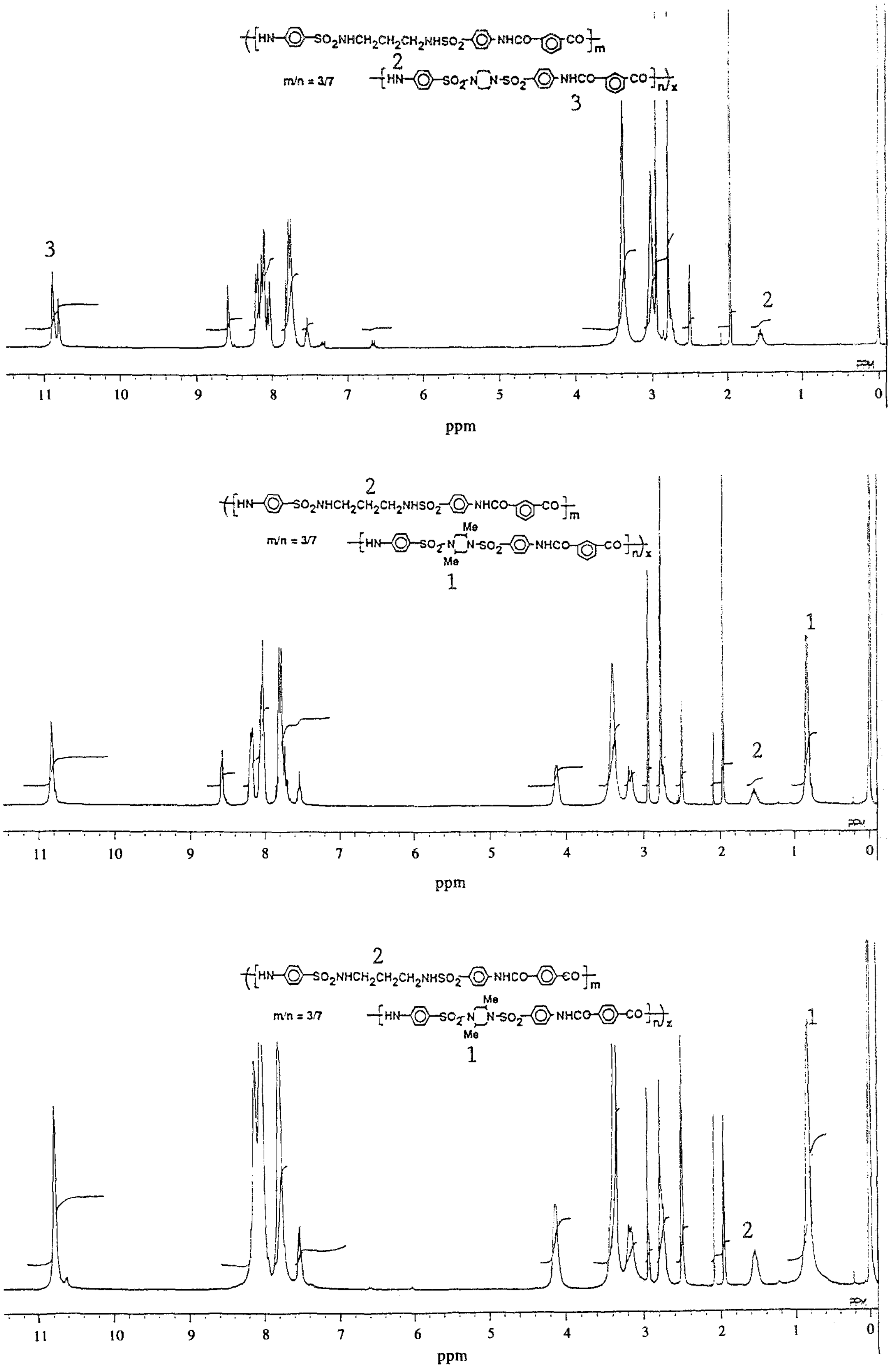

Figure 2 ^{1}H n.m.r. spectra of copolymers **2d**, **4d** and **5d** in DMSO-d_6; *represents peaks from residual DMAc

Table 3 Solubility of the poly(amide-sulfonamide)s[a]

	Solvent[b]						
Polymer	Acetone	Methanol	Ethyl acetate	Methylene chloride	DMF	DMAc	DMSO
2a	–	–	–	–	+	+	+
2b	–	–	–	–	+	+	+
2c	–	–	–	–	+	+	+
2d	–	–	–	–	+	+	+
2e	–	–	–	–	+	+	+
2f	–	–	–	–	+	+	+
3a	–	–	–	–	–	–	–
3b	–	–	–	–	–	–	–
3c	–	–	–	–	–	–	–
3d	–	–	–	–	–	–	–
3e	–	–	–	–	–	–	–
3f	–	–	–	–	–	–	–
4a	–	–	–	–	+	+	+
4b	–	–	–	–	+	+	+
4c	–	–	–	–	+	+	+
4d	–	–	–	–	+	+	+
4e	–	–	–	–	+	+	+
4f	–	–	–	–	+	+	+
4g	–	–	–	–	+	+	+
5a	–	–	–	–	+	+	+
5b	–	–	–	–	+	+	+
5c	–	–	–	–	+	+	+
5d	–	–	–	–	+	+	+
5e	–	–	–	–	+	+	+
5f	–	–	–	–	+	+	+

[a] (+) Soluble at room temperature; (–) insoluble

[b] All polymers are soluble in concentrated H_2SO_4

the polymer series **3a**–**3f** are likely to be above 300°C, as a result of their high rigidities (*Table 4*). The rigidity of the molecules could be reduced by substituting isophthaloyl chloride with terephthaloyl chloride or piperazine with the less compact 2,5-dimethylpiperazine in the polymer backbone. Significantly lower T_g values were observed from these structural variations. However, for series **2** and **4**, fluctuations in the T_g values were observed when changing the ratio of the two diamino monomers. In contrast, a gradual decrease in the T_g was observed for the polymer series **5** (see *Figure 3*) by increasing the relative amount of **1c** in the composition. The weight loss below 120°C from t.g.a. studies shows water contents for the individual ppolymers from 1.7 to 7.7%. Since all of the polymer samples were dried at 70°C for 24 h in a vacuum oven prior to the measurements, these percentage weight losses below 120°C should provide a good estimation of the relative hydrophilicity of the different PASAs. The polymers have good thermal stabilities, as indicated by the reasonably high temperatures recorded (> 380°C) before a 10% weight loss occurs. A set of typical thermograms of the series **5** copolymers is shown in *Figure 4*.

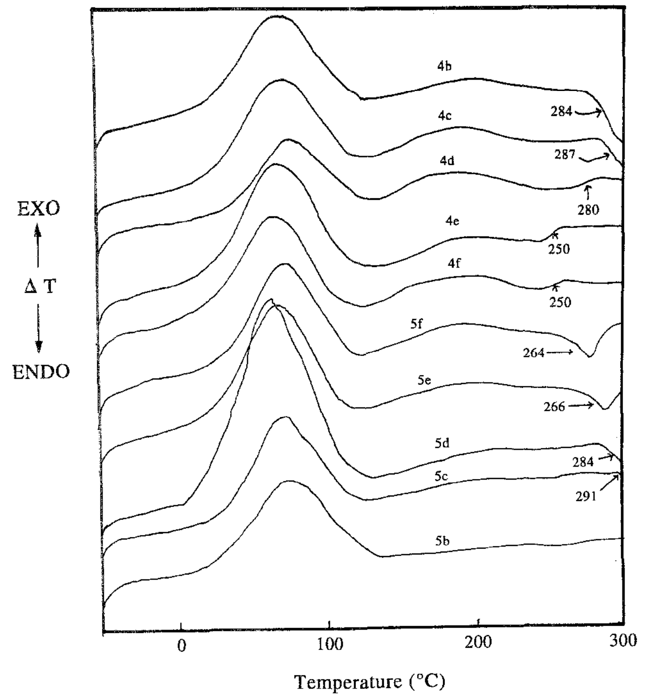

Figure 3 D.s.c. curves obtained for members of the PASA series **4** and **5** over the range from –50 to 300°C

X-ray diffraction studies. The relationship between the extent of copolymerization and the degree of crystallinity for the PASA series **2**, **4** and **5** was investigated by

Table 4 Thermal properties of the poly(amide-sulfonamide)s

Polymer	Wt loss before 120°C (%)[a]	10% Wt loss[a] (°C)	*RW* at 600°C[a,b] (%)	T_g[c] (°C)
2a	5.3	390	40.3	–
2b	6.0	387	44.1	279
2c	5.0	382	43.8	–
2d	6.5	392	43.9	255
2e	4.9	382	42.6	256
2f	4.8	391	38.1	259
3a	3.2	394	38.7	–
3b	3.6	397	42.3	–
3c	2.3	406	44.7	–
3d	1.7	408	41.8	–
3e	4.8	405	40.4	–
3f	3.5	417	40.8	–
4a	4.2	388	45.8	–
4b	5.3	406	41.9	284
4c	3.9	383	54.5	288
4d	4.8	390	48.8	280
4e	6.7	383	50.0	250
4f	3.8	402	46.0	250
5a	5.9	408	41.4	–
5b	5.4	407	47.6	–
5c	6.0	393	40.1	291
5d	7.7	388	36.5	284
5e	5.6	383	39.8	266
5f	7.1	378	31.5	264

[a] Measured by t.g.a. under a nitrogen atmosphere at a heating rate of 10°C min^{-1}

[b] *RW* = residual weight

[c] Determined by d.s.c. up to 300°C at a heating rate of 10°C min^{-1}

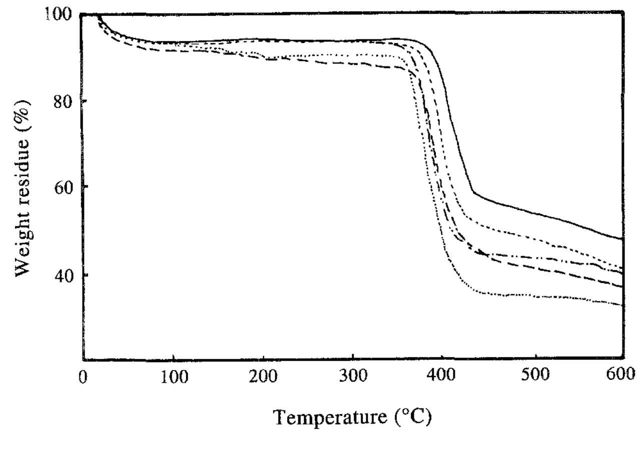

Figure 4 T.g.a. curves obtained for members of the PASA series **5** at a heating rate of 10°C min^{-1}: (- - -) **5b**; (. . . .) **5c**; (— — —) **5d**; (— ·· — ·· —) **5e**; (. . . . .) **5f**

X-ray (2θ = 5–40°C). The results obtained are shown in *Figure 5*. In general, most of the polymers showed a reasonable degree of crystallinity, with only a few of them being completely amorphous. However, no simple relationship between the degree of crystallinity and the polymer composition was observed. Most of the polymers of series **2** and **4** exhibited two strong peaks at around 9 and 17°.

CONCLUSIONS

Four series of random poly(amide-sulfonamide)s have been prepared from the reaction of terephthaloyl chloride/isophthaloyl chloride with different ratios of two diamino monomers in DMAc, by using low-temperature solution polymerization reactions. They were adequately characterized by a wide range of spectroscopic and physical methods. Most of the copolymers had intrinsic viscosities greater than 0.4 dl g^{-1} and showed good potential for use as membrane materials. A study of the reverse osmosis properties of these new materials is now underway.

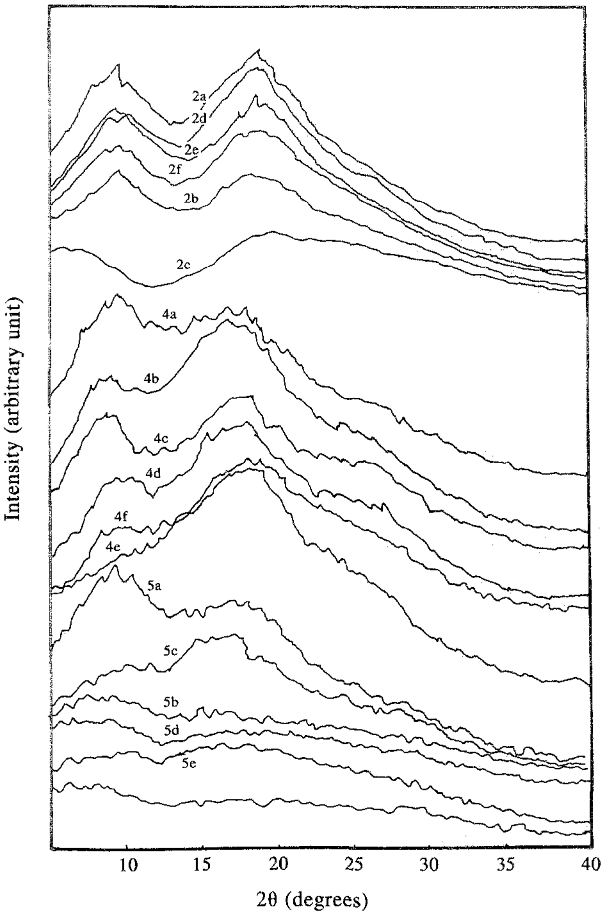

Figure 5 X-ray diffraction diagrams obtained for members of the PASA series **2**, **4** and **5**

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