Synthesis, Characterization, and Pervaporation Performance of Random Copolymers of Poly(amidesulfonamide)s (PASAs)

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ABSTRACT: Stimulated by the outstanding membrane properties of poly(amidesulfonamide)s (PASAs), 2 series of copolymers were synthesized by low-temperature solution polycondensation of either the diamino monomer *N,N'*-bis(4-aminophenylsulfonyl)piperazine (**1A**) or *N,N'*-bis(4-aminophenylsulfonyl)-2,5-dimethylpiperazine (**1B**) with a mixture of isophthaloyl and terephthaloyl chloride. All of these copolymers were adequately characterized by intrinsic viscosity measurements, infrared (IR) spectroscopy, ^{1}H and ^{13}C nuclear magnetic resonance, differential scanning calorimetry, thermogravimetric analysis, and wide-angle X-ray diffraction. The effects of various feed ratios of isophthaloyl–terephthaloyl chloride on the physical properties of the copolymers were investigated. In particular, the crystallinity of PASA copolymers was found to be trimmed down by copolymerizing diamino monomer **1A** or **1B** with increasing fraction of isophthaloyl chloride. It was envisioned that when the crystallinity of the PASA membranes decreased, permeation flux would be preferably increased at a minimum sacrifice of separation characteristics in the pervaporation process. Experimental findings, however, revealed that the resulting permeation flux and separation factor of pervaporation membranes derived from various copolymers were both within the same order of magnitude. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 47–60, 1998

Key words: poly(amidesulfonamide)s; membrane materials; pervaporation; random copolymers

INTRODUCTION

Membrane technology represents one of the most effective and energy saving means applicable to a wide range of separation processes, including reverse osmosis (RO), pervaporation, ultrafiltration, and gas separation.[1] Membrane materials play a vital role in all separation processes. Therefore, continuous development of new membrane materials with outstanding separation characteristics is crucial to sustain and expand the growth of membrane separation technology. In response to this research challenge, we have synthesized and characterized a new series of homopolymers and copolymers of poly(amidesulfonamide)s (PASAs).[2,3] They possess several desirable properties, as follows: high viscosity, capable of forming tough membranes; high chemical stabilities resistant to attack of strong acid and alkali; good thermal stabilities; and sufficient hydrophilicity, favoring the permeation of water flux. Furthermore, their applications in RO process were demonstrated.[4,5] To extend the use of this new material, we have recently reported the pervaporation properties of some selected PASAs in dehydration of alcohols.[6] A fairly high separation factor for preferential permeation of water
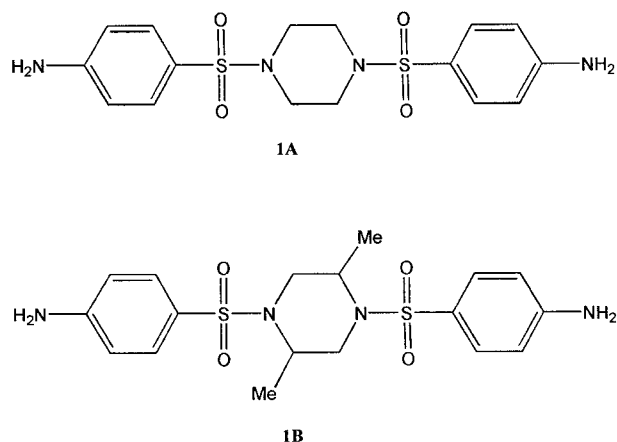
Figure 1 Structure of diaminomonomers **1A** and **1B**.

was observed when PASAs homopolymers were used as membrane barriers in the pervaporation separation of aqueous alcohol mixtures. In particular, homopolymers formed from diamino monomer **1A** or **1B** with isophthaloyl chloride demonstrated a reasonable balance of permeation flux and separation factor in dehydration of ethanol. However, all of the trial PASAs exhibit a permeation flux below 35 g m^{-2} h^{-1}. To have a real application prospect in pervaporation, the permeation flux through the membranes has yet to be further improved. For glassy polymers such as PASAs, pervaporation is believed to be a diffusion-controlled process.[7,8] One of the rational thoughts to increase the diffusivity of these materials is to trim down their degree of crystallinity. The present work represents our effort to achieve this goal by copolymerizing **1A** or **1B** with a mixture of terephthaloyl and isophthaloyl chlorides. The physical and spectroscopic properties of new materials in relation to their structure variations were investigated. The pervaporation performance of the materials in dehydration of ethanol was assessed.

EXPERIMENTAL

Diamino Monomers

The preparation of the diamino monomers **1A** and **1B** has been described elsewhere[2] (Fig. 1). They were purified by dissolving in minimum amount of hot dimethylformamide (DMF) and then reprecipitated in methanol prior to the use in polymerization.

Polymer Syntheses

The polymers were synthesized by the low-temperature polycondensation reaction. The following experimental procedure is representative of the general method used for the preparation of copolymers of PASAs.

A PASA copolymer of **A** series with 50% of isophthaloyl moiety was prepared by reacting N,N'-bis(4-aminophenylsulfonyl)piperazine (**1A**) with a phthaloyl chlorides mixture composed of isophthaloyl chloride and terephthaloyl chloride in a 1 : 1 molar ratio. The mixture was prepared by melting an equal weight of isophthaloyl and terephthaloyl chloride in a round-bottom flask under nitrogen atmosphere. Polymerization was carried out by dissolving 0.9739 g (2.46 mmol, 1 eq.) of diamino monomer **1A** in 15 mL of anhydrous N,N-dimethylacetamide (DMAc) in a 50-mL round-bottom flask equipped with a magnetic stirrer and a stopper. Slightly heating was required for complete dissolution. After cooling to room temperature, the solution was cooled to −17°C with an ice-salt bath. To this was added with stirring 0.4991 g (2.46 mmol, 1 eq.) of the 1 : 1 phthaloyl chloride mixture. 5 mL of anhydrous DMAc was used for rinsing. During polymerization, phthaloyl chlorides dissolved, and the viscosity of the polymer solution gradually increased. The reaction was kept at −17°C for 45 min. The liberated HCl was neutralized by adding 0.4 mL (2.46 mmol, 2 eq.) of pyridine after polymerization. The mixture was further stirred at room temperature for 1 h. The polymer was precipitated by dropping the polymer solution into large quantity of water. Threads of polymer were collected, washed, and soaked overnight in water until no more milky was observed. It was finally dried overnight in a vacuum oven at 80°C. The yield was found to be quantitative.

Polymer Characterization

Each of the copolymers was characterized by measuring its intrinsic viscosity, infrared (IR) spectroscopy, ^{1}H and ^{13}C nuclear magnetic resonance (NMR), wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). IR spectra of the copolymers were determined as polymer films on a Perkin–Elmer Paragon 1000PC Fourier transform infrared (FT IR) spectrometer. If the copolymers were insoluble in DMAc, potassium bromide pellets would be used instead. Dimethyl-d_6-sulfoxide (DMSO-d_6) and N,N-dimethylfor-

mamide-d_7 (DMF-d_7) were used as solvents for NMR measurement, and tetramethylsilane (TMS) was added as the internal reference. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a Joel JNM-EX270 spectrometer at 270 MHz and 67.8 Hz, respectively. The intrinsic viscosity was determined in DMAc in an Ubbelohde viscometer thermostated at 25.0°C. The following equation was used to calculate the intrinsic viscosities [η]s of the polymers:

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

where c is the concentration and η_{sp} and η_r are the specific viscosity and relative viscosity, respectively.[9] The crystallinity of the copolymers, unless specified, was determined as films from the WAXD patterns obtained at ambient temperature with a diffraction angle 2θ ranged from 5 to 40°, using a Rigaku D-MAX X-ray diffractrometer and monochromatic nickel-filtered CuK$_\alpha$ radiation. Glass transition temperature (T_g) and melting point (T_m) were determined on a Shimadzu DSC-50 differential scanning calorimeter in a nitrogen atmosphere at a heating rate of 20°C/min. The DSC coordinates of temperature and power were calibrated against indium. For each polymer sample, 2 scans from -40 to 340°C were performed, and the T_g and T_m of the copolymer were determined from the second scan. Thermal stability of the polymers was assessed by TGA on a Shimadzu TGA-40 thermogravimetric analyzer at a heating rate of 20°C/min up to 480°C in a nitrogen atmosphere.

Membrane Preparation and Pervaporation Experiments

The pervaporation membranes were symmetric and nonporous. The general procedure for the preparation of pervaporation membranes was previously described.[6] The thickness of the membranes was kept at around 30 μm. Prior to the pervaporation experiments, the membrane was preconditioned in the feed solution for at least 4 h. The pervaporation apparatus used in this work was the same as reported in the previous study,[6,8] with the effective membrane area in the cell being 33.18 cm[2]. The membrane was supported by a filter paper over a perforated metal disc of 6.5 cm in diameter. The cell was loaded with 50 mL of 90 wt % aqueous ethanol solution at 20°C. A vacuum pump (Edwards E2M-15) maintained the downstream presssure at 0.3–0.5 mm Hg. The perme-

ate was condensed in a cold trap cooled by liquid nitrogen, and the permeate rate (J) was determined by measuring the weight of the permeate. The compositions of the feed solutions and the permeates were measured by a Shimadzu GC-8A gas chromatography equipped with a 1-m-long column packed with Hayesep DB and a thermal conductivity detector. The separation factor $\alpha_{H2O/EtOH}$ was calculated from the following equation:

$$\alpha_{H2O/EtOH} = \frac{Y_{H2O}/Y_{EtOH}}{X_{H2O}/X_{EtOH}}$$

where X_i and Y_i are the weight fraction of species i in the feed and permeate, respectively.

RESULTS AND DISCUSSION

Polymer Synthesis

The diamino monomer N,N'-bis(4-aminophenylsulfonyl)piperazine **1A** and N,N'-bis(4-aminophenylsulfonyl)–2,5-dimethylpiperazine **1B** were synthesized with an overall yield of 57 and 49%, respectively, from p-acetamidobenzenesulfonyl chloride via a two-step reaction sequence. By using the low-temperature solution polymerization technique, 2 series of copolymers (that is, **Am** and **Bm**) containing a total of 10 new PASAs were obtained in excellent yields (>95%) (Table I, column 4). At -17°C, in anhydrous DMAc, most of the polycondensation reactions could go to completion without immature precipitation. The PASA random copolymers were labelled either as **Am**XX% or **Bm**XX%, where the first character, **A** or **B**, represented the polymer derived from the diamino monomer **1A** or **1B**, respectively. The next character, **m**, denoted the isophthaloyl moiety whose molar percentage XX% was estimated by the ^{1}H-NMR analysis (vide infra). If the copolymer was insoluble in either DMSO-d_6 or DMF-d_7, the XX value was the molar percentage of isophthaloyl chloride used in the feed of the polymerization.

Solubilities and Intrinsic Viscosities

Similar to other PASAs, most of the newly prepared PASAs were found to be only soluble in aprotic polar solvents like DMF, DMAc, and DMSO. The **Bm** copolymers, in which the appendage of methyl groups in the piperazine ring

Table I   Characterization of PASAs

| | Molar % of Isophthaloyl Moiety | | | | | T_d | |
Copolymer	Feed	Copolymer[a]	Yield %	$[\eta]$[c] dL g^{-1}	T_m[e] °C	mid (°C)[f]	Char (%)[g]
PASAs Derived from *N,N′*-bis(4-aminophenylsulfonyl)piperazine							
Am84%	83	84.2	99.5	0.63	300.2	385	48.2
Am66%	65	66.4	99.0	0.63	302.6	389	50.0
Am51%	50	50.9	97.3	0.59	301.3	394	46.2
Am35%	35		98.2	insoluble[d]	309.8	396	50.0
Am17%	17		98.7[b]	insoluble[d]	—	409	47.1
PASAs derived from *N,N′*-bis(4-aminophenylsulfonyl)-2,5-dimethylpiperazine							
Bm82%	83	81.7	96.3	0.40	304.5	390	55.4
Bm64%	65	63.8	97.7	0.52	306.1	404	55.9
Bm50%	50	50.3	99.4	0.80	309.4	397	56.5
Bm35%	35	34.8	98.4	0.89	313.5	415	59.4
Bm16%	17	16.0	95.3	0.82	—	409	54.1

[a] Estimated by ^{1}H-NMR analysis.
[b] The polymer was precipitated out during polymerization.
[c] Intrinsic viscosity was determined at 25.0°C in DMAc by the single point method.[9]
[d] The polymer was insoluble in DMAc.
[e] Melting point was determined from the second scan of DSC thermogram, as shown in Figure 6 (a) and (b).
[f] Decomposition temperature was determined from the mid of tangent intersections in the TGA thermogram at a heating rate of 20°C/min in a nitrogen atmosphere.
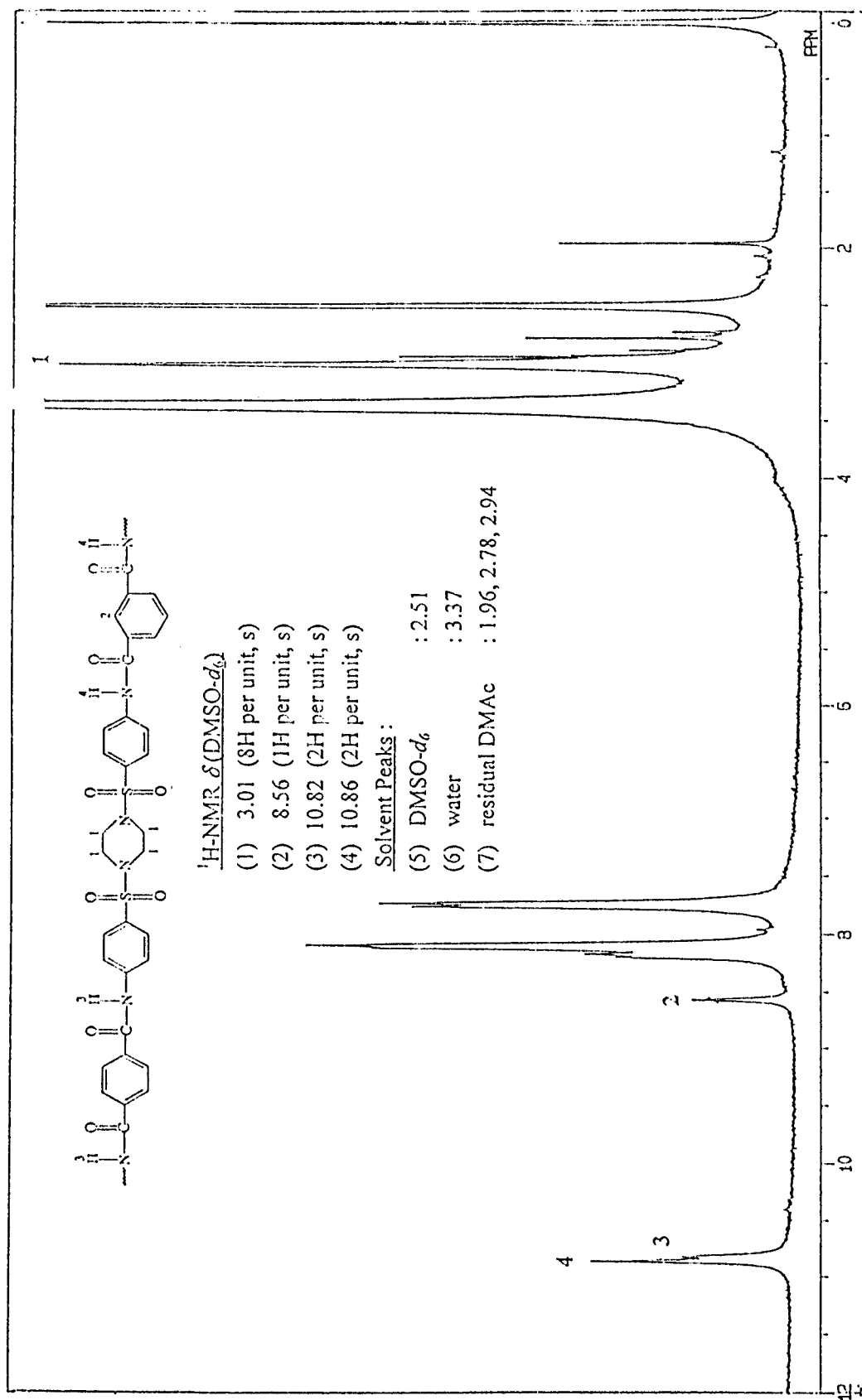[g] Determined as percentage by weight of residue remaining after heating at 480°C.

reduced the intermolecular chain interaction, were generally more soluble than the corresponding **Am** copolymers. The relative amount of the terephthaloyl moiety in the copolymers would also affect their solubilities. The symmetrical *p*-phenylene linkage of the terephthaloyl moiety allowed both the retention of axial symmetry and the free dispose of amide groups for attaining dense packing. Because of these 2 structural characteristics, the crystallinity of **Am** 35% and **Am**17% was so high that they were insoluble in DMAc. The solubility of **Am**17% was so low that it precipitated out during the early stage of polymerization. Even though all of the **Bm** copolymers were soluble in DMAc, the polymer solution of copolymers with the highest terephthaloyl content (that is, **Bm**16%) were found to gel on standing, indicating that its chain regularity or crystallinity was the highest among the **Bm** copolymers. The intrinsic viscosity $[\eta]$ of the soluble PASAs was mostly between 0.5 and 0.9 dL g^{-1}, and membranes of sufficient toughness could be routinely prepared from these copolymers (Table I, column 5).
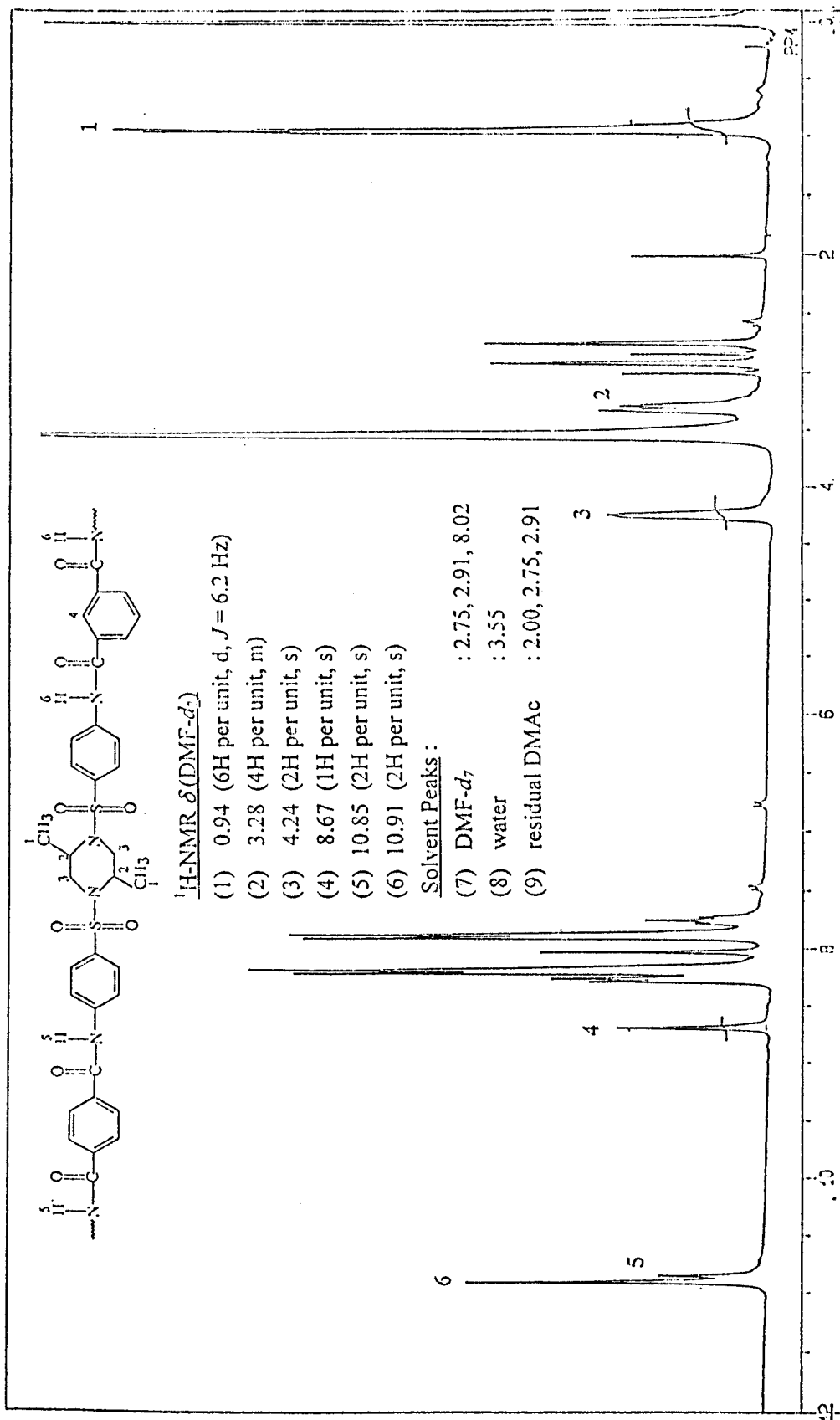
Spectroscopic Characterization

The chemical structures of PASA copolymers were characterized by the combined methods of IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

Careful examination of the IR spectra of the **Am** and **Bm** copolymers revealed that the characteristic group frequencies of each series were almost identical. In general, these IR spectra were featured by the presence of the asymmetric and symmetric sulfonamide O=S=O stretch at 1315 and 1151 cm^{-1}, respectively. The formation of *trans*-amide linkage in PASAs was evident by the appearance of strong amide bands at 3350–3300, 1680, 1536, and 1264 cm^{-1}, which were corresponding to amide NH stretch and amide I, II, and III mode, respectively. The broad absorption band centered at 3350–3300 cm^{-1} was assigned to the hydrogen-bonded NH stretch of the amide groups in the copolymers.

The structure and composition of PASAs can be deduced from ^{1}H NMR technique. The ^{1}H-NMR spectra of **Am** and **Bm** copolymers as exemplified by **Am**66% and **Bm**82% are shown in Figure 2 (a) and (b), respectively. The chemical shifts and signal assignments of the ^{1}H-NMR spectra of PASAs

^{1}H-NMR δ(DMSO-d_6)

(1) 3.01 (8H per unit, s)
(2) 8.56 (1H per unit, s)
(3) 10.82 (2H per unit, s)
(4) 10.86 (2H per unit, s)

Solvent Peaks :

(5) DMSO-d_6 : 2.51
(6) water   : 3.37
(7) residual DMAc   : 1.96, 2.78, 2.94

(a)

Figure 2 ^{1}H-NMR spectrum of (a) **Am**66% copolymer in DMSO-d_6 and (b) **Bm**82% copolymer in DMF-d_7.

¹H-NMR δ(DMF-*d₇*)

(1) 0.94 (6H per unit, d, J = 6.2 Hz)
(2) 3.28 (4H per unit, m)
(3) 4.24 (2H per unit, s)
(4) 8.67 (1H per unit, s)
(5) 10.85 (2H per unit, s)
(6) 10.91 (2H per unit, s)

Solvent Peaks :

(7) DMF-*d₇*   : 2.75, 2.91, 8.02
(8) water   : 3.55
(9) residual DMAc : 2.00, 2.75, 2.91

(b)

Figure 2.   *(Continued from the previous page).*

Table IIa   Observed Chemical Shifts of Proton Resonates for Am: ^{1}H-NMR δ (DMSO-d_6) in Am Copolymers

Copolymer	H_1	H_2	H_3	H_4
n	8	1	2	2
Am84%	3.01	8.56	—	10.86
Am66%	3.01	8.56	10.82	10.86
Am51%	3.02	8.56	10.82	10.86

n is the number of hydrogen nuclei per repeating unit comprising a peak.
The chemical structure is as follows:.
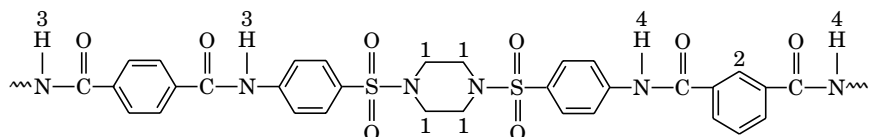
are compiled in Table II (a) and (b). The composition of various copolymers, with respect to the relative amount of isophthaloyl and terephthaloyl repeating units, can be estimated from the relative intensities of the selected signals of the 2 phthaloyl subunits. In the ^{1}H-NMR spectra of PASAs, the resonates at δ 7.5–8.6 were assigned to aromatic ring protons. This aromatic region can be divided into 2 portions. The first portion of aromatic resonates at δ7.5–8.3 is so complicated that they cannot be resolved. However, for isophthaloyl moiety, because of the additive deshielding effect caused by the 2 *meta* disposition carbonyl groups, their common β-proton resonates at δ8.6, which is more downfield than the rest of aromatic protons. By using this resonance peak at δ8.6 for 1 proton as the marker for isophthaloyl moiety, and comparing its intensity with that of the 8 methylene proton signal of piperazine moiety at δ3.0 or with the 2 methine proton signal of 2,5-dimethylpiperazine at δ4.2, the isophthaloyl molar % in the **Am** and **Bm** copolymers can be calculated.

Within the accuracy of the spectroscopic method, the copolymer composition estimated from the ^{1}H-NMR studies was found to be close to the respective feed composition (Table I, column 3). Therefore, it is conceivable to assume that the

Table IIb   Observed Chemical Shifts of Proton Resonates for Bm: ^{1}H-NMR δ(DMF-d_7) of Bm Copolymers

Copolymer	H_1	H_2	H_3	H_4	H_5	H_6
n	6	4	2	1	2	2
Bm82%	0.94	3.28	4.24	8.67	10.85	10.91
Bm64%	0.81	3.15	4.14	8.55	10.78	10.81
Bm50%	0.81	3.14	4.13	8.55	10.78	10.81
Bm35%	0.82	3.15	4.13	8.55	10.78	—
Bm16%	0.82	3.16	4.12	8.54	10.77	—

n is the number of hydrogen nuclei per repeating unit comprising a peak.
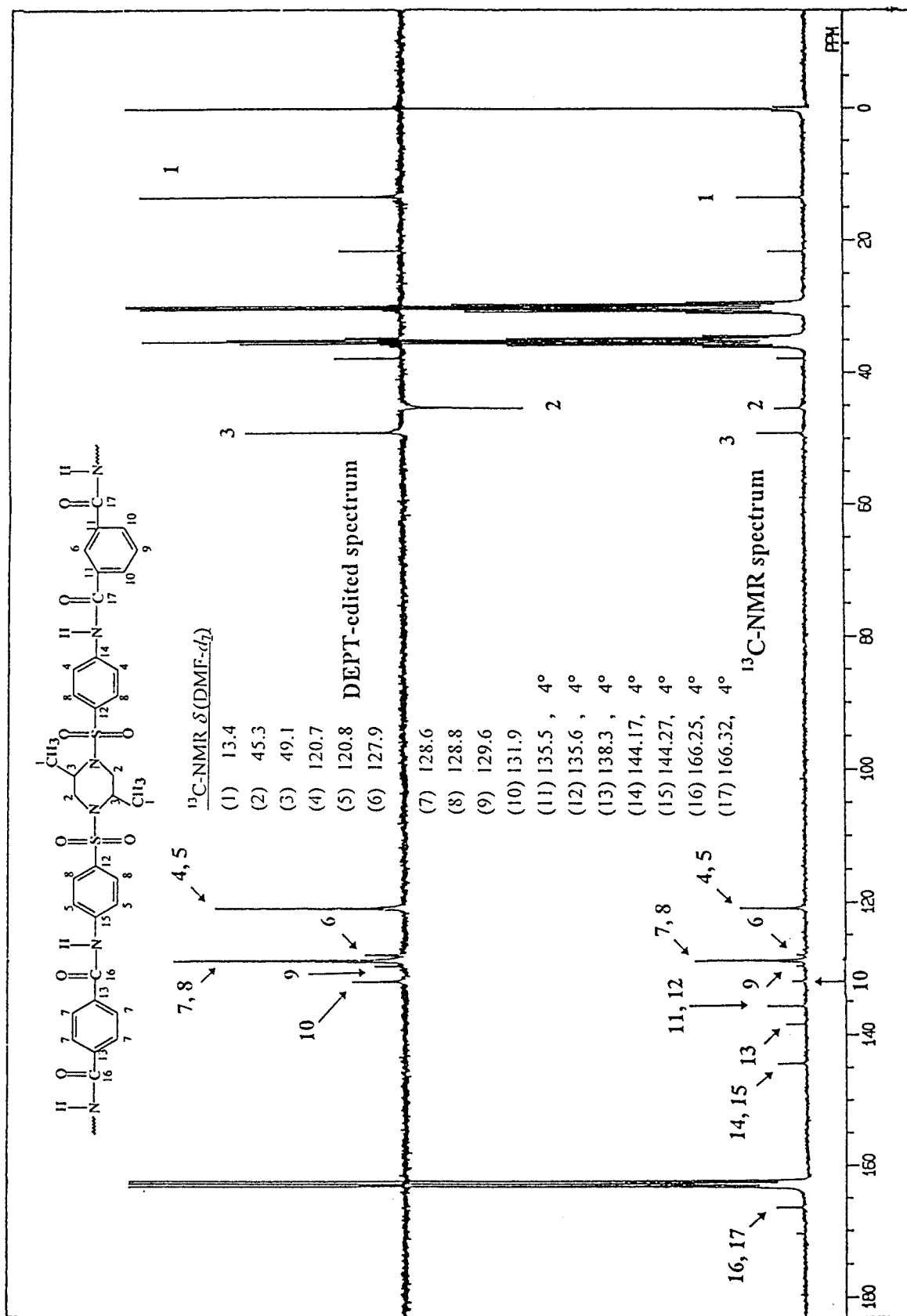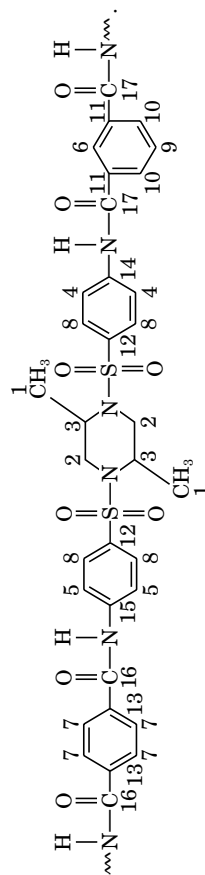The chemical structure is as follows:
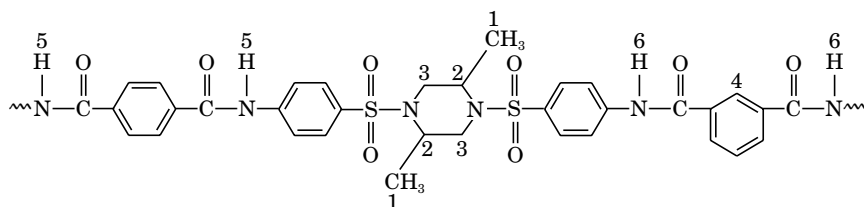
Figure 3 ^{13}C-NMR (bottom) and EDPT-edited (top) spectra of **Bm**50% copolymer in DMF-d_7.

Table III   Observed Chemical Shifts of Carbon Resonates for Bm Copolymers, Their Assignments, and Calculated Values

Carbon	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}
n^a	2	2	2	2	2	1	4	4	1	2	2	2	2	1	1	2	2
Type^b	1°	2°	3°	3°	3°	3°	3°	3°	3°	3°	4°	4°	4°	4°	4°	4°	4°
Cal'd δ^d				118.0	118.0	126.1	127.4	128.1	128.7	130.7	133.6	129.9	136.9	144.3	144.3		
Obs'd δ^c																	
Bm82%	13.3	45.2	48.9	120.6	—	128.1	128.6	128.7	129.2	131.8	135.3	135.5	138.3	144.06	—	—	166.3
Bm64%	13.4	45.3	49.0	120.7	120.8	128.2	128.6	128.8	129.4	131.9	135.5	135.6	138.3	144.18	144.23	—	166.3
Bm50%	13.4	45.3	49.1	120.7	120.8	127.9	128.6	128.8	129.6	131.9	135.5	135.6	138.3	144.17	144.27	166.25	166.3
Deviation^e				2.7	2.8	1.8	1.2	0.7	0.9	1.2	1.9	5.7	1.4	−0.1	0.0		

The chemical structure is as follows:

[a] Number of carbon nuclei per repeating unit comprising a peak.
[b] Type of carbon nuclei: primary (1°), secondary (2°), tertiary (3°), and quaternary (4°).
[c] Observed ^{13}C chemical shifts from ^{13}C-NMR spectra.
[d] ^{13}C chemical shifts for aromatic carbons calculated by the additivity rule based on the empirical substituent increments.
[e] Deviation = observed − calculated, based on the values of **Bm**50% copolymer.

reactivity of diamino monomer **1A** (or **1B**) toward terephthaloyl or isophthaloyl chloride in the polymerization reaction is similar such that random copolymers were produced in these experiments.

Because of the better solubility properties of **Bm**50%, **Bm**64%, and **Bm**82%, they were subjected to detailed ^{13}C-NMR studies. For each of these **Bm** copolymers, there are 17 types of chemically different carbons, 3 of which are aliphatic carbons, C_1–C_3; 12 are aromatic carbons, C_4–C_{15}; and 2 of which are amide carbonyl carbons, C_{16}–C_{17}. Assignment of carbon signals of the noise-decoupled ^{13}C-NMR spectra of the copolymers can be simplified by the reference to the corresponding DEPT-edited spectra and the revelation of the empirical calculation for the chemical shift of various aromatic carbon nuclei. For instance, differentiation of the methyl, methylene, methine, and quaternary carbon nuclei of the molecule can be achieved by direct comparison of the noise-decoupled ^{13}C-NMR spectrum of **Bm**50% with its DEPT-edited spectrum (Fig. 3). Furthermore, by using the additivity rules for effect of substituents on the ^{13}C-chemical shifts of substituted benzenes, the ^{13}C-chemical shift of aromatic carbons of the copolymers can be estimated.[10] A fairly good agreement between the observed and calculated ^{13}C chemical shift of the aromatic carbons confirms the validity of the carbon signal assignments (Table III). In addition, the signal assignments were fully compatible with the results of the DEPT experiments. Even though the peak intensity of ^{13}C signals cannot be used to deduce the number of carbon nuclei comprising a particular peak, interesting results were obtained by comparing the relative intensity of aromatic carbons in the **Bm** copolymer series. The intensity h of various carbon resonates of the isophthaloyl and terephthaloyl moiety (that is, C_1 to C_6) was first normalized with the signal intensity of the corresponding methine carbon (δ49.1) of the 2,5-dimethylpiperazine moiety of the same molecule to give the normalized peak intensity f. In a plot of f of phthaloyl ring carbons versus isophthaloyl molar % shown in Figure 4, a least-squares fit line with a linear coefficient r greater than 0.99 was obtained for each of the phthaloyl carbons. As the intensity of individual carbon signal was governed by its relaxation time in the spin transition process, the present findings indicated that the composition of PASA copolymers appeared to be a crucial factor affecting the relaxation time of the excited carbon nuclei.


isophthaloyl moiety
(m-phenylene linkage)

terephthaloyl moiety
(p-phenylene linkage)
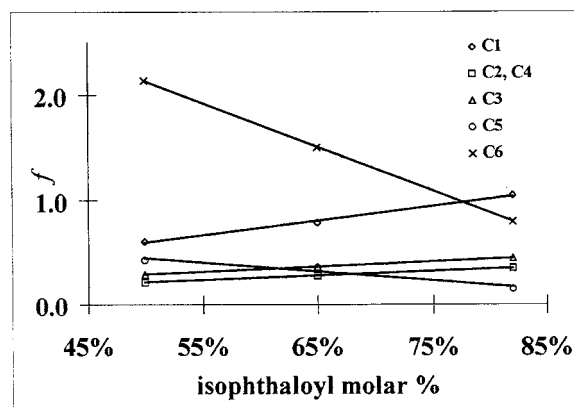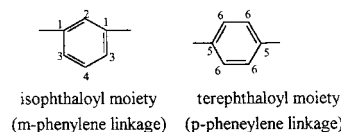
^{a} f = normalized peak intensity of C_i to $C_{\delta 49.1}$; the ^{13}C-chemical shifts of isophthaloyl carbons were at δ 135.5 (C_1), 127.9 (C_2), 131.9 (C_3) and 129.6 (C_4), whereas those of terephthaloyl carbons were at δ 138.3 (C_5) and 128.6 (C_6).

Figure 4 Plot of f of the phthaloyl ring carbons versus isophthaloyl molar percentage in **Bm** copolymer.

Crystallinity

The relative degree of crystallinity for the PASA copolymers was investigated by wide-angle X-ray diffraction (WAXD) ($2\theta = 5$–$40°$), and their X-ray diffraction (XRD) patterns are shown in Figure 5, in which they are stacked and are of same chart magnification for comparison. In a relative sense, the **Am** copolymers exhibited a higher degree of crystalinity because their diffraction patterns were much sharper than those of the **Bm** copolymers. The increase in crystallinity in **Am** copolymers was explained by better and, thus, close-packing of the polymer backbones. The diffraction pattern of **Am**17% was the sharpest among these PASA copolymers, indicating that its recrystallinity was the highest. Because of this reason, its solubility was the lowest among the **Am** and **Bm** copolymers, as indicated by its early precipitation during polymerization. The **Bm** copolymers were essentially amorphous because their diffraction patterns shown in Figure 5 were broad and diffuse. The amorphous behavior of the **Bm** copolymers was ascribed by the chain disorder induced by the methyl groups substitution in the piperazine moiety, which deterred the polymer chains from close packing. Similar amorphous WAXD patterns were observed for polyamides synthesized by Idage et al.[11] and Hsiao and Yang.[12]
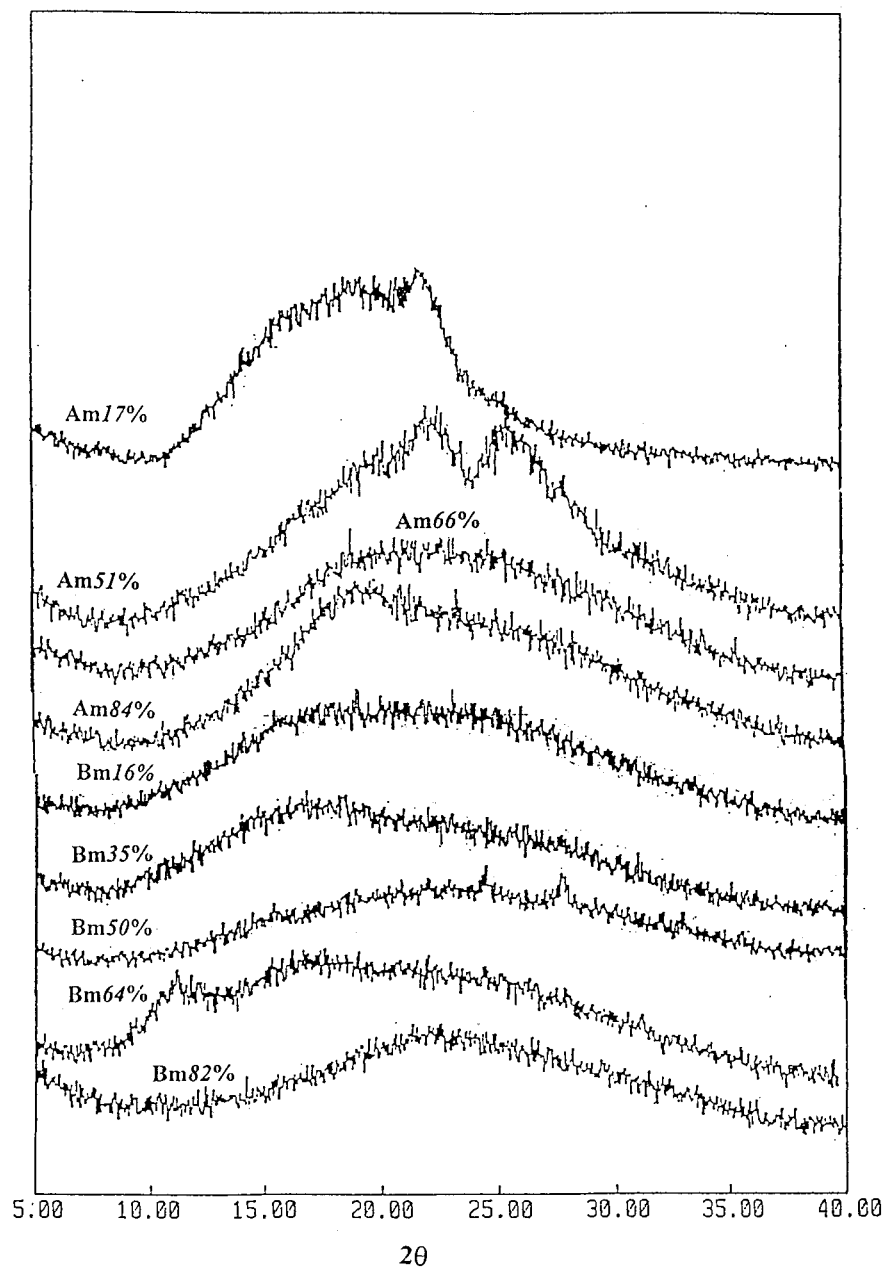
Figure 5 X-ray diffraction diagrams of PASA polymer films, from top to bottom: **Am**17% (powder), **Am**51%, **Am**66%, **Am**84%, **Bm**16%, **Bm**35%, **Bm**50%, **Bm**64%, and **Bm**82%.

Thermal Characterization

The thermal properties of polymers were evaluated by DSC and TGA. The DSC thermograms of the PASA copolymers are shown in Figure 6, in which an anonymous broad peak centered at 70–90°C is observed for each copolymer. This peak was probably came from the bound water in the copolymers, which could not be removed by vacuum drying at 80°C. Because of these broad peaks, the glass transition temperatures of the polymers could not be determined from the thermograms. The amount of bound water was estimated to be around 6–8% by weight from the TGA studies. The melting of a perfectly crystalline substance is characterized by a sharp melting endotherm and a well-defined melting point T_m.

THERMAL ANALYSIS DATA
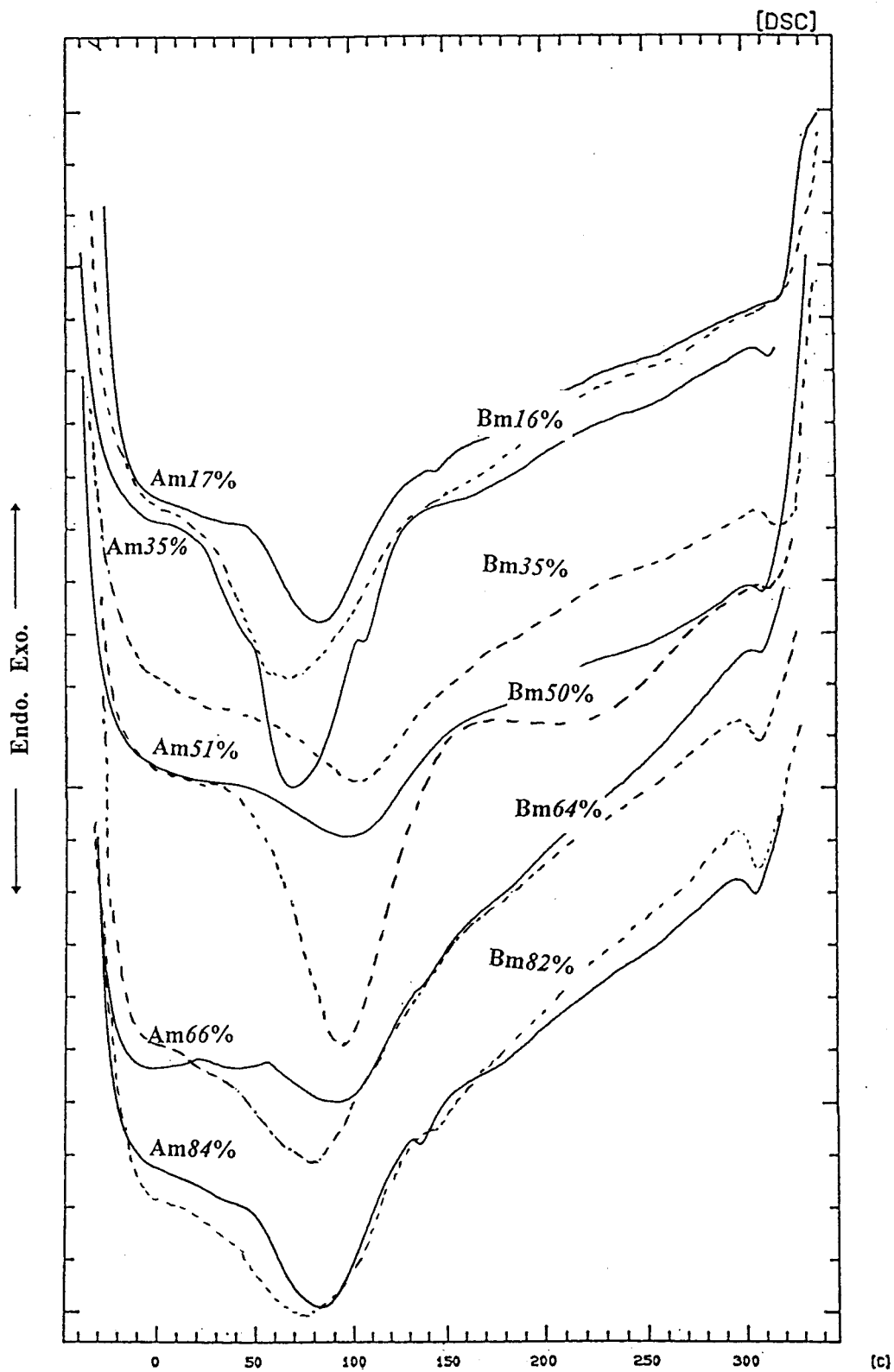
Figure 6 Second-scan DSC thermograms of **Am** copolymers (——) and **Bm** copolymers (-----) at a heating rate of 20°C/min in nitrogen atmosphere.

Table IV   Pervaporation of a 90 Wt % Aqueous Ethanol Solution through PASA Membranes[a]

Copolymer	$[\eta]^c$ dL g^{-1}	t^d μm	Weight Fraction of Water in Feed (X_w)	Permeate (Y_w)	α^e	J^f g m^{-2} h^{-1}
PASAs derived from *N,N'*-bis(4-aminophenylsulfonyl)piperazine						
Am100%[b]	0.85				57.2	31.3
Am84%	0.63	28	0.143	0.711	14.7	41.3
		28	0.158	0.831	26.2	36.6
PASAs derived from *N,N'*-bis(4-aminophenylsulfonyl)-2,5-dimethylpiperazine						
Bm100%[b]	0.85				39.7	34.4
Bm82%	0.40	32	0.158	0.588	7.6	31.9
Bm64%	0.52	30	0.125	0.761	22.3	30.4
		32	0.125	0.725	18.5	29.8
Bm50%	0.80	25	0.158	0.752	16.2	40.2
		25	0.158	0.755	18.4	45.9
Bm35%	0.89	28	0.143	0.758	18.8	46.5
		33	0.158	0.753	13.6	28.7

[a] Operating temperature was 20.0°C and downstream pressure was 0.3–0.5 mm Hg.
[b] Values abstracted from Chan et al.[6] for comparison.
[c] Intrinsic viscosity was determined at 25.0°C in DMAc by the single point method.
[d] Membrane thickness in μm.
[e] α = separation factor = $\dfrac{y_w/(1-y_w)}{x_w/(1-x_w)}$.
[f] J = permeation flux determined from the weight of permeate collected within a prescribed period of time.

In this study, the melting points of the polymers were evaluated from the second scan of the DSC thermograms because the second scan melt endotherm was more pronounced than that of the first. This observation is common for semicrystalline materials. Thus, the melting points of the copolymers were deduced from Figure 6 and were shown in Table I (column 6). For unknown reasons, no distinct T_m was observed for copolymer **Am**17% and **Bm**16%. In addition, the melting points of **Bm** copolymers having the same molar percentage of isophthaloyl moiety were generally higher than those of **Am** copolymers by 3 to 5°C. This implied that **Bm** copolymers were more rigid than **Am** copolymers, even though the latter had higher crystallinity, as found in the WAXD studies. Similar phenomenon was observed in the thermal stability indicated from the TGA studies. The char percentages at 480°C along either **Am** or **Bm** series were nearly the same, with an average value of 48.3% for **Am** copolymers and 56.3% for the **Bm** copolymers. The higher char percentage

and T_m of **Bm** copolymers could be explained by the increase in chain rigidity due to the methyl group substitution in piperazine moiety, which somewhat outweighed their decrease in crystallinity. In other words, chain rigidity was a factor more important than crystallinity in determining the thermal properties of PASA copolymers.

Performance of Pervaporation Membranes

In search for new polymeric materials for membrane applications, PASA membranes were found to have the desired properties, such as toughness, flexibility, and stability to heat and corrosive chemicals. Recently, we reported that in the dehydration of alcohol–water binary mixture by pervaporation technique, in contrast to other PASA copolymers, the membrane prepared from **Am**100% and **Bm**100% exhibited the best compromise among processability, permselectivity, and permeability.[6] Since permeated molecules can only diffuse through the amorphous phase or the interstices between the crystallites of a poly-

meric membranes, we envisaged that permeability and permselectivity of the membrane material should vary with its degree of crystallinity. In this study, in order to attain an insight into the relationship between crystallinity and pervaporation properties of a class of material, monomer **1A** and **1B** was copolymerized with various mixtures of isophthaloyl and terephthaloyl chloride.

Using our homemade pervaporation apparatus, nonporous symmetric membranes of PASA copolymers were fabricated and employed for a separation of 90 wt % aqueous ethanol solution. Solubility is one of the most important factors in preparing casting solutions for good membrane properties. It was found that copolymers with higher crystallinity had poor solubility and processability. Therefore, among the **Am** copolymers, only **Am**84% could be used for membrane preparation. In addition, among the 5 newly prepared **Bm** copolymers, **Bm**16% was not suitable for membrane preparation, as its polymer solution was gelled on standing. The separation factor α of PASA membranes found in Table IV are all greater than unity, indicating that all of these membranes are water-preferential permeable materials. Since the results of swelling experiments and solubility parameter calculations both indicated PASA membranes are intrinsically hydrophobic,[8] the pervaporation process of this type of membrane material is believed to be diffusion-controlled. In general, the selection factor α and the permeation flux shown in Table IV of PASA membranes was between 8 and 57 and between 29 and 47 g m^{-2} h^{-1}, respectively. Originally, we envisioned that when the crystallinity of PASAs was decreased by copolymerizing with larger percentage of isophthaloyl chloride, the permeation flux would be enhanced preferably at a minimum sacrifice of permselectivity. However, from this study, to our disappointment, the separation factor and permeation flux of PASA membranes were found to be both within the same order of magnitude in comparison with the related homopolymers. In other words, among the PASA copolymers synthesized in this study, even though the membranes prepared from **Am**84% and **Bm**82% had higher molar percentage of the isophthaloyl moiety, the resulting decrease in crystallinity had little impact in enhancing the permeation flux. Therefore, crystallinity, which was one of the second-order polymer structures,[13] was important in determining the solubility and processability, but exerted little influence in the pervaporation performance of PASA membranes.

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