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Synthesis and Properties of Polyamides of 2,2'- [Isopropylidenebis-(p-phenyleneoxy)] diacetic Acid*

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ABSTRACT

A group of six semiaromatic polyamides of 2,2'-[isopropylidenebis-(p-phenyleneoxy)] diacetic acid (Bisacid A₂) were synthesized by low-temperature solution polycondensation techniques. Six different diamines were condensed independently with Bisacid A₂ chloride in a mixture of N-methylpyrrolidone (NMP) and hexamethylphosphoramide (HMPA). The polymers were obtained in 82-95% yield and possessed inherent viscosities in the range from 0.32 to 0.63 dL/g. The polyamides were characterized by IR and ¹H-NMR spectra. The molecular weight and molecular weight

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distribution of the polyamides were determined by gel-permeation chromatography. The thermal stability, thermal degradation kinetics, crystallinity, density, and solubility were also determined. A model diamide (MDA) was synthesized from aniline and Bisacid A₂ chloride to confirm the formation of polyamides from diamines.

INTRODUCTION

Extensive investigations have been carried out in the field of wholly aromatic polyamides and related polycondensates, which led to the commercial development of Nomex and Kevlar aromatic polyamides by Du Pont [1-5]. The p-linked aromatic polymers have been of special interest because of their high modulus and strength, but most of these polymers have the practical limitation of insolubility in most of the aprotic solvents and, hence, of limited processability. With a view to increasing the solubility and hence the processability of totally aromatic polyamides, we attempted and succeeded in the synthesis of several polyamides from Bisacid A₂ and aromatic diamines with flexibilizing spacers between the phenylene units. The bispolyamides (BPA) were characterized by IR and ¹H-NMR spectra. The inherent viscosity, density, percent crystallinity, thermal stability, thermal degradation kinetics, glass-transition temperature T_g and melting point T_m were also determined. The molecular weight distribution (MWD) were derived from gel-permeation chromatographic analysis.

A model diamide (MDA, see Experimental) was also synthesized from Bisacid A₂ chloride and aniline for comparison of its IR and ¹H-NMR spectra with those of the corresponding polyamides. The preparation and initial evaluation of polyamides from Bisacid A₂ and p- and m-phenylenediamines (Bisparamid A₂ and Bismetamid A₂, respectively) were reported by Lenk and co-workers [6-9].

EXPERIMENTAL

Infrared spectra were run on a Perkin-Elmer 283 IR Spectrophotometer by a KBr pellet technique. Proton NMR spectra were recorded on Varian-90 (90 MHz) and Jeol-90 MHz FT-NMR spectrometers at room temperature in hexamethylphosphoramide using TMS as the internal reference. The thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and thermomechanical analysis (TMA) were done on Du Pont 990 and Du Pont 1090 thermal analyzers at a heating rate of 10°C/min under a nitrogen atmosphere.

The molecular weights were determined on a Knauer HPLC equipped with Knauer variable UV detector. The GPC columns used in this work were silica-based LiChrospher Si 1000 and LiChrospher Si 4000 connected in sequence. DMAc was used as the eluent. The universal calibration method [10-12], using polystyrene standards supplied by Herbert Knauer & Co. (West Germany), was used for calibration of the GPC columns. The number-average molecular weight (\bar{M}_n) and weight-average molecular weight (\bar{M}_w) were calculated by the ASTM method [13].

X-ray diffractograms were recorded with a Philips X-ray diffractometer (vertical goniometer type) using nickel filtered $\text{CuK}\alpha$ radiation. The elemental analyses were done on a Perkin-Elmer 240 instrument. The inherent viscosities were determined in DMAc at 30°C with an Ubbelohde suspension-type viscometer. The densities of the polyamides were determined with a small pycnometer with hexane at 30°C. Melting points were uncorrected and determined on a Kofler block.

Bisacid A₂ [14, 15] was prepared from Bisphenol A and monochloroacetic acid in alkaline medium and recrystallized from acetic acid (50%), mp 169°C.

Bisacid A₂ chloride [15] was obtained by the action of thionyl chloride on the corresponding acid. Excess thionyl chloride was removed by distillation. Bisacid A₂ chloride was purified by the literature method [15] and was obtained as a viscous brown oil which neither crystallizes nor vacuum distills without decomposition.

Diamines. Commercially available benzidine (Fluka) was used as such without further purification. The diamines, 4,4'-diaminodiphenylmethane [16], 4,4'-diaminodiphenylethane [17, 18], 4,4'-diaminodiphenyl ether [19], 4,4'-diaminodiphenyl sulfide [20], and 4,4'-diaminodiphenyl sulfone [21], were synthesized according to literature methods.

Commercially available hexamethyl phosphoramide (HMPA), N-methylpyrrolidone-2 (NMP) and N,N-dimethylacetamide (DMAc) were each purified by vacuum distillation over phosphorous pentoxide to clear, colorless liquids and kept dried over Molecular Sieves until used. The solvents DMF and DMSO were distilled before use.

Synthesis of Polyamides [22-25]

The bispolyamides described in the present work were prepared as follows: The calculated amount of Bisacid A₂ chloride (0.0125 mol), dissolved in 10 mL dry CCl_4 , was added all at once to a vigorously stirred solution of the diamine (0.0125 mol) in a mixture of NMP (33.30 mL) and HMPA (16.70 mL) kept at a temperature of -10 to -15°C. Stirring was discontinued after 2 h, and the reaction mixture

was allowed to stand overnight, gradually attaining room temperature. The reaction mixture was then worked up by agitating the contents with excess water in a blender to wash away the solvent, and the polyamide was collected by filtration. This washing procedure was repeated several times with water, dilute hydrochloric acid, hot water, and finally with methanol. The collected polymer was dried in a vacuum oven at 90°C for 8 h.

The model diamide 2,2'-[isopropylidenebis-(p-phenyleneoxy)] diacetanilide (MDA) was synthesized exactly like the polyamides using 1 mol of Bisacid A₂ chloride and 2 mol of aniline in DMAc at 0 to -10°C. It was recrystallized from benzyl alcohol. Yield 82%, mp 180°C.

Analysis: Calculated: C, 75.26; H, 6.12; N, 5.67%. Found: C, 75.20; H, 6.11; N, 5.69%.

RESULTS

The yields and properties of the polyamides such as inherent viscosity, density, percent crystallinity, glass transition temperature T_g , melting point T_m , number-average molecular weight \bar{M}_n , weight-average molecular weight \bar{M}_w , and polydispersity D are tabulated in Table 1. The GPC patterns of the polyamides are presented in Fig. 1.

A summary of the IR absorption frequencies and their appropriate assignments for all materials is presented in Table 2. The ¹H-NMR spectral data in HMPA for the model diamide (MDA) and the polyamides (BPA-I to BPA-VI) are given in Table 3. The thermal stabilities and thermal degradation kinetics of the polyamides are summarized in Table 4. The thermograms of all polyamides are presented in Fig. 2. The effect of molecular weight on the thermal stability of BPA-IV, as ascertained by TGA, is illustrated in Fig. 3. The TMA and DSC patterns of the polyamides are given in Figs. 4 and 5, respectively. The solubilities of polymers in various solvents are summarized in Table 5. The x-ray diffractograms are presented in Fig. 6.

DISCUSSION

The polyamides were prepared by the low-temperature solution polycondensation technique [22-25] in a solvent mixture of NMP and HMPA (2:1). Aromatic acid chlorides are found to react with amide solvents like DMAc and NMP at elevated temperatures [26]. Moreover, amide solvents tend to acylate primary diaramines and oligo-diamines at room temperature. Further, in the polycondensation of aromatic acid dichlorides in amide solvents, transacylation and transamidation were claimed to occur [27]. These side reactions are mini-

TABLE I. Preparation and Properties of Bispolyamides

Polyamide code	Yield, %	η_{inh}^a	Density, g/cm^3 ^b	Crystallinity, % ^c	T_g^d	T_m^e	\bar{M}_n^f	\bar{M}_w^f	D^g
BPA-I	85	0.63	0.76	33	67.7	271	53 780	89 810	1.67
BPA-II	90	0.32	0.82	35	68	195	40 240	76 450	1.90
BPA-III	95	0.36	h	30	64	185	45 420	89 480	1.97
BPA-IV	92	0.42	0.68	34	73.8	242	49 260	65 020	1.32
BPA-V	82	0.33	0.71	23	62	265	42 300	83 750	1.98
BPA-VI	95	0.36	0.74	22	59	232	43 860	81 580	1.86

^aDetermined on a 0.5-g/dL solution in DMAc at 30°C.

^bDetermined pycnometrically with hexane at 30°C.

^cDetermined from XRD.

^dDetermined from TMA; $\Delta T = 5^\circ C/min$.

^eDetermined on a Kofler block.

^fMeasured by GPC.

^g $D = \bar{M}_w/\bar{M}_n$ = polydispersity.

^hDensity could not be determined because the polymer floats on hexane.

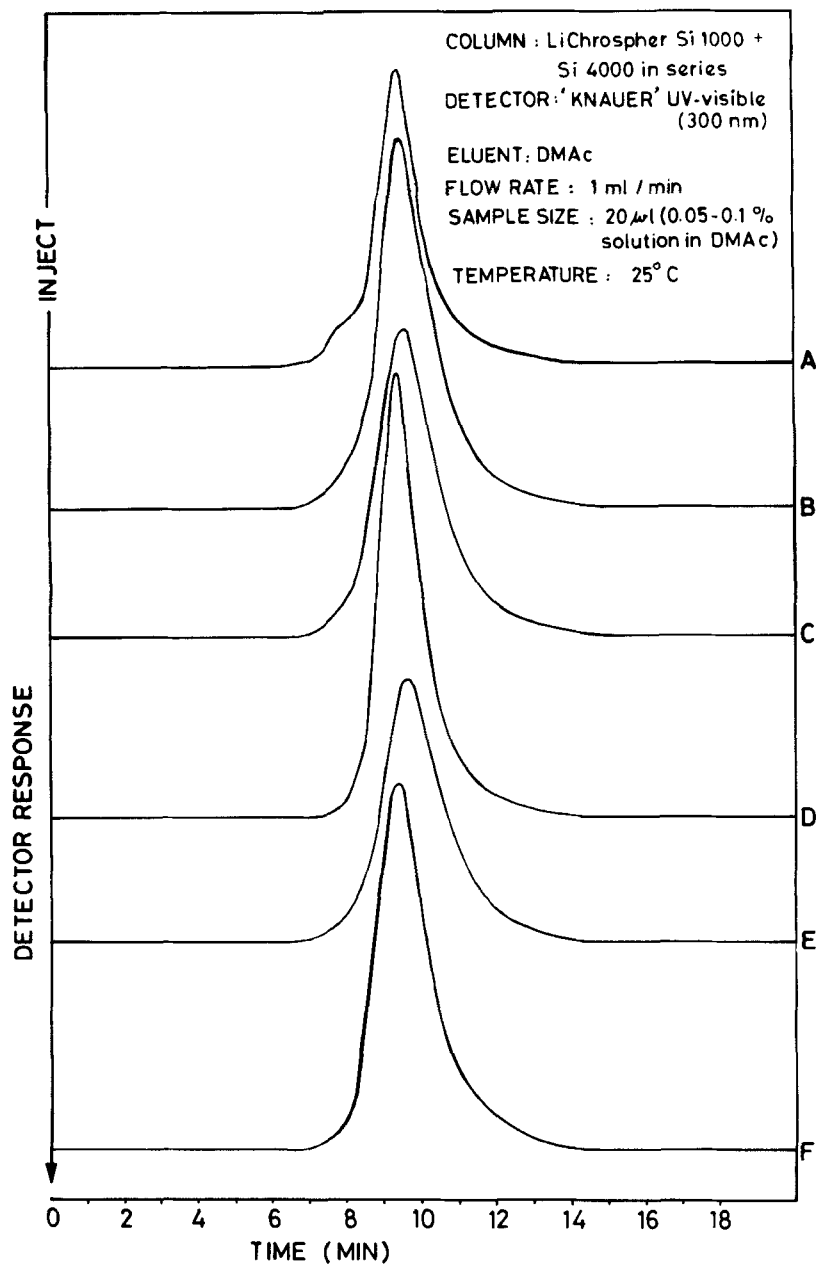


FIG. 1. Gel-permeation chromatography patterns of polyamides.
 (A) BPA-I, (B) BPA-III, (C) BPA-III, (D) BPA-IV, (E) BPA-IV, and
 (F) BPA-VI.

TABLE 2. Infrared Absorption Frequencies of Model Diamide and Polyamides: ^a Frequency in cm⁻¹

MDA	BPA-I	BPA-II	BPA-III	BPA-IV	BPA-V	BPA-VI	Assignment
685(s)	635(w)	635(m)	635(m)	640(w)	635(m)	635(s)	Out-of-plane bending of C-H bonds of aromatic rings
750(s)	725(w)	725(w)	725(w)	725(w)	725(w)	720(w)	
825(s)	825(s)	830(s)	830(s)	835(s)	830(s)	745(m) 830(s)	
-	-	-	-	-	700(w)	-	Aromatic C-S stretching frequency
1010(m)	1010(m)	1010(m)	1015(m)	1020(m)	1015(s)	1010(m)	In-plane bending of C-H bonds
1060(s)	1060(s)	1060(s)	1060(s)	1065(s)	1065(s)	1060(m)	
1100(m)	1115(w)	1110(m)	1110(m)	1110(m)	1110(s)	1110(s)	
-	-	-	-	-	-	1150(s)	Symmetric stretching of sulfone group
1180(s)	1180(s)	1180(s)	1185(s)	1190(m)	1185(s)	1185(s)	C-O-C asymmetric stretching
1300(m)	1300(m)	1300(s)	1300(s)	1310(m)	1310(s)	1300(s)	Aromatic C-N stretching

(continued)

TABLE 2 (continued)

MDA	BPA-I	BPA-II	BPA-III	BPA-IV	BPA-V	BPA-VI	Assignment
1440(s)	1420(m)	1415(s)	1420(s)	1420(m)	1400(s)	1410(s)	C=C ring stretching
1500(s)	1500(s)	1510(s)	1510(s)	1505(s)	1510(s)	1510(s)	Amide II band due to inter- action of N-H bending and C-H stretching
1530(s)							
1600(s)	1600(s)	1600(s)	1610(s)	1615(m)	1590(s)	1600(s)	C=C ring stretching
1685(s)	1690(s)	1680(s)	1690(s)	1690(s)	1690(s)	1700(s)	Amide I band due to C=O stretching
2920(w)	2940(w)	2930(w)	2940(m)	2940(w)	2940(w)	2940(w)	Aliphatic C-H stretching
2960(w)	2980(m)	2980(m)	2970(m)	2980(m)	2980(m)	2980(m)	
3050(m)	3050(m)	3040(m)	3040(m)	3060(m)	3050(m)	3060(m)	Aromatic C-H stretching
3120(w)	3110(w)	3120(w)	3140(w)	3140(w)	3110(w)	3110(w)	Overtone of amide II band
3300(b)	3320(b)	3330(w)	3320(m)	-	-	3350(w)	N-H stretching (H- bonding)
3400(s)	3410(s)	3410(s)	3400(s)	3420(s)	3390(s)	3400(s)	N-H stretching (free)

^aw = weak, m = medium, s = strong, b = broad.

TABLE 3. $^1\text{H-NMR}$ Spectral Data ^a for Model Diamide and Polyamides in HMPA

Code	Description of peaks, multiplicity, ^b number of protons, ^c peak assignment
MDA	4.54(s, 4H) -2CH ₂ flanked by O and CO
	6.96(m, 14H) -Aromatic protons of Bisacid A ₂ ring + m- and p-protons of aniline ring
	7.55(d, 4H) -o-Protons of aniline ring
	10.62(s, 2H) -Amide protons
BPA-I	4.54(s, 4H) -2CH ₂ flanked by O and CO
	6.84-7.74(m, 16H) -Aromatic protons
	11.14(s, 2H) -Amide protons
BPA-II	4.74(s, 4H) -2CH ₂ flanked by O and CO
	7.01-7.68(m, 16H) -Aromatic protons
	11.11(s, 2H) -Amide protons
BPA-III	4.58(s, 4H) -2CH ₂ flanked by O and CO
	6.98-7.68(m, 16H) -Aromatic protons
	11.11(s, 2H) -Amide protons
BPA-IV	4.61(s, 4H) -2CH ₂ flanked by O and CO
	6.88-7.74(m, 16H) -Aromatic protons
	11.11(s, 2H) -Amide protons
BPA-IV	4.54(s, 4H) -2CH ₂ flanked by o and CO
	6.88-7.68(m, 16H) -Aromatic protons
	11.28(s, 2H) -Amide protons
BPA-VI	4.64(s, 4H) -2CH ₂ flanked by O and CO
	6.91-7.91(m, 16H) -Aromatic protons
	11.22(s, 2H) -Amide protons

^aChemical shift (δ ppm, relative to TMS).

^bs = singlet, d = doublet, m = multiplet.

^cDetermined by relative areas under the peak.

TABLE 4. Thermal Stabilities and the Thermal Degradation Kinetics of the Polyamides in Nitrogen^a

Code	Temperature at various percentage decompositions, °C						ipdt, °C	ΔE , ^c kcal/mol	n ^d
	2	10	20	30	40	T _{max} ' ^b °C			
BPA-I	320	395	415	430	440	430	310	42	0.27
BPA-II	270	385	415	430	445	430	337	23	0.27
BPA-III	270	390	410	425	435	420	277	45	0.34
BPA-IV	320	385	410	420	435	430	377	26	0.33
BPA-V	280	380	405	420	430	420	333	40	0.22
BPA-VI	360	400	420	430	445	430	345	43	0.20

^aRate of heating, 10°C/min.^bTemperature at which maximum rate of weight loss occurs.^c ΔE = activation energy of the thermal decomposition reaction.^dn = order of decomposition reaction.

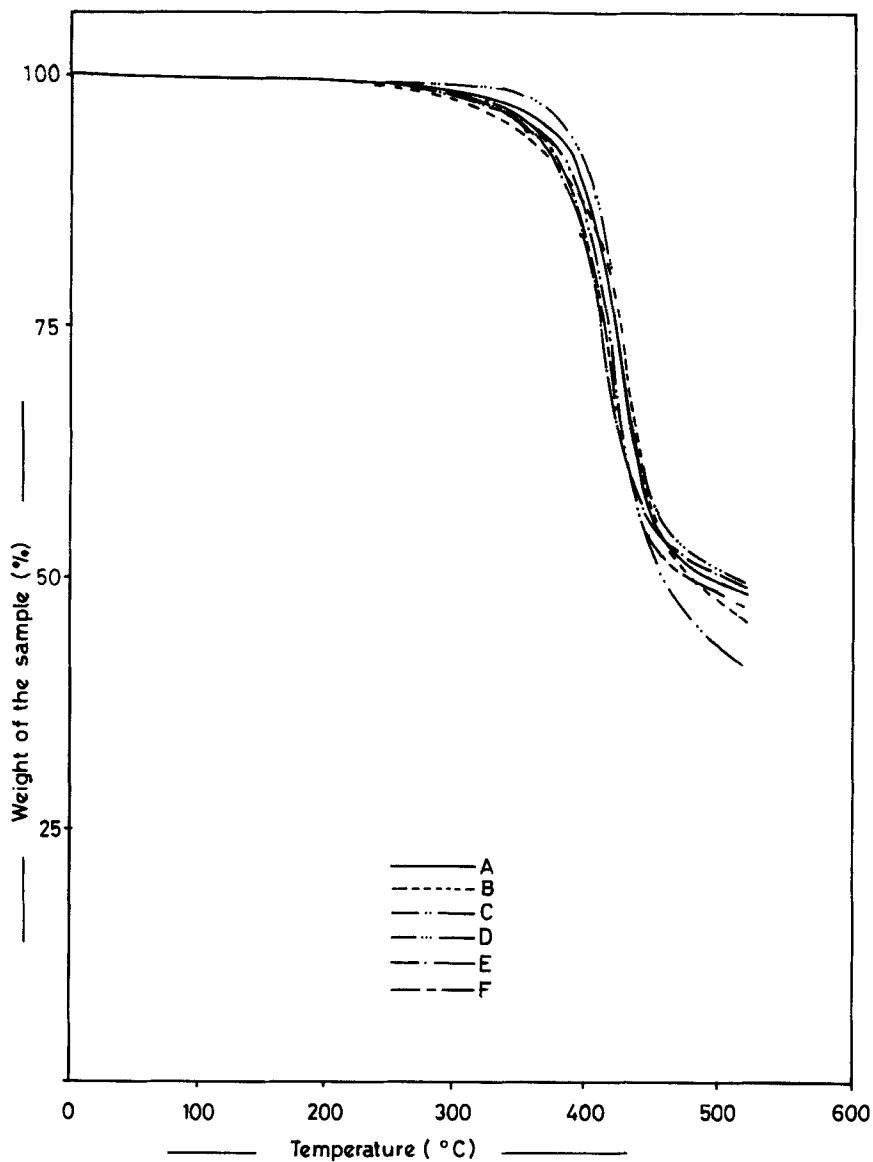


FIG. 2. Thermogravimetric analysis in N_2 . (A) BPA-I, (B) BPA-II, (C) BPA-III, (D) BPA-IV, (E) BPA-V, and (F) BPA-VI. Heating rate, $10^\circ C/min$.

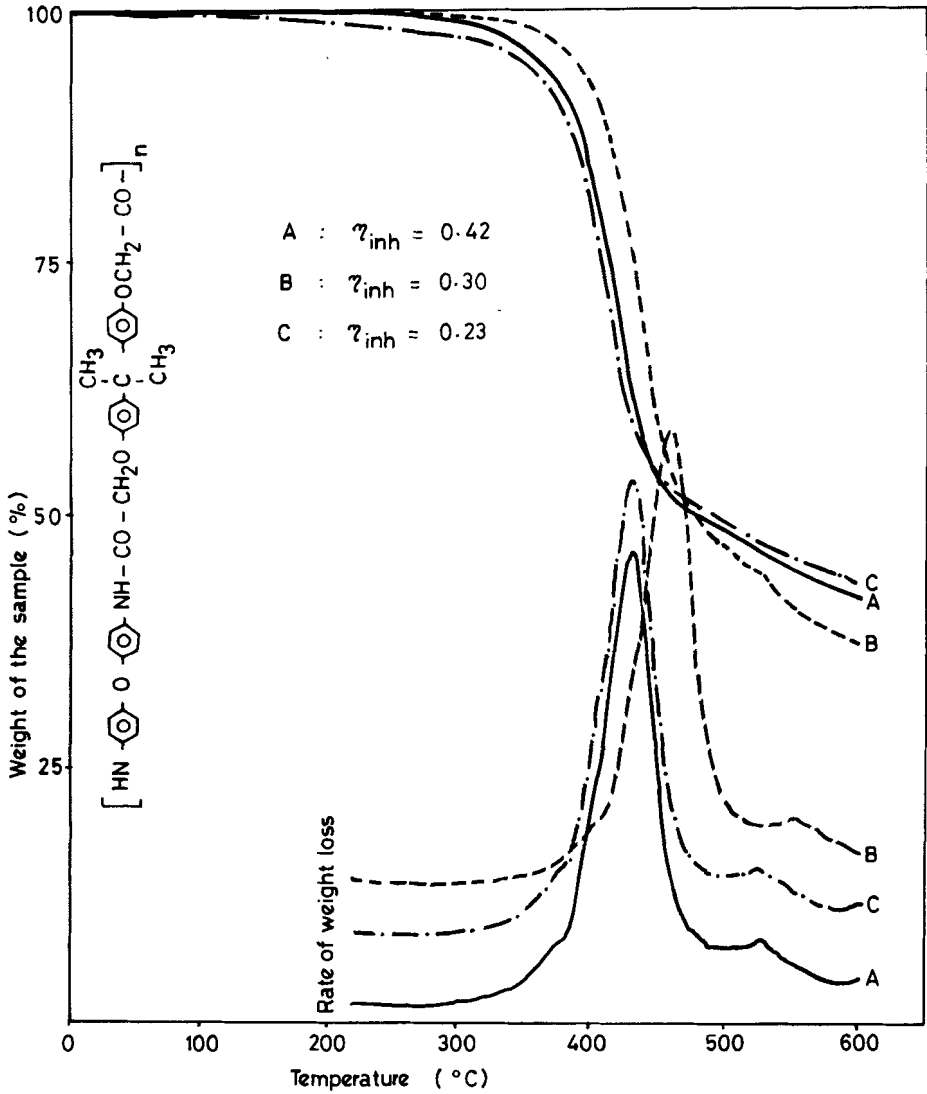


FIG. 3. Effect of molecular weight on the thermal stability of BPA-IV.

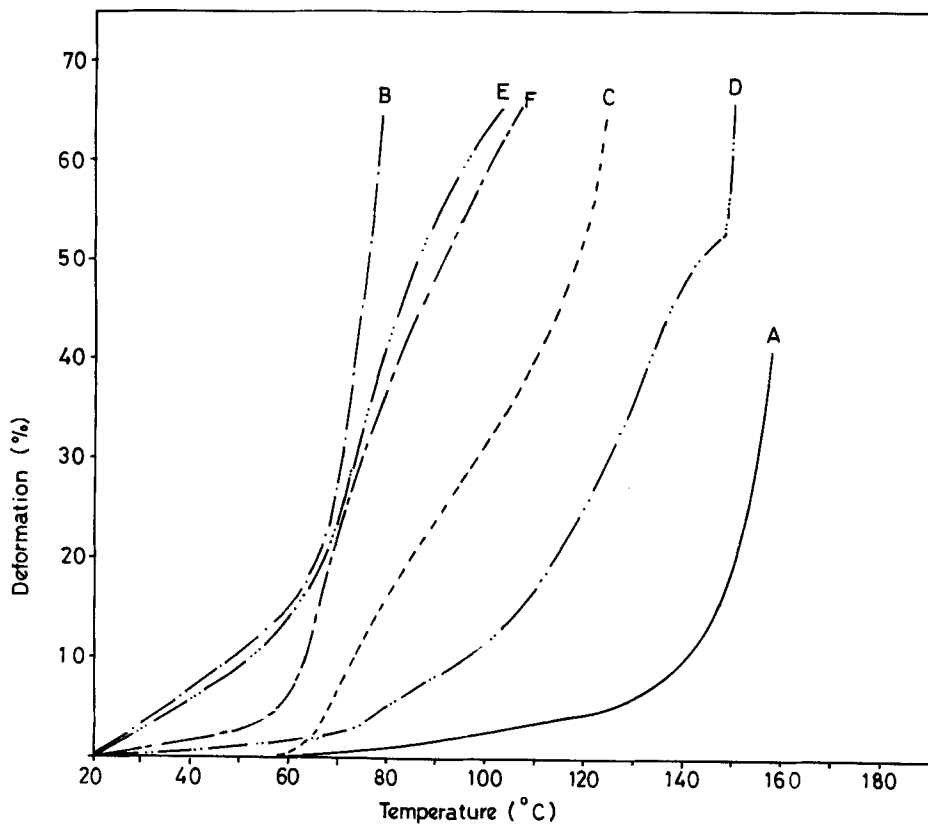


FIG. 4. Thermomechanical curves of polymers. (A) BPA-I, (B) BPA-II, (C) BPA-III, (D) BPA-IV, (E) BPA-V, and (F) BPA-VI. Heating rate, 5°C/min.

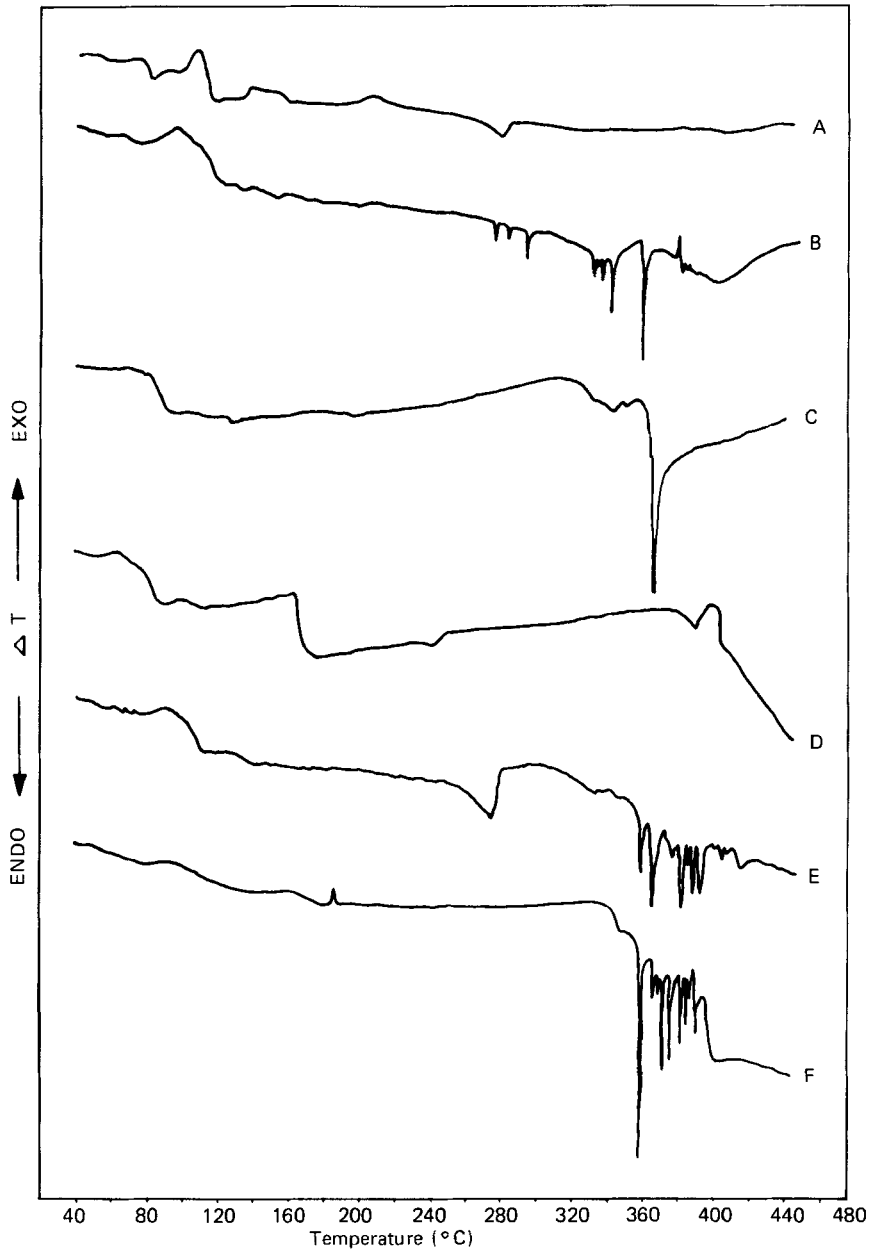


FIG. 5. Differential scanning calorimetry of Bispolyamides in N_2 . (A) BAP-I, (B) BPA-II, (C) BPA-III, (D) BPA-IV, (E) BPA-V, and (F) BPA-VI. Heating rate, $5^\circ\text{C}/\text{min}$.

TABLE 5. Solubilities of Polyamides^a

Polyamide	Concentrated H ₂ SO ₄	HMPA	NMP	DMAC	DMF	DMSO	TFE ^b	THN ^c	THF ^d	Formic acid
BPA-I	SS	SS	SS	SS	SS	SS	I	I	I	I
BPA-II	SS	SS	SS	SS	SS	SS	I	I	I	I
BPA-III	SS	SS	SS	SS	SS	SS	I	I	I	I
BPA-IV	SS	SS	SS	SS	SS	SS	I	I	I	I
BPA-V	SS	SS	SS	S	S	S	I	I	I	I
BPA-VI	SS	SS	SS	SS	SS	S	I	I	I	I

^aSS = soluble at room temperature, S = soluble on heating, I = insoluble.

^bTrifluoroethanol.

^cTetrahydrophthalene.

^dTetrahydrofuran.

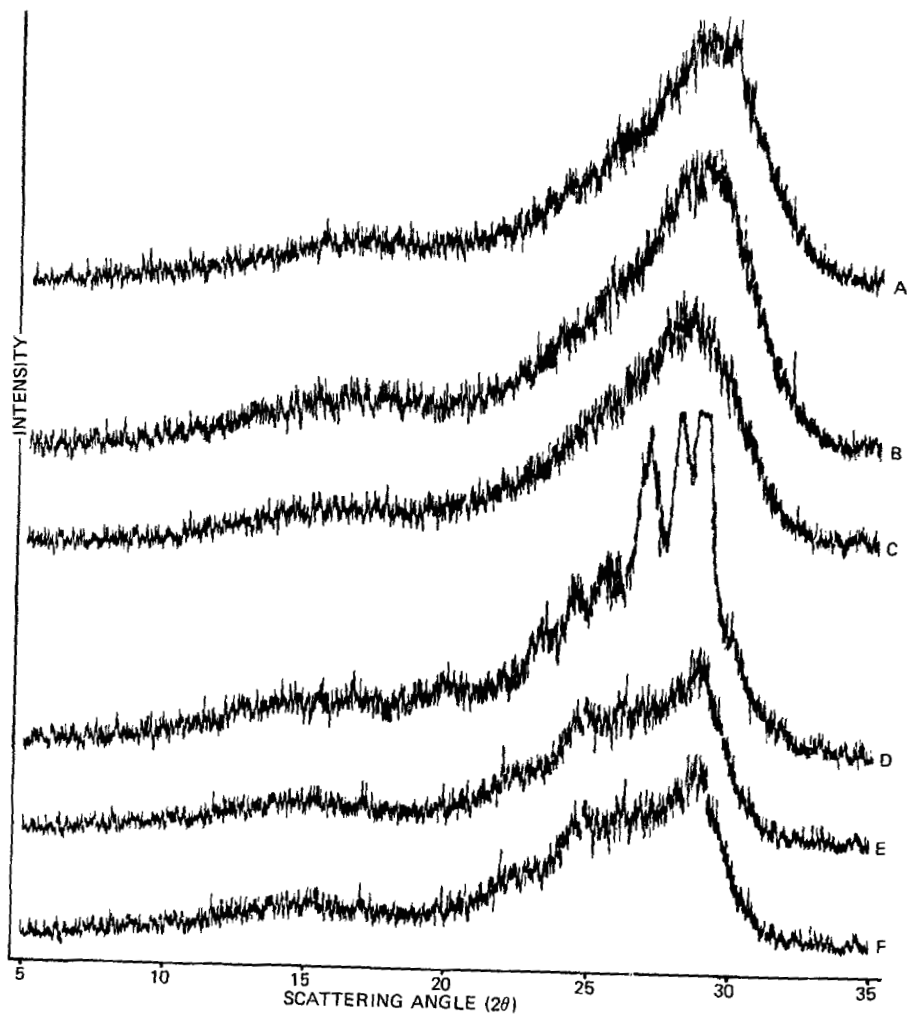


FIG. 6. X-ray diffraction diagrams. (A) BPA-I, (B) BPA-II, (C) BPA-III, (D) BPA-IV, (E) BPA-V, (F) BPA-VI.

mal at low temperatures (-10 to -15°C), and hence all polycondensation reactions were carried out at -10 to -15°C. The polymerization proceeded rapidly with yields in the range from 82 to 95% to give high molecular weight polyamides having η_{inh} 0.32 to 0.63 dL/g (Table 1).

The \bar{M}_n values of the polyamides are in the range from 40 000 to 54 000. All polyamides have polydispersities of 1.32 to 1.98 (Table 1).

The IR spectra of aromatic polyamides are elaborately discussed in the literature [28-30]. The model diamide (MDA) and the polyamides show carbonyl absorption around 1680 cm^{-1} . This absorption, known as the amide I band, arises from the carbonyl stretching of N-H bending and C-N stretching of the C-N-H group, is identified near 1510 cm^{-1} . The N-H stretching band near 3280 cm^{-1} is characteristic of secondary amide linkages.

The lowering of the usual carbonyl frequency from 1715 to 1680 cm^{-1} is due to the resonance effect [28]. Because the diamide and polyamides were examined in the solid state, hydrogen bonding [29] could be the major contributing factor of their lower carbonyl absorption frequency. The model diamide and all polyamides have an absorption at about 3400 cm^{-1} which is attributed to N-H stretching free of H-bonding.

The absorption at 700 cm^{-1} (w) observed for BPA-V is attributed to the aromatic C-S stretching frequency, and the absorption peak at 1150 cm^{-1} (s) found for BPA-VI is due to the symmetric stretching of the sulfone group.

The $^1\text{H-NMR}$ spectral data (Table 3) further confirm the structure of the model diamide and the polyamides. The amide protons were found at δ 10.62-11.28 ppm. The aliphatic protons could not be identified specifically due to serious interference from the solvent, HMPA, which has a strong absorption at δ 2.48-2.52 ppm. The spectra of the model diamide is well resolved, whereas those of the polyamides are found to be broad with poor resolution.

The thermal stabilities of these polyamides, as measured by dynamic TGA methods, are quite comparable (Fig. 2 and Table 4). BPA-II and BPA-III start decomposing at a lower temperature (270°C), taking 2% decomposition as the criterion. But at higher temperatures, all the polyamides have more or less the same rate of decomposition, having T_{max} 420-430°C. All the polyamides are found to have high char yields (40-45%) on decomposition. Cyclization and crosslinking reactions are probably responsible for these high char yields [31].

In order to have a semiquantitative idea of the relative thermal stabilities of the polyamides, the integral procedural decomposition temperature (ipdt) were calculated from the primary thermograms in the temperature range from 100 to 650°C [32]. According to the ipdt values (Table 4), BPA-III is least stable among these bispolyamides, and that is quite expected because of the presence of the weak ethylenic linkage in the polymer backbone. The ipdt values are found to have no direct relation to the molecular weights. BPA-III, having a higher molecular weight compared to BPA-II and BPA-V, is found to have a

lower ipdt value. These results show that the degradation reaction is not by endgroup initiation. If it were by endgroup initiation, a polymer with a lower molecular weight, having more endgroups per unit weight of the material, would be expected to have a lower ipdt value [33]. Again, BPA-IV, having different molecular weights as given by different η_{inh} values, was the subject of further studies. The thermal stability of this polymer as given by the T_{max} values is found to be quite independent of the molecular weight (Fig. 3). If the mechanism of degradation is by endgroup initiation, the T_{max} values would have a direct relation to the molecular weight [34].

The activation energy and the order of thermal decomposition reaction (Table 4) were calculated by the method of Freeman and Carroll [35] as modified by Anderson and Freeman [36]. Since the polymers have high char yields on breakdown, only the initial portion (5-25%) of the decomposition was examined for calculation of kinetic parameters. A wide range of activation energies (23-45 kcal/mol) were observed for these polyamides (Table 4). The activation energy calculated is for the overall degradation reaction comprising initiation, propagation, and termination reactions, and, as such, does not bear any direct relation to the thermal stability [37]. For example, the least stable polymer, BPA-III, according to the ipdt value, has a maximum ΔE value of 45 kcal/mol. Fractional orders in the range from 0.20 to 0.34 (Table 4) were observed for the degradation reactions. Since only the intermediate portion (5-25%) is examined for the calculation of kinetics parameters, a fractional order for the decomposition reaction is quite expected. For these polyamides, the region between 5 and 25% degradation appears to involve the transition from zero-order to first-order kinetics [36].

The polyamides have T_g values in the range 59-73.8°C as obtained from thermomechanical analysis (Table 1 and Fig. 4). All polymers except BPA-III showed an endotherm on the DSC curves in this temperature range, corresponding to the glass transition (Fig. 5). For BPA-III, a broad endothermic transition started at 88°C and this probably corresponds to above T_g transitions of the $T_{\ell\ell}$ type [38].

The exotherms at 109 and 96°C in the DSC curves of BPA-I and BPA-II, respectively, probably correspond to crystallization exotherms. The exotherms at 211 and 190°C observed for BPA-I and BPA-VI, respectively, are probably due to an α - β transition corresponding to a transition from intramolecular H-bonding to intermolecular H-bonding [39, 40]. The endotherms at 275 and 274°C found for BPA-I and BPA-V, respectively, correspond to crystalline melting. The three weak endothermic peaks observed for BPA-II at 273.6, 275.7 and 277.1°C probably correspond to initial weight-loss endotherms. The endotherms observed at temperatures of 320 to 400°C for BPA-II, BPA-III, BPA-V, and BPA-VI correspond to weight loss endotherms. For BPA-I and BPA-IV, the weight loss endotherms are not pronounced, probably be-

cause the weight-loss endotherms are overlapped by the cyclization and crosslinking exotherms.

The crystallinity of the polyamides has been calculated by the literature method [41, 42] (Table 1 and Fig. 6). The polymers are found to be partially crystalline and the crystallinity is in the range from 22 to 35%. BPA-V and BAP-VI are found to have the lowest crystallinity among these polyamides. This is attributed to the presence of bulky groups like S and SO₂ which prevent the regular close packing of the polymer chains required for high crystallinity [43]. All the polyamides are readily soluble in concentrated H₂SO₄ and organic solvents like HMPA, NMP, DMAc, DMSO, and DMF (Table 5). None of these bispolyamides is soluble in THF, THN, TFE, and formic acid. Thus, an increase in the solubility and, hence, an improvement in the processability of polyamides resulted from the incorporation of flexibilizing spacers on the polymeric backbone.

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REFERENCES

- [1] W. B. Black, *J. Macromol. Sci.-Chem.*, **A7**, 3 (1973).
- [2] W. B. Black, *Trans. N. Y. Acad. Sci.*, **32**, 765 (1970).
- [3] J. Preston, *Polym. Eng. Sci.*, **15**(3), 199 (1975).
- [4] E. I. du Pont de Nemours & Co., U.S. Patent 3,006,899 (1961).
- [5] J. Preston and F. Dobinson, *J. Polym. Sci., Part B*, **2**, 1171
- [6] R. S. Lenk, J. L. White, and J. Fellers, *Polym. Sci., Eng. Rep.*, **56** (1975).
- [7] R. S. Lenk, J. L. White, and J. Fellers, *Ibid.*, **58** (1975).
- [8] R. S. Lenk, J. L. White, and J. F. Fellers, *J. Appl. Polym. Sci.*, **21**(6), 1539 (1977).
- [9] R. S. Lenk, J. L. White, and J. Fellers, *Polym. J.*, **9**(1), 9 (1977).
- [10] Z. Grubisic, M. Picot, P. Gramain, and H. Benoit, *J. Appl. Polym. Sci.*, **16**, 2931 (1972).
- [11] J. Cazes and R. Dobbins, *J. Polym. Sci., Part B*, **8**, 785 (1970).
- [12] F. Mc Crackin, *J. Appl. Polym. Sci.*, **21**, 191 (1977).
- [13] ASTM D 3536-76.
- [14] R. S. Lenk and J. F. Kinstle, *J. Appl. Polym. Sci.*, **21**(6), 1469 (1977).

- [15] R. S. Lenk, J. L. White, and J. F. Fellers, Ibid., 21(6), 1543 (1977).
- [16] J. T. Scanlan, J. Am. Chem. Soc., 57, 887 (1935).
- [17] H. A. Stransbury Jr. and W. R. Proops, J. Org. Chem., 26, 4162 (1961).
- [18] L. M. Litvineko and N. F. Lerchenko, Zh. Obshch. Khim., 29, 3079 (1959); Chem. Abstr., 57, 13060d (1962).
- [19] G. A. Reynolds, J. Am. Chem. Soc., 73, 4996 (1951).
- [20] Y.-L. Chi and J.-Y. Moh, K' o Hsueh T' ung Pao, 2, 50 (1957); Chem. Abstr., 53, 188961 (1959).
- [21] A. M. Von Arendock and E. C. Keliderer, J. Am. Chem. Soc., 62, 3521 (1940).
- [22] T. I. Bair, P. W. Morgan, and F. L. Killian, Macromolecules, 10, 1396 (1977).
- [23] P. W. Morgan, J. Polym. Sci., Part C, 4, 1075 (1963).
- [24] L. Starr, J. Polym. Sci., Part A-1, 4, 3041 (1966).
- [25] J. Preston, Ibid., 4, 529 (1966).
- [26] G. I. Braz, N. N. Voznesenkaya, and A. Ya. Yakubovich, Zh. Org. Khim., 9(1), 114 (1973); Chem. Abstr., 78, 110809P (1973).
- [27] N. N. Voznesenkaya, G. I. Braz, and A. Ya. Yakubovich, Vysokomol. Soedin, Ser. A, 14(8), 1822 (1972).
- [28] R. M. Silverstein, G. C. Bassler, and T. C. Morrill, Spectrometric Identification of Organic Compounds, Wiley, New York, 1974.
- [29] D. A. Skoog and D. M. West, Principles of Instrumental Analysis, Holt, Rinehart and Winston, New York, 1971.
- [30] C. J. Pouchert, The Aldrich Library of Infrared Spectra, Aldrich Chemical Company, Milwaukee, Wisconsin, 1975.
- [31] Y. P. Khanna and E. M. Pearce, J. Appl. Polym. Sci., 27(6), 2053 (1982).
- [32] C. D. Doyle, Anal. Chem., 33, 77 (1961).
- [33] I. K. Varma, V. S. Sundari, and D. S. Varma, J. Appl. Polym. Sci., 22, 2857 (1978).
- [34] Y. P. Khanna and E. M. Pearce, J. Polym. Sci., Polym. Chem. Ed., 19, 2817 (1981).
- [35] E. S. Freeman and B. Carroll, J. Phys. Chem., 62, 344 (1958).
- [36] D. A. Anderson, and E. S. Freeman, J. Polym. Sci., 54, 253 (1961).
- [37] E. M. Pearce, Private Communication.
- [38] R. F. Boyer, Rubber Chem. Technol., 36, 1303 (1963).
- [39] R. S. Lenk, J. Polym. Sci., Macromol. Rev., 13, 355 (1978).
- [40] W. Sweeny, U.S. Patent 3,287,324 (1966).
- [41] H. P. Klug and L. E. Alexander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, Wiley, New York, 1954.
- [42] P. H. Hermans and A. Weidinger, J. Polym. Sci., 4, 135 (1949).
- [43] M. Srinivasan, K. J. Scariah, V. N. Krishnamurthy, and K. V. C. Rao, J. Polym. Sci., Polym. Chem. Ed., In Press.

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