Synthesis and Study of New Fluorescent Copolyamides

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ABSTRACT: New fluorescent aromatic copolyamides were synthesized by condensing (i) a mixture of 4,4'-[1,4-phenylenebis(methyldiylne nitrilo)]-di(benzoyl chloride) (I) and terephthaloyl chloride (II) with 4,4'-diaminodiphenyl ether and 4,4'-diaminobibenzyl and (ii) a mixture of monomer (III) and monomer (II) with 4,4'-diaminodiphenyl methane by a low temperature solution polycondensation method.¹

Monomer (III)

The copolyamides were characterized by solubility tests, viscosity measurements, UV, IR, emission spectroscopy, TGA, and DSC data. The spectral and thermal properties of the copolyamides are correlated to their structure and the effect of the new fluorescent diacid monomer unit and terephthaloyl unit on the thermal degradation of the copolymer was also studied.

KEY WORDS Fluorescence / Polycondensation / Copolyamides / Extension of Conjugation / Azomethine Linkage / Terephthaloyl Group / Schiff's Base / Thermal Stability / Glass Transition Temperature /

Completely aromatic polyamides such as poly(*p*-phenylene terephthalamide) and polyamides synthesized from aromatic diamines and terephthaloyl chloride are well known for their chain stiffness and thermal stability.^{2,3} It was of considerable interest to investigate the thermal stability and other physical properties of these aromatic polyamides from terephthaloyl chloride by incorporating some new monomer units (comonomer) in the polymer backbone. The aromatic azomethine linkage is of special interest owing to the *syn-anti* isomerism exhibited by it and its effect on the thermal and photochromic properties⁴ of polymers warrants investigation. An aromatic azomethine group is fluorescent⁵ and it has been reported⁶ that the azomethine linkage ($-\text{C}=\text{N}-$) in polyaromatic Schiff's bases provides greater stability toward thermal degradation compared to the amide ($-\text{C}-\text{N}-$) group in polyamides. However no detailed investigation has

been made on the effect of systematic modification of polyamides by the incorporation of the azomethine linking group in the aromatic polyamide backbone. In this paper, we report our results on the synthesis and characterization by solubility, viscosity, spectral (UV, IR, and emission spectroscopy), and thermal (TGA and DSC) studies of the new fluorescent aromatic copolyamides prepared by the condensation of diamines with a mixture of (i) monomer (I) and monomer (II) and (ii) monomer (III) and monomer (II) in a 1 : 1 ratio. The thermal stabilities of these polyamides is possibly associated with the effect of azomethine linking group on the polymer backbone.

EXPERIMENTAL

Chemicals

4,4'-Diaminodiphenyl ether (Fluka AG) was used without further purification. 4,4'-Diaminobibenzyl

(Fluka AG) was recrystallized from dilute alcohol, and 4,4'-diaminodiphenylmethane (Koch-light) from dry benzene. The diacid chloride (I) was prepared as reported in our previous paper,⁷ by condensing terephthalaldehyde with 4-aminobenzoic acid and refluxing the pure diacid with excess of thionyl chloride in the presence of traces of pyridine

as catalyst. Terephthaloyl chloride (II) was also prepared from terephthalic acid by the above method. The diacid chloride (III) was prepared by the above method using its diacid (monomer VI) obtained by the condensation of terephthalic acid and 4,4'-diaminodiphenylmethane.

Monomer (VI)

The polymerization solvent *N,N*-dimethylacetamide (BDH, England) was treated with potassium hydroxide pellets and distilled over phosphorous pentoxide prior to use. Lithium chloride (SD's) was dried at 100°C in vacuum before use. Lithium carbonate (SD's) was used as it was.

Polymerization

All copolyamides were synthesized by the low temperature solution polycondensation method. In a typical experiment, the polymerization was carried out by adding a 1 : 1 mixture of diacid chlorides (I) and (II) to the chilled diamine solution in DMA/LiCl. The polymerization reached almost completion after ~1 h at -10°C. The temperature was then raised to 25°C and the mixture stirred for one more hour to increase the viscosity. A sufficient amount of lithium carbonate was added to neutralize the liberated HCl. Finally, the reaction mixture was filtered through a coarse glass frit and precipitated in cold water. Repeated water and acetone washes followed by vacuum drying of the filtered polymer at 80°C ensured a lithium free, monomer free, and moisture free copolyamide.

Characterization of the Copolyamides

Solubility. Solubility tests were carried out in DMA, DMSO, NMP, DMF, trifluoroacetic acid, and concentrated sulphuric acid. The effect of the addition of LiCl to DMA on the solubility of the copolyamides was also observed.

Viscosity. Viscosity measurements were carried out in an Ubbelohde suspended level viscometer at 25°C in concentrated sulphuric acid (0.1 g dl⁻¹).

Infrared spectra. The IR spectra of the copolyamides were taken in KBr pellets in a Beckman IR-20 spectrophotometer.

Ultraviolet Spectra. The UV spectra of the monomers and copolyamides were recorded with a Carl-Zeiss UV-VIS specord instrument in dry DMA.

Emission Spectra. The emission spectra of the monomers and copolyamides were recorded with an Aminco-Bowman spectrofluorometer in dry DMA in 10 mm cells.

Thermo-Gravimetric Analysis (TGA). The TGA data were obtained using a Du Pont 951 Thermal Gravimetric Analyser with a heating rate of 10°C min⁻¹ in nitrogen atmosphere.

Glass Transition Temperature (*T_g*). The glass transition temperature *T_g* was determined as the temperature corresponding to one-half the increase in heat capacity at the transition in DSC traces.⁸

Differential Scanning Calorimetry (DSC). The DSC data were obtained using a Du Pont 910 differential scanning calorimeter at a heating rate of 10°C min⁻¹ in nitrogen atmosphere.

RESULTS AND DISCUSSION

The polymerization procedure may be represented by the following reaction scheme.

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Table I. Synthesis conditions and inherent viscosities of the copolyamides

Diamine	Diacid-chlorides ratio	Polyamide	Yield	Color	$[\eta]_{inh}^a$
1 : 1	PS-A	96	Yellowish red	0.86
1 : 1	PS-B	87	Orange red	0.72
1 : 1	PS-C	95	Flesh red	0.67

^a 0.1 g dl⁻¹ of concd H₂SO₄ (98%) at 25°C.

The color and inherent viscosities of the copolyamides are shown in Table I. From the viscosity data, it was observed that the molecular weight of the copolyamides was low. The high moisture sensitivity of the monomers (I) and (III) may be the cause for the lower molecular weight of the prepared polymers. The solubilities of the copolyamides are summarized in Table II. All three copolyamides were found to be easily soluble in concd H_2SO_4 and soluble in trifluoroacetic acid (TFA). The appreciable acid-base interaction between the above solvent molecules and the solute polymer molecules should be the cause for the high solubility. The copolyamides however were found to be insoluble in formic acid which is a good solvent only for aliphatic polyamides. The copolyamides were also found to be partially soluble in DMA and the

Table II. Copolyamide solubility

Solvent ^b	Solubility ^a		
	PS-1	PS-2	PS-3
Concd H ₂ SO ₄	++	++	++
CF ₃ COOH	+	+	+
HCOOH	—	—	—
DMA	±	±	±
DMA/LiCl	±	±	±
DMSO	—	—	—
DMF	—	—	—
NMP	—	—	—

^a Solubility: (++) easily soluble; (+) soluble; (±) partially soluble or swelling; (−) insoluble.

^b DMA, dimethylacetamide; DMSO, dimethyl sulfoxide; DMF, dimethylformamide; NMR, *N*-methylpyrrolidone.

Figure 1. The absorption and emission spectra of monomer IV and monomer VI, copolyamides PS-A, PS-B, and PS-C.

addition of LiCl increased their solubility⁹ to a small extent. In all cases, it was difficult to redissolve the copolyamides in DMA or DMA/LiCl after the copolymers were precipitated from the reaction solutions (DMA/LiCl) by suitable nonsolvents. The copolyamides were also found to be insoluble in DMSO, DMF, and NMP.

The absorption and emission maxima of the monomer 4,4'-[1,4-phenylene bis-(methylidyne nitrilo)]-di-(benzoic acid) (IV), monomer (VI), and the copolyamides prepared are shown in Figure 1. The monomer (IV) and (VI) showed absorption maxima at 292 and 278 nm. Monomer IV showed an emission maximum at 450 while monomer VI, at 425 and 500 nm. The NMR spectra of monomer VI were taken in trifluoroacetic acid using HMDS as the internal reference and are shown in Figure 4. Multiplets in the region 7.1 to 8.0 δ are observed for the aromatic protons. A singlet at 9.0 δ corresponding to the azomethine proton and another singlet at 3.7 δ for benzyl protons are also observed (Ph-CH₂-Ph). The copolyamides PS-A, PS-B, and PS-C showed absorption maxima at 306, 306, and 294 nm and emission maxima at 625, 650, and 675 nm respectively. The increase in both the absorption and emission maxima in going from the monomers

to the polymers may be attributed to the extension of conjugation brought about by the amide group^{10,11} formed during polymerization.

The IR spectra of the copolyamides are shown in Figure 2. In all the copolyamides, the stretching frequency of the carboxyl carbonyl group (1680—1690 cm⁻¹) of the monomer (IV), monomer (VI) and terephthalic acid was absent and instead, the IR band corresponding to amide carbonyl (1645—1650 cm⁻¹) appeared. The disappearance of the two bands corresponding to the primary amino group at 3400—3500 cm⁻¹ followed by the appearance of a single band at 3290—3300 cm⁻¹ on polymerization was also confirmed. From the IR data, the formation of amide linkages during polymerization could be deduced. The —C=N— stretching frequency was found to occur in the range 1600—1605 cm⁻¹ in all three copolyamides. The experimentally determined percentage values of carbon, hydrogen, and nitrogen present in the monomers IV, and VI and polymers PS-A, PS-B, and PS-C were found to agree with the calculated values (Table IV). From the above spectral and elemental analyses data, the structures of the copolyamides have been confirmed as follows:

Figure 2. IR spectra of the copolyamides PS-A, PS-B, and PS-C.

PS-B

PS-C

Figure 3. TGA and DSC curves of copolyamides PS-A and PS-B.

Table III. Copolyamides thermal data

Copolyamides	DSC			TGA	
	Endotherm °C	Exotherm °C	Glass transition temp, T_g °C	Thermal stability	
				Temperature of 10% weight loss	Temperature of 50% weight loss
				°C	°C
PS-A	87 (sharp)	420 (broad)	145	325	540
PS-B	80 (broad) 255	450 (broad)	180	350	550
PS-3 ^a	80, 240 (sharp)	415 (broad)			
	155 (broad)	445 (starts)	160	268	575
PS-4 ^a	80—130 (broad)	315 (sharp)			
		400 (starts)	235	200	675

^a PS-3 and PS-4 are simple polyamides synthesized by condensing monomer I with 4,4'-diaminobenzyl and 4,4'-diaminodiphenyl ether.

Thermal Properties

The TGA and DSC curves of PS-A and PS-B are shown in Figure 3. The thermal analysis data are given in Table III. From the TGA curves of PS-A and the polyamide PS-4¹² it was found that the

introduction of terephthaloyl group, by as much as 50% in the polymer backbone, changed the thermal behavior of the copolyamide PS-A considerably. In the case of polyamide PS-4, a 50% weight loss occurred at 675°C whereas the copolyamide PS-A

Figure 4. NMR spectrum of monomer VI.

Table IV. Elemental analysis data of monomers and polymers

Monomer/Polymer	Elemental analysis					
	C%		H%		N%	
	(Found)	(Calcd)	(Found)	(Calcd)	(Found)	(Calcd)
Monomer IV (mp > 300°C)	70.71	70.96	4.47	4.33	7.23	7.52
Monomer VI (mp > 300°C)	75.05	75.31	4.96	4.79	5.87	6.06
PS-A	74.59	74.81	4.70	4.42	9.51	9.70
PS-B	77.92	78.18	5.31	5.20	9.22	9.43
PS-C	79.17	79.39	5.29	5.08	8.58	8.82

showed a 50% weight loss at 540°C. From this, it is evident that the introduction of a terephthaloyl group decreases the thermal stability of the copolyamide considerably. A similar effect was also observed in the case of PS-B. Though the glass transition temperature of copolyamide PS-A is lower (145°C) compared to that of the polyamide PS-4 (235°C),¹² the difference in the T_g s of copolyamide PS-B (180°), and polyamide PS-3 (160°C)¹² is quite small. Thus, the incorporation of a terephthaloyl unit in the backbone of a polyamide changes the glass

transition temperature also.

The change in T_g value of the copolyamide PS-A from that of the simple polyamide PS-4 may be attributed to a configuration which effects the close packing of the polyamide and copolyamide chains. In the case of PS-4, the presence of an ether linkage (—O—) in the diamine part influences the polymer chain to assume preferentially a helical structure. Now, the close packing of the helical polymer chains may lead to high crystallinity, thereby increasing the T_g value (235°C). As the linear tere-

phthaloyl group is introduced into the backbone of PS-4, the helical structure is disturbed in the resulting copolyamide PS-A, thus decreasing the crystallinity and hence the T_g value. (145°C).

In the case of PS-3,¹² the $-\text{CH}=\text{N}$ -linkage in the diacid part may have a *syn-anti* configuration. In order to achieve maximum crystallinity through close packing, this linkage should have *anti* configuration which may not be realized in polymer PS-3 thus leading to a lower T_g value (160°C). The introduction of the linear terephthaloyl unit introduces more linearity in the copolyamide (PS-B) chains thus leading to an increase in crystallinity. Therefore the T_g value of the copolyamide PS-B is slightly higher (180°C) than that of PS-3.

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