

Processable heat-resistant polymers: 14. Polyamides and polyamideimides containing azo linkages

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Diamines containing azo groups were synthesized by reacting sulphanilamide or *p,p'*-di(aminophenyl) sulphone with aniline. These diamines were used for the synthesis of polyamides and polyamideimides by interfacial and solution polycondensation techniques. The polymers were characterized by elemental (N and S) analyses and by i.r. and u.v. spectroscopy. The physical, chemical, thermal and electrical properties of the polymers were studied. The polymers were found to be soluble in highly polar solvents. The thermal stability of polyamideimides is superior to that of polyamides. X-ray diffraction and electrical behaviour of the polymers were also reported.

Keywords Azo linkage; interfacial polycondensation; solubility parameter; polyamide; polyamideimide; imidodicarboxylic acid

INTRODUCTION

Different types of polymers having azo linkages have been reported in the literature¹⁻⁵. According to recent reports polyamides (PA) having azo groups may be prepared from diacid chlorides and diamines having preformed azo groups in either of the reactants⁶⁻⁹. The present communication is mainly concerned with the synthesis of diazodiamines and copolymers (polyamides (PA) and polyamideimides (PAI)) from these diamines by solution or interfacial polycondensation techniques.

EXPERIMENTAL

Reagents

Trimellitic anhydride (TMA) (Amoco Chemical Corporation, USA) was used after crystallization from acetic anhydride¹⁰. Adipic acid, *p*-aminobenzoic acid (BDH, India), sulphanilamide (IDPL, India) and *p,p'*-di(nitrophenyl) sulphone (HOC, India) were crystallized from ethanol. Thionyl chloride (SD, India) and aniline (BDH, India) were distilled before use. *N,N*-dimethyl formamide (DMF) (E. Merck, India) was dried over phosphorus pentoxide and distilled under reduced pressure (~20 torr). All other solvents used were pure grade.

Monomer synthesis

4,4'-Bis(aminophenyl) sulphone (DADPS)^{11,12} was prepared by reducing di(nitrophenyl) sulphone with stannous chloride and HCl in ethyl acetate medium¹².

Adipoyl chloride was prepared by reacting adipic acid and thionyl chloride¹³.

N-(*p*-Carboxyphenyl) trimellitimide (IDCA)^{14,15} was prepared by reacting TMA and *p*-aminobenzoic acid¹⁵.

The diacid chloride of IDCA¹⁶⁻¹⁸ was prepared by reacting IDCA with thionyl chloride for 14 h.¹⁸

Aminosulphonamide azobenzene (ASAB) was prepared by reacting sulphanilamide and aniline in acid medium following the standard procedure¹⁹. Crystallization from ethanol yielded a yellowish brown powder: yield, 56–59%; melting point, 202°–203°C. Nitrogen content: Calc. 20.03, Found 20.31. Sulphur content: Calc. 11.59, Found 11.92.

p,p'-Bis-aminoazobenzene) sulphone (BAABS) was prepared by the same procedure¹⁹. Crystallization from ethanol gave a yellowish brown powder: yield, 52–54%; melting point, 196°–197°C. Nitrogen analysis: Calc. 18.42, Found 18.31. Sulphur analysis: Calc. 7.02, Found 6.78.

Polymer synthesis

The polymers (PA and PAI) were prepared from adipoyl chloride or the diacid chloride of IDCA with ASAB or BAABS following two different methods.

Synthesis of the polymers by direct polycondensation technique (method A). 1.83 g (10 mmol) of adipoyl chloride or 3.48 g (10 mmol) of the diacid chloride of IDCA in 25 ml DMF were stored together under nitrogen in a tube. The mixture was cooled to 0°C when 2.76 g (10 mmol) of ASAB or 4.56 g (10 mmol) of BAABS and 1.58 g (20 mol) of pyridine were added. The solution was stirred at room temperature (30°–40°C) for 12 h, and then poured into ice/water, filtered, washed with cold water and chloroform, and finally purified from DMF solution by precipitation with methanol.

Synthesis of the polymers by interfacial polycondensation technique (method B). The polycondensation reaction by the interfacial method was carried out using the standard procedure²⁰.

Characterization of the polymers

Viscosity measurements. Viscosity measurements were carried out in 0.5% (w/v) solutions in DMF at 30°C using a Ubbelohde suspended level viscometer.

Density measurements. The density of the polymer samples was determined in dry benzene at 30°C by means of a small pycnometer.

Spectroscopy. I.r. spectra were recorded with a Perkin-Elmer 237B spectrophotometer using nujol mull, u.v. spectra with a Carry-17D UV spectrophotometer in ethanol for monomers, in acetone for PAs and in DMF for PAIs, and n.m.r. spectra of the monomer with a Varian 60 MHz NMR using DMSO-d₆ solvent and trimethyl silane as internal standard.

X-ray diffraction. X-ray diffraction diagrams for the polymers were recorded with a Dorn I (USSR) X-ray diffractometer using N-filtered Cu K α radiation.

Thermal behaviour. Thermogravimetric analysis (t.g.a.) and differential thermal analyses (d.t.a.) for polymers were made simultaneously with a Hungarian Mom Derivatograph of Paulik-Paulik Erdey System. The measurements were recorded in air at a heating rate of 10°C min⁻¹.

Isothermal ageing. The polymers were heated in an air circulating ageing oven at 100°C for PA and at 200°C for PAI for different time intervals.

Electrical properties. The dielectric constant (ϵ'), dielectric loss ($\tan \delta$) and electrical conductivity (σ) with frequency, f , of the polymers were measured at room temperature ($\sim 30^\circ\text{C}$) with a polymer pellet of 1.253 cm diameter and thickness 0.211 cm for PA-1, 0.231 cm for PAI-1, 0.262 cm for PA-2 and 0.206 cm for PAI-2 by using a Radio Capacitance Bridge (Type 716C) at 10^3 and 10^4 Hz.

RESULTS AND DISCUSSION

Characterization of monomers and polymers

The diamines containing azo groups, ASAB and BAABS, are characterized by i.r.²¹, u.v.²², n.m.r.²³ spectroscopy and elemental (nitrogen and sulphur) analysis.

The physical properties of the polymers (PA and PAI) are shown in Table 1. The repeat unit was confirmed by elemental analyses (nitrogen and sulphur), i.r. and u.v. spectroscopy. The characteristic i.r. bands for PA-1 and PA-2 are observed near 1640–1650 cm⁻¹ due to amide groups, at 3250–3400 cm⁻¹ due to –NH– stretching of amides, near 1150 and 1300 cm⁻¹ (PA-1) for SO₂ stretching of sulphonamides, and at 1160 and 1320 cm⁻¹ (PA-2) due to the sulphone groups. The –N=N– stretching bands in both polymers are observed at their respective places. The i.r. spectra for polyamideimides (PAI-1 and PAI-2) show the characteristic absorption bands near 1785, 1725 and 725 cm⁻¹ due to imides and near 1640–1650 cm⁻¹ due to amide groups. The presence of a broad band near 3300 cm⁻¹ is the characteristic –NH– stretching absorption band of amides and the –SO₂– stretching band of sulphonamides or sulphones are observed at their respective places mentioned earlier.

The u.v. spectra of the polymers show that there is a small peak near 358 nm for PA-1, PA-2 and PAI-1 and 362 nm for PAI-2 which correspond to the presence of azo groups (–N=N–) in the polymers.

Solution viscosity behaviour

Inherent viscosity measurements (Table 1) indicated that the polymers were of low molecular weight. The polymers prepared by method A possess relatively higher inherent viscosity compared with the polymers prepared by method B. Similar observations have been reported by Imai *et al.* for other polyamideimides²⁴.

All the polymers (PA and PAI) form stable solutions in DMF and other polar solvents. However, the decrease of solution viscosity with time is rather higher in PAs than PAIs. This may be due to degradation of the polymer chain by solvents.

X-ray diffraction study of polymers shows that polyamides are partially crystalline whereas polyamideimides are amorphous. The higher crystallinity of the former may be due to the presence of the smaller –(CH₂)₄– unit that may readily fit into the crystal lattice.

Thermal behaviour

Thermogravimetric analyses (t.g.a.) and differential thermal analyses (d.t.a.) for polymers in air are shown in Figures 1 and 2. T.g.a. data indicate that initial weight losses of about 9% (PA-1), 13% (PA-2), 13% (PAI-1) and 4% (PAI-2) occur at 100°–110°C. This is due to the loss of moisture or entrapped solvent present in the polymers.

Table 1 Yield and physical properties of the polyamides and the polyamideimides

Polymer code	Method of polymerization	Yield (%)	Inherent ^a viscosity (dl g ⁻¹)	Density (g cm ⁻³)	T_m^b (°C)	Nitrogen (%)		Sulphur (%)	
						Calc.	Found	Calc.	Found
PA-1	A	88–90	0.26	1.19	246	14.50	14.01	8.29	7.67
	B	78–82	0.14	1.18	–	14.50	14.03	8.29	7.92
PA-2	A	81–85	0.29	1.23	255	14.84	14.32	5.65	5.07
	B	73–76	0.13	1.22	–	14.84	14.18	5.65	5.51
PAI-1	A	72–74	0.18	1.19	348	10.16	9.82	5.80	5.29
	B	66–67	0.11	1.17	–	10.16	9.78	5.80	6.02
PAI-2	A	68–72	0.20	1.24	360	10.94	10.60	3.98	3.53
	B	65–66	0.14	1.23	–	10.94	10.89	3.98	3.62

^a Measured in DMF (0.5 wt% solution) at 30°C

^b Calculated from d.t.a. curves (Figures 1 and 2)

Subsequently there are weight losses of about 12% (PA-1) and 2% (PAI-1) at 300°C and 13% (PA-2) and 8% (PAI-2) at 355°C. The degradation of the polymer follows a complex process and maximum weight loss occurs at 350–600°C. The melting temperature, T_m , as evident from the d.t.a. curves, is found to be 246°C (PA-1), 255°C (PA-2), 348°C (PAI-1) and 360°C (PAI-2). The d.s.c. curve for PAI-2 in nitrogen atmosphere also shows a melting point in nearly the same temperature region.

The loss of weight after heating the polymers (PAs at 100°C and PAIs at 200°C) in air for 12 h is shown in Table 2, which indicates that PAIs possess better thermal stability than PAs.

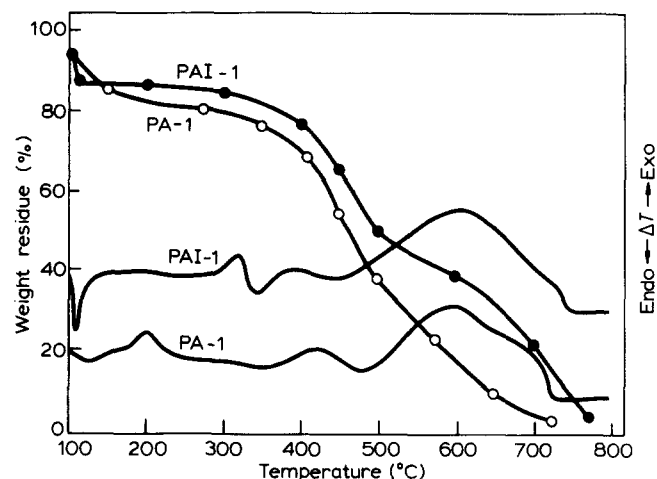


Figure 1 Differential thermal analysis (d.t.a.) and thermogravimetric analysis (t.g.a.) of the polymers recorded in air at a heating rate of $10^\circ\text{C min}^{-1}$

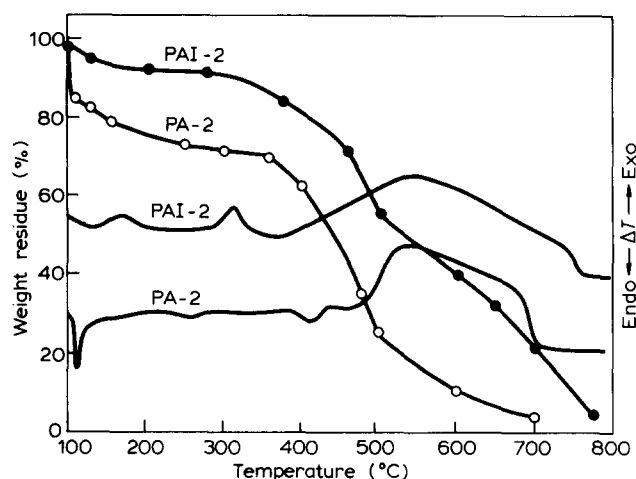


Figure 2 D.t.a. and t.g.a. of the polymers recorded in air at a heating rate of $10^\circ\text{C min}^{-1}$

Table 2 Isothermal ageing of the polyamides and the polyamideimides

Polymer	Weight loss (%) after heating in air at different intervals		
	1 h	6 h	12 h
PA-1 ^a	6.8	1.3	0.8
Cumulative weight loss	—	10.1	12.6
PA-2 ^a	11.6	0.7	0.8
Cumulative weight loss	—	15.6	17.8
PAI-1 ^b	8.8	1.5	0.5
Cumulative weight loss	—	16.1	17.9
PAI-2 ^b	5.2	1.4	1.1
Cumulative weight loss	—	9.2	14.2

^a Measured at 100°C

^b Measured at 200°C

Electrical properties

The variation of dielectric constant (ϵ'), dielectric loss ($\tan \delta$) and electrical conductivity (σ) of polymers with frequency, f , (10^3 and 10^4 Hz) at room temperature ($\sim 30^\circ\text{C}$) is shown in Table 3. The dielectric constant of the polymers decreases with frequency, due to the fact that the alternating electric field tends to orient the polar groups in the direction of the applied field²⁵. With the increase of frequency the orientation of the polar groups gradually decreases and hence the dielectric constant also decreases. The dielectric loss of the polymers increases slightly with change of frequency from 10^3 to 10^4 Hz. The electrical conductivity of all the polymers at 10^3 and 10^4 Hz is found to be 8.48×10^{-11} – 2.07×10^{-10} $\text{ohm}^{-1} \text{cm}^{-1}$. The higher conductivity value of these polymers arises due to the heterogeneity of the sample, conducting impurities, molecular weight distribution and crystal defects, and gradually exerts its influences in the lower frequency region²⁶.

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Table 3 Electrical behaviour of the polyamides and the polyamideimides^a

Polymer code	Dielectric constant, ϵ'		Dielectric loss, $\tan \delta$		Electrical (a.c.) conductivity, σ ($\text{ohm}^{-1} \text{cm}^{-1}$)	
	10^3 Hz	10^4 Hz	10^3 Hz	10^4 Hz	10^3 Hz	10^4 Hz
PA-1	6.62	6.31	0.049	0.059	1.8×10^{-10}	2.07×10^{-10}
PA-2	6.27	6.16	0.038	0.042	1.32×10^{-10}	1.44×10^{-10}
PAI-1	5.92	5.81	0.031	0.038	1.02×10^{-10}	1.22×10^{-10}
PAI-2	5.87	5.76	0.026	0.033	8.48×10^{-11}	1.05×10^{-10}

^a Measured at room temperature ($\sim 30^\circ\text{C}$)

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