SHORT COMMUNICATIONS

Synthesis of Poly(amide-imide)s from *N,N'*-(Pyromellitoyl)diglycine

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Earlier reports from our laboratory described the synthesis of certain new polyamides and polyimides containing azo and ether linkages in the main chain.^{1,2} Yang³ has reported the synthesis of several poly(amide-imide)s from *N,N'*-bis(chloroformylmethyl)pyromellitimide. In this paper we present the synthesis of three new poly(amide-imide)s and a copoly(amide-imide) from the same diacid chloride. Aromatic poly(amide-imide)s are noted for their outstanding thermal stability.⁴

EXPERIMENTAL

N,N'-Bis(chloroformylmethyl)pyromellitimide (2) was prepared as reported by Yang³ and melted at 240°C (lit.³ mp 240°C). 4,4'-Diaminoazobenzene was prepared by the method of Witt and Kopetschni.⁵ It was recrystallised from ethanol; mp 251°C (lit.⁵ mp 246°C). 4,4'-Diaminodiphenyl ether (Fluka; mp 188°C), 4,4'-diaminodiphenylsulphone (Fluka; mp 174°C) and 1,5-diaminonaphthalene (Fluka; mp 188°C) were recrystallised from alcohol.

N,N-Dimethylacetamide (Seramac Solvent, India) was dried first over KOH pellets and then distilled over P₂O₅ (bp 161—162°C).

Polycondensation was carried out as follows. In a 100 ml 3 necked flask with an N₂ inlet at the bottom, 1.06 g (0.005 mol) of the amine (3) was added to 25 ml of dried DMAc containing 5% LiCl. After stirring for a few minutes under nitrogen, 1.845 g (0.005 mol) of diacid chloride (2) was added. The temperature of the flask was maintained at 0—5°C, using an ice salt mixture. Stirring was continued for about an hour at this temperature and for about 3 h at room temperature. The viscous solution obtained was poured into water to precipitate the polymer. The polymer obtained was washed with water several times and finally with methanol. It was dried under vacuum at 100°C for 8 h.

RESULTS AND DISCUSSION

The synthesis of the poly(amide-imide)s can be represented by the following general equation.

Table I. Poly(amide-imide) properties

Polymer	Colour	Yield	η_{inh}^a	Spectra	
		%	dl g ⁻¹	UV-vis (nm)	IR (cm ⁻¹)
4a	Orange	96	0.86	234, 428	1680, 1720
4b	Orange yellow	96	0.58	234, 434	1780, 3330
4c	Colourless	96	0.58	234	1550, 1250
4d	Colourless	84	0.45	232, 222	720

^a Measured at a concentration of 0.5 g dl⁻¹ in DMA/LiCl at 25°C.

Figure 1. IR spectrum of polymer, **4a**.

The properties of the poly(amide-imide)s are given in Table I. All the polymers were insoluble in common organic solvents. The polymers were also insoluble in polar solvents such as DMAc, NMP, DMF, and DMSO, but soluble when these solvents contained 5% LiCl. Polymers **4b** and **4c** were partially soluble in *m*-cresol, due to the presence of flexible groups such as $-O-$ and $-\text{S}-$, which reduce the

chain rigidity. Polymers **4a** and **4b** have high chain rigidity due to the presence of rigid azo groups, leading to poor solubility. Furthermore, **4d** with its fused ring system has very low solubility.

The inherent viscosity of the polymers varies from 0.45 to 0.86. The inherent viscosity of copolymer **4b** prepared with the two diamines was in between those of the polymers prepared from the diamines individually. The synthesis of the poly(amide-imide) with an inherent viscosity of 0.46

Figure 2. TG curves of the poly(amide-imide)s in N₂.

Figure 3. DTA curves of the poly(amide-imide)s.

from 4,4'-diaminodiphenyl ether has already been reported.³

Two bands, one in the UV region and another in the visible region, were observed for polymers **4a** and **4b**. The visible absorption was due to the presence of the azo chromophore in the main chain. Polymers **4c** and **4d** had absorption only in the UV region since they were colourless. The IR spectrum of polymer **4a** is give in Figure 1. All the polymers showed almost identical spectra.

The heat resistivity of the polymers was studied by thermogravimetry. The temperature at which a 20% weight loss occurred was taken for comparing the thermal stability of the polymers. The results

Polymer	4a	4b	4c	4d
Temp of 20% wt. loss	390	385	395	385

indicate that the thermal stability of all the polymers is almost the same. However, Figure 2 shows

that the degradation of polymer **4a** is slow when compared to the others. This decomposition takes place mainly in two steps, at almost the same temperature for all the polymers (Figure 3), indicating that the nature of the decomposition may be similar for all the polymers. Further work on the improvement of the molecular weight and preparation of the films is now in progress.

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