

Synthesis of Aromatic-Aliphatic Polyamides Containing Azo Linkage

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SUMMARY

Two inherently coloured polyamides containing aromatic azo unit in their backbone were synthesised from 4,4'-diaminoazobenzene (1) and two aliphatic dicarboxylic acid chlorides (2a, 2b) using N-methyl pyrrolidone (NMP) and N,N-dimethyl acetamide (DMAc) as solvents by the low temperature solution polycondensation method. The polymers were characterised by inherent viscosity, solubility, infra-red and UV-visible spectroscopy. Thermogravimetric analysis of the polymers was carried out to study polymer stability.

INTRODUCTION

In recent years, a number of polymers incorporating the azo (-N=N-) group as an integral part of the main chain, have been reported. Presence of the azo chromophore in a polyamide backbone increases chain stiffness and imparts colour to the polymer. The growing interest in these polymers is also due to their possible use as high grade pigments of good fastness to light and as materials which exhibit photochromic and photocontractible behaviour (RIORDAN and BLAIR, 1979). Recently NANJAN et al (1979, 81) from this

laboratory reported the synthesis, characterisation and spinning of some aromatic polyamides containing azo linkage in the polymer backbone. Although a number of aliphatic-aromatic polyamides have been reported in the literature, reports on the synthesis of azo group containing aliphatic-aromatic polyamides which are expected to be fibre forming are only scanty. In this paper, the authors report the synthesis of two such aromatic-aliphatic polyamides containing azo group in the backbone.

EXPERIMENTAL

4,4'-Diaminoazobenzene (1) was prepared by the method of WITT and KOPETSCHNI (1912). p-Nitroaniline (Riedel) in dil. H_2SO_4 was converted to 4,4'-dinitroazobenzene containing small amounts of the corresponding azoxy compound by the oxidative coupling with $K_2S_2O_8$. The crude dinitro mixture was then subjected to reduction with NaSH in boiling aqueous ethanol. The diamine after purification and recrystallisation from ethanol melted at 251°C.

Adipoyl chloride was prepared by refluxing adipic acid (Loba-chemie, India) with excess of thionyl chloride in benzene for 3 hrs. B.p. 121-122°C/11 mm.

Azeloyl chloride was prepared in a similar manner from azeloic acid (Koch-Light) B.p. 147-148°C/5-6 mm.

N-Methyl pyrrolidone (Koch-light), was dried first over KOH pellets, then over P_2O_5 and finally distilled over freshly added P_2O_5 . B.p. 196-197°C.

N,N-Dimethyl acetamide (Ceramic solvents,

India) was purified in a similar manner. B.p. 161-162°C.

Polymerization : 4,4'-Diaminoazobenzene (around 1g) was stirred in 30 ml of DMAc or NMP in a nitrogen atmosphere at -10 to -5°C. After 15 min stirring, an exact equivalent of the diacid chloride (2a or 2b) in 4 ml of dry THF was added in drops to the stirred solution. The stirring was continued for a further period of 30 min. The cooling bath was removed and calculated amount of Li_2CO_3 was added with stirring and the contents were left overnight. The polymer, precipitated in water, was washed with water, dil HCl, dil Na_2CO_3 , water and then with acetone. It was finally dried in vacuum over P_2O_5 at 100°C.

Viscosity measurements of 0.5% solutions were made in 98% H_2SO_4 at 25°C in a Ubbelohde suspended type viscometer. Freshly prepared solutions were used to exclude the possibility of degradation.

Solubility was tested by taking about 1-2 mg of the polymer in 2-3 ml of the solvent. If insoluble in cold, the solution was subjected to heating.

UV-visible spectra of the polymers were recorded in 98% H_2SO_4 with a Carl-Zeiss UV-VIS Spectord spectrophotometer using closed cells.

Infra-red spectra were recorded with Beckman IR-20 spectrophotometer using KBr discs.

Thermogravimetric analysis of the two polymers were carried out in air using a Rigakudenki DTA-TGA thermo analyser at a heating rate of 10°/min.

RESULTS AND DISCUSSION

Synthesis of the two polyamides can be represented as follows:

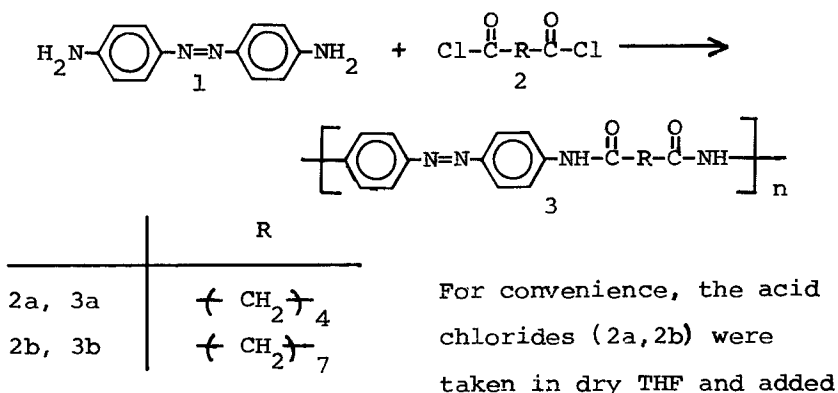


TABLE 1

Properties of the polymers 3a and 3b

Medium	Colour	Yield (%)	η_{inh} (dl/g)	Spectra		
				UV-VIS λ_{max} (nm)	IR (cm ⁻¹)	
3a	DMAc	Brown	93	0.21	238, 430	1665, 3290
	NMP		95	0.21		
3b	DMAc	Yellow	91	0.10	243, 454	1665, 3290
	NMP		89	0.12		

was obtained as hard, dense and crystalline form whereas 3b was obtained as highly amorphous light-weight material. 3b readily gave a powder on grinding while 3a gave a powder only on prolonged grinding. Crystalline nature of 3a which is derived from

an even carbon diacid chloride may be due to the possible 'tactic chain order' (TSVETKOVA and SHTENNIKOVA, 1978) existing in its crystal lattice as a consequence of the interchain attraction and stereoregular packing of the polymer chains. Such a packing is not likely in 3b which is derived from the odd carbon diacid chloride (STATTON, 1959).

Use of either DMAc or NMP as the polymerization solvent seems to have no effect on the molecular weight of the polymers as exemplified by almost the same inherent viscosity values obtained in both the cases.

The two polymers 3a and 3b were tested for solubility in a variety of solvents. Both 3a and 3b were insoluble in common organic solvents like THF, benzene and chloroform. But in more polar solvents like NMP, DMAc, DMSO, DMF and pyridine the two polymers are very sparingly soluble at room temperature. However, on heating, 3b dissolved in NMP, DMAc and DMSO, whereas heating caused no significant change in the solubility of 3a. Solubility of aromatic polyamides generally depends upon the extent of interchain hydrogen bonding, rigidity of the polymer backbone and molecular weight of the polymer sample. For a given volume of polymer in the bulk phase, 3a with its smaller repeat unit length is expected to contain a large number of interchain hydrogen bonds than 3b. Also the molecular weight of 3a is higher than that of 3b (Table 1). This explains the poor solubility of 3a when compared to 3b. Both the polymers are soluble in

98% H₂SO₄.

Infra-red spectra of the two polymers were almost identical. This is due to the similarity in structure of the two polymers. The polymers showed the characteristic amide carbonyl and amide N-H stretchings at 1665 and 3290 cm⁻¹ respectively. The azo group frequencies (1405, 1590 cm⁻¹) were observed for both the polymers (LEFEVRE et al 1953, UNEO 1957).

The UV-visible spectra of the polymers are of interest because of their azo chromophore. In the UV-visible spectra two bands were observed for both the polymers, one in the UV region and the other in the visible region. λ_{\max} values are given in Table-1. The band in the UV-region arises due to $\pi \rightarrow \pi^*$ transition and that in the visible region is due to $n \rightarrow \pi^*$ transition. It was observed that the absorbance value decrease with time in conc. H₂SO₄ for both the polymers pointing to solvolytic degradation. However, λ_{\max} is not shifted to a new wavelength. This solvolytic degradation was also noted in the course of viscosity measurements.

Thermooxidative stability of the two polymers as indicated by their percent weight loss with temperature is given below.

	WEIGHT LOSS IN PERCENT									
	5	10	15	20	25	30	35	40	45	
Polymer 3a Temp in °C	331	375	394	414	433	472				
Polymer 3b Temp in °C	340	342	346	362	389	424	452	471	488	

Both the polymers 3a and 3b were stable upto 300°C. 3a suffers a gradual decomposition with temperature while a rapid weight loss of about 10% was noted for 3b in the temperature range 340-346°. The thermal data shows that 3a is more stable than 3b. For example, at 470°C, the percent weight loss of 3a is only 30 compared to 40 for 3b. The higher stability of 3a may be attributed to its higher molecular weight and crystalline nature involving greater interchain hydrogen bonding. Further work on improvement of molecular weight and fiber studies are in progress.

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