Synthesis and characterization of inherently coloured azo polyamides

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Six intrinsically coloured azo polyamides have been prepared by interfacial polycondensation and characterized by visible, ultra-violet and infra-red spectroscopy, viscometry and differential thermal analysis.

INTRODUCTION

Much interest has been aroused over the past few years in the synthesis of polymers which have a chromophoric system forming part of their structure. A number of polymers incorporating the azo chromophore have been prepared. Some of the interest in this type of polymer is due to their possible use as high grade pigments of good fastness to light, also as materials which exhibit photochromic and photocontractile behaviour. Most of the azo polymers, which have been reported in the literature, may be broadly classified into three groups:

(a) polymers formed by modification of existing polymers[1-6];

(b) addition polymers which have azo structures appended to the polymer backbone and are obtained from azo compounds carrying olefinic groups[5,7-10];

(c) polymers which have azo groups as an integral part of the main chain[10-30].

Of the third group, polyesters and polyamides prepared by polycondensation of azobenzene derivatives have received most attention. The azo polyamides now reported are of this type. Several reviews dealing with inherently coloured polymers have been published[31-34].

Azo polyamides have been shown to be formed on adding azodibenzoic acids during the polymerization of ε-caprolactam[20]. Melt polycondensation methods were used by Bykov[21] to give a polyamide from 2,2'-azodibenzoic acid and 1,6-diaminohexane, that from the 4,4'-azo diacid could not be prepared under these conditions. Low temperature polymerization methods have been used for azo polyamides. A Du Pont patent[22] claims the preparation of coloured polymers containing an azo, azine or anthraquinone chromophore. A number of azo polyamides are described, prepared by solution or interfacial polycondensation procedures. Bykov *et al.*[23,24] have used various substituted azo diacid chlorides in the synthesis of azo polyamides. During studies of photoisomerization behaviour of molecules, Morawetz and coworkers[10,25,26] synthesized a number of azo copolyamides involving 4,4'-azodibenzoyl chloride and uncoloured diacid chlorides with diamines including 4,4'-diaminoazobenzene. Other azo polyamides and copoly-amides using 4,4'-azodibenzoyl chloride as one of the reactants have been reported[27-30].

In the present work, six azo polyamides have been prepared using interfacial polycondensation techniques, from respectively, 3,3'-azodibenzoyl chloride and 4,4'-azodibenzoyl chloride with each of the diamines, 1,6-diaminohexane, piperazine and *trans*-2,5-dimethylpiperazine. Five of these polymers have not been previously reported; the polymer from 4,4'-azodibenzoyl chloride and *trans*-2,5-dimethylpiperazine is reported in a patent[22] but only a few properties are described; it is claimed that this polymer has pronounced resistance to light.

The six polyamides reported in this work have the structures shown in *Figure 1*. The names of the polymers and the codes used to simplify reference to the polymers, for this publication, are given in *Table 1*. The azo diacid chlorides were synthesized as described below, the diamines were commercially available. 1,6-Diaminohexane was chosen as an example of a primary diamine. Piperazine, a cyclic secondary diamine, is known to give soluble polyamides. Polyamides from *trans*-2,5-dimethylpiperazine are generally of high molecular weight when prepared by interfacial polycondensation, and have greater solubility than those derived from piperazine.

EXPERIMENTAL

Azodibenzoic acids

3,3'-Azodibenzoic acid. This was prepared by the sodium perborate/acetic acid oxidation of 3-aminobenzoic acid. To a vigorously stirred solution of sodium perborate tetrahydrate (135 g) in glacial acetic acid (750 cm³), was added slowly a solution of 3-aminobenzoic acid (103 g, 0.75 mol) in glacial acetic acid (750 cm³). The temperature was maintained at 40°C for 3 hours. After cooling to room temperature, the solid obtained was filtered off, washed with acetic acid and water, and air-dried. It was a mustard-yellow powder, 47% yield; m.p. 345°C (dec); λ_{max} (0.1M NaOH) 319 nm (log ϵ 4.12), 425 nm (log ϵ 3.04).

This azo diacid has been prepared by a number of methods but it is probable that many of those mentioned in
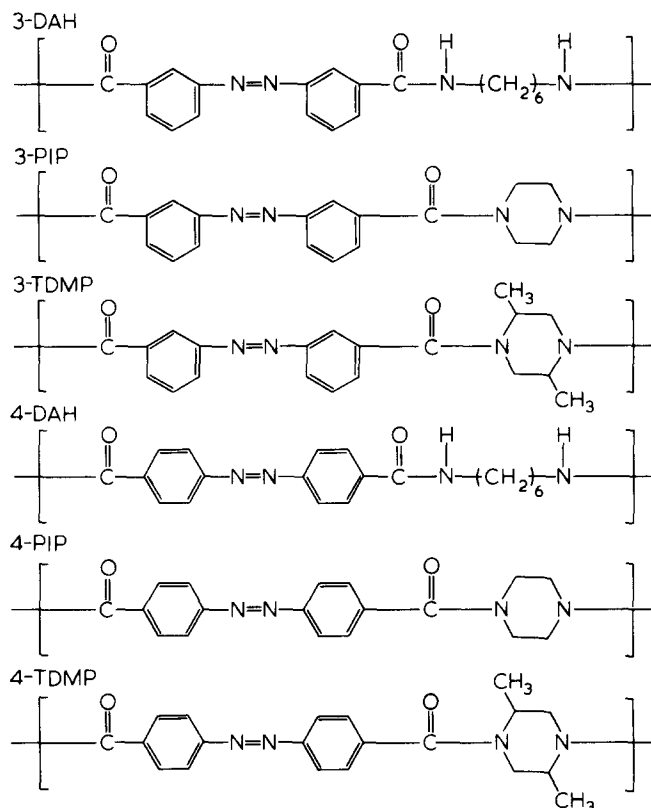
3-DAH

3-PIP

3-TDMP

4-DAH

4-PIP

4-TDMP

Figure 1 Structures of the azo polyamides

the early literature, and involving reduction of 3-nitrobenzoic acid, gave products contaminated with the azoxy compound. A copper—ammonia hydroxylamine reducing agent was used by Atkinson *et al.*[35] and Bogolovskii[36] for the decomposition of diazotised 3-aminobenzoic acid. The 3,3'-azodibenzoic acid obtained was reported as having a melting point of 340°C (dec).

4,4'-Azodibenzoic acid. This was prepared by the method of Tomlinson[37] involving the glucose reduction of alkaline 4-nitrobenzoic acid solution to the hydrazo diacid, followed by air oxidation. The resulting orange pink powder gave 77% yield, melting point $> 360°C$, λ_{max} (0.1M NaOH) 230 nm (log ϵ 4.08), 331 nm (log ϵ 4.38), 431 nm (log ϵ 3.13). Spectroscopic data were not reported by Tomlinson. The data reported above are in agreement with those of Reid and Pritchett[38] who prepared small quantities of this azo diacid by the reduction of 4-nitrobenzoic acid using zinc dust and sodium hydroxide, following by air oxidation.

These azo diacids are very insoluble substances which decompose at relatively high temperatures. The azo diacids, prepared as described above, were of sufficiently high purity to be used directly in the synthesis of the azo diacid chlorides, required for the polymer syntheses.

Azodibenzoyl chlorides

3,3'-Azodibenzoyl chloride. This was prepared by the reaction of 3,3'-azodibenzoic acid with thionyl chloride. 34.0 g (0.12 mol) of 3,3'-azodibenzoic acid and 72.0 g (0.60 mol) anhydrous sodium carbonate were thoroughly mixed by shaking. To this mixture was added 360 cm^3 (5.00 mol) of thionyl chloride and the mixture refluxed for 3 h. Excess thionyl chloride was removed by distillation.

The crude diacid chloride was dissolved by refluxing with portions of 80°—100°C petroleum ether. This extract was

filtered hot, concentrated by distillation, and allowed to cool; the crystals which deposited were recrystallized from petroleum ether. They were orange crystals: 51% yield; m.p. 97—98°C. Composition found: C, 54.87%; H, 2.72%; Cl, 22.95%; N, 9.40%. $C_{14}H_8Cl_2N_2O_2$ requires C, 54.72%; H, 2.62%; Cl, 23.09%; N, 9.12%; λ_{max} (cyclohexane) 247 nm (log ϵ 4.55), 315 nm (log ϵ 4.32), 444 nm (log ϵ 2.67).

Korshak *et al.*[18] have claimed the synthesis of this compound and report a melting point of 83.5°—84.5°C. Diazotized 3-aminobenzoic acid was decomposed to give the azo diacid. No details are given but the method used is probably similar to that due to Bogolovskii[36] and involves a copper—ammonia/hydroxylamine reducing agent. Conversion of the azo diacid to the azo diacid chloride was effected using thionyl chloride.

Because of the difference in melting point, the azo diacid chloride was also prepared, in this present work, using Korshak's method. The diacid, obtained with 85% yield and m.p. 330°C (dec), was less pure than that obtained by the perborate oxidation procedure — λ_{max} (0.1 M NaOH) 320 nm (log ϵ 4.10), 420 nm (log ϵ 2.83). On forming the diacid chloride, using thionyl chloride, the crude product had a melting point of 92°—93°C. After careful purification by recrystallization, the melting point was raised to 94°—95°C and vacuum sublimation of a small sample gave a melting point of 96°—97°C.

That this purified sample of the azo diacid chloride was identical with the 3,3'-azodibenzoyl chloride prepared in this present work, was shown by mixed melting point and spectroscopic studies. The samples, prepared by the two routes, had identical infra-red, visible and ultra-violet spectra. λ_{max} for the pure 3,3'-azodibenzoyl chloride, prepared by Korshak's method for this present work, are given: 246 nm (log ϵ 4.53), 315 nm (log ϵ 4.27), 444 nm (log ϵ 2.66). This data gives indirect confirmation of the authenticity of the azo diacid chloride prepared by the first route described above. It is therefore concluded that the melting point of 83.5°—84.5°C, as reported by Korshak, is that for an impure sample. There is also the possiblity of an error in the literature.

4,4'-Azodibenzoyl chloride. This was prepared from 4,4'-azodibenzoic acid and thionyl chloride using the method due to Tomlinson[37]. Isolation and recrystallization of the product were similar to that described for the 3,3'-isomer. Red needles were formed with 47% yield; m.p. 164—165°C (lit. 164°C). Composition found: C, 54.45%; H, 2.76%; Cl, 23.25%, N, 9.18%. $C_{14}H_8Cl_2N_2O_2$ requires C, 54.72%; H, 2.62%; Cl, 23.09%; N, 9.12%. λ_{max} (cyclohexane) 233 nm (log ϵ 3.89), 333 nm (log ϵ 4.54), 472 nm (log ϵ 2.82). Spectroscopic data were not reported by Tomlinson.

PREPARATION OF THE AZO POLYAMIDES

The polymerization in each case was by interfacial polycondensation[22,41], carried out in a Braun Multimix blender.

Table 1 Azo polyamides

Polyamide	Code
Poly(3,3'-azodibenzoyl-1,6-diaminohexane)	3-DAH
Poly(3,3'-azodibenzoyl-piperazine)	3-PIP
Poly(3,3'-azodibenzoyl-*trans*-2,5-dimethylpiperazine)	3-TDMP
Poly(4,4'-azodibenzoyl-1,6-diaminohexane)	4-DAH
Poly(4,4'-azodibenzoyl-piperazine)	4-PIP
Poly(4,4'-azodibenzoyl-*trans*-2,5-dimethylpiperazine)	4-TDMP

Table 2 Polymer properties

Polymer	Colour	Yield (%)	η_{inh}	Decomposition temperature (°C)	λ_{max}* (nm)
3-DAH	Orange	95	1.31	370	
3-PIP	Orange	72	1.03	370	319,442
3-TDMP	Orange	72	1.39	380	320,443
4-DAH	Reddish orange	92	1.23	385	—
4-PIP	Reddish orange	95	1.21	405	327,446
4-TDMP	Reddish orange	95	4.05	405	331,446

* λ_{max} for the corresponding azo diacid chlorides, using chloroform as solvent, are given: 3,3'-azodibenzoyl chloride 316,442 nm; 4,4'-azodibenzoyl chloride 335,470 nm

A solution of the required diamine (0.006 mol) was made in a suitable volume of water (45 cm^3); to this solution was added sodium carbonate (0.01 mol), the acid acceptor. The solution was added to the blender and an emulsion formed by adding dichloromethane (13 cm^3), with high speed stirring. To this rapidly stirred emulsion was added, as quickly as possible, a solution of the appropriate freshly recrystallized azo diacid chloride (0.005 mol) in dichloromethane (27 cm^3). Rapid stirring was continued for 5—7 min, and the polymer isolated, if necessary, collected, rinsed, and dried in a vacuum oven at 60°C. Isolation procedures depended on whether the polymer precipitated rapidly (3-DAH and 4-DAH) when filtration was suitable, or formed viscous solutions or dispersions (3-PIP, 4-PIP, 3-TDMP, 4-TDMP) when an addition of hexane was made to completely precipitate the polymer, before filtration.

After-treatment of the polymers was consistent with the removal of unreacted materials, sodium chloride and low molecular weight species, under conditions giving minimum degradation of the polymer.

Viscometry

Viscosity measurements were made at 25°C using *m*-cresol as solvent for all the azo polyamides, except 3-DAH and 4-DAH where concentrated sulphuric acid was used. The concentration used throughout was 0.5 g/100 cm^3.

Results are expressed as inherent viscosity (logarithmic viscosity number), where:

$$\eta_{inh} = \frac{[\ln \eta_{rel}]}{c}$$

Thermal behaviour

Differential thermograms were obtained for the various polymers with a DuPont Model 900 Thermal Analyzer, using a heating rate of 15°C/min.

Ultra-violet and visible spectra

These were recorded on a Unicam SP800 recording spectrophotometer. 0.1 M aqueous sodium hydroxide was used as solvent for the spectra of the azo diacids, and cyclohexane and chloroform for the azo diacid chlorides, while chloroform was suitable for three of the azo polyamides.

Because of solubility difficulties, 1,1,2-trichloroethane/formic acid azeotrope was used for determination of the spectra of the 4-PIP polymer. Attempts were made to record the spectra of the more insoluble azo polyamides, 3-DAH and 4-DAH, using concentrated sulphuric acid, however solution of these polymers was accompanied by some polymer decomposition.

Infra-red spectra

These were recorded using a Unicam SP200 prism spectrophotometer, range 650—5000 cm^{-1}, with the carefully dried sample, in each case, incorporated in a potassium bromide disc.

Solubility

Solubility experiments, for the various polymers, were carried out using 0.1 g polymer in 3—5 cm^3 of the selected solvent at room temperature. If there was no evidence of solution after 2—3 h, the solvent was heated to its boiling point. If solution occurred on heating, the solution was allowed to cool to ascertain if the polymer remained in solution or precipitated.

RESULTS AND DISCUSSION

Table 2 gives properties of the six azo polyamides prepared. As expected, polymers prepared from 4,4'-azodibenzoyl chloride are much redder in colour than those from the 3,3'-isomer. Interfacial polycondensations are capable of giving high yields of polymer. The lower yields obtained with the 3-PIP and 3-TDMP polymers may be due to some solution of these polymers in the organic solvent phase used in the polymerization, together with removal of low molecular weight material by the rinsing procedures used.

Inherent viscosity

Inherent viscosity (logarithmic viscosity number) has been widely used for characterizing condensation polymers, especially those prepared by interfacial methods. For the azo polyamides described in this work, inherent viscosities have been determined. The results are given in *Table 2*. In all cases the inherent viscosities are high, particularly so with the polymers derived from *trans*-2,5-dimethylpiperazine. The result for 4-TDMP (4.05) compares favourably with that reported for this polymer (2.19) by Du Pont[22]. That 3-TDMP gives a lower inherent viscosity (1.39) as compared with 4-TDMP, may be due to a number of factors: (i) 3,3'-azodibenzoyl chloride is more unsymmetrical than the 4,4'-isomer; (ii) the rates of hydrolysis of the two azo diacid chlorides may be quite different; (iii) the greater solubility of the 3-TDMP polymer in the organic solvent phase during polymerization. Korshak *et al.*[39] in a study of the formation of various polyarylates, suggested that the low molecular weight of some of the products was due to excessive solubility of the polymer in the solvent used, leading to rapid rupture of the growing chains.

A number of empirical relationships have been proposed relating various viscosity numbers with molecular weights for selected polymers. One of these, due to Korshak and Pavlova[40], for polyamides in *m*-cresol is $\eta_{sp}/c = 0.522 \times 10^{-6} \times M^{1.26}$ (where $c = 0.5$ g/100 cm^3). Applying this relationship to those azo polyamides which are soluble in *m*-cresol, the following molecular weights were obtained: 3-PIP, 1.9×10^4; 4-PIP, 2.4×10^4; 3-TDMP, 2.7×10^4; 4-TDMP, 1.25×10^5.

It should be pointed out that the relationship used can only be approximate, however it seems reasonable to conclude that the molecular weights are in the range 1.5×10^4 to 1.5×10^5. That this conclusion is satisfactory is confirmed by some relationships between inherent viscosity and molecular weight given by Morgan[41] for a series of samples of a related polymer, poly(terephthaloyl-*trans*-2,5-dimethylpiperazine).
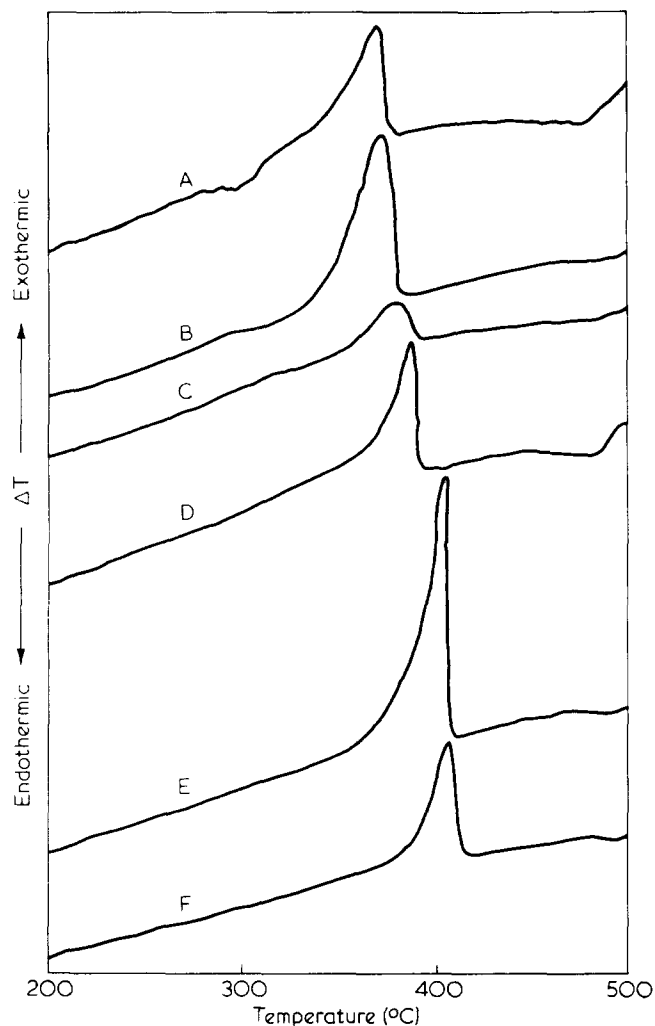
Figure 2 Differential thermograms of (A) 3-DAH; (B) 3-PIP; (C) 3-TDMP; (d) 4-DAH; (E) 4-PIP; (F) 4-TDMP

Thermal behaviour

Features such as chain rigidity, strong interchain attraction, stereoregularity and high crystallinity contribute to the high melting points generally found with polyamides[41–47]. An increase in melting point occurs if linear structures are replaced by cyclic structures, especially when the latter are combined on an axis of linear symmetry. When piperazines, with their rigid structure, are combined with aromatic diacids, the resulting polyamides have high melting points (350°– 400°C or higher[48–51]), particularly when the rings are linked via the 1,4-positions.

Azo polyamides prepared by various workers, from terephthaloyl chloride and 2,4-diaminoazobenzene[52] (320°C dec), from adipoyl chloride and 4,4′-diaminoazobenzene[22] (>400°C), and from 2,2′-azodibenzoic acid and 1,6-diaminohexane[21] (250°C) have the melting points given in parentheses. Korshak and coworkers[15–18] found that polyesters from 4,4′-azodibenzoic acid have higher melting points than those from 3,3′-azodibenzoic acid, also that polyesters based on these azo diacids and hydroquinone have melting points of >400°C. The hydroquinone ring structure confers pronounced chain rigidity.

It is apparent that the azo polyamides, prepared in this present work, should have high melting points, probably in excess of 400°C. The melting point of 4-DAH might be expected to be greater than the 370°C reported for

poly(hexamethylene terephthalamide)[41], due to the plurality of rings and the effect of the conjugated –N = N– group. High melting points are to be expected for 3-PIP, 4-PIP, 3-TDMP and 4-TDMP polymers because of the additional presence of piperazine or substituted piperazine ring structures. Although the 3,3′ polymers are less symmetrical than the 4,4′-, melting points in excess of 400°C are likely in both cases, since the azo polyesters based on hydroquinone, mentioned above, have melting points >400°C and polyesters are generally lower melting than polyamides. Poly(terephthaloyl-*trans*-2,5-dimethylpiperazine)[50] has a melting point >400°C.

It is evident from the differential thermograms shown in *Figure 2* for the various azo polyamides, now reported, that these polymers have high thermal stability. Thermal breakdown occurs between 370° and 405°C and before fusion temperatures are reached. The sharp exotherms associated with decomposition (temperatures are given in *Table 1*), occur at lower temperatures for the 3,3′-polymers, as compared with the 4,4′-polymers. This may be attributed to differences in structural regularity, the 4,4′-structures giving more compact packing of the chains. The exotherms corresponding to decomposition combined with the narrow temperature range of their occurrence (370°–405°C), irrespective of polymer structure, would suggest that the first step in the thermal degradation process for each azo polyamide may be the elimination of the azo group, possibly as molecular nitrogen. The first step in the thermal degradation of some azo polymers, prepared by oxidative coupling of primary aromatic amines, has been ascribed to such a process[13].

The thermograms recorded for two uncoloured polyamides, poly(isophthaloyl-*trans*-2,5-dimethylpiperazine) and poly-(terephthaloyl-*trans*-2,5-dimethylpiperazine), prepared for some photodegradation studies[53], show no endotherms or exotherms up to at least 400°C. These polymers are similar in structure to 3-TDMP and 4-TDMP, respectively, but they do not have the azo chromophoric system. This gives support to the suggestion that elimination of the azo group may be the first stage in the thermal decomposition of the azo polyamides.

Ultra-violet and visible spectra

Polymers containing the azo chromophore give characteristic ultra-violet and visible spectra. The spectra of a few azo polymers have been reported[12,17–21,24,31,54]. Ultra-violet and visible spectra have been obtained for four of the azo polyamides described in this present work, λ_{max} values are given in *Table 2*. Typical visible spectra (0.400 g/l solutions) and ultra-violet spectra (0.016 g/l solutions) are shown in *Figure 3*.

For visible spectra, it is clear that on comparing λ_{max} values for the polyamides, with λ_{max} values for the azo diacid chlorides from which they are derived, there is little difference for the 3,3′-polymers but a marked difference for the 4,4′-polymers. This may be due to a change in conjugation on forming polymers from 4,4′-azodibenzoyl chloride. While –COCl groups in the 4- and 4′- positions to the azo linkage have a marked effect on conjugation and consequently change the light absorption characteristics, there is little effect with –COCl groups in the 3- and 3′- positions.

The low intensity band for azobenzene and its derivatives in the visible region is associated with a n–π^* transition. This transition for the 4,4′-azodibenzoyl chloride (λ_{max} 470 nm) exhibits a marked bathochromic shift compared with azobenzene. Spectral data given for *trans*-azobenzene
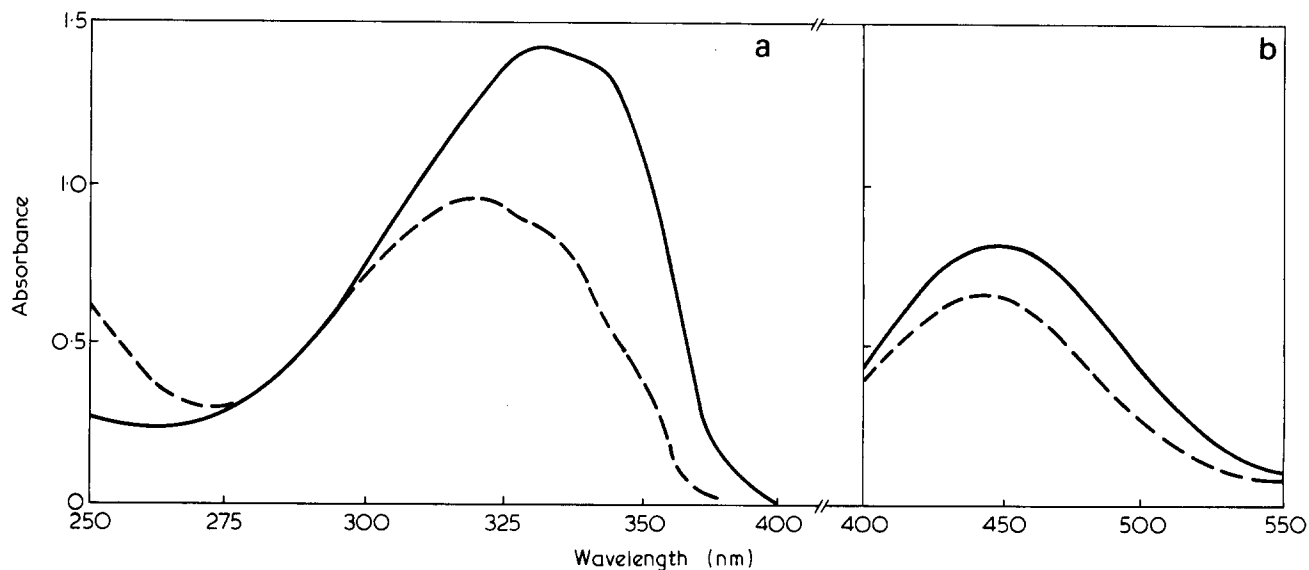
Figure 3 (a) Ultra-violet and (b) visible spectra of the azo polyamides, 3-TDMP (— — —) and 4-TDMP (———), in chloroform
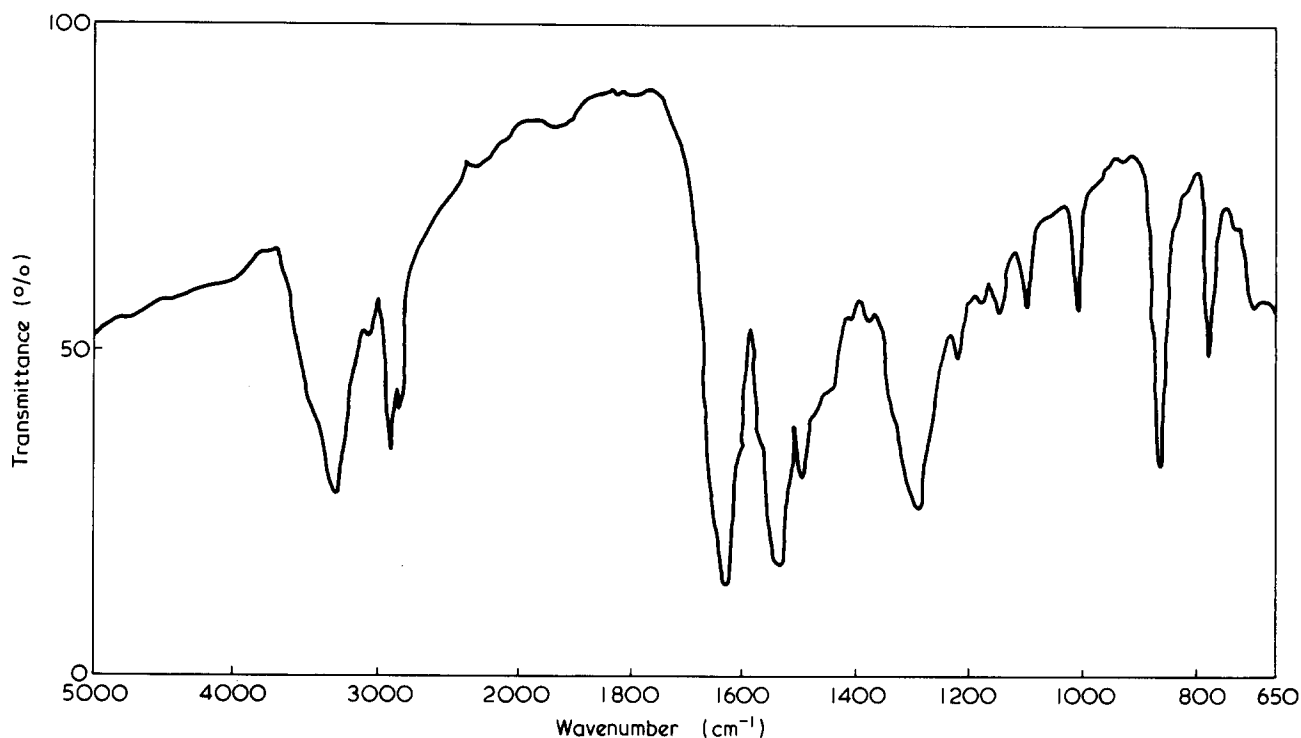

Figure 4 Infra-red spectrum of the azo polyamide, 4-DAH

in the literature vary according to the worker, the instrument used and the solvent, but typical values[55] are λ_{max} 228 nm (log ϵ 4.15), 319 nm (log ϵ 4.34) and 443 nm (log ϵ 2.70). The band in the visible region for 3,3'-azodibenzoyl chloride shows little difference in λ_{max} as compared with azobenzene.

With ultra-violet spectra, the bands for the azo polyamides do not show marked changes from those for the corresponding azo diacid chlorides. The 4,4'-azodibenzoyl chloride shows a marked bathochromic shift (λ_{max} 335 nm) as compared with the 3,3'-isomer (λ_{max} 316 nm). A similar but smaller displacement is also evident in the derived polymers.

The high intensity bands between 310 and 360 nm in azobenzene and its derivatives are due to π—π* transitions. The band at 335 nm for the 4,4'-azodibenzoyl chloride is very intense and shows a bathochromic shift, as compared with

azobenzene. For the 3,3'-azodibenzoyl chloride, the band at 316 nm shows little shift or change in intensity, as compared with azobenzene.

It is apparent that while change from —COCl to —CON(R)—, in forming a polyamide from the 4,4'-azodiacid chloride, gives an appreciable change in spectral characteristics, a similar change is not apparent in the case of the 3,3'-isomer.

Infra-red spectra

These have been recorded for all six polyamides. A typical example, that for 4-DAH, is reproduced in *Figure 4*. Bands which are common to all polymers and for which assignments are proposed are:

1270 ± 20 cm^{-1} (C—N stretching)

Table 3 Polymer solubility

Solvent	Polyamide					
	3-DAH	4-DAH	3-PIP	4-PIP	3-TDMP	4-TDMP
Acetone	I	I	V.S.S.	I	V.S.S.	V.S.S.
Dichloromethane	I	I	S.S.	V.S.S.	S.	S.S.
Chloroform	I	I	S	S.S.	S	S
N,N-dimethylformamide	S.S.	V.S.S.	S.S.	S.S.	S.S.	S.S.
m-Cresol	S.S.	V.S.S.	S	S	S	S
98% Formic acid	S.S.	I	S	S.S.	S	S
Trifluoroacetic acid	S	S	S	S	S	S
5M Hydrochloric acid	I	I	I	I	I	I
Conc. sulphuric acid	S	S	S	S	S	S
Chloroform/formic acid azeotrope 85/15 w/w	V.S.S.	I	S	S.S.	S	S
1,1,2-Trichloroethane/formic acid azeotrope 60/40 w/w	S.S.	I	S	S	S	S

I = insoluble; V.S.S. = very slightly soluble; S.S. = slightly soluble; S = soluble

1630 ± 10 cm^{-1} (C=O stretching)

2950 ± 50 cm^{-1} (aromatic C–H stretching or C–H stretching in –CH$_2$–)

For the polyamides with –CONH– groups, 3-DAH and 4-DAH, additional bands include:

1530 cm^{-1} (N–H bending and/or C–N stretching)

3300 cm^{-1} (N–H stretching)

The band at 3300 cm^{-1} indicates considerable hydrogen bonding in polyamides[56].

For the polyamides based on piperazine or *trans*-2,5-dimethylpiperazine, 3-PIP, 4-PIP, 3-TDMP and 4-TDMP, the band at 3300 cm^{-1} is absent. The polymers 3-TDMP and 4-TDMP have a band at 1330 cm^{-1}, this is probably due to C–CH$_3$ bonds. The –N = N– frequency of aromatic azo compounds is difficult to identify in the infra-red, the frequencies are not only weak but are overlaid by other aromatic bands[57].

Solubility

The solubility characteristics of the azo polyamides are shown in *Table 3*. These are in general agreement with those observed for aromatic polyamides and piperazine based polyamides[41,47,50,58].

Polymers which exhibit hydrogen bonding, 3-DAH and 4-DAH, are very insoluble, except in trifluoroacetic acid and concentrated sulphuric acid. 3-DAH, due to the asymmetry of its structure, is more soluble than its isomer, e.g. it can be dissolved to some extent in hot *m*-cresol. The very slight solubility shown by 3-DAH and 4-DAH in some other solvents may be due to low molecular weight material in the polymer sample. This material is commonly present in polymers prepared by interfacial polycondensation.

The 3-PIP, 4-PIP, 3-TDMP and 4-TDMP polyamides are soluble in a range of solvents and solvent mixtures. The 3,3'-polymers, as expected, are more soluble than the 4,4'-polymers; this is in agreement with the findings of Korshak and Vinogradova[15] that polyesters of 3,3'-azodibenzoic acid are more soluble than those from 4,4'azodibenzoic acid. The polyamides based on *trans*-2,5-dimethylpiperazine exhibit greater solubility than those based on piperazine.

Of the solvents listed in *Table 3*, the most effective was

found to be the azeotrope, 1,1,2-trichloroethane/formic acid 60/40 w/w. It was found possible to cast strong films of 3-TDMP and 4-TDMP from this solvent mixture.

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