

## Synthesis and characterization of new polyamides and copolyamides containing 6,6'-sulfonediquinoline units

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### Summary

Aromatic polyamides were obtained by the direct polycondensation reaction of a new monomer containing a 6,6'-sulfonediquinoline unit with various aromatic diamines. The polymers were characterised by elemental, infrared, wide angle X-ray diffraction and thermal analysis. The polyamides, possessed inherent viscosities in the range 0.24 - 0.43 dl g<sup>-1</sup>, 10% weight loss in nitrogen and air above 410°C and glass transition temperatures in the range 170-220°C. The polyamides obtained by reaction with 4,4'-methylenedianiline and 4,4'-sulfonyldianiline were soluble on heating in N-methyl-2-pyrrolidinone and partially soluble in dimethylacetamide. Solubility and thermal properties of copolyamides, prepared from the reaction of 4,4'-oxydianiline with the new monomer and the 4,4'-dicarboxydiphenyl sulfone, were also studied.

### Introduction

Aromatic polyamides are of commercial importance and academic interest (1) because they exhibit good mechanical properties combined with an excellent thermal stability. However, the processing of these polymers by thermoplastics methods has been extremely difficult because in many cases they do not melt below their decomposition temperature (2). Moreover they are insoluble in organic solvents. The need for engineering plastics overcoming these problems recently increased and to make aromatic polyamides more processable, various attempts have been made to reduce their melting temperature or improve their solubility. One approach to increase solubility of aromatic polyamides is the introduction of flexible groups into the polymer chain. Unfortunately, the loss of thermal stability is often a consequence of the reduced chain stiffness. On the other hand, Hirsch and Lilyquist (3) reported that quinoline has the highest decomposition temperature of all aromatic rings and the introduction of this rigid moiety into the polymer chain leads to materials displaying excellent oxidative and thermal stability (4-8).

The goal of better solubility together with retained high thermal stability could be achieved in preparing polyamides starting from monomers containing diquinoline rings bridged by flexible groups or by group active in disrupting polymer chain planarity. Previous paper (9) reported the syntheses of polyamides containing 6,6'-methylenediquinoline units and the introduction of diquinoline units appeared particularly interesting because some of the resulting polymers showed a good solubility in aprotic solvents still maintaining high ultimate use temperatures.

This paper reports on the synthesis of 6,6'-sulfonediquinaldic acid where the diquinoline units are bridged by sulfonyl unit that is active for disrupting polymer chain

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planarity (10). The synthesis of polyamides and copolyamides obtained starting from this new monomer are reported and the influence of the incorporation of this moiety into the polymer backbone on properties of polyamides has been studied. The results have been compared with those obtained for polyamides containing only one quinoline ring per repeat unit.

## Experimental

### Materials

"Sulfo mix" (a solution of *m*-nitrobenzenesulfonic acid in sulfuric acid) was prepared as described by Utermohlen (11). Crotonaldehyde (Aldrich Co.) was distilled before use. *N*-methyl-2-pyrrolidinone (NMP) was refluxed over  $\text{CaH}_2$  for 8 h and distilled under reduced pressure. It was then refluxed in the presence of  $\text{P}_2\text{O}_5$  and freshly distilled before use. Triphenyl phosphite (TPP) was purified by fractional distillation under vacuum. Pyridine (Py) was refluxed in an inert atmosphere in the presence of NaOH for 6 h, distilled and stored over 4 Å molecular sieves. Reagent grade calcium chloride and lithium chloride (Aldrich Co.) were dried for 16 h at 180°C under vacuum. Reagent grade aromatic diamines (Aldrich Co.) such as *p*-phenylenediamine (PPD) and 4,4'-oxydianiline (ODA) were purified by sublimation; 4,4'-methylenedianiline (MDA) was crystallised twice from toluene; 4,4'-sulfonyldianiline (DAS) and 1,5-diaminonaphthalene (DAN) were crystallised from ethanol. 4,4'-Dicarboxydiphenyl sulfone (DCDPS) was prepared according to the literature (12). Other reagents were commercial materials.

### Instrumental

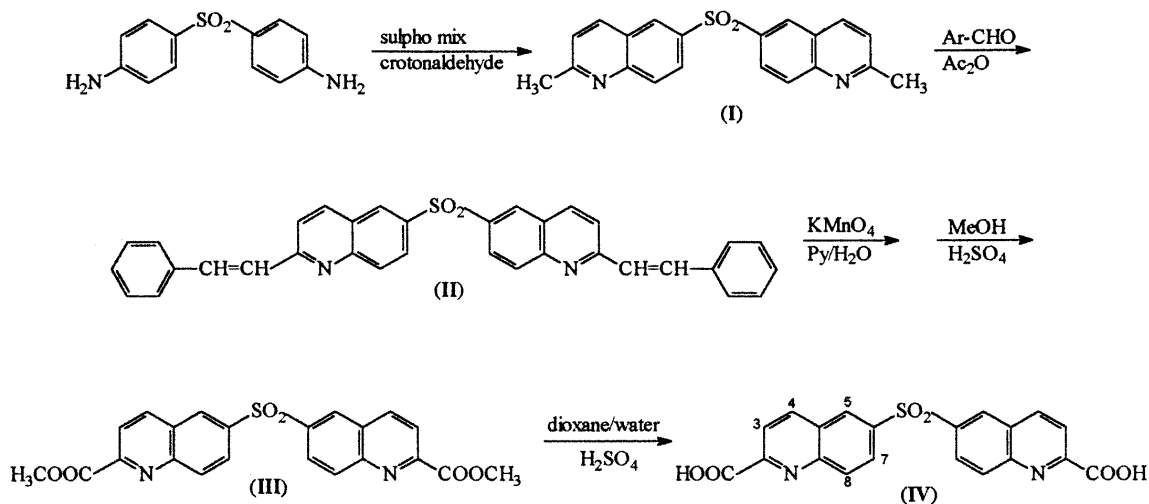
All melting points of low molecular weight materials were determined on a Buchi 530 capillary melting point apparatus and are uncorrected. Infrared (i.r.) spectra were recorded in potassium bromide pellets on a Perkin Elmer FT-1725-X spectrophotometer over the range 4000-600  $\text{cm}^{-1}$ , and nuclear magnetic resonance (n.m.r.) spectra were obtained with a Bruker AC 200 instrument using  $\text{Me}_4\text{Si}$  as internal reference. Elemental analyses were conducted on a Carlo Erba Elemental Analyser, model 1106. Inherent viscosities ( $\eta_{\text{inh}} = \ln \eta_r / C$  at polymer concentration  $C = 0.5 \text{ g dl}^{-1}$ ) were measured with an Ubbelohde suspended-level viscometer at 30°C using concentrated sulphuric acid as the solvent. Thermogravimetric analyses (t.g.a.) were performed with a Mettler M3 thermobalance at a heating rate of 10°C  $\text{min}^{-1}$  in  $\text{N}_2$  flow (25  $\text{ml min}^{-1}$ ) or in static air. Temperature of 10% weight loss was taken as decomposition temperature ( $T_d$ ). Differential scanning calorimetry (d.s.c.) measurements were made using Mettler DSC 30 with Al pans at a heating rate of 20°C  $\text{min}^{-1}$  in  $\text{N}_2$ . Char yields ( $C_y$ ) were calculated as the percentage of solid residue after heating from room temperature to 700°C in  $\text{N}_2$ . The X-ray diffraction patterns were obtained at room temperature irradiating the polymer powders with a Cr  $K_\alpha$  radiation and collected using a flat film camera. The sample to film distance was 75 mm.

### Monomer synthesis (Scheme 1)

#### Synthesis of 6,6'-sulfonediquinaldine (I)

To a stirred mixture of 4,4' sulfonyldianiline (18 g, 0.072 mol), 50 g of sulfo mix and 10 ml of water, heated to 140°C, crotonaldehyde (16.85 g, 0.240 mol) was slowly

SCHEME 1



added during 1 hour, keeping the temperature at 140°C. The solution was stirred at this temperature for an additional 4 hours and then poured into ice and water. The mixture was made alkaline (pH=8) with sodium hydroxide solution. An ice bath was used to control the exothermic neutralisation reaction. The precipitate was filtered, washed with water and dried. The solid was crystallised from toluene (m.p.250-1°C; yield 60%). Anal.Calcd. for  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{SO}_2$ : C, 68.94; H, 4.63; N, 8.04; S, 9.20. Found: C, 68.70; H, 4.55; N, 8.15; S, 9.05.  $^1\text{H-n.m.r.}$  ( $\text{CDCl}_3$ ):  $\delta=7.41$  (d,  $\text{H}_3$ , 1H);  $\delta=8.19$  (d,  $\text{H}_4$ , 1H);  $\delta=8.59$  (s,  $\text{H}_5$ , 1H);  $\delta=8.09$  (s,  $\text{H}_7$  and  $\text{H}_8$ , 2H). i.r.:  $3058\text{ cm}^{-1}$  ( $\nu_{\text{as}} \text{CH}_3$ ) and  $2916\text{ cm}^{-1}$  ( $\nu_{\text{s}} \text{CH}_3$ );  $1612\text{-}1492\text{ cm}^{-1}$  (C-C and C-N ring stretching);  $1317$  ( $\nu_{\text{as}} \text{SO}_2$ ) and  $1148\text{ cm}^{-1}$  ( $\nu_{\text{s}} \text{SO}_2$ ).

#### Synthesis of 6,6'-sulfonyl-2,2'-styryldiquinoline (II)

A mixture of **I** (10.35 g, 0.03 mol), benzaldehyde (19 g, 0.18 mol) and acetic anhydride (37 g, 0.36 mol) was allowed to reflux for 4 hours. The mixture was then cooled and the solid filtered, washed with acetic anhydride and ethyl alcohol (m.p.=262-3°C, 70% yield). Anal. Calcd. for  $\text{C}_{34}\text{H}_{24}\text{N}_2\text{SO}_2$ : C, 77.84; H, 4.61; N, 5.34; S, 6.11. Found: C, 77.95; H, 4.55; N, 5.21; S, 6.15.  $^1\text{H-n.m.r.}$  ( $\text{DMSO-d}_6$ ):  $\delta=8.00$  (d,  $\text{H}_3$ , 1H);  $\delta=8.62$  (d,  $\text{H}_4$ , 1H);  $\delta=8.79$  (s,  $\text{H}_5$ , 1H);  $\delta=8.16$  (s,  $\text{H}_7$  and  $\text{H}_8$ , 2H);  $\delta=7.92$  (d,  $\text{H}_9$ , 1H);  $\delta=7.49$  (d,  $\text{H}_{10}$ , 1H);  $\delta=7.73$  (dd,  $\text{H}_6$ , 2H);  $\delta=7.41$  (m,  $\text{H}_{\text{mp}}$ , 3H). i.r.:  $3041\text{ cm}^{-1}$  (olefinic C-H stretch);  $1608\text{ cm}^{-1}$  (C=C stretch);  $1320$  ( $\nu_{\text{as}} \text{SO}_2$ ) and  $1151\text{ cm}^{-1}$  ( $\nu_{\text{s}} \text{SO}_2$ ).

#### Synthesis of 6,6'-sulfonyl dimethyl diquinaldine dicarboxylate (III)

Potassium permanganate (18.07 g) was slowly added (2 hours) to a stirred mixture of **II** (10 g), pyridine (150 ml) and water (10 ml). The mixture was maintained at 0°C and stirring was continued for 4 hours. The mixture was acidified with diluted sulphuric acid to pH 4. It was then treated with a solution of sodium metabisulphite until there was a complete change in the colour of the solution. The precipitate was then filtered, washed with water to eliminate inorganic salts and pyridine, dried (5.8 g, yield 75%) and added to a solution of 250 ml of methanol containing 3 ml of concentrated sulphuric acid. The mixture was allowed to reflux overnight, then it was cooled and the precipitate was filtered and stirred in a solution of sodium bicarbonate. The solid was

filtered and crystallised from dioxane (m.p.302-3°C, 75% yield). Anal.Calcd. for  $C_{22}H_{16}N_2SO_6$ : C, 60.54; H, 3.69; N, 6.42; S, 7.35. Found: C, 60.17; H, 3.74; N, 6.52; S, 7.34.  $^1H$ -n.m.r. ( $CDCl_3$ ):  $\delta=8.32$  (d,  $H_3$ , 1H);  $\delta=8.49$  (d,  $H_4$ , 1H);  $\delta=8.72$  (d,  $H_5$ , 1H);  $\delta=8.21$  (dd,  $H_7$ , 1H);  $\delta=8.42$  ( $H_8$ , 1H);  $\delta=4.09$  (s,  $CH_3$ ). i.r.:  $1720\text{ cm}^{-1}$  (C=O stretch);  $1201\text{ cm}^{-1}$  (acetate  $CC(=O)-O$  stretch);  $1320$  ( $\nu_{as}\text{ SO}_2$ ) and  $1151\text{ cm}^{-1}$  ( $\nu_s\text{ SO}_2$ ).

#### Synthesis of 6,6'-sulfonediquinaldic acid (IV)

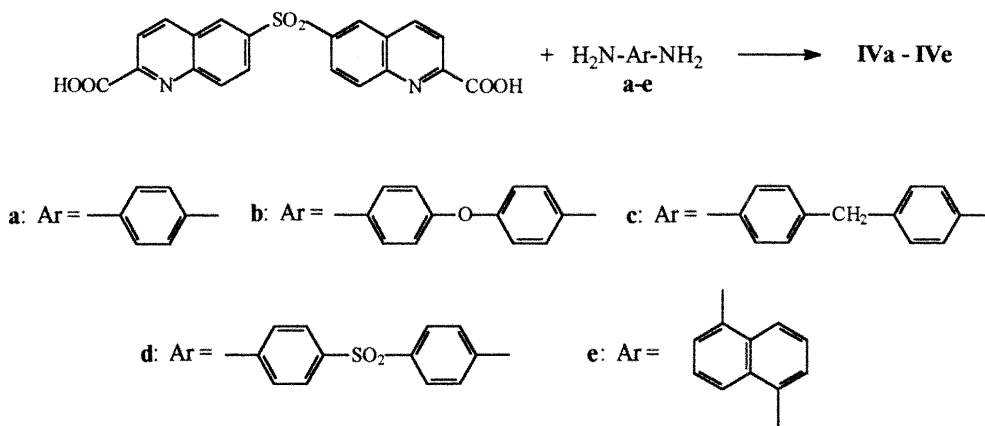
4 ml of concentrated sulfuric acid were slowly added to a heated stirred mixture of **III** (2.0 g) in 300 ml of a solution of dioxane/water (70/30). The solution was refluxed for 36 hours, the solid was filtered, washed with water and suspended in a dilute sodium hydrogencarbonate solution for 1 hour. The white solid was collected by filtration, washed with water and dried (m.p.:  $315^\circ\text{C}$ ; 60% yield). Anal.Calcd. for  $C_{20}H_{12}N_2SO_6$ : C, 58.82; H, 2.96; N, 6.86; S, 7.85. Found: C, 59.10; H, 2.95; N, 6.95; S, 7.91.  $^1H$ -n.m.r. (DMSO- $d_6$ ):  $\delta=8.24$  (d,  $H_3$ , 1H);  $\delta=9.01$  (s,  $H_5$ , 1H);  $\delta=8.85$  (d,  $H_4$ , 1H);  $\delta=8.32$  (dd,  $H_7$  and  $H_8$ , 2H);  $\delta=13.71$  (s, OH). i.r.:  $3414\text{ cm}^{-1}$  (O-H stretch);  $1730\text{ cm}^{-1}$  (C=O stretch);  $1321$  ( $\nu_{as}\text{ SO}_2$ ) and  $1147\text{ cm}^{-1}$  ( $\nu_s\text{ SO}_2$ ).

#### Polymer synthesis (Scheme 2)

A typical example of solution polymerisation is as follows: a solution of NMP (3 ml) and Py (0.8 ml) containing LiCl (0.1 g) and  $CaCl_2$  (0.2 g) was added to a mixture of diacid **IV** (0.5104 g, 0.00125 mol), ODA (0.2503 g, 0.00125 mol) and TPP (0.7757 g, 0.0025 mol). The mixture was maintained under stirring and in nitrogen atmosphere at  $105^\circ\text{C}$  for 3 h. The resulting reaction mixture, after cooling, was poured into methanol (200 ml), and the precipitated polymer was separated by filtration and extracted with methanol overnight. The collected polymer was dried under vacuum for 12 h at  $150^\circ\text{C}$ . The yield was 95% and  $\eta_{inh}$  of the polymer in concentrated sulphuric acid was  $0.36\text{ dl g}^{-1}$ . The i.r. spectrum (KBr) showed absorptions at  $3282\text{ cm}^{-1}$  (N-H stretch),  $1669\text{ cm}^{-1}$  (C=O stretch),  $1596\text{ cm}^{-1}$  (N-H bend) and  $1411\text{ cm}^{-1}$  (C-N stretch). The other polymers were synthesised by analogous procedures.

Copolymerisations of **IV** / DCDPS and ODA (Scheme 3) were carried out by using phosphorylation route at  $105^\circ\text{C}$  for 6 h and using different mole percentages of the diacids.

SCHEME 2



## Results and discussion

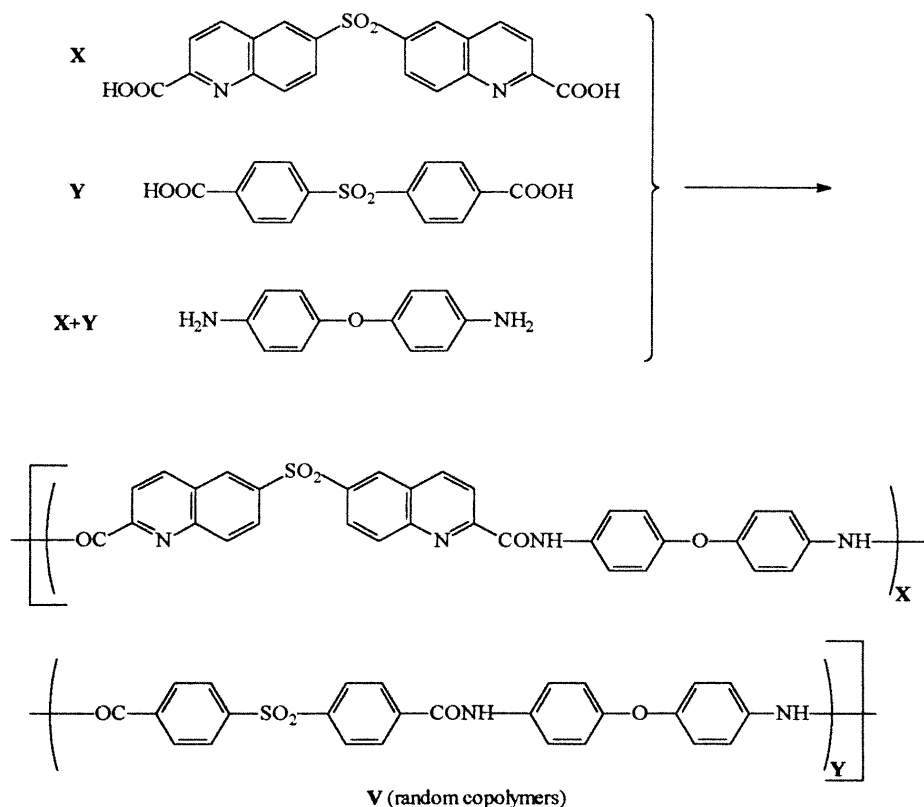
### Monomer synthesis

In this paper, we report the synthesis and characterisation of polyamides obtained starting from a new monomer containing diquinoline units bridged by a sulfone group. The new monomer (**IV**) was synthesised according to Scheme 1. The 6,6'-sulfonediquinoline (**I**) was prepared by application of the typical Skraup synthesis starting from 4,4'-sulfonyldianiline and crotonaldehyde in the presence of an oxidising agent (sulfo mix). The used molar ratio of aldehyde to amine was 3.34:1 (13) and the temperature was maintained at 140°C. The styryl derivative (**II**) was obtained by reaction of **I** with benzaldehyde in acetic anhydride. Oxidation with potassium permanganate and the following esterification with methanol gave compound **III** that was purified by crystallisation and then hydrolysed in a solution of dioxane/water using concentrated sulfuric acid as catalyst and compound **IV** was obtained. All compounds were characterised by elemental analysis, n.m.r. and i.r. and the results are in accord with the proposed structures.

### Synthesis of polyamides

Polyamides **IVa-IVe** were synthesised by direct polycondensation of dicarboxylic acid **IV** with aromatic diamines **a-e** using triphenyl phosphite and pyridine as condensing agents (14-15) (Scheme 2). The reactions have been carried out in NMP solution of the diacid and diamines in the presence of LiCl and CaCl<sub>2</sub>, in a nitrogen atmosphere and at a temperature of 105°C.

SCHEME 3



**Table 1. Mole percentage of feeding of diacids used in preparation of copolyamides VCo1-3**

	X (mol %)	Y (mol %)
<b>V-Co1</b>	25	75
<b>V-Co2</b>	50	50
<b>V-Co3</b>	75	25

The copolyamides **VCo1-3** were synthesised according to Scheme 3, using different mole percentages of the diacids (Table 1).

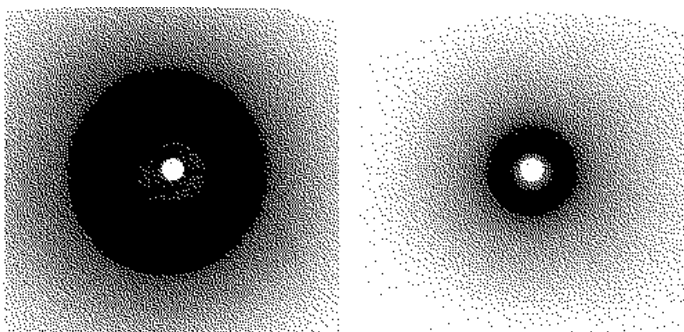
All the polymerisations proceeded in homogeneous solution and the yields of the polymers were quantitative. The elemental analysis values of the polymers and of the copolymers were in accord with the proposed structures. The i.r. spectra showed absorptions bands at 1321-1147  $\text{cm}^{-1}$  ( $\text{SO}_2$ ), while the presence of absorptions bands near 3300  $\text{cm}^{-1}$  (N-H stretch), near 1730  $\text{cm}^{-1}$  due to amide C=O and near 1400  $\text{cm}^{-1}$ , due to amide C-N, confirmed the structure of polyamides.

The inherent viscosities, obtained in concentrated sulfuric acid, were in the range 0.24 -0.43  $\text{dl g}^{-1}$ . Due to the poor solubility of our polymers at room temperature in NMP or DMAc (Table 2), it was not possible to evaluate their molecular weights by GPC measurements. However, to get an impression about the molecular weights, it could be worth applying the Mark-Houwink equation ( $[\eta] = K M_w^\alpha$ ) to our results. For poly(*p*-phenylene terephthalamide) (PPD-T) values of  $K = 8 \times 10^{-3}$  and  $\alpha = 1.09$  have been reported for sulfuric acid solution (16). After the determination of the intrinsic viscosity, such values have been used to calculate  $M_w$  of our polymers. The values found for  $M_w$  stay in the range 1800-3500.

**Table 2. Solution Viscosities, Thermal Characterisation and Solubility<sup>a</sup> of Polymers IVa-IVe and Copolyamides VCo1-3.**

Polymer	$\eta_{\text{inh}}^b$	$T_d^c$ (°C)	$T_d^d$ (°C)	$T_g^e$ (°C)	$C_y^f$	Solubility	
						NMP	DMAc
<b>IVa</b>	0.29	432	434	220	49	-	-
<b>IVb</b>	0.36	412	422	210	54	-	-
<b>IVc</b>	0.29	431	444	170	51	+	±
<b>IVd</b>	0.24	457	467	190	54	+	±
<b>IVe</b>	0.38	410	432	-	50	-	-
<b>V-Co1</b>	0.28	420	429	170	54	±	-
<b>V-Co2</b>	0.34	441	448	177	58	+	±
<b>V-Co3</b>	0.43	425	451	175	57	+	+

<sup>a</sup> Tested with 0.2 g of polymer in 2 ml of solvent. <sup>b</sup> Measured in concentrated sulfuric acid at 30°C ( $c=0.5 \text{ g dl}^{-1}$ ). <sup>c</sup> Temperature of 10% weight loss determined in nitrogen atmosphere. <sup>d</sup> Temperature of 10% weight loss determined in static air. <sup>e</sup> Determined in "as made" samples. <sup>f</sup> Char yields calculated as the percentage of solid residue after heating from room temperature to 700°C under nitrogen. <sup>g</sup> +, soluble on heating; ±, partially soluble on heating; -, insoluble.



**Figure 1. WAXD of polymers IVa (left) and IVb (right).**

Wide angle X-ray diffraction measurements, made on "as made" polymer powders, showed that all the polymers were amorphous (Figure 1). This result can be explained taking into account the influence of the SO<sub>2</sub> bridging group. In fact it is known that the introduction of sulfone group in polymers such as poly(ether ketone)s produces higher solubility and lower crystallinity because of the disruption of the polymer chain planarity due to different bond angles (105° for Ar-SO<sub>2</sub>-Ar, with respect to 124° for Ar-CO-Ar and Ar-O-Ar (10)) resulting in a lower interaction between the chains. In our polyamides the moiety containing the sulfone group is sufficient to promote a drop of crystallinity.

#### *Thermal properties of polyamides*

The thermal behaviour of the synthesised polyamides was evaluated by t.g.a. and d.s.c. and the values of T<sub>d</sub>, T<sub>g</sub> and C<sub>y</sub> are summarised in Table 2 (T<sub>g</sub> values were all taken from "as made" samples). It has to be taken into account that these measurements provide a preliminary guide to thermal stability because chemical reactions, such as crosslinking, can set in well below the temperatures at which volatile products are evolved. Due to the presence of polar amide linkages, the polyamides absorb significant amounts of moisture and the t.g.a. curves showed small weight losses in the range of 50-150°C due to water desorption. Slow heating up to 100°C followed by cooling to room temperature in flowing nitrogen removed most of moisture (17-19).

All the polymers were stable up to 410°C in both air and nitrogen (Table 2) and they show almost the same stability in both conditions. This high thermal stability is confirmed by the values of C<sub>y</sub> reported in Table 2. In fact C<sub>y</sub> is one of the criterion for the evaluation of the thermostability of a polymer (20-21). For all the obtained polymers C<sub>y</sub> were always higher than 49 % and reached 58%. T<sub>g</sub> values were in the range 170-220°C.

#### *Solubility*

Solubility of the polymers in NMP and DMAc at 10.0% (w/v) is summarised in Table 2. Only the polymers obtained starting from MDA and DAS (**IVc** and **IVd**) were soluble on heating in NMP and partially soluble in DMAc. This behaviour can be explained through the enhancement of the chain flexibility induced by the methylene group of the diamine moiety in polymer **IVc** and to the lower interaction between the chains due to the bond angle of 105° present in the -Ar-SO<sub>2</sub>-Ar- moiety of the diamine in polymer **IVd**. It was expected that also the presence of the ether bond, such as in polymer **IVb**, obtained starting from **IV** and ODA, would improve chain flexibility and then solubility. But results show that polymer **IVb** is not soluble thus indicating that such

increase of flexibility is at least counterbalanced by the higher rigidity induced by the diquinoline unit. This hypothesis is partially supported by the fact that on preparing copolyamides starting from ODA with various molar ratio of **IV** and DCDPS as diacids (**VCo1-3** - scheme 3) we observed an increase of solubility using higher percentage of DCDPS. This behaviour is due to the lower rigidity of phenyl group of DCDPS in comparison with the diquinoline unit, confirmed by the lower, but still high,  $T_g$  values of the copolymers respect to the one of polymer **IVb**. In fact it is known that one of the most important factors influencing the value of the  $T_g$  is the chain flexibility (22).

In conclusion the introduction in polyamides of diquinoline units bridged by a sulfone group results in amorphous materials. The polyamides containing this unit show good thermal stabilities and good  $T_g$  values for polymers of this class. The introduction of the diquinoline moiety results interesting in polymers where it is combined with MDA and DAS; these polymers are in fact soluble in aprotic solvents.

### Acknowledgements

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