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Synthesis and characterisation of new polyamides containing 6,6′-oxy or 6,6′-carbonyldiquinoline units

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Abstract

A series of new polyamides has been prepared from new monomers containing 6,6′-oxy or 6,6′-carbonyl diquinoline units with various aromatic diamines by the phosphorylation route. The polymers, having inherent viscosity in the range 0.29–1.04 dl g^{-1}, were obtained in quantitative yield, had excellent thermal stability as shown by 10% weight loss temperatures in nitrogen and air (above 435 and 420°C, respectively) and high glass transition temperatures (in the range of 230–310°C). Some of them were semicrystalline. The polymers were characterised by elemental and infrared analysis and GPC. The solubility in *N*-methylpirrolidinone was very good for all polymers. The properties of these polymers are compared with those of corresponding polyamides having only one quinoline ring per repeat unit and with those of some other polymers reported in literature.

Keywords: Quinoline; Polyamides; Direct polycondensation

1. Introduction

In the last few decades, thermally stable polymers have received extensive interest due to the increasing demands for high temperature polymers as replacements for metals or ceramics in the automotive, aerospace and microelectronics industries. Aromatic polyamides are certainly one of the most successful classes of high temperature polymers: they possess thermal stability, chemical resistance, low flammability and have excellent mechanical properties when used as fibres [1–3]. However, they encounter processing difficulties due to limited solubility in organic solvents and high glass transition (T_g) or melting temperatures (T_m), caused by the chain stiffness and intermolecular hydrogen-bonding between amide groups [4]. To develop high performance materials, modifications increasing the solubility and lowering the transition temperatures while maintaining the rod-like characteristic and thermal stability are of particular interest. The knowledge of the relationships between the chemical structures of the monomers and the properties of the polymers is an important prerequisite for the development of new plastics and the improvement of existing ones.

In recent years interest has been focused on the synthesis of rigid-rod polyamides by incorporating aromatic rings into the polymer backbone. The increased number of aromatic rings enhances the rigidity of the polymer backbone and their polarisable π-electrons lead to strong intermolecular interactions increasing the transition temperatures of these polymers. Rigid-rod polymers also exhibit high thermal stability and exceptional mechanical, optical and morphological properties. Particularly, Hirsch and Lilyquist [5] reported that quinoline has the highest decomposition temperature of all aromatic rings so extensive research has been devoted to the synthesis of polyquinoline. They show a wide range of chain stiffness (from relatively flexible polymers with a low T_g to rod-like macromolecules with a high T_g) and excellent thermal stability, with initial weight losses occurring between 500 and 600°C [6–11]. Thus the introduction of quinoline units into the polymer backbone of aromatic polymers such as polyesters, polyamides etc. could influence the T_g, the T_m and the degree of crystallinity. Previous papers, reporting the syntheses of polyamides [12–14], poly(arylene ether)s [15,16] and polyesters [17] containing quinoline units in the chain, confirmed the positive influence of the introduction of this heterocyclic unit. This positive influence can be improved by introducing diquinoline moieties in the polymer repeat unit [18,19].

To improve solubility with slight reduction in thermal properties, a successful method is the incorporation of aryl

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ether units in the polymer backbone. This trade-off is a natural outcome of the flexible linkages, which inhibit packing and decrease the co-planarity of the aromatic rings, thus reducing the inter and intra-chain interactions to enhance solubility. However, lowering the segmental rotational barrier and increasing the degrees of freedom also lowers the T_g. A similar effect, but to a lower extent, is shown by the introduction of ketone groups.

In a continuation of the study on the influence of the presence of diquinoline units in the polymer backbone, we think that the goal of better solubility together with retained high thermal stability could be achieved in preparing polyamides starting from monomers containing quinoline rings bridged by flexible groups. The present article describes successful syntheses of two novel diquinoline monomers, 6,6′-oxy and 6,6′-carbonyl diquinaldic acids, where the quinoline units are bridged with flexible ether and carbonyl groups, respectively. Polymers have been synthesised by a direct phosphorylation reaction of these new monomers and various diamines; their solubility and thermal behaviour have also been discussed. The influence of the incorporation of these moieties into the polymer backbone on the properties of obtained polyamides has been studied. The results have been compared with those of corresponding polyamides having only one quinoline ring per repeat unit and with those of polyamides containing quinoline rings bridged by sulfonyl or methylene units.

2. Experimental

2.1. Materials

"Sulfo mix" (a solution of *m*-nitrobenzenesulfonic acid in oleum) was prepared as described by Utermohlen [20]; crotonaldehyde was distilled before use.

N-methyl-2-pyrrolidinone (NMP) was refluxed over CaH_2 for 8 h and distilled under reduced pressure. It was then refluxed in the presence of P_2O_5 and freshly distilled before use. Triphenylphosphite (TPP) was purified by fractional distillation under vacuum. Pyridine (Py) was refluxed in an inert atmosphere in the presence of NaOH for 6 h and stored on 4 Å molecular sieves. LiCl (Aldrich Co.) was dried for 16 h at 180°C under vacuum. Reagent grade aromatic diamines (Aldrich Co.) *p*-phenylene diamine (PPD) and 4,4′-oxydianiline (ODA) were purified by sublimation; 4,4′-methylene dianiline (MDA) was crystallised twice from toluene; 4,4′-sulfonyldianiline (DAS) and 1,5-diaminonaphthalene (DAN) were crystallised from ethanol; 4,4′-diaminobenzophenone (ABP) was crystallised from ethanol/water. Other reagents were commercial materials.

2.2. Instruments

All melting points of low molecular weight materials were determined on a Buchi 530 capillary melting point apparatus and are uncorrected.

IR spectra were recorded in potassium bromide pellets on a Perkin Elmer FT-1725-X spectrophotometer over the range 4000–600 cm^{-1}.

Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker AC 200 Instrument using Me_4Si as internal reference.

Elemental analyses were conduced on a Carlo Erba Elemental Analyzer-Mod 1106.

Inherent viscosities ($\eta_{inh} = \ln \eta_r / C$ at polymer concentration $C = 0.5$ g dl^{-1}) were measured with an Ubbelohde suspended-level viscometer at 30°C using NMP or concentrated sulphuric acid as solvents.

Quantitative solubility was determined using 0.05 g of polymer in 1 ml of solvent.

The molecular weight results were generated using a HP 1100 gel permeation chromatography (GPC) instrument operated at 70°C, using NMP as carrier at a flow rate of 1 ml/min. Separations were accomplished using a PLgel 5 μm mixed-D column from Polymer Labs, a refractive index detector and toluene as internal standard. Solution concentrations were 5 mg/1 ml in NMP; they were filtered through 0.45 μm membranes of PVDF and samples of 20 μl of the filtered polymer solution were injected into the columns. The results are the average of two injections. Calibration was performed using narrow polydispersity polystyrene standards in weight average molecular weights in the range 2500–650 000 Da.

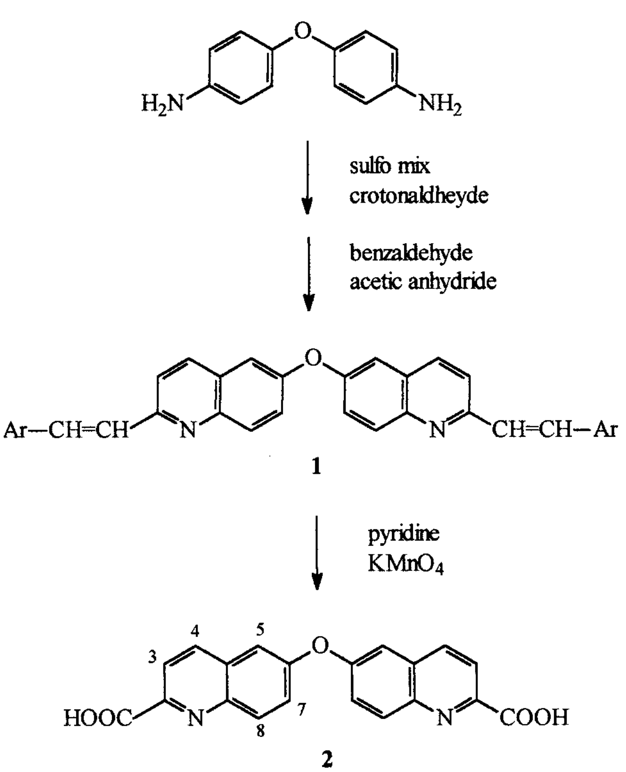
Thermogravimetric analyses (TG) were performed with a Mettler M3 thermobalance at a heating rate of 10°C min^{-1} in N_2 flow (25 ml min^{-1}) or in static air. Decomposition temperatures (T_d) were taken as the temperatures of 2, 5 and 10% weight loss. Char yields (C_y) were calculated as the percentage of solid residue after heating from room temperature to 700°C in N_2.

Differential scanning calorimetry (DSC) measurements were made using a Mettler DSC 30 with Al pans at a heating rate of 20°C min^{-1} in N_2.

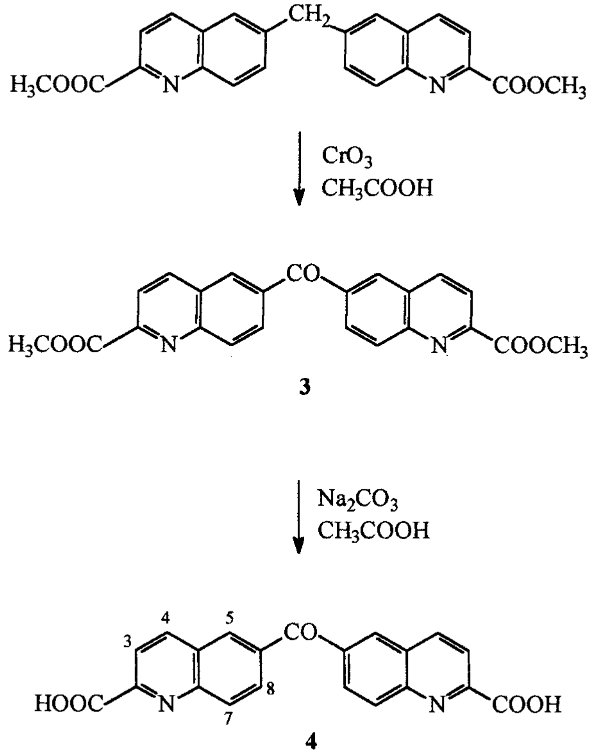
2.3. Monomer synthesis

Monomer **2** was synthesised according to Scheme 1.

*Synthesis of 6,6′-oxy-2,2′-styryldiquinoline (**1**).* Crotonaldehyde (11.70 g, 0.167 mol) was slowly added over 2 h, keeping the temperature at 140°C, to a stirred mixture of 4,4′-oxydianiline (10 g, 0.05 mol), 30 g of sulfo mix, and 10 ml of water. The solution was stirred at this temperature for an additional 5 h and then slowly poured into ice and water. The mixture was neutralised with sodium hydroxide solution and then made alkaline (pH = 8–9) with an ammonium hydroxide solution. An ice bath was used to control the exothermic neutralisation reaction. The precipitate was filtered, washed with water and dried at 35°C. The solid was extracted in soxhlet with petroleum ether (75–120°C) and the solvent was distilled under vacuum. To 10.62 g of the obtained residue, corresponding to 6,6′-oxydiquinaldine, benzaldehyde (22.47 g) and acetic anhydride (43.24 g) were



Scheme 1.



Scheme 2.

added and the mixture was heated overnight and then cooled. The solid was filtered, washed with acetic anhydride, dried and crystallised from dioxane (yield 70%; m.p. 213–214°C).

Anal. Calcd for $C_{34}H_{24}N_2O$: C, 85.69; H, 5.08; N, 5.88. Found: C, 85.22; H, 5.15; N, 5.94. ^{1}H NMR ($CDCl_3$): $\delta = 7.20 - 7.70$ (m, 18H); $\delta = 7.55$ (dd, H_7, 2H); $\delta = 8.00$ (d, H_4, 2H); $\delta = 8.12$ (d, H_3, 2H). IR: 3035 cm^{-1} (olefinic C–H stretch) and 1640 cm^{-1} (C=C stretch).

Synthesis of 6,6′-oxydiquinaldic acid (2). Potassium permanganate (23.89 g) was slowly added (2 h) to a stirred mixture of compound **1** (10 g), pyridine (190 ml) and water (10 ml). The mixture was maintained at 0°C and stirring was continued overnight. The mixture was neutralised with sulphuric acid, then acidified to pH 4–5 with acetic acid and treated with a solution of sodium metabisulfite until there was a complete change in the colour of the solution. The precipitate was filtered, washed with water to eliminate inorganic salts and pyridine and dried. The obtained diacid was treated with a 0.5% potassium hydroxide solution. The solution of the soluble salt was filtered and the filtrate was acidified with acetic acid to pH 4–5. The white precipitate was filtered, washed, dried and crystallised from dioxane (yield 68%; m.p. 255–256°C).

Anal. Calcd for $C_{20}H_{12}N_2O_5$: C, 66.67; H, 3.36; N, 7.77. Found: C, 65.62; H, 3.65; N, 7.59. ^{1}H NMR (DMSO-d_6): $\delta = 7.71$ (d, H_5, 2H); $\delta = 7.77$ (dd, H_7, 2H); $\delta = 8.10$ (d, H_8, 2H); $\delta = 8.25$ (d, H_4, 2H); $\delta = 8.47$ (d, H_3, 2H). IR: 3081 cm^{-1} (O–H stretch); 1697 cm^{-1} (C=O stretch); 1245 cm^{-1} (C–O–C stretch).

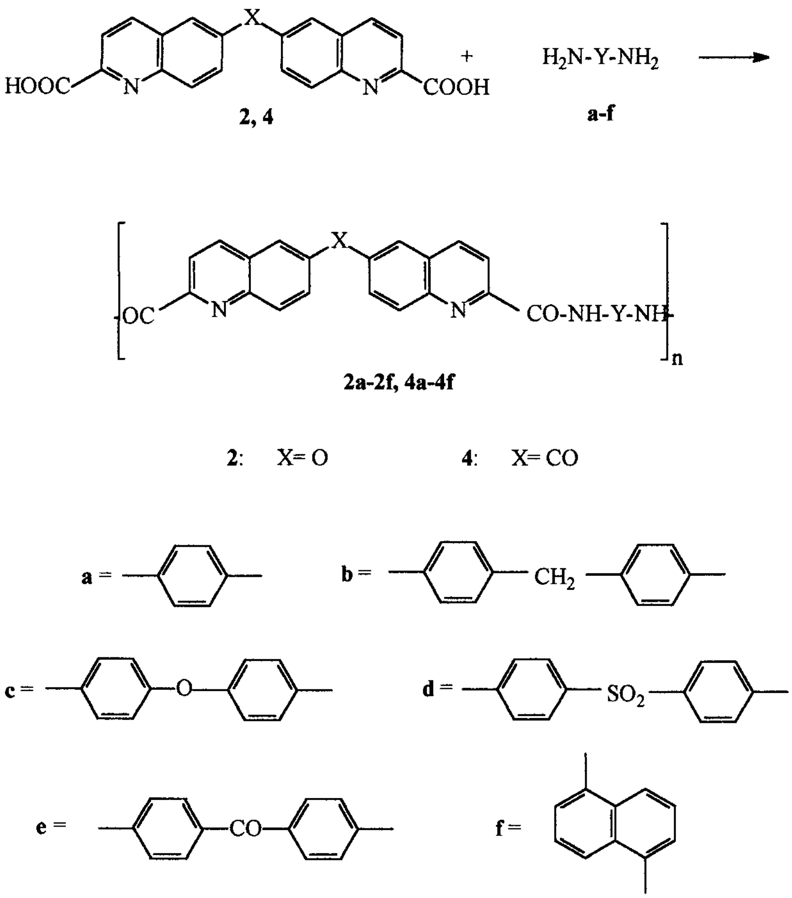
Monomer **4** was synthesised according to Scheme 2.

Synthesis of 6,6′-carbonyl dimethyl diquinaldine dicarboxylate (3). To a refluxing solution of 6,6′-methylene dimethyl diquinaldine dicarboxylate [18] (3 g, 0.0078 mol) in 30 ml of acetic acid, chromium trioxide in excess (0.0145 mol) was added slowly over 8 h and then the solution was allowed to reflux overnight. The white solid was filtered and washed with hot acetic acid and then with cold water. The solid was suspended in a cold solution of sodium bicarbonate, filtered, dried and crystallised from dioxane (60% yield, m.p. 254–255°C).

Anal. Calcd for $C_{23}H_{16}N_2O_5$: C, 69.00; H, 4.03; N, 7.00. Found: C, 68.25; H, 4.16; N, 7.21. ^{1}H NMR ($CDCl_3$): $\delta = 4.13$ (s, CH_3); $\delta = 8.25 - 8.50$ (m, 10H). IR: 1705 cm^{-1} (carboxylic C=O stretch); 1658 cm^{-1} (carbonylic C=O stretch) and 1211 cm^{-1} (acetate CC(=O)–O stretch).

Synthesis of 6,6′-carbonyldiquinaldic acid (4). 1.85 g of compound **3**, 300 ml of 2.5% sodium carbonate solution and 40 ml of dioxane were allowed to reflux for 36 h. The white salt was filtered, washed with hot dioxane and water and then it was suspended in 250 ml of an aqueous solution of acetic acid (10% v/v) overnight. The solid was collected by filtration and washed with water (85% yield; m.p. 305–306°C).

Anal. Calcd for $C_{21}H_{12}N_2O_5$: C, 67.74; H, 3.25; N, 7.52. Found: C, 65.98; H, 3.38; N, 7.36. ^{1}H NMR (DMSO-d_6): $\delta = 8.21$ (d, H_4, 2H); $\delta = 8.29$ (dd, H_7, 2H); $\delta = 8.35$ (d, H_8, 2H); $\delta = 8.63$ (d, H_5, 2H); $\delta = 8.77$ (d, H_3, 2H). IR: 3029 cm^{-1} (O–H stretch); 1703 cm^{-1} (carboxylic C=O stretch) and 1658 cm^{-1} (carbonylic C=O stretch).



Scheme 3.

2.4. Polymer synthesis

A typical example of polymerisation is as follows: a solution of NMP (5 ml) and Py (1.25 ml) containing 8 wt% (LiCl (0.5 g) was added to a mixture of diacid (0.00125 mol), diamine (0.00125 mol) and TPP (0.00250 mol). The mixture was maintained under stirring and in a nitrogen atmosphere at 110°C for 5 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 100°C. The yield was higher than 95% for all polymers.

3. Results and discussion

In this paper we report the synthesis and characterisation of polyamides obtained starting from two new monomers containing quinoline units bridged by ether or carbonyl groups. The new monomer **2** was synthesised according to Scheme 1, by the application of the typical Skraup synthesis to 4,4′-oxydianiline and crotonaldehyde, using a solution of nitrobenzene and oleum (sulfo mix) as oxidising agent; from the obtained 6,6′-oxydiquinaldine, by reaction with benzaldehyde in acetic anhydride, the styryl derivative **1** was prepared. Oxidation with potassium permanganate gave compound **2** that was purified and then characterised. Monomer **4** was obtained, according to Scheme 2, by oxidation of 6,6′-methylene dimethyl diquinaldine dicarboxylate with chromium trioxide [18]; the obtained compound **3** was hydrolysed with a sodium carbonate solution and then treated with an aqueous solution of acetic acid giving monomer **4**.

All compounds were characterised by elemental analysis, NMR and IR and the results are in agreement with the proposed structures.

Polyamides **2a**–**2f** and **4a**–**4f** were synthesised by direct polycondensation of dicarboxylic acids **2** and **4** with aromatic diamines **a**–**f** using triphenyl phosphite and pyridine as condensing agents (Scheme 3). The reactions were carried out in NMP solution of the diacid and diamines in the presence of 8% by weight of LiCl, in a nitrogen atmosphere and at a temperature of 110°C. All the polymerisation proceeded in homogeneous solutions and the yields of the polymers were quantitative. Polycondensations promoted by triphenylphosphite can produce polymers contamined with P-derivatives, but the elemental analyses (Table 1) and ^{31}P NMR did not show evidence of presence of P. The values obtained from the elemental analyses, lower

Table 1
Solution viscosities, elemental analysis and solubility of polymers

Polymer	η_{inh} (dl g^{-1})	Elemental analysis (%)[a]					Solubility[b]	
		Formula	C	H	N	S	DMAc	NMP
2a	1.04[c]	$(C_{26}H_{16}N_4O_3)_n$ $(432.44)_n$	70.84 (72.22)	3.83 (3.73)	12.79 (12.96)	–	±	+
2b	0.65[d]	$(C_{33}H_{22}N_4O_3)_n$ $(522.56)_n$	74.76 (75.85)	4.31 (4.24)	10.64 (10.72)	–	−	++
2c	0.84[c]	$(C_{32}H_{20}N_4O_4)_n$ $(524.54)_n$	72.97 (73.27)	3.96 (3.84)	10.64 (10.68)	–	−	+
2d	0.45[d]	$(C_{32}H_{20}N_4O_5S)_n$ $(572.59)_n$	66.05 (67.12)	3.62 (3.52)	9.67 (9.78)	5.54 (5.59)	++	++
2e	0.57[c]	$(C_{33}H_{20}N_4O_4)_n$ $(536.55)_n$	72.60 (73.87)	3.86 (3.76)	10.32 (10.44)	–	−	−
2f	0.72[c]	$(C_{30}H_{18}N_4O_3)_n$ $(482.50)_n$	74.02 (74.68)	3.83 (3.76)	11.52 (11.61)	–	+	+
4a	0.48[c]	$(C_{27}H_{16}N_4O_3)_n$ $(444.45)_n$	72.23 (72.97)	3.71 (3.63)	12.46 (12.61)	–	+	+
4b	0.86[d]	$(C_{34}H_{22}N_4O_3)_n$ $(534.57)_n$	75.79 (76.39)	4.24 (4.15)	10.41 (10.48)	–	−	++
4c	0.62[d]	$(C_{33}H_{20}N_4O_4)_n$ $(536.55)_n$	73.17 (73.87)	3.84 (3.76)	10.36 (10.44)	–	+	++
4d	0.34[d]	$(C_{33}H_{20}N_4O_5S)_n$ $(584.61)_n$	67.08 (67.80)	3.52 (3.45)	9.51 (9.58)	5.42 (5.48)	++	++
4e	0.40[c]	$(C_{34}H_{20}N_4O_4)_n$ $(548.56)_n$	73.44 (74.45)	3.77 (3.67)	10.07 (10.21)	–	+	+
4f	0.29[c]	$(C_{31}H_{18}N_4O_3)_n$ $(494.51)_n$	74.52 (75.30)	3.72 (3.67)	11.24 (11.33)	–	+	+

[a] Calculated values are reported in parentheses.

[b] Tested with 0.05 g of polymer in 1 ml of solvent: ++, soluble; +, partially soluble; ±, partially soluble on heating; −, insoluble (DMAc: dimethylacetamide).

[c] Measured in concentrated sulfuric acid at 30°C ($c = 0.5$ g dl^{-1}).

[d] Measured in NMP.

than the calculated ones, have to be attributed to the hygroscopic characteristics of amide groups. The IR spectra of the polymers showed the characteristic amide absorption bands near 3330 cm^{-1} (N–H stretch), near 1690 cm^{-1} (C=O stretch) and near 1405 cm^{-1} (C–N stretch); the polymers obtained starting from monomer **2** showed the characteristic ether absorption near 1250 cm^{-1} (C–O–C stretch), while in the polymers deriving from monomer **4** the stretching absorption band of the carbonyl bridging the quinoline rings, that in the monomer occurs at 1658 cm^{-1}, is present as a shoulder due to the overlap with the carbonyl stretching band of the amide group (Fig. 1).

The inherent viscosities were in the range of 0.45–1.04 dl g^{-1} for polymers of series **2** and in the range of 0.29–0.86 dl g^{-1} for polymers of series **4**. They were determined in concentrated sulphuric acid or NMP, depending on the solubility of the polymer (Table 1).

Solubility behaviour of polymers is given in Table 1. All the polymers were soluble in concentrated sulphuric acid and the ones obtained by reaction with DAS (**2d** and **4d**) were completely soluble in DMAc and NMP, due to the presence, in the polymer backbone, of sulfonyl group that is active in disrupting polymer chain planarity increasing the solubility. The semicrystalline polymers were less soluble in DMAc and NMP which is in agreement with the general rule that solubility decreases with increasing crystallinity; in particular, polymer **2e** was completely insoluble both in DMAc and NMP. For all polymers, the solubility was higher in NMP than in DMAc; in fact, except polymer **2e**, all the polymers were soluble or partially soluble in NMP without heating (Table 1).

Gel permeation chromatography (GPC) is a very convenient method for the determination of molar masses. However, since it is related to the hydrodynamic radius of the polymers in solution, it does not yield absolute values. Calibration with polystyrene may result in questionable results when the polarity and backbone stiffness of the polymers studied deviate strongly from those of polystyrene. Only for the polymers soluble in NMP it was possible to determine the molecular weight distribution. It was essentially unimodal with no evidence of oligomeric or unreacted species for polymers **4b** and **4c**, while for the other polymers two narrow distributions were observed (Table 2).

The thermal behaviour of the synthesised polyamides was evaluated by TGA and DSC and the T_d, T_g, T_m and C_y values are summarised in Table 3. A slow heating up to 100°C followed by cooling to room temperature in flowing nitrogen was made to remove most of the moisture absorbed by the polyamides, due to the presence of polar amide linkages. The T_ds, determined under N_2, of the polymers **2a**–**2f** were in the range 295–405°C (2% weight loss), 410–440°C (5% weight loss), and 435–455°C (10% weight loss) (Fig. 2), while the ones of the polymers **4a**–**4f**, were in the range 320–350°C (2% weight loss), 400–420°C (5% weight loss), and 440–450°C (10% weight loss) (Fig. 3). The polymers showed almost the same stability in air. The char yield (C_y) was in the range 57–60% for most of the polymers, confirming their high thermal stability. The T_gs were detected in the second heating after annealing for 30 min at 250°C: they were in the range 230–305°C for polymers **2a**–**2f** and in the range 235–310°C for polymers **4a**–**4f** depending on the starting monomer and diamine component structure. Only for polymer **4f** no T_g was detected. T_g is known to depend on several factors (chain symmetry, polar groups, cross-linking, intermolecular forces etc.) but it primarily depends on the rigidity of the polymer chain. In fact, the increase of the rigidity of the polymer backbones increases the energy barrier for segmental motion, mobility is hindered and

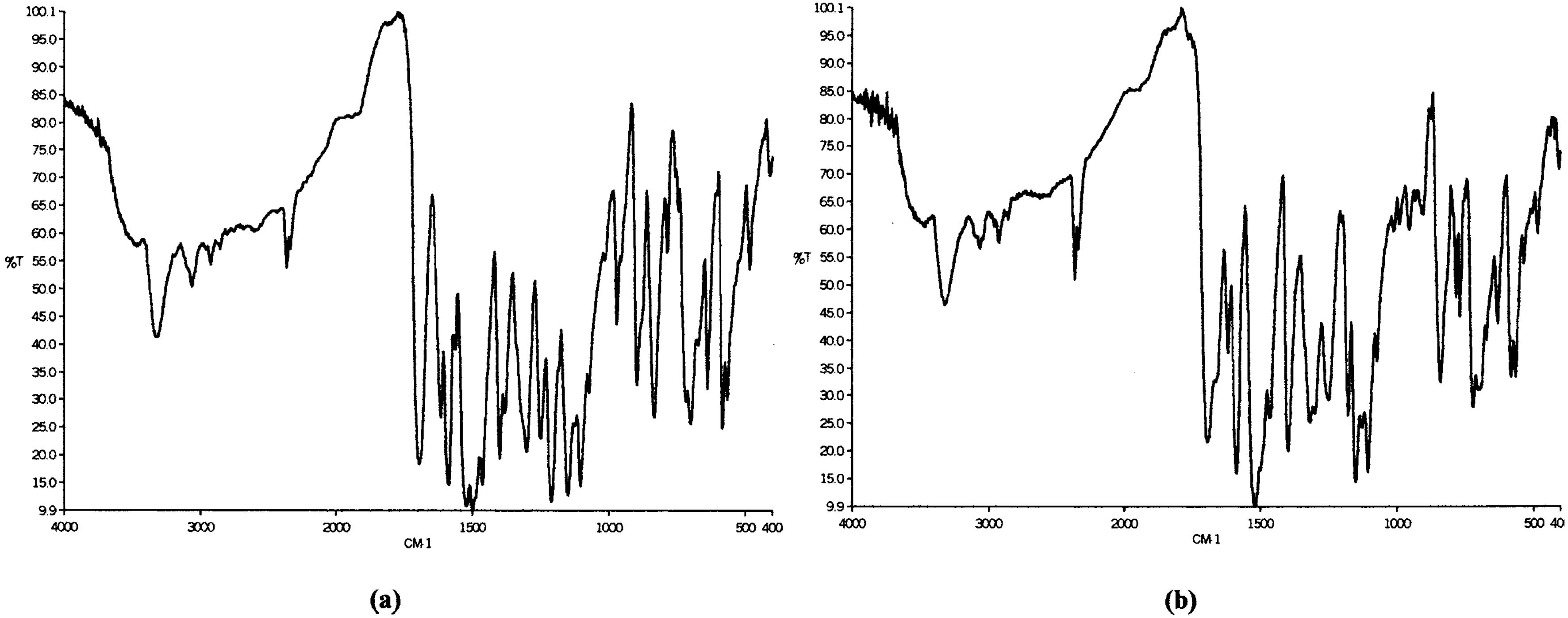


Fig. 1. IR spectra of polymers **2d** (a) and **4d** (b). **2d** band assignments: 3328 cm^{-1} (N–H stretch); 1695 cm^{-1} (amidic C=O stretch); 1401 cm^{-1} (C–N stretch); 1251 cm^{-1} (C–O–C stretch). **4d** band assignments: 3318 cm^{-1} (N–H stretch); 1695 cm^{-1} (amidic C=O stretch) and shoulder 1660 cm^{-1} (C=O stretch); 1398 cm^{-1} (C–N stretch).

Table 2
Molar masses (determined using narrow polydispersity polystyrene standards) of soluble polyamides

Polymer	M_n (g mol^{-1})		M_w (g mol^{-1})		M_w/M_n	
2b	31 185	568 479	46 913	671 627	1.50	1.18
2d	15 319	631 018	28 947	681 910	1.9	1.00
4b		709 660		1 042 295		1.47
4c		593 600		915 360		1.54
4d	10 286	448 850	18 320	589 270	1.78	1.31

hence T_g increases. Polymers obtained by reaction with DAS were amorphous and showed higher T_g values (305°C for **2d** and 310°C for **4d**) with respect to the other polymers. It is because sulfonyl group present in the moiety of the diamine is active to disrupt chain planarity owing to the different bond angles [21]. Polymer **2a**, **2c**, **2e** and **2f** showed an endothermic peak at 460°C, due to degradation. Polymers obtained by reaction with PPD and ABP were semicrystalline both in series **2** and **4**, particularly polymer **2e** "as made" showed a T_g at 230°C, an exothermic crystallisation peak at 279°C and T_m at 380°C (Fig. 4), after heating

Table 3
Thermal characterisation of polymers (* — exhotermic crystalisation peak at 279°C)

Polymer	T_d[a] (°C)	T_d[b] (°C)	T_d[c] (°C)	T_d[d] (°C)	T_d[e] (°C)	T_d[f] (°C)	T_g(°C)	T_m (°C)	C_y[g]
2a	295	410	435	305	405	435	240	410	59
2b	370	420	440	395	425	445	245	–	57
2c	405	440	455	400	430	450	270	380	58
2d	340	420	440	375	420	445	305	–	45
2e	340	415	440	360	415	440	230*	380	50
2f	355	425	445	365	420	445	275	–	60
4a	320	420	450	310	405	440	235	410	62
4b	350	405	445	380	410	440	265	–	63
4c	330	400	440	290	375	420	260	–	64
4d	335	420	450	320	400	435	310	–	57
4e	350	420	450	335	410	445	270	405	60
4f	345	415	445	330	410	445	–	–	70

[a] Temperature of 2% weight loss determined in nitrogen atomosphere.
[b] Temperature of 5% weight loss determined in nitrogen atomosphere.
[c] Temperature of 10% weight loss determined in nitrogen atomosphere.
[d] Temperature of 2% weight loss determined in static air.
[e] Temperature of 5% weight loss determined in static air.
[f] Temperature of 10% weight loss determined in static air.
[g] Char yield calculated as the percentage of solid residue after heating from room temperature to 700°C under nitrogen.

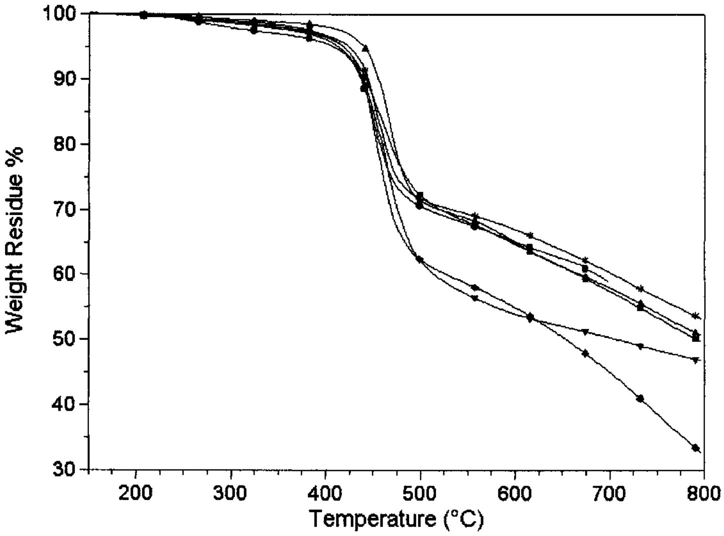
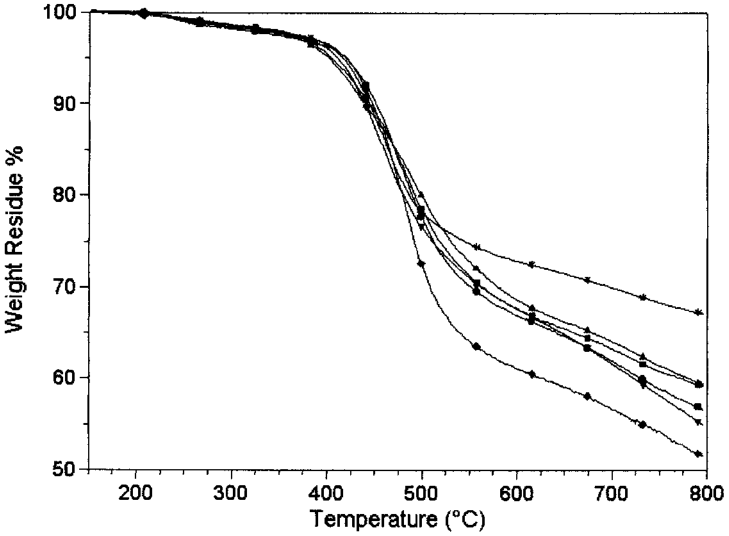


Fig. 2. TGA curves in nitrogen of polyamides **2a** (●); **2b** (■); **2c** (▲); **2d** (◆); **2e** (▼); **2f** (*).



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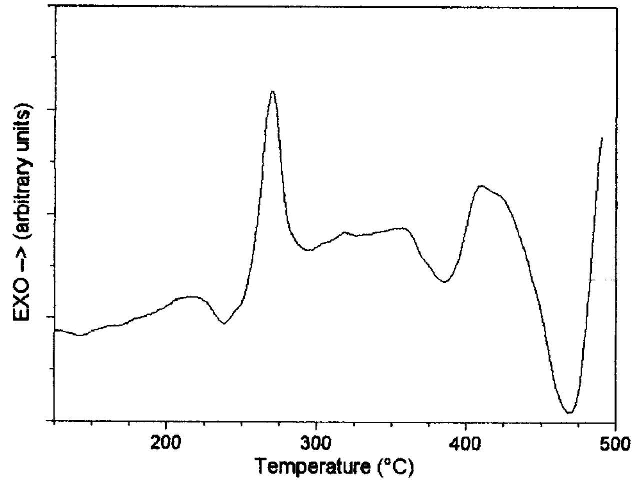
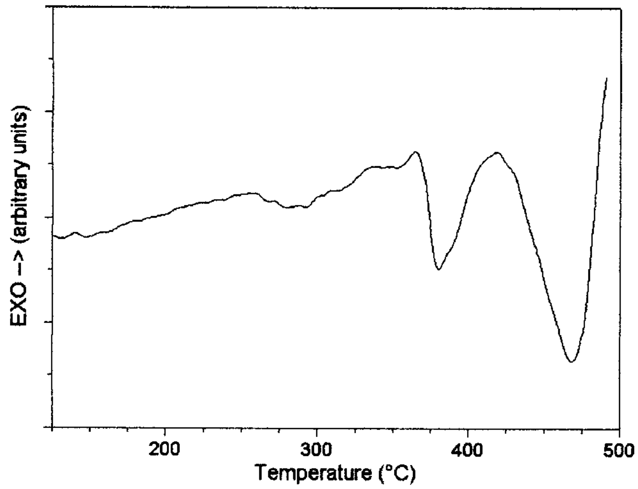


(a)

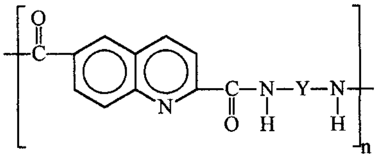


(b)

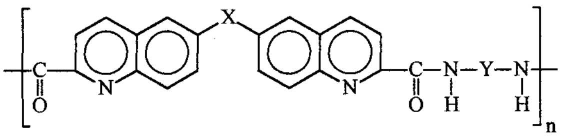
Fig. 4. DSC curve of polyamide **2e**: (a) run on "as made" sample; and (b) re-run after heating to 370°C and cooling.

to 370°C, cooling and re-run, the T_g increased to 275°C. Also polymer **2c** was semicrystalline ($T_g = 270°C$; $T_m = 380°C$); for the other polymers, although annealing experiments at $T > T_g$ for 1/2 h were performed, no evidence of melting transition was obtained.

In previous papers we reported the syntheses of polyamides containing in the repeat units, only one quinoline ring [12] (**5**) or quinoline units bridged by methylene [18] or sulfone [19] groups (**6** and **7**, respectively) and now it can be interesting to compare the properties of all these polyamides with those of the polymers reported here, and to rationalise the structure–property relationships taking into account the influence of three factors: (1) the number of quinoline moieties present in the repeat unit; (2) the unit bridging the two quinoline units; and (3) the structure of the diamine component.



5



6 ($X = CH_2$)

7 ($X = SO_2$)

In order to evaluate the effect of the number of quinoline moieties present in the repeat unit we can compare the properties of the polymers of series **2**, **4**, **6** and **7** with those of polyamides of series **5**. These last polymers were soluble only in concentrated sulphuric acid and thermal analysis showed high T_d values [12], T_g values in the range 288–298°C and T_m higher than 400°C and very close to the decomposition temperature [22]. The comparison provided evidence that in the series with diquinoline units the solubility was greatly improved in almost all polymers while the T_d and T_g values remained comparable. The slightly lower T_gs observed for the polymer obtained by reaction with MDA in series **6** and for all series **7** polymers were probably due to the polymer low molecular weights.

As regards the presence of the different unit bridging the two quinoline rings, it does not seem to influence the thermal stability; in fact all the polymers containing diquinoline units showed temperatures of 10% weight loss higher than 400°C. Instead it is evident an influence on the crystalline domain presence; in fact in series **2** and **4** the T_g values were in the range 230–310°C and only the polymers obtained by reaction with PPD and ABP (in both series) and ODA (in series **2**) were semicrystalline. In series **6**, all polymers were semicrystalline with T_gs ranging between 259–294°C (only polymers obtained by reaction with MDA showed a lower T_g), while in series **7** all polymers were amorphous with T_gs in the range 170–220°C. Concerning the solubility, polyamides of series **2** and **4** showed very good results; in fact, except for polymers **2e**, they were soluble or partially soluble in NMP. In series **6** only polymers obtained by reaction with ODA and MDA showed good solubility in NMP and DMAc, while for series **7** polymers only the ones obtained by reaction with MDA and DAS were soluble in the same solvents.

Taking into account the effect of the diamine component, the best results were obtained with MDA, ODA and DAS with regard to solubility improvement, with DAS, PPD and DAN with respect to the T_g increase, and with PPD and ABP in order to obtain semicrystalline polymers.

In conclusion, the introduction of quinoline units bridged by an ether or carbonyl group in polyamides resulted in amorphous or semicrystalline materials. The polyamides showed good thermal stability, high T_g values and very good solubility in aprotic solvents such as NMP. By comparison with some other polymers containing different bridging groups, the best results, regarding thermal stability and solubility, were shown by the polyamides containing quinoline rings bridged by ether or carbonyl units.

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