

SYNTHESIS AND CHARACTERIZATION OF NEW POLYAMIDES CONTAINING 6,6'-METHYLENEDIQUINOLINE UNITS

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ABSTRACT

Aromatic polyamides have been synthesised from a new monomer containing a 6,6'-methylenediquinoline unit by reaction with various diamines by the phosphorylation route. The polymers have been characterised by elemental analysis, i.r., thermogravimetric analysis and differential scanning calorimetry. The polyamides, obtained in quantitative yield, possessed inherent viscosities in the range 0.20-0.85 dl g⁻¹, 10% weight loss in nitrogen and air above 420°C and glass transition temperatures in the range 184-294°C. The polyamides obtained by reaction of this new monomer with 4,4'-oxydianiline and 4,4'-methylenedianiline were soluble on heating in N-methyl-2-pyrrolidone and partially soluble in dimethylacetamide. The properties of these polymers are compared with those of corresponding polyamides having only one quinoline ring per repeat unit.

(Keywords: diquinoline unit; polyamides; direct polycondensation, thermal properties).

INTRODUCTION

During the last thirty years extensive research has been devoted to the synthesis of organic polymers for use in high temperature applications. The driving force is due to the demand from the air and space industries for new materials with low densities to be used in structural applications. The research in this field has resulted in development effort directed toward high performance polymers that remain a key item for future technologies. Typical examples of high performance polymers are polyarylate and aromatic polyamides.^{1,2} They exhibit excellent mechanical strength per unit weight, high thermal stability combined with low flammability, chemical resistance as well as good electrical properties. On the other hand these outstanding combinations of properties are counterbalanced by many problems with respect to processability, in fact they have high melting temperatures and are only sparingly soluble.³

Because for unfilled thermoplastic polymers the ultimate use-temperature is limited to the T_g , while the melting temperature (T_m) determines the temperature to be reached for processing, it is desirable to have a polymer with a high T_g and a T_m as low as possible. Thus in the synthesis of any thermally stable polymer a compromise has to be reached between thermo-mechanical properties and processability. Therefore it is very important to study various structure-property relationships in order to predict the effects of structural modifications on polymer properties.

The temperature at which the T_g and T_m occur in polymers depends upon the cohesive energy of the polymer chains in the amorphous and crystalline regions,^{4,5} hence they are both influenced by the polymer structure. Chain immobility, caused by polymer backbone rigidity, and interchain attractions, such as hydrogen bonding or dipole-dipole attraction, increase T_g and T_m .⁶ The incorporation of aromatic rings in the polymer chain not only increases chain stiffness, but also introduces structures that possess good thermal and oxidative stability. Therefore thermally stable polymers generally consist of aromatic or heteroaromatic structures.

Hirsch and Lilyquist⁷ reported that quinoline has the highest decomposition temperature of all aromatic rings. Interests in the syntheses of aromatic polyquinoline have increased rapidly during the past decade because these materials display excellent oxidative and thermal stability and polyquinoline have been reported⁸⁻¹² with a wide range of chain stiffness, that can be altered from relatively flexible polymers with a low T_g to rod-like macromolecules with a high T_g . All the polymers showed an excellent thermal stability, with initial weight losses occurring between 500 and 600°C. Most of the materials were soluble in common organic solvents and had a low degree of crystallinity^{13,14}. The introduction of quinoline units into the polymer backbone of aromatic polymers could influence T_g , T_m , degree of crystallinity and thermal stability.

Previous papers reported the syntheses of new quinoline monomers¹⁵, polyamides^{16,17}, poly(arylene)ethers^{18,19} and polyesters²⁰ containing quinoline units in the chain. The thermal properties of the obtained polymers confirmed the positive influence of the introduction of heterocyclic units. It could be hypothesised that this positive influence could be improved by introducing two quinoline moieties in the polymer repeat unit. Hence in this paper we report of aromatic polyamides, obtained by a direct phosphorylation reaction^{21,22}, containing diquinoline units in the polymer backbone. The synthesis proceeded starting from the new monomer 6,6'-methylenediquinaldic acid. The influence of the incorporation of this moiety into the polymer backbone on properties of the obtained 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 Utermohlen²³. Crotonaldehyde was distilled before use.

N-methyl-2-pyrrolidone (NMP) was refluxed over CaH₂ for 8 h and distilled under reduced pressure. It was then refluxed in the presence of P₂O₅ 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 and stored over 4 Å molecular sieves. LiCl (Aldrich Co.) was 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.

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 cm⁻¹, and nuclear magnetic resonance (n.m.r.) spectra were obtained with a Bruker AC 200 instrument using Me₄Si as internal reference. Elemental analyses were conducted on a Carlo Erba Elemental Analyser, model 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 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 min⁻¹ in N₂ flow (25 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 min⁻¹ in N₂. Char yields (C_y) were calculated as the percentage of solid residue after heating from room temperature to 700°C in N₂.

Monomer synthesis

Synthesis of 6,6'-methylenediquinaldine (1)

To a stirred mixture of 4,4' methylenedianiline (15.46 g, 0.078 mol), 50 g of sulfo mix and 10 ml of water, heated to 140°C, crotonaldehyde (18.51 g, 0.264 mol) was slowly 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 neutralised with sodium hydroxide solution and then made alkaline (pH=8) with a sodium carbonate solution. An ice bath was used to control the exothermic neutralisation reaction. The precipitate was filtered, washed with water and dried at 100°C. The solid was extracted with toluene, the solvent was distilled under vacuum and the residue was then purified by chromatography on silica gel using ethyl acetate as eluant (m.p.134-135°C; yield 41%).

Anal.Calcd. for C₂₁H₁₈N₂: C, 84.53; H, 6.08; N, 9.38. Found: C, 84.13; H,6.20; N, 9.50.

¹H-n.m.r. (CDCl₃): δ=2.73 (s, CH₃); δ=4.31 (s, CH₂); δ=7.25 (d, H₃, 2H); δ=7.57 (H₅ and H₇, 4H); δ=7.96 (m, H₄ and H₈, 4H).

i.r.: 2962 cm⁻¹ (ν_{as} CH₃) and 2850 cm⁻¹ (ν_s CH₃); 1598-1480 cm⁻¹ (C-C and C-N ring stretching).

Synthesis of 6,6'-methylene-2,2'-styryldiquinoline (2)

A mixture of **1** (8 g, 0.027 mol), benzaldehyde (17 g) and acetic anhydride (35 g) was heated for 4 hours at 140°C. The mixture was then cooled and the solid filtered, washed with water, dried and crystallised from acetic anhydride (m.p.=210-211°C, 80% yield).

Anal. Calcd. for C₃₅H₂₆N₂: C, 88.58; H, 5.52; N, 5.90. Found: C, 88.75; H, 5.40; N, 5.75.

¹H-n.m.r. (CDCl₃): δ=4.30 (s, CH₂); δ=7.30-7.69 (m, 20H); δ=8.03 (d, H₄ and H₇, 4H).

i.r.: 3029 cm⁻¹ (olefinic C-H stretch); 1636 cm⁻¹ (C=C stretch).

Synthesis of 6,6'-methylene dimethyl diquinaldine dicarboxylate (3)

Potassium permanganate (19.11 g) was slowly added (2 hours) to a stirred mixture of compound **2** (9.56 g), pyridine (200 ml) and water (10 ml). The mixture was maintained at 0°C and stirring was continued for 1 hour. The mixture was then neutralised to pH 7 with diluted sulphuric acid and

acidified to pH 4 with acetic acid to avoid the protonation of quinolinic nitrogen. It was then treated with a solution of sodium methabisulphite 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 and added to a solution of 100 ml of methanol containing 2 ml of concentrated sulphuric acid. After reflux for 6 hours, the mixture was filtered and slowly added to a solution of ice and water. The precipitate was filtered and washed with cold water and with a cold solution of sodium bicarbonate. The crude product was crystallised from toluene (m.p.223-224°C, 65% yield).

Anal.Calcd. for C₂₃H₁₈N₂O₄: C, 71.49; H, 4.69; N, 7.25. Found: C, 71.66; H, 4.60; N, 7.30.

¹H-n.m.r. (CDCl₃): δ=4.08 (s, CH₃); δ=4.41 (s, CH₂); δ=7.66 (m, H₅ and H₇, 4H); δ=8.23 (m, H₃, H₄ and H₈, 6H).

i.r.: 1713 cm⁻¹ (C=O stretch); 1209 cm⁻¹ (acetate CC(=O)-O stretch).

Synthesis of 6,6'-methylenediquinaldic acid (4)

2.05 g of compound **3** and 200 ml of 5% sodium carbonate solution were allowed to reflux overnight. The solution was filtered and the filtrate was neutralised with diluted sulphuric acid and then acidified with acetic acid to pH 3-4. The white solid was collected by filtration, washed with water, dried and crystallised twice from N,N-dimethylformamide and a solution of methanol/water (30/70) (m.p.=251°C, 60% yield).

Anal.Calcd.for C₂₁H₁₄N₂O₄: C, 70.38; H, 3.94; N, 7.82. Found: C, 70.25; H, 3.88; N, 7.75.

¹H-n.m.r. (DMSO-d₆): δ=4.45 (s, CH₂); δ=7.82 (d, H₇, 2H); δ=7.99 (s, H₅, 2H); δ=8.11 (m, H₃ and H₈, 4H); δ=8.50 (d, H₄, 2H).

i.r.: 3425 cm⁻¹ (O-H stretch); 1707 cm⁻¹ (C=O stretch).

Polymer synthesis

A typical example of solution 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 (0.4479 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°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 100°C. The yield was 95% and η_{inh} of the polymer in concentrated sulphuric acid was 0.85 dl g⁻¹.

RESULTS AND DISCUSSION

In this paper, we report the synthesis and characterisation of polyamides obtained starting from a new monomer containing diquinoline units bridged by a flexible group as methylene. The new monomer (**4**) was synthesised according to Scheme 1. The 6,6'-methylenediquinaldine (**1**) was prepared by application of the typical Skraup synthesis starting from 4,4'-methylenedianiline and crotonaldehyde, using as oxidising agent a solution of nitrobenzene and oleum (sulfo mix). The used ratio of aldehyde to amine was 1.67:1²⁴, the temperature was carefully maintained at 140°C, because at lower temperature the yield was poor and at higher temperature a complicate mixture of products, difficult to separate and to characterise, was obtained. The styryl derivative (**2**) was obtained by reaction of **1** with benzaldehyde in acetic anhydride. Oxidation with potassium permanganate and the following esterification with methanol gave compound **3** that was purified by crystallisation and then hydrolysed with 5% sodium carbonate solution to give **4**. All compounds were characterised by elemental analysis, n.m.r. and i.r. and the results are in accord with the proposed structures.

Polyamides **4a-e** were synthesised by direct polycondensation of dicarboxylic acid **4** with aromatic diamines **a-e** using triphenyl phosphite and pyridine as condensing agents^{21,22}(Scheme 2). The reactions have been 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 105°C. The temperature was carefully controlled because its increase beyond this value causes a drop in polymer viscosity, probably due to the decrease of interactions between Py and TPP in a range close to the boiling temperature of Py. All the polymerisations proceeded in homogeneous solution and the yields of the polymers were quantitative. The elemental analysis values of these polymers are listed in Table 1. In all cases, however the found values of carbon were lower than the calculated values for the proposed structure and this could be attributed to the hygroscopic characteristics of amide groups²⁵, and not to the incomplete removal of NMP bound to the polyamide chains. In fact elemental analysis and TGA measurements made after drying the polymers for 12 h at temperatures above T_g under high vacuum, did not show any relevant change with respect to the values obtained with the samples dried as reported in the experimental section. The i.r. spectra of the polymers (Table 1) showed the N-H stretching near 3330 cm^{-1} and the presence of absorption bands at 1680 cm^{-1} , due to amide C=O, and at 1400 cm^{-1} , due to amide C-N stretch, confirmed the structure of the polyamides.

The solubility of the polyamides is given in Table 2. Polymers **4b** and **4c** were soluble on heating in NMP and partially soluble in DMAc, the other polymers showed no solubility in these solvents due to their rigid structure³.

The inherent viscosities, obtained in concentrated sulphuric acid, were in the range 0.20-0.85 dl g⁻¹ (Table 2).

The thermal behaviour of the synthesised polyamides was evaluated by t.g.a. and d.s.c. and the values of T_d, T_g, T_m and C_y are summarised in Table 2 (T_g and T_m values were all taken from “as made” samples except for sample **4b**). 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 the moisture²⁶⁻²⁸. All the polymers were stable up to 420°C in both air and nitrogen (Table 2 and Figure 1) and they showed almost the same stability in both conditions. One of the criterion that has been used to describe polymer stability at high temperature is the char yield (C_y)^{3,29}, defined as the amount of carbonised residue determined at 700°C in nitrogen. For all the obtained polymers it was above 46% (Table 2). In polymer **4b**, the T_g was determined only after quenching, in fact quenching from the elevated temperature to room temperature in air shows more amorphous samples so that T_g could be easily detected in the second heating trace of d.s.c. Sample **4c** showed two endothermic transitions indicating two melting points for corresponding crystalline polymorphs (Figure 2).

To rationalise the structure-properties relationships three factors have to be taken into account: i) the effect of the structure of the diamine deriving moiety; ii) the effect of the methylene bridging the two quinoline units and iii) the effect of the number of quinoline moieties present in the repeat unit.

Polyamides **4a**, **4d** and **4e** had T_g close to 290°C, polymer **4b** showed a T_g of 259°C while polymer **4c** (Table 2) showed a T_g value of 184°C. It is known³⁰ that one of the most important factors influencing the value of the T_g is polymer chain flexibility. The higher T_g values found for polymers **4a**, **4d** and **4e** can be ascribed to the influence of the moiety introduced into the polymer chain by the diamine monomer. Polymer **4a** and **4e** contain moieties particularly rigid such as *p*-phenylene and 1,5-naphthalene³¹, while polymer **4d** contains sulphone groups that, because of the high polarity of the sulphone link³², induces an increase of the energy barrier for segmental motion. The more flexible the chains are, such as those containing ether linkages or linear alkylene groups,

the lower are T_g s. In polymer **4b** the chain flexibility is due to the ether groups, while in polymer **4c** the flexibility is greatly increased by the presence of the methylene groups coming from MDA.

The presence of a methylene group bridging the two quinoline units will influence properties such as solubility, thermal stability, T_g and T_m . In order to evaluate these effects, it could be useful to compare the properties of the polymers reported here with those of polyamides that we reported in a previous paper¹⁶. In the polymer backbone of those polyamides one quinoline moiety was present per repeat unit. They were soluble only in concentrated sulphuric acid and thermal analysis showed high T_{ds} ¹⁶, T_g s in the range 288-298°C and T_m higher than 400°C and very close to decomposition temperature³³. The comparison evidences that in the series reported here only polymers derived from ODA and MDA are influenced to a large extent by the modification of the polymer backbone. In fact because the methylene bridge could promote a drop in thermal stability it could be expected that the polymers reported here show lower T_{ds} . Actually thermal stability is negatively affected only, and to a low extent, in the polymers prepared using as diamines ODA and MDA. In the same two polymers T_g s decrease but maintain still high values (259 and 184°C respectively) and T_m s are about 100°C lower and are far from the T_{ds} . In these two polymers also the solubility is improved and in fact they are soluble on heating in NMP and partially soluble in DMAc, while the corresponding polymers with one quinoline unit were soluble only in concentrated sulphuric acid.

In conclusion, the knowledge of the relationship between the chemical structures of monomers and the properties of the polymers is an important prerequisite for the development of new plastics and the improvement of existing ones. Therefore the present paper aimed to study the properties of polyamides containing diquinoline units bridged by a flexible group as methylene and to compare the behaviour of these polymers with those of the corresponding polyamides containing one quinoline ring in the repeat unit. It is interesting to note that the polyamides containing diquinoline units show high thermal stabilities and excellent T_g s for polymers of this class. Moreover, the introduction of diquinoline moieties results in particularly interesting polymers when combined with ODA and MDA that contain flexible groups. In fact for these polymers, with respect to those containing one quinoline unit, the thermal stability hasn't decreased, T_m s have decreased, T_g s maintained still high and the solubility in aprotic solvents increased; all these properties make these new polymers potentially better processable, still maintaining high ultimate use temperatures.

Studies are in progress to study the effect of introduction in the polymer backbone of moieties containing diquinoline units bridged by groups such as SO₂, O and CO.

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References

1. Cassidy, P.E., *Thermally Stable Polymers*, Dekker, New York, 1980.
2. (a) Critchley, J.P., Knight, G.J., Wright W.W., *Heat-Resistant Polymers*, Plenum Press, New York (1983); (b) Belbin, G.R., Staniland, P.A., *Phil.Trans.R.Soc.Lond.*, 1987, **A322**, 451.
3. Yang, H.H., *Aromatic High-Strength Fibers*, Wiley, New York, 1989.
4. Billmeyer, F.W., "*Textbook of Polymer Science*", 2nd ed. Wiley-Interscience, New York, 1971.
5. Conley, R.T., "*Thermal Stability of Polymers*", Marcell Dekker, Inc., New York, 1970, vol.1.
6. Frazer, A.H., "*High Temperature Resistant Polymers*", in *Polymer Reviews*, Mark, H.F. and Immergut, E.H. (Eds), Interscience, New York, 1968, vol.17.
7. Hirsch, S.S. and Lilyquist, M.R., *J.Appl.Polym.Sci*, 1967, **11**, 305.
8. Norris, S.O. and Stille, J.K., *Macromolecules*, 1976, **9**, 496.
9. Beever, W.H. and Stille, J.K., *Macromolecules*, 1979, **12**, 1033.
10. Sybert, P.D. and Beever, W.H., *Macromolecules*, 1981, **14**, 493.
11. Stille, J.K., *Macromolecules*, 1981, **14**, 870.
12. Kim, K., Park, S.Y., Kim, Y.J., Kim, N., Hong, S.I., Sasabe, H., *J.Appl.Polym.Sci.*, 1992, **46**, 1.
13. Harris, S.O. and Stille, J.K., *Macromolecules*, 1976, **9**, 496.
14. Wrasidlo, W. and Stille, J.K., *Macromolecules*, 1976, **9**, 505.
15. Bottino, F.A., Di Pasquale, G., Pollicino, A., Recca, A., Staniland, P.A., *J.Heterocyclic Chem.*, 1989, **26**, 929.
16. Bottino, F.A., Di Pasquale, G., Pollicino, A., *Makromol.Chem.Rapid Commun.*, 1993, **14**, 523.
17. Lee, C.J., Park S.K., Kim, S.Y., Lee, Y.J., Min, B.G., Son, T.W., Kim, B.C., *Polym.Intern.*, 1995, **36**, 203.
18. Bottino, F.A., Di Pasquale, G., Pollicino, A., *Eur.Polym.J.*, 1995, **1**, 35.
19. Bottino, F.A., Di Pasquale, G., Leonardi, N., Pollicino, A., *J.Polym.Sci.Polym.Chem.Ed.*, 1995, **33**, 843.
20. Markova, G., Vasnev, V., Mamo, A. Recca, A., *Polymer*, 1994, **9**, 2007.
21. Yamazaki, N., Matsumoto, M., Higashi, F., *J.Polym.Sci.Polym.Chem.Ed.*, 1975, **13**, 1373.
22. Higashi, F., Ogata, S., Aoki, Y., *J.Polym.Sci.Polym.Chem.Ed.*, 1982, **20**, 2081.
23. Utermohlen, W.P., *J.Org.Chem.*, 1943, **8**, 544.
24. Bowen, D.M., Belfit, R.W.Jr., Walser, R.A., *J.Am.Chem.Soc.*, 1953, **5**, 4307.
25. Yang, P. and Chen, W.T., *J.Polym.Sci.Polym.Chem.*, 1993, **31**, 1571.27.
26. Morgan, P.W., *Macromolecules*, 1977, **10**, 1381.
27. Bair, T.I., Morgan, P.W., Killian, F.L., *Macromolecules*, 1977, **10**, 1396.

28. Chatfield, D.A., Einhorn, I.N., Mickelson, R.W., Futrell, J.H., *J.Polym.Sci.Polym.Chem.Ed.*, 1979, **17**, 1353.
29. Chaudhuri, A.K., Min, B.Y., Pearce, E.M., *J.Polym.Sci.,Polym.Chem.Ed.*, 1980, **18**, 2949.
30. Ridway, J.S., *J.Polym.Sci.*, 1970, **8**, 3089.
31. Bottino, F.A., Di Pasquale, G., Leonardi, N., Pollicino, A., *Polymer*, in press.
32. Carlier, V., Devaux, J., Legras, R., McGrail, P.T., *Macromolecules*, 1992, **25**, 6646.
33. Bottino, F.A., Di Pasquale, G. Pollicino, A., *unpublished results*.

Table 1. Elemental Analysis and i.r. data for polymers 4a-e

Polymer	Formula	Elemental Analysis (%) ^a				Infrared Spectra (cm ⁻¹)		
		C	H	N	S	NH	CO	C-N
4a	(C ₂₇ H ₁₈ N ₄ O ₂) _n (430.45) _n	74.80 (75.33)	4.35 (4.21)	12.92 (13.01)		3325	1681	1401
4b	(C ₃₃ H ₂₂ N ₄ O ₃) _n (522.56) _n	75.25 (75.85)	4.28 (4.24)	10.58 (10.72)		3331	1679	1401
4c	(C ₃₄ H ₂₄ N ₄ O ₂) _n (520.59) _n	78.15 (78.44)	4.71 (4.65)	10.63 (10.76)		3334	1684	1402
4d	(C ₃₃ H ₂₂ N ₄ SO ₄) _n (570.62) _n	68.54 (69.46)	3.91 (3.89)	9.71 (9.82)	5.56 (5.62)	3328	1694	1401
4e	(C ₃₁ H ₂₀ N ₄ O ₂) _n (480.52) _n	76.69 (77.49)	4.37 (4.20)	11.56 (11.66)		3339	1690	1427

^a Calculated values are reported in parentheses.

Table 2. Solution Viscosities, Thermal Characterisation and Solubility ^a of Polymers 4a-e

Polymer	η_{inh}^b	$T_d^c(^{\circ}C)$	$T_d^d(^{\circ}C)$	$T_g(^{\circ}C)^e$	$T_m(^{\circ}C)$	C_y^f	NMP ^g	DMAc ^g
4a	0.6 4	447	447	294	412	51	-	-
4b	0.8 5	448	451	259 ^h	326	52	+	±
4c	0. 20	437	449	184	320 337	46	+	±
4d	0.4 6	421	444	289	408	49	-	-
4e	0.3 5	437	440	293	430	53	-	-

^a Tested with 0.2 g of polymer in 2 ml of solvent.

^b Measured in concentrated sulphuric acid at 30°C (c = 0.5 g dl⁻¹).

^c Temperature of 10% weight loss determined in nitrogen atmosphere.

^d Temperature of 10% weight loss determined in static air.

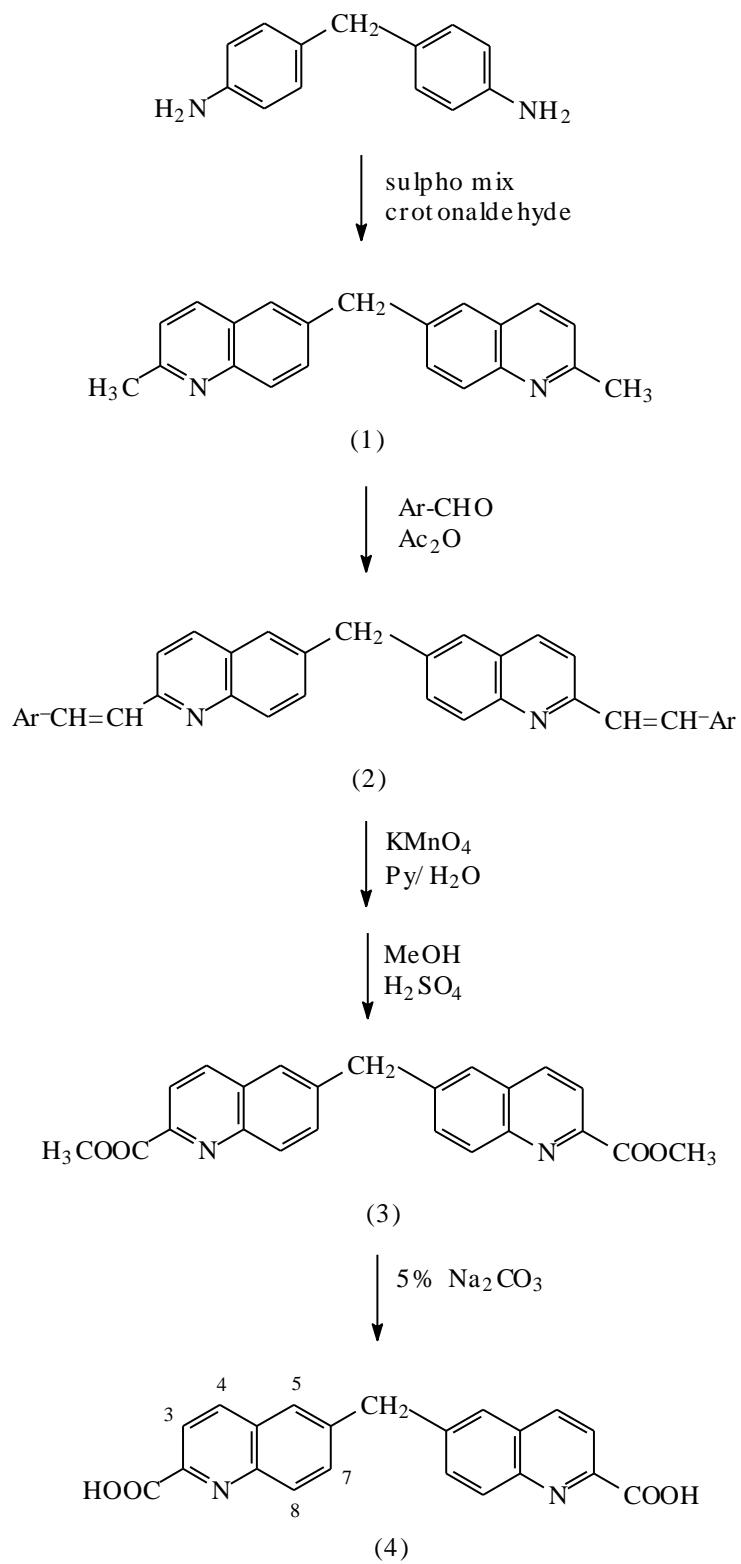
^e Determined in “as made” samples.

^f Char yield calculated as the percentage of solid residue after heating from room temperature to 700°C under nitrogen.

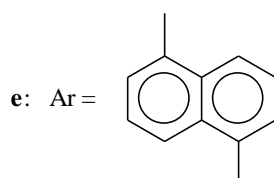
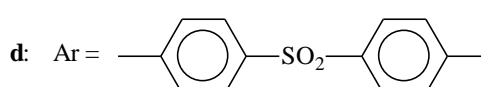
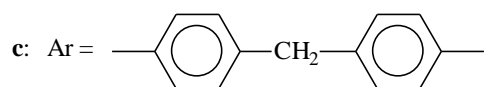
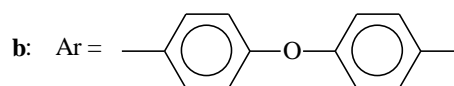
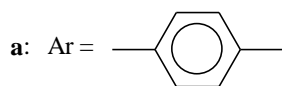
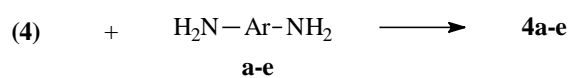
^g +, soluble on heating; ±, partially soluble on heating; -, insoluble.

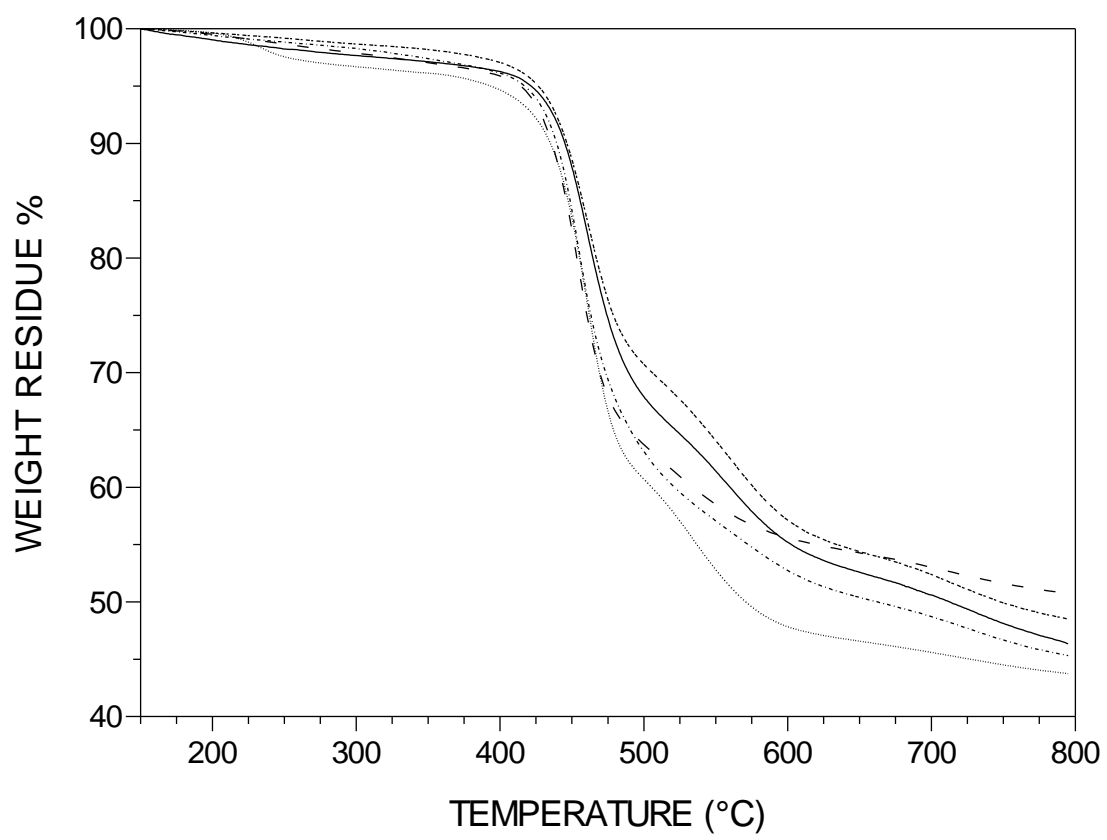
^h Determined after quenching.

SCHEME 1



SCHEME 2





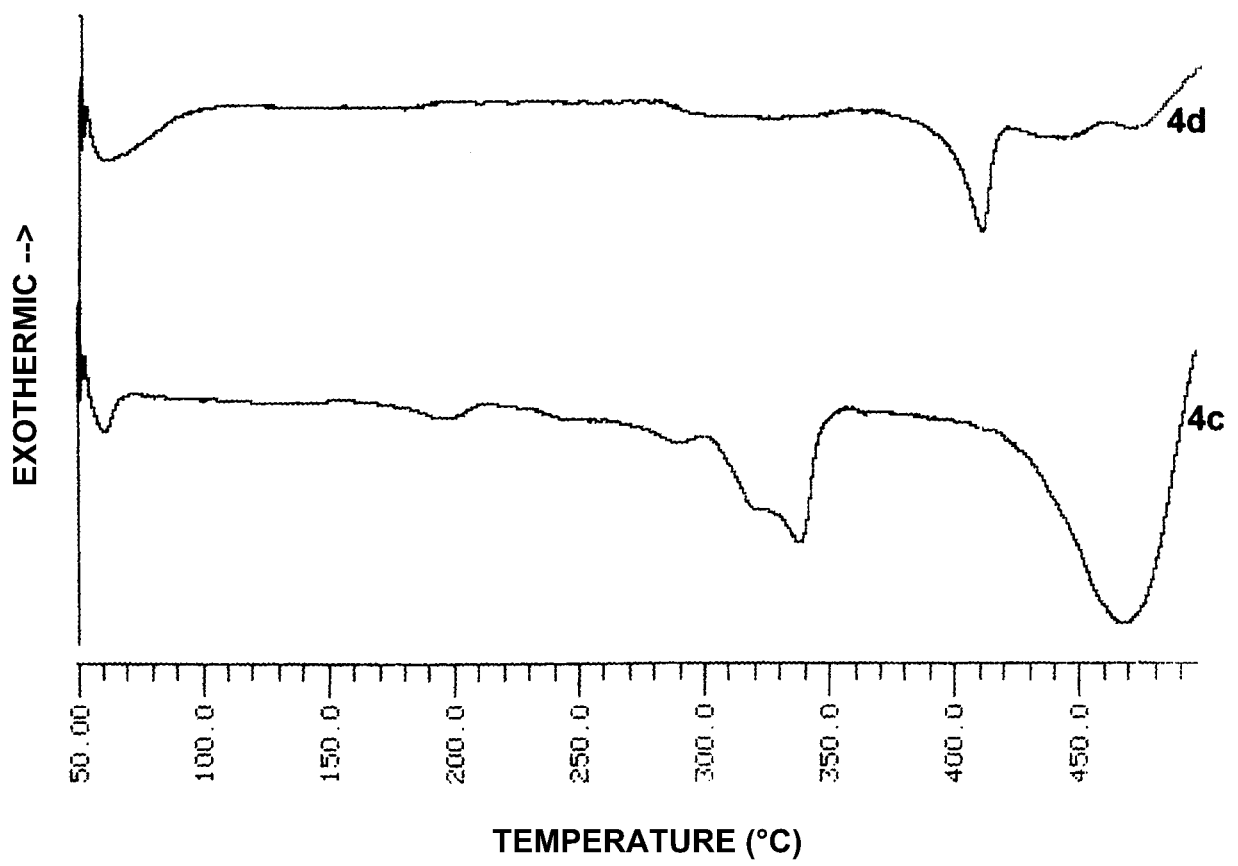


Figure Captions

Fig.1. t.g.a. curves in nitrogen of polymers **4a** (—), **4b** (---), **4c** (⋯), **4d** (- - -), **4e** (- -)

Fig.2. d.s.c. curves of polymers **4c** and **4d**.