

Wholly aromatic polymeric ketones from bis-(α -aminonitrile)s via soluble poly(bisaminonitrile)s

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Condensation of the dianion of the bisaminonitrile α, α' -dicyano- α, α' -bis(dimethylamino)-*m*-xylene (**8**) with bis[*p*-(*p*-fluorobenzoyl)phenyl] ether (**9**) and 2,6-dibromopyridine (**12**) yielded the corresponding new poly(bisaminonitrile)s poly{oxy-*p*-phenylenecarbonyl-*p*-phenylene-[α, α' -dicyano- α, α' -bis(dimethylamino)-*m*-xylyl]-*p*-phenylenecarbonyl-*p*-phenylene} (**10**) and poly[α, α' -dicyano- α, α' -bis(dimethylamino)-*m*-xylyl-2,6-pyridinediyl] (**13**), respectively. Acidic hydrolysis of the readily soluble poly(bisaminonitrile)s **10** and **13** deprotected the carbonyl groups and afforded the new polyketones poly(oxy-*p*-phenylenecarbonyl-*p*-phenylenecarbonyl-*m*-phenylenecarbonyl-*p*-phenylenecarbonyl-*p*-phenylene) (PEK⁴KKK, **11**) and poly(carbonyl-*m*-phenylenecarbonyl-2,6-pyridinediyl) (**14**), respectively. PEK⁴KKK **11** is insoluble in organic solvents, but polyketopyridine **14** is soluble in acidic aqueous media. © 1998 Elsevier Science Ltd. All rights reserved.

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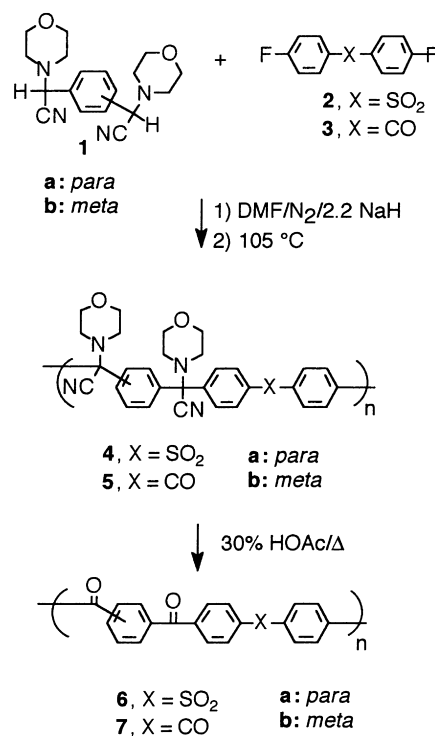
INTRODUCTION

While wholly aromatic polymeric ketones have properties which are desirable, their high degree of structural rigidity and concomitant crystallinity creates solubility problems; high molecular weights are difficult to attain¹. By using α -aminonitrile chemistry, we hoped to circumvent this obstacle by creating precursor polymers which were soluble enough to remain in solution and attain high molecular weight, but which could also be easily modified chemically to produce the desired polymeric ketones.

The first application of α -aminonitrile chemistry to polyketone syntheses occurred in our laboratories in 1991 when Pandya *et al.*² synthesized novel phthaldehyde-based precursor poly(bis- α -aminonitrile)s **4**, which were soluble in solvents such as acetone and THF. Since the aminonitrile unit is analogous to a cyanohydrin moiety and is, in essence, a protected carbonyl group, acidic hydrolysis of the poly(bisaminonitrile)s **4** afforded the new poly(ketone ketone sulfone)s **6**, which exhibited good thermal stability. As expected, poly(ketone ketone sulfone)s **6** were insoluble in all common organic solvents. Although the molecular weight of poly{[α, α' -dicyano- α, α' -bis(*N*-morpholino)-*p*-xylyl]-*p*-phenylenesulfonyl-*p*-phenylene} (**4a**) was low ($M_n = 5$ kg/mol) due to a side reaction of α, α' -dicyano- α, α' -bis(*N*-morpholino)-*p*-xylene (**1a**), this problem was solved by using the *meta*-isomer α, α' -dicyano- α, α' -bis(*N*-morpholino)-*m*-xylene (**1b**) in the synthesis of poly{[α, α' -dicyano- α, α' -bis(*N*-morpholino)-*m*-xylyl]-*p*-phenylenesulfonyl-*p*-phenylene} (**4b**), which was obtained in high molecular weight ($M_n = 32$ kg/mol) and was quantitatively converted to the corresponding all-aromatic poly(*m*-phenylenecarbonyl-*p*-phenylenesulfonyl-*p*-phenylenecarbonyl) (**6b**). In addition, later we demonstrated that this synthetic sequence worked extremely well with

4,4'-difluorobenzophenone (**3**) as the electrophilic partner to produce the poly{[α, α' -dicyano- α, α' -bis(*N*-morpholino)-*m*-xylyl]-*p*-phenylenecarbonyl-*p*-phenylene} (**5b**) with molecular weight (M_n) approaching 40 kg/mol; this polymer was also quantitatively converted to the all-aromatic poly(*m*-phenylenecarbonyl-*p*-phenylenecarbonyl-*p*-phenylenecarbonyl) (**7b**)³. Note that **6** and **7** do not possess ether linkages.

The high molecular weights obtained in the above syntheses demonstrated the exceptional selectivity and reactivity of the



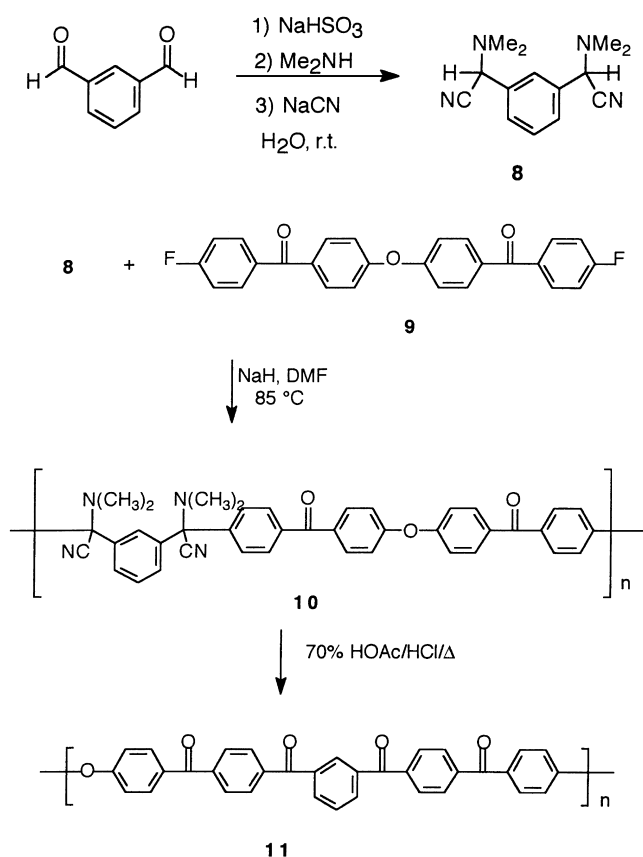
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α -aminonitrile anions, already shown previously in model studies with low molar mass compounds by Albright⁴. We wished to extend this protocol in order to obtain polyketones containing other aromatic moieties.

RESULTS AND DISCUSSION

A wholly aromatic poly(ether ketone ketone ketone ketone)

To demonstrate the versatility of this polymerization process we targeted a polyketone that contained an ether linkage. α, α' -Dicyano- α, α' -bis(dimethylamino)-*m*-xylene (**8**) was chosen as the nucleophilic monomer in this study; it was made in 93% yield from dimethylamine and isophthalaldehyde in a Strecker reaction⁵. **8** is more easily purified than **1b** and has a simpler ¹H n.m.r. spectrum. Condensation of the dianion of **8** with bis[*p*-(*p*-fluorobenzoyl)phenyl] ether (**9**)⁶ was carried out at 85°C in DMF; the higher than normal (25°C) temperature was used because of the limited solubility of **9**.



Purification of the resultant poly{oxy-*p*-phenylenecarbonyl-*p*-phenylene- $[\alpha, \alpha'$ -dicyano- α, α' -bis(dimethylamino)-*m*-xylyl]-*p*-phenylenecarbonyl-*p*-phenylene} (**10**) was achieved by repeated reprecipitations from THF into water and finally methanol. This polymer, because of its atactic nature (two stereocentres per repeat unit) and polar substituents, was quite soluble in such common solvents as acetone and chloroform. D.s.c. analysis indicated that poly{oxy-*p*-phenylenecarbonyl-*p*-phenylene- $[\alpha, \alpha'$ -dicyano- α, α' -bis(dimethylamino)-*m*-xylyl]-*p*-phenylenecarbonyl-*p*-phenylene} (PEKAAK, **10**) was amorphous, with a T_g of 146°C. The proton n.m.r. spectrum revealed an intense dimethylamino singlet at 2.23 ppm as well as several broad resonances in the aromatic region of the spectrum. 2DCOSY n.m.r. spectroscopy was utilized to deduce the coupling pattern of the aromatic

protons in this macromolecule (Figure 1). The i.r. spectrum showed a relatively strong carbonyl absorbance at 1680 cm⁻¹, but the nitrile stretch was too weak to be observed.

G.p.c. analysis of the purified poly{oxy-*p*-phenylenecarbonyl-*p*-phenylene- $[\alpha, \alpha'$ -dicyano- α, α' -bis(dimethylamino)-*m*-xylyl]-*p*-phenylenecarbonyl-*p*-phenylene} (**10**) in chloroform indicated $M_n = 7.4$ and $M_w = 10.7$ kg/mol (polystyrene equivalents), with a polydispersity of 1.43. The relatively low molecular weight is primarily attributed to the fact that difluoro monomer **9** was very insoluble in most solvents, including the reaction solvent, DMF, and difficult to purify as a result*†.

Poly{oxy-*p*-phenylenecarbonyl-*p*-phenylene- $[\alpha, \alpha'$ -dicyano- α, α' -bis(dimethylamino)-*m*-xylyl]-*p*-phenylenecarbonyl-*p*-phenylene} (PEKAAK, **10**) was hydrolysed to poly(oxy-*p*-phenylenecarbonyl-*p*-phenylene-*m*-phenylenecarbonyl-*p*-phenylene-*m*-phenylenecarbonyl-*p*-phenylene) (PEKAAA, **11**) using 70% aqueous acetic acid and a small amount of hydrochloric acid at 90°C. Novel PEKAAA **11** was insoluble in all organic solvents, but was soluble in concentrated sulfuric acid. The 2DCOSY n.m.r. spectrum in D₂SO₄ (Figure 2) very clearly shows the coupling patterns of the aromatic protons in the polymer. The i.r. spectrum revealed no aliphatic C–H stretching and no nitrile stretch, showing that hydrolysis was complete; the carbonyl peak at 1660 cm⁻¹ was broader and an ether stretch was present at 1240 cm⁻¹.

The precursor poly{oxy-*p*-phenylenecarbonyl-*p*-phenylene- $[\alpha, \alpha'$ -dicyano- α, α' -bis(dimethylamino)-*m*-xylyl]-*p*-phenylenecarbonyl-*p*-phenylene} (PEKAAK, **10**) exhibited two stages of weight loss upon heating (Figure 3A); this was most likely due to initial loss of the labile aminonitrile moiety. This polymer lost 5% of its weight at 313°C under a nitrogen atmosphere. As expected, PEKAAA **11** was thermally much more robust, with a 5% weight loss at 492°C (Figure 3A). The d.s.c. thermogram of PEKAAA **11** (Figure 3B) showed a broad glass transition at 185°C and a T_m at 343°C, indicative of a semicrystalline polymeric backbone. Only a T_g at 176°C was seen in the second heating.

A wholly aromatic polyketone without an ether linkage: a poly(ketopyridine)

With α -aminonitrile chemistry, one can incorporate carbonyl groups without the need of ether linkages in the aromatic backbone, as required in classical nucleophilic approaches and most Friedel–Crafts methods¹. We realized that many aromatic dihalides suitable for such polycondensations were available commercially; like difluorobenzophenone (**3**) and bis(*p*-fluorophenyl) sulfone (**9**), 2,6-dibromopyridine (**12**) is also suitably activated

* In other polymerizations with **1b** and **8** we (H. W. Gibson, J. Yang) have observed by g.p.c. the formation of significant amounts of what are believed to be cyclic dimers whose formation would be relatively facile due to the *m*-linkage in the bisaminonitriles; these cyclics are removed by repeated reprecipitations as we have done here³. However, in the present cases we did not examine the g.p.c. traces of the crude polyaminonitriles.

† We have evidence that the anions of **1b** and **8** are capable of attack on the ether linkage, displacing a phenoxide ion, particularly at higher temperatures and when the ether linkage is activated by a carbonyl group at the *para* position as is the case here (J. Yang and H. W. Gibson, in preparation).

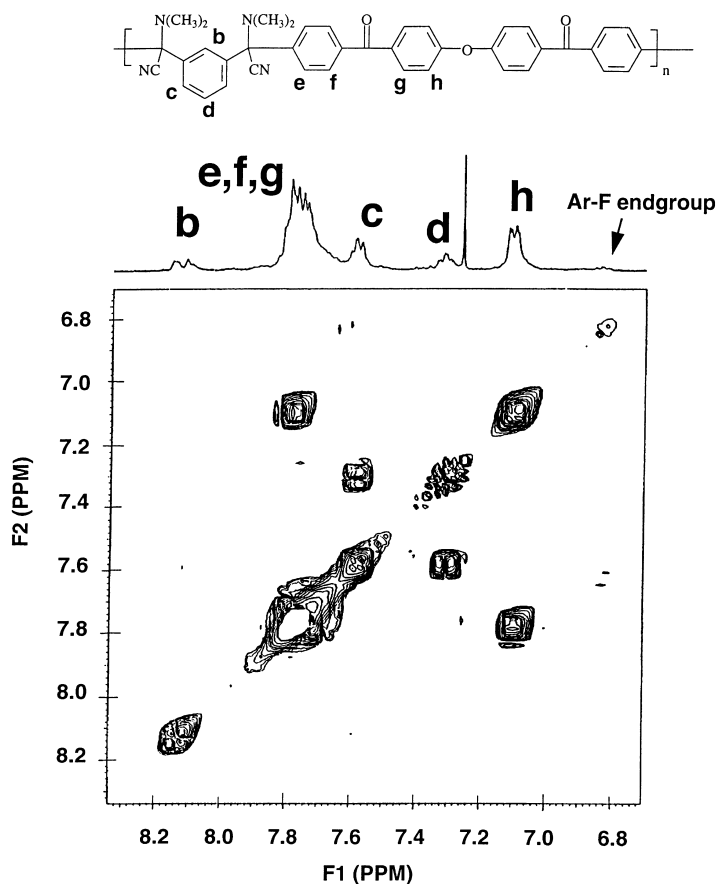


Figure 1 2D COSY n.m.r. spectrum (400 MHz) of poly{oxy-*p*-phenylenecarbonyl-*p*-phenylene- $[\alpha, \alpha'$ -dicyano- α, α' -bis(dimethylamino)-*m*-xylyl]-*p*-phenylenecarbonyl-*p*-phenylene} (**10**) in CDCl_3

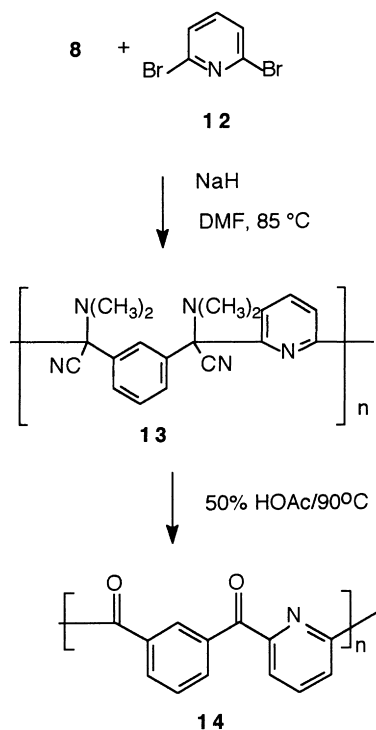
for nucleophilic attack. α, α' -Dicyano- α, α' -bis(dimethylamino)-*m*-xylene (**8**) was reacted with sodium hydride and 2,6-dibromopyridine (**12**) in DMF at 85°C.

G.p.c. analysis of the resultant purified poly[α, α' -dicyano- α, α' -bis(dimethylamino)-*m*-xylyl-2,6-pyridinediyl] (**13**) in chloroform gave a very symmetrical peak corresponding to $M_n = 13$, $M_w = 21.9$, and $M_{z+1} = 50$ kg/mol (PS equivalents), with a polydispersity of 1.68 (see Footnote 1). Poly[α, α' -dicyano- α, α' -bis(dimethylamino)-*m*-xylyl-2,6-pyridinediyl] (**13**) had a T_g of 94°C as determined by d.s.c. and lost 5% of its weight at 206°C (t.g.a.).

Hydrolysis of poly[α, α' -dicyano- α, α' -bis(dimethylamino)-*m*-xylyl-2,6-pyridinediyl] (**13**) with 50% aqueous acetic acid at 90°C afforded the light yellow poly(carbonyl-*m*-phenylenecarbonyl-2,6-pyridinediyl) (**14**) which was soluble in aqueous media at pH values below 6.0, presumably due to protonation of the pyridyl unit. D.s.c. analysis showed that the polymer was semicrystalline, with a T_g of 129°C and a T_m at 170°C. T.g.a. analysis revealed that poly(carbonyl-*m*-phenylenecarbonyl-2,6-pyridinediyl) (**14**) was not very stable thermally, with a 5% weight loss at 242°C (N_2), possibly due to residual protonation of the pyridyl groups after workup and/or water sorption.

EXPERIMENTAL

Melting points were taken on a Mel-Temp II melting point apparatus and are uncorrected. ^1H n.m.r. spectra, recorded in ppm, were obtained using Varian Unity 400 MHz and Bruker WP-270 MHz spectrometers with Me_4Si (TMS) as an internal standard in CDCl_3 , unless otherwise noted. The



following abbreviations are used to denote multiplicities: s (singlet), d (doublet), m (multiplet). I.r. spectra, reported in cm^{-1} , were recorded on Perkin-Elmer and Nicolet Impact 400 infrared spectrometers using pulverized KBr as the medium. Elemental analyses were obtained from Atlantic Microlab (Norcross, GA). Differential scanning calorimetry

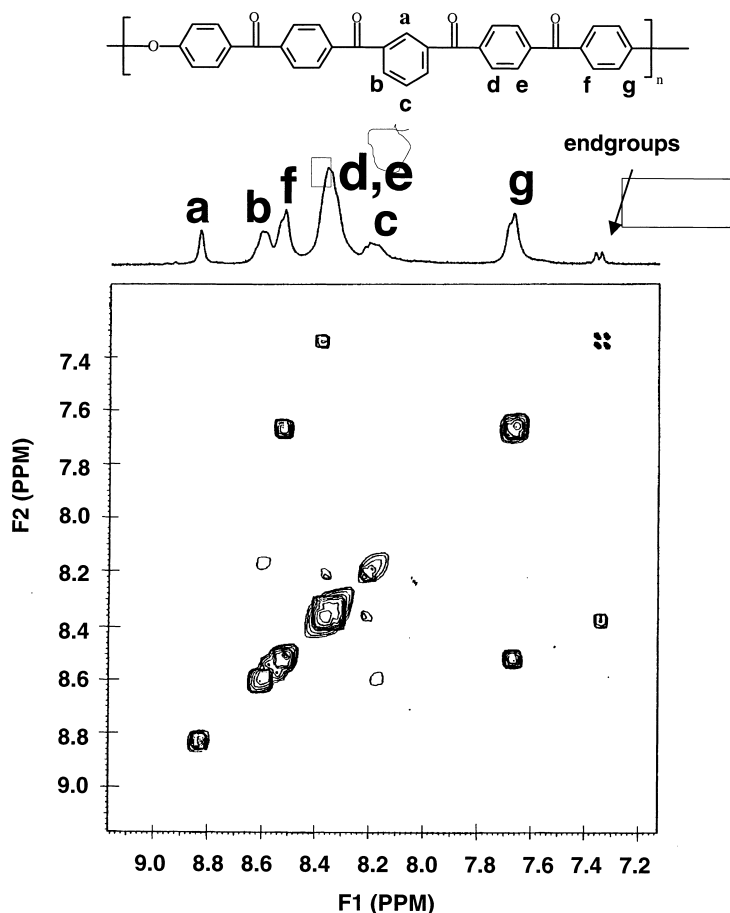


Figure 2 2D COSY n.m.r. spectrum (400 MHz) of poly(oxy-*p*-phenylenecarbonyl-*p*-phenylenecarbonyl-*m*-phenylene-carbonyl-*p*-phenylenecarbonyl-*p*-phenylene) (PEK KKK, **11**) in D₂SO₄

(d.s.c.) was performed on a Perkin-Elmer Series-7 calorimeter under a dry N₂ purge using indium and lead as the calibration standards. Thermogravimetric analysis (t.g.a.) was performed on a Perkin-Elmer TGA-7 analyser under dry N₂ purge. Gel permeation chromatography (g.p.c.) was performed using a Waters model 590 pump, 600E pump controller, WISP 710B autosampler, and Viscotek laser refractometer. A Waters Ultrastayragel column (10 Å pore size) with a flow rate of 1.0 ml/min was used in the analyses. Starting materials were purchased from Aldrich and used as received.

α,α'-Dicyano-*α,α'*-bis(dimethylamino)-*m*-xylene (**8**)

To a 500 ml three-necked round-bottomed flask fitted with a mechanical stirrer and N₂ inlet were added isophthalaldehyde (20.2 g, 150 mmol), NaHSO₃ (31.2 g, 300 mmol), and distilled H₂O (300 ml). When this stirred mixture became homogeneous (2 h), Me₂NH (13.5 g, 300 mmol, in a 40 wt.% solution in H₂O) was added slowly via syringe. The initial white milkiness disappeared within about 10 min, at which time NaCN (14.7 g, 300 mmol) in H₂O (10 ml) was added slowly via a dropping funnel. A thick viscous precipitate appeared immediately, which slowly hardened into a spherical object. Vigorous mechanical stirring gradually dispersed this solid as a white powder after 3 days, at which time it was filtered and dried in a vacuum oven (33.7 g, 93%). Recrystallization from hexanes 3 × afforded pure **8** as colourless needles, mp 143–144°C (28.7 g, 79%). ¹H n.m.r. δ: 7.65 (s, 1 H, Ar-H), 7.53 (dd, *J* = 5 Hz, 2 H), 7.45 (m, 1 H, ArH), 4.87 (s, 2 H, CHCN), 2.37 (s, 12 H, CH₃). I.r. *ν*: 3110–2790 (vs, C-H),

2235 (m, C≡N), 1495 (s, C-N). Elem. anal. calcd. (found) for C₁₄H₁₈N₄: C, 69.39 (69.42); H, 7.48 (7.46); N, 23.12 (23.10).

Poly{oxy-p-phenylenecarbonyl-p-phenylene-[α,α'-dicyano-α,α'-bis(dimethylamino)-m-xylyl]-p-phenylenecarbonyl-p-phenylene} (**10**)

To a 100 ml round-bottomed flask fitted with a reflux condenser and stirring bar were added **8** (2.000 g, 8.26 mmol), **9** (3.419 g, 8.26 mmol) and dry DMF (50 ml). To this heterogeneous mixture was added NaH (0.700 g, 16.7 mmol, 60% dispersion in mineral oil) and the mixture immediately turned green and began to evolve H₂. The suspension was heated to 85°C, at which time **9** slowly dissolved. After stirring at 85°C for 2 days, the homogeneous dark brown solution was cooled and poured into H₂O, giving a grainy precipitate immediately. Filtration and drying under vacuum gave 4.57 g (99%) of a granular polymer, which was redissolved in THF and precipitated twice into H₂O, hot hexanes, and finally MeOH to afford a white powder (4.11 g, 89%). ¹H n.m.r. (Figure 1) δ: 8.2–6.8 (m, 20 H, Ar-H), 2.23 (s, 12 H, CH₃). i.r. *ν*: 3000–2795 (s, aliphatic C-H), 1660 (vs, C=O), 1245 (vs, Ar-O-Ar). G.p.c. (CHCl₃, PS equivalents, kg/mol) *M*_n = 7.4, *M*_w = 10.7, *M*_z + 1 = 20.1, *M*_w/*M*_n = 1.43.

Poly[α,α'-dicyano-α,α'-bis(dimethylamino)-m-xylyl-2,6-pyridinediyl] (**13**)

The reaction was carried out essentially as above at 85°C for 24 h. The product was precipitated from MeOH into H₂O and from THF into hexanes. Yield: 85%. ¹H n.m.r. δ:

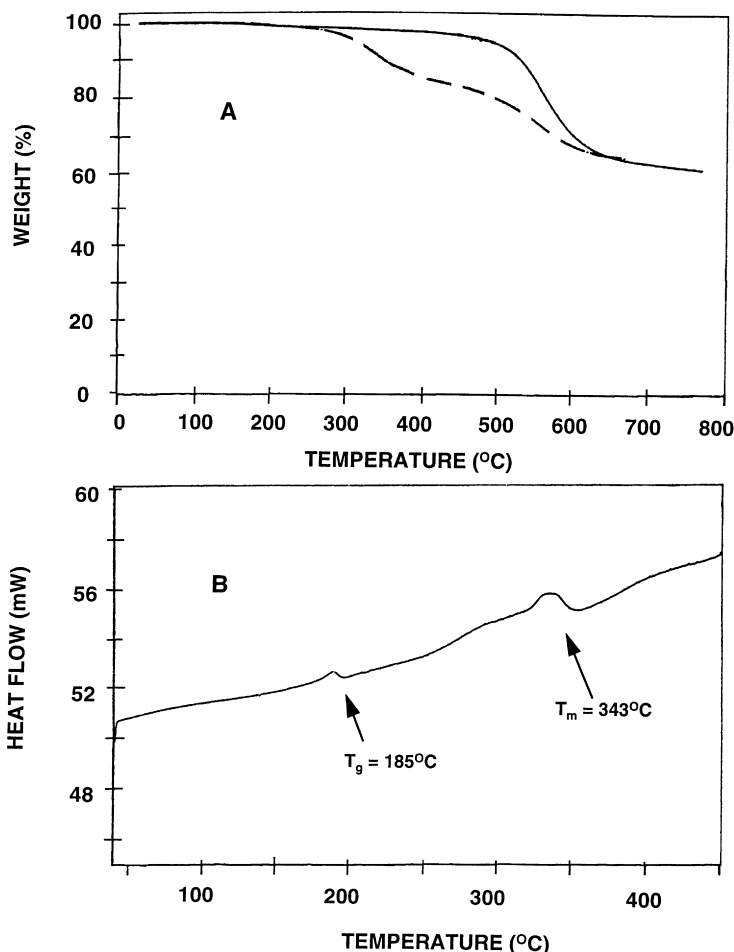


Figure 3 (A) Thermogravimetric analyses of poly{oxy-*p*-phenylenecarbonyl-*p*-phenylene-[α,α' -dicyano- α,α' -bis(dimethylamino)-*m*-xylyl]-*p*-phenylene-carbonyl-*p*-phenylene} (**10**) (dashed line) and poly(oxy-*p*-phenylenecarbonyl-*p*-phenylenecarbonyl-*m*-phenylene-carbonyl-*p*-phenylenecarbonyl-*p*-phenylene) (PEK KKKK, **11**): (solid line); (B) d.s.c. trace (first heating) for poly(oxy-*p*-phenylenecarbonyl-*p*-phenylenecarbonyl-*m*-phenylene-carbonyl-*p*-phenylenecarbonyl-*p*-phenylene) (PEK KKKK, **11**) at 10°C/min

7.78–7.20 (m, 7 H, Ar–H), 4.83 (s, CHCN endgroup), 2.23 (s, 12 H, CH₃). I.r. ν : 3000–2780 (m, aliphatic C–H), 2210, 2190 (vw, CN). G.p.c. (CHCl₃, PS equivalents, kg/mol) $M_n = 13$, $M_w = 21.9$, $M_z + 1 = 50$, $M_w/M_n = 1.68$.

*Poly(carbonyl-*m*-phenylenecarbonyl-2,6-pyridinediyl)* (**14**)

To a 100 ml round-bottomed flask fitted with a reflux condenser and stirring bar were added 0.5 g of **13** and 50% aq. HOAc (~25 ml). The solution was then heated at reflux for 24 h. After cooling, basification with 2 N NaOH was required to precipitate **14**, which was filtered and washed several times with distilled H₂O. Drying under vacuum afforded the polyketone. ¹H n.m.r. (DMSO-*d*₆) δ : 8.58 (s, Ar–H), 8.25 (d, $J = 7.2$ Hz, 2 H, Ar–H), 8.05 (m, 4 H, Ar–H), 7.94 (d, $J = 7.2$ Hz, 2 H, Ar–H), 7.75 (t, $J = 7.6$ Hz, 1 H, Ar–H). I.r. ν : 1655 (vs, C=O).

*Poly(oxy-*p*-phenylenecarbonyl-*p*-phenylenecarbonyl-*m*-phenylene-carbonyl-*p*-phenylenecarbonyl-*p*-phenylene)* (PEK KKKK, **11**)

The procedure above was followed using 25 ml 70% aq. HOAc along with 5 ml of conc. HCl. ¹H n.m.r. (D₂SO₄,

Figure 2) δ : 8.82 (br s, 1 H), 8.63–8.12 (br m, 15 H), 7.63 (br d, 4 H). I.r. ν : 3150–3000 (m, aryl C–H), 1660 (vvs, C=O), 1245 (vvs, C–O–C).

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