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Synthesis of aromatic polyamides containing anthracene units via a precursor polymer approach

Michael A. Rabjohns and Philip Hodge*
Department of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK

and Peter A. Lovell
Manchester Materials Science Centre, University of Manchester and UMIST, Grosvenor Street, Manchester M1 7HS, UK
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The Diels–Alder and retro-Diels–Alder chemistry of anthracene were used to synthesize aromatic polyamides analogous to poly(*p*-phenylene terephthalamide) (PPTA) via soluble precursor polymers. Novel monomers, which are formally Diels–Alder adducts of diaminoanthracenes with maleic- and fumaric-type dienophiles, have been synthesized. Two routes for their preparation were employed: firstly, reduction of 2,6-diaminoanthraquinone to 2,6-diaminoanthracene followed by Diels–Alder reaction and, secondly, nitration of Diels–Alder adducts of anthracene followed by reduction of the nitro groups. These monomers were used to prepare precursor polymers using low temperature solution polycondensation with terephthaloyl chloride and activated polycondensation with terephthalic acid. Copolymers were also prepared with structures closer to PPTA. The precursor polymers were converted into anthracene-containing aromatic polyamides by thermal retro-Diels–Alder reactions at temperatures of about 220°C. Confirmation that the retro-Diels–Alder reaction had taken place was provided by t.g., i.r. and solid-state ^{13}C n.m.r. spectroscopy. © 1997 Elsevier Science Ltd.

(Keywords: aromatic polyamides; precursor polymers; Diels–Alder)

INTRODUCTION

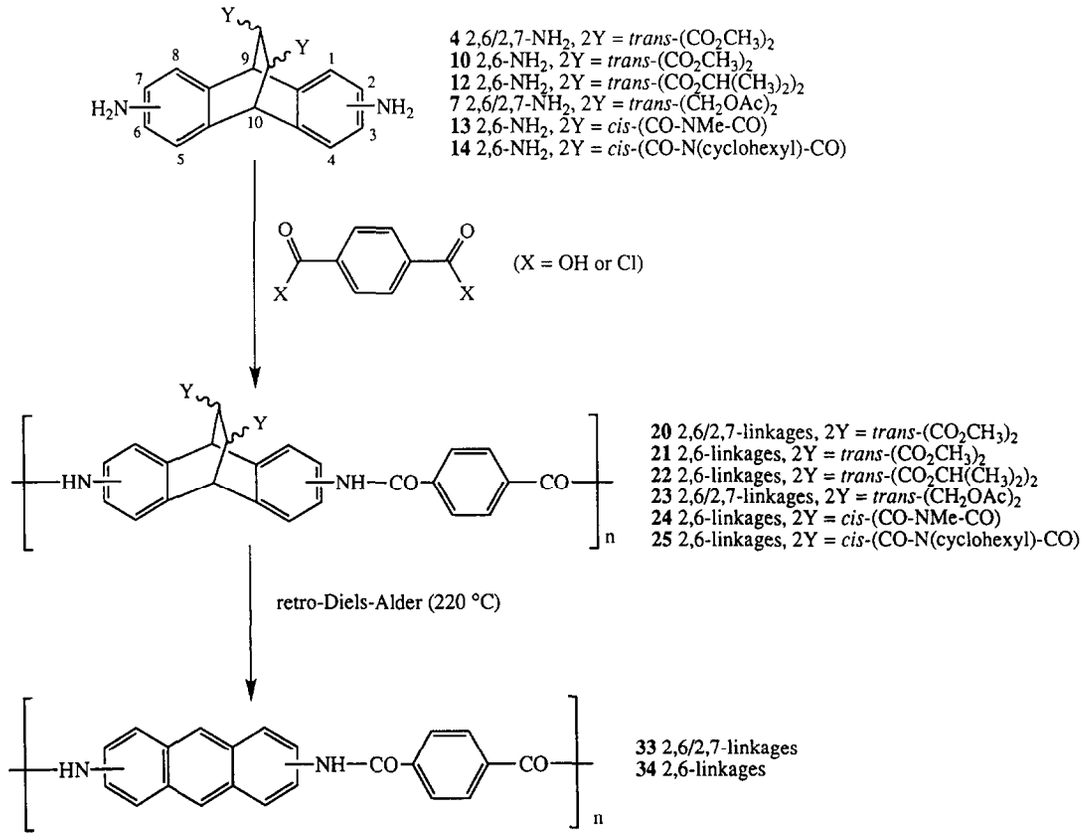
Many high performance polymers are all-aromatic polymers linked by simple units such as amide or ester groups. Such polymers tend to have very high melting points and glass transition temperatures and to be crystalline and insoluble. This causes serious problems with their synthesis and processing. Accordingly, there have been many attempts to prepare such polymers via soluble precursor polymers. The precursor polymer approach involves the preparation of a polymer that is soluble and processable and which can subsequently be converted readily into the required aromatic polymer by a simple chemical reaction. This treatment can take place after the precursor polymer has been made into, for example, a film or a fibre. The precursor method has been applied successfully to several different types of high performance polymer, for example poly(*p*-phenylene)[1], poly(*p*-phenylene vinylene)[2,3] and polyimides[4,5].

Our goal in this project was to prepare aromatic polyamides by a precursor route. The chosen monomers were Diels–Alder adducts of diaminoanthracenes. Once these monomers had been incorporated into polyamide structures, retro-Diels–Alder reactions could be carried out to produce the all-aromatic anthracene-containing polyamides. The approach is shown in *Scheme 1*. There were several reasons for choosing this particular Diels–Alder/retro-Diels–Alder system: (a) if anthracene adducts functionalized in particular positions (2,6-) are used then the eventual aromatic polyamide will contain near-linear anthracene units and thus potentially retain many of the desirable properties that PPTA has due to its extended rod-like structure, (b) anthracene is a reactive diene, readily undergoing Diels–Alder reactions with a wide range of dienophiles[6,7], (c) the Diels–Alder reactions of anthracenes are relatively unaffected by substituents on the peripheral rings[8–10], and (d) the retro-Diels–Alder reactions of anthracene adducts generally take place at temperatures above 200°C[11,12], thus enabling processing of the precursor polymers below this temperature ceiling.

The present work is seen as a first step towards the synthesis of polyamides containing anthraquinone units. Such units are thermally stable and it has been shown recently that the 2,6-anthraquinonediyl moiety is mesogenic[13]. The anthraquinone-containing polymers could be synthesized via precursor polymers in a similar manner to the synthesis of anthracene-containing polyamides described in this paper.

Precursor polymer approaches similar to that described here have already been used to synthesize polyesters, containing anthracene units[14] and poly(acetylene-*co*-phenylene)s[15]. There has also been some previous work relevant to that described here, using ethylene adducts of

* To whom correspondence should be addressed



Scheme 1 Precursor polymer route to anthracene-containing aromatic polyamides

diaminoanthracenes to prepare anthracene-containing polyamides by a precursor route[16]. However, the synthetic strategy described in this paper has distinct advantages over this previous work. Firstly, the use of exclusively 2,6-substituted adducts (compared to 2,6-/2,7-mixtures) has potential advantages in the linearity and crystallinity of the final polymers produced. Secondly, the use of dienophiles other than ethylene makes the monomer synthesis more straightforward and versatile (ethylene is a relatively unreactive dienophile) and has the potential to induce greater solubility in the precursor polymers. Additionally, the temperatures required for cycloreversion of the adducts may be varied by choice of dienophile. In this way the stable temperature range of the precursor polymers may be controlled, enabling the use of various methods of processing.

In this paper we describe the synthesis of Diels–Alder adducts of β,β'-diaminoanthracenes with various dienophiles by two separate routes. We then discuss the polymerization of these diamine monomers to produce soluble precursor polyamides, comparing the results of different methods of polymerization. Finally, we describe the production of anthracene-containing aromatic polyamides by thermal retro-Diels–Alder reactions of the precursor polymers and the confirmation of this process by several methods of analysis.

EXPERIMENTAL

General

Methods of characterization and analysis were as previously described[14] with the addition of the following. In descriptions of ^{1}H n.m.r. spectra all J values are quoted in Hz. Solid state ^{13}C n.m.r. spectra were recorded using a Varian Unity 300 spectrometer equipped with a Doty Scientific Industries CP/MAS probe; spectra were run with a contact time of 2 s and a recycle time of 5 s, using spinning speeds of 4–5 kHz. H.p.l.c. analysis was carried out on solutions (10 mg ml^{-1}) in methanol and the eluent used was a 40/60 mixture of methanol and water (containing 0.5% ammonium acetate); the equipment was a Waters 'Z'-Module with a Novaflak ODS (4 μm) 10 cm × 8 mm ID column and detection was by u.v. at a wavelength of 254 nm. FAB mass spectrometry was carried out using a Kratos Concept spectrometer (with bombardment by xenon atoms and a *m*-nitrobenzyl alcohol matrix). EI mass spectrometry was carried out using a Kratos MS25 spectrometer. Dilute solution viscosity measurements were obtained using Ubbelohde-type viscometers and a water bath thermostatistically controlled to ±0.1°C. Gel permeation chromatography (g.p.c.) measurements were carried out using 0.2% (w/v) solutions in dimethylacetamide (DMAc) at 70°C and 4 μm Styragel columns (10^6, 10^4, 10^3, 500 Å) with DMAc as the eluent; polystyrene standards provided the molecular weight calibration. Wide-angle X-ray scattering was carried out at the Manchester Materials Science Centre, using compacted powder samples. The experiments were conducted using a PW1710 diffractometer and a Cu LFF X-ray tube (40 kV, 30 mA), operating at wavelengths of 1.54060 and 1.54438 Å, over a range of angles (2θ) from 5–90°. Data analysis was performed using PC-APD Diffraction Software.

All solvents used were dried using standard procedures[17], except where stated otherwise below.

Maleic anhydride was recrystallized from chloroform immediately before use. In general, all other reagents from commercial sources were used as received. Exceptions are noted in the individual experimental procedures. All solid products were dried at 50°C *in vacuo* at approximately 10 mmHg for a minimum of 24 h.

For polymerization: p-phenylenediamine and terephthalic acid were used as received (both from Fluka, > 99%). Terephthaloyl chloride was sublimed and stored *in vacuo*. *N*-Methylpyrrolidone (NMP) was fractionally distilled under reduced pressure and then stored over 4A molecular sieves under nitrogen. Pyridine was kept over potassium hydroxide pellets, then stirred for 24 h over calcium hydride, distilled under nitrogen and stored over 4A molecular sieves under nitrogen. Triphenyl phosphite was purified according to a standard procedure[18]. Lithium chloride and calcium chloride were dried *in vacuo* for 24 h at 200°C and stored in a desiccator.

The following compounds were prepared using literature procedures and had satisfactory melting points and ^{1}H n.m.r. spectra: anthracene/dimethyl fumarate adduct[19] (**1**) and anthracene/1,4-dihydroxy-*trans*-2-butene adduct[20] (**2**).

Monomer synthesis

Dimethyl 9,10-dihydro-2,6(7)-dinitro-9,10-ethanoanthracene-11,12-trans-*dicarboxylate (3)*. Adduct **1** (3.22 g, 10 mmol), ammonium nitrate (1.60 g, 20 mmol) and trifluoroacetic anhydride (10 ml, 70 mmol) were placed in a flask equipped with a condenser and a $CaCl_2$ drying tube. Chloroform (10 ml) was added and the mixture was stirred at room temperature for 2 h, after which time it had become homogeneous. The mixture was then poured into water (60 ml) and extracted twice with chloroform. The combined chloroform extracts were washed with water, dried ($MgSO_4$) and evaporated to give 3.54 g (86% yield) of a yellow solid with m.p. = 102–146°C. ^{1}H n.m.r. ($CDCl_3$, 500 MHz): δ/ppm = 8.23 (*d*, J = 2.0, 0.5H), 8.22 (*d*, J = 2.0, 0.5H), 8.14 (*s*, 1H), 8.07 (*m*, 2H), 7.53 (*d*, J = 8.1, 0.5H), 7.52 (*d*, J = 8.1, 0.5H), 7.45 (*d*, J = 8.1, 0.5H), 7.44 (*d*, J = 8.1, 0.5H), 4.96 (*m*, 2H, bridge), 3.63 (*m*, 6H, $-OCH_3$), 3.42 (*m*, 2H, bridgehead). I.r.: $\bar{\nu}$/cm^{-1} = 2955 (*m*, C–H stretch), 1736 (*s*, C=O), 1523 and 1351 (*s*, NO_2 antisym. and sym. stretch). U.v. (95% ethanol): λ_{max}/nm = 273 (ε = 24 800). Analysis: C 58.6%, H 4.1%, N 6.7% (calc. for $C_{20}H_{26}N_2O_8$: C 58.3%, H 3.9%, N 6.8%).

Dimethyl 2,6(7)-diamino-9,10-dihydro-9,10-ethanoanthracene-11,12-trans-*dicarboxylate (4)*. A solution of adduct **3** (5.02 g, 12.2 mmol) in ethyl acetate (100 ml) was prepared and palladium (10% on carbon, 0.65 g) was added. The flask was attached to a standard hydrogenation apparatus operating at atmospheric pressure. After hydrogen take-up had ceased, the catalyst was removed by filtration through Celite and the filtrate evaporated to leave 4.23 g (99% yield) of a yellow solid with m.p. = 98–163°C. The product was purified by column chromatography [silica gel, chloroform/ethyl acetate (1 : 1)]. ^{1}H n.m.r. ($CDCl_3$, 500 MHz): δ/ppm = 7.02 (*d*, J = 7.8, 0.5H), 7.01 (*d*, J = 7.7, 0.5H), 6.94 (*d*, J = 7.8, 0.5H), 6.93 (*d*, J = 7.7, 0.5H), 6.66 (*d*, J = 2.2, 0.5H), 6.65 (*d*, J = 2.2, 0.5H), 6.59 (*d*, J = 2.2, 0.5H), 6.57 (*d*, J = 2.2, 0.5H), 6.36 (*m*, 2H), 4.49 (*m*, 2H, bridge), 3.63 (*s*, 6H, $-OCH_3$), 3.51 (*s*, *br*, 4H, $-NH_2$), 3.37 (*s*, 2H, bridgehead). ^{13}C n.m.r. ($CDCl_3$, 75 MHz): δ/ppm = 172.73, 172.67, 172.5, 144.3, 144.2, 144.1, 144.0, 143.6, 142.8, 141.8, 140.9, 132.9, 312.1, 131.0, 130.1, 124.7, 124.4, 123.9, 123.6, 112.3, 121.1, 111.8, 111.1, 110.9, 52.0, 48.5, 47.9, 47.6, 47.4, 47.2, 47.0, 46.6, 45.8, 45.6, 45.0. H.p.l.c.: peaks at 15.2 min (23%), 16.3 min (24%) and 21.2 min (53%). I.r.: $\bar{\nu}$/cm^{-1} = 3446, 3370 and 3231 (*m*, N–H stretch), 3012 and 2953 (*m*, C–H stretch), 1729 (*s*, C=O stretch), 1626 (arom. ring stretch), u.v. (95% ethanol): λ_{max}/nm = 288, 237 (ε = 4000, 11 600); (after addition of HCl) λ_{max}/nm = 271, 254 (ε = 2500, 2900). M.s. (FAB): m/z = 353 ($[M+H]^+$), 248, 208. Analysis: C 67.8%, H 6.1%, N 8.1% (calc. for $C_{20}H_{20}N_2O_4$: C 68.2%, H 5.7%, N 8.0%).

trans-*11,12-Bis(acetoxymethyl)-9,10-dihydro-9,10-ethanoanthracene (5)*. The diol adduct **2** (0.66 g, 2.5 mmol) was stirred with acetic anhydride (20 ml) and pyridine (5 ml) for 90 min. The mixture was then poured into ice-cold dilute sulfuric acid (200 ml) and stirred for a further 30 min. The product was extracted with ether (40 ml) and washed with saturated aqueous $NaHCO_3$ solution and then with water. The ether solution was dried ($MgSO_4$), filtered and concentrated, leaving a white solid. The yield was 0.85 g (95%) and the product was recrystallized from hexane. M.p. = 107–108°C (lit.[21] m.p. = 108–109°C). ^{1}H n.m.r. ($CDCl_3$, 200 MHz): δ/ppm = 7.18 (*m*, 4H, arom.), 7.02 (*m*, 4H, arom.), 4.17 (*d*, 2H, bridgehead, J = 1.7), 3.77 (*m*, 2H, $-CHCH_2OAc$), 3.48 (*m*, 2H, $-CHCH_2OAc$), 2.01 (*s*, 6H, $-OCOCH_3$), 1.67 (*m*, 2H, bridge). I.r.: $\bar{\nu}$/cm^{-1} = 3023, 2954 (C–H stretch), 1741 (C=O, ester).

trans-*11,12-Bis(acetoxymethyl)-9,10-dihydro-2,6(7)-dinitro-9,10-ethanoanthracene (6)*. This adduct was prepared from adduct **5** using the same reaction conditions as in the synthesis of adduct **3**. The yield was 17.40 g (84%). M.p. = 88–136°C. ^{1}H n.m.r. ($CDCl_3$, 200 MHz): δ/ppm = 8.20 (*m*, 2H), 8.12 (*m*, 2H), 7.51 (*m*, 2H), 4.55 (*m*, 2H, bridgehead, 3.96 (*m*, 2H, $-CH_2OAc$), 3.53 (*m*, 2H, $-CH_2OAc$), 2.11 (*m*, 6H, $-OCOCH_3$), 1.85 (*m*, 2H, bridge). I.r.: $\bar{\nu}$/cm^{-1} = 2949 (*w*, C–H, stretch), 1743 (*s*, C=O, ester), 1523 and 1346 (NO_2). Analysis: C 59.6%, H 4.6%, N 6.7% (calc. for $C_{22}H_{20}N_2O_8$: C 60.0%, H 4.6%, N 6.4%).

trans-*11,12-Bis(acetoxymethyl)-2,6(7)-diamino-9,10-dihydro-9,10-ethanoanthracene (7)*. This adduct was prepared from adduct **6** using the same reaction conditions as in the synthesis of adduct **4**. The yield was 12.86 g (79%). The product was purified by column chromatography [silica gel, chloroform/ethyl acetate (1/2)]. M.p. = 108–152°C. ^{1}H n.m.r. ($CDCl_3$, 500 MHz): δ/ppm = 6.88 (*m*, 2H), 6.60 (*m*, 2H), 6.39 (*m*, 2H), 3.98 (*m*, 2H, bridgehead), 3.82 (*m*, 2H, $-CH_2OAc$), 3.61 (*m*, 2H, $-CH_2OAc$), 3.38 (*s*, *br*, 4H, NH_2), 2.08 (*s*, 6H, $-OCOCH_3$), 1.67 (*m*, 2H, bridge). ^{13}C n.m.r. ($CDCl_3$, 125 MHz): δ/ppm = 170.88, 170.85, 144.8, 144.6, 144.4, 144.3, 142.0, 141.1, 134.1, 133.2, 131.1, 130.1, 126.0, 125.7, 124.0, 123.7, 113.2, 113.04, 113.01, 112.9, 112.5, 112.4, 112.29, 112.26, 112.18, 112.11, 112.06, 112.03, 111.99, 111.3, 111.2, 67.05, 66.96, 66.93, 66.87, 66.82, 66.79, 66.73, 66.70, 46.1, 45.18, 45.14, 45.10, 45.02, 44.92, 43.97, 42.99, 42.80, 42.74, 42.70, 42.50, 42.42, 42.27, 21.01, 20.92. I.r.:

$\bar{\nu}/cm^{-1}$ = 3417, 3366, 3232 (*s*, N–H stretch); 3011, 2946 (*m*, C–H stretch); 1731 (*s*, C=O ester). U.v. (95% ethanol): λ_{max}/nm = 292, 235 (ε = 4200, 15400); (after addition of HCl) λ_{max}/nm = 271, 263 (ε = 1700, 1300). M.s. (FAB): m/z = 381 ($[M + H]^+$). Analysis: C 69.3%, H 6.7%, N 7.7% (calc. for $C_{22}H_{24}N_2O_4$: C 69.5%, H 6.4%, N 7.4%).

*Reduction of 2,6-diaminoanthraquinone to 2,6-diaminoanthracene (**9**).* 2,6-Diaminoanthraquinone (**8**) (13.10 g, 55 mmol) was suspended in 10% sodium hydroxide solution (125 ml) and zinc dust (10 g, 0.15 mol) was added, with mechanical stirring, at room temperature. The mixture was brought to reflux temperature and 95% ethanol (10 ml) was added to prevent violent foaming. Further portions of zinc duct (2 × 10 g, 2 × 0.15 mol) were added after 30 and 60 min had elapsed. The mixture was then heated under reflux with vigorous stirring for 24 h. The solid was filtered off from the mixture and washed with hot water until the washings were clear. This crude product containing zinc residues was subjected to Soxhlet extraction using acetone. Recrystallization of the extract from acetone gave bright yellow crystals (3.40 g, 40% yield) with m.p. = 230°C (dec.). ^1H n.m.r. (DMSO-d_6, 200 MHz): δ/ppm = 8.23 (*s*, 2H, $H_{9,10}$), 8.04 (*d*, 2H, J = 8.9, $H_{4,8}$), 7.33 (*dd*, 2H, J = 2.0, 8.9, $H_{3,7}$), 7.20 (*d*, 2H, J = 1.8, $H_{1,5}$), 5.63 (*s*, *br*, 4H, $-NH_2$). ^{13}C n.m.r. (DMSO-d_6, 75 MHz): δ/ppm = 144.1, 130.7, 128.1, 127.5, 121.4, 121.0, 103.8. I.r.: $\bar{\nu}/cm^{-1}$ = 3399, 3315, 3212 (*m*, N–H stretch); 3007, 2925 (*w*, C–H stretch), 1638 (*s*, arom. ring stretch). U.v. (95% ethanol): λ_{max}/nm = 423, 346, 329, 314, 271 (ε = 540, 460, 670, 770, 670, 11500); (after addition of HCl) λ_{max}/nm = 374, 354, 337, 252 (ε = 670, 750, 560, 20300). M.s. (FAB): m/z = 209 ($[M + H]^+$).

*Dimethyl 2,6-diamino-9,10-dihydro-9,10-ethanoanthracene-11,12-*trans*-dicarboxylate (**10**).* Before use, chlorobenzene was heated under reflux for 24 h over phosphorus pentoxide, then distilled under reduced pressure. A solution of 2,6-diaminoanthracene (**9**) (0.773 g, 3.71 mmol) and dimethyl fumarate (0.994 g, 6.90 mmol) in chlorobenzene (50 ml) was heated under reflux for 3 days, under an atmosphere of nitrogen. The mixture was allowed to cool and most of the chlorobenzene was removed *in vacuo*. The brown oily residue was dissolved in a small volume of chloroform. This solution was added with stirring to a large excess of hexane. The light brown precipitate formed was isolated by filtration, washed with hexane and dried. The yield was 0.95 g (73%). The product was purified by column chromatography [silica gel, chloroform/ethyl acetate (1/1)]. M.p. = 100–158°C. ^1H n.m.r. ($CDCl_3$, 200 MHz); δ/ppm = 7.05 (*d*, J = 7.8, 1H), 6.97 (*d*, J = 7.8, 1H), 6.67 (*d*, J = 2.2, 1H), 6.59 (*d*, J = 2.2, 1H), 6.39 (*dd*, J = 2.2, 7.8, 1H), 6.37 (*dd*, J = 2.2, 7.8, 1H), 4.47 (*s*, 2H, bridge), 3.62 (*s*, 6H, $-OCH_3$), 3.53 (*s*, *br*, 4H, $-NH_2$), 3.35 (*s*, 2H, bridgehead). ^{13}C n.m.r. ($CDCl_3$, 75 MHz): δ/ppm = 172.7, 172.6, 144.2, 144.1, 143.6, 141.8, 132.1, 130.1, 124.7, 124.5, 123.9, 112.1, 111.7, 110.9, 52.0, 47.9, 47.6, 47.5, 45.8. H.p.l.c.: peaks at 15.1 min (50%) and 16.0 min (50%). I.r.: $\bar{\nu}/cm^{-1}$ = 3446, 3370 and 3231 (*m*, N–H stretch), 3012 and 2953 (*m*, C–H stretch), 1729 (*s*, C=O stretch), 1626 (arom. ring stretch). U.v. (95% ethanol): λ_{max}/nm = 288, 237 (ε = 4000, 11600); (after addition of HCl) λ_{max}/nm = 271, 254 (ε = 2500, 2900). M.s. (FAB): m/z = 353 ($[M + H]^+$), 248, 208. Analysis: C 67.9%, H 5.7%, N 7.7% (calc. for $C_{20}H_{20}N_2O_4$: C 68.2%, H 5.7%, N 8.0%).

*Synthesis of diisopropyl fumarate (**11**) from fumaric acid.* A solution of fumaric acid (44.43 g, 0.383 mol) in isopropanol (250 ml) containing concentrated sulfuric acid (5 ml, 2%) was heated under reflux for 72 h. The solvent was removed and the residue was partitioned between water and diethyl ether. The ether layer was washed twice with water dried over $MgSO_4$, filtered and evaporated. The liquid residue was distilled under reduced pressure. The yield of distilled product was 43.20 g (56%). B.p. = 126°C (*ca.* 10 mmHg) (lit.[22] b.p. = 102°C at 9 mmHg). ^1H n.m.r. ($CDCl_3$, 200 MHz): δ/ppm = 6.80 (*s*, 2H, $-CH=CH-$), 5.09 (septet. 2H, $-CH(CH_3)_2$), 1.29 (*d*, 12H, $-CH(CH_3)_2$). I.r. (liquid film): $\bar{\nu}/cm^{-1}$ = 1720 (C=O, ester).

*Diisopropyl 2,6-diamino-9,10-dihydro-9,10-ethanoanthracene-11,12-*trans*-dicarboxylate (**12**).* The method used was the same as for the synthesis of adduct **10**, except that the dienophile was diisopropyl fumarate (**11**). The yield was 7.02 g (53%). M.p. = 100–138°C (dec.). ^1H n.m.r. ($CDCl_3$, 200 MHz): δ/ppm = 7.06 (*d*, J = 7.8, 1H), 6.94 (*d*, J = 7.8, 1H), 6.69 (*d*, J = 2.2, 1H), 6.54 (*d*, J = 2.2, 1H), 6.38 (*m*, 2H), 4.90 (*m*, 2H, $-CH(CH_3)_2$), 4.48 (*s*, 2H, bridge), 3.71 (*s*, *br*, 4H, $-NH_2$), 3.34 (*m*, 2H, bridgehead), 1.22 (*m*, 12H, $-CH(CH_3)_2$). I.r.: $\bar{\nu}/cm^{-1}$ = 3444, 3367 (*m*, N–H stretch), 1722 (*s*, C=O, ester). U.v. (95% ethanol): λ_{max}/nm = 290, 267, 238 (ε = 4800, 8000, 16200); (after addition of HCl) λ_{max}/nm = 251, 243 (ε = 9000, 7600). Analysis: C 70.4%, H 7.0%, N 6.9% (calc. for $C_{24}H_{28}N_2O_4$: C 70.6%, H 6.9%, N 6.9%).

*N-Methyl-2,6-diamino-9,10-dihydro-9,10-ethanoanthracene-11,12-*cis*-dicarboximide (**13**).* The method used was the same as for the synthesis of adduct **10**, except that the dienophile was *N*-methylmaleimide. The yield was 8.01 g (90%). The product was purified by column chromatography [silica gel, chloroform/ethyl acetate (2/3)]. M.p. = 170–172°C. ^1H n.m.r. (DMSO-d_6, 200 MHz): δ/ppm = 7.02 (*d*, 1H, J = 7.8), 6.80 (*d*, 1H, J = 7.9), 6.61 (*d*, 1H, J = 1.9), 6.40 (*d*, 1H, J = 2.1), 6.28 (*dd*, 1H, J = 8.0, 2.2), 6.22 (*dd*, 1H, J = 8.2, 2.4), 4.92 (*s*, *br*, 4H, $-NH_2$). 4.30 (*m*, 2H, bridge), 3.11 (*s*, 2H, bridgehead), 2.4 (*s*, 3H, $-NCH_3$). ^{13}C n.m.r. (DMSO-d_6, 75 MHz): δ/ppm = 177.3, 177.1, 147.0, 146.9, 143.5, 140.7, 129.2, 126.2, 124.6, 124.3, 110.8, 110.4, 110.3, 110.1, 47.4, 47.0, 44.2, 44.1, 23.9. H.p.l.c.: peak at 3.00 min (100%). I.r.: $\bar{\nu}/cm^{-1}$ = 3427, 3351, 3230 (m/s, N–H stretch), 1772 (m) and 1691 (s) (C=O, succinimide). U.v. (95% ethanol): λ_{max}/nm = 390, 341, 288, 238 (ε = 1070, 2100, 5800, 16700); (after addition of HCl) λ_{max}/nm = 390, 340, 261 (ε = 1000, 2000, 4040). Analysis: C 70.7%, H 5.7%, N 12.0% (calc. for $C_{19}H_{17}N_3O_2$: C 71.5%, H 5.4%, N 12.2%).

*N-Cyclohexyl-2,6-diamino-9,10-dihydro-9,10-ethanoanthracene-11,12-*cis*-dicarboximide (**14**).* The method used was the same as for the synthesis of adduct **10**, except that the dienophile was *N*-cyclohexylmaleimide. The yield was 5.24 g (80%). The product was purified by column chromatography [silica gel, chloroform/ethyl

Table 1 Synthesis of polyamides from various diamine monomers and terephthalic acid derivatives

Polymer product	Diamine monomer	Method[a]	Yield/%	η_{inh}[b]/dl g^{-1}	G.p.c. results[c]			D.s.c. endotherm peak/°C	T.g. weight loss onset/°C	Isothermal weight loss		
					M_n	M_w	M_w/M_n			Temp./°C	Found[d]/%	Calc.[e]/%
18	**8**	B	100	0.624[f]	–	–	–	–	–	–	–	–
19	**9**	B	100	–	–	–	–	–	–	–	–	–
20	**4**	A	87	0.153	2900	5450	1.9	282	210	242	29.8	29.9
		B	94	0.181	2060	3600	1.8					
21	**10**	A	46	0.354	4850	7500	1.5	265	211	245	29.8	29.9
		B	74	0.355	3370	5860	1.7					
22	**12**	B	67	0.227	1400	2250	1.6	263	220	246	29.4	37.2
23	**7**	A	78	0.141	1800	4160	2.3	332	270	354	36.3	33.7
		B	96	0.187	2150	5600	2.6					
24	**13**	B	74	0.211	5460	11800	2.2	370	225	300	30.7	24.7
25	**14**	B	98	0.603	1730	3230	1.9	367	235	300	32.1	34.6

D.s.c. and t.g. were both performed at a rate of 10°C min^{-1} under a nitrogen flow
[a] A = acid chloride method; B = Higashi method
[b] Unless indicated otherwise, inherent viscosity measured in NMP at 25°C at a concentration of 1 g dl^{-1}
[c] In solution in DMAc using polystyrene calibration
[d] Weight loss observed in an isothermal experiment after 90 min at the temperature shown
[e] Calculated for complete loss of the dienophile by retro-Diels–Alder reaction and sublimation
[f] Inherent viscosity measured in concentrated H_2SO_4 at 25°C at a concentration of 0.1 g dl^{-1}

Table 2 Synthesis of copolyamides from diamine adduct monomers, *p*-phenylenediamine and terephthalic acid derivatives

Polymer product	Diamine monomer	Mol%[a]	Method[b]	Yield/%	η_{inh}[c]/dl g^{-1}	D.s.c. endotherm peak/°C	T.g. weight loss onset/°C	Isothermal weight loss		
								Temp./°C	Found[d]/%	Calc.[e]/%
26	**4**	10	A	85	0.238	272	230	248	7.2	5.5
27	**4**	20	A	67	0.220	257	220	246	9.0	10.0
28	**4**	50	A	50	0.145	255	218	246	12.2	20.0
29	**10**	20	A	38	0.110	256	209	260	8.9	10.0
			B	92	1.513					
30	**10**	50	A	58	0.266	258	214	246	18.3	20.0
			B	92	1.052					
31	**12**	20	B	100	1.336	257	215	223	13.2	13.4
32	**12**	50	B	76	–	258	210	258	24.8	25.8

D.s.c. and t.g. were both performed at a rate of 10°C min^{-1} under a nitrogen flow
[a] Mol% of diamine monomer, with *p*-phenylenediamine as the remainder of the diamine component
[b] A = acid chloride method; B = Higashi method
[c] Inherent viscosity measured in NMP at 25°C at a concentration of 1 g dl^{-1}
[d] Weight loss observed in an isothermal experiment after 90 min at the temperature shown
[e] Calculated for complete loss of the dienophile by retro-Diels–Alder reaction and sublimation

acetate (1/1)]. M.p. = 150°C (dec.). ^{1}H n.m.r. (DMSO-d_6, 200 MHz): δ/ppm = 7.02 (*d*, 1H, J = 7.8), 6.78 (*d*, 1H, J = 7.9), 6.61 (*d*, 1H, J = 1.9), 6.41 (*d*, 1H, J = 2.1), 6.27 (*dd*, 1H, J = 8.0, 2.2), 6.24 (*dd*, 1H, J = 8.2, 2.4), 5.0 (*s*, *br*, 4H, –**NH$_2$**), 4.3 (*m*, 2H, bridge), 3.0 (*m*, 2H, bridgehead), 1.9–0.8 (*m*, 10H, cyclohexyl). ^{13}C n.m.r. (DMSO-d_6, 75 MHz): δ/ppm = 177.3, 177.1, 147.0, 146.7, 146.3, 143.5, 129.2, 126.2, 124.7, 124.2, 110.52, 110.48, 110.35, 110.13, 50.0, 46.6, 46.3, 44.5, 44.4, 27.7, 25.2, 24.8. I.r.: $\bar{\nu}$/cm^{-1} = 3437, 3355, 3222 (*m*, N–H stretch), 1762 (m) and 1688 (s) (C=O, succinimide). U.v. (95% ethanol): λ_{max}/nm = 340, 291, 239 (ε = 2080, 4600, 16800); (after addition of HCl) λ_{max}/nm = 341, 262 (ε = 1600, 3800). Analysis: C 74.2%, H 6.3%, N 10.4% (calc. for $C_{24}H_{25}N_3O_2$: C 74.4%, H 6.5%, N 10.8%).

Polymer synthesis

All the polyamides prepared were synthesized by one or both of two methods described below (Methods A and B). In all cases the scale of the reaction was the same. Details of the ratios of monomers used, yields and important characterization data are shown in *Tables 1* and *2*.

Example of Method A: synthesis of polymer ***20***. Monomer **4** (1.762 g, 5.000 mmol) was dissolved in a mixture of NMP (50 ml), pyridine (10 ml), calcium chloride (3.0 g) and lithium chloride (1.0 g) in a 250 ml three-necked flask equipped with a mechanical stirrer and a nitrogen inlet. A flow of nitrogen was introduced into the system and the flask was cooled in an ice/water bath to 0–5°C. Terephthaloyl chloride (1.015 g, 5.000 mmol) was added as a solid, with vigorous stirring. The temperature was maintained at 0–5°C for 1 h, then allowed to increase to room temperature. Stirring at room temperature was continued overnight. After a total reaction time of 24 h, the mixture was poured into methanol (500 ml) and stirred. The polymer precipitated was filtered off, washed with copious amounts of water and

methanol, and then dried. The yield was 2.08 g (87%). ^{1}H n.m.r. (pyridine-d_5, 200 MHz): δ/ppm = 10.4 (*s*, 2H, NHCO), 7.8–6.8 (*m*, 10H, arom.), 4.4 (*m*, 2H, bridge), 3.2 (*s*, 2H, bridgehead), 3.0 (*s*, 6H, $-OCH_3$). I.r.: $\bar{\nu}/cm^{-1}$ = 3308 (*s*, *br*, N–H stretch), 1728 (*s*, C=O, ester), 1654 (*s*, C=O, amide). U.v. (DMF): λ_{max} = 294 (ε = 32 000).

Example of Method B: synthesis of polymer ***20***. A 250 ml three-necked round bottom flask was fitted with a condenser, mechanical stirrer and a nitrogen inlet. The flask was placed in a thermostatically controlled constant temperature oil bath at 115°C, and flushed with nitrogen. The flask was charged with terephthalic acid (0.831 g, 5.000 mmol), monomer **4** (1.762 g, 5.000 mmol) and the solvent mixture consisting of NMP (40 ml), pyridine (10 ml), calcium chloride (3.0 g) and lithium chloride (1.0 g). The mixture was stirred vigorously and a solution of triphenyl phosphite (3.10 g, 10.0 mmol) in NMP (10 ml) was added. The reaction mixture was stirred at 115°C for 2.5 h, then cooled, precipitated into methanol, filtered, washed with copious amounts of water and methanol, and then dried. The yield was 2.31 g (96%). Spectroscopic data were as for the polymer **20** prepared by method A.

Example of retro-Diels–Alder reaction: synthesis of polyamide ***33*** *from precursor polymer* ***20***. Precursor polyamide **20** (0.160 g) was ground to a fine powder and spread on a glass petri dish. This sample was placed in a vacuum oven and heated under vacuum (approximately 1 mmHg) at 220°C. The sample was removed and weighed at intervals. A constant weight was reached after 5 h. The yield of polyamide **33** was 0.112 g (100%).

Table 3 Synthesis of final polyamides by retro-Diels–Alder reaction of precursor polymers

Final polymer	Precursor polymer	Weight loss	
		Found[a]/%	Calc.[b]/%
33	**20**	29.9	29.9
34	**21**	28.4	29.9
38	**29**	9.8	10.0
39	**30**	20.6	20.0

[a] Weight lost on heating for 5 h *in vacuo* at 220°C
[b] For complete loss of the dienophile by retro-Diels–Alder reaction and sublimation

I.r.: $\bar{\nu}/cm^{-1}$ = 3202 (*m*, N–H stretch), 1656 (*s*, C=O, amide).

Details of all the large scale retro-Diels–Alder reactions are contained in *Table 3*.

RESULTS AND DISCUSSION

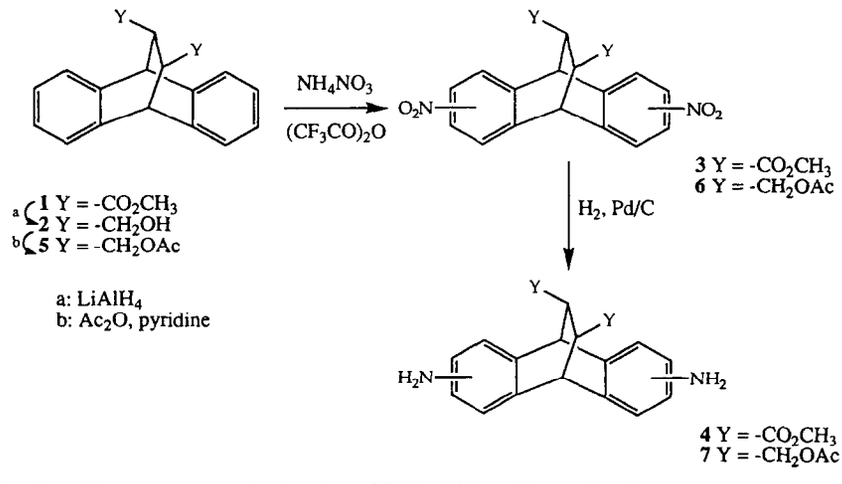
Monomer synthesis

Two synthetic approaches to the synthesis of monomers based on Diels–Alder adducts of β,β'-diaminoanthracene were used. One was to take preformed Diels–Alder adducts of anthracene and introduce the diamine functionality by nitration, followed by reduction of the nitro group. The second approach started from the commercially available 2,6-diaminoanthraquinone. Reduction of this compound to 2,6-diaminoanthracene followed by Diels–Alder reaction yielded the required type of monomer. Both of these routes were investigated and the results are presented in the following sections.

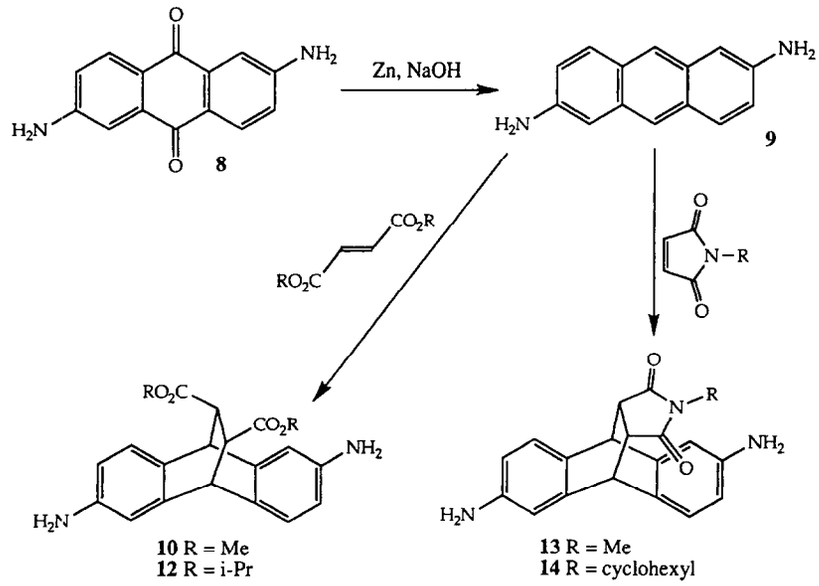
Nitration of anthracene Diels–Alder adducts. The mild nitration of anthracene adducts is known to proceed exclusively with substitution at the β-positions[16,23] (i.e. 2, 3, 6, 7) and with only one nitro group introduced per aromatic ring. Since the nitration of the second ring occurs without any additional selectivity, the product is essentially an equimolar mixture of the 2,6- and 2,7-isomers. This synthetic approach has some disadvantages, which will be elaborated on later, but since it provides easy access to diaminoanthracene adduct monomers, the approach was utilized in the present work.

Nitration of the adduct **1**, prepared by the Diels–Alder reaction of anthracene with dimethyl fumarate, produced the β,β'-dinitroanthracene adduct **3** in 86% yield. Catalytic hydrogenation of this dinitro adduct produced the β,β'-diaminoanthracene adduct **4** in 99% yield; see *Scheme 2*. Adduct **5** was prepared by reduction of adduct **1** to the diol **2** followed by acetylation. Application of the nitration-reduction sequence of adduct **5** produced the diamino adduct **7** in an overall yield of 45% for the four steps from adduct **1**.

Reduction of 2,6-diaminoanthraquinone and subsequent Diels–Alder reactions. The synthetic route from 2,6-diaminoanthraquinone (**8**) to 2,6-diaminoanthracene



Scheme 2 Synthesis of diamine adduct monomers via nitration of Diels–Alder adducts of anthracene



Scheme 3 Synthesis of diamine adduct monomers via Diels–Alder reactions of 2,6-diaminoanthracene

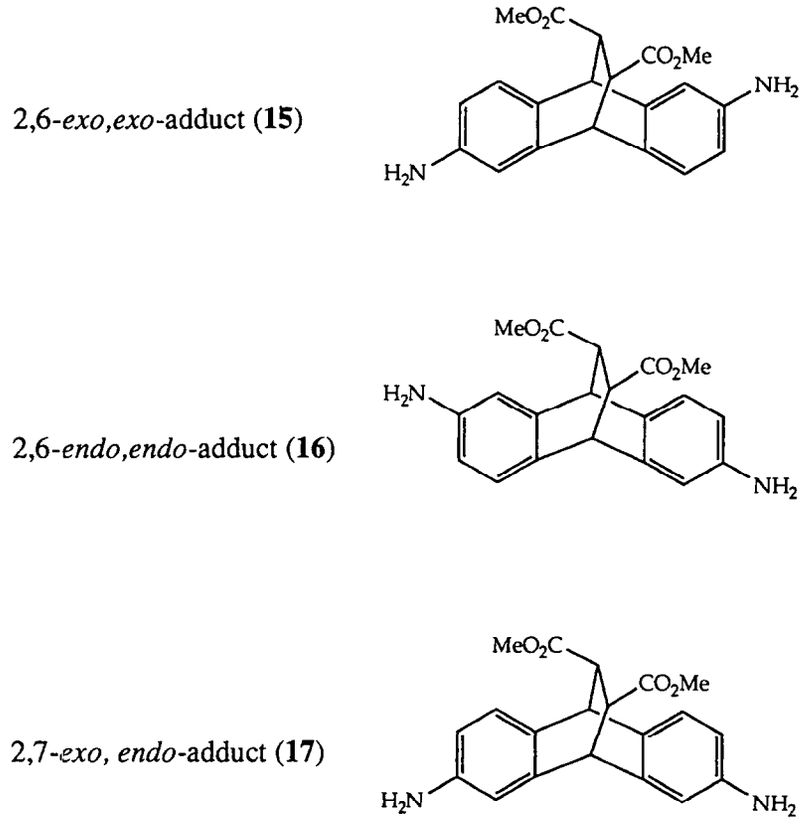


Figure 1 Possible Diels–Alder adducts from 2,6-/2,7-diaminoanthracene and dimethyl fumarate

Diels–Alder adducts for use as monomers is outlined in *Scheme 3*. Reduction of 2,6-diaminoanthraquinone in one step using zinc and sodium hydroxide gave 2,6-diaminoanthracene (**9**) in yields of 25–40%. Reactions of **9** in chlorobenzene at reflux temperature with dimethyl fumarate, diisopropyl fumarate, *N*-methylmaleimide and *N*-cyclohexylmaleimide gave Diels–Alder adducts **10**, **12**, **13** and **14** respectively in yields of 53–90%.

Isomerism of the products 4, 7, 10 and 12. Each of the final products **4**, **7**, **10** and **12** from the monomer synthesis was, as expected, a mixture of isomeric racemates. Consistent with this they all displayed broad melting point ranges (up to 50°C in breadth). The number of racemates which could possibly be present in a given product depends on the stereochemistry of the dienophile used and on the 2,6- or 2,6-/2,7-substitution pattern of the anthracene moiety. Monomer **4**, for example, is derived from a *trans*-dienophile and the amino groups may be in the 2,6- or 2,7-positions. There are, therefore, the three possible racemates shown in *Figure 1*. The numbers of possibilities for other products are given in *Table 4*.

H.p.l.c. analysis was used to determine the number of racemates present in products **4** and **10**. In each case the

Table 4 Isomers of β,β'-diaminoanthracene adducts

Anthracene substitution	Dienophile stereochemistry	Number of diastereomers	Examples
2,6	*cis*	1	**13**, **14**
2,6	*trans*	2	**10**, **12**
2,6/2,7	*cis*	2	–
2,6/2,7	*trans*	3	**4**, **7**

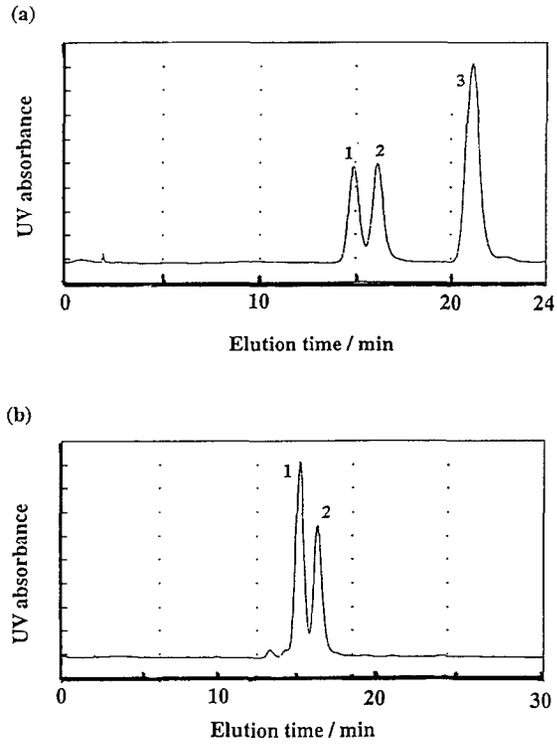


Figure 2 H.p.l.c.chromatograms of monomers **4** and **10**. (a) Monomer **4**; peaks 1, 2 and 3 integrals in the ratio 23/24/53. (b) Monomer **10**; peaks 1 and 2 integrals in the ratio 50/50

expected number of isomers (see *Table 4*) was found. The two racemates present in product **10** are also present in product **4**. This allows the assignment of h.p.l.c. peak 3 (see *Figure 2*) to the 2,7-diamino compound **17** and peaks 1 and 2 to the 2,6-diamino compounds **15** and **16** (see *Figure 1*). For product **4** the relative areas of peaks 1–3 were in the ratio 23/24/53 respectively. This confirms that the nitration reaction shows no significant preference for one or the other β-positions in adduct **1** (the ratio of 2,6- to 2,7-isomers in product **4** is 47/53). It is also evident that the Diels–Alder reaction of 2,6-diaminoanthracene (**9**) with dimethyl fumarate to produce **10** exhibits no preference for the formation of isomers **15** and **16**, since the h.p.l.c. analysis of **10** shows peaks 1 and 2 in the ratio 50/50.

In an attempt to further identify the isomers present in product **4**, the product was subjected to column chromatography. This afforded small samples of each of racemates **15**, **16** and **17** (see *Figure 1*). The ^{1}H n.m.r. spectra of these were recorded. The aromatic resonances showed small differences, as can be seen from the data in *Table 5*. It should be noted here that in compound **15** the two sets of aromatic protons are in the same environment; the same is true with **16**. However, with compound **17** the two sets are different. Thus, in agreement with the h.p.l.c. results, isomer **17** is confidently assigned the

Table 5 ^{1}H n.m.r. spectra[a] (aromatic region) of the isomers of the β,β'-diaminoanthracene/dimethyl fumarate adducts **4** and **10**[b]

(a) 2,6-isomer **15**:	7.05 (*d*, 2H, J = 7.9, $H_{4,8}$) 6.59 (*d*, 2H, J = 2.2, $H_{1,5}$) 6.38 (*dd*, 2H, J = 7.8, 2.3, $H_{3,7}$)
(b) 2,6-isomer **16**:	6.97 (*d*, 2H, J = 7.8, $H_{4,8}$) 6.67 (*d*, 2H, J = 2.2, $H_{1,5}$) 6.37 (*dd*, 2H, J = 7.8, 2.2, $H_{3,7}$)
(c) 2,7-isomer **17**:	7.07 (*d*, 1H, J = 7.8) 6.95 (*d*, 1H, J = 7.8) 6.68 (*d*, 1H, J = 2.2) 6.61 (*d*, 1H, J = 2.2) 6.40 (*dd*, 1H, J = 7.8, 2.3) 6.37 (*dd*, 1H, J = 7.8, 2.3)

[a] All spectra were measured in solution in $CDCl_3$ at 500 MHz. Chemical shift values given are δ/ppm; J values are in Hz
[b] For the structures tentatively assigned to isomers **15** and **16** and firmly assigned to isomer **17**: see *Figure 1*

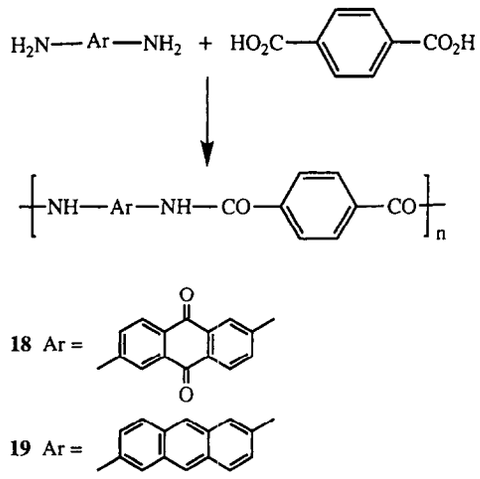
structure shown in *Figure 1*. In the ^{1}H n.m.r. spectrum of adduct **13**, the set of aromatic protons closer to the imide carbonyls are shifted downfield relative to those on the other aromatic ring, the α-protons being shifted by 0.20 and 0.21 ppm and the β-proton by 0.06 ppm. Assuming an ester group causes downfield shifts for nearby protons, albeit smaller shifts than the conformationally rigid imide group, then spectrum (i) in *Table 5* and h.p.l.c. peak 2 can be tentatively assigned to compound **15** and spectrum (ii) and h.p.l.c. peak 1 to compound **16**.

Polymer synthesis

There are several established methods for the synthesis of polyamides. The two used in the present work were (a) the low-temperature solution polycondensation reaction between a diamine and a diacid chloride[24] and (b) the direct reaction between a diamine and a diacid with the aid of a condensation agent, such as triphenyl phosphite and pyridine (Higashi method)[25–28]. These methods were regarded as suitable for the present study because PPTA has been successfully prepared by both methods[24–28].

Direct synthesis of polyamides containing anthraquinone and anthracene units. For comparison purposes, anthraquinone- and anthracene-containing polyamides were synthesized initially by a direct (non-precursor route). Thus, 2,6-diaminoanthraquinone and 2,6-diaminoanthracene were reacted with terephthalic acid using the Higashi method[25–28], to form aromatic polyamides **18** and **19**, as shown in *Scheme 4*. In both reactions the product was a gel, suggesting the formation of reasonably high molecular weight polymer. The anthraquinone-containing polyamide **18** was insoluble in all solvents tried except concentrated sulfuric acid, for which a 0.1 g dl^{-1} solution had an inherent viscosity of 0.62 dl g^{-1}. This is a reasonably high value, taking into account that the 2,6-diaminoanthraquinone used to prepare this polymer was used from a commercial source without purification. The anthracene-containing polyamide **19** was insoluble in a wide range of solvents. Since the 9,10-positions of anthracene are much more reactive to electrophiles than normal aromatic compounds, it is possible that electrophilic aromatic substitution reactions occurred during the polymerization. This could result in crosslinking, thus rendering the polymers insoluble.

These initial experiments highlight the need for



Scheme 4 Direct synthesis of polyamides containing anthracene and anthraquinone units

precursor routes in order to obtain well characterized products of this type with significant molecular weight.

Synthesis of homopolyamide precursor polymers. Precursor polyamides were prepared by the reaction of each of the six adduct monomers **4**, **7**, **10**, **12**, **13** and **14** with terephthalic acid (or terephthaloyl chloride): see *Scheme 1*. Yields and relevant characterization data are given in *Table 1*. The precursor polymers were characterized as follows.

Solubility. The solubility of precursor polymers is a property that is of some importance in determining their usefulness, since the ability to be handled, characterized and processed in common solvents is a desirable characteristic. Solubilities were measured at a concentration of $10\,mg\,ml^{-1}$ in a range of solvents of different polarities. The precursor homopolyamides **20–25** were all soluble in polar aprotic solvents such as NMP, DMSO and pyridine, but insoluble in other organic solvents such as THF, acetone, dichloromethane and methanol. Thus, no significant effect on solubility was observed when different adduct structures were used. The solubility of these precursor polymers in some common organic solvents represents a marked improvement on the ethylene-bridged adduct precursor polyamides prepared by Frazer *et al.*[16]. The latter were very soluble in solvents such as *m*-cresol or mixtures of 1,1,2,2,-tetrachloroethane and phenol. The increased solubility of the present precursor polyamides enables characterization by solution n.m.r. and the estimation of molecular weight by g.p.c., as well as facilitating processing in less aggressive solvents.

Spectroscopic measurements. All the precursor homopolyamides were characterized by ^1H n.m.r., i.r. and u.v. spectroscopy, and in some cases also by ^{13}C n.m.r. spectroscopy. The spectra obtained were fully consistent with the proposed structures; the data for polymer **20** is given in the Experimental section as an example.

Molecular weight measurements. The inherent viscosities of the precursor homopolyamides measured in solution in NMP were in the range $0.1–0.8\,dl\,g^{-1}$. Dilute solution viscometry, however, is not an accurate method for comparing molecular weights in the absence of a standard sample.

Molecular weights were estimated by end-group analysis using ^{13}C n.m.r. spectroscopy. The carbonyl regions (160–210 ppm) of the spectra of the polyamides **21**, **23** and **25** were examined. Resonances due to the amide and ester groups in the polymer structures were observed, but no additional resonances due to acid end groups were seen above the background. From the signal-to-noise ratios in these regions, assuming that there is one acid end-group per polymer chain, it was calculated that the *minimum* values of M_n for the polymers **21**, **23** and **25** were 6500, 8200 and 5400 respectively.

A third method used to estimate molecular weight was g.p.c. The g.p.c. results suggested that all the polymers had low molecular weights. Values of M_n were in the range 1400–5600 and M_w/M_n was in the range 1.5–2.6. In the cases where direct comparison is possible with the ^{13}C n.m.r. end-group analysis, the values of M_n obtained by g.p.c. for the polymers **21**, **23** and **25** were 3370, 2150 and 1730 respectively. The g.p.c. results are lower than the minimum values from end-group analysis by factors of 2–4. It is therefore likely that there are similar discrepancies for all these polymers and that the actual values of M_n are at least in the range 5000–20 000.

There are further valid reasons for thinking that M_n has been underestimated by g.p.c. The low values obtained for these polymers, if correct, should in some cases mean the observation of discrete peaks for oligomers in the chromatograms. This was not the case; for all the polymers a single continuous trace was observed. It may be that these polyamides adsorb onto the g.p.c. column through their numerous polar groups, so increasing the retention time for the polymers and thereby reducing the molecular weight value recorded.

Thermal analysis. A summary of the differential scanning calorimetry (d.s.c.) and thermogravimetry (t.g.) results is shown in *Table 1*. Typical examples of d.s.c. and t.g. traces are shown in *Figure 3*, for polyamide **21**. By d.s.c. none of the precursor polyamides exhibited a glass transition temperature or melting point. In all cases a broad endothermic peak was observed above 200°C, with a maximum in the temperature range 250–330°C. In the t.g. traces of the polymers, weight loss was observed above 200°C. Both these features were attributed to the occurrence of the retro-Diels–Alder reaction. The dienophiles generated in these reactions are volatile and account for the weight losses observed. When compared to the retro-Diels–Alder reactions of the ethylene adduct polyamides prepared by Frazer *et al.*[16] (t.g. onset temperature for weight loss at 250°C), it is evident that some of these polymers undergo the retro-Diels–Alder reactions at lower temperatures (fumarate and maleimide adduct-containing polymers; **20**, **21**, **22**, **24** and **25**) and one at higher temperatures (1,4-diacetoxy-*cis*-2-butene adduct-containing polymer **23**): see *Table 1*.

In t.g., when heating was continued after retro-Diels–Alder reaction had finished, further weight loss was observed with the onset around 410°C, as can be seen in *Figure 3b*. This indicated that decomposition of the final polymers occurs at this temperature in an inert atmosphere (nitrogen).

X-ray scattering. Wide-angle X-ray scattering (WAXS) measurements were made on compressed powder samples of a few selected polymers. The homopolyamides **20**, **21** and **23** all showed broad diffuse patterns. This suggests that crystallinity is low and that these precursor polyamides are amorphous. The

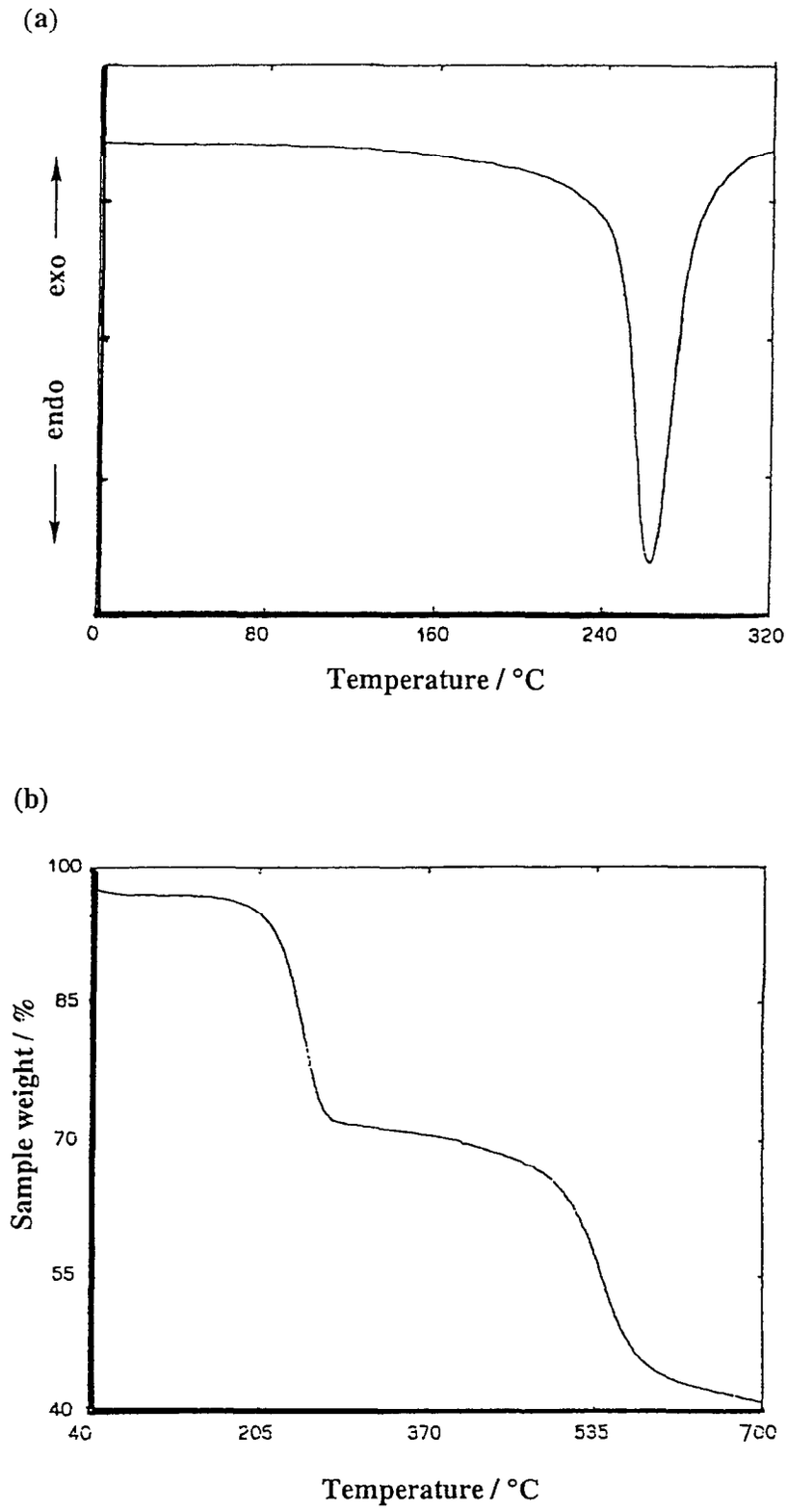
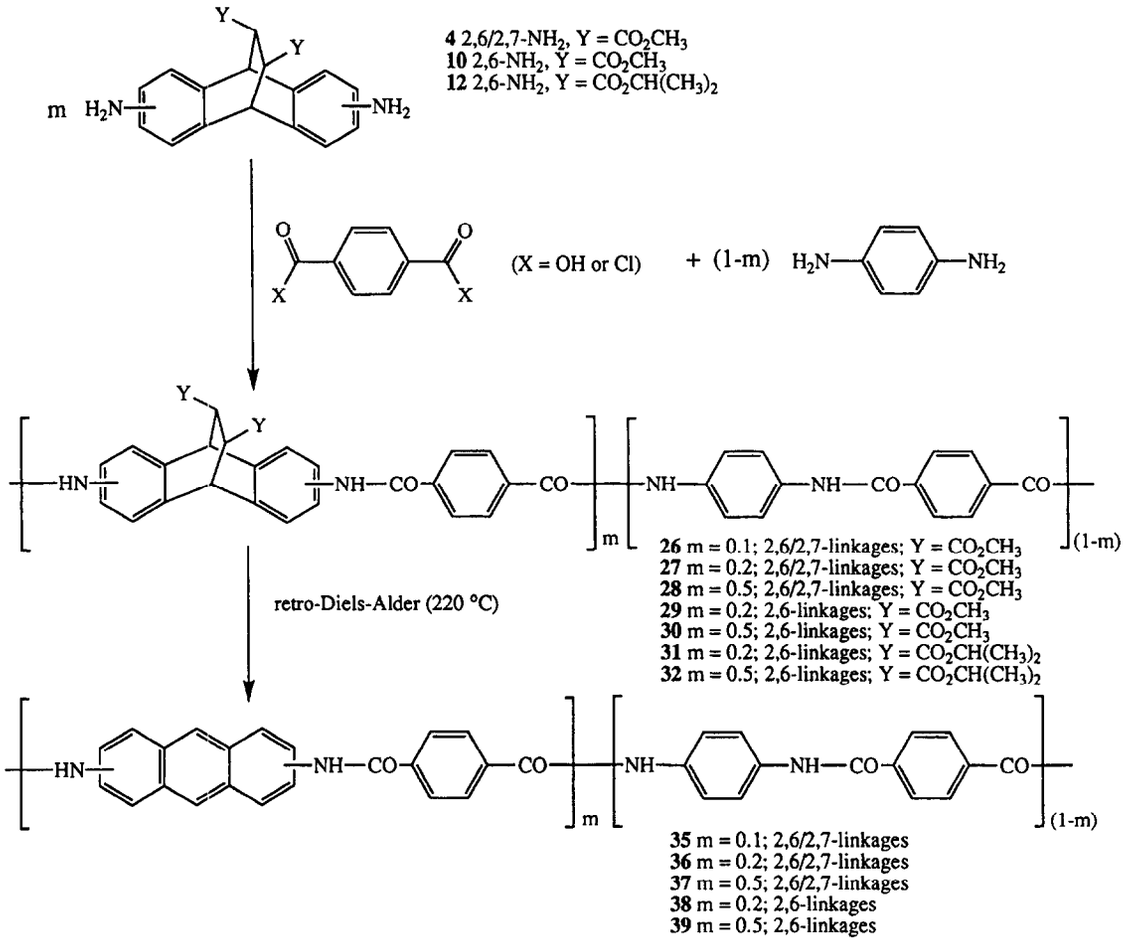


Figure 3 D.s.c. and t.g. of polyamide **21**. (a) D.s.c. (heating rate 10°C min^{-1}, under N_2). (b) T.g. (heating rate 10°C min^{-1}, under N_2)

precursor polyamides prepared by Frazer *et al.*[16] were also non-crystalline. This is in contrast to Kevlar fibres, which are highly crystalline[29].

Synthesis of copolyamide precursor polymers from adduct monomers and p-*phenylenediamine*. Copolymers were prepared by the reaction of various proportions of adduct monomers **4**, **10** and **12** and *p*-phenylenediamine with terephthalic acid. Both the acid chloride route and the Higashi method were used. The amount of adduct monomer included was 10, 20 or 50 mol% of the diamine portion. The reactions are summarized in *Scheme 5* and the yields and characterization data are given in *Table 2*.

The aim of synthesizing processable precursor copolymers was not achieved, as all these copolymers were insoluble in all the organic solvents used for testing (including methanol, acetone, THF, pyridine, DMSO,



Scheme 5 Precursor polymer route to copolyamides containing anthracene units

DMF, NMP and NMP containing 5% LiCl). Even in what was potentially the most favourable case, polymer **32**, where 50% of the diisopropyl fumarate adduct **12** was used, no significant increase in solubility was observed. However, some copolymers exhibited partial solubility in amide solvents such as NMP and DMF. The copolymers were characterized by i.r. spectroscopy.

The only satisfactory solvent identified was 98% sulfuric acid. Molecular weights were examined by viscosity measurements in 98% sulfuric acid: see *Table 2*. It is evident that the copolyamides prepared by the Higashi method all had significantly higher inherent viscosities than those prepared by the acid chloride route. These results are in contrast to the results of the homopolymerizations of the adduct monomers, where the inherent viscosity was apparently independent of the method of polymerization. The inherent viscosities of the copolymers were in some cases greater than $1\,g\,dl^{-1}$. Although it is not possible to quantitatively compare these values with the viscosity of PPTA in sulfuric acid solution, the data indicate that the copolymers are of moderately high molecular weight.

Analysis of the copolymers by d.s.c. and t.g. gave similar results to those observed for the homopolymers. The retro-Diels–Alder reaction was again observed by weight loss (t.g.) and endothermic peaks in d.s.c. *Table 2* summarizes these results. In some cases the weight losses observed in isothermal experiments do not agree closely with the calculated values. This fact, combined with the observation of partial solubility for some copolymers, suggests that a true copolymerization did not occur, as one co-monomer was much more reactive than the other. Thus, it could be that *p*-phenylenediamine is more reactive than the diamine adduct monomers. This could lead to copolymers with fractions differing in composition. The adduct-rich fractions would be more soluble and could therefore be washed out during the work-up procedure, leaving the isolated copolymer deficient in the adduct structure and therefore exhibiting lower weight loss than the calculated value.

Analysis of one copolymer (**29**) by WAXS showed that it was partially crystalline, with two sharp peaks corresponding to spacings of 4.3 and 3.8 Å, but it also exhibited a large broad peak, as for the precursor homopolyamides, which indicated the presence of substantial amorphous regions.

Production of aromatic polyamides from the precursor polymers by the retro-Diels–Alder reaction. As described in the preceding sections, analysis of the precursor polyamides by d.s.c. and t.g. provided a method for studying the retro-Diels–Alder reactions of these polymers and enabled the identification of suitable conditions for carrying out these reactions. For the production of the final polymers on a scale larger than that used for t.g. measurements, four precursor polymers were chosen, namely the homopolyamides **20** and **21** and the copolyamides **29** and **30**. The retro-Diels–Alder reaction of the homopolyamides is shown in *Scheme 1*; the copolymers undergo the reaction in an analogous way to produce the final copolymers shown in *Scheme 5*. *Table 3* summarizes the results obtained. In all four cases

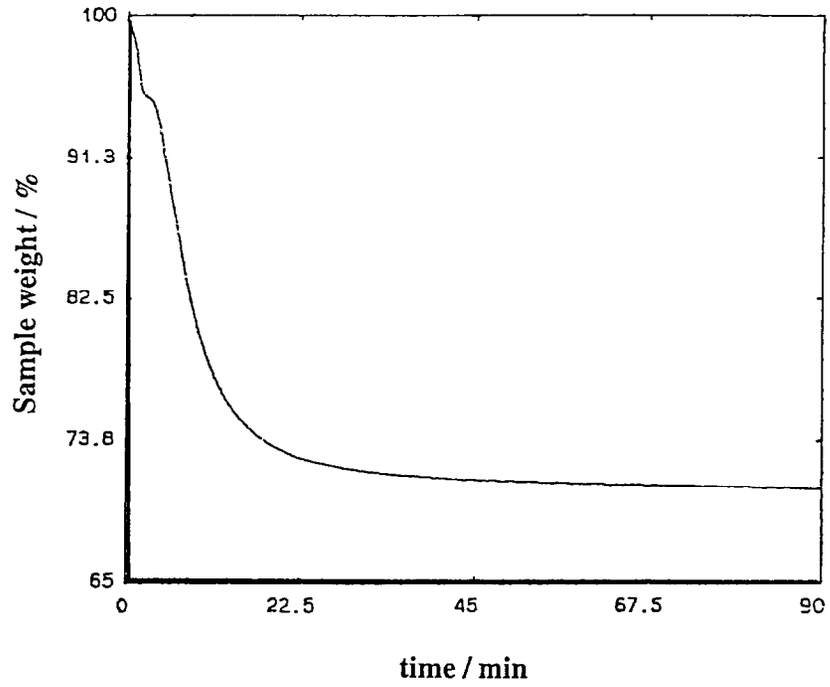


Figure 4 Isothermal weight loss of polyamide **21** at 235°C under N_2

a sample of the precursor polymer was ground to a fine powder, spread on a pre-weighed glass petri dish and heated *in vacuo* at 220°C. At intervals, the sample was removed from the vacuum oven and weighed until, after 5 h, weight loss had ceased. The weight loss was in each case in good agreement with the amount calculated for sublimation of the dienophile following completion of the retro-Diels–Alder reaction.

All the final polymers were insoluble in all organic solvents tried, and in sulfuric acid. They were characterized by i.r. spectroscopy. This showed the absence of ester carbonyl groups. The i.r. spectra of the final homopolyamides **33** and **34** were essentially identical to the i.r. spectra of the anthracene-containing polyamide **19** prepared by direct reaction and of the analogous polymer prepared by Frazer *et al.*[16].

Solid state ^{13}C n.m.r. spectra were obtained for these final polyamides. The spectra confirmed that the retro-Diels–Alder reactions had taken place, by showing the absence of resonances due to aliphatic carbons in the 50 ppm region.

The retro-Diels–Alder reactions were investigated further by a series of *isothermal* weight loss experiments carried out on the precursor polymers. A typical example is shown in *Figure 4*. The weight loss in these experiments initially followed a straight line, then gradually the curve flattened out, until eventually no further weight loss was observed. It should be noted that the initial kink in the curve shown in *Figure 4* occurred during the brief (*ca.* 5 min) rapid heating period during which the temperature of the sample was raised from 20°C to 235°C, at which temperature it was subsequently maintained. The kink may in part be due to a significant change in the ease with which the dimethyl maleate can diffuse out of the matrix as the latter becomes increasingly dense. The total weight loss observed in these various experiments was generally in good agreement with those calculated for complete loss of the dienophile by retro-Diels–Alder reaction and sublimation, as can be seen from the data in *Tables 1* and *2*.

CONCLUSIONS

Diels–Alder adducts of β,β'-diaminoanthracenes have been prepared successfully by two distinct routes. The first of these was by the nitration of anthracene adducts followed by reduction of the dinitro adducts thus formed. The second approach was the reduction of 2,6-diaminoanthraquinone to 2,6-diaminoanthracene followed by Diels–Alder reactions.

Anthracene- and anthraquinone-containing aromatic polyamides were prepared directly by the Higashi method. These polymers were insoluble in all organic solvents tested. The anthraquinone-containing polyamide was soluble in concentrated sulfuric acid, but the anthracene-containing polyamide was not.

Soluble precursor polyamides have been prepared, with M_n in the range 5000–20 000, by the reaction of several diaminoanthracene Diels–Alder adducts with terephthalic acid or terephthaloyl chloride. The molecular weights obtained were similar from the two polymerization methods. While these homopolyamides are significantly more soluble than the ethylene-bridged adduct polymers synthesized by Frazer *et al.*[16], the variations employed in adduct structure did not result in any significant differences in solubility among the precursor polymers.

Copolymers have also been prepared using these adducts as co-monomers (up to 50 mol%) with *p*-phenylenediamine. These copolymers are produced in higher molecular weight using the Higashi method. The precursor copolymers were, however, not soluble in organic solvents.

These adduct-containing polyamides and copolyamides were readily converted into the corresponding all-aromatic anthracene-containing polyamides via the retro-Diels–Alder reaction. Conditions for the retro-Diels–Alder reactions were established using d.s.c. and t.g. results. The reactions were complete within 5 h at the appropriate temperature (220–350°C, depending on the

type of dienophile in the adduct structure). The occurrence of the retro-Diels–Alder reactions was confirmed by the weight loss observed, solid state ^{13}C n.m.r. and i.r. spectroscopy. The different temperatures required for the retro-Diels–Alder reactions mean that in this general approach the stable temperature range of the precursor polymer can be controlled by choice of dienophile.

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