polymer report

Synthesis of acetylene-terminated monomers: 1,1′-(1-methylethylidene)bis[4-(4-ethynylphenyl)methoxy]benzene and 1,3-bis[(4-ethynylphenoxy)methyl]benzene

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The new acetylene-terminated monomers 1,1′-(1-methylethylidene)bis[4-(4-ethynylphenyl)methoxy]benzene and 1,3-bis[(4-ethynylphenoxy)methyl]benzene (**VI**) were prepared in 50% and 60% overall yield, respectively. The three-step synthesis involved: (a) a Williamson reaction between α,4-dibromotoluene and bisphenol A, or α,α′-dichloro-*m*-xylene and 4-bromophenol, giving the bromo-terminated compounds 1,1′-(1-methylethylidene)bis[4-(4-bromophenyl)methoxy]benzene or 1,3-bis[(4-bromophenoxy)methyl]benzene, respectively; (b) palladium-catalysed cross-coupling with 2-methyl-3-butyn-2-ol, affording the corresponding alkynyl tertiary alcohols from which catalyst residues were removed by treatment with diaminoethane; and (c) removal of the acetone protecting group in the presence of KOH. The low melting point of **VI** (102–104°C) makes it suitable for catalysed cure studies.

(Keywords: acetylene-terminated monomers; synthesis; characterization)

INTRODUCTION

Acetylene-terminated monomers (ATMs) are cured to give high-performance resins, which can replace, for example, epoxies for use under hot wet conditions[1–3]. For an investigation into the effects of catalysts on resin structure[4], ATMs were required (a) free of oligomers so that they could be fully characterized and (b) with low melting points to enable low-temperature cure to take place. With these aims, various ATMs were prepared. The synthesis and characterization of two of the novel monomers are described here.

EXPERIMENTAL

I.r. spectra were recorded from Nujol mulls of CsI discs by use of a Perkin–Elmer 728 spectrometer connected to a Perkin–Elmer 360 data station. ^1H n.m.r. spectra were run on either a Perkin–Elmer R32 90 MHz CW or a Bruker WP-80-SY 80 MHz FT spectrometer, and $^{13}C\{^1H\}$ spectra on this latter instrument operating at 20.115 MHz. Mass spectra were obtained by use of an AE1 MS9 mass spectrometer. Elemental analyses were carried out by Butterworth Laboratories, Twickenham, except those for trace Pd and Cu residues, which were determined by Rooney Laboratories using atomic absorption spectroscopy. Triethylamine was redistilled over powdered potassium hydroxide.

1,1′-(1-Methylethylidene)bis[4-(4-bromophenyl)methoxy]-benzene (I)

A mixture of α,4-dibromotoluene (50 g, 0.2 mol), bisphenol A (22.8 g, 0.1 mol) and anhydrous potassium carbonate (40.4 g, 0.29 mol) in *N,N*-dimethylacetamide (400 ml) was stirred at 110°C under nitrogen for 4 h. The crude product was precipitated by addition of 5% aqueous sodium hydroxide (600 ml) to the reaction mixture at 50°C, and was washed thoroughly with water and dried under vacuum at 90°C. Dropwise addition of a solution of the crude product in dichloromethane (60 ml) to methanol (400 ml) precipitated colourless crystals of **I**, which were filtered off and dried under vacuum at 90°C (yield 80%; m.p. 143–145°C). Found: C, 61.55; H, 4.60; Br, 28.14; O, 5.71. $C_{29}H_{26}Br_2O_2$ requires: C, 61.50; H, 4.63; Br, 28.23; O, 5.65.

I.r. (CsI) (cm^{-1}): 3030w, 2960w, 2910w, 2870w, 1910vw, 1605m, 1590m, 1505s, 1485m, 1465m, 1400m, 1375m, 1290m(br), 1240s(br), 1180s, 1155vw, 1105w, 1085vw, 1065m, 1020m, 1010s, 960vw, 945w, 870m, 830s, 810s, 760w, 735w, 710vw, 565s, 515m, 485vw, 430vw. ^1H n.m.r. ($CDCl_3$, tetramethylsilane (TMS) standard) δ_H (ppm): 1.63 (6H, s, CH_3), 4.96 (4H, s, OCH_2), 6.7–7.6 (16H, m, arom.). $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$, TMS standard) δ_C (ppm): 31.0 (C2), 41.6 (C1), 69.1 (C7), 114.2 (C5), 121.6 (C11), 127.7 (C4), 128.9 (C9), 131.5 (C10), 136.2 (C8), 143.4 (C3), 156.3 (C6). M.s. (70 eV), *m/e* 566 (M^+).

1,1′-(1-methylethylidene)bis[4-(4-ethynylphenyl)methoxy]-benzene (III)

To a refluxing mixture of **I** (17 g, 0.03 mol) and 2-methyl-3-butyn-2-ol (7.6 g, 0.09 mol) in anhydrous triethylamine (150 ml) under nitrogen was added bis(triphenylphosphine)palladium dichloride (0.05 g, 0.07 mmol), copper(I) iodide (0.05 g, 0.26 mmol) and triphenylphosphine (0.25 g, 0.95 mmol). After 10 h under reflux, the hot reaction mixture was filtered to remove precipitated Et_3NHBr, and the solvent was evaporated from the filtrate at 80°C under vacuum. The residue was taken up

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in chloroform (150 ml), washed with 10% aqueous HCl (2 × 40 ml) and dried over anhydrous potassium carbonate. To eliminate palladium and copper residues, diaminoethane (10 ml) was added and the solution was stirred at 60°C for 30 min, washed thoroughly with water and then dried over anhydrous potassium carbonate. The solvent was removed at 50°C under vacuum, and the crude product was purified in 10 g batches by flash chromatography on neutral alumina with dichloromethane (500 ml) followed by methanol (300 ml) as eluents. Removal of the solvent at 60°C under vacuum from the methanol fraction afforded the intermediate alkynyl tertiary alcohol **II**.

The protecting group was removed by heating under reflux a solution of **II** in toluene (150 ml) in the presence of powdered potassium hydroxide (4 g), the liberated acetone being distilled off. When acetone formation had ceased, the hot mixture was treated with activated charcoal (3 g) and then filtered. The filtrate was washed thoroughly with water, dried over anhydrous magnesium sulfate and the solvent was removed at 70°C under vacuum to afford the crude product. Purification by flash chromatography on neutral alumina (1/1 n-hexane/dichloromethane eluent) followed by recrystallization from methanol gave colourless crystals of pure **III** (yield 62%; m.p. 146–148°C). Found: C, 86.92; H, 6.09; Br, 0.086; O, 6.91; Pd, < 1 ppm; Cu, < 1 ppm. $C_{33}H_{28}O_2$ requires: C, 86.81; H, 6.18; O, 7.01.

I.r. (CsI) (cm^{-1}): 3300m, 3290m, 3040w(br), 2970m, 2920w, 2880w, 2870w, 2110vw, 1920vw(br), 1605m, 1580w, 1505s, 1465w, 1450m, 1410w, 1380m, 1360w, 1310w, 1295w, 1235s, 1180m, 1120w, 1105w, 1085vw, 1045m, 1020m, 875w, 860w, 830s, 770w, 650m, 590w, 580w, 560w, 530w, 510w. ^1H n.m.r. ($CDCl_3$, TMS standard) δ_H (ppm): 1.63 (6H, s, CH_3), 3.06 (2H, s, $C\equiv CH$), 5.03 (4H, s, OCH_2), 6.7–7.6 (16H, m, arom.). $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$, TMS standard) δ_C (ppm): 31.0 (C2), 41.7 (C1), 69.5 (C7), 77.3 (C13), 83.4 (C12), 114.2 (C5), 121.6 (C11), 127.1 (C9), 127.7 (C4), 132.8 (C10), 138.1 (C8), 143.5 (C3), 156.5 (C6). M.s. (70 eV), *m/e* 456 (M^+).

1,3-Bis[(4-bromophenoxy)methyl]benzene (*IV*)

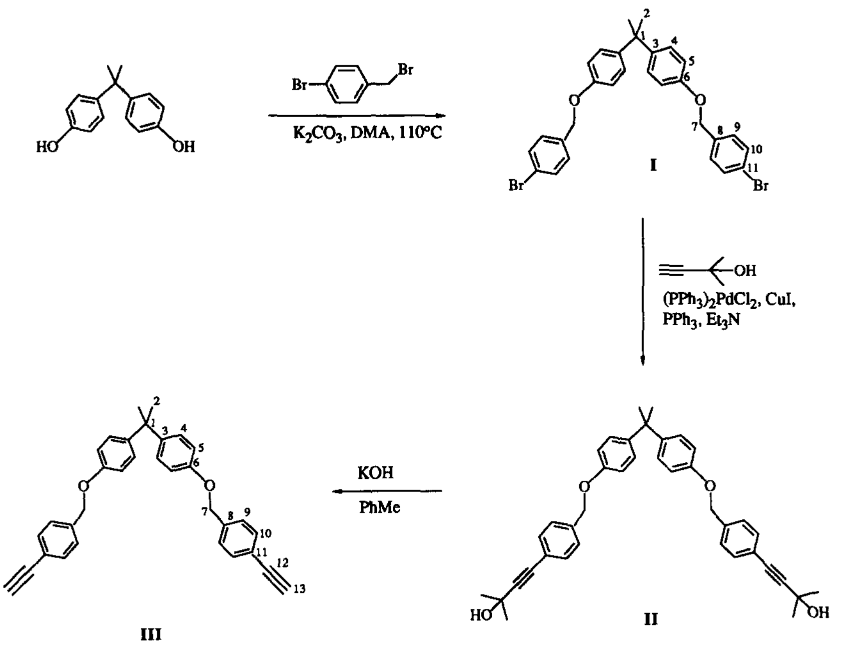
Using the same experimental procedure described above for **I**, **IV** was prepared from α,α′-dichloro-*m*-xylene (35 g, 0.2 mol), 4-bromophenol (70.9 g, 0.41 mol) and anhydrous potassium carbonate (82.8 g, 0.6 mol) in *N*,*N*-dimethylacetamide (500 ml). Dropwise addition of a solution of the crude product in dichloromethane (100 ml) to methanol (500 ml) precipitated colourless crystals of **IV**, which were filtered off and dried under vacuum at 70°C (yield 92%; m.p. 92–95°C). Found: C, 53.70; H, 3.60; Br, 35.10; O, 7.60. $C_{20}H_{16}Br_2O_2$ requires: C, 53.60; H, 3.60; Br, 35.66; O, 7.14.

I.r. (CsI) (cm^{-1}): 3090w, 3060w, 3030w, 2940w, 2870w, 1910vw, 1880vw, 1850vw, 1590m, 1575m, 1485s, 1465m, 1450w, 1430w, 1405w, 1385m, 1370m, 1300m, 1285s, 1240s(br), 1170m, 1115w, 1100w, 1070m, 1030m, 1010m, 1000m, 895m, 835s, 805m, 790s, 770w, 705s, 650s, 580vw, 560w, 505s, 480w, 430w. ^1H n.m.r. ($CDCl_3$, TMS standard) δ_H(ppm): 5.12 (4H, s, OCH_2), 6.8–7.6 (12H, m, arom.). $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$, TMS standard) δ_C (ppm): 70.0 (C5), 113.3 (C9), 116.7 (C7), 126.2 (C1), 127.0 (C4), 128.9 (C2), 132.3 (C8), 137.1 (C3), 157.8 (C6). M.s. (70 eV), *m/e* 448 (M^+).

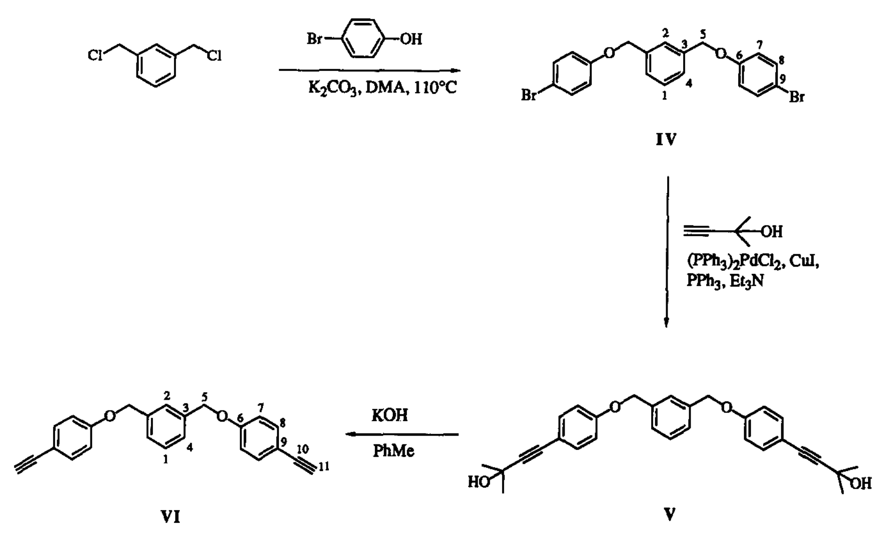
1,3-Bis[(4-ethynylphenoxy)methyl]benzene (*VI*)

By using the same experimental precedures as for the preparation of **III**, **IV** was converted into **V**, which afforded colourless crystals of **VI** (yield 65%; m.p. 102–104°C) following elimination of the acetone protecting group and purification by chromatography and recrystallization from methanol. Found: C, 84.91; H, 5.35; Br, 0.051; O, 9.69; Pd, < 1 ppm; Cu, < 1 ppm. $C_{24}H_{18}O_2$ requires: C, 85.18; H, 5.36; O, 9.46.

I.r. (CsI) (cm^{-1}): 3290s, 3090w, 3060w, 3030w, 2940w, 2870w, 2110w, 1880vw(br), 1605s, 1570m, 1505s, 1485m, 1460m, 1440w, 1410w, 1380m, 1360m, 1300m, 1285s, 1235s(br), 1170s, 1110m, 1090w, 1050m, 1020m, 1000m, 990m, 940w, 890m, 830s, 810m, 790m, 770m, 740m, 690m, 660m, 640m, 620m, 590m, 530s, 510w, 475w, 450m, 410w.



Scheme 1



Scheme 2

^{1}H n.m.r. ($CDCl_3$, TMS standard) δ_H (ppm): 2.98 (2H, s, $C\equiv CH$), 5.05 (4H, s, OCH_2), 6.7–7.6 (12H, m, arom.). $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$, TMS standard) δ_C (ppm): 69.8 (C5), 76.0 (C11), 83.6 (C10), 114.6 (C9), 114.9 (C7), 126.3 (C1), 127.1 (C4), 128.9 (C2), 133.6 (C8), 137.0 (C3), 159.0 (C6). M.s. (70 eV), *m/e* 338 (M^+).

RESULTS AND DISCUSSION

The two new ATMs 1,1′-(1-methylethylidene)bis[4-(4-ethynylphenyl)methoxy]benzene (**III**) and 1,3-bis[(4-ethynylphenoxy)methyl]benzene (**VI**) were prepared as shown in *Schemes 1* and *2*, respectively.

The first step in each case is a Williamson reaction with anhydrous potassium carbonate at 110°C in *N*,*N*-dimethylacetamide, giving the intermediate bromo-terminated compounds **I** and **IV**. Thus, reaction between bisphenol A and α,4-dibromotoluene afforded **I** in 80% yield after recrystallization. Likewise, 4-bromophenol was treated with α,α′-dichloro-*m*-xylene to give **IV** in 92% yield. To our knowledge neither compound has been reported previously, but the *para*-substituted isomer of **IV**, 1,4-bis[(4-bromophenoxy)methyl]benzene, has been claimed to be a useful fungicide and herbicide[5].

The bromo-terminated compounds **I** and **IV** were converted into the desired ATMs using the method developed by Sabourin[6]. Thus, the protected alkynyl tertiary alcohols **II** and **V** were prepared by treatment of **I** and **IV**, respectively, with 2-methyl-3-butyn-2-ol in refluxing triethylamine, the reaction being catalysed by bis(triphenylphosphine)palladium dichloride and copper(I) iodide together with triphenylphosphine. Copper and palladium catalyst residues present in **II** and **V** were reduced to <1 ppm by treatment with aqueous HCl followed by diaminoethane. Finally, the protecting group was removed by heating under reflux a solution in toluene in the presence of KOH, the acetone formed being distilled out. Purification of the crude compounds by flash chromatography followed by recrystallization from methanol gave **III** in 50% and **VI** in 60% overall yield. Elemental analysis showed both compounds to be essentially free of Br-terminated material.

The low melting point of **VI** (102–104°C), reflecting the *meta*-substitution at the central benzene ring, makes it suitable for catalysed cure studies. The relatively high melting point of **III** (146–1148°C) can be compared to that of the *meta*-substituted isomer 1,1′-(1-methylethylidene)bis[4-(3-ethynylphenyl)methoxy]benzene (102–104°C)[7].

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