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Synthesis of adamantyl and benzoxazole substituted poly(*m*-phenylene)s via the nickel catalysed coupling of aryl chlorides

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Poly(*m*-phenylene)s (PMP) with 1-adamantyl and 5-methyl-2-benzoaxozole or 2-benzoaxazole substituents *ortho* and *meta* to the backbone were synthesized via the nickel(0) catalysed dehalogenative coupling of aryl dichlorides. *Ortho* substituted polymers, which can have head-to-head and head-to-tail linkages, displayed better solubility in common organic solvents. The benzoxazole-containing PMPs exhibited excellent thermal stability in air by dynamic t.g.a. (thermogravimetric analysis) with values of 5% weight loss of 530–600°C while the adamantyl-substituted polymer showed a much lower thermal stability (5% weight loss at 370°C). All benzoxazole-functionalized polymers exhibited relatively high glass transition temperatures of 221–250°C. No glass transition was observed for the adamantyl-substituted PMP before the onset of decomposition at 350°C. Polymer number average molecular weights ranged from only 2000–4500 relative to polystyrene standards, indicating the need for further development of polymerization conditions. Copyright © 1996 Elsevier Science Ltd.

(Keywords: nickel catalysed; poly(*m*-phenylene)s; adamantyl; benzoxazole)

Introduction

Polyphenylenes are well known for their excellent thermal stability, with *para*-linked materials exhibiting rigid-rod properties. These polymers also display electrical conductivity and electroluminescence which may lead to the development of useful polymeric electrooptic devices[1,2]. Many polyphenylenes, especially the unsubstituted poly(*p*-phenylene), have proven difficult to synthesize due to lack of solubility of the polymer or difficulty in achieving the conversion necessary to develop high molecular weight[3]. Recently, nickel-catalysed aryl coupling reactions have been developed which allow the formation of polymers under mild conditions if the resulting polymers are amorphous and soluble in the polymerization solvent[4,5]. Coupling reactions using Ni(cod)$_2$ require equimolar amounts of this expensive, air-sensitive complex. Polymerizations conducted with the NiCl$_2$/Zn/triphenylphosphine system have the advantage of being catalytic in nickel complex which is regenerated *in situ*[6]. This coupling reaction has been shown to work well with aryl chlorides, bromides, triflates[7], and mesylates[8], and tolerates a wide variety of substituents. Little work has been reported on *meta*-linked polyphenylenes; we are aware of only two papers describing incorporation of *meta*-units. One deals with random *para*/*meta* copolymers[9] and the other reports several copolymers but only one example of a methyl ester substituted *meta*-phenylene homopolymer of low molecular weight[10].

The present report describes a series of all-*meta* polyphenylenes (PMP) obtained from 4- or 5-(2-benzoxazole)- and 5-(1-adamantyl)-substituted-1,3-dichlorobenzenes. The combination of the *meta*-linked phenylene backbone and pendant functional groups impart increased solubility while maintaining high thermal stability. Tailoring of the pendant functional groups will allow the synthesis of a broad range of thermally stable polymers with high glass transition temperature and useful properties.

Experimental

The structures of monomers **1–4** and synthesis results are summarized below. The corresponding polymer structures (**1a–4a**) are described in *Table 1* along with characterization results.

Synthesis of 1,3-dichloro-5-(1-adamantyl)benzene (1). 1-Bromoadamantane (10.0 g, 46.5 mmol) was dissolved in 1,3-dichlorobenzene (10.3 g, 70 mmol) in a 50 ml round-bottom flask. Aluminium chloride (0.2 g, 1.5 mmol) was added to the flask and the contents heated at 60°C for 24 h under nitrogen. The reaction mixture was poured into 150 ml of stirring methanol to precipitate the product and extract unreacted dichlorobenzene and bromoadamantane. The crude product was collected by filtration, dried, and sublimed at 130°C. The white crystalline mass composed of product **1** and a small amount of adamantane by-product was recrystallized from benzene/ethanol to give **1** as colourless crystals; mp 141–144°C; yield 67%; ^{13}C n.m.r. spectrum (75.469 MHz, CDCl$_3$) δ 28.7, 36.5, 42.9, 123.9, 125.6, 134.6, 154.8; Anal. Calcd. for $C_{16}H_{18}Cl_2$: 68.34; H, 6.45. Found: C, 68.37; H, 6.21.

Synthesis of 2-(3,5-dichlorophenyl)benzoxazole (2). 3,5-Dichlorobenzoic acid (10.0 g, 52.4 mmol) and 30 ml of thionyl chloride were combined in a 100 ml round-bottom flask. Five drops of DMF (*N,N*=dimethyl formamide) were added as catalyst and the reaction

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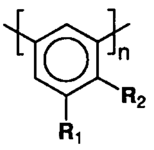
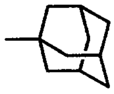
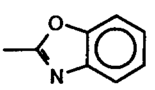
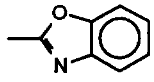
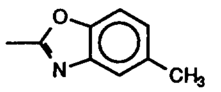
Table 1 Structures and results for adamantyl and benzoxazole substituted poly(*m*-phenylene)s



R_1	R_2	Polymer	M_n[a]	M_w/M_n	T_g (°C)[b]	T.g.a. 5% wt. loss in air (°C)[c]
	H	**1a**	2000	1.6	n.d.[d]	370
	H	**2a**	—[e]	—	250	600
H		**3a**	4500	1.9	229	570
H		**4a**	4400	1.6	221	530

[a] G.p.c. (gel permeation chromatography) values based on polystyrene standards in THF (tetrahydrofuran)

[b] T_g reported as inflection point on d.s.c. (differential scanning calorimetry) trace. Heating rate of 10°C min^{-1}

[c] Heating rate of 20°C min^{-1}

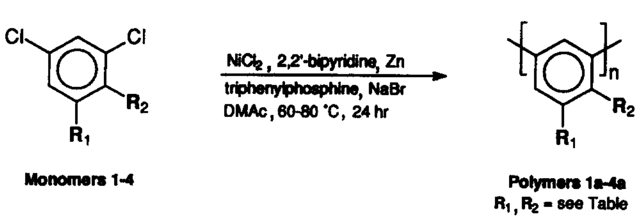
[d] No T_g observed up to onset of decomposition at 350°C

[e] Polymer insoluble in all solvents tested except concentrated sulfuric acid

mixture was stirred at 60°C for 2 h until a clear yellow solution formed. Excess thionyl chloride was removed from the 3,5-dichlorobenzoyl chloride by vacuum distillation. The acid chloride was cooled to 0°C in a ice-water bath. The resulting crystalline mass was dissolved in 15 ml of 1-methyl-2-pyrolidinone (NMP). To this solution was added pyridine (4.3 ml, 52.4 mmol). A solution of 2-aminophenol (5.71 g, 52.4 mmol) in 15 ml of NMP was added dropwise to the reaction flask over 30 min with stirring under nitrogen at 0°C. After stirring an additional 1 h at 0°C, 10 ml of toluene was added to the reaction mixture and the flask was fitted with a Dean–Stark trap. The flask contents were heated to reflux for 24 h with a heating mantle, and water removed by azeotropic trapping. The reaction mixture was allowed to cool to 80°C, then poured into 200 ml of stirring methanol. The resulting brown precipitate was collected by filtration, dried, and sublimed at 150°C to give a light-yellow crystalline solid. Recrystallization from benzene gave **2** as white needles; mp 137–138°C; yield 37%; ^{13}C n.m.r. spectrum (75.469 MHz, $CDCl_3$) δ 110.7, 120.4, 125.0, 125.7, 125.9, 129.7, 131.1, 135.7, 141.6, 150.7, 160.2; Anal. Calcd. for $C_{13}H_7Cl_2NO$: C, 59.12; H, 2.67; N, 5.30. Found: C, 59.07; H, 2.76; N, 5.37.

Synthesis of 2(2,4-dichlorophenyl)benzoxazole (3). To a 250 ml 3-neck round-bottom flask was added 85% *o*-phosphoric acid (83 g). The flask was immersed in a room temperature water bath. Phosphorous pentoxide (as P_2O_5) (57 g, 0.4 mol) was added to the mechanically stirred acid over 2 min. The heterogeneous mixture was stirred for 4 h at 60°C under nitrogen to form a viscous solution. 2-Aminophenol (11.5 g, 0.1 mol) was added to the reaction flask and stirred for 2 h at 60°C to form a dark-blue solution. 2,4-Dichlorobenzoic acid (20 g, 0.1 mol) was added to the flask with slow stirring. The reaction was heated at 110°C for 18 h to give a dark-green heterogeneous mixture. Phosphorous pentoxide (30 g, 0.21 mol) was added to the flask and the reaction mixture stirred for 24 h at 140°C. The dark-green homogeneous solution was cooled to 80°C and slowly poured into 1 l of rapidly stirring water. The resulting pink precipitate was washed three times with water, collected by filtration, dried, and sublimed at 150°C to give a white crystalline mass contaminated with a bright orange by-product. Column chromatography of the sublimed material (silica-gel, benzene eluent) and subsequent concentration of the product eluent fraction at elevated temperature and cooling gave white needle crystals of **3**; mp 130–132°C; yield 80%; ^{13}C n.m.r. spectrum (75.469 MHz, $CDCl_3$) δ 110.7, 120.5, 124.6, 124.8, 125.7, 127.3, 131.2, 132.4, 134.2, 137.4, 141.6, 150.4, 160.0; Anal. Calcd. for $C_{13}H_7Cl_2NO$: C, 59.12; H, 2.67; N, 5.30. Found: C, 59.28; H, 2.58; N, 5.33.

Synthesis of 5-methyl-2-(2,4-dichlorophenyl)benzoxazole (4). *Monomer* **4** was synthesized according to the procedure described for monomer **2**. The crude product was sublimed at 150°C to give a white crystalline mass contaminated with a highly coloured orange by-product. Column chromatography of the sublimed material (silica-gel, benzene eluent) and subsequent concentration of the eluent at elevated temperature and cooling gave white needle crystals of **4**; mp 128–130°C; yield 57%; ^{13}C



Scheme 1 Dehalogenative coupling polymerization of monomers 1–4

n.m.r. spectrum (75.469 MHz, $CDCl_3$) δ 110.0, 120.3, 124.8, 126.9, 127.3, 131.2, 132.4, 134.1, 134.6, 137.3, 141.8, 148.7, 160.0; Anal. Calcd. for $C_{14}H_9Cl_2NO$: C, 60.46; H, 3.26; N, 5.04. Found: C, 60.67; H, 3.09; N, 5.21.

General polymerization scheme. A typical polymerization (*Scheme 1*) consisted of reacting $NiCl_2$ (1 mol%), triphenylphosphine (0.5 eq), Zn powder (3 eq), NaBr (1 M), and 2,2′-bipyridine (1 mol%; this component is optional) in *N*,*N*-dimethylacetamide (DMAc) at 60°C under N_2. After *in situ* formation of the reddish-brown catalyst solution was achieved (*ca.* 30 min), monomer was added and allowed to react for 24 h at 60–80°C to give the corresponding polymer (*Table 1*). The adamantyl-substituted monomer was polymerized in a mixture of DMAc/THF in order to better solubilize the resulting all-hydrocarbon polymer. The heterogeneous polymerization mixtures were filtered to remove excess zinc and then precipitated into methanol. The solid was washed with HCl/methanol to remove unreacted zinc and organic impurities and washed with water to remove salts. Moderate to high yields of polymer were obtained upon vacuum drying.

Results and discussion

Monomers. A variety of adamantane derivatives have been reported over the years, including phenyl and chlorophenyl derivatives made via Friedel–Crafts alkylation[11]. Similarly, benzoxazole monomers and polymers can be obtained using poly(phosphoric acid)[12] or reaction of *o*-aminophenols with acid chlorides followed by *in situ* cyclization[13]. We followed these methods in synthesizing the new compounds described here.

Gas chromatographic analysis of monomer **1**, produced by the Friedel–Crafts alkylation of 1,3-dichlorobenzene with 1-bromoadamantane, revealed 96% *meta* alkylation (regiochemistry confirmed by n.m.r.) with the remaining 4% *ortho* to one of the chlorines. Product yield of monomer **3** from the polyphosphoric acid (PPA) reaction was much higher than the yields of monomers **2** and **4** obtained using NMP. The PPA route also obviated the need to synthesize the intermediate acid chloride. Correct spectral and elemental analysis results were obtained for all monomers (see Experimental).

Polymers. The adamantyl-substituted PMP (polymer **1a**) precipitated from the DMAc/THF solvent mixture during polymerization, but showed good solubility in pure THF and chloroform. Poor solubility of **1a** in polar aprotic solvents is attributed to the all-hydrocarbon nature of the polymer as no crystallinity (that would limit solubility) was evident by d.s.c. Analysis of polymer **1a** by ^{13}C n.m.r. indicated a significant degree of polymerization as evidenced by the peak at 141 ppm (trace b, *Figure 1*) characteristic of the quaternary carbons of the PMP backbone. The quaternary carbons *ipso* to the chlorines in monomer **1** (trace a, *Figure 1*) at 134 ppm are not evident in the spectrum of the polymer.

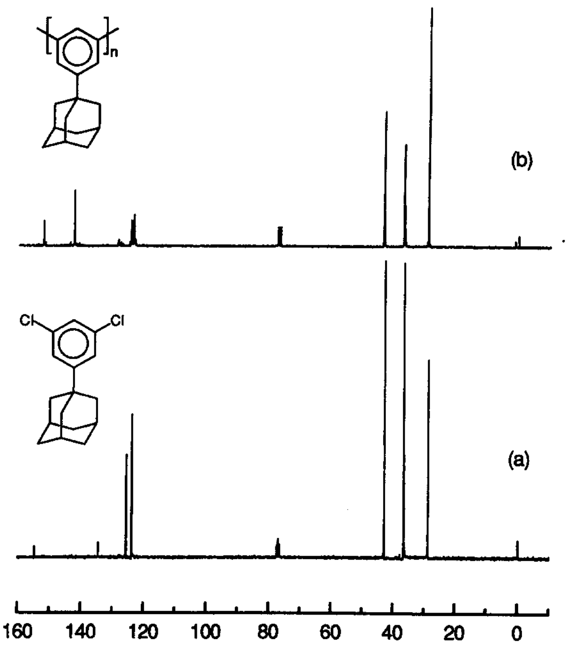


Figure 1 ^{13}C n.m.r. of (a) 1,3-dichloro-5-(1-adamantyl)benzene monomer **1** and (b) adamantyl-substituted poly(*m*-phenylene) **1a**

Polymer **2a** also precipitated during polymerization in DMAc. Observation of a crystalline melting transition at 320°C by d.s.c. is presumably due to solvent induced crystallization since it is not seen on re-scans of melted samples. Once precipitated from the reaction mixture, **2a** was only soluble in concentrated sulfuric acid, consistent with crystallinity inhibiting solvation. Benzoxazole-containing polymers **3a** and **4a** remained in solution during polymerization and displayed good solubility in chloroform and THF, presumably due to occasional head-to-head rather than head-to-tail linkages which give a more random structure to the polymers; no crystallinity was apparent by d.s.c.

Glass transition temperatures for the pendant benzoxazole PMPs **2a–4a** ranged from 221 to 250°C. No T_g was observed for the pendant adamantyl PMP before the onset of decomposition at 350°C. Thermal stability (t.g.a.) in air was also much lower for this aliphatic-containing polymer which displayed a 5% weight loss at 370°C. Thermal stabilities for the pendant benzoxazole polymers **2a–4a** were much higher, ranging from 530 to 600°C in both air and nitrogen.

The adamantyl-substituted PMP (**1a**) possessed a number average molecular weight, relative to polystyrene standards, of 2000. The low molecular weight of **1a** is attributed to precipitation of the polymer during synthesis, and further work is underway involving polymerization in THF. The soluble, pendant-benzoxazole polymers **3a** and **4a** showed molecular weights of 4500 and 4400, respectively. It is known that reductive chlorine elimination from aryl chlorides can occur during nickel coupling reactions, effectively end-capping the polymers. In fact, deliberate addition of proton sources to the reaction is an effective means of reducing aryl halides to the corresponding arenes[5]. Low molecular weights for the soluble benzoxazole-containing polymers may also be due to metal–ligand aryl exchange reactions that have been shown to occur with palladium–triphenylphosphine complex mediated couplings[14]. Aryl transfer from the catalyst complex to the growing polymer would serve much the same purpose as reduction to the arene, in that further chain extension would be prohibited. This aryl transfer may be expected to occur in the nickel–triphenylphosphine mediated coupling reactions as well. We are investigating changes in solvent, temperature and catalyst ligands that we hope will allow formation of higher molecular weight polymer. It is clear from these preliminary results, however, that polymerization of *m*-dichlorosubstituted aromatics is facile and gives as high molecular weights as for *p*-dichloro derivatives, although routine formation of commercially useful molecular weights is not yet possible. This approach does make available several families of new polymers from commercially available or easily synthesized starting materials that are of interest for a number of applications as high performance, thermally stable materials.

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