Synthesis and characterization of pendantly amine functionalized poly(arylene ether sulfone)

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The synthesis of new pendantly functionalized polyaromatic thermoplastics using pre-functionalized monomers is reported. These will have potential applications as either toughening agents in thermosetting resins or, with the incorporation of crosslinking moieties, as matrices in their own right.

(Keywords: pendant; amine functionalization; poly(arylene ether sulfone))

Introduction

Much recent work has been directed towards the synthesis and development of functionalized polyaromatic thermoplastics, both as potential toughening agents for thermosetting resins and as high performance composites using the functionality to achieve crosslinking or chain extension[1,2]. One approach towards the incorporation of pendant functionalization involves the post-functionalization of polymers such as the modified poly(ether sulfone)s. However, this approach sometimes requires quite severe chemical conditions which may lead to polymer degradation. An alternative approach involves the preparation of pre-functionalized monomers and their subsequent polymerization. The polymers obtained would have potential applications as either toughening agents in thermosetting resins or with the incorporation of crosslinking moieties as matrices in their own right[3].

This work has established successful synthetic routes to a functionalized monomer compatible with poly(ether sulfone)-type chemistry; this has been purified and fully characterized. Reaction profiles have been developed and optimized so as to achieve the polymerization of this monomer unit without the loss of the desired pendant functionalization during the polymerization.

Results and discussion

Monomer **3** (*Scheme 1*) was obtained by the reaction of difluoronitrobenzene and potassium xanthate and successive oxidation of the sulfur functionality by the use of chromic anhydride, followed by reduction of the nitrate groups.

The polymer synthesis is based on the reaction of 4,4′-difluoro-2,2′-diaminodiphenylsulfone ($DFDASO_2$) with bisphenol S (Bis S) and 4,4′-difluorodiphenylsulfone (DFDPS), with the aim of producing polymers comprising the repeat unit shown in *Formula 1*. As a control experiment, the reaction of DFDPS with Bis S was also carried out. The analytical data on the obtained materials indicated the presence of hyroxy-ended polymer with degradation of the pendant amino groups starting at 285°C.

As a consequence of the previous experiment, a 5% excess of the fluoro-monomers was used to ensure fluoro-group termination in the resultant polymer and a maximum temperature of 265°C was maintained. The d.s.c. and g.p.c. results pertaining to each pendantly (amine) functionalized polymer are reported in *Table 1*.

The control experiment involving DFDPS and Bis S produced a polymer of high molecular weight. However, the calculated value of the number average molecular weight suggested that branching could be taking place along the polymer backbone. For the functionalized systems, the relationship between M_w and M_n correlated well for a linear polymer.

^1H and ^{13}C n.m.r. confirmed the presence of amine groups both ‘in-chain’ and at the chain ends giving rise to a fluorine-terminated polymer.

After establishing ‘in-chain’ functionalization, a further aim of the work will be the introduction of chemical crosslinks into the polymer backbone by the conversion of the amine groups into maleimide functionalities which, under thermal conditions, could crosslink with themselves to produce a crosslinked thermoplastic varying in degrees of crosslink density depending upon the initial level of ‘in-chain’ functionalization.

Experimental

Synthesis of monomer 3 (Scheme 1). Into a 100 ml conical flask equipped with a magnetic stirrer and reflux condenser were placed 15.9 g (0.1 mol) of 2,5-difluoronitrobenzene, 16 g (0.1 mol) of potassium xanthate and 50 ml of 95% ethanol. The mixture was heated under reflux for 24 h. The product, which precipitated from solution during the course of the reaction, was collected by filtration under vacuum, washed twice with hot ethanol and once with hot water and dried under vacuum to afford 12.8 g (83%) of 4,4′-2,2′-difluorodinitrodiphenylsulfur (**1**) as yellow crytals, m.p. 159–160°C. ^1H n.m.r. ($CDCl_3$): δ 7.26 (2H, d); δ 7.34 (2H, d); δ 7.86 (2H, dd). Mass spectrum: m/z 312 M^+.

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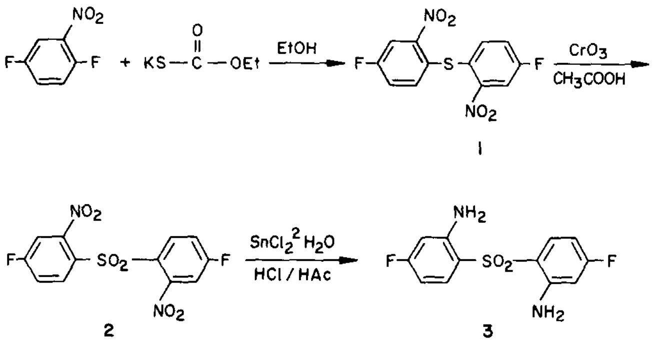
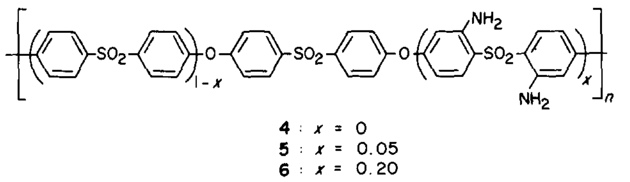


Scheme 1



Formula 1

Table 1 Data obtained from d.s.c. and g.p.c. for polymers **4**–**6**

Polymer	T_g (°C)	M_w	M_n
4	229	80400	21900
5	224	32000	13600
6	221	25400	9630

Into a 250 ml conical flask equipped with a magnetic stirrer were placed 100 ml of acetic acid, 5 g (0.016 mol) of **1** and 7.5 g of chromic anhydride. A mixture of sulfuric acid (3 ml) and water (7 ml) was added. The brown mixture was allowed to reflux overnight and then poured onto crushed ice. A solid was collected by filtration and dried under vacuum to afford 5 g (91%) of 4,4′-difluoro-2,2′-dinitrodiphenylsulfone (**2**) as white powder, m.p. 146–148°C. ^{1}H n.m.r. ($CDCl_3$): δ 7.46–7.74 (4H, m); δ 8.48 (2H, dd). Mass spectrum: m/z 344 M^+.

A hot solution (200 ml) of **2** (4 g, 0.012 mol) in acetic acid was added to 17.32 g tin dichloride dihydrate dissolved in 6.4 ml of hydrochloric acid. The mixture was heated under reflux for 30 min, poured onto crushed ice and then into a cold 10% KOH solution (2 l) maintaining pH > 10.

The slurry was extracted with dichloromethane. The organic layer was washed with water, dried over Na_2SO_4, and rotoevaporated. The crude product was purified by silica gel column chromatography using dichloromethane as eluent, to afford 1.4 g (43%) of 4,4′-difluoro-2,2′-diaminodiphenylsulfone ($DFDASO_2$) (**3**) as white crystals, m.p. 127–129°C. ^{1}H n.m.r. ($CDCl_3$): δ 5.17 (4H, bs); δ 6.27–6.60 (4H, m); δ 7.75 (2H, dd). Mass spectrum: m/z 284 M^+.

Polymerization of DFDPS with Bis S (**4**). As a control experiment, the reaction of DFDPS with Bis S was carried out following known procedures[4]. The adopted profile was: DFDPS (6.42 g, 0.02525 mol) and diphenylsulfone (DPS) (29.97 g) were charged to a 250 cm^3 round-bottomed flask equipped with N_2 inlet, mechanical stirrer, thermocouple and condensation apparatus. The mixture was heated to ~120°C and K_2CO_3 (3.46 g, 0.025 mol) was added with subsequent addition of Bis S (6.26 g, 0.025 mol) over a period of 15 min. A series of temperature increases was then applied with temperature holds at 140°C for 60 min, 185°C for 60 min, 225°C for 60 min, 265°C for 60 min and 285°C for 60 min.

The toffee-like polymer was discharged, allowed to solidify, then leached using 100 ml of a 4:1 mixture of methanol:acetone and subsequently water.

Polymerization of DFDPS with $DFDASO_2$ and Bis S (**5**). DFDPS (6.099 g, 0.0239 mol), $DFDASO_2$ (0.359 g, 0.00126 mol) and DPS (30.03 g) were charged as described above. After the addition of K_2CO_3 (3.455 g, 0.025 mol) and Bis S (6.256 g, 0.025 mol), a temperature profile identical to that in the previous experiment was adopted. Samples were taken at each of the temperature holds; those taken at 185 and 225°C were soluble in the leaching solvent; those taken at 265 and 285°C yielded cream-coloured powders after leaching.

Elemental analysis ($C_{24}H_{16.1}O_6N_{0.1}S_2$). Calculated: C, 61.86%; H, 3.48%; N, 0.30%. Found: C, 61.34%; H, 3.45%; N, 0.16%.

The ^{1}H n.m.r. spectrum in dimethylsulfoxide gave: δ 6.59 (1H, dd); δ 6.71 (1H, dd); δ 7.83 (1H, dd); δ 6.15 (2H, s). The ^{13}C n.m.r. spectrum further evidenced the presence of the amino groups by 149 ppm quaternary carbon adjacent to amine.

Polymer **6** was synthesized using the above procedure. Elemental analysis for polymer **6** ($C_{24}H_{16.4}O_6N_{0.4}S_2$). Calculated: C, 61.26%; H, 3.51%; N, 1.19%. Found: C, 60.60%; H, 3.55%; N, 1.03%.

Differential scanning calorimetry. The scans were carried out in a Mettler DSC 20 at a rate of 20°C min^{-1}. The procedure was as follows: heating; holding for 2 min; cooling; reheating on a sample that was dried at 80°C in a vacuum oven.

The glass transition temperature can thus be located with the onset and the middle-point.

Gel permeation chromatography. G.p.c. analysis was used to determine both M_n and M_w, and to obtain the differential weight fraction curves. Polystyrene was used as a calibration.

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