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Anhydride-Containing Polysulfones Derived from a Novel A_2X-Type Monomer

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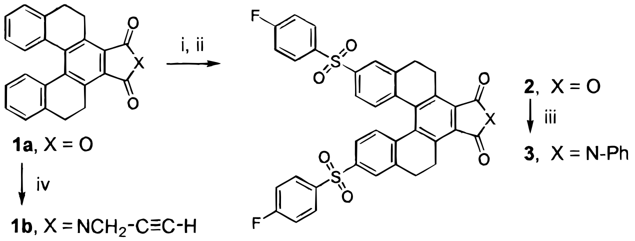
The good chemical resistance, high tensile strength, and thermal and hydrolytic stability of polysulfones have rendered this class of materials, such as Udel resin, successful in many applications.[1] To further tailor the properties of polysulfones for more specific applications, a reactive functional group is often required and introduced, through which polymer transformations such as grafting and cross-linking could be performed. The carboxylated polysulfones[2] and nitrated polysulfones[3] were previously prepared through electrophilic substitution reactions on the parent polysulfones. This route often results in polymer degradation, with the exception of the amination of lithiated polysulfones using azides and other electrophilic NH_2 synthons.[3] There have been few examples of the preparation of functionalized polysulfones through a polycondensation process. The direct polycondensation of sulfonated 4-chlorophenyl sulfone with 4,4′-isopropylidenediphenol (BPA)[4] and of bis(4-fluorophenyl)-3-aminophenylphosphineoxide with BPA[5] produced polysulfones containing the sulfonic acid and amino groups, respectively.

Anhydride groups are useful as reactive sites along polymer main chains or at chain ends because they can react with many types of molecules such as amines, alcohols, and epoxides. Anhydride-containing polysulfones may also have additional characteristics such as an enhanced adhesion property for potential applications as reactive polymer modifiers, compatibilizers, and coupling agents to reduce the interfacial tension between the inorganic fillers and the polymer. However, a direct introduction of the anhydride group into a polysulfone is difficult, whereas nucleophilic and electrophilic polycondensations using anhydride-containing monomers are also troublesome due to involvement of the reactive anhydride group during polymerization. Accordingly, the *N*-phenylimido group, which is chemically inert under polycondensation conditions, has been used as a latent anhydride group and introduced into polysulfones by nucleophilic polycondensation of an appropriately functionalized bisphenol.[6] The imide group in the polymer could undergo a facile transimidization at elevated temperatures with hydrazine and amino acids to afford polysulfones containing reactive amine and acid groups.[6] A simple, high-yield conversion of the *N*-phenylimido group to an anhydride group in a polysulfone by a saponification process seems desirable but has not been found in the literature.

Compound **1a** (5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride) contains an anhydride group and has been derivatized to an AB-type amino-anhydride monomer and AA-type diamines for the preparation of a series of novel polyimides.[7] With proper substitutions on the two benzene rings in compound **1a**, a novel A_2X-type dihalide monomer can be realized, where X represents the anhydride or its imide precursor and A corresponds to the fluorine. The use of an A_2X-type dihalide as a monomer in a polycondensation should offer a route to a variety of anhydride-containing polysulfones from the breadth of commercially available bisphenols. In this paper, the synthesis and polymerization of the novel difluoride monomer **3** and its polymer transformation to yield the corresponding anhydride-containing polysulfones are reported.

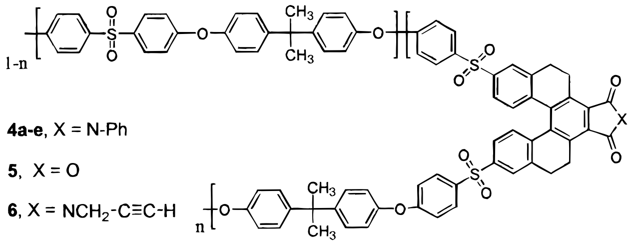
Scheme 1. Syntheses of Monomer 3 and Model Compound 1b



Reagents and solvents: i, $HClSO_3$, CH_2Cl_2; ii, $AlCl_3$, fluorobenzene, nitrobenzene; iii, aniline, DMAc; iv, propargylamine, DMAc.

The synthesis of monomer **3** was accomplished in three steps from compound **1a** (Scheme 1). Chlorosulfonation of compound **1a** using chlorosulfonic acid gave the corresponding bischlorosulfonyl derivative,[8] which then reacted with fluorobenzene in the presence of aluminum chloride to afford the difluoro-anhydride **2** in good yield.[9] The imidization of **2** with aniline gave monomer **3**, which appeared to be noncrystalline and showed a glass transition at 141 °C by differential scanning calorimetry (DSC).[10]

Polycondensation of **3** was accomplished using a recently reported process which involves the use of cesium carbonate as a base and magnesium hydroxide to aid in the removal of displaced fluoride.[11] A series of copolymers **4a**−**d** and homopolymer **4e** were prepared through the polycondensation of **3** with 4-fluorophenyl sulfone and BPA. All polymers were isolated as yellow amorphous powders.



Incorporation of monomer **3** into polysulfones **4** was confirmed by IR, ^1H NMR and UV/vis spectroscopic methods. All polymers displayed carbonyl peaks due to the *N*-phenyl imide at 1770 and 1710 cm^{-1} in their IR spectra, which corresponded exactly to those of monomer **3**. The ^1H NMR spectra of polysulfones **4** showed the presence of the ethylene protons from **3** at 2.5, 3.0, and 4.2 ppm and the methyl protons from BPA at 1.69 ppm, further indicating the incorporation of **3**. To quantify the content of **3** incorporated into copoly-

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Table 1. Characterization of Polysulfones Derived from Difluoride 3

polymer	**3** in feed[a] (mol %)	**3** in polymer[b] (mol %)	T_g[c] (°C)	T_d[d] (°C)	M_w[e]	M_n[e]	M_w/M_n	η_{inh}[f] (dL/g)
4a	5	4.9	200	500	126 000	54 000	2.33	0.64
4b	20	16	213	436	33 800	16 900	2.00	0.35
4c	35	29	231	469	21 700	11 400	1.90	0.33
4d	50	42	251	408	19 300	9 900	1.95	0.33
4e	100	100	290	433	18 800	12 600	1.50	0.19

[a] Mole fraction of **3** used in feed. [b] Mole fraction of **3** incorporated in the polymer, as determined from the UV/vis calibration curve. [c] From DSC analysis under nitrogen at a heating rate of 10 °C/min. [d] Onset temperature for 5% weight loss, as assessed by TGA under nitrogen at 10 °C/min. [e] Measured by GPC relative to polystyrene standards. [f] Inherent viscosity in $CHCl_3$ at 25 ± 0.1 °C (0.5 g/dL).

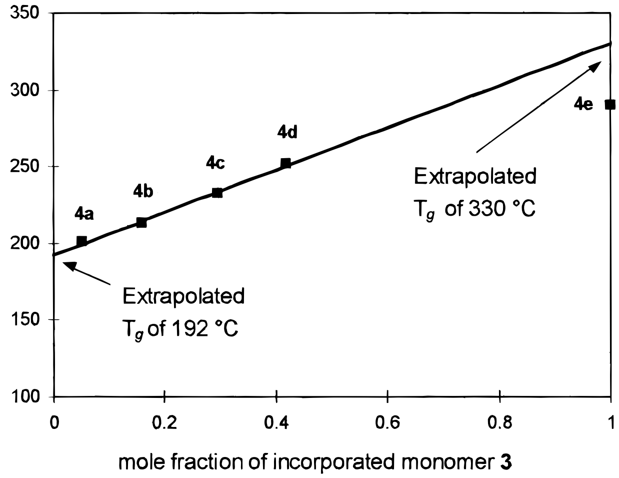

Figure 1. T_g value versus mole fraction of monomer **3** incorporated in a polysulfone.

mers **4**, UV/vis spectroscopy was used to construct a Beer–Lambert calibration curve of absorbency versus monomer concentration. From this calibration curve, the mole fraction of monomer **3** in copolymers **4** was determined to be in the range 4.9–42% (Table 1). A linear relationship between the mole percentage of incorporated **3** and the measured glass transition temperature (T_g) of copolymers **4** was found (Figure 1). The T_g values of polysulfones **4a**–**d** ranged from 200 to 251 °C (Table 1). It was apparent that the increase in chain rigidity of the resulting polymers due to the presence of the rigid tetrahydro[5]helicene moiety has a significant effect on T_g. The higher the content of **3** in the polymer, the higher the T_g of the polymer. With a measured T_g of 290 °C, homopolymer **4e** is an anomaly to this linear relationship. However, the higher molecular weight **4e** would have a very high T_g, close to 330 °C, as extrapolated from the graph in Figure 1. Furthermore, the extrapolated T_g of 192 °C for the parent polysulfone falls in the range of reported T_g values (184–195 °C).[12]

Gel permeation chromatography (GPC) measurements, relative to polystyrene standards, showed a decrease in molecular weight as the content of **3** increased in polysulfones. Due to the U-shape molecular structure of **3**, the hydrodynamic volume of the polymers becomes increasingly smaller and subsequently retention times become longer. The measured inherent viscosity values of polysulfones **4a**–**e** exhibited a similar trend. Polysulfone **4e** had a much lower viscosity (0.19 dL/g) than copolymers **4a**–**d** (0.64–0.33 dL/g). Attributed to the molecular structure of monomer **3**, the apparent molecular weights of all polymers **4a**–**e** should be lower than the actual values.

The actual molecular weight could be determined from end-capped polysulfones. The same copolymerization of **4b** was performed in the presence of 1 mol % excess of 4-fluorophenyl sulfone and 2 mol % of 3,5-di-*tert*-butylphenol relative to BPA. The resulting end-capped polysulfone had a T_g of 212 °C, similar to that (213 °C) of the copolymer **4b**, but had a slightly lower inherent viscosity (0.28 dL/g) and a lower molecular weight (M_n 14 700) by GPC. From the ^1H NMR spectrum of the end-capped polysulfone, the actual number-average molecular weight was calculated to be 45 300 using the ratio of the integrals of the methyl peak of BPA and the *tert*-butyl peak of the end groups, which is higher than the one determined by GPC. By comparing with a viscosity of 0.35 dL/g and an apparent number-average molecular weight of 16 900 for polymer **4b**, all polysulfones containing the U-shape-like tetrahydro[5]helicene unit should therefore have much higher molecular weights than their apparent molecular weights determined by GPC.

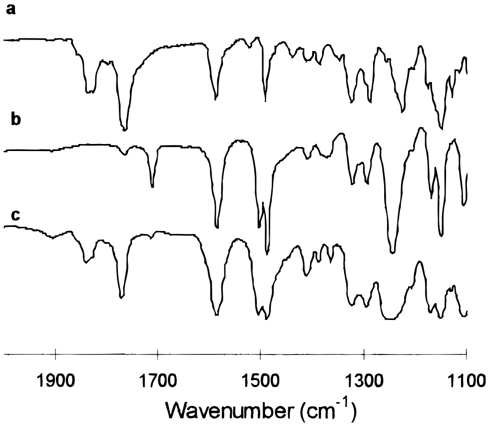

Figure 2. IR spectra (1100–1950 cm^{-1}) of (a) anhydride **2**, (b) imide polymer **4b**, and (c) anhydride polymer **5**.

When the parent polysulfone was subjected to the treatment of ethanolic potassium hydroxide in DMAc at 100 °C, polymer chain degradation occurred within 0.5 h by GPC analysis. Without DMAc, a suspension of the polysulfone in ethanol was treated with KOH under the same temperature and no degradation was detected over a long period of time. The testing results imply that transformation of the phenylimido group into an anhydride group in a polysulfone should be done under heterogeneous base hydrolysis conditions. Thus, the treatment of **4b** as a fine suspension in ethanolic potassium hydroxide at 70 °C within 30 min led to a complete hydrolysis of the imide group.[13] No polymer degradation was apparent by GPC analysis. For comparison, the IR spectrum of anhydride polymer **5** is shown together with those of anhydride **2** and the precursor imide polymer **4b** (Figure 2). The disappearance of the carbonyl stretch of the imide functionality at 1710 and 1767 cm^{-1} and the appearance of the characteristic carbonyl stretch of the anhydride moiety at 1837 and 1767 cm^{-1} indicate clearly the successful transformation of the imide group to an anhydride

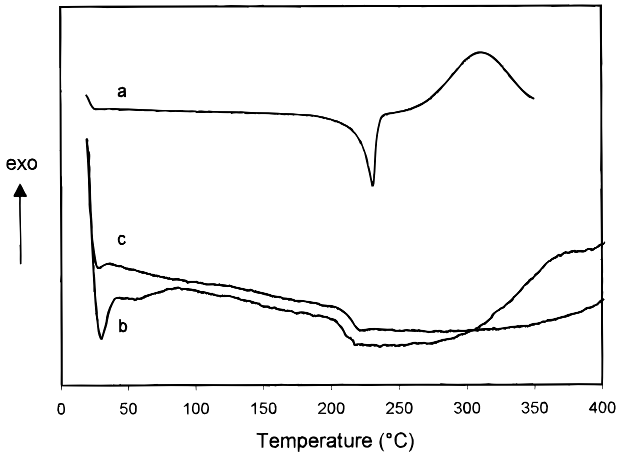

Figure 3. DSC traces of (a) compound **1b** and polysulfone **6**: first scan (trace b) and second scan (trace c) at a heating rate of 10 °C/min in nitrogen.

functionality. The thermal properties of anhydride containing polysulfone **5** remained unchanged, having a T_d of 410 °C and a T_g of 210 °C.

To demonstrate the accessibility of the anhydride group, a cross-linking experiment was performed using propargylamine. The model propargylimide **1b** was prepared,[14] which underwent an exothermic reaction at 311 °C, as indicated by DSC (Figure 3, trace a). The anhydride-containing copolymer **4b** was converted to the corresponding propargylimide **6** under the same conditions as for the preparation of the model compound and was thermally cross-linked. DSC study of polymer **6** indicated that an exothermic cross-linking occurred at about 300 °C (Figure 3, trace b). In the subsequent scan, there was no exothermic peak (Figure 3, trace c), implying the completion of cross-linking. The cross-linked copolymer was no longer soluble but swelled in conventional solvents (e.g., chloroform) and had a slightly increased T_g.

In conclusion, the incorporation of a latent anhydride group into the polysulfone main chain, subsequent functional group transformation, and polymer cross-linking have been successfully demonstrated.

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(9) In a flame-dried, 250 mL, three-necked flask equipped with a condenser, a nitrogen inlet/outlet, and a magnetic stirrer was dissolved the sulfonyl chloride[8] (12.0 g, 21.9 mmol), derived from the chlorosulfonation of compound **1**, in nitrobenzene (65 mL) upon heating. To the above cooled red solution were added anhydrous $AlCl_3$ (14.5 g, 109 mmol) and fluorobenzene (42.0 g, 438 mmol), resulting in a dark purplish/black mixture. The mixture was heated to 135 °C for 3.5 h. The solution was cooled to room temperature and then added to an aqueous HCl solution (10% v/v, 250 mL). After they were stirred vigorously for 18 h, the layers were partitioned and the aqueous layer was extracted once with methylene chloride (25 mL). The organic phases were combined and concentrated to give a solution containing the product and nitrobenzene. The product was precipitated into aqueous methanol (90%, 1 L). The solid was collected on a sintered glass filter funnel, dissolved in acetone, and again precipitated into aqueous methanol (90%) to remove any residual nitrobenzene. The pale yellow solid **2** was collected and used without further purification: 9.2 g (63%); T_m 303 °C (DSC); ^{1}H NMR (400 MHz, $CDCl_3$) 8.00 (q, 2H), 7.90 (s, 1H), 7.47 (d, 1H), 7.24 (t, 2H), 7.16 (d, 1H), 4.00 (d, 2H), 2.90–3.10 (M, 4H), 2.55 (M, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.98, 164.43, 162.34, 141.87, 140.89, 140.54, 139.68, 137.07, 137.02, 136.99, 131.02, 130.78, 130.69, 127.31, 126.87, 125.25, 116.96, 116.74, 28.08, 23.89; ^{19}F NMR (300 MHz, $CDCl_3$) 27.30 (relative to trifluoroacetic acid); IR (KBr) 1837 and 1769 cm^{-1} (C=O, anhydride); MS (FAB, *m/e*, relative intensity %) 669 (M + H$^+$, 32.4).

(10) In a 50 mL, two-necked, round-bottomed flask fitted with a nitrogen inlet/outlet and a Dean–Stark trap was dissolved anhydride **2** (4.0 g, 6.0 mmol) in DMAc (25 mL) and chlorobenzene (10 mL) under nitrogen. Aniline (0.8 mL, 9.0 mmol) was then added. The solution was stirred at room temperature for 30 min and heated to reflux overnight. More chlorobenzene was added (30 mL) to azeotropically distill off water. The reaction solution was poured into acidic ethanol (5 mL HCl/100 mL). The resulting solids were dissolved in chloroform (10 mL), passed through a short column packed with silica gel (10 g), and eluted with chloroform (100 mL). After removal of chloroform and drying at 70 °C under vacuum (5 mmHg) for 24 h, monomer **3** was obtained as a beige, amorphous powder: 3.3 g (74%); T_g 141 °C (DSC); ^{1}H NMR (400 MHz, $CDCl_3$) 8.00 (q, 4H), 7.89 (s, 2H), 7.53–7.38 (m, 7H), 7.26–7.16 (m, 6H), 4.20 (d, 2H), 2.90–3.10 (m, 4H), 2.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 167.10, 166.94, 164.39, 141.18, 140.64, 139.37, 138.19, 137.74, 137.14, 131.46, 131.04, 130.77, 130.67, 129.16, 128.31, 127.19, 127.12, 126.72, 125.10, 116.94, 116.72, 28.47, 23.71; ^{19}F NMR (300 MHz, $CDCl_3$) 27.58 (relative to trifluoroacetic acid); IR (KBr) 1764 and 1710 (C=O, imide) cm^{-1}; MS (FAB, *m/e*, relative intensity %) 744 (M + H$^+$, 100.0).

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(13) A chloroform solution of **4b** (150 mg/10 mL) was added into ethanolic potassium hydroxide solution (1 pellet of KOH/35 mL) to form a fine suspension. The suspension was heated to 70 °C for 30 min with stirring and the hydrolysis was monitored by IR. After it was cooled to ambient temperature, the suspension was acidified with concentrated HCl. The resulting polymer was collected by filtration, redissolved in $CHCl_3$, filtered through a pad of Celite to remove inorganic salts, and precipitated into ethanol. Polymer **5** was subjected to heating at 185 °C under high vacuum for 14 h, to ensure a complete formation of the anhydride.

(14) The same procedure as ref 10 was employed with the following exceptions: **1a** (0.500 g, 1.42 mmol), propargylamine (0.086 g, 1.56 mmol), DMAc (5 mL), chlorobenzene (5 mL), and an additional 5 mL of chlorobenzene after 18 h. Compound **1b** was obtained as a yellow amorphous powder: 0.464 g (84%); mp 231 °C (DSC); ^{1}H NMR (200 MHz, $CDCl_3$) 7.32–6.90 (m, 8H), 4.43 (s, 2H), 4.1 (d, 2H), 2.85–2.92 (m, 4H), 2.55 (m, 2H), 2.21 (s, 1H); IR (KBr) 1758 and 1713 (C=O, imide) cm^{-1}; MS (EI, *m/e*, relative intensity %) 389 (M$^+$, 90.0).

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