Amino-Functionalized Poly(arylene ether ketone)s

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ABSTRACT: Amino-functionalized poly(arylene ether ketone)s have been synthesized by nucleophilic aromatic substitution from isomeric amino-functionalized monomers and Bisphenol A. The polymerizations have been found to proceed without any side reactions. The polymers were characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy and gel permeation chromatography. The glass transition temperatures and thermal stabilities of the isomeric polymers have been determined by differential scanning calorimetry and thermogravimetry. A strong dependence of the glass transition temperature on the position of the amino function in the polymer backbone was observed. This could be explained by inter- or intramolecular hydrogen bonding. Owing to the good reactivity of the amine groups, those polymers will then allow further modifications and easily lead, for example, to amide formation or to the grafting of various molecules.

Introduction

Poly(arylene ether)s are high-performance engineering thermoplastics, widely used in electronic, electric, aircraft, and aerospace industries.[1] At first, considerable effort was made to modify their chemical structure, essentially in order to improve their thermal properties. In the last few years, more attention was paid to their functionalization.[2−5] This could be achieved either by chemical modification of the polymer or by direct synthesis using functionalized monomers. Aldehyde and carboxylic acid functionalized poly(arylene ether ketone)s, for example, were obtained by chemical modification of methyl-substituted polymer, synthesized using methylhydroquinone as one of the comonomers. The methyl-functionalized polymer obtained was later converted into the corresponding bromomethyl derivative and further transformation led to aldehyde and carboxylic acid functionalized polymers.[2,3] Recently, the synthesis of amino-functionalized polysulfones by transformation of commercially available polymers was reported.[4,5] However, postfunctionalization of a polymer is often difficult to control and can sometimes lead to its degradation. The reduction of nitro-substituted poly(ether sulfone)s to give aminated polymers, for example, did not proceed as expected, reduction often being incomplete or leading to side reactions.[6] Also, the nitration of poly(ether sulfone) showed the occurrence of chain scission, as indicated by a reduction in inherent viscosity. In the case of poly(arylene ether ketone)s, a reduction in inherent viscosity upon sulfonation using chlorosulfonic acid has also been observed.[7,8] It should be noted in this context that Kim et al. encountered difficulties with completing the decomposition of the amine chlorostannate complex, obtained by the reduction of poly (3,3′-dinitro-4,4′-benzidineisophthalamide) with stannous chloride, owing to the inability of NaOH to diffuse through the rigid polymer matrix.[9] In another instance, involving the reduction of nitro-substituted poly(1-vinylpyrene) using stannous chloride, elemental analysis indicated a significant decrease in the nitrogen content, probably due to the partial cleavage of some of the nitro-substituted pyrene units back to pyrene.[10]

Another way of introducing functional groups into a polymer backbone involves the end-capping of the growing polymer chain upon treatment with appropriately monofunctionalized monomers. Amino-terminated poly(aryl ether ketone)s were synthesized in this way.[11−13] It appears, however, that such a functionalization becomes more and more difficult with the increasing degree of polymerization.

Obtaining a functionalized polymer by direct synthesis from functionalized monomers is an attractive approach, since the number of functional groups on the polymer backbone can be controlled; however, the function chosen has to be compatible with the polymerization conditions used. In the case of poly(arylene ether ketone)s, due to the vigorous conditions of the nucleophilic substitution, synthesis of ester-substituted PEEK failed.[1] On the other hand, aminated poly(ether sulfone)s have already been successfully synthesized using an amino-functionalized monomer.[14] Direct synthesis of poly(ether ketone)s containing pentanoic acid side chains also succeeded and allowed their transformation by condensation of the carboxylic group with several amines.[15]

In this article, we report the synthesis of two isomeric amino-functionalized poly(arylene ether ketone)s and their characterization. The advantage of amino groups being that they can be readily transformed into various other functionalities owing to their good reactivity. Thus, the polymers could then be easily modified by reaction with oligomers or polymers containing proper functionalities to give graft copolymers, allowing the careful tuning of the thermal and mechanical properties of the poly(ether ketone)s.

Experimental Section

Measurements. Melting points were determined by a Buchi melting apparatus and are uncorrected. IR spectra were recorded on a Nicolet 320 FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using Varian Gemini 200 and Bruker AC 300 instruments. Mass spectra were recorded on a Fisons Trio 2000 under electron impact conditions.

Differential scanning calorimetry was performed either on a DSC I Mettler TC 10 A or a DSC II Mettler TC 11. The DSC curves obtained during the second heating scan were taken into consideration. The samples were heated at a rate of 10 °C/min under flowing nitrogen gas. Thermogravimetric analyses were performed on a Mettler TC 10A at a heating rate of 10 °C/min under a nitrogen atmosphere. GPC analyses were done with a Waters chromatography system with a Permagel 10^3−10^6 Å polystyrene standards column using tetrahydrofuran or dimethylformamide (DMF) as eluent.

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Materials. 5-Aminoisophthalic acid, nitroterephthalic acid, succinic anhydride, and sulfolane were obtained from commercial sources and used without any further purification. Bisphenol A was recrystallized from a toluene−acetic acid (4:1 v/v) mixture. *N*-Methyl-2-pyrrolidinone and toluene were purified by drying over calcium hydride overnight, followed by distillation, and stored over type 4 Å molecular sieves. Potassium carbonate was dried at 125 °C for 24 h prior to use.

2-Nitroterephthaloyl Dichloride. Thionyl chloride (50 mL) was poured into a 100 mL round-bottomed flask containing 2-nitroterephthalic acid (7.00 g, 33 mmol). A few drops of pyridine were added, and the reaction mixture was refluxed until a clear solution was obtained. The excess thionyl chloride was then removed under vacuum. A dark brown, oily liquid was obtained and further dried under vacuum. Yield: 8 g (98%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.9 (s, 1 H), 8.55 (d, 1 H), 7.90 (d, 1 H).

2-Nitro-1,4-bis(4-fluorobenzoyl)benzene (6). To a stirred solution of 2-nitroterephthaloyl chloride (8.00 g, 32 mmol) in fluorobenzene (50 mL) was added anhydrous aluminum chloride (12.95 g, 97 mmol) portionwise over $^{1}/_{2}$ h at room temperature. After completion of the addition, 20 mL of fluorobenzene was added and the reaction mixture was allowed to stir at room temperature for an additional $^{1}/_{2}$ h, at the end of which the flask was heated slowly to reflux. The mixture was held under refluxing condition for 12 h and then cooled to room temperature. The aluminum chloride complex was decomposed by adding ice cold dilute HCl (1:1), and the product was separated by extracting with dichloromethane which was washed subsequently with sodium bicarbonate solution and water and dried over anhydrous magnesium sulfate. Dichloromethane was then removed under vacuum. The residue was recrystallized from ethanol. A pale yellow crystalline solid was obtained. Yield: 9.82 g (88%). Mp 120−122 °C. IR (KBr, cm^{-1}): 1665, 1650 (C=O), 1600 (C=C), 1540, 1354 (−NO_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.58 (s, 1 H), 8.15 (dd, 1 H), 7.85 (m, 4 H), 7.61 (d, 1 H), 7.20 (m, 4 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 193.5, 192.8, 167.1 (J_{C-F} = 251 Hz), 166.7 (J_{C-F} = 253 Hz), 147.7, 140.9, 139.3, 136.8, 134.7 (J_{C-F} = 9.7 Hz), 133.9 (J_{C-F} = 10.0 Hz), 133.6, 131.0, 127.0, 117.9 (J_{C-F} = 22.2 Hz), 117.6 (J_{C-F} = 22.0 Hz). MS (*m*/*z*): 367.1 ($M^{\bullet+}$). Anal. Calcd for $C_{20}H_{11}F_2NO_4$: C, 65.63; H, 3.21; N, 3.31. Found: C, 65.79; H, 3.18; N, 3.50.

2-Amino-1,4-bis(4-fluorobenzoyl)benzene (1). 2-Nitro-1,4-bis(4-fluorobenzoyl)benzene (**6**) (26.00 g, 71 mmol), stannous chloride dihydrate (30.00 g, 133 mmol), and ethyl acetate (150 mL) were stirred under argon at room temperature. The mixture was heated to reflux. After 1 day of reaction, the mixture turned into a clear orange solution. The mixture was cooled to room temperature, and addition of NaOH resulted in the precipitation of yellow solids which were filtered and dried. Recrystallization from toluene yielded a bright yellow amorphous solid. Yield: 20.8 g (87%). Mp: 159−61 °C. IR (KBr, cm^{-1}): 3447, 3329 (N−H), 1634, 1618 (C=O), 1598 (C=C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.89 (m, 2 H), 7.73 (m, 2 H), 7.52 (d, 1H), 7.15 (m, 5 H), 6.92 (dd, 1 H), 6.1 (s, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.8, 196.0, 166.5 (J_{C-F} = 251 Hz), 165.6 (J_{C-F} = 250 Hz), 152.7, 143.1, 137.4, 135.18, 134.9, 134.3 (J_{C-F} = 9.4 Hz), 133.4 (J_{C-F} = 9.1 Hz), 120.5, 119.6, 117.4 (J_{C-F} = 22.8 Hz), 117.1 (J_{C-F} = 22.5 Hz), 115.9. MS (*m*/*z*): 337.2 ($M^{\bullet+}$). Anal. Calcd for $C_{20}H_{13}F_2NO_2$: C, 71.21; H, 3.88; N, 4.15. Found: C, 71.59; H, 3.95; N, 4.26.

5-*N*-Succinimidoisophthalic Acid (7). 5-Aminoisophthalic acid (18.11 g, 0.1 mol) was dissolved in DMF (150 mL). To this solution was added succinic anhydride (10.00 g, 0.1 mol), followed by 50 mL of toluene. The mixture was heated at 80 °C for 2 h, and then the temperature was increased to 140−145 °C, the water formed upon condensation being removed azeotropically with toluene in a Dean-Stark trap. After the toluene was removed completely (~5 h), the reaction mixture was cooled to room temperature, precipitating needlelike solids. The solids thus obtained were filtered, washed repeatedly with water, and dried. Yield: 20 g (76%). Mp: >300 °C. IR (KBr, cm^{-1}): 3300−2800 (−OH), 1780, 1719 (imide C=O), 1708 (C=O (−OH)). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 8.47 (s, 1 H), 8.10 (s, 2 H), 2.79 (s, 4 H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 177.0, 166.1, 133.7, 132.3, 132.1, 129.5, 26.9. MS (*m*/*z*): 263.1 ($M^{\bullet+}$). Anal. Calcd for $C_{12}H_9NO_6$: C, 54.76; H, 3.44; N, 5.32. Found: C, 54.85; H, 3.49; N, 5.29.

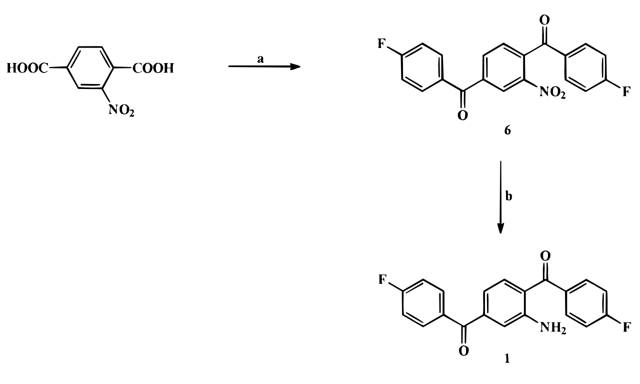
5-*N*-Succinimidoisophthaloyl Dichloride. To 5-*N*-succinimidoisophthalic acid (15 g, 57 mmol) was added 60 mL of thionyl chloride, followed by a few drops of pyridine, and then the mixture was refluxed for 6 h. A clear solution was obtained, and the excess thionyl chloride was removed under vacuum. The product was then dried under vacuum. The gray solid thus obtained was used without further purification for the synthesis of 5-*N*-succinimido-1,3-bis(4-fluorobenzoyl)benzene. Yield: 16 g (93%). ^{1}H NMR ($CDCl_3$, 200 MHz); δ 8.85 (s, 1 H), 8.45 (s, 2 H), 2.95 (s, 4 H).

5-*N*-Succinimido-1,3-bis(4-fluorobenzoyl)benzene (8). A suspension of 5-*N*-succinimidoisophthaloyl chloride (15 g, 0.05 mole) in fluorobenzene (100 mL) was heated to 60 °C under an inert atmosphere until a homogeneous solution was obtained. The flask was then cooled to 40 °C and 2 g of $AlCl_3$ was added. The heating of the oil bath was stopped at this stage, and an additional 18 g of $AlCl_3$ (a total of 20 g, 0.15 mol) was added in 2 g portions, until the evolution of gas subsided after each of the previous additions. An additional 20 mL of fluorobenzene was added, and the reaction mixture was refluxed for 16 h. The excess fluorobenzene was removed under vacuum, and the flask was then cooled to room temperature. The aluminum chloride complex was decomposed by adding ice-cold dilute HCl (1:1). The resulting solid was filtered and dried. The product was purified by recrystallization from acetone after treating the solution with activated charcoal. Yield: 16 g (76%). Mp: 189−191 °C. IR (KBr, cm^{-1}): 1780, 1716 (imide C=O), 1666 (C=O), 1597 (C=C). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 7.97 (m, 7 H), 7.45 (t, 4 H), 2.85 (s, 4 H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 193.0, 176.9, 167.4 (J_{C-F} = 250 Hz), 137.8, 133.6, 133.3 (J_{C-F} = 9.5 Hz), 133.1, 133.0, 131.7, 130.2, 117.9 (J_{C-F} = 22.5 Hz), 116.3, 115.9, 28.9. MS (*m*/*z*): 419.2 ($M^{\bullet+}$), 324.1, 123 (base peak). Anal. Calcd for $C_{24}H_{15}F_2NO_4$: C, 68.73; H, 3.60; N, 3.34. Found: C, 68.65; H, 3.64; N, 3.29.

5-Amino-1,3-bis(4-fluorobenzoyl)benzene (2). Compound **8** (15 g, 36 mmol) was dissolved in 75 mL of toluene and 60 mL of 10% NaOH solution was added. The mixture was heated at 80 °C overnight and then poured into a 500 mL beaker. The bright yellow, needlelike crystals, which appeared upon cooling, were filtered, washed with water, and dried. The product was then recrystallized from toluene. Yield: 10 g (83%). Mp 164−166 °C. IR (KBr, cm^{-1}): 3472, 3383 (N−H), 1659, 1649 (C=O), 1596, 1590 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.84 (dd, 4 H), 7.43 (s, 1 H), 7.38 (s, 1H), 7.14 (t, 4 H), 4.00 (s, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 195.8, 166.1 (J_{C-F} = 251 Hz), 150.9, 139.3, 135.2, 134.0 (J_{C-F} = 9.3 Hz), 119.6, 119.5, 117.1 (J_{C-F} = 22.0 Hz); MS (*m*/*z*): 337 ($M^{\bullet+}$), 123 (base peak), 95.1. Anal. Calcd $C_{20}H_{13}F_2NO_2$: C, 71.21; H, 3.88; N, 4.15. Found: C, 71.10; H, 3.79; N, 4.22.

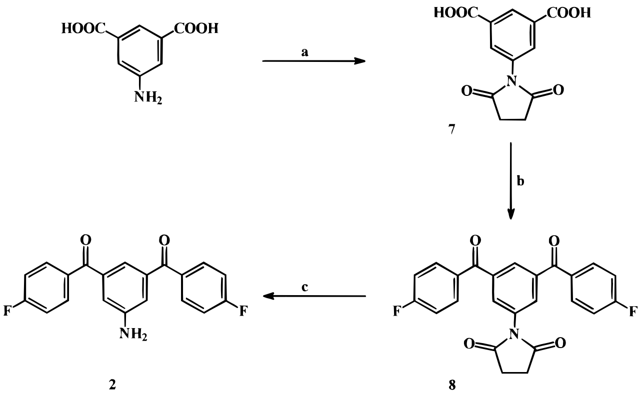
Polymer Synthesis. Polymer 3 from Monomer 1 and BPA. In a three-necked flask, equipped with a stirrer, a Dean-Stark trap fitted with a condenser, and an argon inlet, was placed monomer **1** (3.37 g, 0.01 mol) and BPA (2.28 g, 0.01 mol). Toluene (8 mL) was used to wash any remaining solids stuck to the opening of the flask. Sulfolane (8 mL) was added to the content of the flask. Potassium carbonate (2.76 g, 0.02 mol) was added to the suspension. The temperature was then increased to 140−150 °C for 2 h under a stream of argon to azeotrope off the water formed with toluene. The temperature was then increased to 180 °C. After 1 h of reaction and an apparent increase in the viscosity, sulfolane (8 mL) was added. After another hour, the resulting viscous solution was cooled down, diluted with THF, filtered, and finally precipitated into methanol containing a few drops of HCl. The resulting fibrous polymer was filtered and dried in a vacuum oven at 60 °C. Yield: 5.35 g (92%). IR (film, cm $^{-1}$): 3477, 3370 (−NH_2), 1634 (C=O), 1610, 1592 (C=C), 1239 (C−O−C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.8 (d, 2 H), 7.7 (d, 2 H), 7.5 (d, 2 H), 7.2 (m, 5 H), 7.0 (m, 8 H), 5.9 (s, 2 H), 1.6 (s, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.0, 194.9, 162.1, 161.1, 158.5, 153.1, 146.9, 146,7, 146.6, 142.4, 133.6, 133.5, 132.5, 131.7, 131.1, 128.3, 127.7, 119.7, 119.5, 117.1, 117.0, 114.9, 42.3, 30.9.

Scheme 1. Synthesis of 2-Amino-1,4-bis(4-fluorobenzoyl)benzene (1)



a. $SOCl_2$; $AlCl_3$, fluorobenzene
b. $SnCl_2$, EtOAc

Scheme 2. Synthesis of 5-Amino-1,3-bis(4-fluorobenzoyl)benzene (2)



a: Succinic anhydride, DMF, toluene
b: $SOCl_2$; $AlCl_3$, fluorobenzene
c: Toluene, 10% NaOH

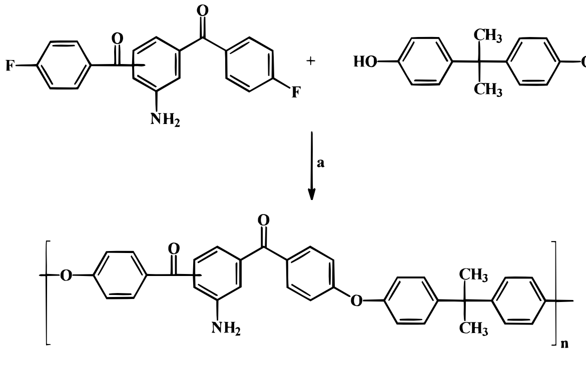
Polymer 4 from Monomer 2 and BPA. The same method described above for polymer **3** was used with monomer **2** (1.91 g, 5.7 mmol), BPA (1.29 g, 5.7 mmol), potassium carbonate (1.80 g, 13.6 mmol), sulfolane (14 mL), and toluene (11 mL). Yield: 2.90 g (95%). IR (film, cm^{-1}): 3465, 3371 ($-NH_2$), 1654 (C=O), 1591 (C=C), 1241 (C—O—C). ^1H NMR (DMSO-d_6, 300 MHz): δ 7.8 (m, 4 H), 7.3 (m, 7 H), 7.0 (m, 8 H), 5.7 (s, 2 H), 1.6 (s, 6 H). ^{13}C NMR (DMSO-d_6, 50 MHz): δ 194.2, 161.0, 155.0, 152.7, 149.2, 147.3, 146.4, 140.23, 138.0, 132.1, 131.4, 128.2, 127.2, 119.3, 118.1, 117.6, 116.9, 114.7, 41.8, 30.4.

Amidation of Polymer 4 (5). Polymer **4** (0.500 g, 0.10 mmol) was dissolved in NMP (10 mL) and pyridine (0.1 mL). Acetyl chloride (0.090 g, 0.12 mmol) in NMP (5 mL) was then added dropwise to the mixture. The solution was stirred overnight at room temperature. The reaction mixture was then heated to 100 °C for 1 h and finally poured into methanol. The solids obtained were filtered, dissolved in chloroform, and precipitated again in methanol. Yield: 0.49 g (98%). IR (film, cm^{-1}): 3320 (—NH), 1678, 1659 (C=O), 1591 (C=C), 1243 (C—O—C). ^1H NMR (DMSO-d_6, 300 MHz): δ 10.3 (s, 1 H), 8.2 (s, 2 H), 7.8 (d, 4 H), 7.5 (s, 1 H), 7.2 (d, 4 H), 7.0 (s, 8 H), 2.0 (s, 3 H), 1.6 (s, 6 H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 194.9, 170.4, 162.8, 154.2, 148.1, 141.2, 139.3, 133.9, 132.4, 129.8, 126.3, 124.4, 121.0, 118.5, 43.4, 32.0, 25.5.

Results and Discussion

Monomer Synthesis. Two isomeric diketone monomers, 2-amino-1,4-bis(4-fluorobenzoyl)benzene (**1**) and 5-amino-1,3-bis(4-fluorobenzoyl)benzene (**2**), were synthesized according to Schemes 1 and 2, respectively.

Scheme 3. Polymer Synthesis of 3 and 4



a. Sulfolane, K_2CO_3, toluene

The nitro precursor **6**, which had been obtained by the Friedel—Crafts acylation of fluorobenzene with 2-nitroterephthaloyl chloride in the presence of $AlCl_3$, was reduced by stannous chloride dihydrate in ethyl acetate according to a general method reported in the literature.[16,17] The reduction proceeded smoothly, as expected, and in high yield. The amino compound **1** was obtained as a pure material after two recrystallizations from toluene. The IR spectrum showed strong absorptions in the region 3300—3400 cm^{-1}, due to the symmetric and asymmetric N—H stretching frequencies. In the ^1H NMR spectrum, the amino protons occur at $\delta = 6.1$, indicating that the protons attached to the nitrogen atom are highly acidic, owing to the presence of electron-withdrawing carbonyl groups in the ortho position. Hence the amino group should be a poor nucleophile. Apart from the molecular ion at m/z 337.2, an ion at m/z 336 with a relative intensity of 92% appears in the mass spectrum, which could be due to the loss of a proton from the amino group.

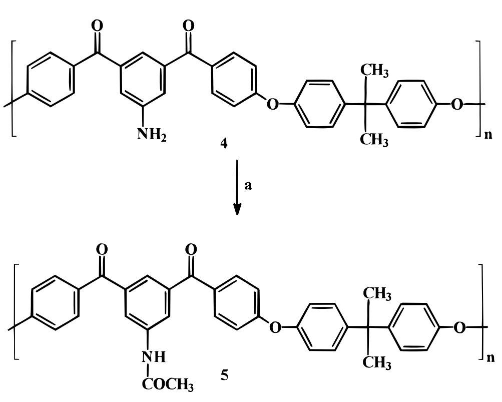
The isomeric amino-functionalized monomer **2** was prepared as shown in Scheme 2, starting from 5-aminoisophthalic acid. This route does not involve any functional group transformation, as for the synthesis of **1**, but a protection and deprotection step. Succinic anhydride was used to protect 5-aminoisophthalic acid. Friedel—Crafts acylation with the resulting compound **7** led to the difluoro ketone **8** which was easily deprotected with sodium hydroxide in toluene to yield the expected monomer **2**. The IR spectrum showed the same characteristic peaks as found for compound **1**. The amino group protons of **2** appear at $\delta = 4.0$ in ^1H NMR spectroscopy.

Polymer Synthesis. The polymerization was carried out by heating an equimolar mixture of monomers and potassium carbonate in sulfolane under inert atmosphere using toluene to remove the water formed during the polymerization as an azeotrope (Scheme 3). The mixture was first stirred at 140 °C for 2 h to assure complete dehydration and was finally heated to 180 °C. After an apparent increase in viscosity, the reaction was stopped and the polymer was precipitated with methanol. The resulting fibers were then purified to allow their characterization.

Due to difficulties experienced in the characterization of polymer **4**, as emphasized later in the article, amidation of the amino group was performed. Polymer **4** was reacted under usual amidation conditions with acetyl chloride to give polymer **5** in high yield (Scheme 4).

Polymer Characterization. Polymers **3** and **4** appeared as yellow fibrous solids, whereas **5** was colorless. Polymers **3** and **5** displayed excellent solubility

Scheme 4. Transformation of Polymer 4 into Polymer 5



a: CH_3COCl, NMP, pyridine

in chlorinated hydrocarbons, tetrahydrofuran (THF), *N*,*N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidinone (NMP), whereas polymer **4** was not soluble in chloroform, dichloromethane, or THF, and yielded gel-like solutions in dipolar aprotic solvents, but could be solubilized in the latter solvents containing 5% LiCl. The structures of all polymers were confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectrometry. Bands due to the N—H symmetric and asymmetric as well as C═O and C—O—C stretchings were found in both spectra of polymers **3** and **4**. In the IR spectrum of polymer **5**, disappearance of the sharp amine absorptions and appearance of an additional carbonyl absorption are observed (Figure 1a,b).

The ^{1}H NMR spectrum of polymer **3** is given in Figure 2. The amine protons of polymer **3** appear at $\delta = 5.9$ and the two methyl ones at $\delta = 1.6$. Two carbonyl signals are found in the ^{13}C NMR spectrum at $\delta = 197.0$ and 194.8, due to the asymmetric nature of monomer **1** in polymer **3**. For polymer **4**, the amine protons appear at $\delta = 5.7$ in the ^{1}H NMR spectrum. ^{13}C NMR spectroscopy shows only one carbonyl peak at $\delta = 194$, as expected, due to its more symmetric nature. After amidation of the amine function (polymer **5**), additional peaks at $\delta = 2.0$, indicating the methyl group, and at $\delta = 10.3$, for the N−H proton, proving the amidation reaction, appeared in the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum a peak at $\delta = 25.4$ proved the presence of a methyl group. The spectra demonstrated the total conversion of the amine function into the acetamide.

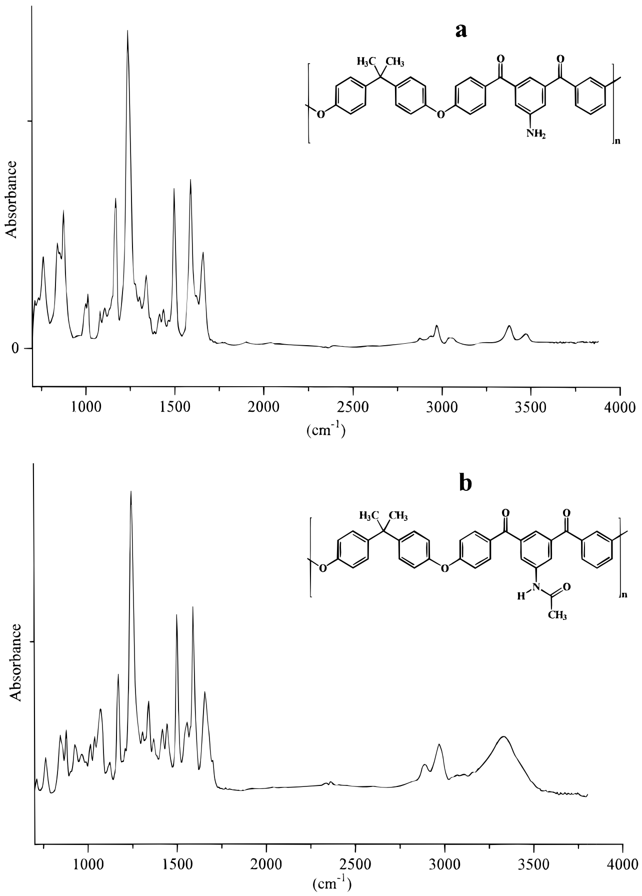


Figure 1. (a) IR spectrum of polymer **4**. (b) IR spectrum of polymer **5**.

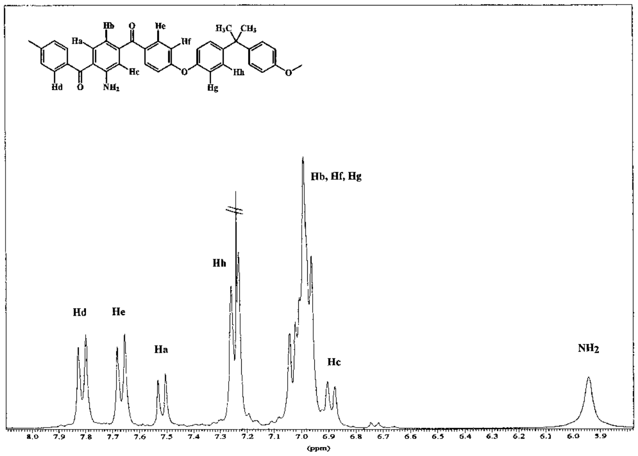


Figure 2. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of polymer **3**.

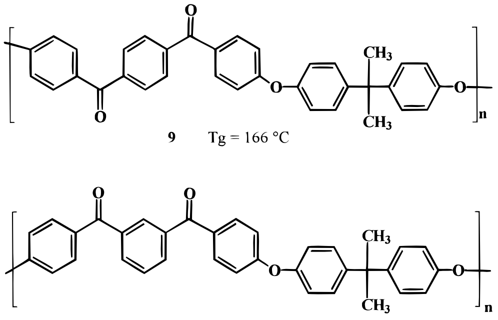
Even though the polymerization was carried out in the presence of free amino groups, side reactions were not observed. Two possible side reactions could be anticipitated in this case, ketimine formation, involving the reaction between amino and carbonyl groups, or the amino group itself acting as a nucleophile under basic conditions. Concerning these two reactions, aminophenols have already been used as nucleophiles to displace halogens activated by various groups without any side reactions.[18−20] When, for example, a mixture of aniline and various differently substituted benzophenones was heated in a solution of NMP/toluene in the presence of anhydrous potassium carbonate at 170 °C for 7 h, no reaction was found to occur and the starting materials were recovered unchanged.[11,18] Various diamines containing carbonyl and ether groups have also been synthesized by reacting 4-aminophenol with difluoro compounds activated by one or more carbonyl groups. Though the reaction temperatures were lower in these cases (around 140 °C), the reaction time was much longer than that employed in our case.[19,20] The use of 4-aminophenol was also successful in the synthesis of a more nucleophilic diamine from 4,4′-dichlorodiphenyl sulfone under more basic conditions involving caustic alkali without any undesirable reactions.[21,22] Compared to the amino compounds discussed above, the amino monomers **1** and **2**, used in our case, are less nucleophilic and compound **1** is moreover sterically hindered. Reports on the preparation of high molecular weight aromatic polyketimines by step-growth polymerization reactions of a diamine with a diketone are scarce due to the nonquantitative nature of these reactions, owing to the steric hindrance and the insolubility of the resulting products.[23] In fact, ketimine forming reactions

Table 1. Characterization of Polymers 3-5

polymer	10^4M_n[a]	10^4M_w[a]	T_g[b] (°C)	TGA[c] (°C)
3	1.96	6.79	190.8	490
4	3.73	7.76	*d*	493
5	2.88	9.32	197.3	422

[a] Measured by GPC relative to polystyrene standards. [b] Second scan at a heating rate of 10 °C/min. [c] Onset temperatures for 10% weight loss. [d] Not observed.

Chart 1. Structure and T_g of Unsubstituted Poly(arylene ether ketone)s 9 and 10



9 Tg = 166 °C

10 Tg = 155 °C

are more favored in neutral solvents under acid-catalyzed conditions.[24]

GPC analysis was performed in THF for polymers **3** and **5** and in dimethylformamide (DMF) for polymer **4**. The molecular weights, measured relative to polystyrene standards, showed that high molecular weight polymers were obtained (Table 1). GPC traces were monomodal in the case of polymers **3** and **5**, but trimodal curves were observed in DMF for polymer **4**. In this case, the result listed in Table 1 only relates to the lower molecular weight fraction. We believe that the high molecular weight fraction is related to aggregation phenomena and results from the problems in dissolving this polymer. Another explanation could arise from an affinity of the polymer toward the column substrate.[25,26] These facts were further demonstrated by the GPC results of polymer **5**, which showed a regular monomodal trace.

None of the polymers showed any crystalline behavior on the DSC trace. In contrast to polymers **3** and **5**, polymer **4** showed no detectable glass transition temperature (T_g) (Table 1). This could be explained by the formation of hydrogen bonds between protons of the amino function and oxygen atoms of the carbonyl groups in polymer **4**, in which case the conformation allows interchain interactions, leading to hindrance in the mobility of the polymer chains. No confirmation of this explanation could be found in the IR spectrum, since the bands corresponding to these particular hydrogen bonds are usually large and weak. However, the solubility behavior of the polymer, especially its higher solubility in polar aprotic solvents containing LiCl, also suggests the presence of such interactions between the polymer chains. Moreover, the fact that monomer **2** is only soluble in polar aprotic solvents accounts for the formation of hydrogen bonds, those solvents being known for their solvating effect.

The T_g of amidated polymer **5** (197 °C), in which case less hydrogen bondings would remain, is then comparable to that of **3** (191 °C). The amino- and amido-functionalized poly(arylene ether ketone)s **3** and **5** show higher glass transition temperatures than the corresponding unsubstituted polymers **9** and **10** (Chart 1), respectively. For example, a polymer based on 1,4-bis(4-chlorobenzoyl)benzene and Bisphenol A has a T_g of 166 °C[27] while that of the corresponding amino group containing polymer **3**, described herein, is 191 °C. Similarly, a polymer based on Bisphenol A and 1,3-bis(4-fluorobenzoyl)benzene shows a T_g of 155 °C[28] while the corresponding acetamide-functionalized polymer **5** shows in our study a T_g of 197 °C.

The higher T_g of the poly(arylene ether ketone)s containing amino or acetamido groups compared to the corresponding unsubstituted polymers **9** and **10** is due to the increased interaction between the polymer chains caused by the hydrogen bonding between the protons of the amino group and the oxygen atom of the carbonyl group. The absence of any exothermic transition indicates that reactions such as cross-linking between amino and carbonyl functions leading to the ketimine formation do not take place. The nonoccurrence of cross-linking is further proven by the constant T_g even in the third scan, despite heating the polymers to a temperature of 360 °C in each of the previous scans.

Thermal stabilities of the polymers were assessed by thermogravimetry. A 10% weight-loss occurred above 420 °C for all polymers. Polymer **5** was less thermally stable than the amino-functionalized polymers, as expected by the presence of an additional aliphatic methyl group.

The mechanical properties are also expected to be enhanced by the increased interactions between the polymer chains

Summary

Two isomeric amino-functionalized poly(arylene ether ketone)s were synthesized from activated difluoro monomers substituted with a free amino group and Bisphenol A. The polymerization reaction proceeded without any detectable side reaction. The functionalized polymers were found to possess higher glass transition temperatures than the corresponding unsubstituted polymers. Work on the transformation of the amino-functionalized polymers by amidation with various carboxylic acids as well as grafting with defined carboxy-functionalized oligobenzamides and oligobenzoates currently under investigation will be reported in the near future.

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