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Synthesis and Properties of Flexible Poly(ether ketone) Backbones, Grafted with Stiff, Monodisperse Side Chains

A. Le Guen, M. Klapper,* and K. Müllen

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

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ABSTRACT: Poly(arylene ether ketone)s with pendant, monodisperse oligobenzamide and oligobenzoate side chains facilitated a study of the effect of hydrogen bonding on chain interactions. A stepwise condensation reaction between acid chlorides and amine or alcohol functions was used to synthesize new series of carboxy-terminated oligobenzamides and oligobenzoates. These oligomers as well as benzoyl chloride were then reacted with two isomeric amino-functionalized poly(arylene ether ketone)s, to lead to modified polymers **10**−**13**. The polymers were charaterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy and gel permeation chromatography. The influences of the length and chemical nature of the side chain on the thermal and mechanical properties were studied. The transformed polymers showed different thermal and mechanical behavior, depending on the length and chemical nature of the side chain. Polymers with pendant oligobenzoates, for example, had lower T_gs and Young's modulus in comparison to the respective polymers with oligobenzamide side chains. These results establish the considerable importance of hydrogen bonding on the improvement of the polymer properties.

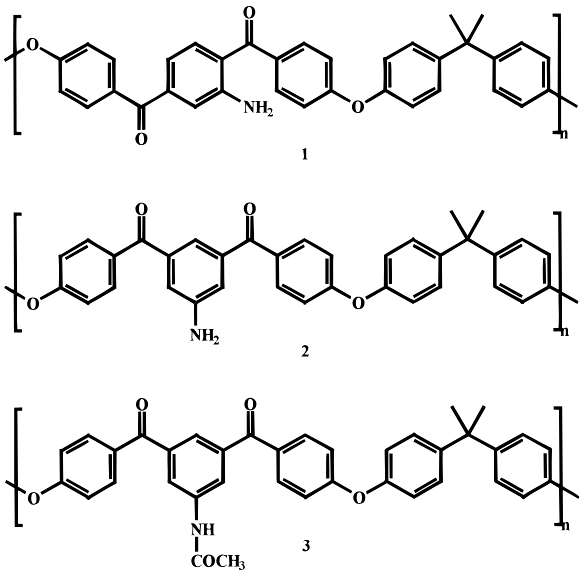
Introduction

Poly(ether ether ketone) (PEEK) is a well-known high-performance engineering thermoplastic.[1] Due to its good solvent resistance, high thermal stability, and excellent mechanical strength, it can be used as a matrix resin for advanced composite materials in aircraft and automobile industries. In the past few years, research has concentrated on the modification of poly(arylene ether ketone)s in order to improve their thermal properties. The polymer transformation can be effected either by intramolecular reactions, using the reactivity between the functions in the polymer backbone to increase the chain stiffness[2,3] or lead to new polymer structures,[4−6] or by intermolecular reactions, attaching molecules onto the polymer backbone to generate polymers with side chains and thus modifying the properties of the initial polymer.[7]

Recently, we reacted living anions of polystyrene and polyisoprene with the carbonyl groups of poly(ether ketone)s to lead to graft copolymers.[7] Such types of polymers are often used as compatibilizers, coatings, surface modifiers, or adhesives.[8] Poly(arylene ether ketone)s and poly(arylene ether sulfone)s containing carboxylic acid functions have also been modified by condensation with amine-terminated alkyl chains.[9−11] This transformation resulted in polymers with alkyl side chains showing very high thermal stability; however, a decrease in the glass transition temperature (T_g) of the initial polymer was also observed.

Recently, the synthesis of amino-functionalized poly(arylene ether ketone)s **1** and **2** (Chart 1) has been reported by us.[12] Amino groups were found useful as attachment sites along the polymer chains since they are reactive and easily form covalent bonds with other functionalities under mild conditions.

Chart 1. Isomeric Amino- and Acetamido-Functionalized Poly(arylene ether ketone)s 1, 2, and 3



Our goal was to keep the inherent properties of the initial poly(ether ketone)s, e.g., good solubility as well as easy processability, and combine them with improved mechanical strength and stability over a wide temperature range. The association of the flexible main chain from the poly(ether ketone) with stiff side chains, capable of forming hydrogen bonds, could result in interesting modifications of the properties of the initial material, such as toughening and improved thermal properties, thanks to the possible ordering of the side chains through H-bonding.

Grafting of polyamides was the method of choice to increase interactions between the polymer chains and thus lead to better mechanical properties. However, the insolubility and lack of processability of the polybenzamides hampered their use in our case, due to the problems concerning the characterization of the resulting material. We thus synthesized a series of soluble, well-defined, monodiperse oligomers to allow for an easy tuning of the solubility vs thermal behavior of the modified polymers. The substitution of rigid-rod aromatic polyimides[13] and aromatic polyamides[14−16] with short oligobenzamides has already been studied. The

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introduction of aromatic amides as side chains on the polymer backbone increased the solubility as well as the glass transition temperatures (T_g) of the resulting polymers, whereas the introduction of an oxybenzoyl group only improved their solubility. We were interested in studying the effect of grafting onto poly(arylene ether ketone)s on the thermal and mechanical properties and on the solubility behavior. In this paper, we report the modification of the amino-functionalized poly(arylene ether ketone)s by reaction with defined oligobenzamides and oligobenzoates and examine its effect on the thermal and mechanical properties and on the solubility behavior, depending on the size and chemical nature of the side chain.

Experimental Section

The functionalized poly(arylene ether ketone)s **1**−**3** were synthesized according to a procedure already reported by us.[12] All solvents were dried and freshly distilled. All other materials were obtained from commercial sources and used without any purification unless otherwise stated. 4-Aminobenzoic acid was recrystallized from a mixture of toluene/methanol (1/1).

IR spectra were recorded on a Nicolet 320 FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker AC 300 and AC 500 instruments. Mass spectra were recorded on a Fisons Trio 2000 under electron impact conditions.

Differential scanning calorimetry was performed on either 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 500 at a heating rate of 10 °C/min under nitrogen atmosphere. GPC analyses were done with a Waters chromatography system with Permagel 10^3−10^6 Å polystyrene standards column, connected to a UV−vis detectometer, using tetrahydrofuran or dimethylformamide (DMF) as eluent. All stress−strain measurements were conducted with an Instron model 6022 instrument at room temperature with rectangles cut out of compression molded films or films cast from solutions.

4-(Benzoylamino)benzoic Acid (4). 4-Aminobenzoic acid (13.7 g, 0.10 mol) was dissolved in a mixture of dioxane (100 mL) and pyridine (8 mL) at 50 °C under argon. The solution was then allowed to cool in an ice bath, and benzoyl chloride (15.5 g, 0.11 mol) in dioxane (100 mL) was added dropwise. The reaction mixture was stirred overnight and allowed to warm to room temperature. The mixture was then poured into ice−water, and the resulting precipitate was filtered off, washed several times with water, and finally recrystallized from methanol to give **4** in high yield: 20.2 g (82%); IR (cm^{-1}, KBr) 3340 (NH), 1681, 1666, 1652 (C═O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.49 (s, 1 H), 7.98−7.92 (m, 6 H), 7.58−7.53 (m, 3 H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 168.42, 167.45, 144.77, 136.16, 133.28, 131.68, 129.90, 129.25, 127.07, 121.01; MS (*m*/*z*) 241.1, 105.1, 77.1. Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.56; N, 5.81. Found: C, 69.70; H, 4.64; N, 5.86.

4-(Benzoylamino-1,4-benzoylamino)benzoic Acid (5). 4-(Benzoylamino)benzoic acid (5.43 g, 22 mmol) was refluxed in freshly distilled thionyl chloride (30 mL) with a few drops of pyridine for 4 h. The excess thionyl chloride was then distilled off, and the resulting solid was dried under vacuum. The acid chloride thus obtained was dissolved in dry *N*,*N*-dimethylacetamide (DMAc, 15 mL) under argon. 4-Aminobenzoic acid (2.74 g, 20 mmol) and pyridine (1 mL) in DMAc (15 mL) were added dropwise to the acid chloride solution at 0 °C, and the resulting mixture was then stirred overnight at room temperature. The temperature was raised to 80 °C and maintained for 1 h. The resulting solution was poured into ice−water and the precipitate obtained filtered off, washed several times with water and finally recrystallized from DMAc/H_2O (9:1): yield 5.1 g (71%); IR (cm^{-1}, KBr) 3332 (NH), 1681, 1656, 1607 (C═O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.52 (s, 1 H), 10.42 (s, 1 H), 8.05−7.94 (m, 10 H), 7.63−7.54 (m, 3 H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 168.61, 167.55, 166.94, 145.06, 144.12, 136.30, 133.46, 131.83, 130.92, 130.27, 130.08, 129.40, 127.09, 121.14; MS (*m*/*z*) 360.1, 105.0, 77.0. Anal. Calcd for $C_{21}H_{16}N_2O_4$: C, 70.00; H, 4.44; N, 7.77. Found: C, 69.99; H, 4.43; N, 7.80.

4-(Benzoylamino-1,4-(benzoylamino-1,4-benzoylamino))benzoic Acid (6). 4-(Benzoylamino-1,4-benzoylamino)benzoic acid (2.22 g, 5.8 mmol) was refluxed in freshly distilled thionyl chloride (30 mL) with a few drops of pyridine for 6 h. The excess thionyl chloride was then distilled off, and the resulting solids were dried under vacuum. The acid chloride thus obtained was dissolved in dry *N*,*N*-dimethylacetamide (DMAc, 10 mL) under argon. 4-Aminobenzoic acid (0.73 g, 5.8 mmol) and pyridine (0.5 mL) in DMAc (10 mL) were added dropwise to the acid chloride solution at 0 °C, and the resulting mixture was then stirred overnight at room temperature. The temperature was then raised to 80 °C and maintained for 1 h. The resulting solution was poured into ice−water and the precipitate obtained filtered off, washed several times with water, and finally recrystallized from DMAc: yield 1.4 g (50%); IR (cm^{-1}, KBr) 3341 (NH), 1681, 1658, 1606 (C═O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.54 (s, 1 H), 10.45 (d, 2 H), 8.05−7.94 (m, 14 H), 7.64−7.51 (m, 3 H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 167.39, 166.29, 165.68, 165.61, 143.78, 142.00, 142.85, 135.02, 132.20, 130.57, 129.61, 129.47, 129.00, 128.81, 128.13, 125.85, 119.86, 119.81; FD-MS (*m*/*z*) 479.1. Anal. Calcd for $C_{28}H_{21}N_3O_5$: C, 70.15; H, 4.38; N, 8.77. Found: C, 69.52; H, 4.33; N, 8.80.

4-Benzoyloxybenzoic Acid (7). 4-Hydroxybenzoic acid (34.5 g, 0.25 mol) was dissolved in 200 mL of icy water containing sodium hydroxide (20.0 g, 0.50 mol). Benzoyl chloride (38.5 g, 0.27 mol) was added dropwise over 15 min to the solution, and the mixture was stirred for another 30 min. Ice-cold hydrochloric acid was then added, and the resulting solid was filtered off, washed with water, and recrystallized from ethanol: yield 36 g (62%); IR (cm^{-1}, KBr) 3200−2600 (O═C−OH), 1736, 1702 (C═O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 8.12 (d, 2 H), 8.05 (d, 2 H), 7.74 (t, 1 H), 7.59 (t, 2 H), 7.41 (d, 2 H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 167.09, 164.60, 154.30, 134.56, 131.26, 130.23, 129.39, 129.36, 129.01, 122.44; FD-MS (*m*/*z*) 242.2. Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.13. Found: C, 69.45; H, 4.14.

Benzyl 4-(Benzoyloxy-1,4-benzoyloxy)benzoate (8). 4-(Benzoyloxy)benzoic acid (5.00 g, 20.0 mmol) was refluxed in freshly distilled thionyl chloride (30 mL) with a few drops of pyridine for 2 h. The excess thionyl chloride was then distilled off, and the resulting solids were dried under vacuum. The acid chloride thus obtained was dissolved in dry dioxane (30 mL) and pyridine (20 mL) under argon. Benzyl 4-hydroxybenzoate (5.15 g, 22.5 mmol) in dioxane (20 mL) was added dropwise to the acid chloride solution at 0 °C, and the resulting mixture was then stirred overnight at room temperature. The temperature was then raised to 80 °C and maintained for 1 h. The resulting solution was poured into ice−water and the precipitate obtained filtered off, washed several times with water, and finally recrystallized from ethanol: yield 7.12 g (79%); IR (cm^{-1}, KBr) 1736, 1702 (C═O); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.14−8.09(m, 2 H), 8.07−7.98 (m, 4 H), 7.52−7.46 (m, 1 H), 7.39−7.33 (m, 2 H), 7.31−7.12 (m, 9 H), 5.2 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.6, 164.4, 163.8, 155.4, 154.6, 136.0, 133.9, 131.9, 131.3, 130.2, 129.0, 128.6, 128.6, 128.2, 128.1, 127.8, 126.6, 122.1, 121.7, 66.8; FD-MS (*m*/*z*) 451.8. Anal. Calcd for $C_{28}H_{20}O_6$: C, 74.34; H, 4.42. Found: C, 74.34; H, 4.37.

4-(Benzoyloxy-1,4-benzoyloxy)benzoic Acid (9). The removal of the protecting group was accomplished according to a procedure found in the literature.[17] Compound **8** (1.06 g, 2.3 mmol) was dissolved in 10 mL of DMAc under argon. The reaction vessel was immersed in a water bath at 25 °C, and 10% palladium−carbon (1.06 g) was added under strong agitation. 1,4-Cyclohexadiene (2.2 mL, 23.5 mmol) was then dropped carefully into the reaction mixture. After 12 h of reaction, the mixture was filtered through Celite, washed with DMAc, and evaporated under reduced pressure. The resulting powder was recrystallized from ethanol: yield 0.65 g (78%); IR (cm^{-1}, KBr) 3200−2600 (O═C−OH), 1732, 1702, 1683 (C═O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 8.26−8.21 (m, 2 H), 8.17−8.13 (m, 2 H), 8.07−8.02 (m, 2 H), 7.79−7.73 (m, 1 H), 7.64−7.52 (m, 4 H), 7.46−7.41 (m, 2 H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 166.5, 164.1, 163.5, 155.0, 154.0, 134.2, 131.6, 130.9, 129.8, 128.9, 128.6, 128.5, 126.3, 122.6, 122.0; MS (*m/z*) 362.1 (M$^+$). Anal. Calcd for $C_{21}H_{14}O_6$: C, 69.61; H, 3.87. Found: C, 69.10; H, 3.81.

Modification of Aminopoly(ether ketone)s 1 and 2 into 10a−c, 11a−d, 12a,b, and 13a,b. The two isomeric poly(arylene ether ketone)s **1** and **2** were reacted with each member of the series of oligobenzamides previously synthesized, as well as with benzoic acid and the oligobenzoates, leading to polymers **10a**−**c**, **11a**−**d**, **12a,b** and **13a,b**. A typical procedure follows:

4-(Benzoylamino)benzoic acid (0.46 g, 1.9 mmol) was refluxed in freshly distilled thionyl chloride (10 mL) with a few drops of pyridine for 4 h. The excess thionyl chloride was then distilled off, and the resulting solid was dried under vacuum. The acid chloride thus obtained was dissolved in dry DMAc (5 mL) under argon. The amine-functionalized poly(ether ketone) (1.01 g, 1.85 mmol) and pyridine (0.5 mL) in DMAc (10 mL) were added dropwise to the solution, and the resulting mixture was then stirred at room temperature for 1 day in the case of polymer **1** or 2 days for polymer **2**. After being heated at 80 °C for 2 h, the solution was precipitated into ice−water, and the resulting polymer flakes were filtered off and washed several times with water. They were then dissolved in tetrahydrofuran (THF), reprecipitated in methanol, filtered off, and dried in a vacuum oven at 100 °C for 1 day.

Reaction of polymer **1** with benzoyl chloride (**10a**): yield 90%; IR (cm^{-1}, film) 3400−3200 (N−H), 1683, 1660, 1656 (C═O), 1242 (C−O−C); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 11.56 (s, 1 H), 9.10 (s, 1 H), 7.98 (d, 2 H), 7.91 (d, 2 H), 7.77 (d, 2 H), 7.73 (d, 1 H), 7.53−7.45 (m, 4 H), 7.27−7.22 (m, 4 H), 7.05−6.99 (m, 8 H), 1.70 (s, 6 H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 198.0, 194.3, 165.9, 162.5, 153.2, 147.2, 140.2, 134.3, 133.2, 132.8, 132.7, 132.3, 128.9, 128.5, 128.4, 127.4, 126.1, 122.8, 119.9, 119.8, 117.2, 42.4, 30.9.

Reaction of polymer **1** with oligobenzamide **4** (**10b**): yield 92%; IR (cm^{-1}, KBr) 3400−3200 (N−H), 1663, 1658, 1654 (C═O), 1241 (C−O−C); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.61 (s, 1 H), 10.44 (s, 1 H), 8.06 (s, 1 H), 7.94−7.83 (m, 6 H), 7.72−7.68 (m, 4 H), 7.60−7.47 (m, 5 H), 7.31−7.20 (m, 4 H), 7.04−6.93 (m, 6 H), 6.81 (m, 2 H), 1.59 (s, 6 H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 193.4, 193.0, 165.8, 164.7, 161.4, 160.7, 153.1, 153.0, 152.6, 152.5, 146.6, 146.1, 142.5, 139.8, 136.5, 134.5, 134.2, 132.5, 132.1, 131.9, 131.6, 130.7, 128.3, 128.2, 128.2, 127.7, 119.6, 119.2, 118.9, 117.2, 117.0, 42.0, 30.5.

Reaction of polymer **1** with oligobenzamide **5** (**10c**): yield 93%; IR (cm^{-1}, KBr) 3400−3200 (N−H), 1655 (C═O), 1241 (C−O−C); ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.49 (s, 1 H), 10.31 (s, 1 H), 10.22 (s, 1 H), 8.15 (s, 1 H), 7.97−7.87 (m, 8 H), 7.74−7.39 (m, 8 H), 735−7.19 (m, 6 H), 7.15−6.98 (m, 6 H), 6.89−6.85 (m, 2 H), 1.63 (s, 6 H).

Reaction of polymer **1** with oligobenzoate **7** (**12a**): yield 96%; IR (cm^{-1}, film) 1743, 1656 (C═O), 1242 (C−O−C); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 11.64 (s, 1 H), 9.10 (d, 1 H), 8.18 (d, 2 H), 8.08 (d, 2 H), 7.92 (d, 2 H), 7.80−7.73 (m, 3 H), 7.65−7.60 (m, 1 H), 7.52 (d, 3 H), 7.42−7.34 (m, 2 H), 7.27 (d, 4 H), 7.07−6.99 (m, 8 H), 1.71 (s, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 197.8, 194.1, 164.9, 164.6, 162.4, 154.0, 153.1, 147.1, 147.0, 146.9, 146.8, 142.7, 140.0, 133.8, 133.2, 132.7, 132.6, 132.1, 131.7, 130.7, 130.2, 129.1, 128.9, 128.6, 128.4, 128.4, 126.0, 122.8, 122.8, 122.2, 119.9, 119.8, 117.1, 42.4, 31.0.

Reaction of polymer **1** with oligobenzoate **9** (**12b**): yield 93%; IR (cm^{-1}, film) 1743, 1658 (C═O)1242 (C−O−C); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 11.63 (s, 1 H), 9.10 (s, 1 H), 8.28−8.18 (m, 4 H), 8.08 (d, 2 H), 7.92 (d, 2 H), 7.80−7.72 (m, 3 H), 7.67−7.62 (m, 1 H), 7.53−7.48 (m, 3 H), 7.38−7.34 (m, 4 H), 7.27 (d, 4 H), 7.06−7.00 (m, 8 H), 1.71 (s, 6 H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 198.2, 194.5, 165.3, 164.9, 164.2, 162.8, 155.8, 154.4, 153.4, 147.6, 140.4, 134.4, 133.1, 133.0, 132.3, 131.2, 130.7, 129.4, 129.1, 128.8, 128.8, 127.1, 126.4, 123.2, 122.6, 122.5, 120.3, 120.2, 117.5, 42.8, 31.4.

Reaction of polymer **2** with benzoyl chloride (**11a**): yield 95%; IR (cm^{-1}, film) 3400−3200 (N−H), 1656 (C═O), 1243 (C−O−C); ^{1}H NMR (THF-d_8, 300 MHz) δ 9.85 (s, 1 H), 8.44 (s, 2 H), 7.96 (d, 2 H), 7.87 (d, 4 H), 7.80 (s, 1 H), 7.52−7.42 (m, 3 H), 7.32 (d, 4 H), 7.03 (d d, 8 H), 1.70 (s, 6 H); ^{13}C NMR (THF-d_8, 75 MHz) δ 193.7, 166.4, 162.7, 154.3, 147.8, 140.7, 139.4, 135.8, 133.1, 132.4, 132.3, 129.2, 129.0, 128.3, 126.3, 124.9, 124.8, 120.4, 117.7, 43.0, 31.2.

Reaction of polymer **2** with oligobenzamide **4** (**11b**): yield 92%; IR (cm^{-1}, film) 3400−3200 (N−H), 1656 (C═O), 1244 (C−O−C); ^{1}H NMR (THF-d_8, 300 MHz) δ 9.81(s, 1 H), 9.69 (s, 1 H), 8.44 (s, 2 H), 7.97−7.90 (m, 6 H), 7.86 (d, 4 H), 7.78 (s, 1 H), 7.48−7.42 (m, 3 H), 7.30 (d, 4 H), 7.01 (d d, 8 H), 1.68 (s, 6 H); ^{13}C NMR (THF-d_8, 75 MHz) δ 193.7, 166.4, 165.9, 162.7, 154.3, 147.75, 143.7, 140.8, 139.4, 136.2, 133.1, 132.4, 132.2, 130.3, 129.2, 129.0, 128.3, 126.1, 124.9, 120.4, 120.3, 119.9, 117.8, 117.7, 117.5, 43.0, 30.5.

Reaction of polymer **2** with oligobenzamide **5** (**11c**): yield 92%; IR (cm^{-1}, KBr) 3400−3200 (N−H), 1656 (C═O), 1243 (C−O−C); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.53 (s, 1H), 10.48 (s, 1H), 10.39 (s, 1H), 8.51 (s, 2 H), 8.01−7.95 (m, 10 H), 7.81 (d, 4 H), 7.64 (s, 1 H), 7.58−7.51 (m, 3 H), 7.25 (d, 4 H), 7.01 (d d, 8 H), 1.59 (s, 6 H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 193.6, 166.1, 165.5, 165.4, 161.5, 152.8, 146.8, 142.9, 142.7, 140.0, 137.9, 134.8, 132.6, 131.1, 129.3, 128.8, 128.7, 128.5, 128.4, 128.3, 127.9, 124.2, 119.7, 119.6, 117.1, 41.9, 30.4.

Reaction of polymer **2** with oligobenzamide **6** (**11d**): yield 89%; IR (cm^{-1}, KBr) 3400−3200 (N−H), 1660 (C═O), 1241 (C−O−C); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.52−10.38 (m, 4 H), 8.50 (s, 2 H), 8.20−7.93 (m, 14 H), 7.81 (d, 4 H), 7.64−7.24 (m, 4 H), 7.04−6.99 (m, 4 H), 6.64 (m, 8 H), 1.59 (s, 6 H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 193.8, 167.3, 166.3, 165.7, 165.6, 161.7, 153.0, 146.9, 143.0, 142.8, 138.1, 135.0, 132.8, 132.2, 131.3, 130.6, 129.6, 129.4, 129.0, 128.8, 128.6, 128.1, 119.8, 117.3, 42.2, 30.8.

Reaction of polymer **2** with oligobenzoate **7** (**13a**): yield 93%; IR (cm^{-1}, film) 1742, 1656 (C═O), 1244 (C−O−C); ^{1}H NMR (THF-d_8, 300 MHz) δ 10.01 (s, 1 H), 8.46 (s, 2 H), 8.17−8.15 (d, 2 H), 8.08−8.05 (d, 2 H), 7.88−7.86 (d, 4 H), 7.80 (s, 1 H), 7.67−7.63 (m, 1 H), 7.54−7.49 (m, 2 H), 7.39−7.30 (m, 6 H), 7.06−7.00 (t, 8 H), 1.69 (s, 6H); ^{13}C NMR (THF-d_8, 75 MHz) δ 193.2, 165.3, 164.4, 162.3, 154.3, 153.8, 147.3, 140.2, 139.0, 134.0, 132.8, 132.7, 131.9, 130.2, 129.8, 129.3, 128.9, 128.7, 125.8, 124.5, 122.0, 119.9, 117.2, 42.5, 30.7.

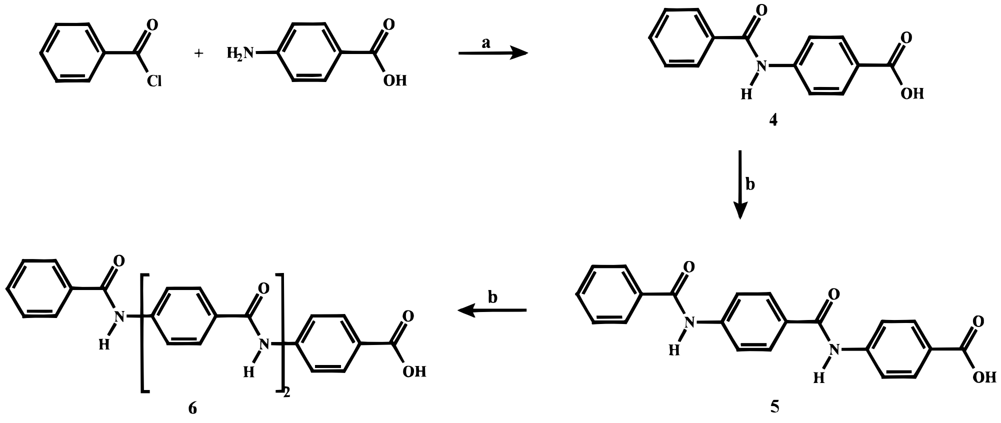
Reaction of polymer **2** with oligobenzoate **9** (**13a**): yield 90%; IR (cm^{-1}, film) 1742, 1656 (C═O), 1243 (C−O−C); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 9.96 (s, 1 H), 8.46 (s, 2 H), 8.27−8.17 (m, 4 H), 8.07 (d, 2H), 7.88−7.80 (m, 5H), 7.70−7.64 (m, 1H), 7.56−7.51 (m, 2 H), 7.46 (d, 2 H), 7.39 (d, 2 H), 7.32 (d, 4 H), 7.05−7.00 (m, 8 H), 1.68 (s, 6 H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 192.4, 164.5, 163.4, 162.9, 161.5, 155.2, 153.5, 153.1, 146.5, 139.4, 138.2, 132.1, 131.9, 131.1, 131.1, 129.5, 128.9, 128.5, 128.2, 127.9, 126.4, 123.6, 121.7, 121.2, 119.1, 116.4, 41.8, 30.0.

Results and Discussion

Synthesis of New Series of Oligobenzamides and Oligobenzoates. The syntheses of the oligobenzamides were achieved in good yields from acid chlorides and amines, as shown in Scheme 1. The condensations were typically carried out in anhydrous dimethylacetamide (DMAc) or dioxane in the presence of pyridine. Thionyl chloride was used to convert the carboxylic acid into an acid chloride.

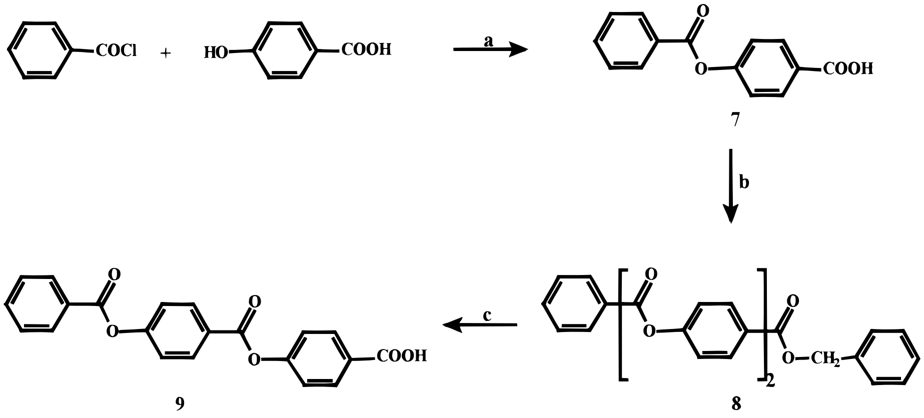
The oligobenzoate **7** was synthesized under Schotten−Baumann conditions, according to a method reported in the literature (Scheme 2).[18] The synthesis of oligobenzoate **9** was not as straightforward as in the case of oligobenzamides and required the use of a benzyl protecting group. The deprotection was effected in high yield, as reported in the literature.[16]

Scheme 1. Synthesis of the Oligobenzamides 4−6



a. Dioxane, pyridine
b. $SOCl_2$, pyridine; DMAc, pyridine, p-aminobenzoic acid

Scheme 2. Synthesis of the Oligobenzoates 7 and 9



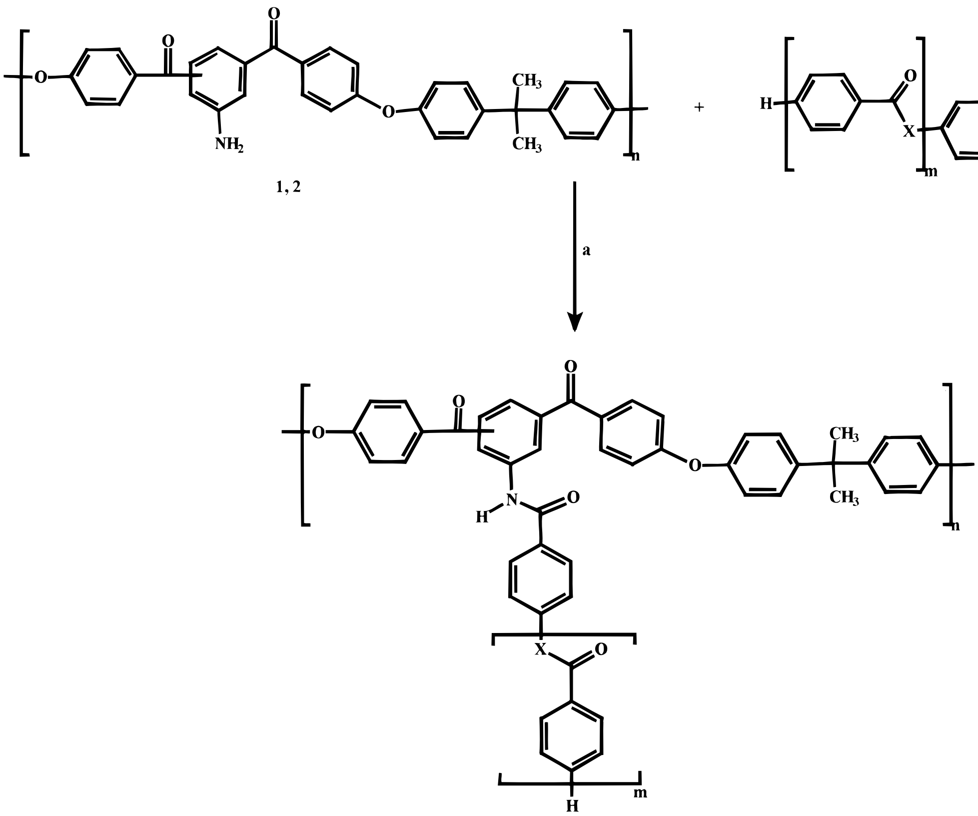
a. H_2O, NaOH
b. $SOCl_2$, pyridine; p-benzyl hydroxybenzoate, dioxane, pyridine
c. 10% Palladium-carbon, cyclohexadiene, DMAc

The structures of oligomers **4**−**9** were confirmed by IR, NMR spectroscopy, and mass spectrometry. The IR spectra of all oligomers show absorptions in the region 3000−2400 cm^{-1} due to the carboxylic acid stretch, a strong band at 3330 cm^{-1} appeared for the NH stretch of the amide of compounds **4**−**6,** and an additional ketone stretching at 1736 cm^{-1} proved the successful synthesis of the oligobenzoates **7** and **9**. In the ^{1}H NMR spectrum, the amide protons of **4**−**6** occur between δ = 10.4 and 10.5, and the carbonyl carbons are found between δ = 165 and 169 in the ^{13}C NMR spectra. Field desorption mass spectrometry (FD-MS) gives a molecular mass at *m/z* 241.1, 360.1, 479.1, and 242.0 for compounds **4**, **5**, **6**, and **7**, respectively, and electron impact mass spectrometry (EI-MS) gives a molecular peak for **9** at 362.1.

Modification of the Amine-Functionalized Poly(arylene ether ketone)s. The synthesis of isomeric amine-functionalized poly(arylene ether ketone)s **1** and **2** (Chart 1) has already been reported by us in a previous article.[19] In that publication, polymer **2** had also been successfully condensed with an acid chloride to yield the acetamide functionalized polymer **3**.[17] The oligomers previously synthesized were converted into their acid chlorides with thionyl chloride and were then reacted overnight with the amine-functionalized polymers in DMAc in the presence of pyridine (Scheme 3). Benzoyl chloride was also used directly in the polymer modification. Polymer **1** yielded the series of polymers **10a**−**c** and **12a,b**, and polymer **2** led to polymers **11a**−**d** and **13a,b**. Differences in the reactivity of the isomeric poly(arylene ether ketone)s could be observed. For example, the use of a large excess of acid chloride and longer reaction times were necessary to carry out the reaction with polymer **1**, whereas polymer **2**, although difficult to dissolve, reacted easily and quantitatively, as proven by the neat ^{1}H and ^{13}C NMR spectra obtained. The lower reactivity of polymer **1** can be explained by the steric hindrance caused by the ortho substitution of the amine group and by its reduced nucleophilicity, owing to the presence of an electron-withdrawing carbonyl group in the ortho position. Polymer **2**, in which the amine function is in the meta position, allows less steric strain from the benzoyl groups and thus enables a better access of the amine to reactive acid chlorides.

The structures of the transformed polymers were confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. The IR spectra of polymers **10a**−**c** and **12a,b** show a large band in the region 3200−3400 cm^{-1} due to the NH amide stretch as well as multiple bands between

Scheme 3. Modification of the Poly(arylene ether ketone)s



10a, 11a: X = NH, m = 0;
10b, 11b: X = NH, m = 1;
10c, 11c: X = NH, m = 2;
11d: X = NH, m = 3;
12a, 13a: X = O, m = 0;
12b, 13c: X = O, m = 1;

1650 and 1670 cm^{-1}, corresponding to the different ketone stretching frequencies, and the ester of **12a,b** gives rise to a sharp band at 1743 cm^{-1}. The same band is observed for the NH stretch in polymers **11a**−**d** and **13a,b**; however, in this case, the carbonyl stretch gives rise to a broad absorption, centered at 1656 cm^{-1}. Additionally, a band at 1742 cm^{-1} indicates the presence of the ester carbonyl group in polymers **13a,b**.

A gradual change in structures from polymer **1** and **2** through addition of oligoamide side chains is revealed by ^{1}H and ^{13}C NMR spectroscopy. The amine-functionalized poly(arylene ether ketone)s were quantitatively transformed into their amide counterpart; no amine function remains, as demonstrated by the shift of the signals in the ^{1}H NMR spectra. The ^{1}H NMR spectra of modified polymers **10a**−**c** and **12a,b** appear very clean, showing no sign of any unreacted polymer. Most characteristic is the absorption of the amide protons, observed between $\delta = 11.6$ and 10.44. In the ^{13}C NMR spectra, carbonyl signals are found at $\delta = 197.9$ and 194.3, as expected for the two ketones in the polymer backbone, due to the asymmetry, and between $\delta = 165.9$ and 164.7 for the amide and ester signals.

The amide protons appear between $\delta = 10.5$ and 9.7 for polymers **11a**−**d** and **13a,b**. Thus, ^{1}H NMR spectroscopy is found to be a good method to prove the successful addition of oligomers on the poly(arylene ether ketone) backbone, since the integration of the amide region against the aliphatic one allows the determination of the exact number of amide protons. The methyl protons are observed, as expected, at $\delta = 1.6$, and the protons in the ortho position of the graft typically give rise to a singlet at $\delta = 8.4$ in THF-d_8 and at $\delta = 8.5$ in DMSO-d_8. The chemical displacements within a series of modified polymers are similar (Figure 1, polymers **11a,b**). However, the intensities of the peaks vary with the length of the side chain. In ^{13}C NMR spectra, the carbonyl groups of the polymer backbone appear at $\delta = 193.7$ and the ones from the amide or ester groups between $\delta = 166.4$ and 165.4. The methyl carbons are typically found around $\delta = 31$ and the quaternary carbon of the poly(arylene ether ketone) backbone around $\delta = 43$, as expected. Thus, ^{13}C NMR as well the ^{1}H NMR spectrometry gives clear evidence for successful modification and high purity of the resulting polymer.

Not surprisingly, the solubility of the polymers changes according to the side-chain length. All polymers show

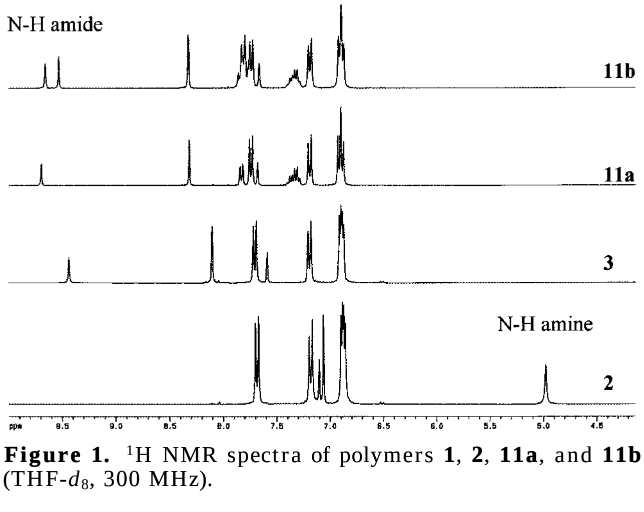


Figure 1. ^{1}H NMR spectra of polymers **1**, **2**, **11a**, and **11b** (THF-d_8, 300 MHz).

Table 1. Characterization of the Polymers

polymer	$T_g{}^a$ (°C)	$T_d{}^b$ (°C)	$M_n{}^c$ (10^{-4})	$M_w{}^c$ (10^{-4})
1	180	470	1.9	4.3
10a	194	460	2.2	4.6
10b	216	435	2.9	9.5
10c	246	418	*d*	*d*
12a	193	398	4.4	12.0
12b	190	392	2.1	4.5
3	197	465	2.9	9.3
11a	201	468	3.6	11.8
11b	221	432	4.3	14.5
11c	228	440	5.9	16.9
11d	234	402	6.4	17.3
13a	199	398	3.5	10.3
13b	193	395	3.0	9.6

[a] Second scan at a heating rate of 10 °C/min. [b] Onset temperature for 5% weight loss obtained in N_2 atmosphere. [c] Measured by GPC relative to polystyrene standards. [d] No value, due to the insolubility of the polymer.

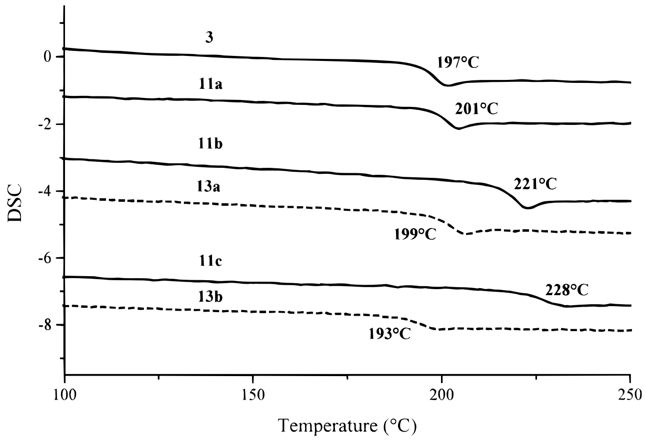


Figure 2. DSC thermograms of acetamide-substituted polymer **3**, polymers grafted with oligobenzamides **11a**−**c**, and polymers grafted with oligobenzoates **13a,b**.

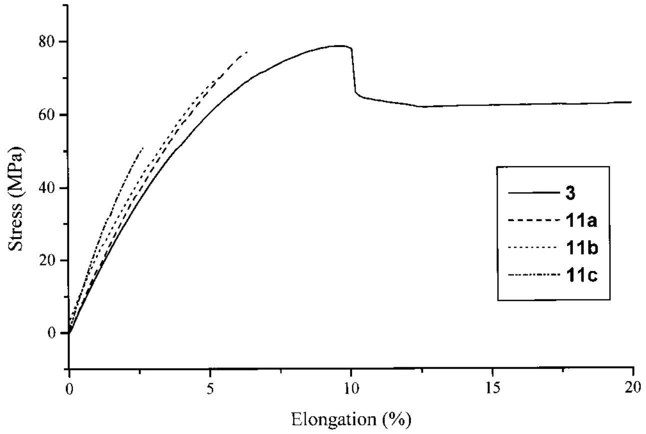


Figure 3. Engineering stress versus elongation for polymers **3** and **11a**−**c**.

good solubility in dipolar aprotic solvents, except **10c**, which only forms gellike solutions. Polymers **10a**, **11a**, **12a,b**, and **13a,b** are also soluble in chlorinated hydrocarbons and tetrahydrofuran. GPC measurements in THF for **10a,b**, **11a,b**, **12a,b**, and **13a,b** and in dimethylformamide for **11c,d**, relative to polystyrene standards, display, as expected, an increase in molecular weight as compared to that of the initial polymer (Table 1). The apparent average molecular weight augments regularly with increasing length of the pendant groups. The GPC curve of polymer **11c,d** is bimodal, an effect which has already been observed in other instances and can be expected in the case of aggregation.[20] Another explanation for that phenomenon could arise from the affinity of the polymer toward the column substrate.[21] Unfortunately, due to the low solubility of the polymers, no further studies could be performed to substantiate these explanations.

To study the significance of the hydrogen bonds between the side chains on the thermal properties of the polymers, it was desired to compare polymers with pendant groups of the same length and stiffness but different chemical nature. In this regard, the comparison of the effect of oligobenzamides, capable of forming hydrogen bonds, to that of oligobenzoates, with similar chain stiffness yet unable to give rise to such interactions, was found important. As expected, introducing side chains onto the polymer backbone affected the glass transition temperatures (T_g) and thermal stability. As shown in Table 1, the T_gs of the modified polymers are in the range 194−246 °C for **10a**−**c**, and 201−234 °C for **11a**−**d** (Figure 2), varying according to the oligobenzamide used. Polymers **12a,b** display T_gs of 193 and 190 °C, and the T_gs of polymers **13a,b** appear at 199 and 193 °C, respectively. In general, introducing side chains on a polymer backbone is likely to decrease its T_g, due to the new degree of mobility introduced. In our case, the steric hindrance introduced by the side groups causes the increased restriction of free rotation of the bond connecting the benzene to the carbonyl groups and reduces the overall chain mobility, thus increasing the T_g of all polymers. The result of this effect can be directly observed upon addition of one benzoyl group onto the backbone, the T_gs of polymers **10a** and **11a** displaying a clear increase as compared to their unsubstituted counterparts. Besides, the highly polar nature of the benzamide side groups and their ability to form hydrogen bonds leads to an additional improvement in the thermal properties of the poly(ether ketone), as can be seen for polymers **10b,c** and **12b**−**d**, in which cases the T_g increases with the length of the side chain. Also, the modification of polymer **1**, in which the steric hindrance is playing a more important role than for polymers derived from **2**, due to the ortho position of the substituent, leads to a more significant increase of the thermal properties (from 180 to 246 °C for polymer **1** to **10c**, as compared to a change from 197 to 234 °C for polymer **3** to **11d**). It should be noted that similar trends have been observed in polyamide or polyimide containing a meta or ortho oligobenzamide side chain.[7,8] Furthermore, the evident decrease in T_g from polymers **10b,c** to **12a,b**, and from **11b,c** to **13a,b**, resulting from the exchange of the amides for ester links, certainly confirms that, in the absence of strong interchain interactions, the longer side chains lead to a decrease of the T_g.

Thermogravimetry of the pendant poly(ether ketone)s **10a**−**c**, **11a**−**d**, **12a,b**, and **13a,b** and the unmodified **1** and **2** indicates that, in most cases, the presence of a benzamide or benzoate pendant group results in a small to moderate decrease in thermal stability, ranging from 5 to 45 °C in nitrogen. The transformed polymers **10a**−**c**, **11a**−**d**, **12a,b**, and **13a,b** exhibit 5% weight loss at temperatures from 392 to 468 °C, which compares favorably with the results for the unsubstituted polymers **1** and **2**, 470 and 465 °C, respectively. The polymers with oligobenzoate side chains generally prove to be less thermally stable than their counterparts

Table 2. Mechanical Properties of Polymers 3, 11a–c, and 13a

polymer	E′ (Gpa)	stress at yield (MPa)	strain at yield (%)	stress at break (MPa)	strain at break (%)
3	1.67	78.5	9.67	63.0	26.08
11a	1.97	76.9	6.80	76.9	6.80
11b	2.23	70.1	6.14	70.1	6.14
11c	2.52	50.9	5.57	50.9	5.57
13a	1.97	68.7	4.85	68.7	4.85

[a] The data were obtained from the average values of five rectangular samples (4 cm × 1 cm) cut in films obtained from solution. Crosshead speed, 1 mm min^{-1}; room temperature.

bearing oligobenzamides. However, no significant decomposition is observed below 400 °C.

The results of mechanical studies gave further evidence for the ability of the side chains to significantly affect the ordering of the main chain and thus strengthen the polymer. The plot of the engineering stress versus elongation for representative samples of the polymers is illustrated in Figure 3.

Young's modulus increases regularly with the length of the oligobenzamide side chain introduced, from 1.67 Gpa for **3** to 2.52 Gpa for **11c** (Table 2). This suggests that polymer **11c** is the stiffest material among the series of polymers studied, which can be explained by the strengthening induced by the hydrogen bonds formed between the side chains introduced on the polymer backbone. Polymer **3** is the most ductile material, with a maximum elongation of 26%, compared with the brittle polymers **11a–c**, displaying maximum elongation between 6.80 and 5.6%, the brittleness increasing with side-chain length.

As expected, Young's modulus decreases when oligoamide is replaced by oligobenzoate pendant groups of equal length. Polymer **13a** displays a Young's modulus comparable to that of **11b**, as expected since both polymers contain the same amount of amide functions, thus affecting their strength similarly.

Thus, the results of both thermal and mechanical studies establish the considerable importance of hydrogen bonding on the improvement of the polymer properties of **10** and **11** with the side chain length.

Conclusion

The two amine-functionalized poly(arylene ether ketone)s previously synthesized were successfully modified by condensation with carboxy-terminated oligobenzamides as well as benzoyl chloride. The poly(ether ketone)s exhibit different reactivities toward the transformation: the ortho-substituted amino polymer is found to be less reactive than the meta-substituted one, due to steric hindrance and low nucleophilicity of the amine function. The transformed polymers show different thermal and mechanical behavior, depending on the length and chemical nature of the side chains. In general, polymers with pendant oligobenzoates have lower T_gs in comparison to the respective polymers with oligobenzamide side chains. Moreover, whereas the T_gs increase with the length of the side chain in the case of oligobenzamides, the longer oligoesters induce a decrease of the T_gs, thus leading us to the conclusion that hydrogen bonding of the side chains plays a crucial role in the improvement of the polymer properties of **10a–c** and **12a–d**. Mechanical measurements allowed further confirmation of this hypothesis, demonstrating the ability of the oligobenzamide side chains to affect the strength and ductility of the polymer.

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