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Poly(arylene ether)s Containing 2,2′-Dibenzoylbiphenyl Units from Isomeric 2-Chlorofluorobenzophenones

Chunhao Zhang and Zhi Yuan Wang*

Department of Chemistry, Carleton University, Ottawa, Ontario, Canada K1S 5B6

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ABSTRACT: High molecular weight, amorphous, soluble poly(arylene ether)s containing 2,2′-dibenzoylbiphenyl units are synthesized, based on the difluoro monomers derived from 2-chlorofluorobenzophenones, by a nickel(0)-catalyzed coupling reaction. The glass transition temperatures range from 156 to 230 °C. The 5% weight losses from these polymers by thermal gravimetric analysis occur all above 460 °C in nitrogen and 448 °C in air.

Introduction

Poly(arylene ether)s such as PEEK[1] and Udel[2] are an important class of high-performance thermoplastics. The combined chemical, physical, and mechanical properties of these materials have led to their use in a variety of applications as coatings, adhesives, and matrix resins for advanced composites.[3,4] These aromatic polymers have functionalities like ether, ketone, and sulfone. They can be constructed via the formation of the ether bond by nucleophilic substitution reactions of activated dihalides with bisphenols[3,5,6] or masked bisphenols[7,8] and sodium carbonate in the presence of silica/Cu catalyst.[9] An alternative route involves electrophilic (Friedel–Crafts) acylation of arene.[3,10] It has also been shown that a nickel(0)-catalyzed coupling reaction can be utilized for the preparation of these polymers through the aryl–aryl bond formation.[11]

Modifications on the properties of poly(arylene ether)s have been focused on the changes of substitution patterns and the "core angle" (the valence angle between the exocyclic bond) of aromatic units in polymers[12] and the incorporation of heterocycles[13] into the polymer backbone. So far, para-directed structural units such as 4,4′-biphenyl or 1,4-phenylene predominant the primary structure of polymer. The change of the substitution pattern from a para to a meta substitution can alter the properties of polymers as the chain linearity varies. However, effect of the ortho-substitution pattern on the property of poly(arylene ether)s has not yet been fully explored.

Recently, poly(arylene ether)s with a 1,2-dibenzoyl benzene moiety have been prepared, and show higher T_g's as compared to their analogues containing 1,3- and 1,4-dibenzoylbenzene moieties.[14] It is well worth notice that these polymers undergo cycloaddition reactions to form heterocyclic polymers.[15] Polyamides and polyarylates containing 2,2′-disubstituted biphenyls have been reported.[16] The solubilities of these polymers are greatly enhanced, and thermal stabilities are also retained. Although poly(arylene ether)s with a 3,3′- or 4,4′-dibenzoylbiphenyl unit (B and C, Figure 1) are known,[11a] those with a 2,2′-type structural feature (A, Figure 1) have not yet been reported.

Similar effects may also be predicted for poly(arylene ether)s having a 2,2′-dibenzoylbiphenyl unit (A, Figure 1). The twisted biphenyl structure would result in better solubility and good thermostability for the resulting polymers. In addition, the carbonyl functional groups along the polymer backbone can further be transformed to other functionalities, which produces another type of polymer.[17] Therefore, it is appropriate to investigate a series of poly(arylene ether)s containing this versatile group.

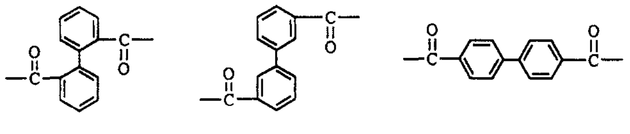
A, 2,2′- B, 3,3′- C, 4,4′-

Figure 1. Isomeric dicarboxybiphenyls.

The polymers of this type can be synthesized either by the polymerization of the monomers containing a 2,2′-disubstituted biaryl or through the formation of the 2,2′-disubstituted biaryl linkage in the polymerization. Certainly, monomers containing such a structural unit can be elaborated based on a biaryl compound, but a variety of structural features would be preserved if they can be made by the formation of the aryl–aryl linkage under mild conditions. The aryl–aryl carbon bond can be formed in many ways such as the classical Ullmann reaction,[18] the palladium-catalyzed coupling or aryl bromide and arylboronic acid,[19] and the nickel-catalyzed coupling of aryl halides.[19] The efficient synthesis of biaryls from aryl chlorides using a catalytic amount of nickel salt, triphenylphosphine, and a reducing metal has now been firmly established.[11,20a,b] In this paper, we report the synthesis of poly(arylene ether)s containing 2,2′-dibenzoylbiphenyl units from isomeric 2-chlorofluorobenzophenones utilizing a nickel(0)-catalyzed coupling reaction.

Experimental Section

General Methods. *N*-Methyl-2-pyrrolidinone (NMP), tetramethylene sulfone (TMSO$_2$), 2-chloro-4′-fluorobenzophenone, 2-chloro-4-fluorobenzoic acid, thionyl chloride (SOCl$_2$), triphenylphosphine, zinc (powder), 3,5-di-*tert*-butylphenol, and other common organic solvents were purchased from Aldrich Chemical Co. and used as received. Anhydrous nickel bromide was obtained from its hydrate (Aldrich) by heating at 100 °C under vacuum for 48 h. *N,N*-Dimethylacetamide (DMAc) (Aldrich) was distilled over P$_2$O$_5$. 4,4′-Isopropylidenediphenol (**3a**, BPA) (Aldrich), 4,4′-(hexafluoroisopropylidene)diphenol (**3b**) (Aldrich), 4,4′-biphenol (**3c**) (Aldrich), 1,4-hydroquinone (**3d**) (Aldrich), and 9,9-bis(4-hydroxyphenyl)fluorene (**3e**) (General Electric Co.) were purified by recrystallization.[4] Aluminum chloride was purchased from Fluka Chemical Corp.

Melting points were taken on a Fisher-Johns melting apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Gemini-200 or a Bruker-400 instrument using tetramethylsilane as an internal reference. A 15-s delay time was set to ensure a correct integration in the ^{1}H NMR study on end-capped polymers. Infrared measurements were performed on a Perkin-Elmer 1600 FTIR instrument. Low resolution mass spectra were obtained on a Du Pont 21-492B instrument.

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Microanalyses were done at Guelph Chemical Laboratories, Ltd., Ontario, Canada. Molecular weights were determined on a Perkin-Elmer LC-250 GPC instrument relative to polystyrene standards using chloroform as an eluent at a flow rate of 1.0 mL/min; an UV detector was set at 254-nm wavelength. Inherent viscosities were measured in a 0.5 g/dL chloroform solution at 25 °C using an Ubbelohde dilution viscometer. The glass transition temperatures were determined by differential scanning calorimetry (DSC) either on a Seiko DSC 220 or a Du Pont DSC 2100 at a heating rate of 10 °C/min under nitrogen, taken as the midpoint of the change in slope of the baseline. Thermal gravimetric analysis (TGA) was performed on a Seiko TG/DTA 220 at a heating rate of 10 °C/min in nitrogen and in air (flow rate of 200 mL/min).

Monomer Synthesis. 2,2′-Bis(4-fluorobenzoyl)biphenyl (**1**). A mixture of $NiBr_2$ (492 mg, 2.25 mmol), zinc dust (4.5 g, 69 mmol), and Ph_3P (4.5 g, 17 mmol) in DMAc (30 mL) was stirred under nitrogen at 50 °C until a red solution was formed. To the resulting solution was added 2-chloro-4′-fluorobenzophenone (10.56 g, 45 mmol) and the reaction mixture was then heated at 80–90 °C for another hour. The mixture was cooled to room temperature and filtered. The filtrate was poured into water (200 mL). The resulting solids were collected by filtration and recrystallized from cyclohexane. The mother liquor contained mainly Ph_3P and was reused in another reaction. After further purification by recrystallization from acetone/MeOH (1/1), the monomer **1** was obtained as colorless crystals. The mean yield for two consecutive reactions was 14.6 g (82%): mp 148.5–149 °C (lit.[21] 136.5–137.5 °C); ^1H NMR (200 MHz, $CDCl_3$) δ 7.73 (4 H, dd, J_{H-F} = 8.7, 5.4 Hz), 7.40–7.31 (8 H, m), 6.94 (4 H, t, $J_{H-F,H-H}$ = 8.6 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 195.78, 167.91, 162.84 (J_{C-F} = 254.8 Hz), 139.89, 137.79, 133.49, 133.44 (J_{C-F} = 9.2 Hz), 132.95, 132.76 (J_{C-F} = 2.9 Hz), 131.35, 130.18, 129.06, 126.81, 115.20, 114.77 (J_{C-F} = 22.0 Hz); MS (*m*/*e*) 275 ($M^{\bullet+} - {}^{\bullet}COPhF$, 100%).

2,2′-Dibenzoyl-5,5′-difluorobiphenyl (**2**). A mixture of $SOCl_2$ (100 mL, excess), 2-chloro-4-fluorobenzoic acid (25.0 g, 143 mmol), and *N*,*N*-dimethylformamide (0.5 mL) was stirred at room temperture for a half hour and then heated at 60 °C until a clear solution was obtained. An excess of $SOCl_2$ was removed by distillation. The residue was distilled under vacuum to give 27.5 g (quantitative) of the 2-chloro-4-fluorobenzoyl chloride as a colorless liquid which was used immediately in the following reaction.

To a mixture of 2-chloro-4-fluorobenzoyl chloride (27.5 g) and benzene (100 mL, excess) in a dry flask was added $AlCl_3$ (23.04 g, 1.2 equiv) in portions at 0–5 °C (ice water bath). After the completion of the addition of $AlCl_3$, the reaction mixture was allowed to warm up gradually and stirred at room temperature overnight. After heating at 50–60 °C for 1 h, the mixture was then poured into ice and treated with 20 mL of aqueous HCl (1 N). The organic layer was partitioned, and the water layer was extracted with chloroform (2 × 100 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. After removal of solvents and vacuum distillation, 2-chloro-4-fluorobenzophenone was obtained as a white solid: 29.2 g (87%): mp 45–47 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (2 H, dd, J = 8.0, 1.1 Hz), 7.56 (1 H, tt, J = 8.0, 1.1 Hz), 7.44 (2 H, t, J = 8.0 Hz), 7.38 (1 H, dd, J_{H-F} = 8.4, 6.0 Hz), 7.18 (1 H, dd, J_{H-F} = 8.6, 2.4 Hz), 7.07 (1 H, td, $J_{H-F,H-H}$ = 8.4, 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.19, 164.52, 162.00 (J_{C-F} = 253.7 Hz), 136.54, 134.83, 134.80 (J_{C-F} = 3.8 Hz), 133.77, 133.00, 132.91 (J_{C-F} = 10.4 Hz), 131.02, 130.93 (J_{C-F} = 9.3 Hz), 130.00, 128.68, 117.77, 117.52 (J_{C-F} = 24.8 Hz), 114.28, 114.07 (J_{C-F} = 23.6 Hz).

2,2′-Dibenzoyl-5,5′-difluorobiphenyl (**2**) was prepared, as described for the synthesis of **1**, from 2-chloro-4-fluorobenzophenone. A typical work-up procedure for a reaction with 15.0 g (64 mmol) of 2-chloro-4-fluorobenzophenone is as follows: The mixture was filtered through Celite and washed with chloroform. The chloroform solution was diluted to ca. 300 mL and washed with H_2O (3 × 100 mL) to remove DMAc. It was then filtered through a pad of silica gel. The filtrate was evaporated to dryness and the residue was recrystallized from ethanol to give white crystalline solids: 11.24 g (88%): mp 129–130 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (4 H, dd, J = 8.2, 1.2 Hz), 7.42–7.37 (4 H, m), 7.26 (4 H, t, J = 8.0 Hz), 7.11 [2 H, dd, J = 9.2 (H–F), 2.5 Hz], 7.03 [2 H, td, J = 8.2 (H–H and H–F), 2.5 Hz]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.90, 164.53, 162.02 (J_{C-F} = 253.0 Hz), 142.53, 142.45 (J_{C-F} = 8.2 Hz), 137.22, 134.30, 134.27 (J_{C-F} = 3.4 Hz), 132.86, 132.01, 131.92 (J_{C-F} = 9.0 Hz), 130.21, 128.05, 118.61, 118.39 (J_{C-F} = 22.5 Hz), 114.19, 113.98 (J_{C-F} = 21.5 Hz). Anal. Calcd for $C_{26}H_{16}O_2F_2$: C, 78.42; H, 4.08; F, 9.53. Found: C, 78.18; H, 4.09; F, 9.31.

Polymer Synthesis. Method A: The following is a typical procedure. In a three-neck flask were placed monomer **1** (1.1949 g, 3.0 mmol), bisphenol **3a** (684.9 mg, 3.0 mmol), K_2CO_3 (829 mg, 6.0 mmol), NMP (9 mL), and toluene (20 mL). The flask was equipped with a Dean-Stark trap connected with a condenser and a nitrogen purge line. The mixture was purged with nitrogen for 20 min before the flask was heated at 120–130 °C (oil bath temperature). The water and toluene were codistilled while deoxygenated toluene was introduced. After about 2–3 h, the temperature gradually rose to 180 °C and was held for 2 h. The resulting viscous solution was cooled to room temperature, diluted with 8.0 mL of NMP, and precipitated into methanol containing a few drops of concentrated HCl. The polymer was purified by dissolving in chloroform, filtering through a pad of Celite, and then precipitating into methanol. After being dried in an oven at 60 °C under vacuum, the fibrous polymer **4a** weighed 1.59 g (89%).

4a: ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (4 H, d, J = 8.5 Hz), 7.42–7.24 (8 H, m), 7.22 (4 H, d, J = 8.7 Hz), 6.92 (4 H, d, J = 8.7 Hz), 6.79 (4 H, d, J = 8.5 Hz), 1.68 (6 H, s); IR (film, cm^{-1}) 1661 ($C{=}O$). **4b**: ^1H NMR (200 MHz, $CDCl_3$) δ 7.68 (4 H, d, J = 8.8 Hz), 7.38–7.23 (12 H, m), 6.89 (4 H, d, J = 9.0 Hz), 6.82 (4 H, d, J = 8.8 Hz); IR (film, cm^{-1}) 1663($C{=}O$). **4c**: ^1H NMR (200 MHz, $CDCl_3$) δ 7.91 (4 H, d, J = 8.8 Hz), 7.75 (4 H, d, J = 8.6 Hz), 7.50–7.24 (8 H, m), 7.00 (4 H, d, J = 8.8 Hz), 6.89 (4 H, d, J = 8.6 Hz); IR (film, cm^{-1}) 1662 ($C{=}O$). **4e**: ^1H NMR (200 MHz, $CDCl_3$) δ 7.71 (2 H, d, J = 6.9 Hz), 7.62 (4 H, d, J = 8.8 Hz), 7.41–7.20 (14 H, m), 7.17 (4 H, d, J = 8.7 Hz), 6.80 (4 H, d, J = 8.7 Hz), 6.73 (4 H, d, J = 8.8 Hz); IR (film, cm^{-1}) 1662 ($C{=}O$).

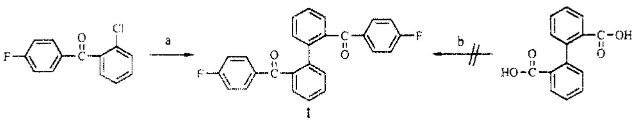
Method B: A mixture of the masked hydroquinone **3f**[22] (562 mg, 2.0 mmol), $KHCO_3$ (801 mg, 8.0 mmol), and monomer **1** (796.6 mg, 2.0 mmol) in $TMSO_2$ (7.0 mL) was purged with nitrogen for 20 min and then heated at 180–190 °C under nitrogen for 2 h. The viscous solution was diluted with 4 mL of $TMSO_2$ and precipitated into methanol containing a few drops of concentrated HCl. The polymer was then purified in the same way as in method A. **4d**: 80% yield; ^1H NMR (200 MHz, $CDCl_3$) δ 7.70 (4 H, d, J = 8.8 Hz), 7.44–7.24 (8 H, m), 7.00 (4 H, s), 6.80 (4 H, d, J = 8.8 Hz); IR (film, cm^{-1}) 1661 ($C{=}O$).

Method C: A typical procedure is as follows. A three-neck flask was charged with monomer **2** (1.1949 g, 3.0 mmol), bisphenol **3d** (330.3 mg, 3.0 mmol), chlorobenzene (1.0 mL), $TMSO_2$ (4.0 mL), and K_2CO_3 (539 mg, 3.9 mmol). The mixture was purged with nitrogen for 20 min and then heated to 235 °C in 15–20 min. The azeotrope of chlorobenzene and water was distilled off at 140–150 °C. After 1 h, the mixture was diluted with 4 mL of $TMSO_2$ and the reaction continued for an additional 2 h. The mixture was then cooled to ca. 160 °C, diluted with 15 mL of 1,1,2,2-tetrachloroethane (TCE), and poured into methanol. The fibrous polymer was further purified in the same way as in method A. The yield was 1.36 g (97%).

5a: ^1H NMR (200 MHz, $CDCl_3$) δ 7.69 (4 H, d, J = 8.2 Hz), 7.42–7.17 (8 H, m), 7.12 (4 H, d, J = 8.9 Hz), 6.97–6.80 (8 H, m), 1.68 (6 H, s); IR (film, cm^{-1}) 1663 ($C{=}O$). **5b**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (4 H, d, J = 7.3 Hz), 7.42–7.38 (4 H, m), 7.32 (4 H, d, J = 8.6 Hz), 7.27 (4 H, t, J = 8.6 Hz), 7.06 (2 H, d, J = 2.4 Hz), 6.96 (6 H, m); IR (film, cm^{-1}) 1666 ($C{=}O$). **5c**: ^1H NMR (200 MHz, $CDCl_3$) δ 7.74 (4 H, d, J = 7.4 Hz), 4.73–7.21 (12 H, m), 7.04 (4 H, d, J = 8.4 Hz), 6.96–6.87 (4 H, m); IR (film, cm^{-1}) 1664 ($C{=}O$). **5d**: ^1H NMR (200 MHz, $CDCl_3$) δ 7.73 (4 H, d, J = 7.7 Hz), 7.45–7.21 (8 H, m), 6.92–6.79 (8 H, m); IR (film, cm^{-1}) 1659 ($C{=}O$). **5e**: ^1H NMR (200 MHz, $CDCl_3$) δ 7.80 (2 H, d, J = 8.2 Hz), 7.62 (4 H, d, J = 7.6 Hz), 7.42–7.21 (10 H, m), 7.21–7.18 (8 H, m), 6.90 (2 H, br.s), 6.81 (6 H, d, J = 8.6 Hz); IR (film, cm^{-1}) 1662 ($C{=}O$).

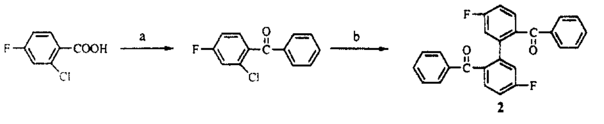
Capping Experiments. In a three-neck flask were placed monomer **1** (1.992 g, 5.000 mmol), bisphenol **3b** (1.664 g, 4.950 mmol), K_2CO_3 (1.383 g, 10.00 mmol), 3,5-di-*tert*-butylphenol (20.63 mg, 0.100 mmol), NMP (16 mL), and toluene (40 mL).

Scheme I. Synthesis of Monomer 1



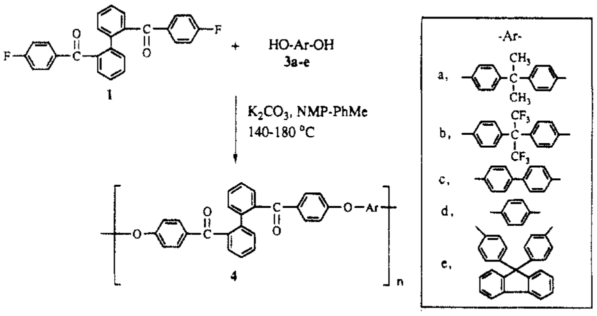
a: $NiBr_2$, Zn, Ph_3P, DMAc, 80-90 °C. b: i, $SOCl_2$, 50 °C; ii, $AlCl_3$, PhF, 25-60 °C.

Scheme II. Synthesis of Monomer 2

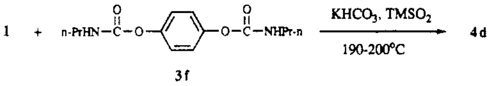


a: i, $SOCl_2$, 50-60 °C; ii, $AlCl_3$, benzene, 60 °C. b: $NiBr_2$, Zn, Ph_3P, DMAc, 80-90 °C.

Scheme III. Synthesis of Poly(arylene ether)s 4



Scheme IV. Synthesis of Polymer 4d Using Masked Hydroquinone 3f



The flask was equipped with a Dean-Stark trap connected with a condenser and a nitrogen purge line. The mixture was purged with nitrogen for 20 min and then heated at 120–130 °C (oil bath temperature) for 2–3 h to remove the azeotrope. The temperature was gradually increased to 180 °C and held for 2 h until a viscous solution was formed. The reaction mixture was diluted with NMP (16 mL) and precipitated into MeOH containing a few drops of concentrated HCl. The polymer **6** was purified as above. The number of repeat units (n) was 105, determined by ^1H NMR.[23] ^1H NMR (200 MHz, $CDCl_3$) δ 7.68 (4 H, d, J = 8.8 Hz), 7.38–7.23 (12 H, m), 6.89 (4 H, d, J = 9.0 Hz), 6.82 (4 H, d, J = 8.8 Hz), 1.28 (s). $[\eta]_{inh}$ = 0.36 dL/g (a 0.5 g/dL solution in chloroform, 25 °C).

Polymer **7** was prepared similarly. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (4 H, d, J = 7.3 Hz), 7.42–7.38 (4 H, m), 7.32 (4 H, d, J = 8.6 Hz), 7.27 (4 H, t, J = 8.6 Hz), 7.06 (2 H, s, J = 2.4 Hz), 6.96 (6 H, m), 1.31 (s). $[\eta]_{inh}$ = 0.42 dL/g (a 0.5 g/dL solution in chloroform, 25 °C).

Results and Discussion

There are three possible approaches to the synthesis of the poly(arylene ether)s containing a 2,2′-dibenzoylbiphenyl unit, including the nucleophilic substitution of activated aromatic dihalides with bisphenols, the electrophilic substitution of arenes with *o*-diphenic acid or its derivatives, and the generation of a biaryl linkage in the polymer forming reactions. Among them, the nucleophilic substitution is the choice of reaction since the difluoride monomer containing a 2,2′-dibenzoylbiphenyl unit can be readily prepared. In this approach, a variety of poly(arylene ether)s can be produced because of the availability of many commercial bisphenols.

Monomer Synthesis. The preparation of the difluoride monomer **1** was initially attempted using the Friedel–Crafts reaction of fluorobenzene and *o*-diphenic acid chloride. However, the reaction failed to produce the desired product due to the competitive intramolecular acylation (Scheme I). Based on the chemistry of the nickel(0)-catalyzed coupling reaction of aryl chlorides, 2-chlorofluorobenzophenones would be ideal candidates for the synthesis of the target monomers. Thus, monomer **1**, 2,2′-bis(4-fluorobenzoyl)biphenyl, was then synthesized by coupling commercially available 2-chloro-4′-fluorobenzophenone in DMAc at 80–90 °C in 82% yield (Scheme I). A greater than 99% conversion of the starting material was observed in less than 1 h. Excess of zinc and triphenylphosphine were removed by filtration and recrystallization from cyclohexane, respectively. The monomer grade compound **1** was obtained after recrystallization twice. Since the mixture of triphenylphosphine and the residual product recovered from the mother liquor can be reused in the next reaction, a nearly quantitative yield should be achieved eventually. The reaction has also been scaled up to 100 g without any difficulties. Similarly, the second monomer, 2,2′-dibenzoyl-5,5′-difluorobiphenyl (**2**), was easily prepared from 2-chloro-4-fluorobenzophenone which was derived from commercially available 2-chloro-4-fluorobenzoic acid (Scheme II). After purification by simple filtration and recrystallization, monomer **2** was obtained in 88% yield.

These monomers are very reactive in the polymerization because of the presence of two carbonyl groups at the para position relative to the fluorine groups. The chemical shifts of the protons at the ortho positions of carbonyl grops for **1** and **2** were found to be ca. 7.45 and 7.75 ppm, indicating a strong electron-withdrawing effect of the carbonyl groups.[13]

Polymer Synthesis. A series of polymers from the difluoride **1** and bisphenols **3a–e** was synthesized by standard nucleophilic condensation polymerization. Polymerizations were performed using a stoichiometric ratio of monomers in the presence of excess (2 equiv) of K_2CO_3 in NMP at ca. 20% solid contents (Scheme III). During the initial stage of reaction, the water being formed was removed as an azeotrope with toluene at 140 °C. Upon completion of the formation of bisphenoxide and dehydration (2–3 h), the reaction mixture was heated up to 180 °C and held for 2–3 h. The resulting polymers were coagulated in an excess of methanol and further purified by dissolving in chloroform, filtering through a pad Celite, and precipitating into methanol. Under these conditions, however, polymer **4d** with moderate molecular weight (η_{inh} = 0.25 dL/g) was obtained from **1** and **3d**, presumably because of the oxidative decomposition of **3d** and/or the cleavage of the resulting polymer by potassium fluoride at elevated temperatures in basic NMP. The chain cleavage during the polymerization was also observed for other polymers such as **4a** if the reaction was kept longer than 6 h at 180–200 °C. The high molecular weight polymer **4d** was then synthesized using the masked hydroquinone (**3f**) in $TMSO_2$ according to a recently reported procedure[8] (Scheme IV). The carbamate protecting group was cleaved *in situ* with potassium bicarbonate and the resulting hydroquinone potassium salt reacted rapidly with the commonomer **1** to form the polymer **4d**. Because there was no water being formed during the polymerization, there was no need to use any azeotroping solvent (e.g., toluene). A high molecular weight polymer could be obtained in about 2 h. A high boiling solvent (e.g., $TMSO_2$) was necessary for keeping the growing polymers in solution since the polymerization of **1** and **3a** in DMAc resulted in the precipitation of oligomers at the early stage of reaction. We also found that no degradation of the growing polymer occurred in less basic solvents like DMAC and $TMSO_2$.

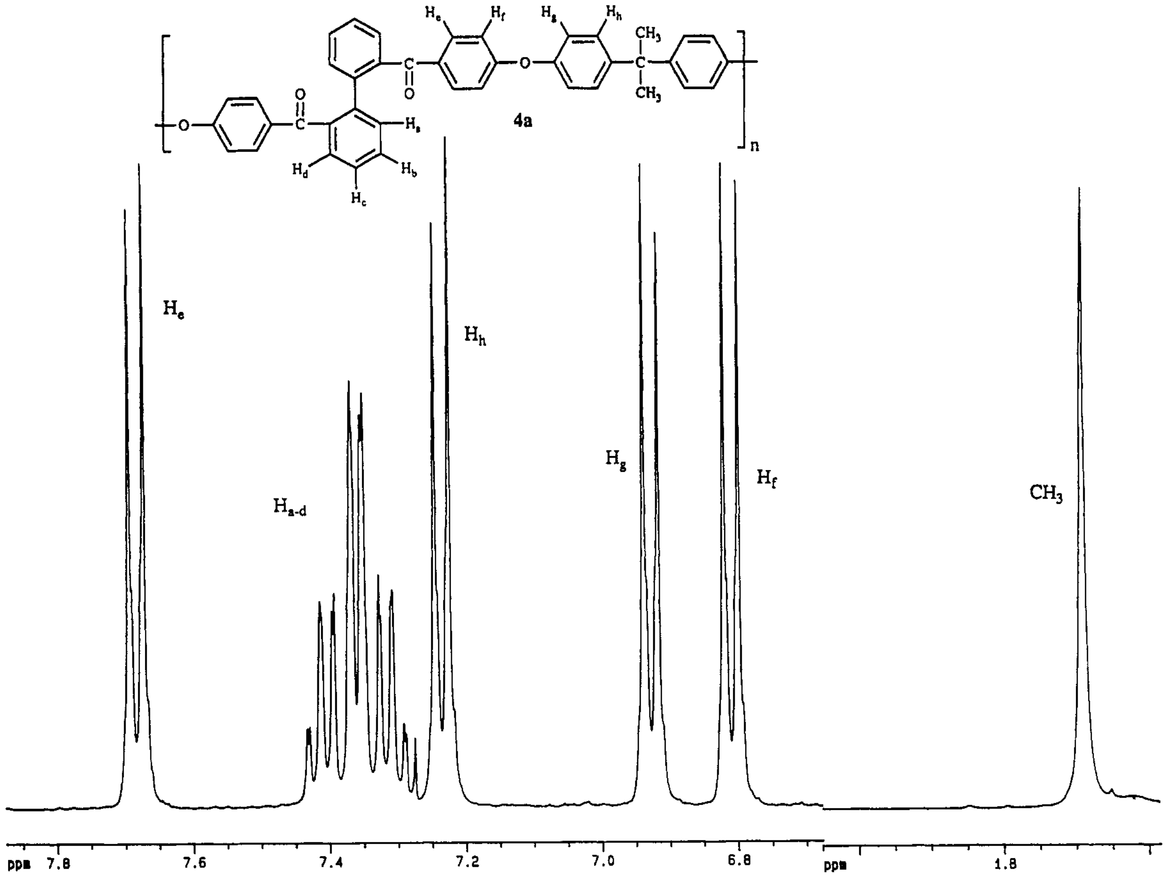
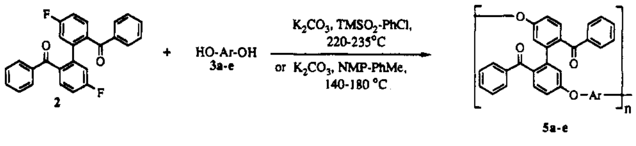


Figure 2. ^{1}H NMR (400 MHz) of poly(arylene ether) **4a** in $CDCl_3$.

Scheme V. Synthesis of Poly(arylene ether)s 5



During the course of our studies, a more convenient method for the synthesis of poly(arylene ether)s was reported,[5] using $TMSO_2$ as a solvent and chlorobenzene as an azeotroping solvent in a higher solid content. It was very successful for the preparation of poly(arylene ether sulfone)s.[5] Therefore, we decided to apply this method to the synthesis of polymers **5**. Thus, polycondensations of the difluoride **2** and bisphenols **3a–e** were conducted in $TMSO_2$ at 30–35% solid contents in the presence of K_2CO_3 (1.3 equiv) (Scheme V). The reaction solution became highly viscous in a couple of hours (the magnetic stirring usually stopped). Dilution was usually needed to maintain the stirring. The polymers **5a–e** were isolated in the same way as for **4a–e**. It should be mentioned that both methods are applicable for the synthesis of polymers **4** and **5**, for the fact that the polymer **5a** is synthesized by the method (NMP, K_2CO_3, 140–180 °C) used for **4a**.

The polymers **6** and **7** with controlled molecular weights were also prepared from monomers **1** and **2** with bisphenol **3b** in the presence of 3,5-di-*tert*-butylphenol as an end-capping agent, respectively. The end-capped polymers were then subjected to the NMR analysis in order to determine the exact molecular weights and compare with those obtained by GPC analysis.

Polymer Characterization and Properties. The structures of polymers **4a–e** and **5a–e** have been confirmed by NMR and IR spectroscopies. For these polymers, the carbonyl absorption in IR is located in the region of 1655–1666 cm^{-1}. The most conclusive evidence is from NMR data. As shown in Figures 2 and 3, the proton and carbon-13 spectra of **4a** are consistent with its structure. The resonance signals corresponding to the aromatic protons of the benzoyl group appear as two sets of doublets at 7.67 and 6.79 ppm; another pair of doublets is at 6.92 and 7.22 ppm due to the protons of the bisphenol unit. The multiple peak at 7.24–7.42 ppm is assigned to the protons on the biphenyl moiety. In the ^{13}C NMR spectrum, as expected, 17 distinguishable lines for each of the different carbon atoms are found. When necessary, the assignment is supported by 2D-COSY experiments. These spectral data (see experimental part) clearly indicate the formation of expected poly(arylene ether)s. The apparent molecular weights measured by GPC are shown in Table I. The number-average molecular weights range from 22 900 to 83 000 g/mol for **4a–e** and 43 100 to 83 700 g/mol for **5a–e**, relative to polystyrene standards. The polydispersity factors lie between 1.97 and 2.78. The high molecular mass of polymers **4a–e** and **5a–e** are also evidenced by their inherent viscosities ranging from 0.42 to 1.15 dL g^{-1} (Table II).

As shown in Table II, the number-average molecular weights of end-capped polymers **6** and **7** are 28700 and 15800 g/mol from GPC analyses, respectively. In comparison, the end group analysis by NMR gives higher values: 73500 g/mol for **6** and 66600 g/mol for **7**. Therefore, the exact molecular weights of these polymers should be higher than the apparent ones determined by GPC. Inherent viscosities of the end-capped polymers are 0.36 dLg^{-1} for **6** and 0.41 dLg^{-1} for **7**.

Polymers **4** and **5** are all amorphous and very soluble in chlorinated solvents such as chloroform, methylene chloride, and TCE. They can be cast into transparent, creasable films. None of them shows any crystalline behavior as assessed by DSC. As shown in Table III, the glass transition temperatures are in the ranges of 172–230

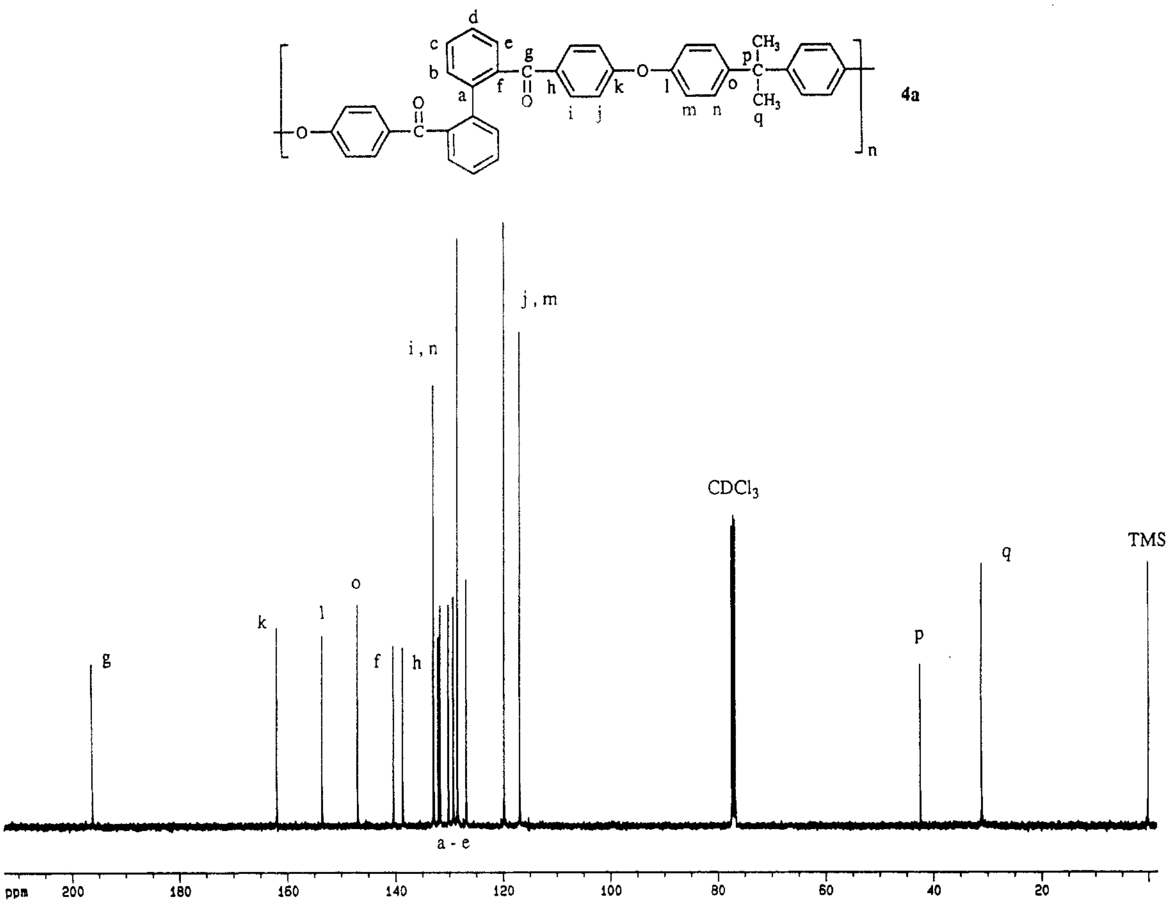


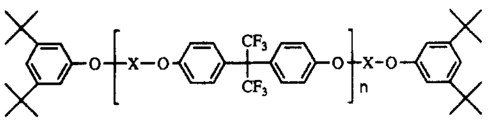
Figure 3. ^{13}H NMR (100 MHz) of poly(arylene ether) 4a in CDCl$_3$.

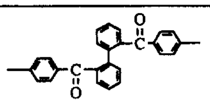
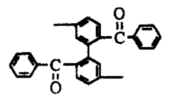
Table I. Synthesis of Poly(arylene ether)s 4a–e and 5a–e

polymer	method	yield (%)	$[\eta]_{inh}$^{a} (dL/g)	M_n ($\times10^{-4}$)	M_w ($\times10^{-4}$)	M_w/M_n
4a	A	89	0.55	5.78	11.4	1.97
4b	A	82	0.50	5.28	12.0	2.27
4c	A	93	0.83	8.30	18.9	2.28
4d	B	80	0.41	2.29	5.03	2.20
4e	A	91	0.52	5.23	10.9	2.09
5a	C (A)	95 (85)	0.55	5.14	10.5	2.05
5b	C	87	1.15	5.78	14.2	2.46
5c	C	89	0.70	4.31	11.4	2.67
5d	C	97	0.71	8.37	23.0	2.75
5e	C	93	0.60	6.22	17.3	2.78

[a] 0.5 g/dL solution in chloroform at 25.0 °C.

Table II. End-Capped Polymers 6 and 7



polymer	-X-	repeat unit	η_{inh}^{a}	M_n ($\times10^{-4}$) NMR	GPC
6		105	0.36	7.35	2.87
7		95	0.42	6.66	1.58

[a] 0.5 g/dL chloroform solution at 25 °C.

Table III. Thermal Properties of Poly(arylene ether)s 4a–e and 5a–e

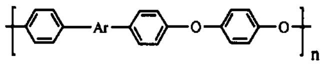
polymer	T_g^{a} (°C)	TGA (°C)^b air	N$_2$
4a	172	453	491
4b	179	516	523
4c	193	505	500
4d	175	504	493
4e	230	521	523
5a	156	473	475
5b	164	480	500
5c	174	448	473
5d	156	448	462
5e	215	460	490

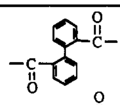
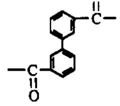
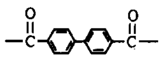
[a] The second run at 10 °C/min. [b] Onset of 5% weight loss at 10 °C/min.

°C for **4a–e** and 156–215 °C for **5a–e**, which vary according to the bisphenol used. The polymers **4e** and **5e** derived from a bulky bisphenol, 9,9′-bis(4-hydroxyphenyl)fluorene (**3e**), have relatively higher T_g's whereas the polymers **4a** and **5a** derived from flexible BPA (**3a**) have lower T_g's. Polymers **5**, which have two pendant benzoyl groups and the biphenyl unit as a part of the polymer backbone, show relatively lower T_g values, about 20 °C lower than those of the corresponding **4a–e** derived from the same bisphenol. The onset of 5% weight loss on the thermograph begins all above 490 °C in nitrogen and 450 °C in air for **4a–e** (Table III). Thermal stabilities of the polymers **5** are yet comparable to those of polymers **4**.

The polymer **4d** has a T_g of 175 °C, which is higher than that (T_g = 154 °C) of polymer **8** with a 3,3′-dibenzoylbiphenyl unit (Table IV).[11a] The increased T_g value of **4d** as compared to the analogous polymer **8** could be attributed to the restricted rotation of a biphenyl bond in the 2,2′-dibenzoylbiphenyl unit.[14] It should be noted that similar trends have been observed in poly(arylene ether)s[14] and polyamides[24] containing an *o*-dibenzoylbenzene moiety. The 10% weight loss for two structurally analogous

Table IV. Comparison of Analogous Poly(arylene ether)s



polymer	-Ar-	T_g (°C)	T_m (°C)	TGA (°C), 10%	
				air	N_2
4d		175		533	521
8		154		570	570
9			323	510	520

polymers **8** and **9** occurs reportedly at 570 °C (air) and 510 °C (air), respectively.[11a] Since the polymer **4d** loses its 10% weight at 533 °C in air (Table IV), these three polymers appear to have similar thermal and thermooxidative stabilities. Both polymers **4d** and **8** are amorphous. Polymer **9** shows no *Tg* but a melting point, which implies that the structural unit C (Figure 1) tends to induce the crystalline blocks while units A and B provide amorphous segments in polymers. Therefore, poly(arylene ether)s with only structural differences like isomeric 2,2′-, 3,3′-, and 4,4′-dibenzoylbiphenyl units should have similar thermal stabilities but may have different glass transition temperatures and crystallinity.

Conclusions

Two new difluoride monomers **1** and **2** are synthesized by the nickel(0)-catalyzed coupling reaction of 2-chloro-4-fluorobenzophenone and 2-chloro-4′-fluorobenzophenone, respectively. Poly(arylene ether)s containing a 2,2′-dibenzoylbiphenyl unit derived from these difluoride monomers are all amorphous and soluble in common organic solvents such as methylene chloride, chloroform, and NMP. Their T_g's and thermal stabilities are comparable to the analogous poly(arylene ether)s having isomeric 3,3′- and 4,4′-dibenzoylbiphenyl units.

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