# Macromolecules

Volume 27, Number 16 August 1, 1994

# Controlled Transformation of 2,2′-Diacylbiphenyl Unit to a Phenanthrene Ring in Poly(arylene ether ketone)

**Zhi Yuan Wang,* Chunhao Zhang, and Frederique Arnoux**

*Ottawa–Carleton Chemistry Institute, Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Canada K1S 5B6*

*Received February 7, 1994; Revised Manuscript Received May 13, 1994*•

ABSTRACT: The degree of conversion of a flexible 2,2′-diacylbiphenyl unit into a rigid phenanthrene ring in poly(arylene ether) can be controlled by varying the amount of thionating agent, e.g., Lawesson's reagent, used in the polymer transformation. When less than 1.5 molar equiv of Lawesson's reagent is used, partial polymer transformation can be achieved, which affords random copolymers containing a different amount of phenanthrene units. The increase in the phenanthrene content in the polymer results in significant increases in the glass transition temperature, the thermal stability, and the solvent resistance.

## Introduction

Intramolecular cyclization of pendant reactive groups to form a fused polycyclic ring in the polymer backbone is a useful polymer transformation process that can be utilized to produce polymers with rare benzenoid structures and unique properties. The cyclization can be effected by thermal, photochemical, and chemical processes. Thermal curing of poly(phenylenequinoxaline)s bearing pendant phenylethynyl groups increased the glass transition temperature and solvent resistance as a result of the formation of a rigid 9-phenyldibenz[*a*,*c*]anthracene ring.[1] The Bergman reaction of soluble alkylated poly(*o*-phenylacetylene)s at elevated temperatures resulted in the formation of ladder-like conjugated aromatic polymers.[2] Irradiation of poly(2,2′-biphenylenevinylene-1,4-phenylenevinylene) in solution as well as in the solid state quantitatively generated a fused dihydrophenanthrene/cyclobutane unit in the polymer.[3] Although thermally and photochemically induced cyclizations do not usually require a chemical reagent and do not generate any byproducts, only a few functional groups are reactive toward heat and light. In contrast, many reactive groups in the polymer can be converted chemically into a cyclic functionality. A ladder-like phenanthridine-based polymer was readily formed via an intramolecular coupling of an amino group and an acyl group located at the 2,2′-positions of the biphenyl moiety in a polymer precursor.[4] A rigid perylene unit in the polymer backbone was derived via a decarboxylation–ring closure from a 1,1′-binaphthyl moiety having two carboxylic acid groups at the 8,8′-positions by heating in alkaline solution.[5] A planar, rigid ladder-type polymer having a fully conjugated *p*-phenylene backbone was synthesized from an alkylated poly(*p*-phenylene) bearing a reactive hydroxylbenzyl group which was converted into a fluorene ring via an intramolecular alkylation upon treatment with a Lewis acid.[6] Recently, we have demonstrated that the polymer precursor containing a 2,2′-diacylbiphenyl unit can be converted chemically into a much more rigid polymer due to the formation of a phenanthrene ring.[7] Changes associated with this structural alteration are the increase in the glass transition temperature up to 100 °C and the improvement in thermal stability. In addition, the solubility and solution viscosity can change depending on the structures of the precursor and resultant polymers. We have also proved that the formation of the phenanthrene ring in the polymer backbone is an exclusively intramolecular process without chain scission and degradation, which means that the precursor polymer and the resultant polymer should have the same number-average molecular weight. Thus, this precursor strategy has been applied to the syntheses of some highly insoluble polymers of high molecular weights[7b] and fully conjugated, phenanthrene-based ladder polymers.[8] It is also conceivable that if a partial cyclization can be achieved in a controlled fashion, a series of copolymers with balanced thermal stability and solubility can be derived from a precursor polymer. The direct synthesis of these copolymers may be very difficult due to the unavailability of suitable reactive monomers. In this paper we report the method for the controlled transformation and the synthesis of a phenanthrene-containing polyether and ether/ketone copolymers from a poly(arylene ether ketone) precursor having a 2,2′-dibenzoylbiphenyl unit.

---

• Abstract published in *Advance ACS Abstracts,* July 1, 1994.

0024-9297/94/2227-4415$04.50/0

## Experimental Section

**General Methods.** *N*-Methyl-2-pyrrolidinone (NMP), tetramethylene sulfone ($TMSO_2$), thionyl chloride, triphenylphosphine, zinc (powder), diphenic acid, 2-chlorobenzoic acid, Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide], boron trichloride in methylene chloride, anisole, and sodium sulfide nonahydrate 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 $P_2O_5$. Aluminum chloride was purchased from Fluka Chemical Corp. Poly(arylene ether ketone) **6** was prepared previously as reported.[9] 1,1,2,2-Tetrachloroethane (TCE), dimethyl sulfoxide (DMSO), and other common organic solvents are reagent grade unless otherwise stated.

The $^1H$ 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 $^1H$ NMR study of partially cyclized polymers **7**. Infrared measurements were performed on a Perkin-Elmer 1600 FTIR spectrometer. Molecular weights were determined by gel permeation chromatography (GPC) relative to polystyrene standards using chloroform as an eluent on a Perkin-Elmer LC-250 GPC instrument at a flow rate of 1.0 mL/min; an UV detector was set at 254-nm wavelength. Thin-layer chromatography was done on silica gel (Kieselgel 60F 254) aluminum-backed plates. Melting points were taken from a Fisher-Johns melting apparatus and are uncorrected. Inherent viscosities were measured in chloroform solution (0.5 g/dL) at 25 °C using an Ubbelohde dilution viscometer. The glass transition temperatures were determined on a Seiko DSC 220 at a heating rate of 10 °C/min in nitrogen (50 mL/min), taken as the midpoint of the change in the slope of the base line. Thermal gravimetric analysis (TGA) was performed on a Seiko TG/DTA 220 at a heating rate of 10 °C/min in nitrogen (200 mL/min). Elemental analysis was done at Guelph Chemical Laboratories Ltd. in Ontario, Canada.

**Monomer Synthesis. 2-Chloro-4′-methoxybenzophenone.** To a solution of 2-chlorobenzoyl chloride (176.0 g, 1.0 mol) and anisole (108.0 g, 1.0 mol) in TCE (500 mL) at 0 °C under nitrogen was added slowly aluminum chloride (160.0 g, 1.2 mol) via a solid addition funnel. After addition, the orange solution was allowed to warm to room temperature and was stirred for 1 h. The reaction mixture was then poured into ice water (1.0 L). The organic layer was partitioned, diluted with methylene chloride (about 200 mL), and washed successively with water (200 mL), aqueous sodium hydroxide (1 N, 2 × 200 mL), water (200 mL), and brine (200 mL). After drying over anhydrous sodium sulfate and removal of solvents at 90 °C under vacuum, the residual oil was diluted with methanol (50 mL). On standing, the product crystallized out as white crystals: 202.0 g (82.1%); mp 79–81 °C (lit.[10] mp 80–81 °C); $^1H$ NMR (200 MHz, $CDCl_3$) 7.82–7.77 (2 H), 7.37–7.35 (4 H), 6.96–6.91 (2 H), 3.87 (3 H).

**2,2′-Bis(4-fluorobenzoyl)biphenyl (1).** An improved procedure is as follows. In a 250 mL, round-bottomed, three-neck flask, a mixture of nickel(II) bromide (2.33 g, 10.66 mmol), zinc dust (21.31 g, 326 mmol), and triphenylphosphine (21.31 g, 80.50 mmol) in dry DMAc (110 mL) was stirred under nitrogen at 50 °C until a red solution was formed (this took ~3 min). To the resulting solution was added 2-chloro-4′-fluorobenzophenone (50.0 g, 167.5 mmol) in one portion. After addition, the mixture turned from a deep red to a coffee color. The reaction mixture was then heated at 80–90 °C for 2 h. Once TLC indicated that the majority of the starting material had been converted to the product or the red color reappeared, indicating the completion of the reaction, the resulting dark reddish brown hot solution was filtered with suction through Celite to remove the residual zinc. The filtrate was distilled under vacuum (water pump) at about 110 °C until almost all (~90% by volume) of the DMAc had been removed and a solid precipitated out. This solid was transferred to a 500 mL beaker and, subsequently, stirred in boiling cyclohexane and filtered when hot to remove the most of the triphenylphosphine, which is more soluble in cyclohexane than the product. The orange product was collected by suction filtration and was then dissolved in a minimum amount of boiling acetone. Hydrogen peroxide (30%) was added until the color disappeared and the solid precipitated out. Once the color had been removed, the complete precipitation was induced by adding water. To further purify if necessary (checked by TLC of the solid), this procedure was repeated using water to dissolve triphenylphosphine oxide and to precipitate the product. The product of monomer grade, free of both triphenylphosphine and its oxide, was obtained as white crystals: 36.2 g (85.5%); mp 148.0–149.0 °C (lit.[7a] mp 148.5–149.0 °C).

**2-(4-Fluorobenzoyl)-2′-(4-hydroxybenzoyl)biphenyl (2).** A mixture of difluoride **1** (10.0 g, 25.1 mmol) and powdered potassium hydroxide (5.60 g, 100 mmol) in DMSO (100 mL) was stirred under nitrogen at room temperature for 72 h. The reaction mixture containing mainly the product **2**, a small amount of **3**, and the unreacted difluoride **1** was then poured into water (200 mL). The solid was collected by filtration. The crude product was dissolved in aqueous potassium hydroxide solution (20%) and filtered. After acidifying with concentrated hydrochloric acid, a white solid precipitated out. The product **2** was isolated by flash chromatography on silica gel (20% ethyl acetate in hexanes). Recrystallization from ether/hexanes gave **2** as small crystals: 5.1 g (51%); mp 162–163 °C; $^1H$ NMR (200 MHz, $CDCl_3$) 7.71 (2 H, dd, $J$ = 8.5, 5.6 Hz), 7.68 (2 H, d, $J$ = 8.4 Hz), 7.48–7.22 (8 H, m), 6.90 (2 H, t, $J$ = 8.4 Hz), 6.60 (2 H, d, $J$ = 8.5 Hz); $^{13}C$ NMR (50 MHz, $CDCl_3$) 196.95, 196.88, 168.08, 162.99, 161.24, 140.07, 139.74, 138.16, 137.81, 133.27, 133.17, 132.98, 132.85, 131.52, 131.42, 130.48, 130.00, 129.34, 129.28, 129.16, 126.92, 126.78, 115.32, 115.08, 114.89; MS (EI, *m/e*, relative intensity) 396 ($M^{+\bullet}$, 0.1), 358 ($M^{+\bullet} - H^\bullet$, 0.5), 275 ($M^{+\bullet} - HOPhCO^\bullet$, 97.3), 273 ($M^{+\bullet} - FPhCO^\bullet$, 100).

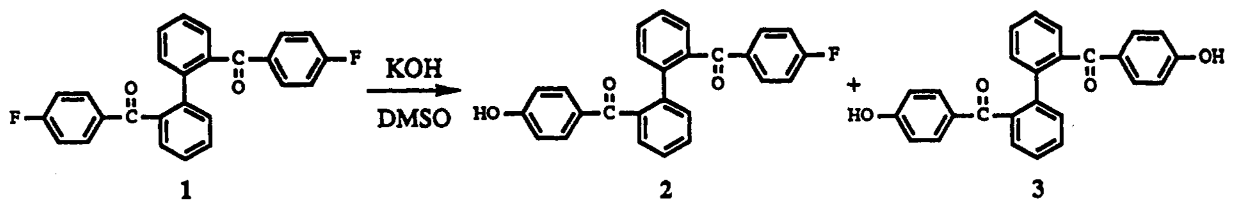
**2,2′-Bis(4-methoxybenzoyl)biphenyl (4).** (a) A mixture of $NiBr_2$ (8.90 g, 40.9 mmol), zinc dust (81.0 g, 1.24 mol), and triphenylphosphine (81.0 g, 0.31 mol) in dry DMAc (1.0 L) was stirred mechanically under nitrogen at 50 °C until a red solution was formed. To the resulting solution was added 2-chloro-4′-methoxybenzophenone (201.0 g, 0.817 mol) in several portions over 15 min, and the reaction mixture was then heated to 80–90 °C for 24 h. The mixture was cooled to room temperature and filtered. The filtrate was poured into water (2 L) with good stirring. After stirring overnight, the solids were collected on the filter funnel and then were stirred in ether (800 mL) for 30 min. The slurry was filtered. The filtrate contained mainly triphenylphosphine. The product on the filter funnel was recrystallized from 2-propanol/cyclohexane as white crystals: 129.0 g (75%); mp 148–150 °C (lit.[11] mp 139–140 °C); $^1H$ NMR (200 MHz, $CDCl_3$) 7.68 (4 H, d, $J$ = 8.9 Hz), 7.45–7.20 (8 H, m), 6.70 (4 H, d, $J$ = 8.9 Hz), 3.78 (6 H, s).

(b) A mixture of diphenic acid (4.84 g, 20.0 mmol) and thionyl chloride (20 mL) was stirred at 50–60 °C overnight. After removal of excess thionyl chloride by distillation, diphenic acid dichloride was vacuum distilled as yellow crystals: 4.17 g (75%); mp 88–90 °C; FTIR (neat, $cm^{-1}$) 1775 (C=O).

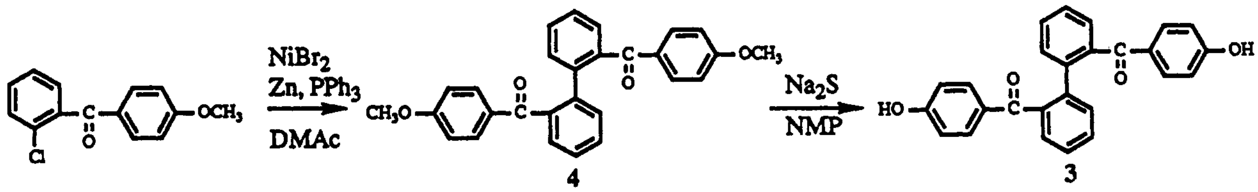
To a mixture of diphenic acid dichloride (1.12 g, 4.0 mmol) and anisole (4.5 mL, excess) was added aluminum chloride (2.3 g, 16 mmol) in portions at 5–10 °C and then stirred at room temperature overnight. The mixture was poured into water containing a few drops of concentrated hydrochloric acid. The mixture was then extracted with chloroform (3 × 100 L), and the combined extracts were washed with water (200 mL). After drying over magnesium sulfate, the solvent was removed under vacuum. The product was purified by recrystallization from ethanol; 1.04 g (61%); mp 148–150 °C.

**2,2′-Bis(4-hydroxybenzoyl)biphenyl (3).** A mixture of **4** (16.0 g, 39.3 mmol) and $Na_2S{\cdot}9H_2O$ (46.9 g, 117.9 mmol), NMP (80 mL), and toluene (80 mL) was heated under nitrogen at 140 °C for 2 h. The water and toluene as an azeotrope were removed from the Dean–Stark trap while fresh toluene was added to maintain the same volume of the reaction solution. Toluene was then completely removed, and the mixture was heated at 160 °C for 4 h. A strong alkaline potassium permanganate solution was used to trap volatile sulfur compounds. The reaction mixture was cooled to room temperature and poured into ether slowly, and the resulting solid was collected by filtration. After dissolving the solid in water, the solution was acidified with concentrated hydrochloric acid to yield white solids. The solid was taken into 20% potassium hydroxide solution, and the solution was filtered.

**Scheme 1. Hydrolysis of the Difluoride 1**



**Scheme 2. Synthesis of Bisphenol Monomer 3**



The filtrate was washed with ether thoroughly. The crude product was then precipitated by the addition of concentrated hydrochloric acid. After recrystallization from ethanol and acetic acid, respectively, the bisphenol 3 was obtained as a white solid: 12.0 g (81%); mp 256–257 °C; $^1$H NMR (200 MHz, CDCl$_3$) 9.17 (2 H, bs), 7.69 (4 H, d $J$ = 8.8 Hz), 7.42–7.22 (8 H, m), 6.79 (m H, d, $J$ = 8.8 Hz); $^{13}$C NMR (50 MHz, CDCl$_3$) 196.12, 162.61, 140.26, 140.22, 133.59, 132.07, 130.32, 130.01, 129.52, 127.52, 115.64; MS (EI, $m/e$, relative intensity) 273 (M$^{+\bullet}$ – HOPhCO$^\bullet$, 100).

**Polymer Synthesis. Poly(arylene ether ketone) 5a.** (a) A three-necked flask was charged with 1 (796.6 mg, 2.0 mmol), 3 (788.8 mg, 2.0 mmol), chlorobenzene (1.0 mL), TMSO$_2$ (3.0 mL), and potassium carbonate (360 mg, 2.6 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 codistilled at 140–150 °C. The reaction continued at 235–240 °C for 4 h. The mixture was then cooled to ca. 160 °C, diluted with 5 mL of TMSO$_2$, and poured into methanol. The fibrous polymer was collected and purified by dissolving in chloroform, filtering through Celite, and precipitating into methanol. The yield of 5a was 1.1 g (73%). $^1$H NMR (200 MHz, CDCl$_3$) 7.72 (4 H, d, $J$ = 8.8 Hz), 7.45–7.22 (8 H, m), 6.89 (4 H, d, $J$ = 8.8 Hz); $^{13}$C NMR (50 MHz, CDCl$_3$) 196.1, 159.8, 140.1, 138.2, 133.1, 132.7, 131.4, 130.3, 129.3, 126.9, 118.2; FTIR (film, cm$^{-1}$) 1662 (C=O); $\eta_{\mathrm{inh}}$ = 0.49 dL/g (0.5 g/dL chloroform solution); $M_w$ = 81700, $M_n$ = 36000, $M_w/M_n$ = 2.27.

(b) A mixture of 2 (792.6 mg, 2.0 mmol), chlorobenzene (0.5 mL), TMSO$_2$ (1.5 mL), and potassium carbonate (360 mg, 2.6 mmol) was purged with nitrogen for 20 min and then heated to 235 °C in 15–20 min. The azeotrope of chlorobenzene and water was codistilled at 140–150 °C, and the mixture was heated at 235–240 °C for 4 h. The reaction mixture was then cooled to ca. 160 °C, diluted with 2 mL of TMSO$_2$, and poured into methanol. The fibrous polymer was further purified as above: 602 mg (77%).

**Poly(arylene ether) 5b.** A mixture of polymer 5a (188 mg, 0.5 mmol) and Lawesson's reagent (405 mg, 1.0 mmol) in dry TCE (20 mL) was purged with nitrogen for 20 min. The mixture was then heated at 140 °C under nitrogen for 4 h. Th resultant polymer precipitated out. The IR analysis showed the absence of carbonyl absorption at 1662 cm$^{-1}$. The reaction mixture was concentrated to about 5 mL and the residue was poured into methanol. The powdery polymer was filtered and washed with hot chloroform continuously in a Soxhlet extractor overnight. The polymer 5b was then dried in an oven at 60 °C under vacuum: 165 mg (96%); FTIR (film, cm$^{-1}$) 3068, 1599, 1504, 1447, 1236, 1169, 1078, 1016, 976, 888, 861, 759, 727, 627. Anal. Calcd for (C$_{26}$H$_{16}$O)$_n$: C, 90.66; H, 4.69. Found: C, 90.29; H, 4.72.

**Calibration of the Percentage of Polymer Conversion vs the Amount of Lawesson's Reagent.** Polymer 6 (293 mg, 0.5 mmol) and Lawesson's reagent (102 mg, 0.25 mmol, 0.5 molar equiv) under nitrogen were mixed in 15 mL of TCE. The mixture was then heated at 140 °C for 4 h. After removal of most of the TCE, the residue was poured into methanol. The polymer was then dissolved in about 20 mL of NMP, and a few drops of 40% aqueous potassium hydroxide solution was added to the NMP solution with stirring. The blue color disappeared rapidly, and the resulting brown solution was further stirred for 10 min. The polymer (256 mg, 92%) was isolated, washed thoroughly with methanol, and dried. The percentage of conversion was determined from the integral ratio of the signals of the "bay" protons on the C4 and C5 of phenanthrene and the protons from the isopropylidene unit in the $^1$H NMR spectrum at 8.17 and 1.62 ppm, respectively. The results are summarized in Table 1.

**Table 1. Amount of Lawesson's Reagent Used and Conversion Percentage of the Polymer 6**

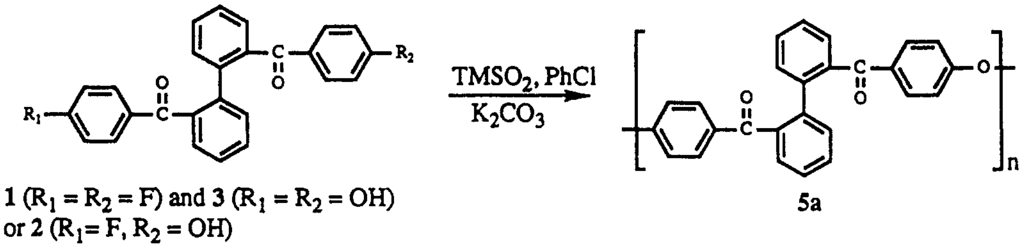
| reagent, molar equiv | 0.25 | 0.40 | 0.50 | 0.75 | 1.00 | 1.25 | 2.00 |
|---|---|---|---|---|---|---|---|
| conv, % | 5.00 | 14.0 | 30.0 | 68.0 | 91.0 | 100.0 | 100.0 |

**Copolymers 5c–e.** A typical procedure is as follows. A mixture of polymer 5a (188 mg, 0.5 mmol) and Lawesson's reagent (81 mg, 0.2 mmol) in dry TCE (15 mL) was purged with nitrogen for 20 min before it was heated at 140 °C for 4 h. The reaction was worked up as described above to give a light blue polymer. The polymer was then dissolved in about 20 mL of NMP, and a few drops of 40% aqueous potassium hydroxide solution was added to the NMP solution with stirring. The blue color disappeared, and the resulting brown solution was further stirred for 10 min. After acidification with concentrated hydrochloric acid, polymer 5c was filtered, washed with water and methanol thoroughly, and dried in an oven at 60 °C under vacuum: 155 mg (90%).

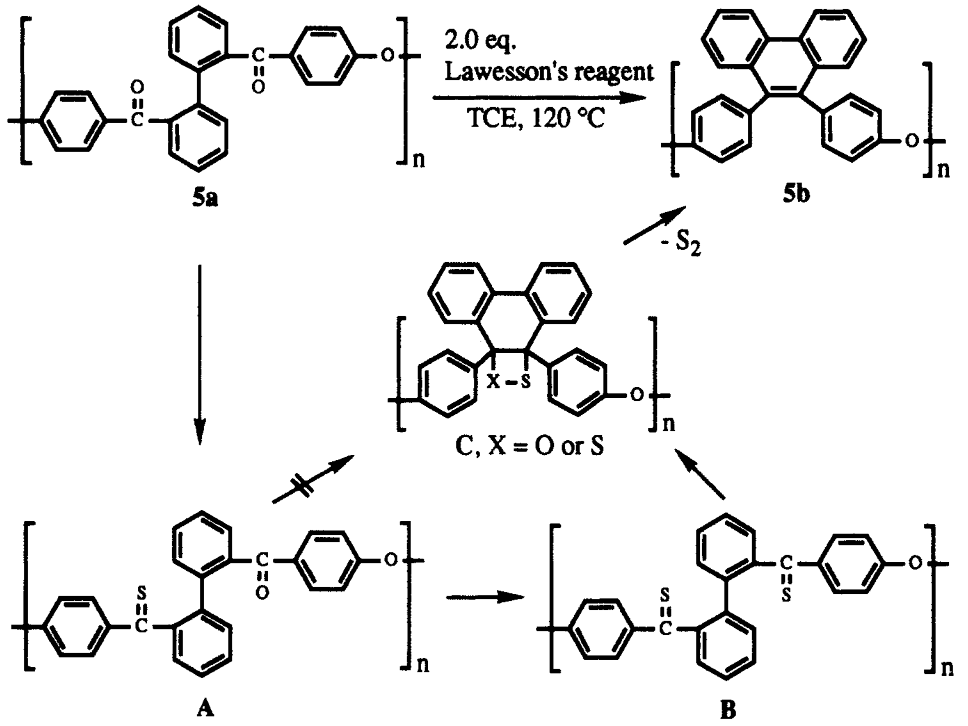
## Results and Discussion

**Monomer Synthesis.** Two types of monomers, AB and AA/BB, can be used for the preparation of the polymer 5a. The AB-type monomer 2 was obtained by the partial hydrolysis of difluoride 1. The synthesis of difluoride 1 was described before[7a] and further modified in this work for large scale production (see Experimental Section). The best results in terms of the yield (51%) and the purity of 2 were obtained when the hydrolysis was done using dry potassium hydroxide powders in DMSO at room temperature. Inevitably, bisphenol 3 was formed along with 2. Using other solvents like $N,N$-dimethylformamide or tetrahydrofuran eithe resulted in a lower yield of desired product or gave no reaction. Monomer 2 was purified first by chromatography to remove 3 and unreacted 1 and then by recrystallization from ether/hexane. Bisphenol 3 was also required as an AA-type monomer for polymer 5a. Although it could be produced by complete hydrolysis of 1, bisphenol 3 was actually prepared according to Scheme 2. Thus, the Ni(0)-catalyzed coupling of 2-chloro-4′-methoxybenzophenone, made by acylation of anisole with 2-chlorobenzoyl chloride, gave compound 4 in high yield. The acylation at low temperature of reactive anisole with diphenic acid dichloride was also successful for the

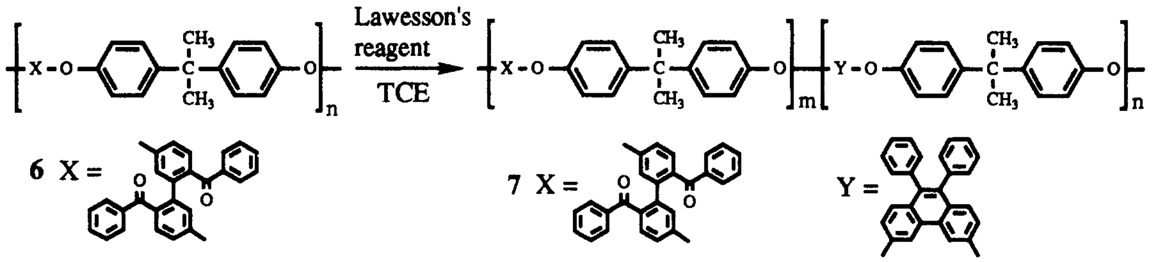
**Scheme 3. Synthesis of the Polyether 5a**



**Scheme 4. Complete Transformation of Poly(arylene ether ketone) 5a to Poly(arylene ether) 5b**



**Scheme 5. Transformation of Polymer 6**



preparation of 4. The subsequent demethylation was best carried out using sodium sulfide in NMP, and the product was purified by recrystallization from acetic acid.[12] Other demethylating reagents such as $BBr_3$ and 48% HBr in acetic acid failed to afford bisphenol 3 in good yields.[13] The lower effectiveness of $BBr_3$ on compound 4 can be attributed to the complex formation between the keto group and the boron reagent which further deactivates the reactivity of the methoxy group toward the boron reagent.

**Polymer Synthesis and Transformation.** Poly(arylene ether ketone) **5a** was synthesized by polycondensations of monomer 2 and monomers 1 and 3, respectively (Scheme 3). Both polymerizations were carried out in $TMSO_2$ using potassium carbonate as a base. The standard $K_2CO_3$/NMP system gave less satisfactory results with respect to molecular weight, presumably due to the cleavage of the resulting polymer by potassium fluoride at elevated temperatures in NMP. Depolymerization by nucleophilic cleavage of aryl ether with fluoride under severe conditions is known.[14] Polymer **5a** was obtained in both cases with an inherent viscosity of 0.49 dL/g. Parent molecular weight was determined by GPC to be $M_w$ = 81700 and $M_n$ = 36000 ($M_w/M_n$ = 2.27). A transparent, tough film can be cast from its chloroform solution.

When polymer **5a** was treated with 2.0 molar equiv of Lawesson's reagent at 120 °C in TCE for 2 h, insoluble polyether **5b** was formed (Scheme 4). This transformation has been confirmed to be a quantitative and nondestructive process.[7] Two thionating reagents, Lawesson's reagent and *in-situ* generated $B_2S_3$, are equally effective at elevated temperatures (>80 °C). The resultant polymer should have the same molecular weight as that of the precursor polymer. We also found that the solubility of the resulting polymer does not affect the degree of polymer conversion but the amount of thionating agent does. According to an MM2-based computational calculation of model compounds and experiments performed by Steliou et al,[15] diatomic sulfur is preferably ejected from an intermediate like **B** having a 2,2′-dithioacylbiphenyl moiety (Scheme

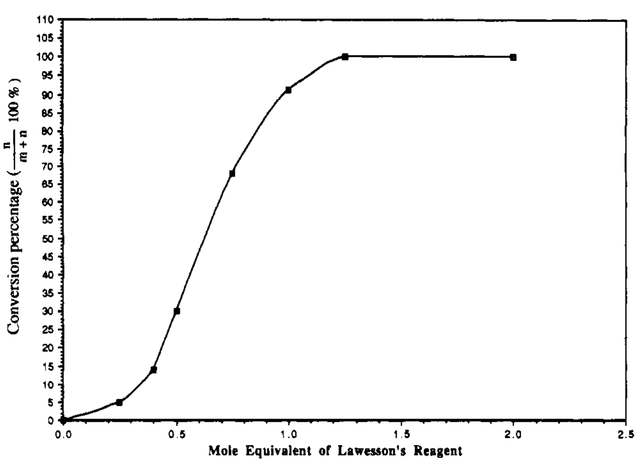


**Figure 1.** Calibration curve of the conversion percentage of polymer **6** vs molar equivalents of Lawesson's reagent.

4). Monothione derivatives of 2,2′-dibenzoyl- and 2,2′-bis(4-methoxybenzoyl)biphenyls are said to be blue and quite stable, but their corresponding bis(thiocarbonyl) analogues are intense blue and spontaneously eject diatomic sulfur to give, through a cyclic 1,2-dithietane intermediate like **C** (X = S), a quantitative yield of 9,10-disubstituted phenanthrenes.[15c] Accordingly, intermediate **A** should not extrude SO via **C** (X = O) to yield polymer **5b**. Furthermore, both intermediates **A** and **B** or the partially cyclized polymer should remain soluble in TCE before the cyclization finishes. However, attempts to isolate the blue thioketone polymer by either lowering the thionation temperature or quenching the reaction have so far failed. Only a partially cyclized thioketone polymer was obtained, suggesting that the cyclization takes place immediately once the thionation of each repeat unit is complete or the cyclization occurs at the temperature that is needed for thionation. Since intermediate **A** does not yield the cyclized product and can be converted back to the starting material by hydrolysis, the ratio of **A** to **B**, which depends on the amount of thionating reagent used, would eventually determine the degree of conversion. In other words, the degree of conversion can be controlled by the amount of Lawesson's reagent.

Polymer **6** ($M_n$ = 51400, $M_w/M_n$ = 2.05, $\eta_{inh}$ = 0.55 dL/g)[9] was used to calibrate the amount of Lawesson's reagent versus the degree of transformation, since polymers **5a** and **6** are similar with respect to their structures and molecular weights and reactivities toward Lawesson's reagent. In addition, the completely cyclized polyether **7** ($m$ = 0) is still soluble in TCE and can be easily characterized by spectroscopic means. Hence, the ratio of phenanthrene to diacylbiphenyl or the percentage of conversion can be determined using the NMR technique according to the ratio of the methyl groups from the isopropylidene part at 1.63 ppm to the aromatic "bay" protons at the C4 and C5 positions of phenanthrene at 8.17 ppm. As shown in Figure 1, complete conversion requires more than 1.25 molar equiv of reagent. Within the range 0.4–1.00 molar equiv, the percentages of conversion vary from 15 to 90, which is close to a linear relation. Therefore, the controlled transformation of polymer **5a** can be achieved according to this calibration curve. In practice, besides the amount of reagent and reaction conditions (tempeature and time), other factors such as the quality of the reagent and the molecular weight of the starting polymer should also be considered.

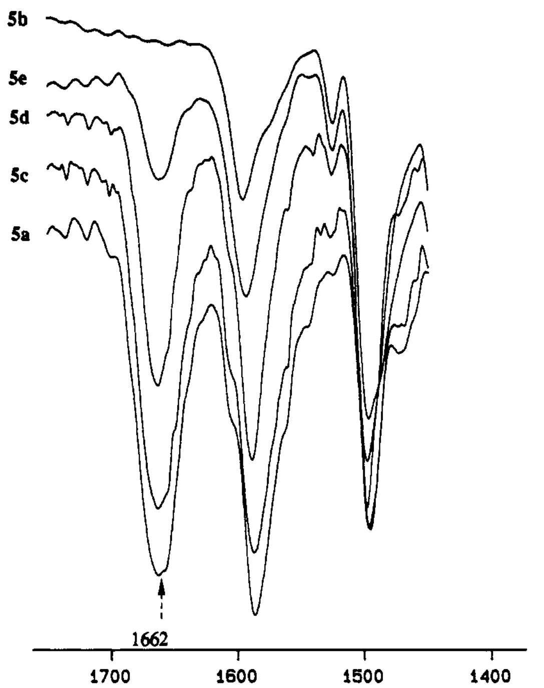


**Figure 2.** IR spectra (1400–1700 cm$^{-1}$ region) of polymers **5a–e**.

Under the same conditions as for the calibration experiment, polymer **5a** was treated with 0.4, 0.55, and 0.8 molar equiv of Lawesson's reagent, respectively. A light blue polymer was first obtained after workup due to the presence of the residual thiocarbonyl groups. Conversion of a thioketone into a ketone was effected by base hydrolysis with a concentrated potassium hydroxide solution in NMP at room temperature. Copolymers **5c–e** thus obtained are expected to contain 14, 41, and 76% of phenanthrene rings, respectively.

**Polymer Characterization.** The structure of polymer **5a** was confirmed by NMR and IR spectroscopy. The solubility of the polymers **5** changed according to the phenanthrene content in the polymer, with polymer **5a** being soluble and polymer **5b** being insoluble in common organic solvents such as chloroform and NMP. Copolymers **5d** and **5e** were partially soluble in hot chloroform, whereas polymer **5c** was soluble in chloroform. Although polymer **5c** was soluble in chloroform, its $^1$H NMR spectrum gave little useful information about its composition and the relative amount of the phenanthrene unit. However, IR proves to be a useful method to qualitatively confirm the successful polymer transformation. The carbonyl absorption for polymer **5a** appears at 1662 cm$^{-1}$ in the IR. As the phenanthrene content increases in the polymers (**5c**, **5d**, **5e**, and **5b**), the intensity of the carbonyl peak decreases (Figure 2), and polymer **5b** shows no absorption at 1662 cm$^{-1}$ at all. Each polymer sample wasmade in the same molar concentration in dry KBr for this IR study.

A gradual change in structures from polymer **6** through partially converted, phenanthrene/ketone copolymers to polymer **7** is revealed by $^1$H NMR. Polymer **6** displays a sharp doublet peak at 7.67 ppm which gradually disappears as the 2,2′-dibenzoylbiphenyl unit is converted in degrees from 14 to 100% (Figure 3). At the same time, two distinct peaks at 8.17 and 7.46 ppm (a doublet) grow by degrees. The copolymers show relatively complex resonance signals (spectra b, c, and d) in comparison with homopolymers **6** and **7** (spectra a and e). In addition, instead of one singlet at 1.63 ppm in spectra a and e, two to three singlet peaks due to the isopropylidene group are seen in spectra b, c, and d.

Crude samples taken directly from polymer transformation reactions showed a band at about 1025–1220 cm$^{-1}$ in the IR spectra attributed to the thioketo group.

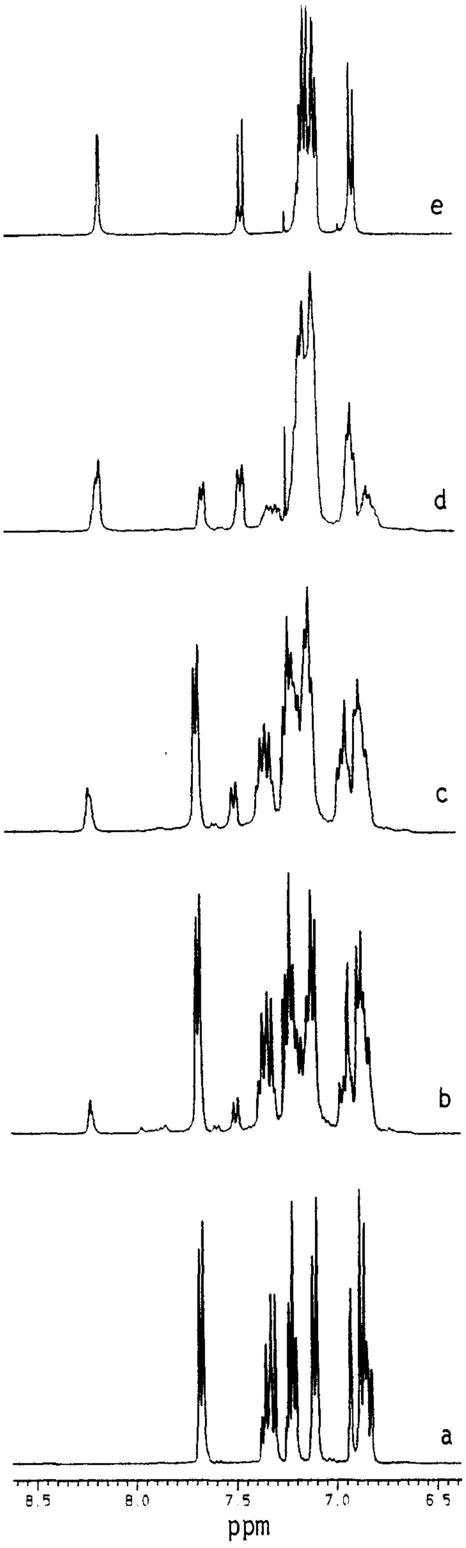


**Figure 3.** $^1$H NMR spectra (6.5–8.5 ppm region) of the polymers derived from **6**: (a) 0% conversion (polymer **6**); (b) 14% conversion; (c) 30% conversion; (d) 86% conversion; (e) 100% conversion (polymer **7**).

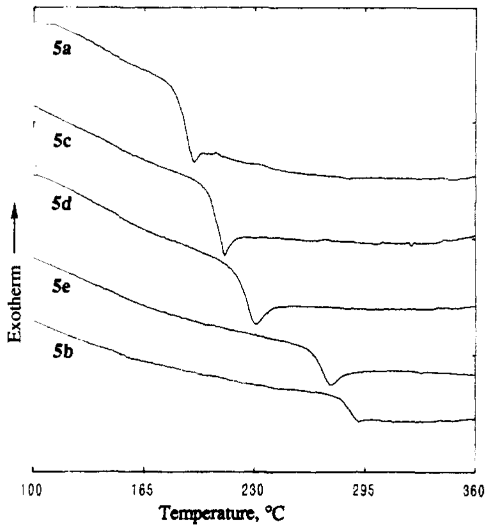
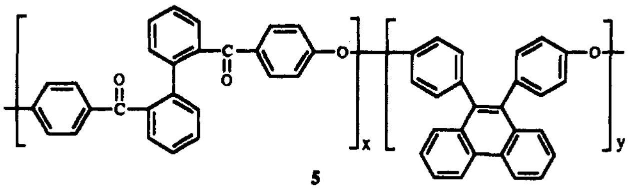


**Figure 4.** DSC thermograms of polymers **5a–e**.

**Table 2. Transformations and Properties of Polymers 5**



**5**

| polymer | Lawesson's reagent, molar equiv | phenanthrene content, % | $T_g$, °C | TGA,[b] °C |
|---|---|---|---|---|
| **5a** | | 0 | 188.2 | 494.0 |
| **5c** | 0.40 | 14[a] | 206.5 | 509.0 |
| **5d** | 0.55 | 41[a] | 224.0 | 513.0 |
| **5e** | 0.80 | 76[a] | 267.0 | 548.0 |
| **5b** | 2.00 | 100 | 285.0 | 590.0 |

[a] Obtained according to the calibration curve (Figure 1). [b] 5% weight loss in nitrogen.

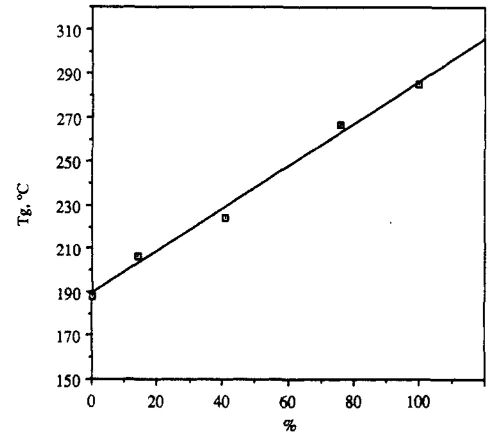


**Figure 5.** Plot of $T_g$ vs phenanthrene content in the polymers **5**.

However, these blue-colored thioketone polymers were quite labile to the hydrolysis. Upon workup and washing with methanol to get rid of the reacted Lawesson's reagent or exposure in air, the blue color gradually faded. Because of the instability, attempts to characterize the thioketone polymer by NMR and elemental analysis failed to provide any meaningful information on the composition and the structure.

Introducing a phenanthrene ring in the polymer backbone also affects the glass transition temperatures and thermal stabilities. DSC thermograms (Figure 4) of copolymers **5c–e** showed a single transition, indicating that they are random copolymers. The $T_g$ increases as the polymer backbone increases its rigidity due to the presence of the phenanthrene ring. From the flexible poly(ether ketone) **5a** to the rigid polyether **5b**, the $T_g$ changed nearly 100 °C (Table 2). The $T_g$'s of the polymers **5** are found to be nearly linear with the content of the phenanthrene unit as shown in Figure 5, which corroborates the validity of the calibration curve (Figure 1) and the completeness of the polymer transformation. The polymer degradation or the miscalculation of the thionating agent would cause the formation of the polymer with either a lower $T_g$ or a higher $T_g$. Since a polycyclic aromatic hydrocarbon is generally more thermally stable than a monocyclic aromatic hydrocarbon, the enhanced thermal stability of the phenanthrene-containing polymers can be expected. The effect of the phenanthrene content of the thermal stability of the polymer was studied by TGA. The onset temperature for 5% weight loss occurred at 494 °C for polymer **5a**, which rose as the phenanthrene content increased and went up to 590 °C for polymer **5b** (Table 2).

## Conclusions

We have demonstrated that the chemical transformation of the 2,2′-diacylbiphenyl unit in a polymer can be controlled by varying the amount of Lawesson's reagent. Poly(arylene ether) **5b**, which has a phenanthrene ring in each repeat unit, was derived from poly(arylene ether ketone) **5a** using 2 molar equiv of Lawesson's reagent. Copolymers containing a certain phenanthrene content were also obtained from polymer **5a** using the calculated amount of Lawesson's reagent. The phenanthrene content or the degree of conversion significantly influences the solubility, the $T_g$, and the thermal stability of the polymer. The polymer transformation method described herein can be applied to other polymer systems that contain the 2,2′-diacylbiphenyl unit to produce copolymers that may not be easily obtainable via a direct polycondensation. Future work will focus on the isolation of soluble blue-colored thioketone polymers for uses as potential thermally curable resins.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

## References and Notes

(1) Lindley, P. M.; Reinhardt, B. A. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1061.
(2) Swager, T. M. S.; Zhou, Q. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *43* (1), 193.
(3) Müllen, K.; Böhm, A.; Fiesser, G.; Garay, R. O.; Mauermann, H.; Stein, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *43* (1), 195.
(4) Tour, J. M.; Lamba, J. J. S. *J. Am. Chem. Soc.* **1993**, *115*, 4935.
(5) Rusanov, A. L. *Russ. Chem. Rev. (Engl. Transl.)* **1992**, *61* (4), 446.
(6) Scherf, U.; Müllen, K. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 489.
(7) (a) Wang, Z. Y.; Zhang, C. *Macromolecules* **1992**, *25*, 5851. (b) Zhang, C.; Wang, Z. Y. *Macromolecules* **1993**, *26*, 3330.
(8) Chmil, K.; Scherf, U. *Macromol. Chem., Rapid Commun.* **1993**, *14*, 217.
(9) Zhang, C.; Wang, Z. Y. *Macromolecules* **1993**, *26*, 3324.
(10) Gibson, M. S.; Vines, S. M.; Walthew, J. M. *J. Chem. Soc., Perkin Trans. 1* **1975**, 155.
(11) Bachmann, E.; Ju-Hwa-Chu, E. *J. Am. Chem. Soc.* **1935**, *57*, 4763.
(12) Newman, M. S.; Sankaran, V.; Olson, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 3237.
(13) (a) McOmie, J. F. W.; West, D. E. *Org. Synth. Collect. Vol. V* **1973**, 412. (b) Kawasaki, I.; Matsuda, K.; Kaneto, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1986.
(14) (a) Attwood, T. E.; Newton, A. B.; Rose, J. B. *Polym. J.* **1972**, *4*, 391. (b) Carlier, V.; Jambe, B.; Devaux, J.; Legras, R.; McGrail, P. T. *Polymer* **1993**, *34* (1), 167.
(15) (a) Steiliou, K.; Salama, P.; Yu, X. *J. Am. Chem. Soc.* **1992**, *114*, 1456. (b) Steiliou, K. *Acc. Chem. Res.* **1991**, *24*, 341. (c) Steiliou, K.; Salama, P.; Brodeur, D.; Gareau, Y. *J. Am. Chem. Soc.* **1987**, *109*, 926.