Introduction of a Phenanthrene Ring into Poly(arylene ether)s via Intramolecular Cyclization of 2,2′-Dibenzoylbiphenyl Units

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ABSTRACT: A new, non-cross-linking route to increase the rigidity in poly(arylene ether)s has been developed, involving the conversion of a 2,2′-dibenzoylbiphenyl unit in the precursor polymer into a phenanthrene ring. Transformation proceeds intramolecularly under mild conditions without degradation. Thermal properties of the phenanthrene-based poly(arylene ether)s are significantly improved in comparison with their precursors.

Introduction

Incorporation of a fused benzenoid group into the backbone of a polymer is one of the possible routes to increase the polymer rigidity or chain stiffness, which usually induces higher crystallinity and increases the glass transition temperature and solvent resistance. A typical example is the introduction of an anthracene ring into poly(phenylquinoxalines), which results in increased creep and craze resistance and higher glass transition temperatures.[1] This structural modification would be a general, unique way to bring in the rigidity in a variety of polymers without sacrificing the thermoplastic characteristics if the desired monomers were readily available and could be polymerized to yield high molecular weight polymers. In fact, the synthesis of bifunctional fused benzenoids is not straightforward, and direct polymerizations of such monomers are often difficult because of the poor solubility of the monomers and the growing polymers.

The solubility problem can be solved by first obtaining a soluble polymer with a removable group, and then generating the target polymer in the following elimination step. Semicrystalline polymers like PEEK have been prepared from soluble precursor poly(arylene ether ketimine)[2] by the hydrolysis of the ketimine. The *tert*-butyl group has been used to enhance the solubility of the precursor PEEK and readily removed via the acid-catalyzed trans-*tert*-butylation to yield PEEK.[3] High molecular weight, insoluble poly(*p*-phenylene) has also been synthesized by aromatization of the O-silylated 1,4-poly(*cis*-5,6-dihydroxy-1,3-cyclohexadiene).[4] Of particular interest is another approach involving a prepolymer containing a reactive pendant group. A new structural unit is created through the reaction of a pendant group upon thermal or chemical treatment. For example, the synthesis of the ladder poly(arylene)s is reported by the conversion of two pendant, neighboring carbonyl groups into a cyclic unit[5] and the introduction of an anthracene ring via intramolecular cyclization of pendant phenylethynyl groups.[1] Conceivably, this approach can be used to solve both problems: the availability of a suitable monomer and the solubility of polymer. However, main concerns are the design of a precursor polymer and the availability of an efficient polymer transformation reaction. In general, any intramolecular reaction that results in the formation of an aromatic ring should be worthy of consideration as a potentially new method for the synthesis of novel polymers. In contrast, the intermolecular reaction will lead to the cross-linking.

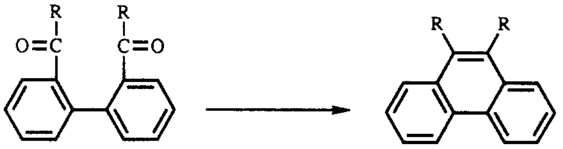

Figure 1. Formation of 9,10-disubstituted phenanthrene from 2,2′-diacylbiphenyl.

The formation of a phenanthrene ring from a flexible 2,2′-diacylbiphenyl is an intramolecular reaction, which can be utilized for polymer synthesis (Figure 1).[6] This enthalpy-controlled reaction has been described in detail, and many substituted phenanthrenes are thermally formed from 2,2′-diacylbiphenyls. The reaction proceeds rapidly in quantitative yield via a dithioketone intermediate **4a** (Scheme III) without any intermolecular dimerization. We have reported the synthesis of a series of soluble, high molecular weight poly(arylene ether)s containing a 2,2′-dibenzoylbiphenyl unit.[7] The feasibility of transforming such polymers into the phenanthrene-containing poly(arylene ether)s has also been demonstrated.[8] In this paper, we report further studies on this new route and the synthesis of two series of the phenanthrene-based poly(arylene ether)s.

Experimental Section

Materials. Poly(arylene ether)s **2** and **5** were prepared previously as reported.[7] Lawesson's reagent,[9] boron trichloride in methylene chloride, tricyclohexyltin chloride, and sodium sulfide nonahydrate were obtained from Aldrich Chemical Co. and used as received. 4-*tert*-Butylphenol (Aldrich) was purified by recrystallization from toluene. *N*-Methyl-2-pyrrolidinone (NMP), 1,1,2,2-tetrachloroethane (TCE), and other common organic solvents were reagent grade unless otherwise stated. Deuterated TCE used for NMR was purchased from Cambridge Isotope Ltd. Tricyclohexyltin sulfide[10] was prepared by refluxing a mixture of tricyclohexyltin chloride and sodium sulfide nonahydrate in 95% ethanol and purified by recrystallization from chloroform/methanol (1/1).

Polymer Characterization. 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 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 the flow rate of 1.0 mL/min; a UV detector was set at 254-nm wavelength. Inherent viscosities were measured in 0.5 g/dL chloroform solution at 25 °C using an Ubbelohde dilution viscometer. The glass transition temperatures were determined either on a Seiko DSC 220 or a Du Pont DSC 2100 at a heating rate of 10 °C/min, 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 air (200 mL/min) and in nitrogen (200 mL/min).

9,10-Bis(4-fluorophenyl)phenanthrene (1). A mixture of 2,2′-bis(4-fluorobenozyl)biphenyl (1.59 g, 4.0 mmol) and Lawes-

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son's reagent (3.24 g, 8.0 mmol) in toluene (60 mL) was heated at reflux under nitrogen for 6 h. The mixture was then cooled and concentrated. The residue was treated with acetone and filtered through a pad of silica gel. The filtered acetone solution was evaporated to give a white solid. After recrystallization from ethyl acetate/cyclohexane (1/1), compound 1 was obtained as white crystals (needles): 0.82 g (56%); mp 256.8–258.1 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ 8.81 (2 H, d, J = 8.4 Hz), 7.72–7.63 (2 H, m), 7.53–7.46 (4 H, m), 7.13–6.90 (8 H, m); ^{13}C NMR (50 MHz, CDCl$_3$) δ 164.02, 159.14, 136.56, 135.34, 135.27, 132.56, 132.40, 131.75, 130.08, 127.63, 126.81, 126.67, 122.60, 115.01, 114.58; HRMS for $C_{26}H_{16}F_2$ calc 366.1243, found 366.1227.

Compound **1** was also synthesized using tricyclohexyltin sulfide and boron trichloride in 82% yield.[7]

Attempted Reaction of 1 with 4-*tert*-Butylphenol. In a three-neck flask were placed **1** (366 mg, 1.0 mmol), 4-*tert*-butylphenol (300 mg, 2.0 mmol), potassium carbonate (276 mg, 2.0 mmol), NMP (5.0 mL), and toluene (10 mL). The mixture was purged with nitrogen for 10 min and then heated up to 140 °C. The azeotropic water was distilled off in 2–3 h. The reaction temperature was then increased to 160–170 °C and reaction continued for 24 h. The displacement of the fluoride group was not observed as monitored by TLC during the reaction. Nearly all of the starting material **1** was recovered after removing the solvent in vacuo and isolating by flash chromatography on silica gel (20% ethyl acetate in hexane).

Transformation of the Polymers 2 to 3. A typical procedure using tricyclohexyltin sulfide–boron trichloride is as follows: A solution of boron trichloride in methylene chloride (1.0 M, 2 mL, 2.0 mmol) was introduced to a mixture of polymer **2a** (293 mg, 0.5 mmol) and tricyclohexyltin sulfide (1.682 g, 2.2 mmol) in dry TCE (30 mL) at room temperature under nitrogen. The mixture was stirred for 20 min at room temperature and then heated at 110–130 °C for 3 h until IR analysis showed the complete disappearance of carbonyl absorption at about 1660 cm^{-1}. A change in color from brown to blue and then to light brown also indicated the completion of reaction. The reaction mixture was then concentrated to about 5–10 mL and poured in methanol. The resultant polymer was purified by dissolving in hot NMP and coagulating in methanol. After washing thoroughly with acetone, ether, and hexanes and dried in an oven at 60 °C under vacuum overnight, white fibrous polymer **3a** (223 mg) was obtained.

3a: 81% yield; ^{1}H NMR (200 MHz, Cl$_2$CDCDCl$_2$) δ 8.73 (2 H, d, J = 8.0 Hz), 7.62–7.57 (4 H, m), 7.49–7.46 (2 H, m), 7.18 (4 H, d, J = 8.3 Hz), 6.97 (4 H, d, J = 7.8 Hz), 6.87–6.80 (8 H, m), 1.62 (6 H, s); IR (film, cm^{-1}) 2967, 1599, 1500, 1239, 1172, 1014, 834, 759, 726. **3b**: 87% yield; ^{1}H NMR (400 MHz, Cl$_2$CDCDCl$_2$) δ 8.71 (2 H, d, J = 8.2 Hz), 7.60–7.57 (4 H, m), 7.43 (2 H, dd, J = 8.4, 6.8 Hz), 7.33 (4 H, d, J = 8.4 Hz), 7.06 (4 H, d, J = 8.5 Hz), 6.90 (4 H, d, J = 8.5 Hz), 6.88 (4 H, d, J = 8.4 Hz); IR (film, cm^{-1}) 2921, 1600, 1501, 1448, 1247, 1175, 1017, 968, 928, 838, 760, 726. **3c**: 83% yield; ^{1}H NMR (400 MHz, Cl$_2$CDCDCl$_2$) δ 8.66 (2 H, d, J = 8.5 Hz), 7.57–7.54 (4 H, m), 7.38 (2 H, t, J = 7.5 Hz), 7.33 (4 H, d, J = 8.6 Hz), 6.97 (4 H, d, J = 8.5 Hz), 6.84 (8 H, t, J = 8.6 Hz); IR (film, cm^{-1}) 3033, 1599, 1491, 1235, 1168, 1016, 866, 760, 726. **3d**: 99% yield; FTIR (KBr, cm^{-1}) 3064, 1584, 1487, 1242, 1152, 866, 780, 726. **3e**: 80% yield; IR (KBr, cm^{-1}) 3063, 1597, 1497, 1446, 1239, 1168, 1013, 827, 725.

Other properties of polymers **3** are presented in Table I.

Transformation of Polymers 5 to 6. A mixture of polymer **5c** (235 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 120–140 °C under nitrogen for 5 h, followed by IR analyses. The reaction mixture was concentrated to dryness under vacuum and the residual polymer was washed with methanol and acetone thoroughly. The resultant polymer was further purified by dissolving in chloroform and precipitating into methanol. After drying in an oven at 60 °C under vacuum overnight, white fibrous polymer **6c** weighed 206 mg.

6a: 91% yield; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 (2 H, s), 7.47 (2 H, d, J = 9.0 Hz), 7.19–7.08 (16 H, m), 6.91 (4 H, d, J = 8.7 Hz), 1.62 (6 H, s); IR (film, cm^{-1}) 2967, 1600, 1499, 1435, 1236, 1184, 973, 823, 756. **6b**: 88% yield; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.28 (2 H, s), 7.54 (2 H, d, J = 8.9 Hz), 7.32 (4 H, d, J = 8.2 Hz), 7.19–7.10 (12 H, m), 6.97 (4 H, d, J = 8.7 Hz); IR (film, cm^{-1}) 3052, 1603, 1508, 1435, 1246, 1173, 969, 827, 700. **6c**: 94% yield; ^{1}H NMR (200 MHz, CDCl$_3$) δ 8.20 (2 H, s), 7.56–7.35 (6 H, m), 7.24–6.96 (16 H, m); FTIR (film, cm^{-1}) 3054, 1600, 1489, 1434, 1232, 972, 823, 701. **6d**: 85% yield; ^{1}H NMR (200 MHz, Cl$_2$CDCDCl$_2$) δ 8.21 (2 H, s), 7.51 (4 H, d, J = 8.3 Hz), 7.24–7.11 (14 H, m); IR (film, cm^{-1}) 2924, 1612, 1491, 1436, 1199, 974, 820, 700. **6e**: 89% yield; ^{1}H NMR (200 MHz, CDCl$_3$) δ 8.18 (2 H, s), 7.63 (2 H, d, J = 8.3 Hz), 7.49–7.05 (24 H, m), 6.85 (4 H, d, J = 8.9 Hz); IR (film, cm^{-1}) 3057, 1599, 1496, 1436, 1237, 973, 824, 746, 701.

Other properties of polymers **6** are presented in Tables II and III.

Transformation of the End-Capped Polymers 7 to 8. The following is a typical experiment. A mixture of polymer **7b** (347 mg, 0.5 mmol) with the number of repeat units of 105[7] as determined by ^{1}H NMR and Lawesson's reagent (405 mg, 1.0 mmol) in dry TCE (25 mL) was purged with nitrogen for 20 min at room temperature. The reaction temperature was increased to 120–140 °C and kept for 3 h. The completion of reaction was confirmed by IR analysis. The reaction mixture was then concentrated to dryness, and the residue was washed with methanol and acetone. The resultant polymer was purified by dissolving in hot TCE and then coagulating in methanol. The fibrous polymer **8b** weighed 271 mg after drying in an oven under vacuum at 60 °C overnight. The number of repeat units was determined to be 105 by ^{1}H NMR. ^{1}H NMR (400 MHz, Cl$_2$CDCDCl$_2$) δ 8.71 (2 H, d, J = 8.2 Hz), 7.60–7.57 (4 H, m), 7.43 (2 H, dd, J = 8.4, 6.8 Hz), 7.33 (4 H, d, J = 8.4 Hz), 7.06 (4 H, d, J = 8.5 Hz), 6.90 (4 H, d, J = 8.5 Hz), 6.88 (4 H, d, J = 8.4 Hz), 1.23 (s).

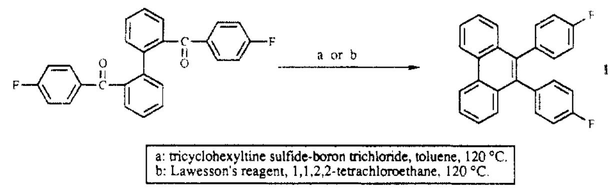
The experiment using the tricyclohexyltin sulfide–boron trichloride reagent gave the same result.

Results and Discussion

To our knowledge, poly(arylene ether)s containing a phenanthrene ring in the polymer backbone have not been described before. The synthesis of these aromatic polymers through the formation of ether linkage via step-growth polymerization would be hampered due to the potential solubility problem of the growing polymers and/or the lack of suitable, reactive monomers. For example, the nucleophilic polycondensation of a dihalide monomer containing a phenanthrene ring with a bisphenol would be quite difficult, if not impossible, because the dihalide monomer may not be reactive enough for a displacement reaction without an activating group. As a control experiment, a mixture of potassium 4-*tert*-butylphenoxide and 9,10-bis(4-fluorophenyl)phenanthrene (**1**) was heated in NMP at 180 °C for 24 h. No displacement reactions were observed, and the starting materials were recovered. The precursor strategy would, therefore, be applicable for the synthesis of a series of such polymers. Prior to our studies on transforming the polymers containing the 2,2′-dibenzoylbiphenyl unit into the phenanthrene-based polymers, the model reaction was investigated.

Model Reaction. One of the well-known methods to form a carbon–carbon double bond by coupling two carbonyl groups is the McMurry reaction.[11] Initial attempts to use this titanium(0)-induced reductive coupling reaction with 2,2′-bis(4-fluorobenzoyl)biphenyl[7] resulted in only a mixture of products derived from both inter- and intramolecular reactions. High dilution is required in order to favor an intramolecular process, but it is not practical for the polymer transformation. Our attention was then focused on the thermal coupling reaction of dithioketone compounds. The cyclization of 2,2′-bis(4-fluorobenzoyl)-biphenyl was first examined using B_2S_3 as a thionating agent generated *in situ* from tricyclohexyltin sulfide and boron trichloride (Scheme I). Complete conversion was observed after refluxing in toluene for a couple of hours. The intermolecular coupling did not occur, and the quantitative formation of a phenanthrene ring was con-

Scheme I. Model Reaction



Scheme II. Transformation of Polymers 2 to 3

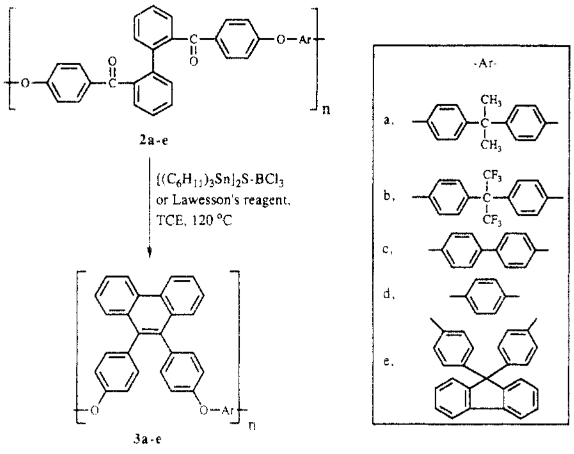


Table I. Characterizations of Poly(arylene ether)s 2 and 3

	yield, %	T_g,[a] °C		TGA (5%, °C), 2		TGA (5%, °C), 3	
Ar	3	2	3	N_2	air	N_2	air
a	81	172	227	491	453	538	524
b	87	179	230	523	516	570	524
c	83	193	251	500	505	588	520
d	99	175	242	493	504	578	556
e	80	230	b	523	521	567	515

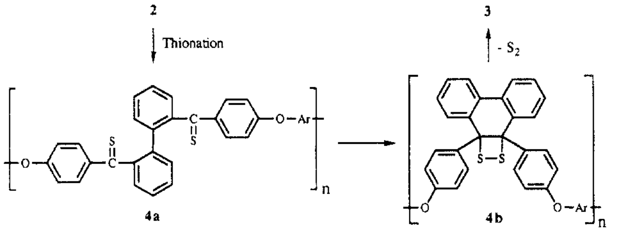
[a] Second run at 10 °C/min. [b] Not observed.

firmed by TLC and NMR analyses. The cyclization with Lawesson's reagent, which is widely used for thionation of ketone, ester, and amide,[9] also gave the desired product, but in a longer reaction time and with an excess of reagents. The yield was also lower due to the difficulties in isolation and purification.

Transformation of Poly(arylene ether)s 2 to 3. Polymers 3 with 9,10-diphenylphenanthrene units were obtained through the transformation of poly(arylene ether)s 2 (Scheme II). The cyclizations were carried out in TCE using either Lawesson's reagent or B_2S_3 *in situ* prepared from tricyclohexyltin sulfide and boron trichloride at relatively low temperatures around 120–140 °C. The tricyclohexyltin sulfide–boron trichloride reagent seems to be more reactive than Lawesson's reagent, but the latter is cheaper and more convenient to use and requires no special handling.

Complete transformations were achieved for each of the polymers 2, and the desired polymers 3 were isolated in good yields (Table I). The reaction was over in 2–3 h, which can be monitored by the disappearance of carbonyl absorption by IR. The color change was also usefully indicative of the complete transformation: from yellow to deep blue developed at the early stage of the reaction, and then back to yellow. The resulting polymers 3 were isolated easily from the reaction mixture by removal of TCE under vacuum and subsequent washing with methanol and acetone. Except for the insoluble polymers **3d** and **3e** which were precipitated out from hot reaction solution, the rest of the polymers were purified by dissolving in a boiling solvent such as TCE or NMP and precipitating into methanol.

Scheme III. Possible Pathway for the Cyclization



As shown in Scheme III, a possible pathway suggested by Steliou[6] for the enthalpically-favored cyclization process involves the 1,2-dithietane intermediate **4b** generated from the dithioketone **4a** and the intramolecular formation of a carbon–carbon double bond upon extrusion of the diatomic sulfur. Isolation of the blue-colored polymers, presumably the thioketone polymers, has not been successful since the dithioketone intermediates are relatively unstable and react rapidly under the conditions necessary for the thionation.

Complete transformations of polymers 2 to the phenanthrene-based polymers 3 have been confirmed by spectroscopic analyses. The IR spectra of polymers **2b** and **3b** are shown in Figure 2. The absorption due to the carbonyl group at 1664 cm^{-1} as seen in the spectrum of **2b** completely disappears in the spectrum of **3b**. In the NMR spectra, one of the structural characteristics of phenanthrene is the resonance peak due to the C_5 and C_6-"bay" protons at 8.0–9.0 ppm.[12] A doublet around 8.70 ppm is observed for polymers 3, except for the insoluble ones **3d** and **3e**. In comparison, a doublet at 8.75 ppm in the spectrum of polymer **3b** with a correct integral is a clear indication of clean intramolecular transformation, which distinguishes **3b** from its precursor **2b** (Figure 3). Structural assignments for each of the polymers 3 have unambiguously been made, with the aid of 2-D COSY experiments when necessary. The ^{13}C NMR spectra were also used to confirm the complete conversion of polymers 2. No signals for either carbonyl (ca. 190 ppm) or thiocarbonyl groups (above 200 ppm) were observed.

Polymers 3 appeared as either white fibers or pale-yellow powders. From polymers 2 to 3, the polymer properties significantly changed. Due to a fused-ring system, the increased rigidity in the polymer backbone led to dramatic increases in both glass transition temperatures (T_g's) and thermal stabilities relative to their precursor polymers 2 (Table I). The T_g's were about 50 °C higher, in the range of 227–251 °C as measured by DSC. Thermal stabilities were also improved as assessed by TGA. The onset of 5% weight loss for each of the polymers 3 was in the range of 537–588 °C. For example, an increase close to 90 °C was found for the polymer **3c** derived from 4,4′-biphenol, compared to its precursor **2c**. In addition, the polymer **3c** showed a melting point of 390 °C as evidenced by a clear endotherm from DSC. Therefore, these polymers should be amenable toward melt processing in spite of their high T_g's. Another notable change for polymers 3 was the increased solvent resistance. All the polymers were insoluble in common organic solvents such as chloroform and methylene chloride at ambient or elevated temperatures. Polymers **3a,b,c** were slightly soluble in hot TCE or NMP. No solvents were found to dissolve polymers **3d** and **3e**.

Transformation of Polymers 5 to 6. Heating a mixture of the polymers 5 and a thionating reagent at 120–150 °C in TCE, a similar procedure as used for the conversion of polymers 2 to 3, gave polymers 6 in excellent yields (Scheme IV). The cyclization reactions required

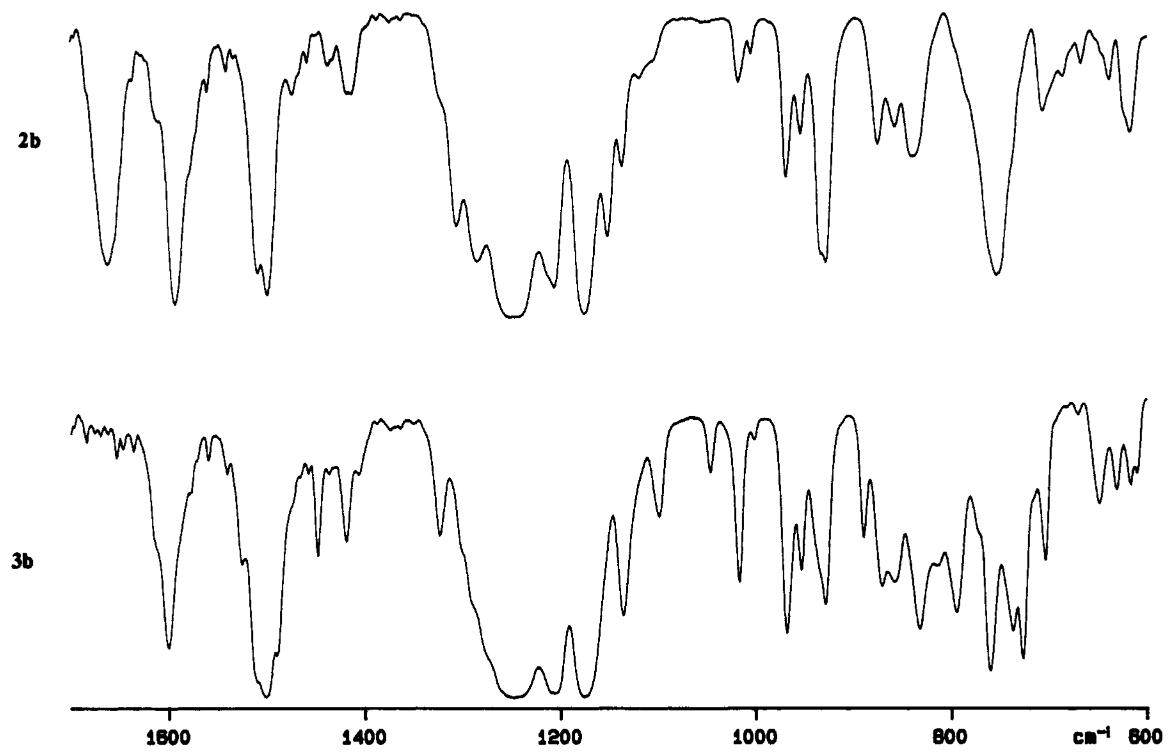


Figure 2. IR spectra of poly(arylene ether)s **2b** and **3b**.

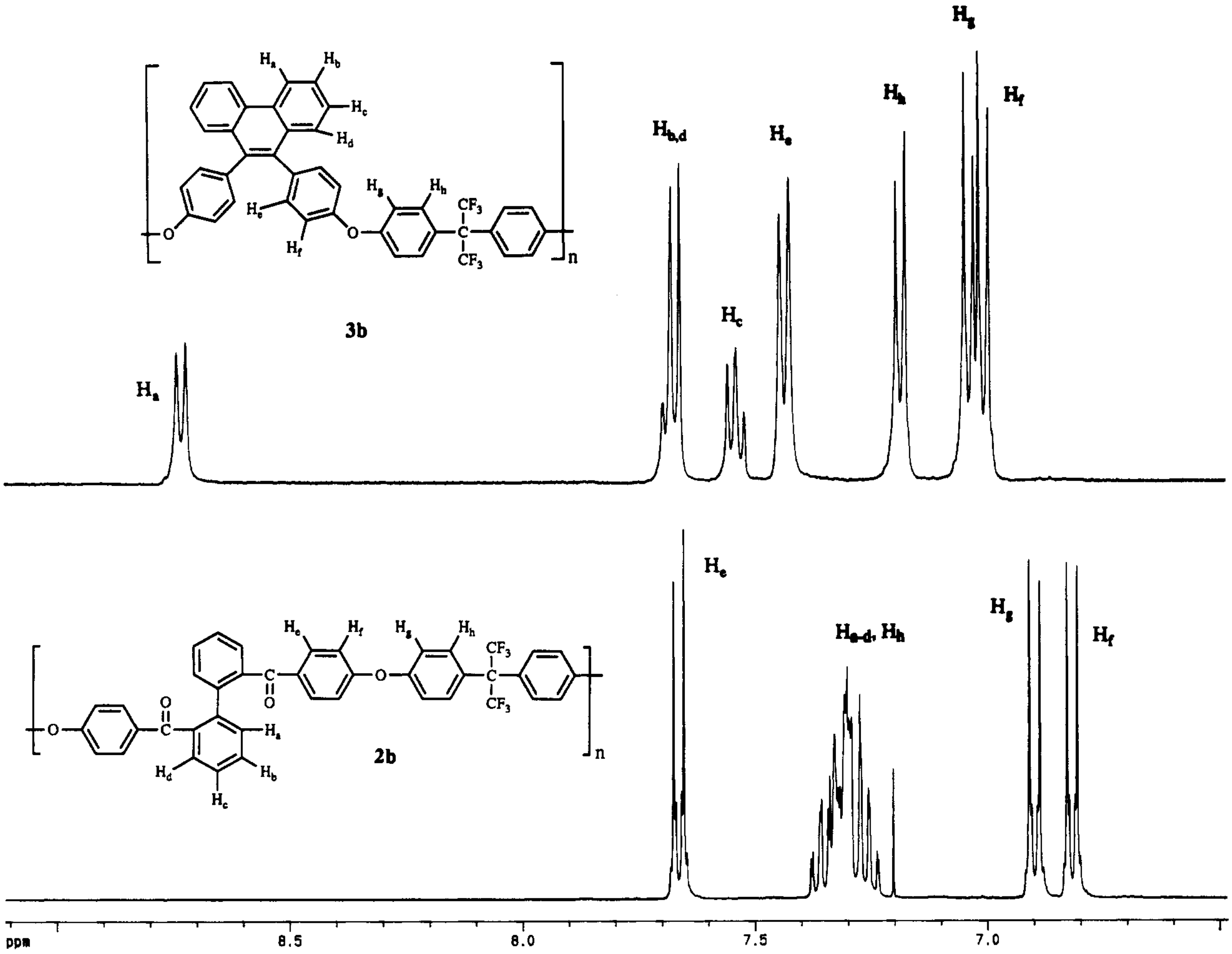


Figure 3. ^{1}H NMR (400 MHz) spectra of poly(arylene ether)s **2b** and **3b**.

4–5 h to complete. Isolation of the polymers **6** was carried out by removing TCE and washing the residue with acetone thoroughly. After purification by dissolving in chloroform or TCE and coagulating in methanol, the polymers were obtained as white fibers. The formation of the desired phenanthrene-based polymers **6** was confirmed in a similar way as for the polymers **3**. For example, the peak at about 1660 cm^{-1} due to the carbonyl group was absent in the IR spectra of polymers **6**. Each ^{1}H NMR spectrum of polymers **6** showed a singlet at about 8.2 ppm attributed

Scheme IV. Transformation of Polymers 5 to 6

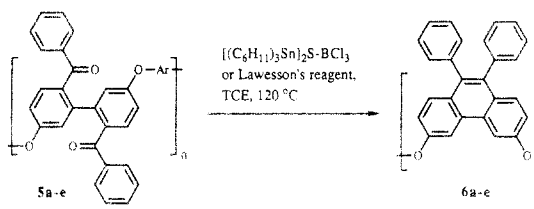


Table II. Synthesis of Poly(arylene ether)s 6 from Poly(arylene ether ketone)s 5

polymer 6	yield (%)	η_{inh}[a,b] (dL/g)	M_w[b] ($\times 10^{-4}$)	M_n[b] ($\times 10^{-4}$)	M_w/M_n[b]
a	91	0.32 (0.55)	6.57 (10.5)	3.12 (5.14)	2.11 (2.05)
b	88	0.50 (1.15)	6.85 (14.2)	2.81 (5.78)	2.43 (2.46)
c	94	0.32 (0.70)	4.79 (11.4)	1.85 (4.31)	2.59 (2.67)
d[c]	85	(0.71)	(23.0)	(8.37)	(2.75)
e	89	0.43 (0.60)	12.2 (17.3)	4.59 (6.22)	2.68 (2.78)

[a] 0.5 g/dL chloroform solution at 25 °C. [b] Data in parentheses are for polymers 5. [c] Insoluble in chloroform.

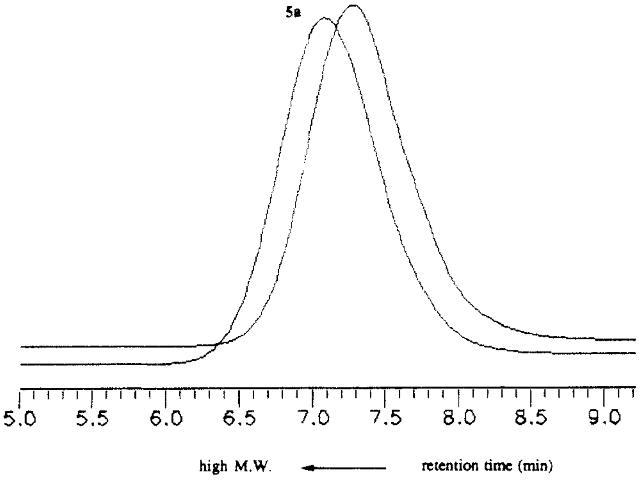


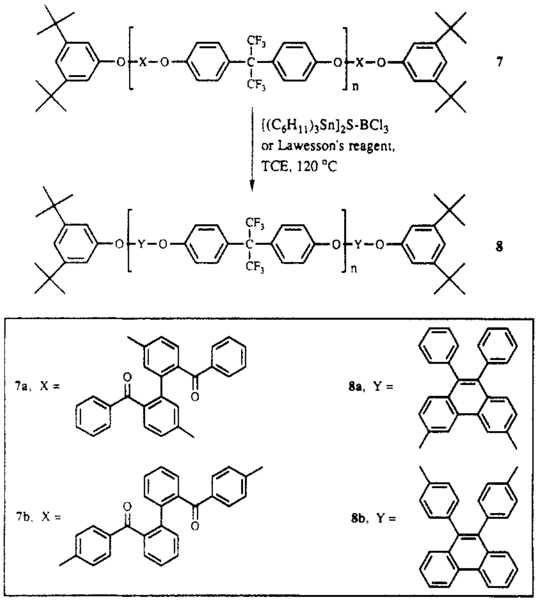
Figure 4. GPC chromatograms of **5a** ($M_n = 5.14 \times 10^4$, $M_w/M_n = 2.05$) and **6a** ($M_n = 3.12 \times 10^4$, $M_w/M_n = 2.11$).

Table III. Comparison of Poly(arylene ether)s 5 and 6

	T_g[a] (°C)		TGA (5%, °C), 5		TGA (5%, °C), 6	
Ar	5	6	N_2	air	N_2	air
a	156	245	473	475	516	499
b	164	253	500	480	518	500
c	174	290	473	448	559	505
d	156	260	462	448	540	502
e	215	324	492	460	559	502

[a] Second run at 10 °C/min.

Scheme V. Transformation of End-Capped Poly(arylene ether)s 7 to 8



to two "bay" protons, indicating the formation of a phenanthrene ring.

The molecular weights of polymers 6 were determined by GPC using polystyrene standards. Going from the flexible 2,2′-dibenzoylbiphenyl moiety to the rigid phenanthrene ring, the polymer chain is obviously shrunk by this structural change. Convincing evidence is from the GPC data (Table II). The apparent molecular weights of polymers 6 decreased in comparison with their precursors 5. Viscosities are additional supporting data. Inherent viscosities of polymers 6 were found to be lower than those of their precursors, ranged from 0.32 to 0.50 dL/g in chloroform (Table II).

To ensure no bond scission during the polymer transformation, a sample of isolated polymer **6a** without purification, which would represent the whole picture of the reaction, was analyzed and compared to its precursor **5a** by GPC. As shown in Figure 4, two polymers **5a** and **6a** have similar polydispersity but different molecular weights. The single GPC trace for the polymer **6a** indicates clearly no degradation. Furthermore, a possible chain cleavage is excluded by NMR studies on the end-capped polymers.

Obviously, the structural difference between the polymers **3** and **6** is that the ether bond is linked directly to the pendant phenyl groups on phenanthrene in the former and to the phenanthrene ring in the latter. Since the chain stiffness should be expected to increase dramatically in the polymers **6**, the increases in T_g's relative to their precursors **5** would be significant. Indeed, large increases (about 100 °C) in T_g's were observed as the polymers **5** were transformed to **6** (Table III), indicating that the bond rotation along the backbone of polymers **6** is more restricted due to a rigid phenanthrene ring. The T_g's for polymers **6** range from 245 to 324 °C as measured by DSC. All polymers are amorphous. Crystalline behaviors are not observed even after annealing above their glass transition temperatures. Thermal stabilities of polymers **6** are also improved in comparison with **5**. Thermogravimetric analyses showed that the 5% weight loss for polymers **6** begun around 500 °C in either air or nitrogen. Due to the meta-linkage of the ether bond and the presence of the pendant phenyl groups, polymers **6** should be more soluble than their analogues **3**. As expected, most of the polymers are soluble in chloroform or TCE at ambient temperatures, except that the polymer **6d** is slightly soluble in hot TCE and NMP. Flexible, transparent films can be made from these polymers by solution casting.

Transformation of the End-Capped Polymers. In order to further confirm that no degradation occurred during the cyclization reaction, the end-capped polymers **7**, which were prepared previously using 3,5-di-*tert*-butylphenol as an end-capping reagent, were treated in the same way as for other polymers (Scheme V). Thus, polymer **7a** with 95 repeat units was treated with Lawesson's reagent or the tricyclohexyltin sulfide–boron trichloride reagent. The GPC analysis showed only a single peak for the resultant polymer **8a**. The NMR study indicated that it had the same number of repeat units, 95, as that of polymer **7a** (Table IV). These results proved that not only does no degradation occur during the transformation but also there is no intermolecular cross-coupling. Similarly, it was confirmed by the NMR analysis that there

Table IV. Characterizations of End-Capped Polymers 7 and 8

polymer	repeat unit $(n)^a$	$\eta_{inh}{}^b$ (dL/g)	M_w ($\times 10^{-4}$)	M_n ($\times 10^{-4}$)	M_w/M_n
7a	95	0.42	3.53	1.58	2.23
8a	95	0.31	3.19	1.45	2.20
7b	105	0.36	5.88	2.87	2.05
8b[c]	105				

[a] Determined by ^{1}HNMR. [b] 0.5 g/dL chloroform solution at 25 °C. [c] Insoluble in chloroform.

was no chain cleavage during the transformation of polymer **7b** to polymer **8b**.

Conclusions

Two series of the phenanthrene-based poly(arylene ether)s from readily available, soluble polymers have been synthesized. Transformations of the precursor polymers by intramolecular cyclizations of the 2,2′-dibenzoylbiphenyl moiety proceed completely under mild conditions without degradation and cross-linking. The dramatic changes in properties such as T_g's, thermal stabilities and solvent resistance (for polymers **3**) are observed. The synthesis of other high-performance polymers containing a phenanthrene ring using this methodology is currently under investigation.

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