Communications to the Editor

Intramolecular Cyclization of 2,2′-Dibenzoylbiphenyl Units as a New Route To Increase the Rigidity and Solvent Resistance in Poly(arylene ether)s

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High-temperature thermoplastics, like poly(ether ether ketone) (PEEK) and poly(phenylenequinoxaline)s, have received considerable attention in the past few years for use in advanced resin matrix composite systems. But many thermoplastic resins are quite sensitive to organic solvents such as brake fluid and also exhibit a low creep resistance at elevated temperatures which prohibit their use in certain structural applications. Efforts to circumvent these problems have centered around the utilization of acetylene thermal curing chemistry. Besides curing acetylene-terminated thermoset oligomers to form a cross-linked polyene network,[1] also studied is a non-cross-linking approach involving an intramolecular cycloaddition reaction of pendant phenylethynyl groups to form a fused anthracene ring.[2] The increased rigidity in the polymer backbone is postulated to increase creep and craze resistance. However, this approach suffers from tedious synthesis of monomers and incomplete intramolecular cyclization. In addition, prolonged heating at elevated temperatures may cause cross-linking, resulting in the brittleness in the polymer.

It is desirable to introduce a rigid, fused aromatic group into high-performance polymers like poly(arylene ether)s in order to improve solvent resistance and other thermal properties, but the direct synthesis of such polymers with high molecular weights would be hampered due to poor solubility of the growing polymer and/or the lack of suitable, reactive monomers. The solubility problem could be overcome by polymerizing a modified monomer, such as 4,4′-difluorobenzophenone *N*-phenylimine for the synthesis of PEEK or other semicrystalline polymers, followed by a postpolymerization transformation like the hydrolysis of ketimine to ketone.[3a,b] Similarly, we reason that both problems, the availability of suitable monomers and the solubility of the polymer, can be solved at the same time if a high molecular weight, soluble polymer can be prepared first and then converted by a simple chemical or thermal process into a desired solvent-resistant polymer. Such a chemical or thermal transformation should result in significant structural changes such as the formation of a new bond or an aromatic ring in the polymer backbone, so that the resulting polymer would become more rigid and solvent resistant and have improved thermal properties. Furthermore, the transformation reaction should proceed rapidly, selectively, and cleanly in an intramolecular fashion. Since the acetylene curing reaction undergoes either intra- or intermolecularly without any significant selectivity, most of its applications are limited within the area of thermoset resins. Generally speaking, an intramolecular carbon–carbon bond-forming reaction requires a specific structural arrangement, like many rearrangement reactions, or a favored enthalpic control.

One of such enthalpy-controlled reactions is the thermal cyclization of labile 2,2′-disubstituted dithiobenzoylbiphenyls generated from the thionation of the corresponding ketone to form fused substituted phenanthrenes.[4a,b] Not only does it result in a significant structural change, from a flexible substituted biphenyl to a rigid substituted phenanthrene, but it also proceeds rapidly at relatively low temperatures (around 80 °C) in quantitative yield without intermolecular dimerization. Thus, a new approach to increase the rigidity and solvent resistance in polymers is designed based on this cyclization chemistry, and its feasibility is demonstrated by synthesizing, as reported herein, a series of non-cross-linked, phenanthrene-based poly(arylene ether)s from readily available poly(arylene ether ketone)s containing 2,2′-dibenzoylbiphenyl units. Poly(arylene ether ketone)s can be prepared in high molecular weights from an activated aryl dihalide containing a 2,2′-dibenzoylbiphenyl moiety and a variety of commercially available bisphenols by step-growth polymerization. The 2,2′-dibenzoylbiphenyl units are then converted into the phenanthrene groups by intramolecular cyclization. The increased rigidity arising from the fused phenanthrene ring would improve the thermal stability and increase the T_g of the polymer.

The monomer for poly(arylene ether ketone)s, 2,2′-bis(4-fluorobenzoyl)biphenyl (1),[5a,b] was synthesized by nickel(0)-catalyzed coupling of commercially available 2-chloro-4′-fluorobenzophenone in high yield (Scheme I). The reaction can be scaled up without any difficulties, and the monomer is purified by simple recrystallization. The cyclization reaction was first tested on the compound 1 using tricyclohexyltin sulfide and boron trichloride as a thionating agent.[4b] After heating for 1–2 h at reflux in toluene, the difluoride 1 was completely converted to 9,10-bis(4-fluorophenyl)phenanthrene.[6] The reaction was clean and quantitative, as indicated by thin-layer chromatography (TLC) analysis. The Lawesson's reagent is also a powerful thionating agent,[7] which converts a ketone, ester, and amide into the corresponding thio analogues. However, it was found to be less effective for this model compound than for the polymers.

Polymerizations of the difluoride 1 with various bisphenols **2a–e** were performed using a stoichiometric ratio of monomers and an excess of potassium carbonate in 1-methyl-2-pyrrolidone (NMP) at 20% solid contents (Scheme II). During the initial stages of the reaction, the water being formed was removed as an azeotrope with toluene (145 °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, subjected to the appropriate solvent rinses, and dried in a vacuum oven at 60 °C overnight. Poly(arylene ether ketone)s **3a–e** were of high molar mass as evidenced by inherent viscosities ranging from 0.41 to 0.83 dL/g. The number-average molecular weights and polydispersity ranged, relative to polystyrene standards by gel permeation

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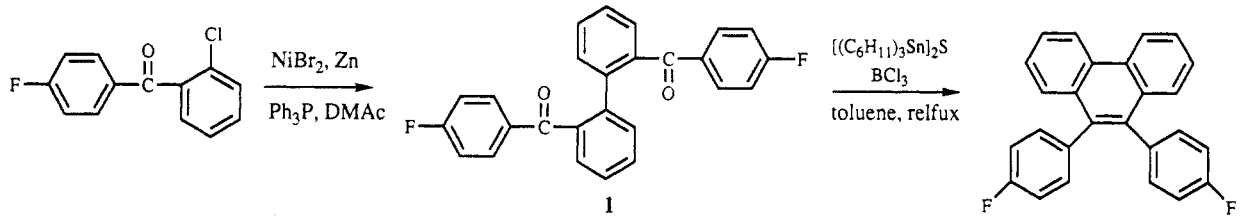
Scheme I
Synthesis of Difluoride Monomer and Model Reaction



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Scheme II
Synthesis of Poly(arylene ether ketone)s 3 and Transformations to Poly(arylene ether)s 4

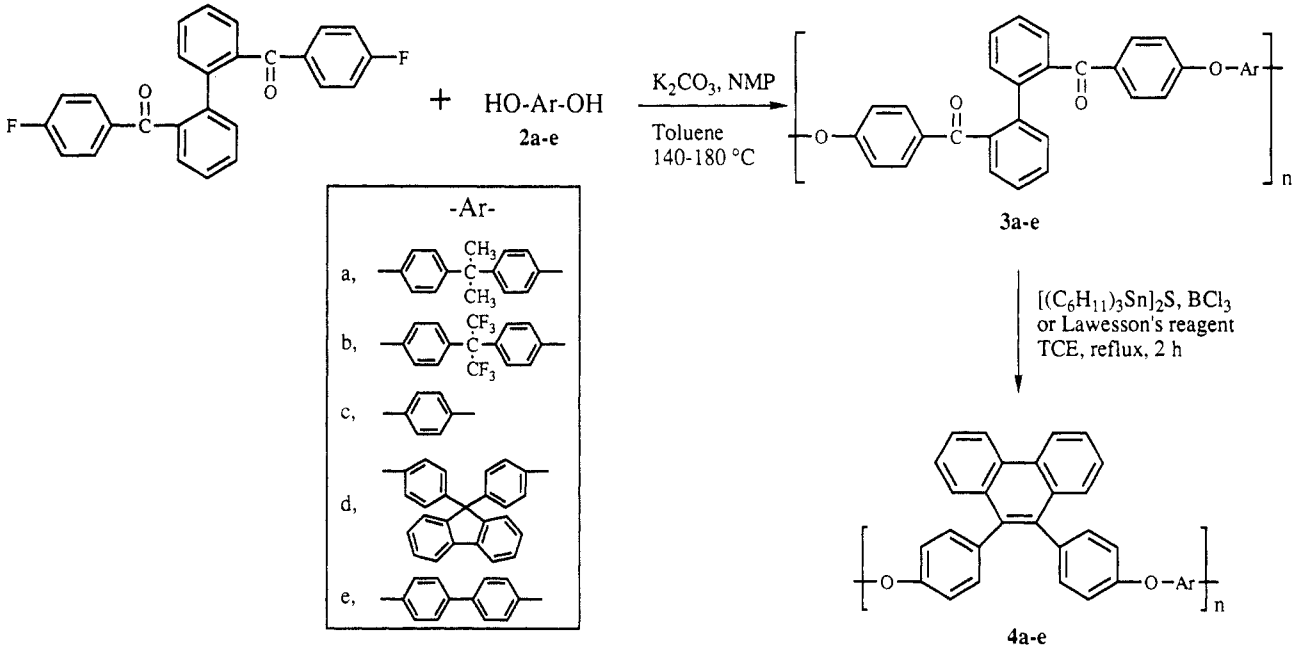
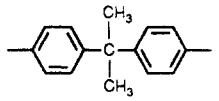
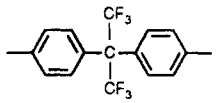
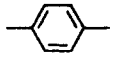
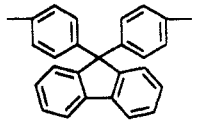
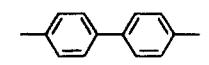


Table I
Characteristics of Polymers 3 and 4

-Ar-	η_{inh},[a] dL/g 3	T_g,[b] °C 3	T_g,[b] °C 4	TGA,[c] °C 3	TGA,[c] °C 4
a, 	0.55	172	227	491	538
b, 	0.50	179	230	523	537
c, 	0.41	175	242	493	578
d, 	0.52	230	*d*	523	567
e, 	0.83	193	251	500	588

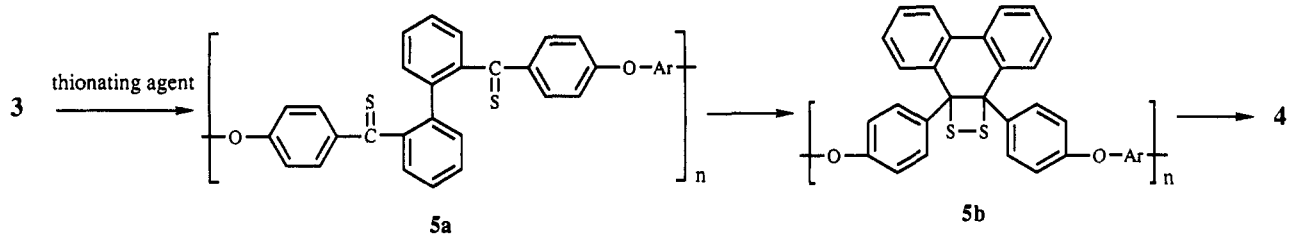
[a] 0.5% solution in chloroform at 25 °C. [b] Performed on a Seiko DSC 220 at a heating rate of 10 °C/min. [c] 5% weight loss in nitrogen, obtained on a Seiko TG/DTA 220 at a heating rate of 10 °C/min. [d] Not observed.

chromatography, from 42 000 to 727 000 and 1.9 to 2.3, respectively. They showed T_g's of 172–230 °C depending on the bisphenol used in the synthesis (Table I). The thermal stabilities, as assessed by 5% weight loss in nitrogen, of the polymers are above 490 °C. All polymers are amorphous, soluble in chlorinated solvents such as methylene chloride, chloroform, and 1,1,2,2-tetrachloroethane (TCE) at ambient temperature, and can be cast into transparent, creasable films.

The cyclization reactions of the 2,2′-dibenzoylbiphenyl group in the polymers **3** were carried out in TCE using either Lawesson's reagent or a tricyclohexyltin sulfide–boron trichloride reagent (Scheme II). The later generates B_2S_3 in situ, an effective thionating agent, only if it is freshly prepared. At about 80–150 °C all cyclizations were found to be complete in less than 2 h, as monitored by FTIR (e.g., a C=O peak). The reaction solution became blue or green at the early stage of the reaction, which indicates the formation of the corresponding thioketones. Subsequent discoloration signals the completion of cyclization. Except that the polymers **4c** and **4d** precipitated out, the rest of resulting polymers remained in a hot reaction solvent. A typical procedure 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 **3a** (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 reaction continued at 110–120 °C for 3 h, followed by FTIR. The reaction mixture was then concentrated to about 5–10 mL and precipitated into methanol. The polymer was purified by dissolving in hot NMP and then pouring into stirred methanol. After washing thoroughly with acetone and drying at 60 °C under vacuum overnight, the fibrous polymer **4a** was obtained (223 mg, 81%).

The structures of the phenanthrene-based polymers were characterized by FTIR and high-resolution ^1H and ^{13}C NMR. The peak at about 1664 cm^{-1} due to the carbonyl group in the polymers **3** disappeared in the FTIR spectra of the polymers **4** and their ^{13}C NMR spectra showed no

Scheme III
Proposed Cyclization Pathway



5a 5b

signals for either carbonyl (at about 196 ppm) or thiocarbonyl groups (at 217 ppm, a typical value for benzothiophenone), indicating a complete conversion. The structures of some of the polymers **4** were unambiguously confirmed by ^{1}H NMR using 2D-COSY experiments. A doublet at 8.23 ppm in ^{1}H NMR spectra is characteristic for the phenanthrene ring and observed with a correct integration, further proving that the reaction proceeds exclusively in an intramolecular fashion.

The polymers **4** showed increased solvent resistance, due to the fact that they are not soluble in chloroform or other common organic solvents and only **4a**, **4b**, and **4e** are slightly soluble in hot TCE or NMP. No suitable solvent was found yet for measuring the viscosities of these polymers. They have higher T_g's, ranging from 228 to 251 °C, in comparison with their precursors (Table I). The thermal stabilities of the polymers **4** were assessed by the weight loss in a variable-temperature thermogram. The onset of 5% weight loss of each of the polymers was in the 537–588 °C range. For example, the polymer containing a biphenyl unit (**4e**) exhibited a significantly higher thermal stability (588 °C for 5% weight loss) than its precursor (**3e**; 500 °C for 5% weight loss). In addition, polymer **4e** showed a melting point of 390 °C measured by differential scanning calorimetry. Thus, these polymers should be amenable toward melt processing in spite of their high T_g's.

The cyclization proceeds via first the formation of a thioketone **5a** and then spontaneous extrusion of diatomic sulfur (S_2) to form a double bond intramolecularly. An attempt to isolate the blue thioketone polymer failed, because once two keto groups in each units were converted to the thioketones the cyclization took place immediately at the temperatures necessary for thionation reaction (e.g., even at 50 °C). The formation of diatomic sulfur is confirmed by trapping with a diene to yield a Diels–Alder adduct.[4a] The proposed pathway for the S_2 extrusion involves a transient 1,2-dithietane intermediate **5b** derived from the thioketone **5a**, and the intramolecular process is preferable to the intermolecular dimerization based on enthalpic consideration (Scheme III).[4b]

In order to investigate if there is any degradation during the polymer transformation or the polymers **4** have the same molecular weights as the polymers **3**, the end-capped polymer **3b** was prepared and subjected to a cyclization reaction. Thus, the polymerization of the difluoride **1** and the bisphenol **2b** was carried out in the presence of a small amount of 3,5-di-*tert*-butylphenol. The number of repeat units (n) of polymer **3b** (η_{inh} 0.36 dL/g in chloroform) was found to be in the range of 105–110 by ^{1}H NMR, close to the designed value (n = 100). After treatment with Lawesson's reagent for 2 h, the resulting polymer **4b** was isolated, purified, and analyzed by NMR. The NMR data showed that the number of repeat units was also in the range of 105–110,[8] meaning no degradation during the cyclization and no intermolecular coupling as well.

Polycondensation of bisphenols **2** with 9,10-bis(4-fluorophenyl)phenanthrene derived from **1** (Scheme I) by nucleophilic displacement would be a direct synthetic approach to polymers **4**. However, this difluoride, due to the lack of a good electron-withdrawing group such as a ketone or sulfone, should not be reactive enough for nucleophilic displacement by a phenol. Indeed, the reaction of this difluoride with potassium 3,5-di-*tert*-butylphenoxide in NMP at 180 °C did not produce any products after 24 h, and both starting materials remained unreacted. In conclusion, our results demonstrated a new route to the synthesis of a rigid, solvent-resistant, fused arene-based high-temperature polymer that could not be made by direct solution polycondensation. Future work in this area will focus on incorporating the 2,2′-dibenzoylbiphenyl unit into other known high-temperature polymer systems such as polyimides and poly(phenylenequinoxaline)s and subsequent conversion to the corresponding phenanthrene-containing polymers. In addition, potential application of this thiocarbonyl coupling chemistry to the development of low-temperature curing resin systems will also be investigated.

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References and Notes

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(3) (a) Mohanty, D. K.; Lowery, R. C.; Lyle, G. D.; McGrath, J. E. *Int. SAMPE Symp. Exhib.* **1987**, *32*, 408. (b) Lyon, K. R.; Geibel, J. F.; McGrath, J. E. *Proc. Am. Chem. Soc. Div. Polym. Mater. Sci. Eng.* **1991**, 249.
(4) (a) Steliou, K.; Salama, P.; Brodeur, Y. *J. Am. Chem. Soc.* **1987**, *109*, 926. (b) Steliou, K.; Salama, P.; Yu, X. *J. Am. Chem. Soc.* **1992**, *114*, 1456.
(5) (a) Backmann, W. E.; Chu, E. J.-H. *J. Am. Chem. Soc.* **1935**, *57*, 1095. (b) A mixture of nickel(II) bromide (492 mg, 2.25 mmol), zinc dust (4.5 g, 69 mmol), and triphenylphosphine (4.5 g, 17 mmol) in 30 mL of dry dimethylacetamide 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 1 h. The mixture was cooled to room temperature and filtered. The filtrate was poured into 200 mL of water. The resulting solids were collected by filtration and recrystallized from cyclohexane. The cyclohexane mother liquor contained mainly triphenylphosphine which was reused. After further purification by recrystallization from acetone–methanol (1:1, v/v), monomer **1** was obtained as colorless crystals: 14.6 g (82% overall yield for two consecutive reactions in same scale); mp 148.5–149 °C (lit.[5a] mp 136.5–137.5 °C).
(6) A solution of boron trichloride in methylene chloride (1.0 M, 2 mL, 2.0 mmol) was introduced to a mixture of monomer **1** (398 mg, 1.0 mmol) and tricyclohexyltin sulfide (1.682 g, 2.2 mmol) in 35 mL of dry toluene at room temperature under nitrogen. After stirring for 10 min at room temperature, the mixture was heated at reflux for 2.5 h. TLC analysis shows complete consumption of the starting material and the

formation of cyclized product. Colors of the reaction solution changed from brown to blue to light brown. The mixture was then evaporated at reduced pressure, and 10 mL of methanol was added to the residue. The resulting mixture was filtered through a pad of silica gel and washed with methanol, acetone, and chloroform, respectively. The combined washings were concentrated, and the residue was purified by flash chromatography (hexanes and then 5% ethyl acetate in hexanes) to give pale yellow powders. After recrystallization from ethyl acetate–cyclohexane (1:1, v/v), the desired product was obtained as white crystals (needle): 297 mg (82%); 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.

(7) Lawesson's reagent: 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide. (a) Pederson, B. S.; Scheibye, S.; Nilsson, N. H.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223. (b) Pederson, B. S.; Scheibye, S.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 229 and 299.

(8) ^{1}H NMR studies were done on a 400-MHz FT-NMR spectrometer using deuterated TCE solvent, and a long delay time (15 s) was set to ensure a correct integration. The same values were obtained from NMR data when the tricyclohexyltin sulfide–boron trichloride reagent was used.