Thiophene-Containing Poly(arylene ether ketone)s. 1. Polymerization of Bis(*p*-fluorobenzoyl)aryl Systems with 4,4′-Isopropylidenediphenol

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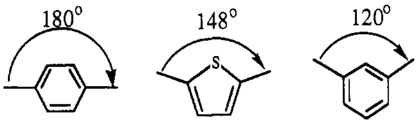
ABSTRACT: A series of poly(arylene ether ketone)s based on bis(*p*-fluorobenzoyl)aryl monomers and 4,4′-isopropylidenediphenol have been synthesized where the central aromatic unit of the activated bishalide monomer was varied to include, 1,4-phenylene, 2,5-thiophene, and 1,3-phenylene structures. All of the polymers were of high molecular weight, including the system using 2,5-bis(*p*-fluorobenzoyl)thiophene, which indicates the inherent stability of the thiophene-containing monomer to the usual polymerization reaction conditions. The effect of varying the exocyclic bond angle of the central aromatic unit on physical properties was investigated. The thiophene-containing poly(arylene ether ketone) showed a glass transition temperature between that of the 1,4- and 1,3-phenylene-based polymers. In addition, the high molecular weight thiophene-containing poly(arylene ether ketone) had comparable thermal stability relative to 1,4- and the 1,3-phenylene-based analogues.

Introduction

Interest in molecular engineering of physical properties for high-performance polymers persists because small alterations of the molecular structure of a polymer can dramatically influence performance and processing properties, properties critical to a polymer's range of applications. Generally, alterations of high-performance polymers focus on changes in the substitution pattern of the aromatic cyclic units comprising the bulk of such polymers. Changes in chain stiffness or rigidity via modification of primary and secondary structures is particularly effective. Para-directed cyclic units (e.g., 1,4-phenylene and 4,4′-biphenyl) dominate the primary structures of high-performance polymers; rotation about the para axis has a fairly low energy barrier, which gives rise to prominent β-relaxations in the dynamic mechanical spectrum for many polymers of this class. Major changes in properties result from introducing deviations in chain linearity, i.e., by using "crankshaft" aromatic units (e.g., 2,6-naphthalene and 3,4′-biphenyl). Meta-directed bonding in phenylene units creates "kinks" or "bends" in the polymer main chain. Such kinks disrupt the linear configuration and thereby reduce polymer crystallinity.

Some of these issues were recently addressed by Cai and Samulski[1] in a study of how modifications of the linearity of molecular structure influenced liquid crystal stability in low molar mass model compounds and in polyesters. They focused on the role of the "core angle" of the aromatic units—the valence angle between the exocyclic bonds—and extended the traditional aromatic units discussed above to include aromatic thiophene moieties. The general concept was to exploit the fact that the exocyclic bond angle of 2,5-thiophene is 148°, in between 180° and 120° associated with *p*- and *m*-phenylene units. To this end, a series of symmetric low molar mass compounds were investigated wherein different central units were incorporated into the core of potential liquid crystal molecules. They concluded that the 2,5-thiophene moiety, interjecting at a 148° core angle, is a viable mesogenic core even though its molecular geometry causes the pendant substituents to deviate from collinearity. These concepts were then extended to the synthesis of thermally tractable liquid crystalline polyesters[2] using 2,5-thiophene diacid chloride and substituted hydroquinones: the *p*-phenylene-based analogues decomposed before melting and the *m*-phenylene-based materials did not exhibit mesomorphism.



Extending this concept, Stompel and Samulski[3] replaced the *p*-phenylene unit (from terephthaloyl chloride) in poly(*p*-phenyleneterephthalamide) with a 2,5-thiophene unit and attained high molecular weight lyotropic liquid crystalline polyamides. More recently, liquid crystalline poly(benzoxazole)s containing 2,5-thiophene linkages were also synthesized.[4] In all of the systems investigated [poly(ester)s, poly(amide)s, and poly(benzoxazole)s], no significant decrease in the thermal stability of the thiophene-containing materials was observed.

Several poly(arylene ether)s, such as Udel poly(ether sulfone) (Amoco) and PEEK poly(ether ether ketone) (ICI), are commercially available. These materials are excellent high-performance engineering thermoplastics and are used in many applications as coatings, adhesives, structural composites, etc. PEEK is characterized by a high melting temperature (343 °C), high rate of crystallization, and high production costs due to the cost of the 4,4′-difluorobenzophenone. Numerous reports have stressed the interesting crystallization attenuations that occur when 1,3-phenylene moieties are substituted for 1,4-phenylene units[5-8] in poly(arylene ether ketone)s.

Realizing that the high-performance properties of the above-mentioned thiophene-based liquid crystalline polymers were being maintained with the added benefits of

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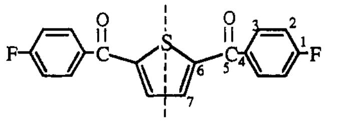
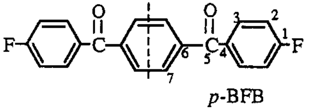
enhanced processibility, we decided to introduce thiophene units into poly(arylene ether ketone)s. The overall objective of modifying poly(arylene ether ketone)s through the introduction of bilateral asymmetry into the polymer backbone (i.e., to replace *p*-phenylene and *m*-phenylene units with 2,5-thiophene units) is twofold: (i) to investigate the compatibility of thiophene units to various polymerization routes to poly(arylene ether ketone)s and (ii) to study in greater detail the geometric constraints of the aromatic units on the thermal and processing properties of amorphous and semicrystalline materials. The dramatic differences between polymers based on 1,4-phenylene versus 1,3-phenylene, independent of polymer class, are well-documented. Often the former are difficult to process (thermally intractable and low solubility), and the latter exhibit poor mechanical properties (negligible crystallinity except in a few systems). By searching intermediate polymer geometries via the thiophene moiety, we anticipate larger thermal processing windows without losing the desirable (liquid) crystalline properties associated with the 1,4-phenylene-based polymeric materials. In addition, the bilateral asymmetry of the heterocycle will certainly influence melting points, rates of crystallization, glass transition temperatures, solubility, miscibility with other polymers, adhesion, etc., relative to conventional phenylene-based materials. This paper represents our first report of systematic investigations of the synthesis and characterization of thiophene-containing poly(arylene ether ketone)s.

Experimental Section

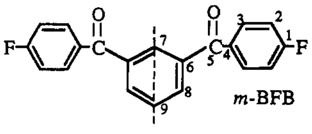
Monomer Synthesis. 2,5-Bis(4-fluorobenzoyl)thiophene (BFTh). In a three-neck, 100-mL flask fitted with a condenser, magnetic stirrer, and nitrogen inlet, 3.46 g (0.026 mol) of anhydrous powdered aluminum chloride (Aldrich) was added to a stirred solution of 2.09 g (0.01 mol) of 2,5-thiophenedicarbonyl chloride[9] in 30 mL (0.32 mol) of fluorobenzene (Aldrich). The mixture was refluxed for 6 h at 80 °C. The excess fluorobenzene was distilled off, and the product was washed with 5% NaOH, 5% HCl, and water. The monomer was filtered and recrystallized three times from acetone. The yield was 2.07 g (63%) (mp 186 °C). ^{1}H NMR (CDCl$_3$, ppm): 7.16–7.29 (m, 4 H), 7.67 (s, 2 H), 7.91–8.02 (m, 4 H). ^{13}C NMR (ppm): 115.8 and 116.0 (F coupling, C$_2$), 131.9 (C$_3$), 133.4 (C$_4$), 133.5 (C$_7$), 148.0 (C$_6$), 164.3 and 167.1 (F coupling, C$_1$), 186.4 (C$_5$).



1,4-Bis(4-fluorobenzoyl)benzene (*p*-BFB) and 1,3-Bis(4-fluorobenzoyl)benzene (*m*-BFB). Both of the phenylene-based monomers (*p*-BFB and *m*-BFP) were synthesized in a manner similar to that described above for BFTh. The yields for polymer-grade *p*-BFB and *m*-BFB were 2.35 (73%) and 1.90 g (59%), and their melting points were 233 and 187 °C, respectively. ^{1}H NMR (ppm): *p*-BFB, 7.13–7.28 (m, 4 H), 7.83–7.94 (m, 4 H), 7.87 (s, 4 H); *m*-BFB, 7.36–7.43 (m, 4 H), 7.72–7.78 (t, 1 H), 7.84–7.90 (m, 4 H), 7.96 (s, 1 H), 7.99–8.03 (d, 2 H). ^{13}C NMR (ppm): *p*-BFB, 115.4 and 115.7 (F coupling, C$_2$), 129.2 (C$_2$), 132.4 (C$_3$), 132.6 (C$_4$), 140.3 (C$_6$), 163.4 and 167.5 (F coupling, C$_1$), 193.8 (C$_5$); *m*-BFB, 115.8 and 116.0 (F coupling, C$_2$), 129.3 (C$_9$), 130.6 (C$_3$), 132.9 (C$_7$), 133.4 (C$_4$), 137.1 (C$_6$), 163.7 and 166.2 (F coupling, C$_1$) 193.7 (C$_5$).



p-BFB



m-BFB

Polymer Synthesis. The poly(arylene ether ketone)s were synthesized in a three-neck, 200-mL flask equipped with a mechanical stirrer, nitrogen inlet, Dean–Stark trap, and condenser. To synthesize the thiophene-based poly(arylene ether ketone), the reaction flask was charged with 1.97 g (0.006 mol) of BFTh, 1.37 g (0.006 mol) of 4,4′-isopropylidenediphenol (Aldrich) (recrystallized from acetone), 1.74 g (0.0126 mol) of dry potassium carbonate, 16 mL of distilled 1-methyl-2-pyrrolidinone (NMP) (Aldrich), and 12 mL of distilled toluene (Aldrich). The reaction mixture was stirred at 140 °C for 3.5 h. Upon dehydration, the toluene was removed and the reaction mixture was stirred for another 3 h at 140 °C. Near-completion of the reaction was qualitatively estimated by a significant viscosity increase. The polymer was precipitated into water, washed with acetone, and dried in vacuo at 120 °C for 24 h. The yield was essentially quantitative. The *p*-phenylene and *m*-phenylene poly(arylene ether ketone) analogues based on *p*-BFB and *m*-BFB were synthesized in a similar manner; however, the polymerizations with *p*-BFB and *m*-BFB necessitated higher temperatures (170 °C) for an additional 8 h to achieve high molecular weights.

Molecular Weight Control. Larger batches of the above-described polymers were also synthesized. These materials were made to have controlled molar masses of approximately 20 000 g/mol. This was accomplished by adding a calculated amount of *tert*-butylphenol (Aldrich) according to the Carothers equation.

Polymer Characterization. Intrinsic viscosity measurements were performed in NMP at 25 °C using a Cannon Ubbelohde dilution viscometer. ^{13}C and ^{1}H NMR studies were done in CDCl$_3$ on a Bruker AC-200 at 50.323 and 200.133 MHz, respectively. Glass transition temperatures were determined using a Seiko DSC 220C. The values reported were obtained from the second heat using a 10 °C/min heating rate and were determined at the midpoint in the transition. Thermogravimetric analyses were performed on a Seiko 320 TG/DTA at a scan rate of 20 °C/min up to 1200 °C in nitrogen and in air.

Results and Discussion

The synthesis of high molecular weight poly(arylene ether ketone) is usually accomplished via either of two methods: (i) Friedel–Crafts acylation routes and (ii) nucleophilic displacement of activated aromatic dihalides.[10,11] The nucleophilic displacement method was employed in this study; polymerizations were carried out using a slight excess of a weak base (potassium carbonate) in a dipolar, aprotic solvent (NMP) at 20–25% solids with an azeotroping reagent (toluene).[12] The polymerization is believed to go through a bimolecular S$_N$Ar mechanism involving the formation of an intermediate: nucleophilic attack by the phenoxide on the activated carbon attached to the halide as the rate-determining step, followed by expulsion of the halide to form the aryl ether linkage. Recent reports[13,14] have suggested that under certain conditions, a competing pathway can complicate the process: an S$_{RN}$1 mechanism with a key step that involves a single electron transfer from the phenoxide to the activated aryl halide. This undesirable mechanism can lead to premature termination steps involving hydrogen atom abstraction yielding an unreactive end group. However, because of the use of activated bisfluoride monomers and the use of 4,4′-isopropylidenediphenol, the S$_{RN}$1 mechanism is believed not to be operative to any deleterious extent.

To investigate in greater detail the role of the aromatic core angle on thermal properties, a series of activated bishalide monomers of the general structure shown in Figure 1 were synthesized. The monomers were easily synthesized by Friedel–Crafts acylation of fluorobenzene with terephthaloyl chloride, 2,5-thiophenedicarbonyl chloride, and isophthaloyl chloride to yield *p*-BFB, 2,5-BFTh, and *m*-BFB, respectively. Both 2,5-BFTh and *m*-BFB had very similar melting points, and *p*-BFB had a melting point ca. 45 °C higher. All of the monomers were synthesized in good yields (≈60%, purified).

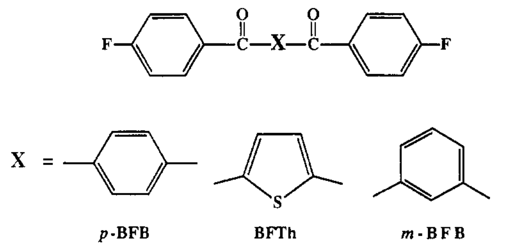


Figure 1. Difluoro monomers derived from terephthaloyl chloride, isophthaloyl chloride, and 2,5-thiophenedicarbonyl chloride.

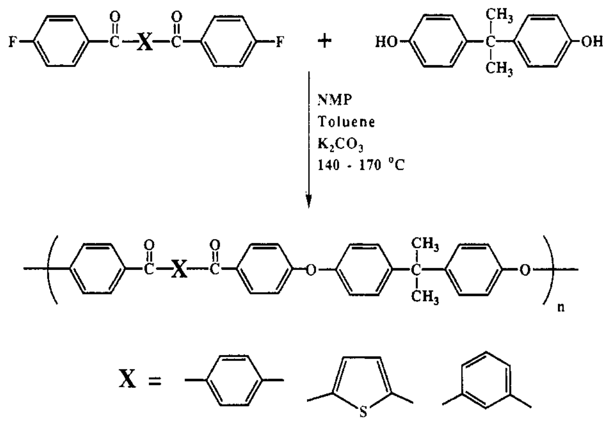


Figure 2. Syntheses of poly(arylene ether ketone)s.

Table I
Poly(arylene ether ketone)s from Bisphenol A and BFTh, *p*-BFB, and *m*-BFB

monomer	intrinsic visc, dL/g	T_g, °C	T (°C) at 5% wt loss (TGA) in nitrogen	in air
m-BFB	0.79	152	493	472
BFTh	1.23	158	496	480
p-BFB	0.92	166	521	509

Poly(arylene ether ketone)s were synthesized from 4,4′-isopropylidenediphenol with each of the activated bisfluoride monomers as shown in Figure 2. The thiophene-based monomer appears to be more reactive than the phenylene-based monomers achieving high molecular weight (as evidenced by a sharp increase in the viscosity of the reaction solution) at lower reaction temperatures and shorter reaction times. All of the polymers were of high molecular weight as indicated by the intrinsic viscosities listed in Table I. The ^{1}H and ^{13}C NMR spectra for the thiophene-containing polymer are shown in Figures 3 and 4, confirming the expected structure. The glass transition temperatures (T_g) of the poly(arylene ether ketone)s series were determined by DSC as shown in Figure 5 for the thiophene-based polymer and are summarized in Table I. An increase in T_g was observed as the core angle of the diketone unit increased from 120° to 180°. The trend in T_g can be related to the aromatic core angle using free-volume arguments.

There is widespread misconception that thiophene-containing polymers are not thermally stable. However, reports[15] on the poor thermal stability of thiophene-containing polymers were derived from studies of very low molar mass materials. In fact, the report on the synthesis of thiophene-based poly(ketone)s, formed via Friedel–Crafts polymerization routes, resulted in materials with 5% weight losses in nitrogen starting at 375 °C. These "polymers" also had inherent viscosities on the order of 0.11–0.27 dL/g and were formed from step-growth reactions having yields ranging from 42% to 95% (with reaction yields on this order of magnitude, the highest degrees of polymerization one could hope to achieve range from 2 to 20). It is therefore not unreasonable to suggest that the observed weight losses in TGA experiments performed on previously reported thiophene-based polymers (in nitrogen) are the result of low molar mass oligomers laden with thermally unstable end groups. Thermogravimetric analyses of our polymers were carried out in nitrogen (Figure 6) and in air (Figure 7). The decomposition temperatures are summarized in Table I. These observations indicate that the thermal and thermooxidative stabilities of the thiophene-containing poly(arylene ether ketone)s are comparable to that for the *m*-phenylene and *p*-phenylene analogues.

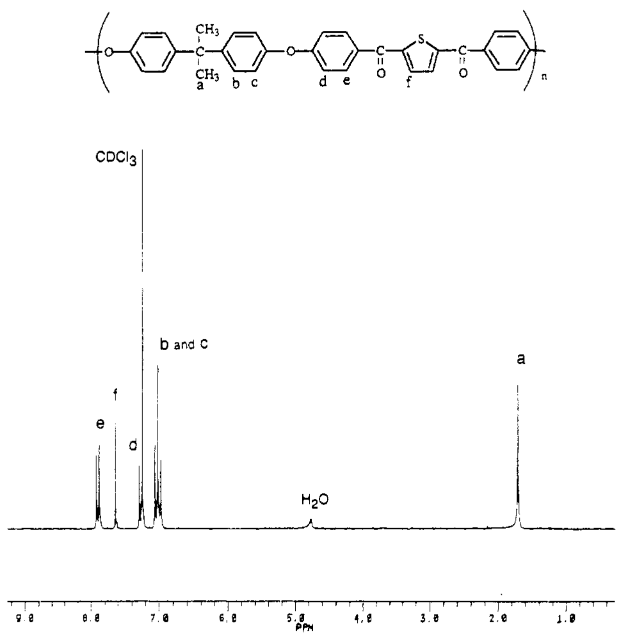


Figure 3. ^{1}H NMR (200.133 MHz) of high molecular weight 2,5-thiophene-based poly(arylene ether ketone) in CDCl$_3$.

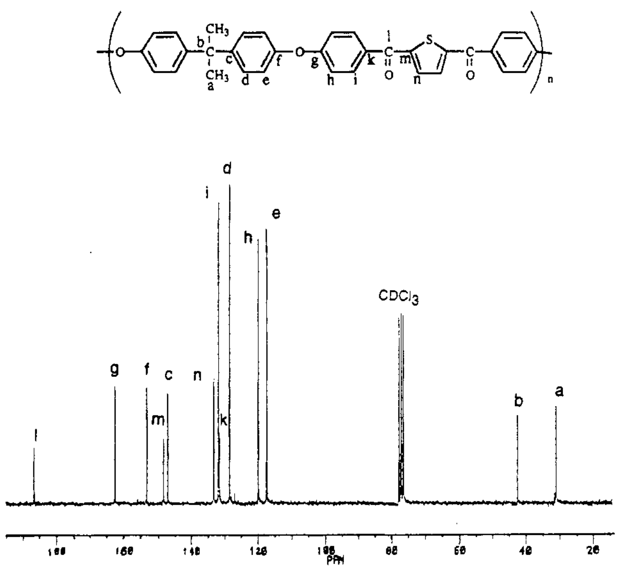


Figure 4. ^{13}C NMR (50.323 MHz) of high molecular weight 2,5-thiophene-based poly(arylene ether ketone) in CDCl$_3$.

The molecular weights of the polymers capped with *tert*-butylphenol were determined by end-group analysis using ^{1}H NMR (Figure 8). The ratio of the integral of the signal from the isopropylidene group in the repeating unit to the integral of the signal associated with the *tert*-butyl group from the end-capper was used to calculate the number-average molar masses of each polymer. The values for the

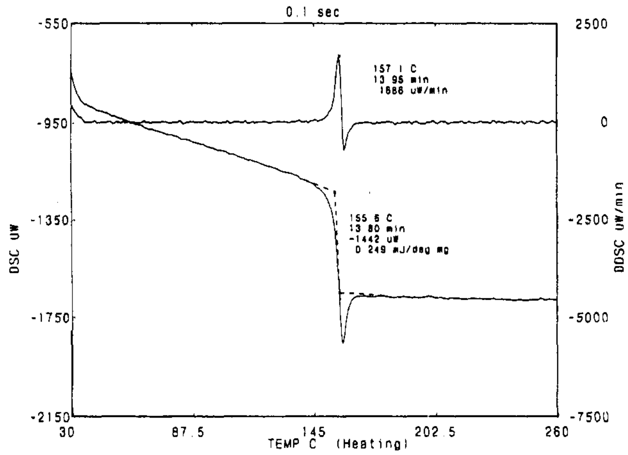


Figure 5. Differential scanning calorimetry (DSC) of 2,5-thiophene-based poly(arylene ether ketone).

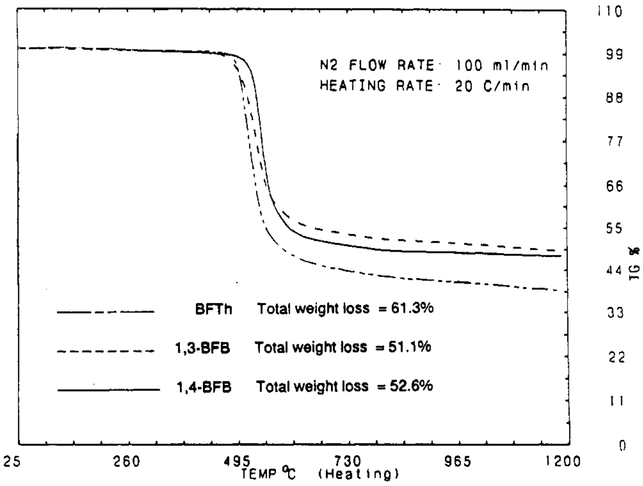


Figure 6. Thermogravimetric analyses (TGA) of poly(arylene ether ketone)s derived from BFTh, *p*-BFB, and *m*-BFB (in nitrogen).

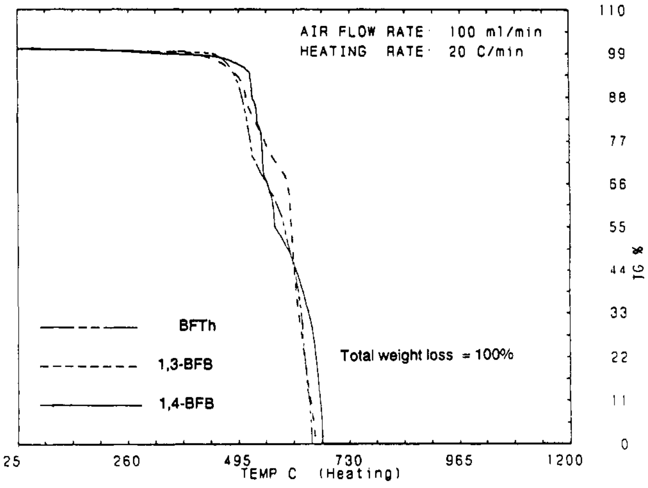


Figure 7. Thermogravimetric analyses (TGA) of poly(arylene ether ketone)s derived from BFTh, *p*-BFB, and *m*-BFB (in air).

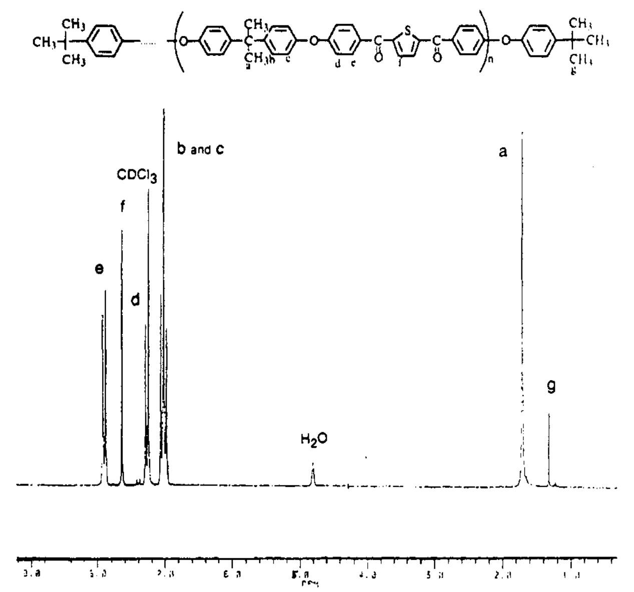


Figure 8. ^{1}H NMR (200.133 MHz) of controlled molecular weight 2,5-thiophene-based poly(arylene ether ketone) end-capped with *tert*-butylphenol.

Table II
Poly(arylene ether ketone)s with Controlled Molar Masses

monomer	intrinsic visc, dL/g	molecular wt
m-BFB	0.37	20 000
BFTh	0.38	24 000
p-BFB	0.49	23 000

number-average molar mass and intrinsic viscosity for each polymer are listed in Table II. Clearly, good molecular weight and end-group control was obtained using the monofunctional reagent *tert*-butylphenol. The intrinsic viscosity of the *p*-phenylene-based polymer (0.49 dL/g) is much higher than the values obtained for the *m*-phenylene and 2,5-thiophene-based polymers (0.37 and 0.38 dL/g, respectively). This result was expected despite the fact that the molar masses of the *p*- and *m*-phenylene-based polymers are approximately the same, reflecting the higher persistence length of the *p*-phenylene-based polymer.

Conclusions

A series of high molecular weight and end-capped poly(arylene ether ketone)s based on bis(*p*-fluorobenzoyl)aryl monomers and 4,4′-isopropylidenediphenol have been synthesized where the central aromatic unit of the activated bishalide monomer was varied to include 1,4-phenylene, 2,5-thiophene, and 1,3-phenylene structures. The system using 2,5-bis(*p*-fluorobenzoyl)thiophene resulted in high polymer at lower reaction temperatures and shorter reaction times than the phenylene-based systems. These results demonstrate the ability of the aromatic heterocycles to withstand the reaction conditions necessary for synthesizing high molecular weight poly(arylene ether ketone)s via the nucleophilic substitution route.

The influence of the variation of the exocyclic bond angle of the central aromatic unit on physical properties was investigated. The thiophene-containing poly(arylene ether ketone) showed a glass transition temperature between that of the 1,4- and 1,3-phenylene-based polymers. In addition, the high molecular weight thiophene-containing poly(arylene ether ketone) had thermal stability comparable to the 1,4- and the 1,3-phenylene-based analogues.

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