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Processible Poly(arylene ether ketone)s That Can Be Cross-Linked to High-Performance Networks

Kenneth A. Walker, Larry J. Markoski, and Jeffrey S. Moore*

The Willard H. Dow Laboratories, Department of Chemistry and the Macromolecular Science and Engineering Center, The University of Michigan, Ann Arbor, Michigan 48109-1055

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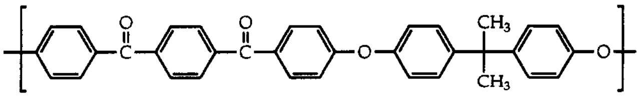
ABSTRACT: High molecular weight copolymers containing 2,5-bis(4-fluorobenzoyl)benzocyclobutene (BFBCB), 1,4-bis(4-fluorobenzoyl)benzene (BFB), and 4,4-isopropylidenediphenol have been synthesized by solution polycondensation. Soluble, amorphous polymers were obtained and no evidence of cross-linking occurred during the polymerization reaction, provided that the temperature was maintained below 150 °C. The polymers were characterized by gel permeation chromatography and by ^{1}H and ^{13}C NMR. The copolymers can be cross-linked well above their glass transition temperature by brief treatment in nitrogen at 400 °C. The cross-linking reaction has been monitored by differential scanning calorimetry, which shows that the heat of the reaction is proportional to the BCB content. The resulting networks are insoluble in all solvents including concentrated sulfuric acid. Thermogravimetric analysis shows that no significant mass loss accompanies the cross-linking reaction.

Introduction

Poly(arylene ether ketone)s and the related poly(arylene ether sulfone)s generally have low flammability, good resistance to strong chemicals, and stability up to moderately high temperatures and can be fabricated using conventional polymer processing methods.[1] Commercially available examples are Udel [poly(ether sulfone) (Amoco)] and PEEK [poly(ether ether ketone) (ICI)]. These materials are high-performance engineering thermoplastics and are used in applications such as coatings, adhesives, and structural composites. These compounds can exist as either semicrystalline or totally amorphous solids, each with distinct properties.

Semicrystalline poly(arylene ether ketone)s have high chemical resistivity and excellent thermal stability, with melting points ranging from 180 to 400 °C. At ambient temperature, these materials are typically only soluble in concentrated sulfuric acid and similar strong acid solvents. Although the melts are generally stable, the high melt transitions make semicrystalline poly(arylene ether ketone)s difficult to process. In contrast, the amorphous analogs are easier to process due to their lower glass transitions and better solubility. Polymers that contain nonlinear bisphenol monomers or ones with bulky side groups exhibit transitions from 150 to 200 °C.[2] These amorphous materials are stable in the melt and are also soluble in many chlorinated organic solvents. Although easier to process, they have somewhat limited applications due to diminished high-performance characteristics. An example of an amorphous poly(arylene ether ketone) is shown (1), which is prepared from the bisfluoro monomer 2 and Bisphenol A. Polymer 1 is an amorphous engineering resin (T_g = 160 °C) with mechanical properties similar to poly(ether sulfone) but with an extraordinarily high elongation at break (150%). In addition, the polymer has a high transparency, high refractive index ($n = 1.664$), low density ($d = 1.2\ \mathrm{g{\cdot}cm^{-3}}$), and low water adsorption, making this material a candidate for optical applications.[3]



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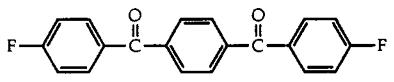

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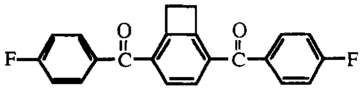
Several attempts have been made to combine the processing advantages found in the amorphous poly(arylene ether ketone)s and the high-performance properties of their semicrystalline counterparts. One has been to vary the proportion of ether and ketone groups[3] which increases the transition temperatures of both the amorphous and semicrystalline phases. Another approach, recently described by DeSimone et al.,[4] involves varying the exocyclic bond angle of the central aromatic unit. Their thiophene-containing poly(arylene ether ketone) showed a glass transition temperature between that of the 1,4- and 1,3-phenylene-based polymers.

Cross-linking of amorphous poly(arylene ether ketone)s has also been used to extend thermal and chemical resistivity.[5] One cross-linking method involved the incorporation of reactive xanthene end groups, while another attempt utilized a xanthene additive to achieve solid-state curing. These approaches suffer from limited processability, uncontrolled cross-link density and heterogeneity, and thermal instability. We are interested in the development of amorphous copolymers based on 1, that can be thermally cross-linked to materials that have properties similar to semicrystalline poly(arylene ether ketone)s. These polymers should still possess the advantages of easy processing characteristic of the amorphous poly(arylene ether ketone)s. For this purpose, we synthesized the thermally reactive monomer 3, designed to lie dormant throughout synthesis and processing but then be triggered to a reactive state at some latter point.



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This monomer was designed with several criteria in mind. First, the monomer's reactivity was chosen such that it would not interfere with synthesis and processing methods typically employed for poly(arylene ether ketone)s. This required a cross-linkable group that would be stable to alkaline conditions up to 200 °C and melts

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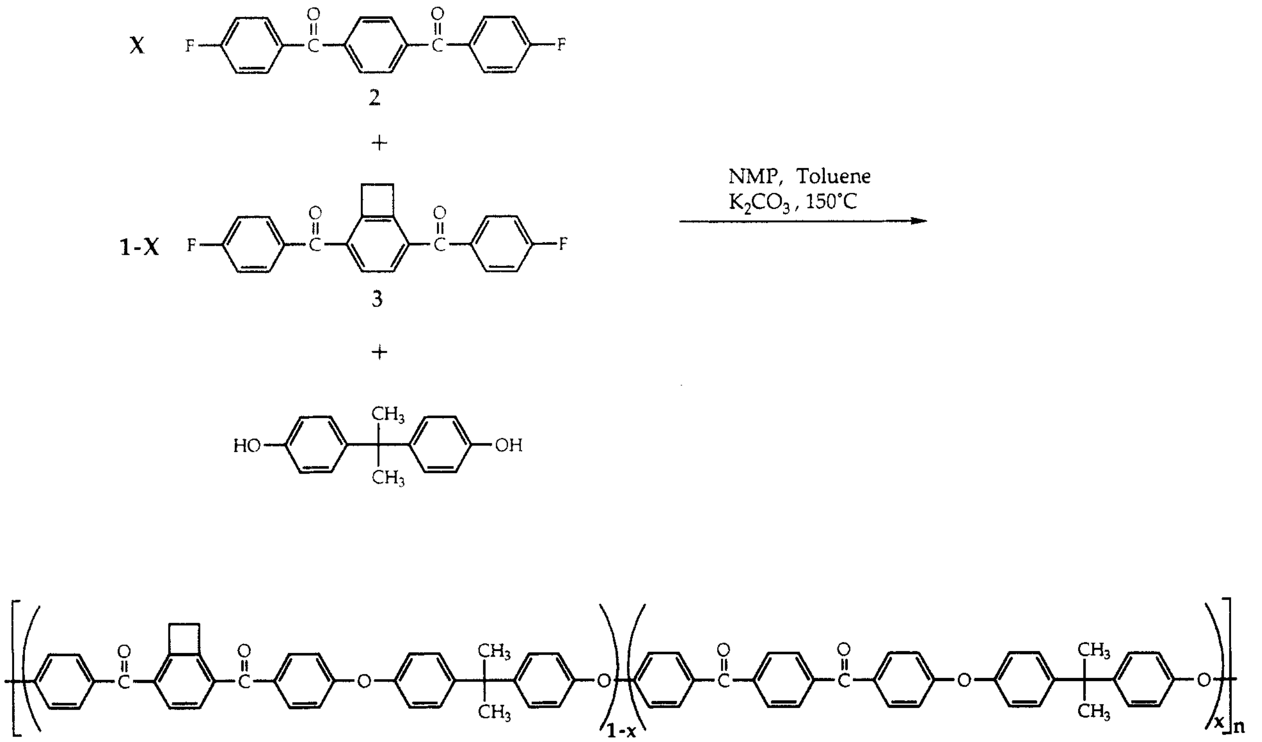
Scheme I. Synthesis of Poly(arylene ether ketone) Copolymers

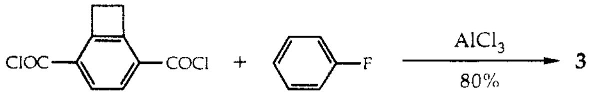


that were stable for short times to temperatures of ca. 250 °C. Second, it was desired to use a comonomer which could be incorporated into the polymer's backbone, so as to exploit the advantages of structosets.[6] Third, cross-linking should occur without evolution of volatile byproducts and should involve a highly reactive intermediate in order to maximize conversion. For this reason, monomer 3 contains the benzocyclobutene (BCB) moiety, which has been shown to be a thermally cross-linkable group.[7] At elevated temperatures, the cyclobutene ring opens to generate the reactive *o*-quinodimethane intermediate, which undergoes cycloaddition chemistry in the presence of reactive dienophiles.[8] In the absence of dienophiles, *o*-quinodimethanes will cyclodimerize,[9] ultimately leading to poly(*o*-xylenes) or dibenzocycloocta-1,5-dienes.[10] Thus, the anticipated cross-linking reactions should not result in a change in mass. Finally, the cross-linking reaction should occur well above the glass transition so that stable melts can be processed.

This paper describes the synthesis and characterization of a series of poly(aryl ether ketone)s copolymers containing bisfluoro monomers 2 and 3. The cross-linking reaction and resulting network were studied by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and solubility experiments. Our findings indicate that these materials have potential as processible amorphous poly(aryl ether ketone)s that can be cross-linked to form high-performance networks.

Results

Monomer 3 was synthesized by Friedel–Crafts acylation of fluorobenzene and benzocyclobutene-2,5-dicarboxylic acid chloride (see eq 1). The synthesis of the acid chloride



(1)

has previously been described.[11] This monomer was a crystalline white solid which was obtained as a single isomer as confirmed by ^{1}H and ^{13}C NMR and GC. The corresponding bisfluoro monomer 2 was synthesized in a similar manner from terephthaloyl chloride. As shown in Scheme I, bisfluoro monomers 2 and 3 were copolymerized with 4,4′-isopropylidenediphenol (Bisphenol A). Polymerization conditions were similar to those described by Rose and Staniland.[12] We found that polymerization could be carried out for periods of ca. 6 h at temperatures of 150 °C without detectable cross-linking. Fortunately, as shown above, these conditions were suitable for obtaining high molecular weight polymers. Higher polymerization temperatures or considerably longer reaction times eventually led to an insoluble and infusible solid, presumably as a result of thermal cross-linking of the cyclobutaarene ring.

Table I. Characterization Data of Poly(arylene ether ketone) Homopolymers and Copolymers

entry	x value	M_n[a]	M_w/M_n	ΔH of reaction (kcal·mol^{-1})
1	1.0	95 000	1.7	0
2	0.75	85 000	1.8	−7.0
3	0.5	125 000	2.0	−11.4
4	0.0	90 000	1.9	−23.9

[a] Relative to polystyrene standards.

The copolymers were isolated by precipitation into water, washed, and dried to remove polymerization solvent. The white to off-white solids displayed excellent solubility in chlorinated hydrocarbons, THF, and *N*-methylpyrrolidinone. Free-standing, transparent films of high quality could be cast from these solvents. Gel permeation chromatography (GPC) in THF relative to narrow polystyrene standards showed that high molecular weight products were obtained (see Table I). The GPC traces were monomodal with polydispersities of ca. 2.0. This distribution is consistent with that expected for condensation polymerizations and is further evidence that significant cross-linking did not occur during polymerization. ^{1}H and ^{13}C NMR spectra confirmed the presence of the cyclobutaarene ring in the homopolymer and copolymers. In the ^{1}H NMR spectrum, a sharp singlet was observed at $\delta = 3.3$ characteristic of the cyclobutene ring. The ratio of this resonance with respect to the

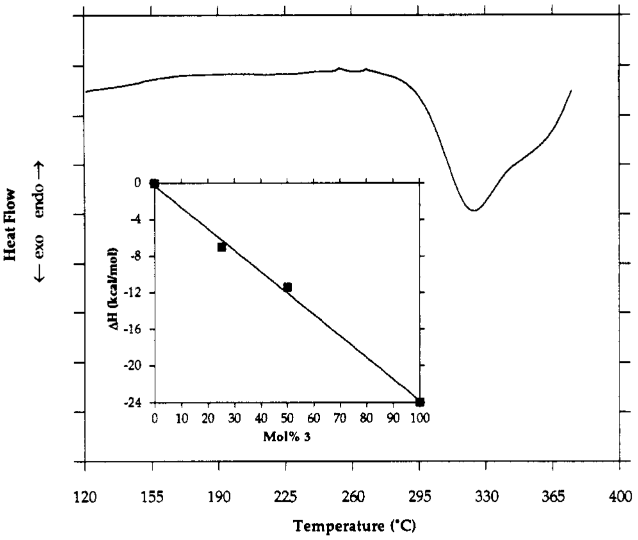


Figure 1. Representative DSC scan (polymer containing 100% 3) and a plot of the enthalpy of the reaction versus comonomer content. All DSC data were recorded using a heating rate of 10 °C/min.

isopropylidene methyl singlet proved to be a reliable check of copolymer composition. Finally, neither the ^{13}C nor the ^{1}H NMR spectra revealed any indication of chain microstructure in the copolymers, which we assume to be random.

The thermal properties of the polymers including the cross-linking reaction were studied by DSC, and a typical heating scan, that for the homopolymer of **3**, is given in Figure 1. For the copolymers and homopolymers, a glass transition (T_g) was observed between 150 and 160 °C. This transition temperature was nearly invariant with copolymer stoichiometry. The T_g was found to be reversible, provided that temperatures did not exceed 200 °C for an extended period of time. At higher temperatures, an irreversible exothermic transition was observed in the range of 300–370 °C, which presumably corresponds to the reaction of the *o*-quinodimethane intermediate. Interestingly, the temperature range for the reaction is significantly higher than that which has been reported[6a] for other BCB-containing compounds. The reaction temperature was also independent of copolymer stoichiometry. Table I shows that the enthalpy of this reaction is directly proportional to the molar content of BCB monomer **3** (see inset, Figure 1). Upon reheating, the cross-linked polymers exhibited no exotherm or observable glass transition temperature up to the decomposition point (ca. 450 °C). The resultant cross-linked networks are insoluble in all solvents at room temperature, including sulfuric acid, while similarly heat-treated polymers containing no BCB monomer remain soluble in chlorinated solvents. Thus, these experiments indicate that the cyclobutaarene ring in monomer **3** is responsible for the cross-linking reaction. TGA data showed that the cross-linking reaction occurs without significant mass loss (<5%) and could be accomplished well below the decomposition temperature (450 °C).

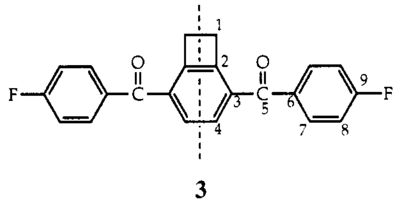
In summary, we have demonstrated the synthesis of amorphous poly(arylene ether ketone)s which incorporate a cross-linkable cyclobutaarene ring in the main chain. The as-prepared polymers can be processed from solution or the melt because of their low glass transition temperature. Thermal exposure to higher temperatures transforms these polymers, without loss of volatiles, into an insoluble, thermally stable network.

Experimental Section

Instrumentation. Gas chromatography analyses were performed on a Hewlett-Packard 5890 GC using a split/splitless injector and flame ionization detector. A fused silica capillary column (0.31 mm × 25 m) was employed (0.52-μm methylsilicone stationary phase). Gel permeation chromatography was performed using a Waters 6000A solvent delivery system and Model 440 absorbence detector at 254 nm. A series of three μ-Styragel columns of pore sizes 500, 10^3, and 10^4 Å were utilized and calibrated with narrow molecular weight polystyrene standards. GPC analyses were performed in THF at 23 °C. DSC and TGA analyses were performed using a Perkin-Elmer 7 apparatus at a rate of 20 °C/min. NMR spectra were recorded on a Bruker AM-300 spectrometer (300-MHz ^{1}H; 75-MHz ^{13}C) and referenced to the residual proton solvent resonance. ^{1}H NMR data are presented in a condensed format as follows: chemical shift (ppm), multiplicity, scalar coupling constant (Hz), integrated intensity. Multiplicities are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet), and broad signals are indicated by br. Carbon NMR shifts are given in ppm and referenced to the solvent ^{13}C signal.

Materials. 1-Methyl-2-pyrrolidinone (NMP) was vacuum distilled off calcium hydride. Toluene was vacuum transferred from sodium benzophone ketyl. 4,4′-Isopropylidenediphenol was recrystallized from acetone prior to use. 1,2-Dihydrocyclobutabenzene 3,6-diacid chloride (XTA) was prepared as previously described.[1] Other reagents were purchased from Aldrich Chemical.

Monomer Synthesis. 2,5-Bis(4-fluorobenzoyl)benzocyclobutene (BFBCB). A three-necked, 250-mL flask fitted with a condenser, magnetic stirrer, and nitrogen inlet is charged with a solution of benzocyclobutene-2,5-dicarboxylic acid chloride (10.0 g, 44 mmol) in fluorobenzene (60 mL). To this solution is added aluminum trichloride (8.65 g, 65 mmol) in one portion. The mixture is refluxed for 12 h, and the excess fluorobenzene is removed under vacuum. The product is washed with 5% sodium hydroxide (100 mL), 5% HCl (100 mL), and water (100 mL) to yield light yellow crystals. Two recrystallizations from acetone yields white crystals of 3,6-bis(4-fluorobenzoyl)-1,2-dihydrocyclobutabenzene (**3**, 12.3 g, yield 80%). ^{1}H NMR ($CDCl_3$): 3.19 (s, 4H), 7.17 (t, 4H), 7.66 (s, 2H), 7.83–7.94 (m, 4H). ^{13}C NMR: δ 30.9 (C_1), 115.8 and 116.0 ($^2J_{CF}$ = 15.0; C_8), 127.1 (C_4), 132.0 and 132.2 ($^3J_{CF}$ = 15.0; C_7), 134.1 (C_3), 135.0 (C_6), 147.3 (C_2), 164.2 and 167.8 ($^1J_{CF}$ = 270.0; C_9), 193.0 (C_5).



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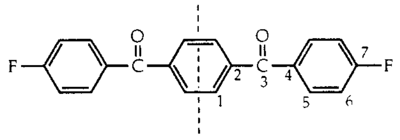
1,4-Bis(4-fluorobenzoyl)benzene (BFB). This monomer was synthesized in a manner similar to that for BFBCB. Two recrystallizations from acetone yields white crystals of 1,4-bis(4-fluorobenzoyl)benzene (BFB) (**2**, 12.1 g, yield 85%). ^{1}H NMR ($CDCl_3$): 7.14–7.24 (m, 4H), 7.85 (s, 4H), 7.86–7.93 (m, 4H). ^{13}C NMR: 115.6 and 115.9 ($^2J_{CF}$ = 22.5; C_6), 129.5 (C_1), 132.6 and 132.8 ($^3J_{CF}$ = 15.0; C_5), 132.8 (C_2), 140.8 (C_4), 164.0 and 167.5 ($^1J_{CF}$ = 262.5; C_7), 194.2 (C_3).



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Polymer Synthesis. To a flask equipped with a mechanical stirrer, a Dean–Stark trap, and a nitrogen inlet is added **3** (2.0901 g, 6 mmol), 4,4′-isopropylidenediphenol (1.37 g, 6 mmol), dry potassium carbonate (1.74 g, 12.6 mmol), dry *N*-methyl-1-

pyrrolidinone (NMP; 16 mL), and dry toluene (12 mL). The reaction mixture is heated to 140 °C under a flow of nitrogen with stirring for 3 h to dehydrate the reaction and remove the toluene. After removal of toluene, the reaction is stirred for another 3 h at 140 °C. The mixture is then precipitated into water, and the polymer is washed with acetone and dried at 60 °C under vacuum for 24 h to yield the poly(ether ether ketone ketone) (3.16 g, yield 98%).

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