

Synthesis and Thermotropic Liquid-Crystalline Behavior of Novel Main-Chain Poly(aryl ether ketones)

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ABSTRACT: Novel aromatic poly(ether ketones) containing bulky lateral groups were synthesized via nucleophilic substitution reactions of 4,4'-biphenol and (4-chloro-3-trifluoromethyl)phenylhydroquinone (CF-PH) with 1,4-bis(*p*-fluorobenzoyl)benzene. The copolymers were characterized by differential scanning calorimetry (DSC), wide-angle X-ray diffraction, and polarized light microscopy observation. Thermotropic liquid-crystalline behavior was observed in the copolymers containing 40, 50, 60, and 70 mol % CF-PH. The crystalline–liquid-crystalline transition [melting temperature (T_m)] and the liquid-crystalline–isotropic

phase transition appeared in the DSC thermograms, whereas the biphenol-based homopolymer had only a melting transition. The novel poly(aryl ether ketones) had glass-transition temperatures that ranged from 143 to 151°C and lower T_m 's that ranged from 279 to 291°C, due to the copolymerization. The polymers showed high thermal stability, and some exhibited a large range in mesophase stability. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1347–1350, 2003

Key words: liquid-crystalline polymers (LCP); synthesis

INTRODUCTION

Among the high-performance polymers currently being examined for use in aerospace and electronics applications are poly(aryl ether ketones) (PAEKs). A high strength, good electrical properties, an excellent thermal stability, and chemical resistance make this class of polymers excellent candidates for advanced materials.^{1,2} However, the high melting temperatures (T_m 's) and high melt viscosities of PAEKs are the primary shortcomings associated with processing these materials.³ To obtain different properties of PAEKs for various applications, structural modifications, such as the introduction of side groups or biphenyl units onto the main chains, have been attempted.^{4,5}

The unique physical and chemical properties of liquid-crystalline polymers (LCPs), such as polyesters and polyamides, allow them to form liquid crystalline (LC) structures at manageable temperatures and be melt processed in the LC state to form high-strength fibers or self-reinforced molded plastics.⁶ Thermotropic liquid-crystalline polymers (TLCPs) are known to have melt viscosities significantly lower than structurally similar isotropic polymers.⁷ Recently, Bennett and Farris⁸ reported the synthesis and characterization of the first thermotropic LC PAEKs. These mate-

rials have potential applications as engineering thermoplastics or fibers. In addition, the materials may be useful as processing aids or reinforcing agents in blending with isotropic PAEKs.

In this study, a series of thermotropic LC PAEK copolymers based on LC biphenyl mesogen and crystal-disrupting (4-chloro-3-trifluoromethyl)phenylhydroquinone (CF-PH) with 1,4-bis(*p*-fluorobenzoyl)benzene (BF) were synthesized via aromatic nucleophilic substitution reactions and were characterized by several experimental techniques.

EXPERIMENTAL

Materials

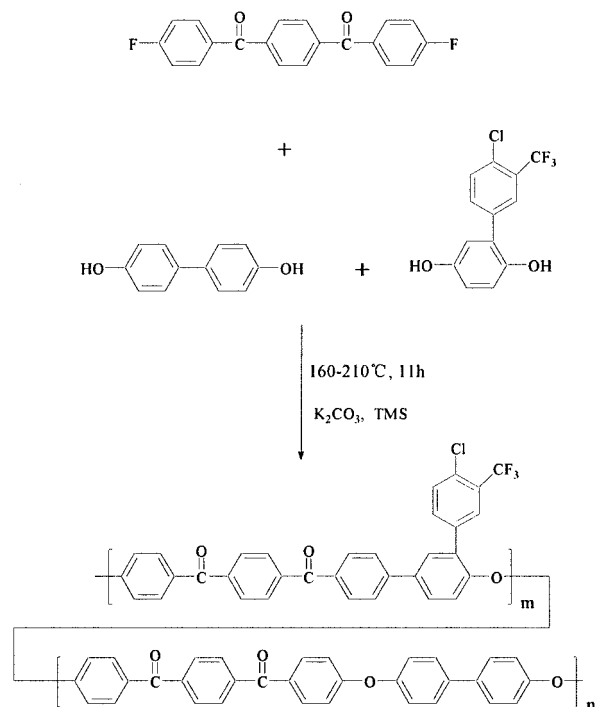
4,4'-Biphenol (BP) was obtained from Honshu Kagaku Ltd. (Japan) in the highest available purity. CF-PH and BF were prepared in our lab by the standard procedures. Anhydrous potassium carbonate (K_2CO_3) was ground and dried at 150°C in an oven before use. Toluene and tetramethylene sulfone (TMS) were obtained from Beijing Chemicals and distilled before use.

Instruments

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 821^e (Switzerland) at a rate of 10°C/min under a nitrogen atmosphere, and the maximum endotherm was taken as the transition temperature. The inherent viscosities (η_{iv} 's) of the polymers were measured in concentrated sulfuric acid

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Scheme 1 Synthesis route of novel PAEK copolymers.

at $25 \pm 0.1^\circ\text{C}$ with an Ubbelohde viscometer (Sigma Aldrich, St. Louis, MO). The decomposition temperatures were determined with a Netzsch Sta 449c (Germany) thermogravimetric analyzer at a heating rate of $20^\circ\text{C}/\text{min}$ in air. LC texture was examined via a Leica DMLP (Germany) optical microscope with a pair of crossed polarizers [polarized light microscopy (PLM)]. Wide-angle X-ray diffraction (WAXD) was carried out on a Japan Rigaku D/max- γA X-ray instrument (Cu $K\alpha$ radiation).

Synthesis

The novel PAEKs were synthesized by solution polycondensation reactions based on BP and hydroquinone containing a bulky pendant group with difluoro monomer. A schematic of the reaction is shown in Scheme 1. In a typical procedure, appropriate molar

ratios of the monomers, BP, CF-PH, and BF were placed in a three-necked flask equipped with a mechanical stirrer, a thermometer, a nitrogen inlet, and a Dean–Stark trap. Calculated potassium carbonate, toluene, and TMS amounts were added into the reactor under a nitrogen atmosphere, and the reaction mixture was heated to a reflux temperature of 160°C and reacted for 3 h to allow phenolate formation. Subsequently, the toluene was distilled over, and the reaction system temperature was gradually raised to 210°C for polymerization over a period of 8 h. The mixture was then coagulated into stirred methanol. The resulting polymer was separated by filtration. The crude product was purified by hot methanol and deionized water several times and was dried at 120°C for 24 h. Then, the white polymer powder was obtained.

RESULTS AND DISCUSSION

A typical aromatic nucleophilic substitution reaction route was used. The reaction included the deprotonation of dihydroxyl monomers and the subsequent aromatic nucleophilic displacement of a fluorine atom from a difluoro monomer. In general, diaryl sulfones are good solvents for crystalline poly(ether ketone) polymers, whereas some polar high-boiling-point solvents are selected as solvents for amorphous systems.⁹ In this system, TMS was selected as the solvent. Toluene was used as an azotroping agent, and its relative amount determined the bisphenolate forming temperature. Anhydrous potassium carbonate, a weak base, was used to deprotonate the hydroxyl groups and to form the bisphenolates. Because the existence of trifluoromethyl groups would enhance the reactivity of chlorine atoms and leads to the occurrence of branched reaction, the polymerization temperature was reduced accordingly. Because of their extended rigid chains and relatively higher crystallinity, PAEKs with no side groups have low solubilities in all known solvents except for concentrated sulfuric acid, whereas all of our copolymers were soluble in a mixed solvent of *p*-chlorophenol/1,1,2,2-tetrachloroethane. This was due to the introduction of the bulky pendant groups,

TABLE I
Properties of Novel PAEKs

Polymer	η_{iv} (dL/g)	T_g^a ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	T_i ($^\circ\text{C}$)	H_m (J/g)	H_i (J/g)	T_d^b ($^\circ\text{C}$)
100BP/100BF	0.41	173	426	—	26	—	523
60BP/40CF-PH/100BF	0.32	150	291	358	6.65	9.87	534
50BP/50CF-PH/100BF	0.36	150	279	371	6.60	9.83	501
40BP/60CF-PH/100BF	0.30	143	289	337	11.96	1.37	500
30BP/70CF-PH/100BF	0.35	143	281	318	11.48	0.72	507
100CF-PH/100BF	0.36	147	—	—	—	—	524

^a The T_g values were measured in the second heating cycle under nitrogen.

^b The temperature at which a 5% weight loss occurred in air.

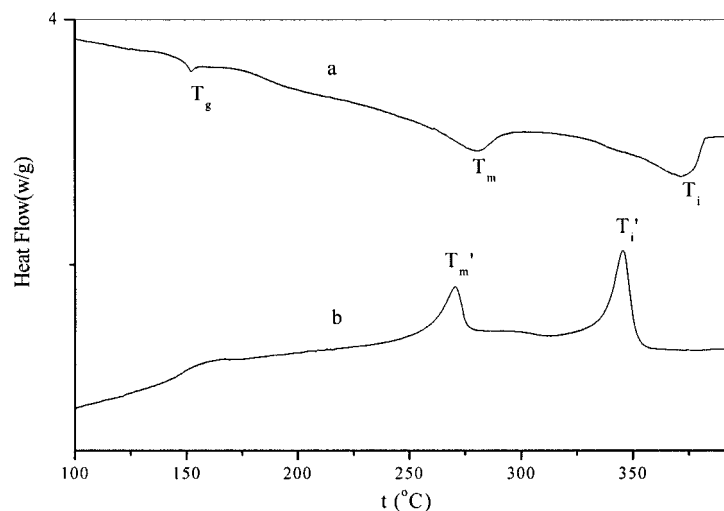


Figure 1 DSC curves of the 50BP/50CF-PH/100BF copolymer in (a) the heating cycle and (b) the cooling cycle.

which reduced the crystallinity and increased the free volume. The results of WAXD showed that they had lower crystallinities than the biphenyldiol-based homopoly(aryl ether ketone)s. However, they were not soluble in common organic solvents despite the good solubility of the homopolymer based on CF-PH.

The data for the thermal properties of the polymers with different compositions are listed in Table I. The DSC curves showed that the glass-transition temperatures (T_g 's) of the polymers ranged from 143 to 173°C. As expected, the melting temperatures (T_m) of the copolymers were lower than that of the isotropic PAEK because of the copolymerization effect of the

side-group monomer. Both the crystalline-to-LC transition (T_m) and the LC-to-isotropic transition [isotropization temperature (T_i)] were observed in the DSC curves of the copolymer, which were further confirmed by PLM. A typical DSC curve is shown in Figure 1. Both cooling and heating curves exhibited two peaks. The one at the low temperature (T_m) was interpreted as the crystal melting transition, and the one at the higher temperature was interpreted as the T_i . The reversibility of the phase transitions was evidenced by the presence of two corresponding peaks at T_i' (the isotropic-to-LC transition) and T_m' (the LC-to-crystalline transition) in the cooling cycle.

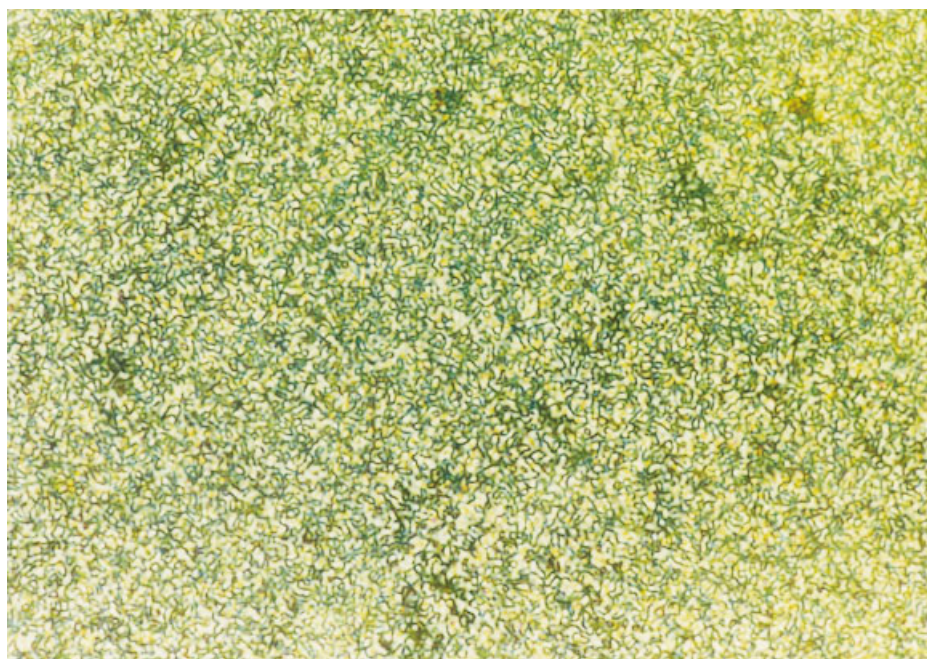


Figure 2 Thread-like texture of the 40BP/60CF-PH/100BF copolymer after cooling from 400 to 320°C, annealing for 1 h, and then quenching to room temperature (crossed polarizer, 400×).

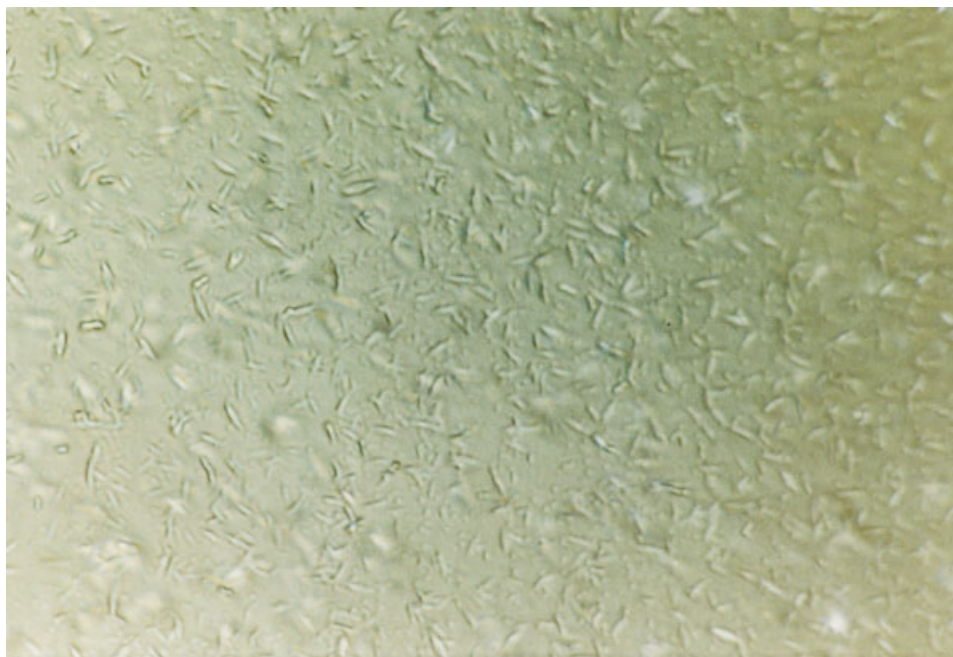


Figure 3 Batonnet texture of the 50BP/50CF-PH/100BF copolymer after cooling from 400 to 320°C, annealing for 1 h, and then quenching to room temperature (crossed polarizers, 400×).

In general, the mesophase stability was measured by the range between T_m and T_i .¹⁰ To our knowledge, the range of mesophase stability for some novel TLCPs was bigger than all of the other known series of PAEKs. The higher range of mesophase stability of the copolymers was consistent with the results reported in the literature.¹¹ This behavior suggested that the thermodynamic stability of the mesophase was effected by geometric repulsive factors more than by the polarizability of the mesogenic groups.

PLM was used to further characterize the thermotropic LC behavior. The samples were heated above the temperature of the isotropic state for a few minutes, subsequently cooled to the LC state, annealed at that temperature for 1 h, and then quickly quenched to room temperature. Each of the copolymers with two first-order phase transitions formed a typical texture in the LC state. Figure 2 shows a typical micrograph of the 40BP/60CF-PH/100BF copolymer. It exhibited a thread-like texture, which is often found in the nematic phase. For the 50BP/50CF-PH/100BF copolymer, a second type of texture, a batonnet texture, was observed (Fig. 3). This batonnet texture showed that the 50BP/50CF-PH/100BF copolymer had an ordered smectic phase.

The thermal stability of all of the polymers was determined in air by thermogravimetric analysis (TGA). The polymers showed a high stability, and the temperature at which a 5% weight loss occurred varied from 500 to 534°C. The good thermal stability of the novel polymers was very helpful for melt processing and LC formation.

CONCLUSIONS

LC properties were obtained for novel PAEK copolymers based on BP and a crystal-disrupting monomer. Melting transition (T_m) and isotropization (T_i) were both observed in the DSC curves. Typical textures of LCPs were observed by PLM. The novel TLCP exhibited a large mesophase stability and a good thermal stability. These materials should have wide application prospects.

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