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## Liquid Crystals

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## Preliminary communication

# The synthesis and thermotropic liquid crystalline behaviour of novel main chain poly(aryl ether ketone)s containing a lateral phenyl group

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Novel main chain poly(aryl ether ketone)s containing a lateral phenyl group were synthesized by nucleophilic substitution reactions of 4,4'-biphenol and phenylhydroquinone with either 4,4'-difluorobenzophenone or 1,4-bis(4-fluorobenzoyl)benzene and their thermotropic liquid crystalline properties were characterized by a variety of experimental techniques. Thermotropic liquid crystalline behaviour was observed in the copolymers containing 50 and 70 mol % biphenol. Melting ( $T_m$ ) and isotropization ( $T_i$ ) transitions both appeared on the DSC thermograms. A banded texture was formed after shearing the sample in the liquid crystalline nematic state. As expected, each of the copolymers had a relatively lower melting transition than the biphenol-based homopoly(aryl ether ketone)s because of the copolymerization effect of the crystal-disrupting monomer phenylhydroquinone.

Poly(aryl ether ketone)s (PAEKs) have been found very useful as advanced materials in applications because of their excellent thermal stabilities and good chemical resistance [1]. However, their highly crystalline properties and high melt viscosities often restrict the use of PAEKs for some applications. To obtain different properties of PAEKs for various applications, changing the molecular structure, for example by the introduction of substituents [2, 3] and a biphenyl unit [4, 5] into the main chain, has been attempted. The introduction of the substituents into the PAEK's backbone could suppress crystallization and improve its solubility, leading to novel applications of PAEK derivatives, but the biphenol-based PAEKs, although they contain the common biphenyl mesogen, have no liquid crystalline properties [4, 5]. Recently, Bennett and Farris [6] reported the synthesis and characterization of novel

thermotropic liquid crystalline poly(aryl ether ketone) copolymers based on the crystal-disrupting substituted hydroquinone and biphenyl mesogenic monomer. These materials have potential applications as engineering thermoplastics or fibres.

In previous papers [7, 8], we have reported a series of thermotropic liquid crystalline poly(aryl ether ketone)s containing a lateral chloro group, the results showing that this class of liquid crystalline polymers exhibits not only the nematic texture, but also a smectic texture. It should be noted that in main chain mesogen–non-mesogen liquid crystalline polymers, smectic phases have been observed only in a very few cases. In this work, a series of poly(aryl ether ketone) copolymers based on 4,4'-biphenol (BP) and phenylhydroquinone (PH) with 4,4'-difluorobenzophenone (DF) or 1,4-bis(4-fluorobenzoyl)benzene (BF) were synthesized by nucleophilic substitution. Thermotropic liquid crystalline behaviour was observed in the copolymers containing 50 and 70 mol % biphenol.

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The synthetic route to the copolymers is illustrated in figure 1. In a typical procedure, 5.35 g (16.61 mmol) of 1,4-bis(4-fluorobenzoyl)benzene, 1.53 g (8.23 mmol) of 4,4'-biphenol and 1.53 g (8.23 mmol) of phenylhydroquinone were placed in a three-necked flask equipped with a platinum thermometer, nitrogen inlet, magnetic stirrer and a Dean–Stark trap. Then 2.5 g (18.09 mmol) of potassium carbonate, 30 ml of xylene and 50 ml of TMSO<sub>2</sub> were added. The temperature was slowly raised to 160°C over a period of 3 h to allow phenolate formation and the water/xylene azeotrope to collect in the trap. Subsequently the reaction temperature was gradually raised to 200–220°C over a period of 8 h to achieve polymerization. The resulting polymer was separated by precipitation by adding the reaction mixture to methanol. The crude product was purified by washing with hot methanol and water.

Thermal analysis was carried out with a Perkin-Elmer DSC-7 instrument with scanning rates of 10°C min<sup>-1</sup> under a nitrogen atmosphere. A polarizing light microscope (PLM) from Opton R Pol was used for texture characterization of the copolymer samples. The wide angle X-ray diffraction (WAXD) was carried out using a D/max-γA X-ray instrument (Cu K<sub>α</sub> radiation). Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGA7 thermogravimetric analyser and a heating rate of 20°C min<sup>-1</sup> and a nitrogen atmosphere. The number-average molecular masses (*M*<sub>n</sub>s) were determined (Varian FT-80A) by <sup>19</sup>F NMR spectroscopy, using trifluoroacetic acid as a reference. The IR analyses (KBr) were obtained on a Nicolet 5DX FTIR spectrophotometer. The IR spectra were consistent with the expected structure, with peaks at 1650 (C=O stretching), 1605 and 1495 (aromatic C=C stretching), 1250, 1170 and 1100 (C–O stretching) cm<sup>-1</sup>.

As mentioned earlier, the biphenol-based homopoly(aryl ether ketone)s have an exceedingly low solubility in all known solvents other than sulphuric acid due to their extended rigid structures and relatively high crystallinity. Incorporating crystal-disrupting phenylhydroquinone moieties is effective in reducing the crystallinity of poly(aryl ether ketone)s. The WAXD results on the copolymers indicated that they had lower crystallinity than the biphenol-based homopoly(aryl ether ketone)s.

The all-substituted poly(aryl ether ketone)s are soluble in organic solvents such as chloroform and DMAc.

The data on the thermal properties and thermotropic behaviour of the new polymers are collected in the table. The *M*<sub>n</sub>s of the copolymers were in the range 4000–6000. All the copolymers had high glass transition temperatures (*T*<sub>g</sub>) in the range of 150–170°C as determined by DSC. The thermal stabilities (*T*<sub>d</sub>) were also checked by TGA in the range of 460–500°C. Both the crystal to liquid crystal transitions (*T*<sub>m</sub>) and the liquid crystal to isotropic transitions (*T*<sub>i</sub>) were observed on the DSC thermograms of the copolymers containing 50 and 70 mol % biphenol, and were further confirmed by PLM observation. As the content of crystal-disrupting co-monomer units increased, the crystalline to liquid crystal transition (*T*<sub>m</sub>) became broader and of smaller intensity, as indicated by the decrease in enthalpy of fusion ( $\Delta H_m$ ) in the table.

For further characterization of the thermotropic liquid crystalline behaviour, the copolymers were evaluated visually using PLM. The thin samples were heated at 400°C for a few minutes, subsequently cooled slowly to give the liquid crystalline state, annealed at this temperature for 0.5 h, and then quenched to room temperature. Each of the copolymers, other than 50BP/50PH/100DF, simply formed a grainy texture that had nematic features. It is interesting to note that Bennett and Farris [6] claimed that 50BP/50PH/100DF with a low molecular mass (*M*<sub>n</sub> = 1850) showed a nematic phase and two other phases (G and smectic B), while the higher molecular mass polymer (*M*<sub>n</sub> = 6600) only formed a nematic phase. In the present work, the *M*<sub>n</sub> is 4000 and the polymer exhibited both a nematic phase and a smectic phase. Figure 2 shows the optical micrographs of copolymer 50BP/50PH/100DF. It displayed the grainy texture with nematic features when the sample was held isothermally at 320°C for 0.5 h. However, after mechanical shearing and slight relaxation, a banded texture can be observed, which is perpendicular to the shear direction. The formation of banded textures after shearing is a nearly ubiquitous characteristic of nematic polymers [9, 10], figure 2(a). Microscopic analysis has shown that, in the banded texture, the director continuously oscillates spatially about the direction imposed by the previous flow

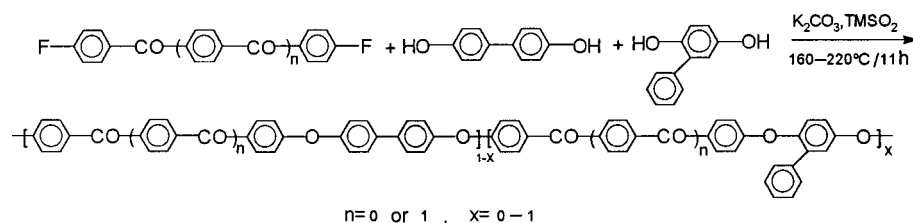


Figure 1. Synthetic route to the novel poly(aryl ether ketone)s.

Table. Thermal Properties of the novel poly(aryl ether ketone)s (see figure 1).

Sample	$n$	$x$	$M_n$	$T_m^a / ^\circ\text{C}$	$T_i^b / ^\circ\text{C}$	$\Delta H_m \text{ J g}^{-1}$	$\Delta H_i \text{ J g}^{-1}$	$T_d^c / ^\circ\text{C}$
70BP/30PH/100DF	0	0.3	4400	320	373	50	5	464
50BP/50PH/100DF <sup>d</sup>	0	0.5	4000	280	335 344	1	66	477
70BP/30PH/100BF	1	0.3	4500	320	374	72	14	495
50BP/50PH/100BF	1	0.5	6300	331	354	5	4	486

<sup>a</sup>  $T_m$ : Cr–mesophase.

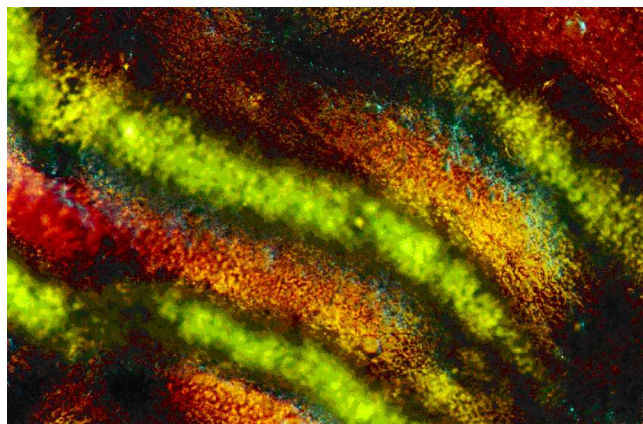
<sup>b</sup>  $T_i$ : nematic–isotropic.

<sup>c</sup>  $T_d$ : decomposition temperature.

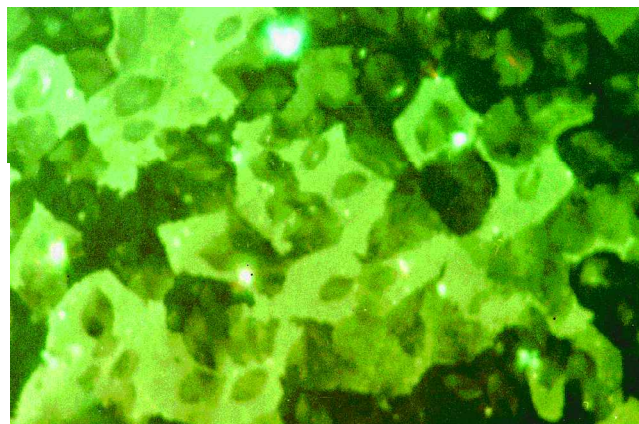
<sup>d</sup> Smectic at 300°C; nematic at 320°C.

[11]. Under a strong mechanical, periodic shear force field, micrometre-size monodomains may also form in the sample in the nematic liquid crystalline temperature range. Defects of observable size of the schlieren type can be found as shown in figure 2(b). This defect is a point singularity with four brushes, which rotate simultaneously with the polarizers. This point singularity has

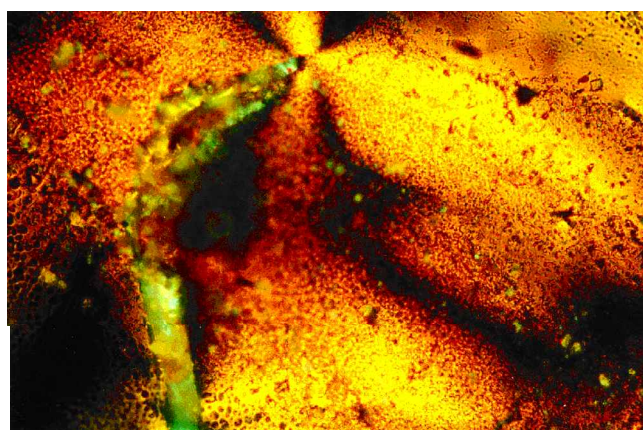
thus an  $S$  value of +1 according to Nehring and Saupe [12]. Although the molecular connectivity between the mesogenic moieties in liquid crystalline polymers may significantly affect the orientation process, a monodomain of a nematic polymer has also been achieved by Yoon *et al.* under strong shearing [13]. After annealing the sample at 300°C for 0.5 h and then air quenching, a



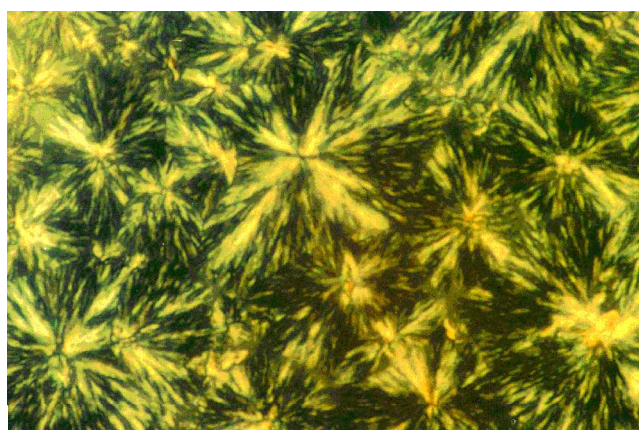
(a)



(c)



(b)



(d)

Figure 2. Optical micrographs of the copolymer 50BP/50PH/100DF after cooling from 400°C to the liquid crystal temperature, annealing for 0.5 h and then quenching to room temperature: (a) banded texture of sample sheared in one direction, diagonally from left lower corner to upper right corner of the picture; (b) monodomain with schlieren texture after strong mechanical shearing from left to right of the picture; (c) mosaic texture; (d) dendritic spherulites.

second type of texture, a mosaic texture, has been observed, which was recorded at room temperature, figure 2(c). This mosaic texture shows that the copolymer 50BP/50PH/100DF also forms a highly ordered smectic phase similarly to low molecular mass liquid crystals [14, 15]. Further cooling resulted in dendritic spherulites, as shown in figure 2(d).

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