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The synthesis and thermotropic liquid crystalline behavior of the novel poly(aryl ether ketone)s containing chloro-side group

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Summary

The novel poly(aryl ether ketone)s containing chloro-side group were synthesized by nucleophilic substitution reactions of 4,4'-biphenol and chlorohydroquinone with either 4,4'-difluorobenzophenone(BP/CH/DF) or 1,4-bis(p-fluorobenzoyl)benzene (BP/CH/BF) and their thermotropic liquid crystalline properties were characterized by a variety of experimental techniques. The thermotropic liquid crystalline behavior was observed in the copolymers containing 50 and 70% biphenol. Melting transition (Tm) and isotropization transition (Ti) both appeared in the DSC thermograms. A banded texture was formed after shearing the sample in the liquid crystalline state. The novel poly(aryl ether ketone)s had relatively higher glass transition temperature (Tg) in the range of 168 ~ 200℃ and lower melting temperature (Tm) in the range of 290 ~ 340℃. The thermal stability (Td) was in the range of 430 ~ 490℃.

Introduction

Poly(aryl ether ketone)s have been found very useful as advanced materials in applications because of their excellent thermal stability and good chemical resistance. However, poly(aryl ether ketone)s have several limitations in processing due to high melting termperature and high melt viscosities (1). Thermotropic liquid crystalline polymers (TLCP) are known to have melt viscosities significantly lower than structurally similar isotropic polymers. Furthermore, the TLCP matherials exhibit anisotropy in extruded and molded articles as a result of preferential orientation of LCP domains or individual chains (2). Recently, Bennett and Farris (3) reported the synthesis and characterization of the novel thermotropic liquid crystalline poly(aryl ether ketone)s. These materials 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 poly(aryl ether kethone)s. In this work, a series of thermotropic liquid crystalline poly(aryl ether ketone)s based on chlorohydroquinone and biphenyl mesogen with either 4,4'-difluorobenzophenone or 1,4-bis(p-fluorobenzoyl)benzene were synthesized by the nucleophilic substitution reaction and

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characterized by several experimental techniques.

Experimental

Materials

The material 4,4'-biphenol was obtained from Honshu Kagaku Ltd. in the hightest available purity. Chlorohydroquinone (Tokyo Kasei Co. Ltd.) was recrystalized from chloroform. Anhydrous potassium carbonate was ground and dried in an oven at 150℃. The xylene and tetramethylene sulfone ($TMSO_2$) were distilled under vacuum before use. 4,4'-difluorobenzophenone and 1,4-bis(p-fluorobenzoyl)benzene were prepared in our laboratory by the standard procedures.

Synthesis

The synthesis route of the copolymers is illustrated in a schematic (Fig.1). In a typical procedure, a three-necked flask was outfit with a platinum thermometer, nitrogen inlet, magnetic stirrer and a Dean-Stark trap. Appropriate mole ratio of the monomers were added into the reactor under nitrogen atmosphere. The temperature was slowly raised to 160℃ over a periord of 3h to allow phenolate formation and water / xylene azeotrope distillation which was collected in the trap. Subsequently the reaction temperature gradually raised to 200 ~ 220℃ for polymerization over a period of 8h. The resulting polymer was seperated by precipitation of the reaction mixture in methanol. The crude product was purified by hot methanol and water.

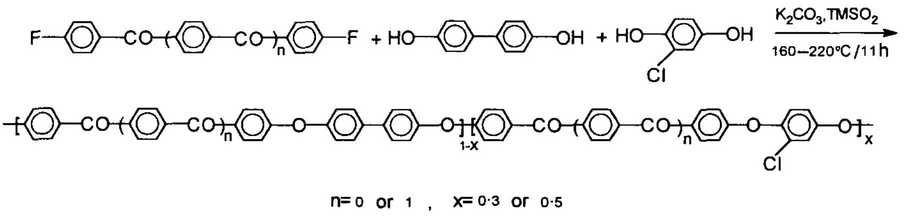

Fig.1 The synthesis route of poly(aryl ether ketone) copolymers

Characterization

The thermal analysis was carried out with a Perkin-Elmer DSC-7 instrument. The temperatures and heat flow scales were carefully calibrated by using standard materials indium and tin over a wide timperature range. Heating and cooling rates of 10℃/min were used under nitrogen atmosphere and the maximum of endotherm was taken as the transition temperature. A polarizing light microscope (PLM) of Opton R Pol was used for texture charaterization of the copolymer samples. The wide angle x-ray diffraction (WAXD) was carried out in Japan D/max-γA X-ray instrument (Cu Kα radiation). The inherent viscosities of the copolymers were measured in a mixed solvent of p-chlorophenol/1,1,2,2-tetrachloroethane at 45℃. Thermogravimetric analysis (TGA) was performed in a Perkin-Elmer TGA7 thermogravimetric analyser, using a heating rate of 20℃/min in nitrogen atmosphere.

Results and Discusion

All of the copolymers were soluble in the mixed solvent of p- chlorophenol/ 1,1,2,2-tetrachloroethane. The inherent viscosity values were in the range of 0.4 ~ 0.7 dl/g (Table1). As well known, poly(aryl ether ketone)s have exceedingly low solubility in all known organic solvents other than sulphuric acid. The low solubility of this kind of polymers is related to their extended rigid structures and relatively high crystallinity (4). In this work, incorporating crystal-disrupting substituted hydroquinone is effective to reduce the crystallinity of poly(aryl ether ketone)s. The WAXD results of the copolymers indicated that they had lower crystallinity than the isotropic poly(aryl ther ketone)s. However, they were not soluble yet in common organic solvents. Their insolubility in the common solvernts clearly demonstrates that their solubility is a complicated consequence of crystallinity and main-chain solvation (5).

Table 1 Thermal Properties and Thermotropic Behavior of The Novel Copolymers

Sample	n	x	$\eta_{i.v.}$ (dl/g)	Tg^a (℃)	Tm (℃)	Ti (℃)	ΔHm (kcal/mol)	ΔHi (kcal/mol)	Td^b (℃)	texture by PLM
70BP/30CH/100DF	0	0.3	0.63	168	338	368	9.5	0.51	430	nematic
50BP/50CH/100DF	0	0.5	0.52	185	336	350	1.6	1.54	458	smectic
70BP/30CH/100BF	1	0.3	0.68	197	318	353	3.7	0.67	487	nematic
50BP/50CH/100BF	1	0.5	0.41	190	289	314	0.55	2.69	490	smectic

a. The Tg were measured in the second heating cycle.
b. The temperature at which a 5% weight loss occured.

The data of the thermal properties and themotropic behavior are collected in Table 1. All of the copolymers had higher glass transition temperatures (Tg) between 168 ℃ and 200℃ as determined by DSC. As expected, each of the copolymers had relatively lower melting transition Tm (290 ~ 340 ℃) than the isotropic poly(aryl ether ketone) containing biphenyl because of the copolymerization effect of the side-group monomer. The thermal stability (Td) were also measured by TGA in the range of 430 ~ 490℃. Both the crystalline-to-LC transitions (Tm) and the LC-to-isotropic transitions (Ti) were observed in the DSC thermograms of the copolymers, which were further confirmed by PLM observation. As the content of nonmesogenic comonomer units increased, the crystalline-to-LC transition (Tm) became broader and of lesser intensity. The later was indicated by the decrease in heat of fusion (ΔHm) in Table1. The ΔHi values of the copolymers containing 70% biphenol were 0.5 ~ 0.7kcal/mol which implied that they underwent nematic-to-isotropic transition, while the ΔHi values of the copolymers containing 50% biphenol were 1.5 ~ 2.7kcal/mol which suggested that they underwent smectic-to-isotropic transition (6).

For further characterization of the thermotropic liquid crystalline behavior, the copolymers were evaluated by visual observations on PLM. The thin samples were heated at 400℃ for a few minutes, subsequently cooled slowly to liquid crystalline state and annealed at the temperature for 1h, and then quenched to room temperature.

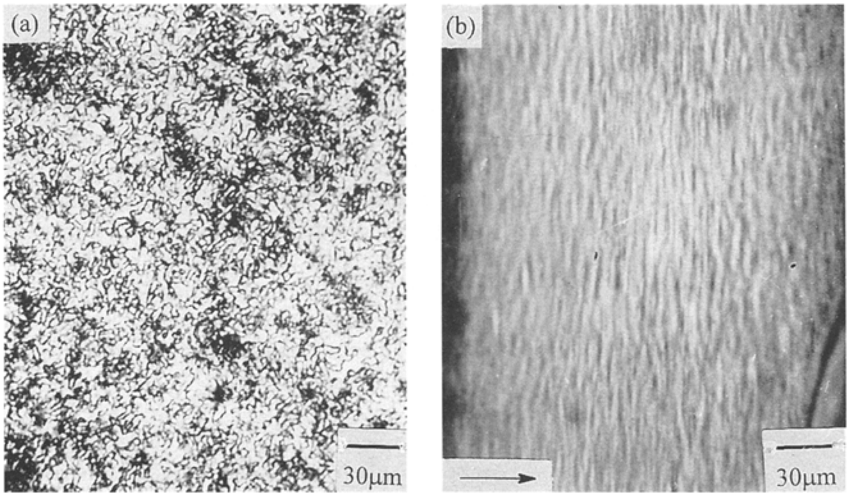

Fig.2 Optical micrographs of the copolymer 70BP/30CH/100DF after cooling from 400℃ to 330℃ and annealing for 1h and then quenching to room temperature, (a) without mechanical shearing and (b) with mechanical shearing. The arrow shows the shear direction.

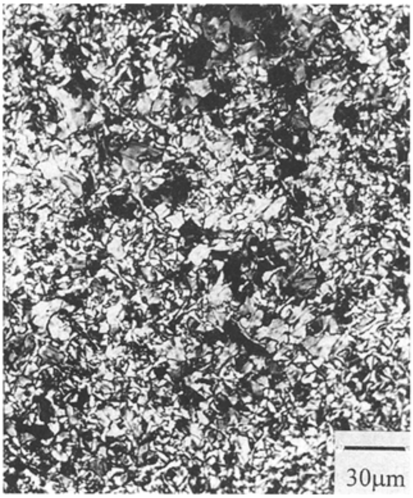

Fig.3 Optical micrograph of the sample 50BP/50CH/100DF after cooling from 400℃ to 300℃ and annealing for 1h and then quenching to room temperature.

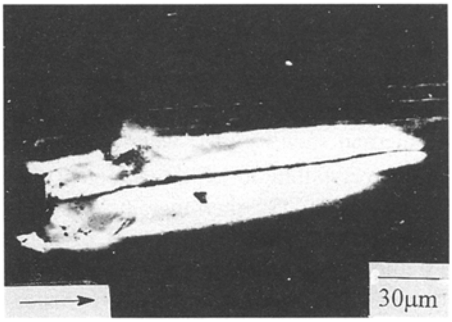

Fig.4 The monodomain of the copolymer 70BP/30CH/100BF after strong mechanical shearing at 350℃ and then air quenching. The arrow shows the shear direction.

Fig.2a shows a photomicrograph of copolymer 70BP/30CH/100DF isothermally heat treated at 330℃ for 1h. It displays a threaded texture, which is often found in the nematic phase. However, after the mechanical shearing and slight relaxation banded texture can be observed. The formation of banded textures after shearing is nearly ubiquitous for nematic polymers (7,8) (Fig.2b). This banded texture which is perpendiculer to the shear direction has a width of about 2μm. For the copolymer 50BP/50CH/100DF, a second type of texture, fanlike textrure, has been observed, which was recorded at room temperature after annealing the sample at 300℃ for 1h and then air quenching (Fig.3). This fanlike texture shows that the copolymer 50BP/50CH/100DF has a ordered smectic phase.

Furthermore, the copolymer 70BP/30CH/100BF exhibited threaded texture, while the copolymer 50BP/50CH/100BF showed fanlike texture, too. The above results are well consistent to the results of DSC. It is interesting to mention here that micrometer-size monodomains may also form in the copolymer 70BP/30CH/100BF in LC state under a strong mechanical, periodic shear force field (Fig.4). In general, one way to obtain monodomain in liquid crystalline polymers is to develop a homogenous orientation of the chain directors parallel to the substrate surface. Mechanical shearing may result in a homogeneous orientation in which the mesogenic moieties lie parallel to the substrate suface (9). Although molecular connectivity between the mesogenic moieties in liquid crystalline polymers may significally affect this orientation process, the monodomain of nematic polymer has also been achieved by Cheng et al. under strong shearing (10).

Conclusion

The thermotropic liquid crystallinity can be achieved in the novel poly(aryl ether ketone)s. The copolymers containing 70% and 50% biphenol mesogen showed nematic and smectic texture, respectively. These copolymers may be of interest as potential engineering thermoplastics, fibers or films with unique anisotropic properties.

Acknowledgment

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