Monodomain Behavior of Liquid Cryslalline Poly(aryl ether ketone) Possessing 3-(Trifluoromethyl)phenyl Group

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SUMMARY

A main-chain liquid-crystalline poly (aryl ether ketone) possessing 3-(trifluoremethyl) phenyl group (FPAEKLCP) has been synthesized from 4,4'-biphenol, 1,4-bis(p-fluorobenzoyl)benzene and a crystal-disrupting substituted monomer, 3-(trifluoremethyl) phenyl-hydroquinone (molar ratio: 1/1/2). The FPAEKLCP showed a crystal-to-liquid crystal transition at 285 °C and liquid crystal-to-isotropic transition at 354 °C in the DSC thermograms. Thin film samples of FPAEKLCP with a thickness from 10 to 100nm prepared on amorphous carbon-coated mica have a monodomain structure with tilted homeotropic orientation due to the surface-induced alignment effect when the samples are annealed at 325 °C, as is obvious from the transmission electron microscopy and electron diffraction observations. The lateral size and thickness of the monodomain increased with increasing isothermal annealing time, indicating that the formation of monodomains is initiated by a uniformly oriented molecular aggregate. The sample annealed at 300 °C no longer show the tilted homeotropic molecular orientation because of the restriction of molecular motion.

Introduction

Main chain thermotropic liquid crystalline polymers (LCPs) have received a great deal of attention over the past two decades because of the unique anisotropic nature of their liquid crystalline phase.[1] The main chain LCPs with alternating mesogenic units and flexible spacers are of ever-increasing interest. Such polymers can form nematic phase and ordered smectic crystal phases.[2-3] Recently, highly ordered smectic and smectic crystal phases have been observed by introduction of rigid mesogenic units and flexible spacers into the polyether backbone.[4-6] The existence of highly ordered smectic crystal phases in main chain LCPs is important concept for scientific understanding of the liquid crystalline state in contrast to the small molecular weight liquid crystals. For the main-chain smectic LCPs, each mesogenic group participates in forming the smectic LC structures, but the polymer chains must adopt a conformation or packing that is compatible with the structure of the smectic LC. The smectic layer structure, which is correlated with the existence of a smectic LC transition, involves two layers, the layer of the mesogens and the layer of the spacers.

Poly (ary ether ketone)s (PAEKs) are one of most important classes of high performance materials.[7-9] The combination of chemical, physical, and mechanical properties of these materials has led to their various applications, such as coatings, adhesives, membranes, and structural composites. However, their high melting transitions, high melting viscosity, and insolubility in common organic solvents obstruct their use for some industrial applications and academic research activities. In order to improve these properties, several strategies for the structural modification of PAEKs have been developed.[10-13] Recently, thermotropic liquid crystalline poly(aryl ether ketone)s have been successfully synthesized by the combination of mesogenic biphenyl units and crystal-disrupting substituents onto the polymer backbone.[14] In such a case, the crystal-disrupting substituents reduce lateral interaction between polymer chains. Accordingly, the crystallization tendency is suppressed and the solubility is improved. The segments containing such a substituent acts as a spacer in a similar manner to a flexible chain. Both nematic and smectic phases have been observed in these materials.

Quite recently, we have synthesized a series of main-chain liquid-crystalline poly (aryl ether ketone)s possessing 3-(trifluoremethyl)phenyl group (FPAEKLCPs) by the reaction of

4,4'-biphenol (BP), 1,4-bis(p-fluorobenzoyl)benzene (BF) and a crystal-disrupting monomer, 3-(trifluoremethyl)phenyl-hydroquinone (FH).[15] The FPAEKLCPs showed grainy, schlieren, fan-like, mosaic, and sanded textures at the LC state in the polarized light microscopy (PLM) observation. In addition to the PLM observation, from the observations of differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) patterns at different temperatures, and transmission electron microscopy (TEM), it has been revealed that the liquid crystalline PAEKs form highly ordered smectic, smectic crystal phase.[16-17]

In the present work, the structure and the morphology of the thin film of FPAEKLCP (BP/FH/BF=1/1/2) prepared on amorphous carbon-coated mica have been investigated by electron diffraction (ED) and TEM experiments. Homeotropic molecular alignment in monodomains has been obtained by using the amorphous carbon-coated surfaces. The surface can induce structural ordering in FPAEKLCP to form orthorhombic lateral packing that does not exist in bulk and fiber samples. The clean glass surface does not induce orthorhombic packing, and in this case only polydomain structures were found.
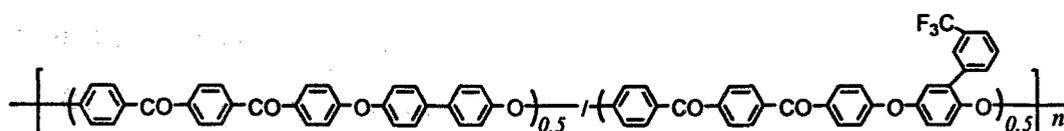
FPAEKLCP

Experimental Part

FPAEKLCP (50BP/50FH/100BF) was synthesized from 4,4'-biphenol (BP), 1,4-bis(p-fluorobenzoyl)benzene (BF) and 3-(trifluoremethyl)phenylhydroquinone (FH) in a molar ratio of BP/FH/BF=1/1/2. The detailed synthetic procedure is as follows:[15]

In a typical procedure, a three-necked flask was equipped with a nitrogen inlet, mechanical stirrer, a thermal meter, Dean-stark trap and a condenser. Appropriate mole ratios of monomers, anhydrous potassium carbonate, solvent (TMS) and xylene (azeotrope) were added into the reactor under nitrogen atmosphere. The temperature was slowly raised to 160 °C over a period of 2hr to allow phenolate formation and water/xylene azeotrope distillation that was collected in the trap. Subsequently, the reaction temperature gradually

195

rose to 220-240 °C for polymerization over a period of 8hr. The resulting mixture was poured into distilled water slowly and then was pulverized into powder prior to filtering, the crude product was purified by hot distilled water to remove the salt and solvent, and then dried at 120 °C in an oven for 24hr and obtained FPAEKLCP.

The films (thickness is 10-100nm) of FPAEKLCP on the amorphous carbon-coated micas were prepared for TEM and ED experiments. A 0.1% (w/w) FPAEKLCP solution in a 40/60 mixed solvent of p-chlorophenol/1,1,2,2-tetrachlorethane (weight ratio 40/60) was cast onto carbon-coated mica. After the solvent evaporated under vacuum, the film was heated at 400 °C, which is above the isotropization temperature, for 5～10min to eliminate previous thermal history. And then rapidly cooled to a preset temperature. After annealing at the temperature for prescribed time. The film was quenched in liquid nitrogen before they were brought back to room temperature. The obtained film was striped, floated onto the surface of water, and collected on copper grids for TEM observation.

Differential scanning calorimetry (DSC) was carried out with a Perkin Elmer model Pyris 1 instrument. The temperature and heat flow scales were carefully calibrated by using the standard materials indium and zinc. Heating and cooling runs were always carried out at a rate 10 °C /min under nitrogen atmosphere. The maximum peak of endotherm was taken as the transition temperature. The wide-angle x-ray diffraction (WAXD) was carried out in Japan D/max-γA X-ray instrument (CuK$_\alpha$ radiation). Liquid crystalline texture was examined via a polarizing light microscope (PLM) (Opton R Pol). The structures and morphology of FPAEKLCP thin films on the amorphous carbon coated surfaces were observed using a JEOL 2010 TEM with a 200-kV accelerating voltage. In order to determine the molecular direction, the samples were also directly examined by electron diffraction (ED) experiments under the TEM. Cali bration of the ED spacing was carried out using gold (Au).


Results and Discussion

Smectic LC Behavior of FPAEKLCP

Figure 1 shows the first cooling DSC thermograms of the FPAEKLCP from 400 °C to 50 °C at 10 °C /min and subsequently reheating over the same temperature range with the same

196

scanning rate. Several peaks are observed in both the heating and cooling curves, which correspond to different phase transitions. Two main first order transitions on the second heating scan are attributed to crystal-to-liquid crystal transition (Tm=285 °C with ΔHm=15J/g) and isotropization of liquid crystal phase (Ti=354 °C with ΔHi=22J/g) respectively. The ΔH_i value of the copolymer is higher than ΔH_m value. This result indicates that the difference in order between the semicrystalline state and mesophase is smaller than the difference between the mesophase and the isotropic melt, and that the mesophases involved have a highly ordered structure. [18]
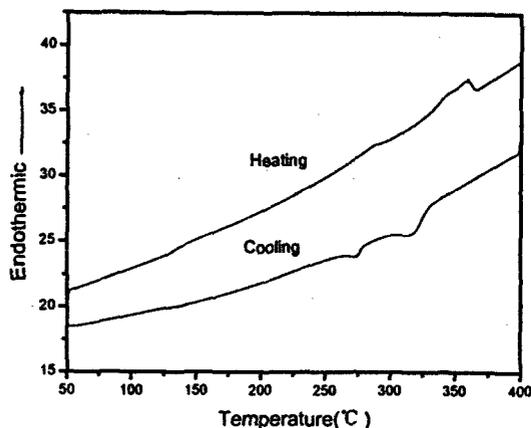

Figure 1. DSC thermograms of FPAEKLCP during the first cooling and second heating scans at a rate of 10 °C/min.
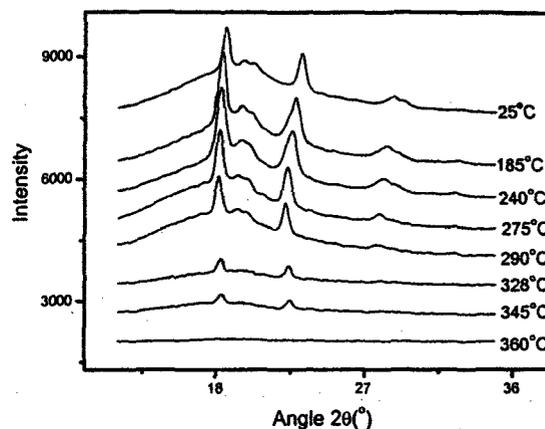
Figure 2. Temperature dependence of X-ray diffraction patterns of FPAEKLCP at a heating rate of 5 °C/min.

Figure 2 shows the change of X-ray diffraction patterns for FPAEKLCP at a heating rate of 5 °C/min. Below the crystal melting temperature (285 °C), strong reflections with four peaks at 2θ=18.4°, 19.6°, 22.7° and 28.5°. which are assigned as (110), (111), (200) and (211), respectively, based on orthohombic packing.[19] It implies that the copolymer has a typical crystal structure, which is similar to other regular member of poly (aryl ether ketone)s family. When the sample is heated into LC temperature range of 285~354 °C, the peak intensity in high-angle region greatly decreased and some peaks were disappeared. In general, these kind of low-angle reflections are related smectic layer structures, while the reflections appearing in high-angle region to the lateral packing of the mesogens. The coexistence of low-angle and high-angle reflections suggests the existence of a highly ordered smectic phase with crystal-like packing of the mesogens. Upon further heating to the isotropic phase (360 °C), all the peaks in low-angle and high-angle regions disappeared.

197
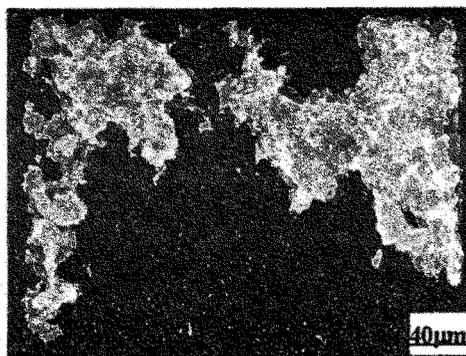
Figure 3. Optical micrograph of the copolymer FPAEKLCP sample
cooled from 400 °C to 325 °C and annealed at 325 °C for
few minutes, and then quenched to room temperature.

The presence of Smectic phase is also in agreement with the results of the optical polarized microscopy. Figure 3 shows a typical very fine mosaic texture of FPAEKLCP sample that was isothermally annealed at a liquid crystalline temperature (325 °C) and then quenched to room temperature. The fine mosiac texture suggests that the copolymer forms a highly ordered smectic phase in a similar manner to small molecular weight liquid crystals.[16, 20]

Formation and Structure of FPAEKLCP Monodomains

For the polymer liquid crystals the surface-induced ordering process is most likely to occur in low-ordered liquid-crystalline states such as the N, S_A, S_C phase because of a relatively low viscosity and large degree of molecular motion. In highly ordered smectic phases, the molecular mobility is restricted due to the formation of highly ordered lateral packing. However, in FPAEKLCP, surface-induced molecular orientation can be achieved in the highly ordered phase.

With thin film samples of FPAEKLCP on the amorphous carbon substrate are cooled from the melt (400 °C) to the smectic phase (325 °C) and isothermally kept at the temperature for 1h (Figure 4a), single-crystal-like ED diffraction patterns related to a monodomain structure can be obtained in 30°-tilted ED observations as shown in Figure 4b. According to the reflection of the ED pattern, the lateral packing symmetry is orthorhombic with lateral lattice sizes of a=7.76Å and b=6.12Å based on the (200) and (110) reflections. Figure 4b shows a representative TEM micrograph of a monodomain of the thin film sample annealed at LC temperature of 325 °C for 1h. The micrograph represents the characteristics of the highly

198

ordered liquid crystal.[21] The monodomain exhibit an elongated shape with the long axis always along the *b*-axis, indicates that the development of the monodomain texture along the *a*-axis and *b*-axis is anisotropic.[22]
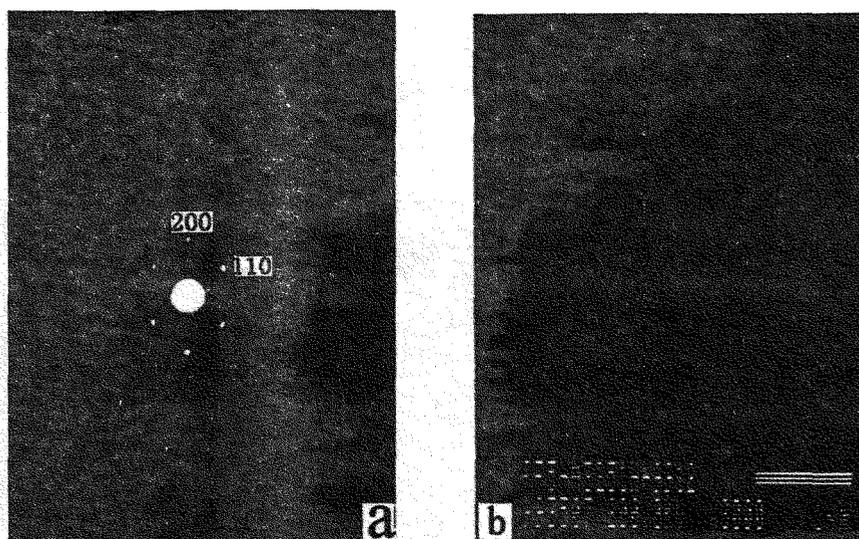

Figure 4. Electric diffraction patterns and the TEM morphological observation of the surface-induced monodomain of the FPAEKLCP thin film annealed at 325 °C for 1h.

The growth of the tilted homeotropic monodomains of FPAEKLCP at 325 °C was observed by TEM. A schlieren pattern is found when the sample is isothermally kept at 325 °C for a few seconds (Figure 5). The schlieren pattern corresponds to the polydomain texture. Further annealing caused the change from randomly oriented polydomains to uniaxially oriented monodomains due to continual orientation. A large and thick monodomain was formed when the thin film was annealed for 1h (Figure 4a). This behavior was also proved by PLM observation.
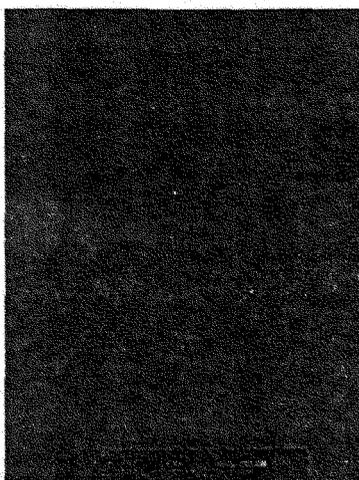
Figure 5. TEM micrographs of FPAEKLCP thin films annealed at 325 °C for 5min.

199

At the initial stage of the monodomain formation, FPAEKLCP molecules have a tendency to form tilted homeotropic orientation in molecular aggregates ("nucleation" process). After the initiation of monodomain, the surrounding molecules continue to migrate toward this domain, orient themselves, and become part of the domain's ordered structure. This process may be defined as a self-assembly behavior for the formation of the ordered structure in FPAEKLCP monodomains.
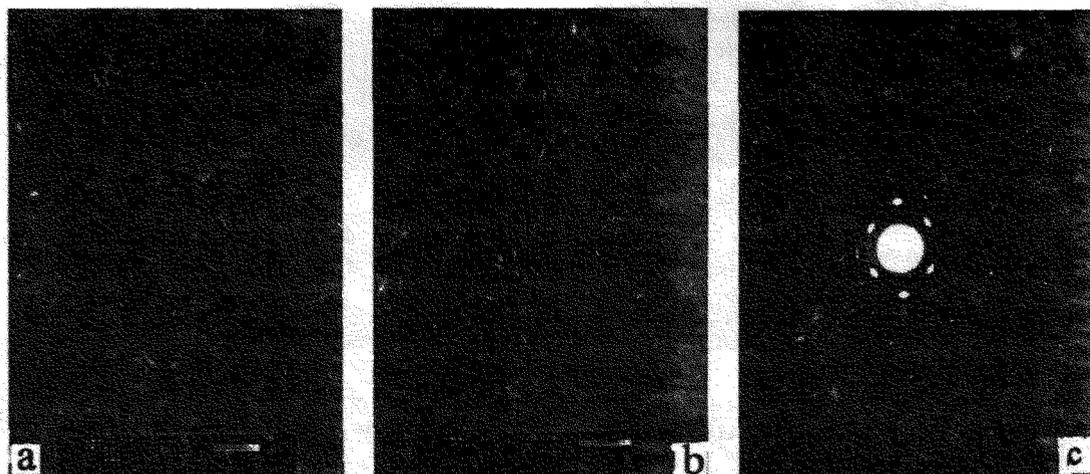
Figure 6. TEM micrographs of FPAEKLCP thin film annealed at (a) 300 °C annealing for 5h and then cooled to room temperature at 5 °C/min, (b) 300 °C for 5h and then quenched to room temperature, and (c) the ED pattern at 300°C for 5h.

FPAEKLCP thin films kept isothermally at different temperatures on carbon-coated substrates exhibit significantly distinguished morphologies as shown in Figure 6. The films annealed at 300 °C showed the texture related to a polydomain structure. The tilted homeotropic molecular alignment can be observed when the samples are kept only at 325 °C. (Figure 4b). The sample annealed at 300 °C for 5h ED diffraction pattern showed only a ring pattern related to polydomains (Figure 6c). It is thought that large-scale molecular motion must be required for the molecules orientation by the surface-induced alignment effect. When the molecules are annealed at below 325 °C, the tilted homeotropic alignment induced by the surface effect can't be attained because of the restriction of chain mobility. Therefore, the morphological layer stacks with homogeneous molecular alignment are observed.

The morphological layer stacks in Figure 4b are similar to that of edge-on lamellar crystals observed in many polymer crystals grown from the melt, such as in the case of poly (aryl ether ketone)s. For the formation of edge-on lamellar crystals in polymer crystallization, the chain molecules are homogeneously oriented and the lamellar crystals are arranged

200

parallel to each other to form the basic component in the construction of spherulites. With increasing crystallization temperature (*i.e.,* lower under cooling) and time, the lamellar thickness increases and the edge-on arrangement becomes more regular, and the spherulitic size increases as well.

Conclusions

The phase structure and order evolution of liquid-crystalline mono- and polydomains for the thin film of FPAEKLCP prepared on the amorphous carbon were investigated based on TEM and ED experiments. when the thin film samples are kept at 325 °C, where FPAEKLCP is at the highly ordered smectic phase, initially observed polydomain structure changed to monodomain structure with annealing time. In the monodomain structure, the molecules had a tilted homeotropic orientation due to the surface-induced alignment effect. The lateral size and thickness of the monodomain increased with isothermal annealing time. The formation of monodomains is initiated by a uniformly oriented molecular aggregate and promoted by a subsequent self-assembly process accompanied by a large scale of molecular motion. This process is conceptually similar to the nucleation-controlled process of polymer crystallization. When the annealing temperature of samples is at 300 °C, the thin films did not show tilted homeotropic molecular orientation because of the restriction of the molecules mobility.

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