

Thermotropic 액정성 Polyesters의 합성 및 특성조사

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Synthesis and Characterization of Thermotropic Liquid Crystalline Polyesters

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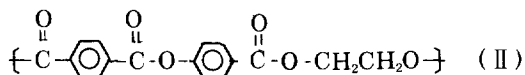
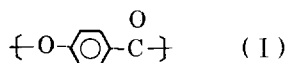
요약: 피리딘 하에서 thionyl chloride를 촉매로 사용하여 *p*-carboxy phenyl terephthalate (CPT) 와 B,D / E,G의 직접축합중합에 의해 랜덤 thermotropic 액정성 copolyesters 를 합성하였으며, 이들 공중합체의 조성이 열적특성, X-선회절 pattern 및 optical texture 에 미치는 영향을 고찰하였다. PCBT는 이중 용융전이, 즉 200-300°C에서 고체-mesophase전이와 240-350°C에서 mesophase-등방성 액체전이를 나타내었다. PCBT의 X-선 회절 pattern에서 $2\theta \approx 16, 19, 24^\circ$ 에서 최대치가 나타났으며, $2\theta \approx 24^\circ$ 의 피크는 mesogenic 단위에 의해 형성된 액정에 기인하며, $2\theta \approx 19^\circ$ 의 피크는 중합체 주쇄에 의해 형성된 일반적인 결정에 기인하는 것으로 나타났다. 또한 PCBT의 optical texture는 nematic상을 나타내었다.

Abstract: Thermotropic liquid crystalline random copolyesters (PCBT) were obtained by the direct polycondensation of *p*-carboxy phenyl terephthalate (CPT) and 1,4-butanediol / ethylene glycol using a catalyst like thionyl chloride in pyridine. Effects of the composition on the thermal property, x-ray diffraction pattern and optical texture are observed. The PCBT showed double melting transition, ie, solid-mesophase transition (T_m) in the range of 200°C and 300°C, and mesophase-isotropic liquid transition(T_i) in the range of 240°C and 350°C. Intense maxima of x-ray diffraction pattern of PCBT are at about $16^\circ, 19^\circ$ and 24° of 2θ . The peak at $2\theta \approx 19^\circ$ is attributed to the crystal according to the crystallization of polymer main chain, and the peaks at $2\theta \approx 24^\circ$ are due to the formation of liquid crystal by mesogenic unit. The optical textures of the polymers correspond to the nematic phases.

INTRODUCTION

Recently, thermotropic liquid crystalline polymers are of considerable interest not only because of their potential as high-strength fibers and plastics, but also because of their structural order in fluid phases. The liquid crystalline behavior of polymer mainly depends on mesogenic units along their backbone. There are two types of liquid crystalline polymers which have mesogenic units either along main chain or as a side chain.¹⁻⁴ The thermotropic liquid crystalline polymers having mesogenic unit along main chain are of considerable practical interest, particularly for the application as high-strength and high modulus fibers, which can be obtained by melt spinning instead of solution spinning as is used for analogous lyotropic liquid crystalline polymers.

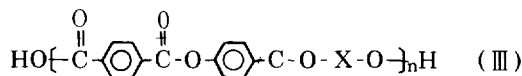
The copolymers incorporating various percentages of 4-oxybenzoyl segments (I), into poly(ethylene terephthalate) (PET) so as to contain segments like II, have been found to be liquid crystal by Jackson.⁵



Melts of the copolymers, containing 40-90 mole % 4-oxybenzole units were reported to exhibit nematic behavior on the basis of the opacity of the melt. Differential scanning calorimetry (DSC) runs in six samples annealed for 30min, at the temperatures between 135 and 200°C gave two or three endotherms. The highest endotherm at 244°C was reported to correspond to the nematic-isotropic transition and was independent of annealing condition and heating rate. The two endotherms of lower temperatures were thought to be attributable to the melting of two crystalline forms which probably differed in crystal size and perfection.

We prepared the random copolyesters (III), (PCBT) by the direct polycondensation of the

CPT, $(\text{HOOC}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{COOH})$ and butanediol (BD)/ethylene glycol (EG) using a catalyst like thionyl chloride in pyridine. The copolyesters exhibit different behavior in viscosity, thermal property, optical texture, and x-ray diffraction pattern with composition.



where X is $(\text{CH}_2)_2$ and $(\text{CH}_2)_4$ with mole ratios of 100/0, 75/25, 50/50, 25/75, 0/100

EXPERIMENTALS

Materials

Butanediol, ethylene glycol and pyridine were purified by vacuum distillation and were kept dried over molecular sieves. Thionyl chloride (extra pure reagent) was used without further purification.

Synthesis of p-Carboxy Phenyl Terephthalate (CPT)

The CPT was synthesized from hydroxybenzoic acid with excess terephthalic acid (TPA) at 240°C for 30min, under nitrogen atmosphere. The CPT was purified by recrystallization from N, N-dimethyl acetamide after washing with methanol. The IR spectrum of the CPT is shown in Fig. 1.

Polymerization⁶

To the cold thionyl chloride (11 mmol) in an ice-water bath pyridine (10ml) was added slowly to keep the reaction temperature low, and the mixture was stirred for 30 min, and treated with the CPT (5m mol) in pyridine (10ml) by dropwise

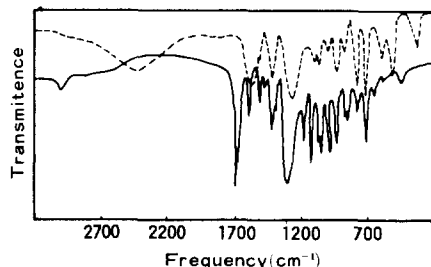


Fig. 1. IR spectrum of CPT(.....) and PCBT-1 (—).

for 20min. The cooling bath was removed, and the resulting mixture was maintained at room temperature for 20 min to complete the reaction. Butanediol (5m mol) in pyridine (10ml) was added all at once, and the whole mixture was heated at 80°C for 4 hrs. The resulting viscous solution was poured into methanol to precipitate polymer, and was washed in boiling methanol, followed by drying at 70°C for 24 hrs under vacuum.

Inherent Viscosity

The inherent viscosities of polymers were determined for a 0.2g/dl solution of the polymer (PCBT) in p-chlorophenol. All measurements were made with an Ubbelohde viscometer in a constant temperature bath at 30°C ± 0.2°C. The inherent viscosity is enumerated by $\eta_{inh} = (2.303 \log t/t_0) / C$ where t_0 and t represent the viscometer flow periods for solvent and polymer solution, respectively, and C is concentration of polymer solution, 0.2 g/dl.

Thermal Analysis

The transition temperatures of polymer powders were determined by a differential scanning calorimeter (DSC 20, Daini Seiko, Japan) under nitrogen gas purging. The samples were heated from room temperature to 280°C at the rates of 5°C/min, 10°C/min, 20°C/min and 40°C/min and cooled at a rate of 10°C/min.

X-Ray Diffraction

X-ray diffractometer system (D/max-III A Type, Rigaku Co. Japan) using Ni-filtered $Cu K\alpha$ radiation has been used to investigate the solid state structure of aromatic copolyesters powder. Some of the powder samples were annealed at

different temperatures.

IR Spectra of Monomer and Polymer

IR spectra of monomer (CPT) and polymer (PCBT) were obtained on a IR spectrophotometer (Perkin-Elmer 1330, USA). The specimen were prepared by the KBr pellet method.

Optical Texture

The texture of the mesophase of polymers were observed on a cross-polarizing microscope equipped with a hot stage during cooling from isotropic melt.

Annealing

The PCBT-1 was cooled to 235°C (the temperature of mesophase formation) from isotropic melt, and annealed for 10 min at that temperature and then quenched to room temperature. The PCBT-3 was quenched to 145°C (the crystallization temperature of polymer main chain) from isotropic melt and annealed for 10 min at that temperature followed by cooling to room temperature.

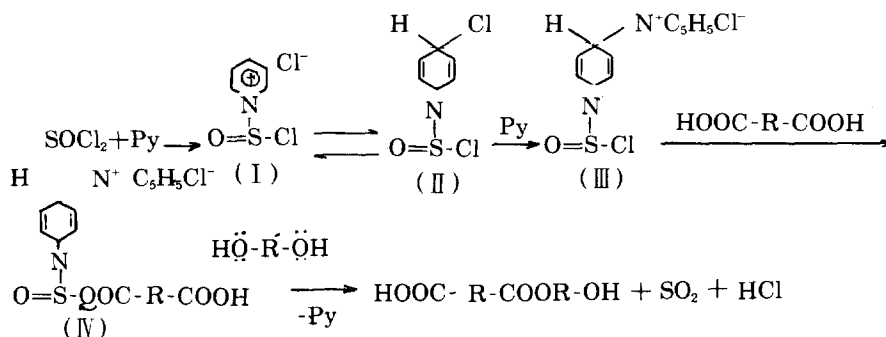
RESULTS AND DISCUSSION

Reaction Mechanism

Thionyl chloride reacts with pyridine (Py) to form 1-chlorosulfinyl pyridinium chloride (I or II), which is converted into III by the reaction with additional pyridine. It was expected that III (or I / II), when treated with a carboxylic acid, forms a carboxylic sulfinic anhydride (IV), which is reactive enough to produce the corresponding carboxylic ester on alcoholysis.^{7,8}

Polymerization Conditions

The effects of reaction temperature from 60°C



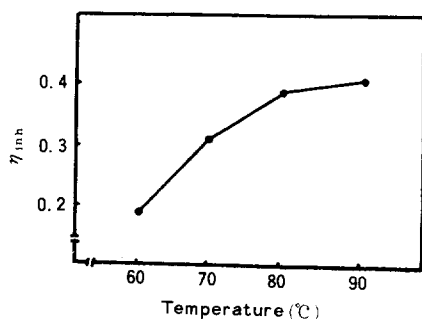


Fig. 2. Inherent viscosity vs. reaction temperature at 4 hr of reaction time.

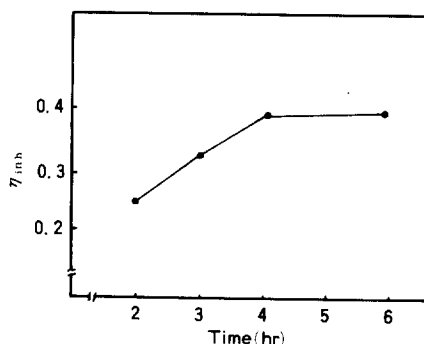


Fig. 3. Inherent viscosity vs. reaction time at 80°C.

to 90°C on inherent viscosities of polymers were shown in Fig. 2. The inherent viscosities of polymer were shown in Fig. 2. The inherent viscosities of polymers were increased with increasing the reaction temperature. The rate of increase was slowed down at 80°C and the polymer was yellowed above this temperature. The reason of yellowing phenomena is not clear, however, it maybe in part due to the SO_2 at the high temperature, and further research should be directed.

Fig. 3 showed the effect of reaction time on the inherent viscosities of polymers. The inherent viscosities of polymer were increased with the reaction time. After about 4 hours, the equilibrium state was established.

The code and inherent viscosity of each polymer which was synthesized at optimum reaction, at 80°C for 4 hrs, are shown in Table 1.

Thermal Properties

Griffin et al.⁹ reported that the thermotropic liquid crystalline polymer with mesogenic unit in its main chain shows the double melting phenomena which are solid-mesophase transition (T_m) at higher temperature than the glass transition temperature, and mesophase-isotropic liquid transition (T_i) at higher temperature than T_m .

As shown in Fig. 4, the DSC curves of liquid crystalline polyesters which were presently synthesized show similar double melting phenomena. Solid-mesophase transition appeared at the temperature between 198 and 213°C. And mesophase-isotropic melt transition appeared at a temperature

Table 1. Synthesis of Copolyesters by Direct Polycondensation

Code	Butanediol / E.C	η_{inh}^a	Yield (%) ^b
PCBT-1	100 / 0	0.34	85
PCBT-2	75 / 25	0.25	83
PCBT-3	50 / 50	0.28	85
PCBT-4	25 / 75	0.26	87
PCBT-5	0 / 100	0.4	84

^a Measured at a concentration of 0.2g/dL in p-chlorophenol at 40°C.

^b Polymerization was carried out at 80°C for 4hr.

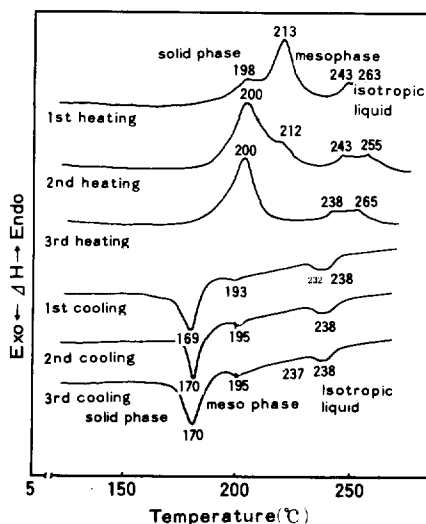


Fig. 4. DSC curves of PCBT-1 at scanning rate of 10°C/min in N_2 gas.

between 243 and 263°C which is higher than T_m . Some of the liquid crystalline polyesters show the similar multiple melting transitions.¹⁰⁻¹²

Noël¹³ reported that this multiple transitions are due to :

- 1) Interconvertible forms of polymer, which differ only in degree of crystal size and perfection.
- 2) Fundamental difference in crystal morphology, for example folded-chain crystals and partially extended chain crystals.
- 3) True polymorphism.
- 4) Solid-mesophase and mesophase-mesophase transition.

The first cooling curves (DSC) show isotropic liquid-mesophase transition at the temperature between 238 and 232°C, and mesophase solid transition at 169°C.

The supercooling of mesophase-solid transition is more significant than that of mesophase-isotropic liquid transition. The formations of main chain crystals are more significantly affected than that of liquid crystals by thermal effect because the behaviors of liquid crystals are due to the mesogenic units. Similar phenomena are reported for other main chain thermotropic liquid crystalline polyesters.^{14,15}

Annealing effects are evident in liquid crystalline polyesters usually involving loss of some solid-solid transitions as well as changes in temperature, shape and area of endothermic / exothermic peaks. The longer relaxation times for polymers and the lack of positional "memory" of polymer segments result in this behavior.⁹

Otherwise second and third cooling curves show similar behavior. And third heating curve also shows the thermal effect like second heating curve, but the extent of changes are small compared to first heating curve.

The thermal behaviors of the random copolymer with various compositions are shown in Fig. 5. There are different multiple transitions of the copolymers. It is assumed that the phenomena of the multiple transitions are presumably due to the complex structures of copolymer with the

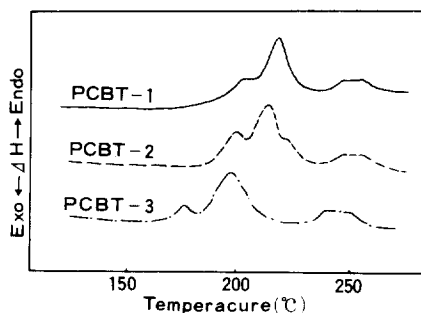


Fig. 5. DSC curves of PCBT with various compositions (heating rate : 10°C / min in N₂ gas).

coexistence of butanediol and ethylene glycol. Furthermore, the x-ray diffraction patterns showed the difference of crystal structures.

It is generally expected that the transition temperatures increase with decreasing the butane diol and increasing the ethylene glycol, but the transition temperatures were decreased. The reason is not clear however this phenomenon are also presumably due to the complex structures of copolyesters.¹³

The mesophase-isotropic phase transition temperatures change a bit with monomer ratio. For the liquid crystalline polymers with same mesogenic units, mesophase-isotropic liquid transition is less affected by flexible spacer than solid-mesophase transition because the formation of liquid crystal are attributed to mesogenic unit.

X-Ray Diffraction

Fig.6 showed the x-ray diffraction of five copolymers. The sharpest and strong peak of all sample were observed at $2\theta=19.5^\circ$. This peak was changed with the content of butanediol, that is, the relative intensity of the peak at $2\theta=19.5^\circ$ increased and the 2θ of the peak decreased with decreasing the butane diol contents. All samples show maximum peaks at the range around $2\theta=16^\circ$, 24° and 28° .

The relative intensity of the peak at $2\theta=16^\circ$ decrease with decreasing the butanediol. Otherwise, the relative intensity of the peak at $2\theta=17^\circ$ shows minimum when butane diol contents was 50mole %, and the peak come close to the peak of 2θ

$=19.5^\circ$ as the butane diol contents increase. Also, the peak at $2\theta=23.4^\circ$ and 24.6° are sharply separated

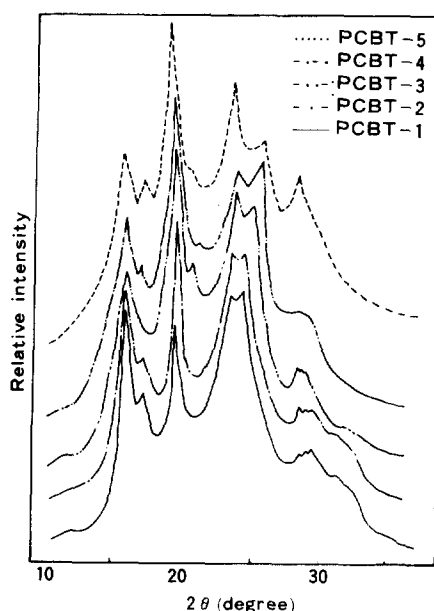


Fig. 6. X-ray diffraction patterns of PCBT with various compositions.

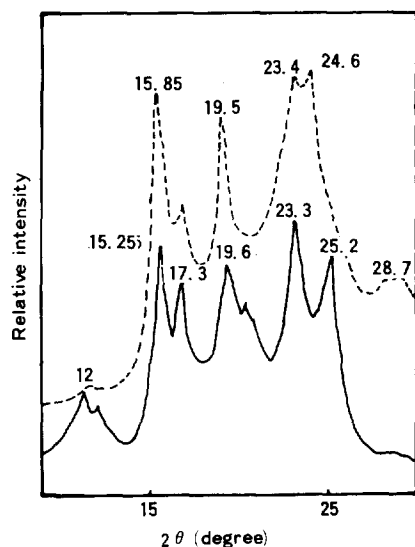


Fig. 7. X-ray diffraction patterns of original PCBT-1 and annealed PCBT-1 at 245°C .

..... original PCBT-1
— annealed PCBT-1

with decreasing butane diol contents, and those become distinct. This phenomenon is considered as the composition of butanediol and ethylene glycol affect crystal structure of the polymer.

Fig. 7 showed the x-ray diffraction of the original PCBT-1, and the PCBT-1 which was annealed for 10 min at the temperature (T_{IN} , 235°C) of isotropic-nematic transition after cooling from isotropic melt to T_{IN} , and then quenched to room temperature. The liquid crystals are formed at T_{IN} , in the case of annealing with above condition. However, they do not pass by general crystallization of polymer main chain since the polymer are directly quenched from T_{IN} (235°C) to room temperature. Therefore, it may be presumed that the PCBT-1 annealed at T_{IN} has the crystal structure attributed to the formation of liquid crystal rather than general crystallization of polymer main chain. As shown in Fig. 7, the double peaks of annealed PCBT-1 at $2\theta=23.3^\circ$ and 25.2° are sharply shown and the two peaks are separated apart. The double peak at $2\theta=15.25^\circ$ and 17.3° were separated sharply. The relative intensity of the peak ($2\theta=12^\circ$) of PCBT-1 annealed at T_{IN} become strong, however, the peak at $2\theta=19.5^\circ$ shows weak and broaden. Consequently, the peak at $2\theta=19.5^\circ$ is attributed to the crystal corresponding to the crystallization of polymer main chain rather than mesogenic unit only, and the peaks at $2\theta=23.4^\circ$ and 24.6° are due to the formation of liquid crystal rather than polymer main chain.

Fig. 8 shows the x-ray diffraction of the original PCBT-3, and the PCBT-3 which was annealed for 10 min at the temperature (T_{C} : 170°C) of nematic-solid transition after quenching from isotropic melt to T_{C} . In the case of annealing with this condition, the general crystallization of polymer main chain are large compared to the formation of liquid crystal, because the polymer was quenched from isotropic melting temperature to the temperature (T_{C}) of general crystallization of polymer. Therefore, it is considered that the crystal structure of PCBT-3 annealed at T_{C} are due to the crystallization of polymer main chain rather than that of the mesogenic unit.

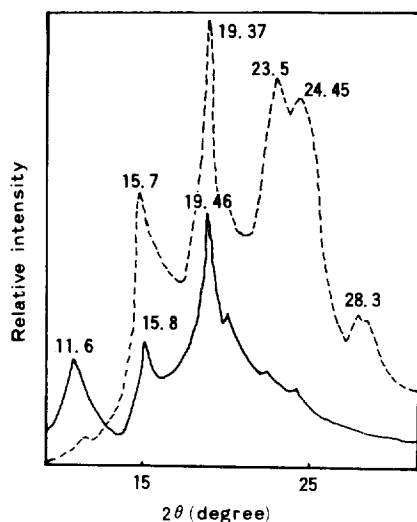


Fig. 8. X-ray diffraction patterns of original PCBT-3 and annealed PCBT-3 at 145°C.

..... original PCBT-3
— annealed PCBT-3



Fig. 9. Photomicrograph of the PCBT-1 at 230°C.

As shown in Fig. 8, the peak of annealed PCBT-3 at $2\theta=19.5^\circ$ and 15.8° have no change with annealing, but the relative intensities of the peak at $2\theta=23.5^\circ$ and 24.5° became very weak while that of the peak at $2\theta=11.6^\circ$ became strong. From, the Fig. 7 and Fig.8, we may conclude that the peak at $2\theta=23.5^\circ$ and 24.5° are due to the formation of liquid crystal by mesogenic unit and the peak at $2\theta=19.5^\circ$ is attributed to general crystal of polymer main chain rather than mesogenic unit.

Optical Texture

Typical optical texture observed with crossed polarizing microscope is shown in Fig. 9. Threaded Schlieren texture can be clearly seen in the photomicrographs. The polymer melts were all turbid between T_m and T_i and revealed strong striae.

CONCLUSIONS

The random copolyesters (PCBT) were obtained by the direct polycondensation of the CPT and butanediol (BD)/ethylene glycol (EG) using a catalyst like thionyl chloride in pyridine under the optimum reaction condition of 80°C and 4 hours. The CPT was synthesized by hydroxy benzoic acid and excess terephthalic acid.

Effects of the composition on the thermal property, x-ray diffraction pattern and optical texture are observed. The conclusions are as follows :

- 1) The PCBT have melting transition temperatures in the range of 200°C and 300°C, and isotropization transitions in the range of 240°C and 350°C. The transitions were significantly affected by compositions of PCBT and annealing
- 2) For the PCBT of various composition, the intense maxima of x-ray diffraction pattern are at about 16° , 19° , and 24° of 2θ . These maxima also change in intensity and position with the monomer ratios (BD/EG) and annealing temperatures. The peak at $2\theta=19^\circ$ is attributed to the crystal according to the crystallization of polymer main chain and the peaks at $2\theta=24^\circ$ are due to the formation of liquid crystal.
- 3) The optical textures of the polymers correspond to the nematic phases.

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