Thermal Properties and Crystalline Structure of Liquid Crystalline Poly(ethylene terephthalate-*co*-2(3)-chloro-1,4-phenylene terephthalate)

DO MOOK RHEE,[1] WAN SHIK HA,[2] JI HO YOUK,[2] DONG IL YOO[3]

[1] Samyang Group Central R&D Center, 63-2 Hwaam-Dong, Yusung-ku, Taejeon, 305-348, Korea

[2] Department of Fiber and Polymer Science, Seoul National University, Shinlim-dong, Kwanak-ku, Seoul, 151-742, Korea

[3] Department of Textile Engineering, Chonnam National University, 300 Yongbong-dong, Puk-ku, Kwangju, 500-757, Korea

ABSTRACT: Thermal properties and crystalline structure of liquid crystalline (LC) poly(ethylene terephthalate-*co*-2(3)-chloro-1,4-phenylene terephthalate) [copoly(ET/CPT)] were investigated using differential scanning calorimetry (DSC), thermogravimetry (TGA), limiting oxygen index (LOI) measurement, electron dispersive X-ray analysis (EDX), X-ray diffractometry, and infrared spectrometry (IR). The thermal transition temperatures of copoly(ET/CPT) were changed with the composition. Copoly(ET/CPT) showed two thermal decomposition steps and the residues at 700°C and LOI values of copoly(ET/CPT) were almost proportional to its chlorine content. The activation energy of thermal decomposition of LC units was very low compared to that of poly(ethylene terephthalate)(PET) units. Crystal structure of copoly(ET/CPT) (20/80) was of triclinic system with the lattice constants of $a = 9.98$ Å, $b = 8.78$ Å, $c = 12.93$ Å, $\alpha = 97.4°$, $\beta = 96.1°$, and $\gamma = 90.8°$, which is very close to that of poly(chloro-*p*-phenylene terephthalte) (PCPT) with the lattice constants of $a = 9.51$ Å, $b = 8.61$ Å, $c = 12.73$ Å, $\alpha = 96.8°$, $\beta = 95.4°$, and $\gamma = 90.8°$. When copoly(ET/CPT)(50/50) was annealed at 220°C in vacuum, crystallization induced sequential reordering (CISR) was not observed but the heat of fusion was slightly increased due to the increase of the *trans* isomer content in PET units. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1286–1294, 2002; DOI 10.1002/app.10451

Key words: poly(ethylene terephthalate-*co*-2(3)-chloro-1,4-phenylene terephthate); poly(chloro-*p*-phenylene terephthlate); thermal transition; thermal stability; crystal structure

INTRODUCTION

Thermotropic liquid crystalline (LC) polyesters can be melt spun into high strength fibers be-cause their chains can spontaneously align parallel along the direction of the flow. However, the main disadvantage of these polymers arising from high chain stiffness is the high melting point, which sometimes prevents processability. In order to reduce the melting point, their chemical structures have been modified by introducing flexible spacers,[1–8] kinked monomers,[9–14] or sub-

---

stituted monomers into the main chain.[15–21] Schaefgen first modified wholly aromatic poly(*p*-phenylene terephthalate) (PPT), which is not melt processable,[22] by introducing a poly(ethylene terephthalate) (PET) unit as a flexible spacer and chlorohydroquinone as a substituted monomer.[15] Poly(ethylene terephthalate-*co*-2(3)-chloro-1,4-phenylene terephthalate) [copoly(ET/CPT)] (41/59 w/w), for example, could be melt spun from its anisotropic melt at 252°C and the resultant fibers exhibited high orientation and high initial modulus. In our previous study,[23] it was reported that the formation of LC copoly(ET/CPT) proceeds through acidolysis, and subsequent polycondensation and the resulting LC copoly(ET/CPT) has a random sequence distribution for all compositions. However, its thermal transitions, thermal stability, and crystal structure with the content the chlorohydroquinone substituent have not been extensively studied thus far. It is known that thermal transition and stability of thermotropic LC polyesters can be affected by both flexible spacers and substituents. Longer flexible spacers apparently impart a higher degree of mobility for the LC units and asymmetric substituents result in the increased separation of LC units along the chain. Eventually, their engineering processes and the resulting physical properties would be also affected by these modifications.[24,25] Furthermore, reorganization of random LC copolyesters into multiblock structures by crystallization induced sequential reordering (CISR) can change their properties. Generally, LC copolyesters with the random sequence distribution have lower transition temperatures than ordered ones.[26]

In this study, thermal properties of copoly(ET/CPT) were investigated according to the composition and its crystalline structure was determined. The effect of annealing of copoly(ET/CPT) on thermal properties, crystalline structure, and sequence distribution was also studied.

EXPERIMENTAL

Synthesis of Copoly(ET/CPT)

A mixture of PET, and the same mole % of chlorohydroquinone diacetate (CHQDA) and terephthalic acid (TPA), completely dried at 60°C in a vacuum oven, was placed in a flask equipped with a mechanical stirrer, a nitrogen inlet, and a re-

ceiver with provision for applying vacuum. The mixture was heated to 280°C at a heating rate of 10°C/min under the nitrogen atmosphere. As the temperature increased, the mixture was melted and acetic acid formed by the reactions of CHQDA with TPA and PET was vigorously evolved. After stirring the reactants for 1 h, the temperature was raised to 290°C while applying vacuum (0.1 Torr), and maintained for a predetermined time to obtain the final product. Copoly(ET/CPT)s are coded according to the feed ratio of CHQDA. For example, copoly(ET/CPT) (50/50) indicates copoly(ET/CPT) prepared with 50 mole % PET and 50 mole % CHQDA (or 50 mole % TPA).

Synthesis of Poly(chloro-*p*-phenylene terephthlate) (PCPT)

A mixture of terephthaloyl chloride, chlorohydroquinone, and pyridine (1/2/21, mole ratio) was charged into a round-bottomed flask equipped with a stirrer and a condenser under the dried nitrogen atmosphere. Benzene was added as a solvent and then the reaction was run at room temperature for 3 h. The final product was filtered and washed with water.

Analyses

Viscosity of 0.5 wt % copolymer solution in phenol/tetrachloroethane (60/40, v/v) was measured using an Ubbelohde viscometer at 20 ± 0.01°C. A 5% solution of copolymer in $CF_3COOD/CDCl_3$ (1/1 v/v) was prepared to determine the sequence length distribution using a Bruker 300 MHz NMR spectrometer. The content of chlorine atoms in copolymer is analyzed by characteristic X-ray obtained from an electron dispersive X-ray analyzer (EDX) equipped in a scanning electron microscope (SEM; Stereoscan 360, Cambridge Instrument Co.). A differential scanning calorimeter (Perkin-Elmer DSC-4) was used to determine the melting temperatures and enthalpies of melting. A heating rate of 20°C/min was used in all thermal analyses and nitrogen gas was purged into the differential scanning calorimetry (DSC) sample cell. Thermal stability was measured using a thermogravimetric analyzer (Perkin-Elmer TGA-2) at a heating rate of 20°C/min under a nitrogen atmosphere. Limiting oxygen index (LOI) was measured on a flame meter according to the standard procedure of ASTM D 4723. The density of LC copolymer was measured in a density-gradient

Table I   Composition Analysis of Copoly(ET/CPT)s

Feed Ratio of CHQDA (or TPA) (mole %)	10	20	30	40	50	60	70
CPT units (mole %)	9.5	21.1	29.4	37.7	47.4	56.6	—
Cl contents (wt %)	1.7	3.6	4.8	6.0	7.3	8.4	9.9

column of carbon tetrachloride and *n*-heptane at 25°C. Infrared spectra were obtained on a Fourier transform infrared (FTIR) spectrometer (Bruker IFS-66) with a KBr pellet at 4 cm^{-1} resolution and over 32 scans. Wide-angle X-ray diffraction (WAXD) patterns were recorded using a diffractometer (Rigaku Denki D/Max3B, Japan) with Ni-filtered CuK$_\alpha$ radiation (λ = 1.5406 Å, 40 kV, 30 mA) in a scan range of $2\theta = 10° \sim 50°$ at a scanning rate of 0.5°/min unless otherwise noted. The samples for WAXD were prepared in the fiber form obtained by melt extrusion using a Koka-type flow tester.

RESULTS AND DISCUSSION

Composition Analysis in Copoly(ET/CPT)

The contents of CPT units and chlorine in copoly(ET/CPT)s were analyzed using a ^{1}H nuclear magnetic resonance (NMR) spectrometer and an EDX equipped in SEM, respectively, and listed in Table I. The contents of CPT units in copoly(ET/CPT)s are slightly different from the amounts of CHQDA and TPA introduced during the preparation. The contents of CPT units in copoly(ET/CPT)s prepared with more than 70 mole % of CHQDA in the feed ratio could not be determined due to their poor solubility to the solvent for ^{1}H NMR analysis.

Thermal Transitions of Copoly(ET/CPT)

Figure 1 shows changes of the melting temperature (T_m) and the crystal transition temperature (T_{ct}) of copoly(ET/CPT)s according to the feed ratio of CHQDA. These transition temperatures are changed according to the composition. Glass transition temperatures (T_g) of copoly(ET/CPT)s prepared with less than 50 mole % of CHQDA are around 75°C and those of copoly(ET/CPT)s prepared with more than 80 mole % CHQDA are around 220°C. Copoly(ET/CPT) (60/40) does not show a melting peak. In the range of 30 ~ 50 mole

% of CHQDA, copoly(ET/CPT)s have two melting peaks. The high melting peak is shifted to higher temperature and the low melting peak to lower temperature as the feed ratio of CHQDA increased. It is therefore considered that these peaks are attributed to the melting of PET (low temperature) and PCPT (high temperature) crystals.

PCPT exhibits T_g, T_{ct}, and T_m at ca. 220, 295, and 352°C, respectively. The results are consistent with those reported by Krigbaum et al.[17] In the case of PPT, T_g and T_m are observed at ca. 267 and 610°C, respectively.[27,28] This indicates that the transition temperatures of PPT are dramatically dropped by introducing the substituent in the main chain. Practically, even a small substituent can reduce the coplanarity of an adjacent rigid rodlike group and increase the diameter or decrease the axial ratio of the rigid rodlike groups.[29] Copoly(ET/CPT) contains PET units as flexible spacers so that it shows lower transition temperatures than PCPT.
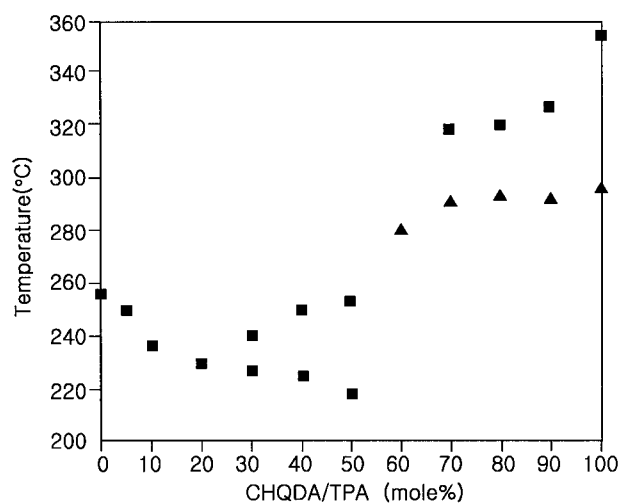

Figure 1   Melting and crystallization transition temperatures of copoly(ET/CPT)s: (■) melting point, and (▲) crystal transition temperature.
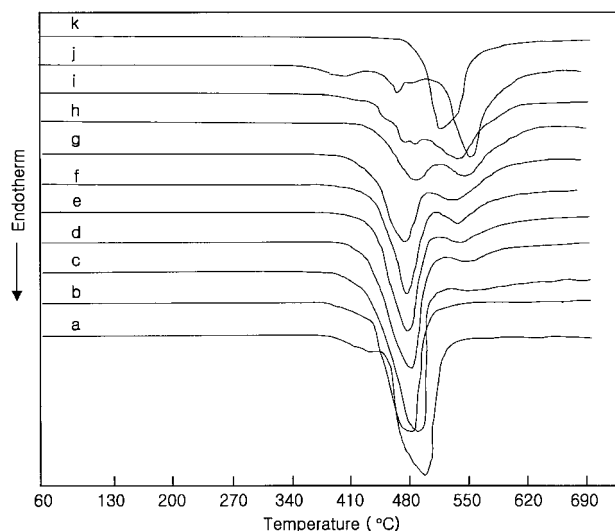
Figure 2 DTG curves of copoly(ET/CPT)s: Feed ratio of CHQDA (a) 5%, (b) 10%, (c) 20%, (d) 30%, (e) 40%, (f) 50%, (g) 60%, (h) 70%, (I) 80%, (j) 90%, (k) PCPT.

When the feed ratio of CHQDA is 60 mole %, only a weak peak around 280°C is observed. Above 70 mole %, two peaks around 290 and 320°C are observed. These two peaks are shifted to higher temperature as the feed ratio of CHQDA increases. They are barely discernable because the asymmetric chloro-1,4-phenylene units are hard to crystallize and their LC transition occurs in the amorphous phase.[30] In this study, isotropic transition temperatures (T_i) of copoly(ET/CPT)s

are not observed up to 370°C, where their thermal decomposition starts.

Thermal Stability of Copoly(ET/CPT)

Figure 2 shows primary differential thermogravimetry (DTG) curves of copoly(ET/CPT)s with the feed ratio of CHQDA. The detailed results of DTG curves are summarized in Table II. The initiation temperature of thermal decomposition (T_i) is the temperature at which the loss of weight is 10 wt %. The maximum rate of thermal decomposition temperature (T_{dm}) is determined from the apex of DTG curve. T_{dm}s and residues at 700°C of copoly(ET/CPT)s are increased with increasing the feed ratio of CHQDA, indicating that the thermal stability of copoly(ET/CPT) is enhanced with increasing CPT units in the main chain. The flame retardance of copoly(ET/CPT) would be improved because of the presence of aromatic units and chlorine substituents in the main chain. The values of LOI for copoly(ET/CPT) (50/50), copoly(ET/CPT) (40/60), and copoly(ET/CPT) (30/70) are 33, 36, and 41%, respectively.

In DTG curves, double peaks are observed for copoly(ET/CPT)s prepared with more than 20 mole % of CHQDA, implying that there are two distinct weight loss stages. These peaks are designated as Peak 1 and Peak 2 for peaks located at low and high temperatures, respectively. PET shows T_{dm} around 490°C, indicating Peak 1 is originated from PET units in copoly(ET/CPT). Peak 2 begins to appear when the feed ratio of

Table II   TGA Results of Copoly(ET/CPT)s

Feed Ratio of CHQDA (or TPA) (mole %)	T_i (°C)	Residue at 700°C (%)	T_{dm}(°C) 1st	T_{dm}(°C) 2nd	E_a (kcal/mole) 1st	E_a (kcal/mole) 2nd
0	437	14.0	491		68.6	
5	462	13.8	492		67.9	
10	438	15.3	483		57.7	
20	452	22.5	487	571	44.1	16.1
30	465	26.7	489	564	47.2	19.0
40	463	30.6	489	552	41.4	21.9
50	469	31.7	488	550	37.8	23.6
60	476	37.9	485	566	33.0	26.9
70	479	38.9	485	561	36.7	25.0
80	476	39.7	482	554	—	25.3
90	483	41.0	478	567	—	35.2
100	484	42.3	—	528	—	34.8

CHQDA is more than 20 mole % and becomes more distinct with increasing the feed ratio of CHQDA. The positions of Peak 1 and Peak 2 move to lower and higher temperatures as the feed ratio of CHQDA increased, respectively. Therefore, it is considered that copoly(ET/CPT) thermally decomposed by two steps due to the different decomposition temperature of PET and LC units. Similarly, two steps of thermal decomposition were reported for segmented polyurethanes,[31–33] in which the first and second stages of the weight loss are assigned mainly due to the decomposition of hard and soft segments, respectively. Since copoly(ET/CPT) has a random sequence distribution for all compositions,[23] it is considered that its decomposition is not affected by the sequence distribution.

For more detailed investigation of the thermal decomposition process of copoly(ET/CPT), two linear relationship regions in TGA curves determined from the regions of Peak 1 and Peak 2 in DTG curves are analyzed. When a polymer thermally decomposes, the weight loss rate is described by the following Arrhenius equation[34]:

$$k_d = [dw/dt] = AW^n e^{-E_a/RT} \qquad (1)$$

where k_d is the thermal decomposition constant, dw/dt is the weight loss rate at a given time, A is the preexponential factor, W is the residual weight of polymer at a given temperature, n is the reaction order, E_a is the activation energy of thermal decomposition, and R is the gas constant. The activation energies of thermal decomposition are determined from a plot of logarithms of reaction rate constant against the reciprocal of temperature and listed in Table II. The activation energy of thermal decomposition of copoly(ET/CPT) for the first stage (Peak 1) is decreased, but that of the second stage (Peak 2) is increased linearly with increasing the feed ratio of CHQDA. This linear relationship supports that copoly(ET/CPT) has the random sequence distribution for all compositions as shown in our previous study.[23] The activation energies of thermal decomposition of LC units obtained are very low compared to those of PET units. This is probably due to chlorohydroquinone units, which can reduce the coplanarity of adjacent LC units and consequently drop the intermolecular interactions.

Crystal Structure of Copoly(ET/CPT)

Figure 3 shows X-ray diffraction patterns of various copoly(ET/CPT)s. PET crystal is clearly ob-
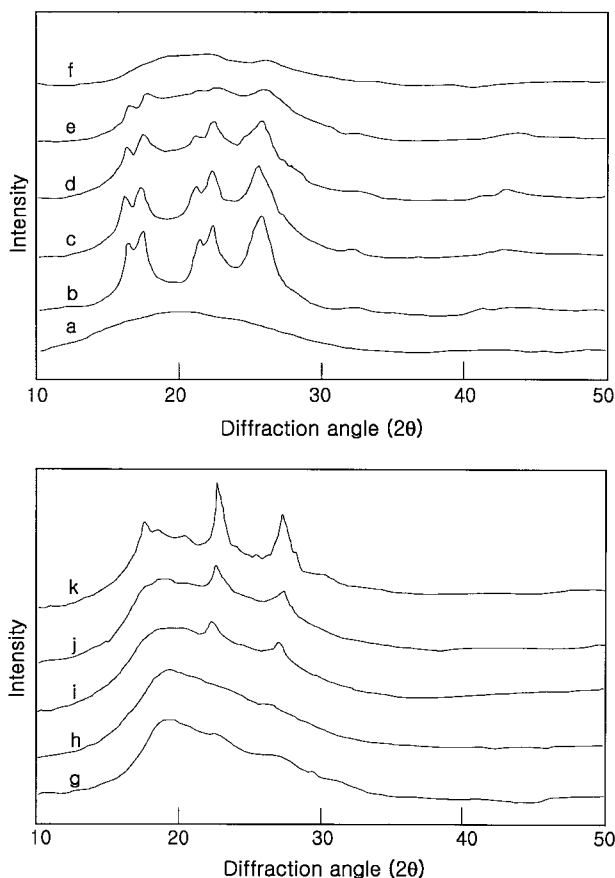

Figure 3   X-ray diffractograms of PET and copoly(ET/CPT)s: (a) amorphous PET, (b) annealed PET at 220°C for 40 h, (c) feed ratio of CHQDA 10%, (d) 20%, (e) 30%, (f) 40%, (g) 50%, (h) 60%, (I) 70%, (j) 80%, (k) 90%.

served for copoly(ET/CPT)s prepared with less than 40 mole % CHQDA, but it disappears above this feed ratio. In the range of 40 ∼ 60 mole % of CHQDA, X-ray diffraction patterns are barely detected except at $2\theta = 20°$. The comonomer concentration in crystal lattice is dependent on the copolymer composition. Above 70 mole % of CHQDA, crystalline structure of PCPT begins to appear. These results are consistent with the thermal transition results obtained by DSC.

Daubeny et al.[35] reported that PET crystal has the lattice constants of $a = 4.56$ Å, $b = 5.94$ Å, $c = 10.75$ Å, $\alpha = 98.5°$, $\beta = 118°$ and $\gamma = 112°$. As shown in Figure 3, the crystalline structure of PET is destroyed with increasing the content of CPT units. Copoly(ET/CPT) (20/80), exhibiting sharp diffraction peaks at $2\theta = 17.33°$, 22.52°, and 27.93°, has the triclinic crystalline structure with the lattice constants of $a = 9.98$ Å, $b = 8.78$

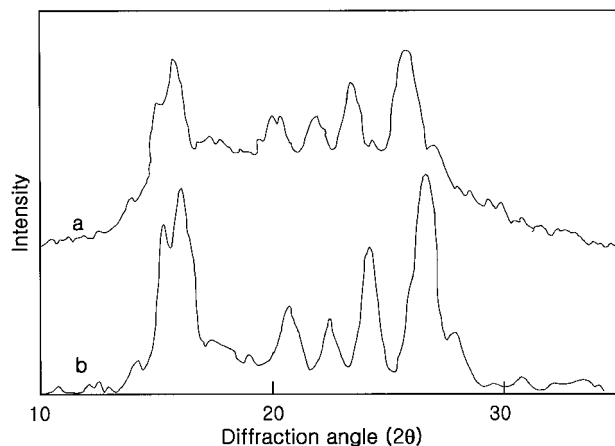**Figure 4** X-ray diffractograms of PCPT at scanning rates of (a) 2°/min and (b) 0.5°/min.

Å, c = 12.93 Å, α = 97.4°, β = 96.1°, and γ = 90.8°. Figure 4 shows X-ray diffraction patterns of PCPT with the scanning rates of 0.5 and 2°/min. The crystalline structure of PCPT is triclinic, which is similar to tetragonal, with the lattice constants of a = 9.51 Å, b = 8.61 Å, c = 12.73 Å, α = 96.8°, β = 95.4°, and γ = 90.8°. The length of chloro-1,4-phenylene is calculated to be 5.51 Å with the lengths of C=C bond in benzene and C—O bond connected to benzene[36] are 1.39 and 1.36 Å, respectively. The length of terephthaloyl unit reported by Blumstein[37] is 7.15 Å. Therefore, the length of CPT unit is calculated to be 12.66 Å. This length is almost the same as that of the c-axis of PCPT, indicating that one repeating unit of PCPT is aligned along with c-axis in the lattice. The degree of crystallinity of PCPT determined

from X-ray diffraction is 14.6% and the density measured is 1.469 g/cm³. The density of amorphous PCPT obtained by quenching is 1.421 g/cm³.[38] Since the number of repeating units in a unit cell calculated from the above results is four, the density of the PCPT crystal calculated from crystal lattice constants is 1.769 g/cm³. Therefore, the density of PCPT calculated from its degree of crystallinity is 1.473 g/cm³, which is very close to the experimental value (1.469 g/cm³).

Annealing of Copoly(ET/CPT)

The properties of random LC copolyesters can be changed by their sequential reorganization into multiblock structures through CISR, which is first proposed by Lenz et al.[39−42] In this study, copoly(ET/CPT) (50/50) was annealed at 220°C in vacuum (0.1 Torr), and changes of its sequence distribution and crystal structure are investigated. In general, an increase of crystallinity and CISR through ester-interchange reaction are expected upon annealing of LC copolyesters. The changes of inherent viscosity and thermal property of copoly(ET/CPT) (50/50) with annealing time are listed in Table III. The inherent viscosity of copoly(ET/CPT) (50/50) is increased with annealing time through the solid-state polymerization. T_m of copoly(ET/CPT) (50/50) is increased from 224.3 to 251.3°C, which is very close to that of PET, after annealing for 40 h. Also, its heat of fusion (ΔH_m) is gradually increased with annealing time. In order to explain this phenomenon, the change of sequence length is traced by ^{1}H NMR spectroscopy. Figure 5 shows the ^{1}H NMR spectrum of copoly(ET/CPT) (50/50). The average

Table III   Thermal Properties of Copoly(ET/CPT) (50/50) Annealed at 220°C in Vacuum

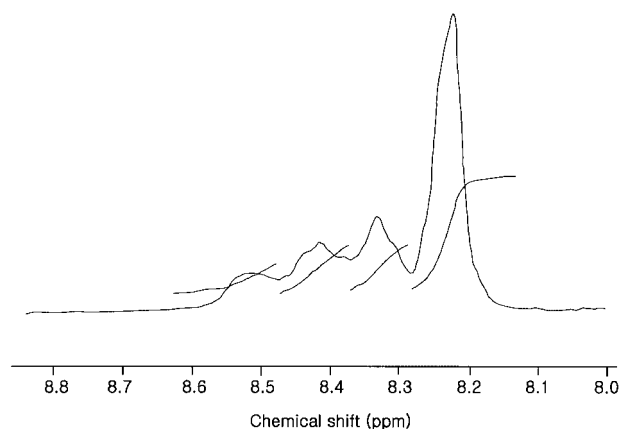| Annealing Time (h)	η_{inh} (dL/g)	T_m (°C)	ΔH_m (cal/g)	T_{dm} (°C) 1st	2nd
0	0.83	—	—	493.0	558.8
1	0.83	224.3	0.42	490.3	555.7
3	0.83	230.7	0.56	490.3	555.0
6	0.87	236.2	0.71	481.5	548.7
10	0.93	240.3	1.11	481.6	551.3
15	1.01	243.3	0.87	478.2	550.2
20	1.04	247.0	1.11	476.8	549.7
30	1.15	254.8	1.68	484.3	559.5
40	1.15	251.3	1.94	481.6	551.1

Figure 5 ^{1}H NMR spectrum of copoly(ET/CPT) (50/50) around 8.4 ppm.

sequence length is analyzed from the proton signals of terephthaloyl units in a range of 8.1 - 8.6 ppm, which split into a multiplet due to three possible environments of terephthaloyl units: ATA, ETE, and ETA, where T, A, and E represent terephthaloyl, chloro-1,4-phenylene, and ethylene units, respectively.[23] Far left (8.48 ∼ 8.64 ppm), far right (8.14 ∼ 8.29 ppm), and two middle peaks (8.29 ∼ 8.38, 8.38 ∼ 8.48 ppm) are ascribed to the proton signals of terephthaloyl units in ETE, ATA, and ETA triad sequences, respectively. Relative concentrations of the three triads are determined from deconvoluted areas of the three signals. The degree of randomness (B) is determined by eqs. (2) and (3):

$$P_{AE} = \frac{P_{ATE}}{2P_{ATA} + P_{ATE}}, \qquad P_{EA} = \frac{P_{ATE}}{2P_{ETE} + P_{ATE}} \quad (2)$$

$$B = P_{AE} + P_{EA} \quad (3)$$

where P_{AE} is the probability of finding an ET unit after an AT unit and P_{EA} the probability of finding an AT unit after an ET unit along a polymer chain. P_{ATE}, P_{ATA}, and P_{ETE} are probabilities of finding ATE, ATA, and ETE triads, respectively. The values of B were 0.93, 0.92, and 0.93 for copoly(ET/CPT) (50/50) annealed for 0, 10 and 40 h, respectively. There is no change in the value of B even after annealing for 40 h within an experimental error range, reflecting that copoly(ET/CPT) (50/50) annealed has almost the random sequence distribution. This indicates that CISR of copoly(ET/CPT) (50/50) is not induced. It

is probably because both components are not crystallized readily and the 50/50 composition is not favorable for CISR. Practically, considering the results of Lenz et al.,[39−42] it is unlikely that copoly(ET/CPT) containing more than 50 mole % of CPT units undergo CISR due to its chemical structure.

Figure 6 shows X-ray diffractograms of copoly(ET/CPT) (50/50) and annealed copoly(ET/CPT) (50/50) at 220°C for 40 h. They show almost the same X-ray diffractogram, indicating that there is no more crystalline structure developed during the annealing. However, in order to explain an slight increase in ΔH_m of copoly(ET/CPT) (50/50), the conformational change of PET units are investigated using IR spectroscopy. In this study, the absorbance ratio of 1337/1578 cm^{-1} is employed to analyze the *trans* isomer content in PET units.[43] Bands at 1337 and 1578 cm^{-1} are ascribed to CH$_2$ wagging(*trans*) and C=C benzene, respectively. When PET is annealed, the absorbance at 1337 cm^{-1} increases but that at 1578 cm^{-1} is not changed.[44] Figure 7 shows the change of the absorbance ratio with annealing time for copoly(ET/CPT) (50/50). The absorbance ratio increases with annealing time, indicating that ΔH_m of copoly(ET/CPT) (50/50) increases as its *trans* isomer content increases in PET units, although it is not detected by X-ray diffraction. T_{dm} is not changed significantly upon annealing as shown in Table III.

CONCLUSIONS

In this study, LC copoly(ET/CPT) was successfully prepared, and its thermal properties and
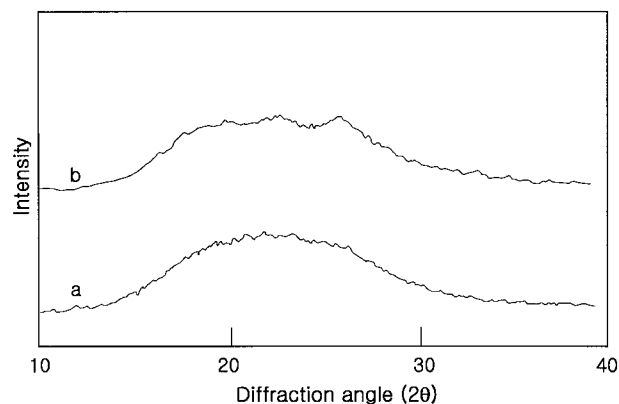

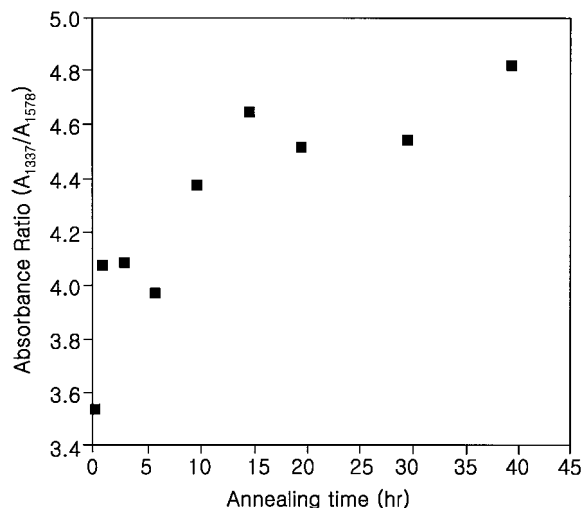**Figure 6** X-ray diffractograms of copoly(ET/CPT) (50/50) (a) before and (b) after annealing at 220°C for 40 h.

Figure 7   Absorbance ratio of 1337/1578 cm^{-1} for co-poly(ET/CPT) (50/50) with annealing time at 220°C.

crystalline structure were investigated with the content of the chlorohydroquinone substituent. The thermal transition temperatures of copoly(ET/ CPT) were changed with the composition. T_is of copoly(ET/CPT)s were not observed up to 370°C, where their thermal decomposition started. Copoly(ET/CPT) thermally decomposed by two steps due to the different decomposition temperature of PET and LC units. Residues at 700°C and LOI values of copoly(ET/CPT) were almost proportional to its chlorine content. The activation energy of thermal decomposition of LC units was very low compared to that of PET units due to chlorohydroquinone units. Crystal structure of copoly(ET/CPT) (20/80) was of triclinic system with the lattice constants of a = 9.98 Å, b = 8.78 Å, c = 12.93 Å, α = 97.4°, β = 96.1°, and γ = 90.8°. When copoly(ET/CPT) (50/50) was annealed at 220°C in vacuum, its molecular weight was increased with annealing time due to the solid-state polymerization but CISR was not observed. The slight increase in ΔH_m was attributed to the increase in the *trans* isomer content of PET units.

REFERENCES

 1. Watanabe, J.; Krigbaum, W. R. Macromolecules 1984, 17, 2288.

 2. Percec, V., Nava, H.; Jonsson, H. J Polym Sci Polym Chem Ed 1987, 25, 1943.
 3. Chen, M. S.; Lee, C.; Chang, N. H.; Chang, B. C.; Tsai, H. B. Polymer 1989, 30, 1472.
 4. Chang, S.; Han, C. D. Macromolecules 1996, 29, 2383.
 5. Gomez, M. A.; Roman, F.; Marco, C.; delPino, J.; Fatou, J. G. Polymer 1997, 38, 5307.
 6. Chang, S.; Han, C. D. Macromolecules 1997, 30, 1656.
 7. Martins, P. C. A.; Novack, K. M.; Gomes, A. S. Polymer 1998, 39, 6941.
 8. Bello, P.; Bello, A.; Riande, E.; Heaton, N. J. Macromolecules, 2001, 34, 181.
 9. Jackson, W. J.; Morris, J. C. U.S. Patent 4,169,933, 1979.
10. Calundan, G. W. U.S. Patent 4,184,996, 1980.
11. East, A. J. U.S. Patent 4,318,841, 1982.
12. Jackson, W. J. Brit Polym J 1980, 12, 154.
13. Jin, J.-I.; Choi, E.-J.; Kang, C.-S. J Polym Sci, Polym Chem Ed 1989, 27, 2291.
14. Cai, R.; Samulski, E. T. Macromolecules 1994, 27, 135.
15. Schaefgen, F. R. U.S. Patent 4,075,262, 1978.
16. Jin, J.-I.; Choi, E.-J.; Jo, B.-W. Macromolecules 1987, 20, 934.
17. Krigbaum, W. R.; Hakemi, H.; Kotek, R. Macromolecules 1985, 18, 965.
18. Shibaev, V. P.; Plate, N. B. Makromol Chem 1980, 181, 1381.
19. Gaudiana, R. A.; Minns, R. A.; Sinta, R.; Weeks, N.; Rogers, H. G: Prog Polym Sci 1989, 14, 47.
20. Harkness, B. R.; Watanabe, J. Macromolecules 1991, 24, 6759.
21. Watanabe, J.; Harkness, B. R.; Sone, M.; Ichimura, H. Macromolecules 1994, 27, 507.
22. Aguilera, C.; Luderwald, I. Macromol Chem 1978, 179, 2817.
23. Lee, D. M.; Ha, W. S.; Youk, J. H.; Yoo, D. I. Fibers and Polymers 2001, 2, 86.
24. Muramatsu, H.; Krigbaum, W. R. J Polym Sci, Polym Phys Ed 1986, 24, 1695.
25. Muramatsu, H.; Krigbaum, W. R. J Polym Sci, Polym. Phys Ed 1987, 25, 803.
26. Ober, C. K.; Lenz, R. W. Macromolecules 1983, 16, 1034.
27. Jin, J.-I. Polymer (Korea) 1981, 5, 349.
28. Jin, J.-I.; Kang, C.-S. Prog Polym Sci 1997, 22, 937.
29. Ober, C. K.; Jin, J.-I.; Lenz, R. W. Liquid Crystal Polymer, Vol. 1; Springer-Verlag: Berlin, 1984.
30. Noel, C.; Friedrich, C.; Laupretre, F.; Billiard, J.; Bosio, L.; Strazielle, C. Polymer 1984, 25, 263.
31. Ferguson, J.; Petrovic, Z. Eur Polym J 1976, 12, 177.

32. Petrovic, Z. S.; Zavargo, Z.; Flynn, J. H.; MacKnight, W. J. J Appl Polym Sci 1994, 51, 1087.

33. Lin, C.-K.; Kuo, J.-F.; Chen, C.-Y. Eur Polym J 2000, 36, 1183.

34. Rabek, J. F. Experimental Methods in Polymer Chemistry; John Wiley & Sons: New York, 1980; p 551.

35. Daubeny, R. deP.; Bunn, C. W.; Brown, C. J. Proc Roy Soc (London) 1954, A226, 531.

36. Weast, R. C. CRC Handbook of Chemistry and Physics, 60th ed.; CRC Press: Boca Raton, FL, 1979; p F-217.

37. Blumstein, A. Polymer Science and Technology; Plenum Press: New York, 1985; p 172.

38. Chang, D.; Miyasaka, K.; Ishikawa, K. Sen-I Gakkaishi 1974, 30, 6.

39. Lenz, R. W.; Go, S. J Polym Sci, Polym Chem Ed 1973, 11, 2927.

40. Lenz, R. W.; Go, S. J Polym Sci, Polym Chem Ed 1974, 12, 1.

41. Lenz, R. W.; Schuler, A. N. J Polym Sci, Polym Symp. 1978, 63, 343.

42. Lenz, R. W.; Jin; J.-I.; Feichtinger, K. A. Polymer 1983, 24, 327.

43. Aharoni, S. M. Makromol Chem. 1978, 179, 1867.

44. Baird, D. G. Polymeric Liquid Crystals; Blumstein, A., Ed.; Plenum Press: New York, 1983; pp 119–143.