Interchange Reaction Kinetics and Sequence Distribution of Liquid Crystalline Poly(ethylene terephthalate-*co*-2(3)-chloro-1,4-phenylene terephthalate)

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Abstract: Liquid crystalline (LC) poly(ethylene terephthalate-*co*-2(3)-chloro-1,4-phenylene terephthalate) [copoly(ET/ CPT)] was prepared using poly(ethylene terephthalate) (PET) as a flexible spacer, terephthalic acid (TPA), and chlorohydro-quinone diacetate (CHQDA). All reactions involved in the copolymerization were investigated using some model compounds: TPA was used for acidolysis, diphenylethyl terephthalate (DPET) for interchange reaction between PET chains, and di-*o*-chlorophenyl terephthalate (DOCT) and di-*m*-chlorophenyl terephthalate (DMCT) for interchange reaction between PET and rigid rodlike segments. Activation energies obtained for the acidolysis of PET with TPA and for interchange reaction of PET with DPET, DOCT, and DMCT were 19.8 kcal/mole, 26.5 kcal/mole, 60.2 kcal/mole, and 45.9 kcal/mole, respectively. This result supports that the copolymerization proceeds through the acidolysis of PET with TPA first and subsequent polycondensation between carboxyl end group and CHQDA or acetyl end group, which is formed from the reaction of CHQDA and TPA. Also, it was found that ester-interchange reaction can be influenced by the steric hindrance. Copoly(ET/ CPT)s obtained had ethylene acetate end groups formed from acetic acid and hydroxy ethylene end groups and showed almost the random sequence distribution for all compositions.

Keywords: Liquid crystalline copoly(ET/CPT), Model compounds, Acidolysis, Interchange reaction, Sequence distribution

Introduction

Thermotropic LC polyesters with nematic phases have difficulties in fiber spinning and plastic molding because of their high melting points. In order to reduce the glass transition temperature and melting point without losing their own physical properties considerably, a variety of chemical structure modifications and/or composition changes have been attempted. The modification of chemical structure was mostly conducted by introducing flexible spacers[1-4], kinked monomers such as *m*-hydroquinone, isophthalic acids, bisphenol A, 4.4'-biphenol, and 6-hydroxy-2-naphthoic acids[5-7], or substituted monomers such as substituted hydroquinones in the main chain[8-10]. Among them, thermotropic LC polyesters having PET units as a flexible spacer[11-13] have drawn great attention from the viewpoints of scientific interest and commercial application since Jackson and Kuhfuss[14] first prepared poly(ethylene terephthalate-co-*p*-hydroxybenzoic acid) by the reaction of PET with *p*-acetoxybenzoic acid using Hamb's method[15]. Schaefgen[8] prepared similar LC copolyesters including copoly(ET/CPT) by the reaction between PET, chloro or methyl substituted hydroquinone, and TPA. The copolyesters contained 15-70 wt% of PET units as a flexible spacer. Symmetrically disubstituted hydroquinones raise the melting points of resulting polymers, while monosubstituted compounds lower them. The fibers readily obtained by spinning their anisotropic melts exhibit high orientation, high initial modulus, and low shrinkage when heated to 160°C. However, the formation mechanism of these LC copolyesters especially in the initial stage has not been extensively studied. On the other hand, it is known that the final properties of these LC copolymers are strongly dependent on the sequence distribution of rigid rodlike segments. There is also reported that melt processible LC copolymers have the random sequence distribution[16,17].

In this study, LC copoly(ET/CPT) was prepared by acidolysis of PET with TPA and polycondensation of carboxyl and acetate groups of CHQDA. The formation mechanism of copoly(ET/CPT), especially in the initial stage, was systematically studied with some model compounds using viscosity measurement and ^{1}H NMR spectroscopy. Its sequence distribution was analyzed using ^{1}H NMR spectroscopy.

Experimental

Synthesis of Chlorohydroquinone Diacetate (CHQDA)

A mixture of 1 mole of chloro-hydroquinone (CHQ, mp: 101~102°C), 2.5 moles of acetic anhydride, and a drop of sulfuric acid was charged into a two-neck flask equipped with a mechanical stirrer. The reactants were slowly heated to 140°C and then refluxed for 2 hrs. The reaction was traced by thin layer chromatography (TLC). Ethyl acetate/n-hexane (1/1, v/v) was used as a TLC solvent. The reaction was run until the CHQ spot was not detected. The precipitate obtained

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by pouring the reaction solution into cold water were stirred in a mixture of 5% aq. NaOH solution and n-hexane (1/1, v/v) at 70°C for 1 hr. Then, *n*-hexane phase was separated and cooled down to room temperature to precipitate chlorohydroquinone diacetate (CHQDA, mp: 71°C). This acetylation reaction is as follows:
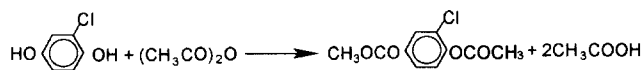

Synthesis of Rigid Model Compounds

A mixture of terephthaloyl chloride, *o*-chlorophenol [(*o*-CP), or *m*-chlorophenol(*m*-CP), or phenylethyl alcohol (PA)], and pyridine (1/2/2.1, mole ratio) was charged into a round bottom flask equipped with a stirrer and a condenser under the dried nitrogen. Benzene was added as a solvent and then the reaction mixture was stirred at room temperature for 3 hrs. After reaction, the product was filtered and washed with pyridine.

Synthesis of Copoly(ET/CPT)

A mixture of PET and the same mole% of CHQDA and TPA completely dried at 60°C under reduced pressure (0.5 Torr) was placed in a flask equipped with a mechanical stirrer, a nitrogen inlet, and a receiver for applying vacuum. The reactants were heated to 280°C by 10°C/min under the nitrogen. As the temperature increased, the reactants were melted and acetic acid, formed by the reactions of CHQDA with TPA and PET, was vigorously evolved. After 1 hr, the temperature was raised again to 290°C *in vacuo* (0.1 Torr), and maintained for predetermined time to obtain the final products.
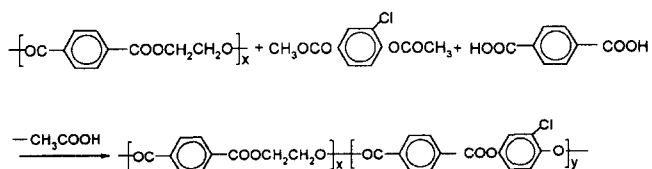
Interchange Reaction

30 g of PET were charged into the reaction vessel equipped with a stirrer under the dried nitrogen. PET was melted at given temperature and then 10 mole% of model compound was introduced into the reaction vessel. An aliquot of reaction product was taken out after given time interval. All samples were washed with tetrachloroethane before analysis.

Measurements of Viscosity and Sequence Length Distribution

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. 5% solution of copolymer in CF₃COOD/CDCl₃ (1/1, v/v) was prepared to

determine the sequence length distribution using a Bruker 300 MHz NMR spectrometer.

Results and Discussion

Interchange Reaction Kinetics

Several reactions can occur in the initial stage of this copolymerization system. Acidolysis between PET and TPA, interchange reactions between PET and CHQDA, and between PET and the resulting rigid rodlike units, and also irregular thermal degradation of ester groups in PET should be taken into consideration. The condensation reaction between carboxyl and hydroxy end groups[18] was ignored in this study because it was restrained in our experimental condition. Zimmerman[19] reported that thermal degradation of PET follows the first-order kinetics. Devaux *et al.*[18] demonstrated that interchange reaction of PET with all bifunctional reactants used follows the second-order kinetics. If the thermal degradation and the interchange reaction occurs simultaneously, the depolymerization at the initial stage is represented as follows:

$$-\frac{dP}{dt} = k_{deg}P + k_2 P[A] \tag{1}$$

where k_{deg} is the rate constant of thermal degradation, k_2 is the rate constant of interchange reaction, P is the concentration of ester groups, and $[A]$ is the concentration of model compounds. All the model compounds used here are bifunctional. Assuming that the thermal degradation of model compounds and reactions between the degraded products and PET are negligible, $[A]$ can be regarded as a constant. Since the reaction between PET and model compounds does not change the concentration of functional chain end groups, the reaction is of the first-order, which has the apparent reaction rate constant k'[18].

$$-\frac{dP}{dt} = P(k_{deg} + k_2[S]) = k'P \tag{2}$$

Integrating equation (2),

$$-\ln(P/P_0) = k't \tag{3}$$

k' is the slope of the plot of $-\ln(P/P_0)$ versus time t. The reaction rate constant, k_2, can be calculated from equation (4).

**Table 1.** Interchange reaction constants of the between PET and some model compounds

Temperature (°C)	PET melt density (g/ml)*	$[A] \times 10^3$ (mole/ml)	$k_{deg} \pm 10^{-6}$ (min⁻¹)
270	1.25	1.3	4.7
280	1.23	1.3	9.0
290	1.21	1.3	16.8

*Measured by Koka flow tester.

$$k_2 = \frac{k' - k_{deg}}{[A]} \tag{4}$$

Zimmerman et al.[19] reported that the thermal degradation rate constants of PET are 25.2×10^{-6} min^{-1}, 47.4×10^{-6} min^{-1}, and 106.8×10^{-6} min^{-1} for a closed system, and 9.0×10^{-6} min^{-1}, 16.8×10^{-6} min^{-1}, and 30.6×10^{-6} min^{-1} for an open system at 280°C, 290°C, and 300°C, respectively. Because the initial interchange reaction in our experiment was carried out under the open system, k_{deg} values obtained by Zimmerman et al.[19] in the open system were used in this study. $k_{deg} = 4.7 \times 10^{-6}$ min^{-1} was used as k_{deg} at 270°C obtained by extrapolating Zimmerman's data. Interchange reaction constants between PET and model compounds are listed in Table 1.

Both apparent reaction rate constant (k) and real reaction rate constant (k_2) were also obtained according to the method of Zimmerman et al.[19]. The concentration of ester groups (P) in reacted PET was calculated from its number average molecular weight (M_n) according to equation (5). M_n was determined by the intrinsic viscosity ([η]) and Mark-Houwink equation[20].
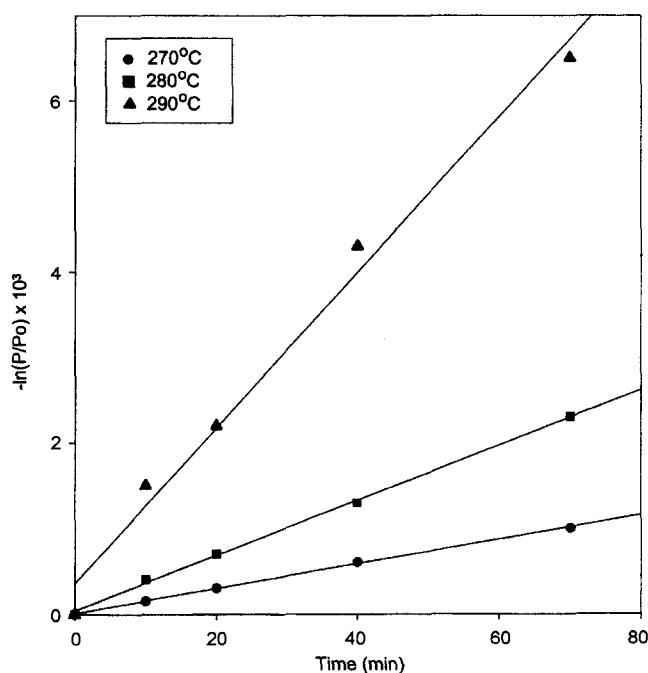
$$P = \frac{1}{M_n} \times DP \times (density) \times 2 \tag{5}$$

$$[\eta] = 1.27 \times 10^{-4} \times (M_n)^{0.86} \tag{6}$$

The number of ester groups in PET is twice as much as that of degree of polymerization of PET[21]. Figures 1 and 2 show changes of the ester linkage concentration with time as the interchange reaction between PET and model compounds proceeds. The reaction between PET and TPA (acidolysis) is very fast and reaches the equilibrium within 40 min, as shown in Figure 2, but the reactions between PET and the other compounds are somewhat slow and exhibits a linear relationship in this experimental condition as shown in Figure 1 for DOCT. The apparent rate constants at the initial reaction stage are summarized in Table 2.

Figure 3 is the plot of reaction rate constants against reciprocal temperature, whose slopes give the activation energies of corresponding reactions by the following Arrhenius equation (equation (7)):

Figure 1. Plots of $\ln(P/P_o)$ vs. interchange reaction time of PET and DOCT.
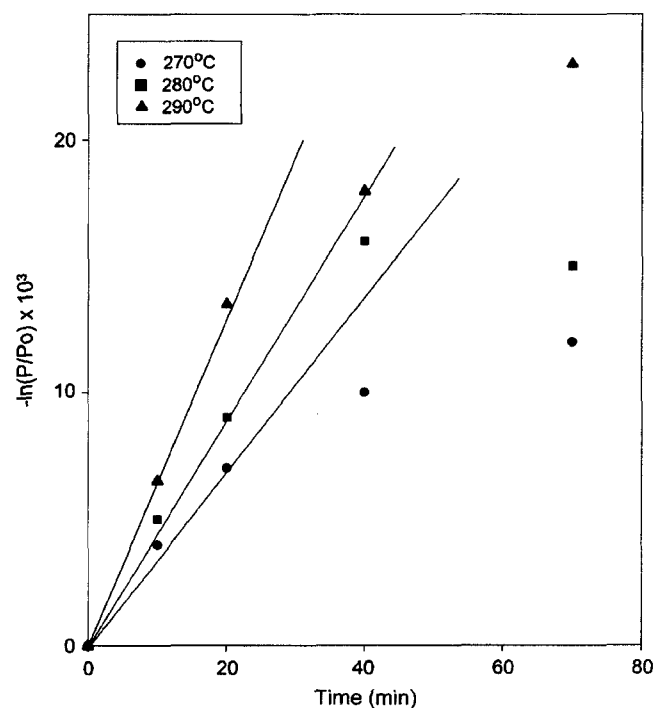
Figure 2. Plots of $\ln(P/P_o)$ vs. interchange reaction time of PET and TPA.

Table 2. Initial apparent reaction rate constants between PET and some model compounds

| Temperature (°C)	Initial apparent reaction rate constants $\times 10^{-5}$ (min^{-1})				
	DOCT	DMCT	TPA	CHQDA	DPET
270	1.450	2.515	1.650	6.582	1.094
280	3.194	5.293	2.355	1.611	1.871
290	8.953	1.089	3.242	4.212	2.658

$$\ln k = \ln A - E_a/RT \tag{7}$$

where k is the rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is the absolute temperature. The activation energies of interchange reaction obtained from equation (7) were listed in Table 3. Activation energy of the acidolysis was 19.8 kcal/mole, and the value was almost the same as those reported by Yoo and Ha[21] (19.3 kcal/mole) and Devaux *et al.*[22] (23.6 kcal/mole). However, different activation energies of interchange reaction were reported by several researchers. Yoo and Ha[21] obtained 54.4 kcal/mole by using benzylbenzoate, Devaux *et al.*[22] obtained 59.5 kcal/mole by using butylbenzoate, and Dröscher and Schmidt[23] obtained 20.3 kcal/mole by using oligoester not having hydroxyl groups. Kim[24] reported that activation energy of interchange reaction between PET and poly(butylene terephthalate) in the melt state is 10.6 kcal/mole. We obtained 26.5 kcal/mole

of activation energy of interchange reaction of PET with DPET. It is likely that the activation energies of interchange reaction reported are dependent on the reaction system. Particularly, it is worth noting that the steric hindrance of model compounds in the interchange reaction may be one of reasons for the difference. Between the activation energies of interchange reaction of DOCT and DMCT with PET, DMCT shows higher activation energy and lower reaction rate than DOCT. This result strongly supports that interchange reaction is influenced by the steric hindrance. The activation energy of interchange reaction between PET and CHQDA is very high and its reaction rate is very slow compared with DOCT and DMCT. This result is in good accordance with that reported using ethylbenzoate and phenyl acetate by Jackson and Kuhfuss[14]. Yokoyama *et al.*[25] reported that activation energies of polycondensation reaction of PET are 18.5 kcal/mole and 40.0 kcal/mole for
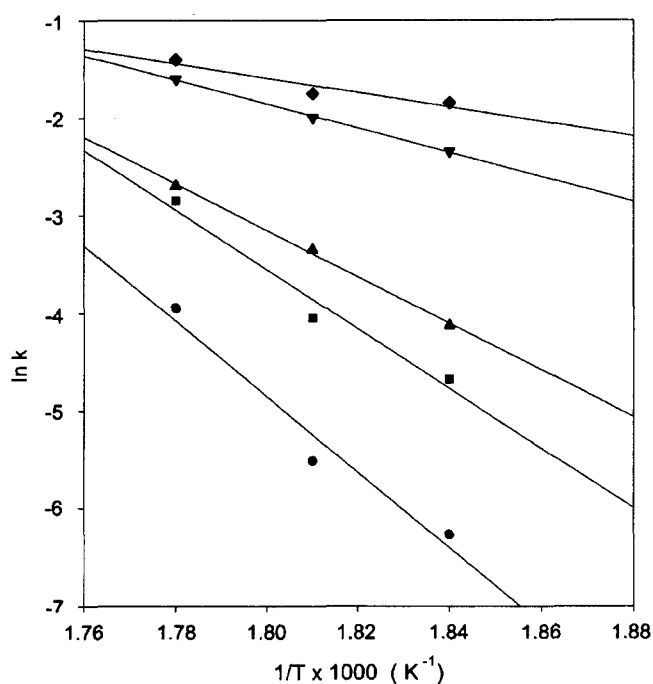

Figure 3. Arrhenius plot of interchange reaction of PET with some model compounds (●: CHQDA, ■: DOCT, ▲: DMCT, ▼: DPET ◆: TPA).
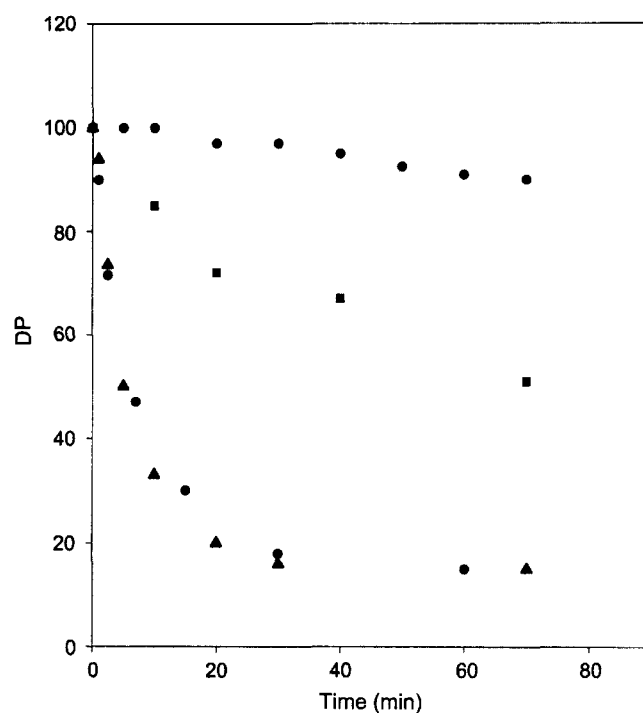
Figure 4. Degree of polymerization of PET vs. interchange reaction time with some model compounds (●: PET, ■: CHQDA, ▲: TPA, ▼: TPA/CHQDA).

Table 3. Kinetic parameters of interchange reaction between PET and model compounds

Model compounds	Rate constant(k_2) $\times 10^2$ (min^{-1})			E_a (kcal/mole)	$\ln A$ (min^{-1})
	270°C	280°C	290°C		
TPA	12.33	17.42	23.63	19.8	16.2
DOCT	0.08	0.18	0.56	60.2	50.9
DMCT	0.16	0.34	0.71	45.9	38.0
CHQDA	0.01	0.05	0.18	87.8	72.2
DPET	8.05	13.70	19.15	26.5	21.9
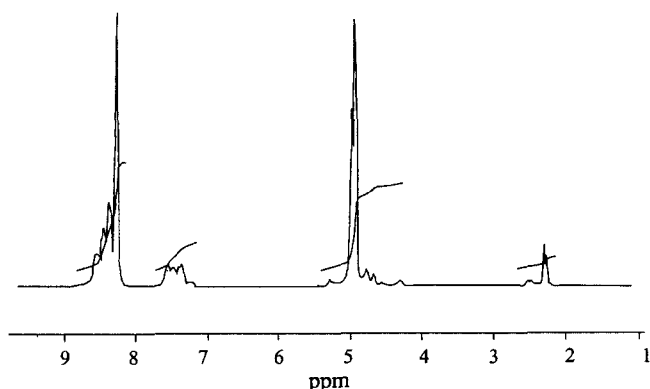
Figure 5. ¹H-NMR spectrum of copoly(ET/CPT) (70/30).

catalytic and non-catalytic reaction, respectively. In the case of DPET, which has similar structure to PET, the activation of interchange reaction is lower than 40.0 kcal/mole. Considering both the structure similarity of PET to DPET and the resulting activation energy values, it is expected that the interchange reaction proceed readily during the polycondensation.

In order to confirm the reactivity of TPA and CHQDA, they were reacted at 290°C. As soon as they were mixed, the

reaction started immediately and acetic acid was evaporated and eventually the reaction mixture was solidified within 20 minutes. Also, 10 mole% of CHQDA and TPA were added onto the PET melt at the same temperature to confirm the reactivity of a PET/CHQDA/TPA ternary system. The chain scission of PET by acidolysis became slightly slower when CHQDA and TPA were poured together into the PET melt than when only TPA was added, as shown in Figure 4. This indicates that the acidolysis by TPA readily occurs at the initial stage of interchange reaction and then the condensation reaction between carboxyl end group and CHQDA (or acetyl end group which is formed by the reaction of TPA and CHQDA) proceeds.

Sequence Length Distribution

The average sequence length of copoly(ET/CPT) was investigated by ¹H-NMR spectroscopy. Figure 5 shows ¹H-NMR spectrum of copoly(ET/CPT) (70/30). The peaks at 4.8~5.0 ppm are assigned to the protons of ethylene units, 8.1~8.6 ppm to terephthaloyl units, and 7.2~7.6 ppm to chloro-1,4-phenylene units, respectively. The peaks at 2.1 ppm were assigned to the protons of ethyleneacetyl formed by the reaction of acetic acid and hydroxyl end groups in PET. The average sequence length was analyzed from the

Table 4. Triad sequences of copoly(ET/CPT)

	Structure of triads	Chemical shift of proton (ppm)	Remarks
ETE	—OCH₂CH₂OOC⟨◯⟩COOCH₂CH₂O—	8.48~8.64	benzene ring protons
ETA	—OCH₂CH₂OOC⟨◯⟩COO⟨◯⟩O— (Cl) —OCH₂CH₂OOC⟨◯⟩COO⟨◯⟩O— (Cl)	8.29~8.48	benzene ring protons of ethylene unit side 8.38~8.29 benzene ring protons of CHQ unit side 8.48~8.38
ATA	—O⟨◯⟩OOC⟨◯⟩COO⟨◯⟩O— (Cl...Cl) —O⟨◯⟩OOC⟨◯⟩COO⟨◯⟩O— (Cl...Cl) —O⟨◯⟩OOC⟨◯⟩COO⟨◯⟩O— (Cl...Cl)	8.14~8.29	benzene ring protons

Table 5. Sequence distribution of copoly(ET/CPT)

Mole % of CHQDA/TPA in feed	Mole % of CPT in copoly(ET/CPT)	P_{ATA}	P_{ATE}	P_{ETA}	P_{ETE}	$<L_{AT}>$	$<L_{ET}>$	B
50/50	47.4	0.279	0.232	0.232	0.254	2.22	2.10	0.927
40/60	37.7	0.203	0.226	0.226	0.362	1.89	2.59	0.915
30/70	28.6	0.122	0.193	0.193	0.483	1.62	3.45	0.908

proton signals split into multiplets due to three possible environments for terephthaloyl units: ATA, ETE, and ETA, where T, A, and E represent terephthaloyl, chloro-1,4-phenylene, and ethylene units, respectively. Chloro-1,4-phenylene group induces the deshielding effect on the protons of terephthaloyl groups[26]. Therefore, the protons of terephthaloyl groups in ATA triad are more deshielded than those of ETA one. All the assignments of the peaks ascribed to terephthaloyl units are listed in Table 4. In addition, the triad sequences of this copolymer and the sequence distributions according to the mole fraction of the CHQDA are given in Table 5.

The degree of randomness(B) and the number-average sequence length of AT ($<L_{AT}>$) and ET ($<L_{ET}>$) are determined by equations (9) and (10):

$$P_{AE} = \frac{P_{ATE}}{2P_{ATA} + P_{ATE}}, \quad P_{EA} = \frac{P_{ATE}}{2P_{ETE} + P_{ATE}} \quad (8)$$

$$B = P_{AE} + P_{EA} \quad (9)$$

$$<L_{AT}> = \frac{1}{P_{AE}}, \quad <L_{TE}> = \frac{1}{P_{EA}} \quad (10)$$

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.

All copoly(ET/CPT)s shows almost the random sequence distribution. When the average sequence length of the rigid rodlike units (AT) is ca. 2 so that the average number of sequentially bonded benzoyl groups is ca. 3~5, the degree of randomness approaches therefore to unity. This indicates that interchange reaction occurs not only between flexible PET chains but also between PET and rigid chloro-1,4-phenylene terephthalate oligomer units.

Acknowledgement

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