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Sequence distribution and crystal structure of poly(ethylene/trimethylene terephthalate) copolyesters

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Abstract

The sequence distribution and the crystal structure of copolyesters synthesized from ethylene glycol, 1,3-propanediol, and dimethyl terephthalate with different molar volume ratios were investigated in this study. The triad sequence probabilities of ethylene/trimethylene terephthalate were characterized from the aromatic quaternary carbons by ^{13}C NMR. The composition of the copolyesters was determined from the aromatic quaternary carbons by ^{13}C NMR, and the methylene protons by ^{1}H NMR. Results show that 1,3-propanediol reacted faster with terephthalic acid in copolyester polymerization than ethylene glycol. The difference in monomer reactivity is significant in the polymerization. Although the constitutional units revealed a random distribution in the molecular chain by ^{13}C NMR, crystallites formed across the full range of ethylene glycol/1,3-propanediol composition by use of differential scanning calorimetry, a hot stage polarizing microscope, and a wide angle X-ray diffraction method. The WAXD deconvolution results show that the major constitutional repeating unit in the molecular chain dominates the crystal structure as a host crystal. The crystal structure was examined by a scanning electron microscope after a solvent etching. Photomicrographs show that the random distribution of the third constitutional unit in the molecular chain of copolyester significantly disturbs the host crystal formation and lamellar orientation.

Keywords: Poly(ethylene/trimethylene terephthalate) copolyester; Sequence distribution; WAXD deconvolution

1. Introduction

In a random copolymer chain, two and more different types of chemical units are joined at random. Numerous experiments have verified that crystallites can form in random copolymers under some circumstances. Flory explained crystallization in random copolymers [1]. Wunderlich introduced kinetic constraints into the Flory model [2]. Based on his 'cold crystallization' model, only nearest neighbors are capable of crystallizing without the redistribution of sequences of like units, while the other types of units incorporated in the crystal are treated as defects. In contrast to the models of homopolymer sequence matching, Windle suggested that the crystallinity in some random copolymers may result from the segregation and lateral matching of similar yet random sequences of the neighboring molecules [3]. Thus, the crystals themselves contain mixtures of the different monomer units, and lack periodicity in the chain direction. They are called non-period-layer crystallites.

A large number of sequence analyses of copolyesters, such as poly(ethylene terephthalate) and poly(butylene terephthalate) [4,5], poly(ethylene terephthalate-*co*-ethylene 5-sodiosulfoisophthalate) [6], poly(ethylene/teramethylene terephthalate) [7], poly(oxybenzoate-*p*-trimethylene terephthalate) [8], and poly(ethylene 2,6 naphthalate)/poly(ethylene terephthalate) [9], have been reported by the selection of the suitable solvent and temperature, and by the use of a nuclear magnetic resonance spectrometer. The chemical constitution and comonomer composition and distribution of poly(ethylene terephthalate-*co*-ethylene 5-sodiosulfoisophthalate) copolymers were assessed by ^{1}H NMR and ^{13}C NMR spectroscopy [10]. Sequence information in copolyesters synthesized from ethylene glycol, 1,4-butanediol, and methyl terephthalate using a ^{13}C NMR

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and the relative amounts of ethylene glycol and 1,4-butanediol in the polyester based on the resonance intensities of ethylene glycol and 1,4-butanediol were reported [7]. The EG/DDP molar fractions of poly(ethylene terephthalate)-*co*-poly(ethylene DDP)s were quantified with the resonance intensities of EG and DDP protons using a ^{1}H NMR [11]. Several theories on the melting temperature of the copolymers have been reported [12,13]. The Gibbs–Thomson equation on the melting temperature of a polymer is well-known [14] and has been applied [15,16]. The relationship between the sequence distribution and the melting temperature for copolymers has been investigated [5,10,17].

There are significant amounts of researches on the crystallization and melting behaviors of poly(ethylene terephthalate) (PET) and poly(trimethylene terephthalate) (PTT) homopolymers [18–26]. Poly(ethylene terephthalate) has two methylene units, and poly(trimethylene terephthalate) has three methylene units in their chemical structure. Both poly(ethylene terephthalate) and poly(trimethylene terephthalate) are members of the thermoplastic aromatic polyester family. Due to various numbers of methylene groups among these polyesters resulting in different chain structures, the chain flexibility of poly(trimethylene terephthalate) should be higher than that of poly(ethylene terephthalate). This fact reflects the difference in the working of chain folding between poly(ethylene terephthalate) and poly(trimethylene terephthalate). Huang reported that the chain folding for nucleation in poly(trimethylene terephthalate) was ca. 4.8 kcal/mol, which is much lower than that of poly(ethylene terephthalate) (ca. 10 kcal/mol) [27,28]. The crystallization rate of poly(trimethylene terephthalate) is faster than that of poly(ethylene terephthalate) [29]. Ward found that poly(trimethylene terephthalate) exhibits better elastic recovery than poly(ethylene terephthalate) [30]. There is a great desire for incorporating a third constitutional unit into the poly(ethylene terephthalate) polymer in order to overcome its undesirable properties. In this paper, we have focused on copolyesters synthesized from ethylene glycol, 1,3-propanediol, and dimethyl terephthalate. The sequence of constitutional units in the molecular chain, and crystallization including the crystal structure of poly(ethylene/trimethylene terephthalate) copolyester were studied.

2. Experimental

2.1. Material preparation

Poly(ethylene/trimethylene terephthalate) (ET) copolyesters were synthesized, with different molar volume ratios, from ethylene glycol (EG), 1,3-propanediol (PDO), and dimethyl terephthalate (TP). The molar volume feed ratios of EG/PDO were 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, and 0/100, respectively. The experimental copolyesters were denoted as ET100 (PET), ET90, ET80, ET70, ET60, ET50, ET40, ET30, ET20, ET10, and ET0 (PTT), respectively. Copolyesters were synthesized by a two-stage reaction sequence (Fig. 1). In the first stage reaction, between dimethyl terephthalate and ethylene glycol/1,3-propanediol was catalyzed through the addition of Ti(O(Bu)). The ester interchange was conducted by stirring for 3 h at 190–220 °C. In the second stage, a further catalyst, Ti(O(Bu))/Sb_2O_3, was added to the mixture. The polycondensation was carried out by stirring for 4 h at 270–280 °C under a vacuum of ca. 60 Pa.

2.2. Characterization

The character and the average composition of the ET copolyesters were determined by a nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR), VARIAN UNITYINOVA 500 NMR spectrometer (Table 1). Samples were dissolved in deutero trifluoroacetic acid (*d*TFA, CF_3COOD) such that polymer concentrations were in the range of 15–20% (wt%). All spectra were operated at ambient temperature, at 499.84 MHz for ^{1}H NMR, and at 125.70 MHz for ^{13}C NMR. The delay time was 0.001 s. Chemical shifts of copolyesters are reported in relation to CF_3COOD. The resonances of CF_3COOD were taken at 11.50 ppm in the ^{1}H NMR spectra and at 113.28–120.47 and 163.48–164.74 ppm in the ^{13}C NMR spectra, respectively. The determination of inherent viscosity was made in 50/50 phenol/tetrachloroethane at 25 °C with an Ubbelohde viscometer. The sample concentration was 0.25 g/mL. The viscosities (η) of the sample were 0.7–0.75 dL/g.

The non-isothermal crystallization and melting behavior were observed with a Du-Pont DSC Q10 instrument using a TA2000 thermal analysis system. The instrument was calibrated with In and Pb. The weight of the samples was in the range of 4–6 mg. The flow rate of the purge gas N_2 was approximately 50 cm^3/min. The heating and cooling rates were 10 °C/min.

The crystal morphology was observed with a Leitz

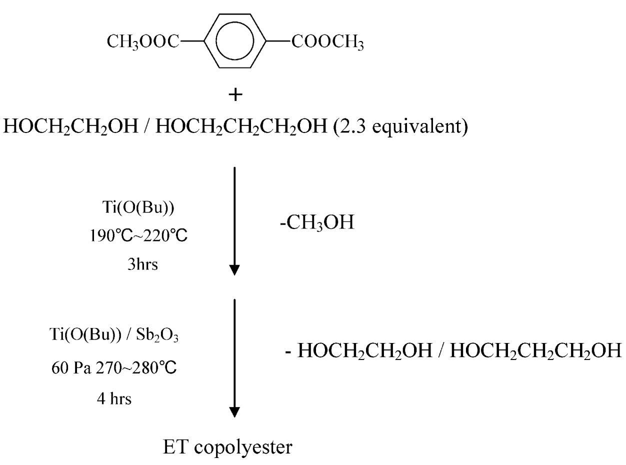


Fig. 1. Synthetic scheme of ET copolyester.

Table 1
Compositions of ET copolyesters

Sample	Feed ratio[a] (EG/PDO)	Triad probabilities (%)			Relative amount[b] (P_{EG}/P_{PDO})	Relative amount[c] (P_{EG}/P_{PDO})	*B*	L_{EG}	L_{PDO}
		P_{ETE}	P_{ETP}	P_{PTP}					
ET100	100/0								
ET90	90/10	67.07	29.00	3.93	82.78/17.22	81.57/18.43	0.96	5.63	1.27
ET80	80/20	43.53	44.78	11.70	66.53/33.47	65.91/34.09	1.00	2.94	1.52
ET70	70/30	26.84	51.69	21.47	52.70/47.30	52.68/47.32	1.04	2.04	1.83
ET60	60/40	18.83	47.89	33.28	41.41/58.59	42.78/57.22	0.98	1.79	2.39
ET50	50/50	10.75	41.42	47.83	28.01/71.99	31.46/68.54	0.96	1.52	3.31
ET40	40/60	8.58	32.42	59.00	20.20/79.80	24.79/75.21	0.87	1.53	4.64
ET30	30/70	4.37	21.16	74.47	14.40/85.60	14.95/85.05	0.83	1.41	8.04
ET20	20/80	4.57	17.52	77.91	6.68/93.32	13.33/86.67	0.76	1.52	9.89
ET10	10/90	0.00	13.97	86.03	4.19/95.81	6.98/93.02	1.08	1.00	13.32
ET0	0/100								

[a] Molar ratio of EG and 1,3-PDO monomers fed for polymerization.
[b] Calculated by ^{1}H NMR.
[c] Calculated by ^{13}C NMR.

(LABORLUX 12 POLS) hot stage polarizing microscope, and a Linkam THMS 600 heater equipped with a LINKAM TMS91 electric microscope controller and Nikon (COOLPIX 990) digital camera. The flow rate of the purge gas N_2 was approximately 90 cm^3/min. For the topographical observation of the inner part of the crystal structure, the specimen was etched with chlorophenol. After being etched the specimen was coated using a JFC-1100E coater with a gold target, for 5 min. The voltage was 1 kV and the electric current was 7.5 mA. The coated specimen was observed using a scanning electron microscope, JEOL JSM-5200. The electric voltage was 20 kV.

For the crystal structure study of the copolyesters, samples were isothermally crystallized for 30 min. The isothermal crystallization temperatures were set according to DSC results. The X-ray diffraction patterns of the samples were obtained using a Rigaku D/max 2550 pc automatic diffractometer with graphite monochrometer-filtered Cu Kα radiation. The electric voltage was 40 kV; electric current was 300 mA; scanning rate was 10 deg/min; and the 2θ scanning angle was 3–70°. The reflection profiles were deconvoluted using the Jade 5 curve-fitting software, Materials Data, Inc., with a peak search method. The FWHM (full width at half maximum) value being used to separate the amorphous phase and crystal reflections was 4.

3. Results and discussion

The chemical shifts in poly(ethylene terephthalate) (ET100) and poly(trimethylene terephthalate) (ET0) homopolymers were determined first. The ^{1}H NMR spectra recorded for ET100 and ET0 homopolymers and ET70 copolyester are shown in Fig. 2. The resonance peaks of benzene proton (TP) (8.44 ppm) and ethylene proton (H_3) (5.12 ppm) were assigned to ET100; and the peaks of benzene proton (TP) (8.53 ppm) and methylene protons $\alpha(H_2)$ (5.06 ppm) and $\beta(H_1)$ (2.80 ppm) for the ester oxygen in 1,3-propanediol unit were assigned to ET0 [8]. The solvent peak of CF_3COOD was at 11.50 ppm.

The spectra of all ET copolyesters recorded the proton resonances in TP (8.20–8.28 ppm), H_1 (2.47–2.54 ppm), H_2 (4.73–4.80 ppm), and H_3 (4.91–4.98 ppm) (Table 2). The expanded ^{1}H NMR spectra of all ET copolyesters, ranging from 1.0 to 6.0 ppm are shown in Fig. 3. It is evident that all of the protons of the ET copolyesters resonate at a higher field than those of the homopolymers. The relative amounts of ethylene glycol and 1,3-propanediol (EG/PDO) in a copolyester, based on the ratio of the downfield peak for ethylene glycol (H_3) relative to the upfield peaks from 1,3-propanediol (H_1), were calculated with the following equations.

$$\mathrm{EG} = \frac{(\mathrm{H}_3/2)}{(\mathrm{H}_1 + \mathrm{H}_3/2)}$$

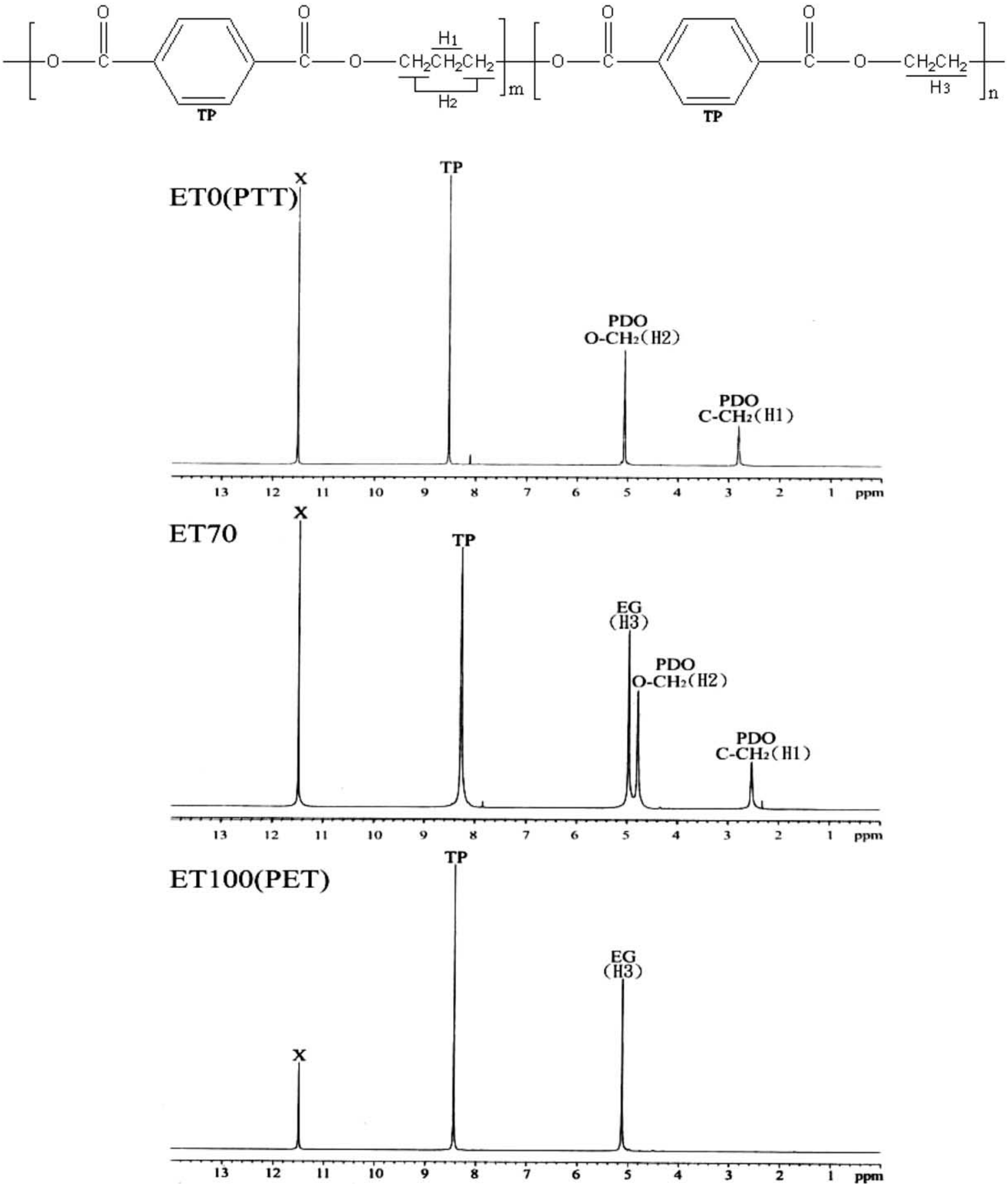


Fig. 2. ^1H NMR spectra of poly(ethylene terephthalate) (ET100), poly(trimethylene terephthalate) (ET0), and ET70 copolyester. Peaks marked by *x* are due to CF_3COOD solvent.

$$\mathrm{PDO} = \frac{H_1}{(H_1 + H_3/2)}$$

The calculated results are given in Table 1. It was found that each of the PDO amounts in the feed ratio of EG/PDO is lower than that in the calculated relative amounts of EG/PDO. For example for ET70, the calculated relative amounts of EG/PDO (P_{EG}/P_{PDO}) was 52.70/47.30 when the feed ratio of EG/PDO was 70/30. This indicates that 1,3-propanediol reacted faster with terephthalic acid than did the ethylene glycol.

In the ^{13}C NMR spectra, four resonance peaks in the spectra of ET100, were assigned as follows: at 66.70 ppm for the ethylene glycol (C_3) unit, at 132.59 ppm for the aromatic alkyl carbon atoms (C_5), 136.08 ppm for the aromatic quaternary carbon atoms (C_7), and at 171.34 ppm for the carbonyl carbon atom (C_{10}), (Fig. 4) [9,31]. The resonance peaks in the spectra of the ET0 are assigned at

Table 2
Chemical shifts (ppm) of ^{1}H NMR spectra for ET copolyesters

Samples	H_1	H_2	H_3	TP
ET100 (PET)	–	–	5.12	8.44
ET90	2.48	4.73	4.92	8.23
ET80	2.49	4.75	4.93	8.24
ET70	2.54	4.80	4.98	8.28
ET60	2.50	4.77	4.95	8.25
ET50	2.50	4.76	4.94	8.22
ET40	2.47	4.73	4.91	8.20
ET30	2.49	4.74	4.93	8.22
ET20	2.48	4.74	4.92	8.21
ET10	2.50	4.76	4.94	8.23
ET0 (PTT)	2.80	5.06	–	8.53

Here, H_1, H_2, H_3, and TP refer to the Fig. 2.

29.70 and 65.93 ppm for the 1,3-propanediol unit (C_1 and C_2), at 132.37 ppm for the aromatic alkyl carbon atoms (C_4), at 136.13 ppm for the aromatic quaternary carbon atom (C_8), and at 171.51 ppm for the carbonyl carbon atom (C_{11}) (Fig. 4) [32]. The resonances of CF_3COOD were taken at 113.28–120.47 ppm and at 163.48–164.74 ppm, respectively.

The three possible triad sequences in ET copolyesters are

-EG-TP-EG-

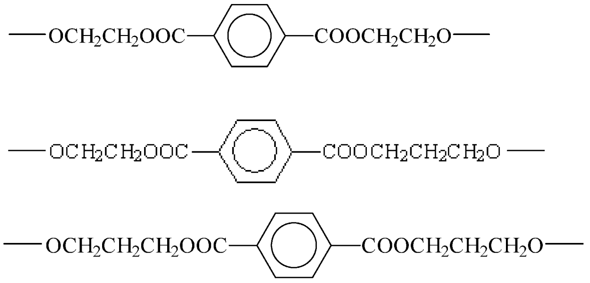
(ETE)

- EG -TP- PDO -

(ETP)

-PDO-TP-PDO-

(PTP)



In comparison with the homopolymers, the spectra of all ET copolyesters showed carbon chemical shifts for C_1 at 29.40–29.70 ppm, C_2 at 65.64–65.93 ppm, C_3 at 66.30–66.70 ppm, C_4 at 132.15–132.40 ppm, C_5 at 132.22–132.59 ppm, C_{10} at 170.98–171.34 ppm, and C_{11} at 171.22–171.51 ppm, respectively. The resonance peaks of C_7 for the EG-TP-EG (ETE) and of C_8 for the PDO-TP-PDO (PTP) sequences were at 135.77–136.08 and 135.90–136.13 ppm, respectively. Two additional resonance peaks for the EG-TP-PDO (ETP) sequence were at 135.08–135.90 ppm for the EG-TP side (C_6) and at 136.05–136.35 ppm for the TP-PDO side (C_9) (Fig. 4). The expanded spectra of the aromatic carbon atoms, in the range of 135.0–137.0 ppm, for all of the copolyesters are shown in Fig. 5. The results show that the relative intensities of the peaks of C_6 and C_9 are almost equal. However, the resonance intensity of C_7 is corresponding to the added EG molar fraction and the resonance intensity of C_8 is corresponding to the added PDO molar fraction (Fig. 5). The relative amounts of EG and PDO in the copolyester were determined from the NMR integration of the total resonance of C_6, C_7, C_8, and C_9. The molar ratios of EG/PDO were calculated by the following equations:

$$\mathrm{EG} = \frac{[C_7 + (C_6 + C_9)/2]}{(C_6 + C_7 + C_8 + C_9)}$$

$$\mathrm{PDO} = \frac{[C_8 + (C_6 + C_9)/2]}{(C_6 + C_7 + C_8 + C_9)}$$

The calculated results of the relative amounts of EG/PDO are given in Table 1. The results calculated from ^{13}C NMR are in good agreement with those calculated by ^{1}H NMR. For example, for ET70 the calculated relative amount of EG/PDO was 52.68/47.32, and the feed ratio of EG/PDO was 70/30.

The number-average sequences of EG-TP-EG (ETE), EG-TP-PDO (ETP), and PDO-TP-PDO (PTP) were calculated by the following equations:

$$\mathrm{EG-TP-EG} = \frac{C_7}{(C_6 + C_7 + C_8 + C_9)}$$

$$\mathrm{EG-TP-PDO} = \frac{(C_6 + C_9)}{(C_6 + C_7 + C_8 + C_9)}$$

$$\mathrm{PDO-TP-PDO} = \frac{C_8}{(C_6 + C_7 + C_8 + C_9)}$$

The calculated number-average sequences of EG-TP-EG (P_{ETE}), EG-TP-PDO (P_{ETP}), and PDO-TP-PDO (P_{PTP}) are given in Table 1. It is evident that the number-average sequence of EG-TP-EG/EG-TP-PDO/PDO-TP-PDO of ET70 was 26.84/51.69/21.47 as the calculated relative amounts of EG/PDO in ET70 was 52.68/47.32.

Values for the number-average sequence length of EG (L_{EG}) and PDO (L_{PDO}) units, given by $L_{\mathrm{EG}} = 2P_{\mathrm{EG}}/P_{\mathrm{ETP}}$ and $L_{\mathrm{PDO}} = 2P_{\mathrm{PDO}}/P_{\mathrm{ETP}}$, are given in Table 1. The randomness B is given by $P_{\mathrm{ETP}}/(2 \times P_{\mathrm{EG}} \times P_{\mathrm{PDO}})$ (Table 1) [7]. For a total randomness of a copolymer, B is equal to 1. For an alternative copolymer, B is equal to 2 and a block copolymer, B is close to zero. Values of B, calculated for all of the copolyesters, range from 0.76 to 1.08. Those values are close to 1. The difference in monomer reactivity may be significant in the polymerization, however, the reaction renders the distribution of the copolyesters as random. The results show that the constitutional repeating

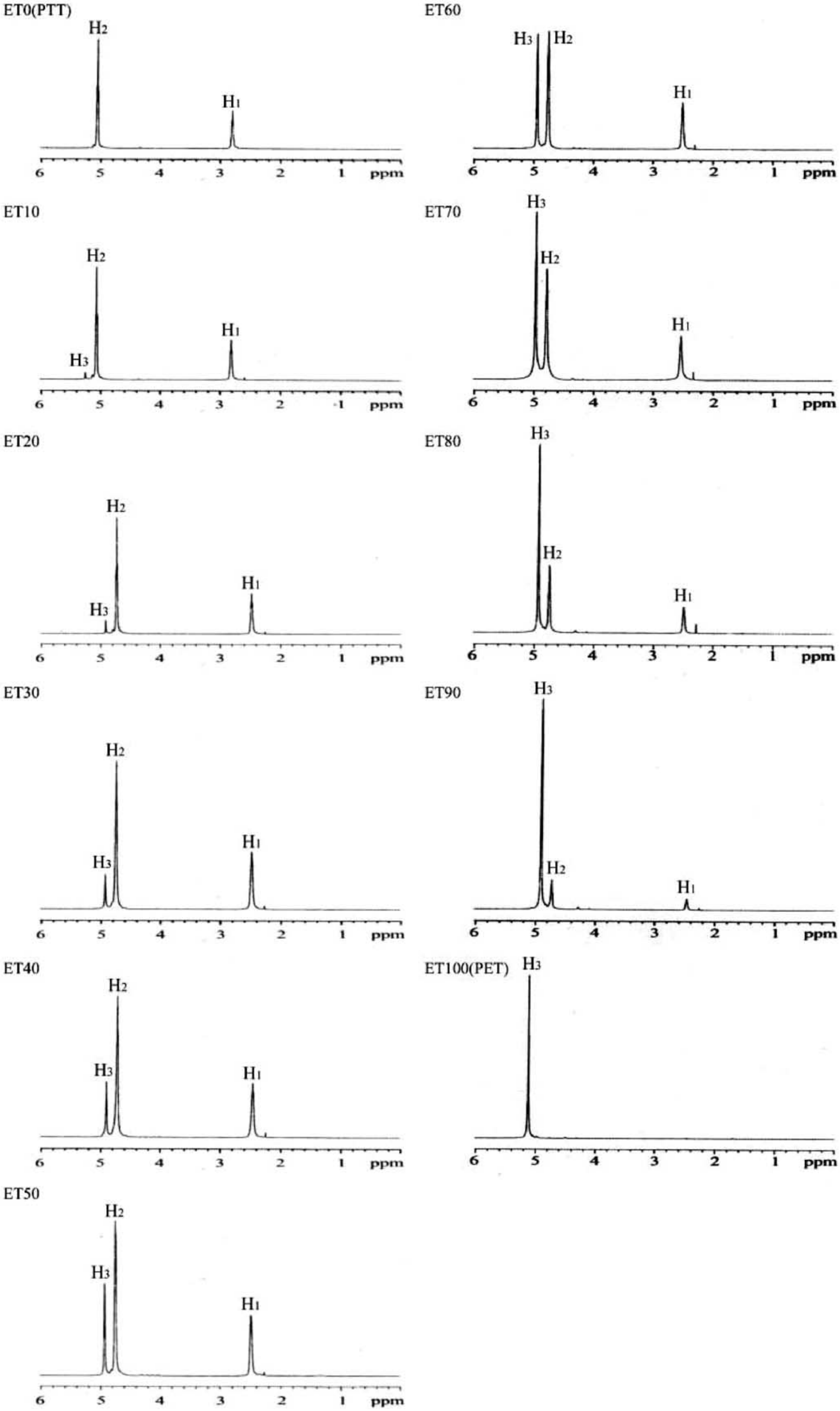


Fig. 3. Expanded ^{1}H NMR spectra of ET copolyesters ranging from 1.0 to 6.0 ppm.

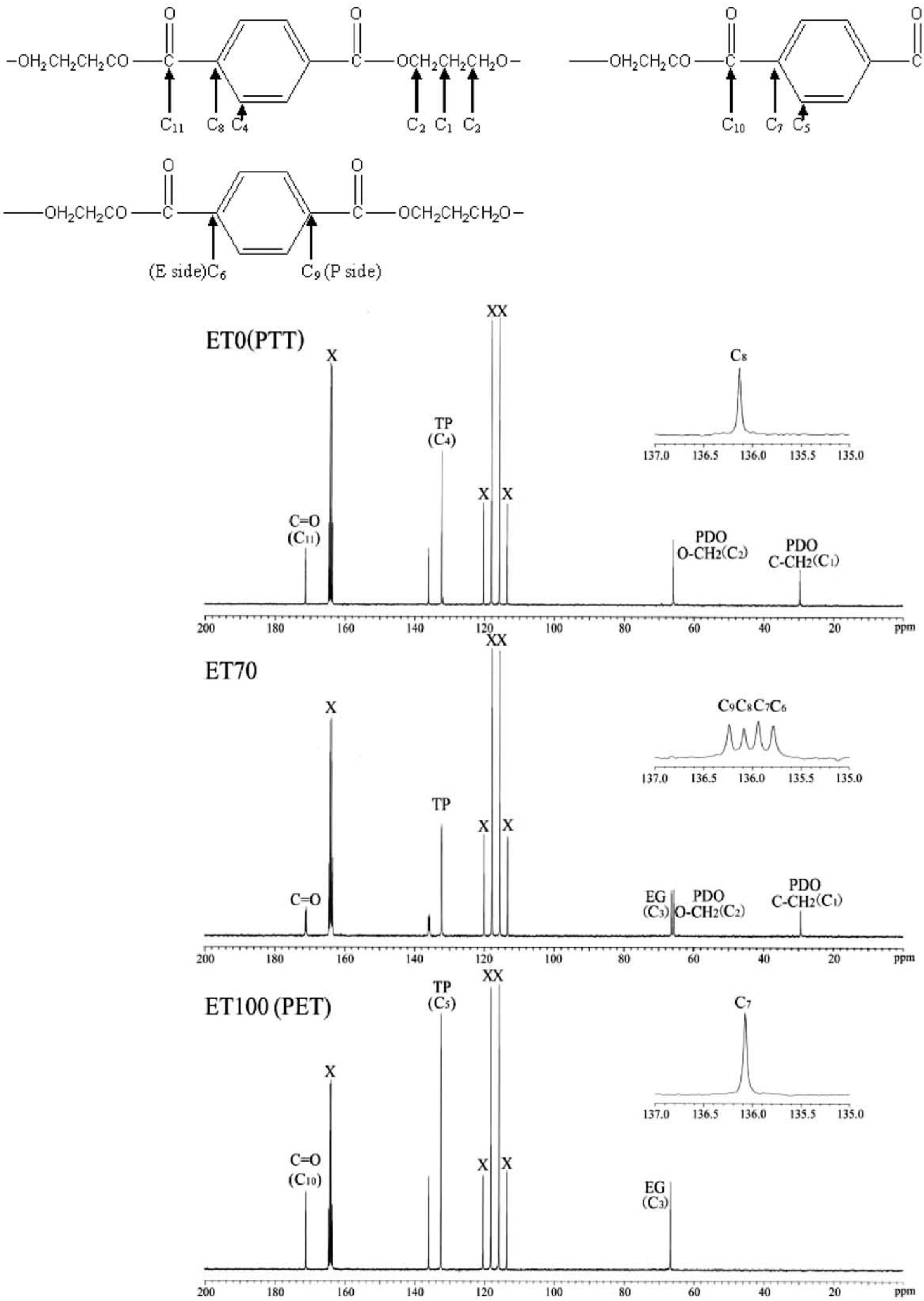


Fig. 4. ^{13}C NMR spectra of poly(ethylene terephthalate) (ET100), poly(trimethylene terephthalate) (ET0), and ET70 copolyester with expanded chemical shifts of aromatic alkyl carbon atoms ranging from 135.0 to 137.0 ppm. Peaks marked by *x* are due to CF_3COOD solvent.

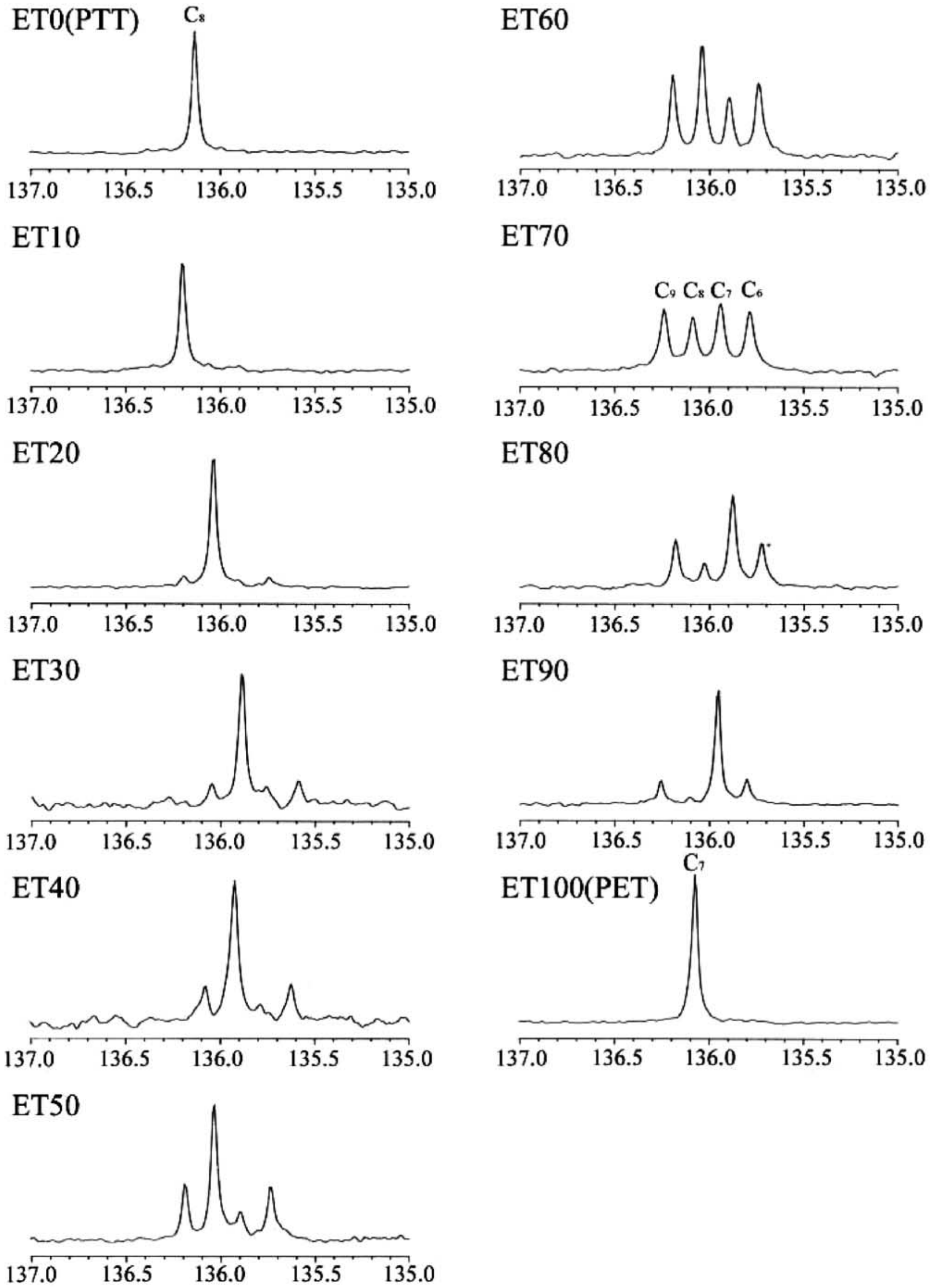


Fig. 5. Expanded ^{13}C NMR spectra of ET copolyesters with chemical shifts of aromatic alkyl carbon atoms ranging from 135.0 to137.0 ppm.

units of ET copolyesters are a random or nearly random distribution in the molecular chain.

In order to study the non-isothermal crystallization and melting behaviors of the copolyesters, samples were melted at 265 °C, with the exception of ET100 at 285 °C, for 3 min, and they were then cooled at 10 °C/min. After that the samples were reheated at 10 °C/min. Fig. 6 shows the crystallization exotherms for copolyesters recorded at 10 °C/min from the melt. Crystals grown on cooling in random copolymers can be observed. However, there is no significant exothermic crystallization peak for the ET80, ET70, ET60, and ET50 copolyesters. For subsequent reheating at 10 °C/min, recrystallization occurred at a lower temperature, for the ET40, ET50, ET60, and ET90 copolyesters (Fig. 7). There are very weak endothermic melting peaks for ET70 and ET80 copolyesters (Fig. 8). The heat of the fusion for the ET70 and ET80 copolyesters is about 0.18 and 0.20 J/g, respectively. A single melting peak was observed for all of the copolyesters. In comparison with homopolymers, it is evident that the melting peak temperature depression of copolyester is significant. A minimum endothermic melting peak temperature occurred

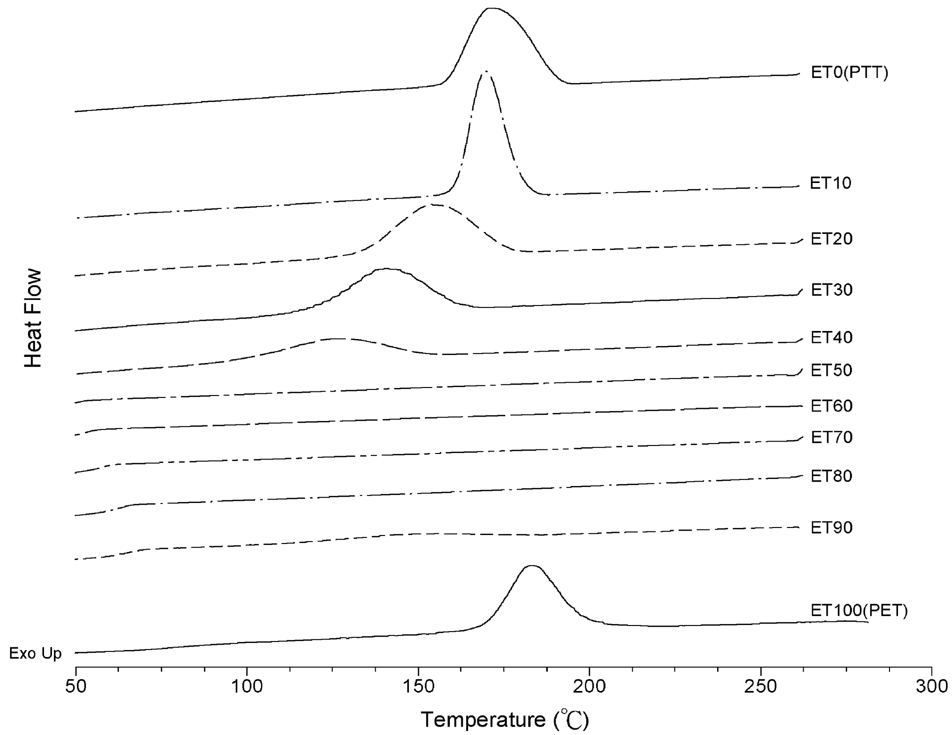


Fig. 6. DSC cooling curves of ET copolyesters at 10 °C/min from the melt for 3 min.

for the ET70 copolyester (Fig. 9). It is evident that crystallization occurred in all of the copolyesters, although a third constitutional unit was incorporated into the PET or PTT homopolymers. The decline of the crystallization and melting peaks can be due to the random distribution of the third constitutional unit into the molecular chain.

Samples melted at 265 °C (ET100 at 285 °C) for 5 min, followed by rapid cooling to the isothermal crystallization

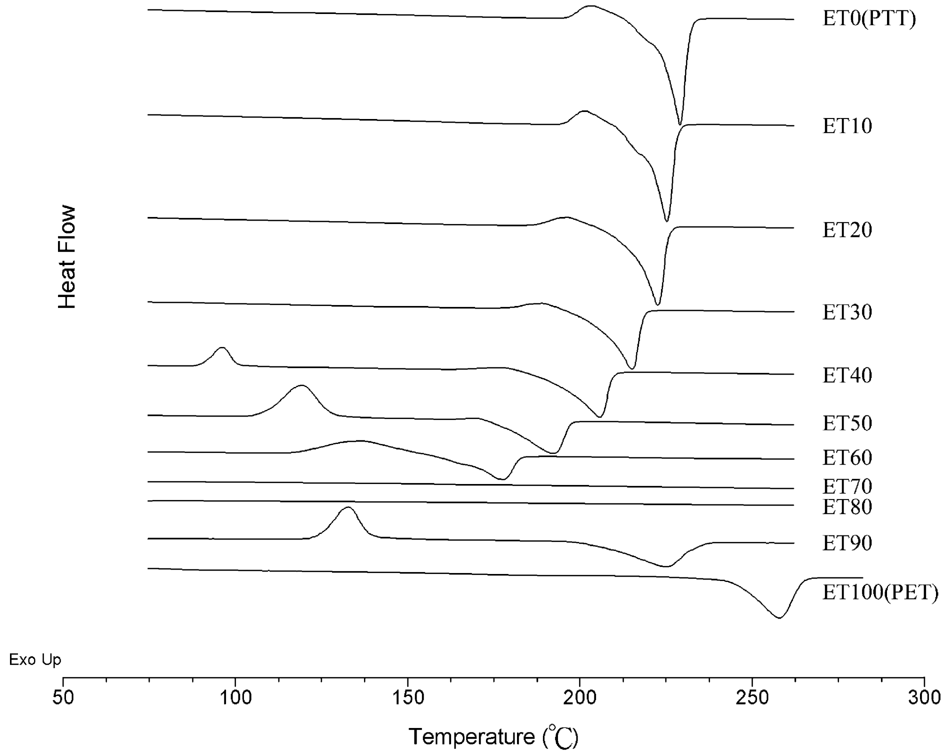


Fig. 7. DSC reheating curves of ET copolyesters. Samples were melt for 3 min, followed by slow cooling at 10 °C/min. Reheating rate: 10 °C/min.

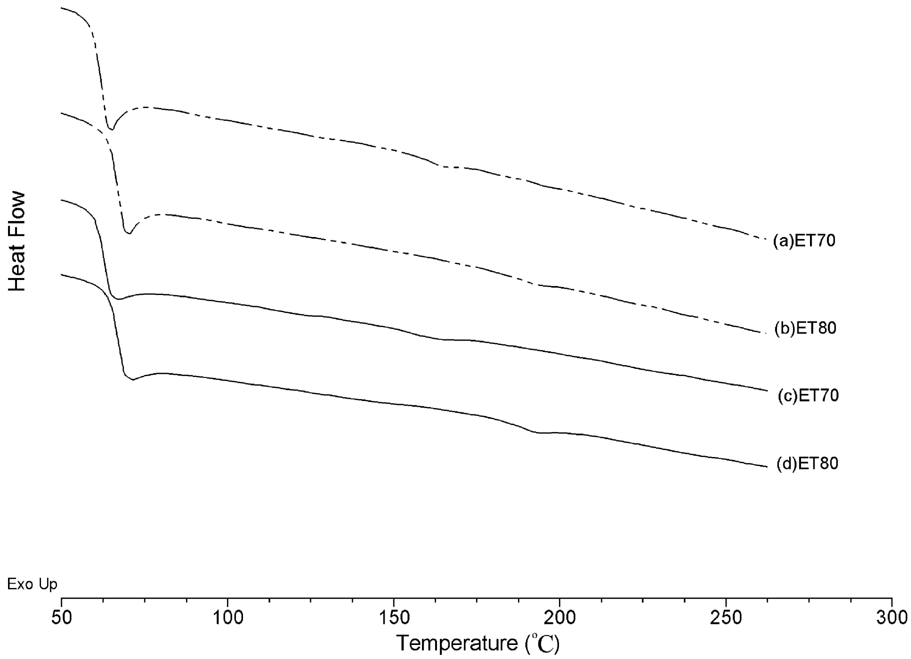


Fig. 8. DSC reheating curves at 10 °C/min of ET70 and ET80 copolyesters. Samples were melted at 265 °C for 5 min, followed by (a) and (b) slow cooling at 10 °C/min, (c) and (d) quickly cooling to isothermal crystallization temperature, ET70 at 110 °C and ET80 at 105 °C, for 30 min.

temperature for 30 min, were used for wide angle X-ray diffraction analysis. The isothermal temperature for each of copolyester was set above their non-isothermal crystallization temperature as follows; ET100 at 200 °C, ET90 at 160 °C, ET80 at 105 °C, ET70 at 110 °C, both ET60 and ET50 at 130 °C, ET40 at 140 °C, ET30 at 150 °C, ET20 at 160 °C, and both ET10 and ET0 at 180 °C. The experimental reflection profiles ranging from 3 to 33° and deconvoluted using Jade 5 curve-fitting software with a peak search method, are shown in Fig. 10. It is evident that two broad curves describe the amorphous phase, and that all crystal reflections are separated.

The crystal reflections of ET100 (PET) and ET0 (PTT) homopolymers are about eight reflections and about 10 reflections, respectively. The reflections of both homopolymers are in reasonable agreement with those reported by Wang, Lu, and Wang [33–35]. In comparison with the reflections of the homopolymers, a new 2θ diffraction peak at ca. 20.72–20.76 was observed on the ET30, ET40, ET50, and ET60 copolyesters (Fig. 10(d)–(g)). From the crystal

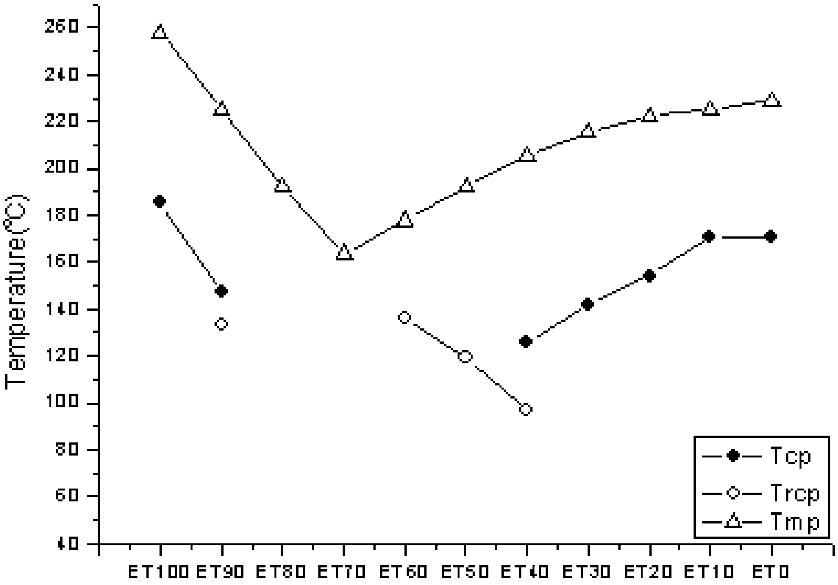
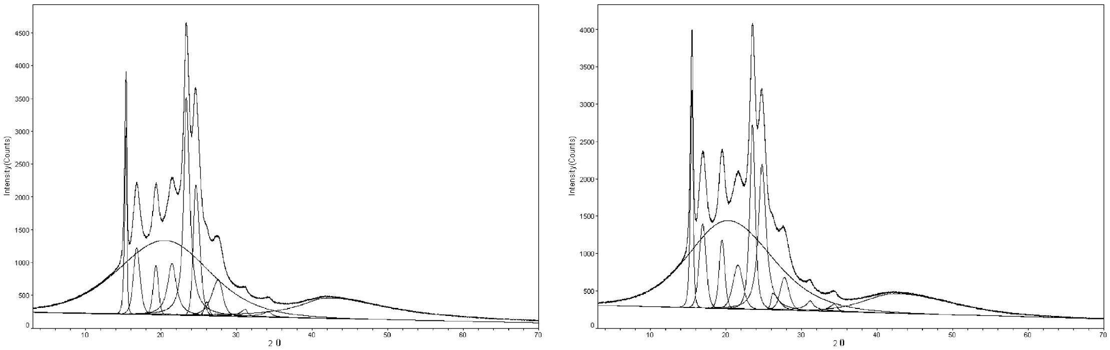
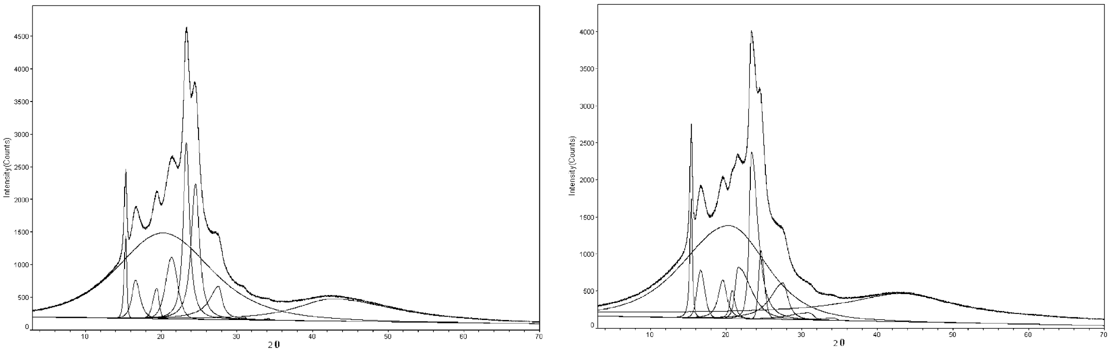


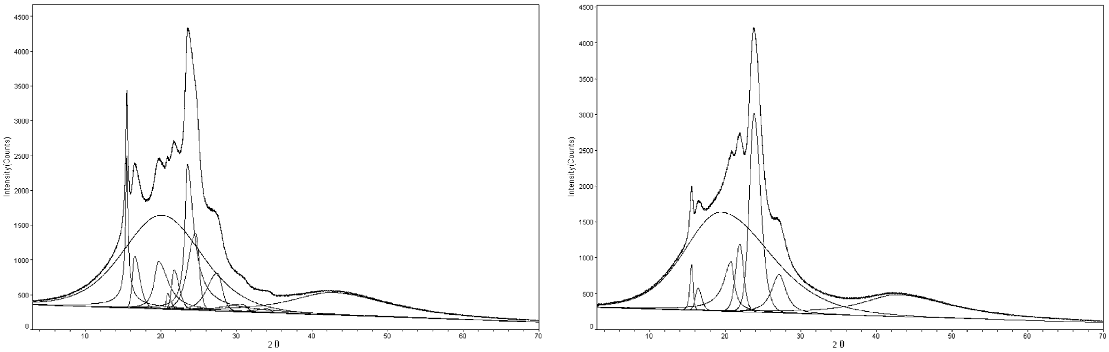
Fig. 9. Crystallization peak temperature (T_{cp}), re-crystallization peak temperature (T_{rcp}), melting peak temperature (T_{mp}) of ET copolyesters. Samples were melted for 3 min and slow cooled at 10 °C/min to 35 °C, followed by reheating at 10 °C/min.



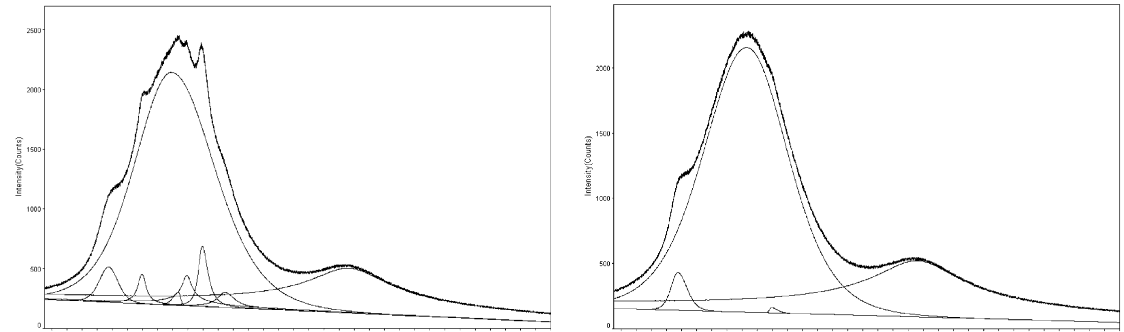
(a) ET0 (PTT) (b) ET10



(c) ET20 (d) ET30

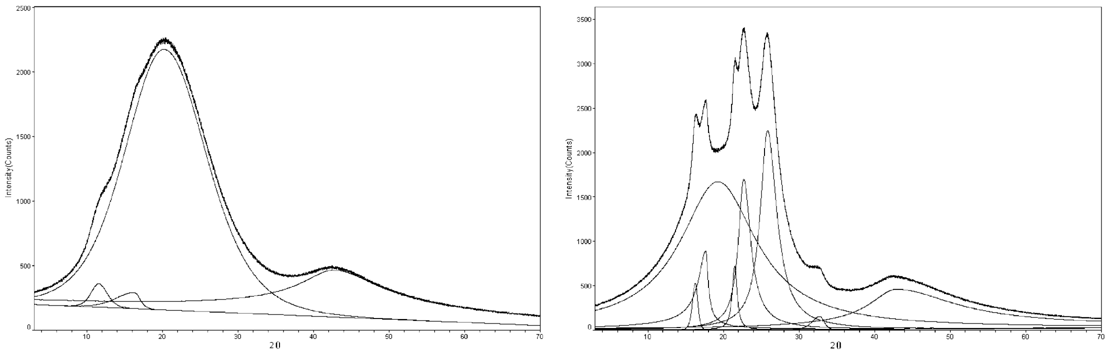


(e) ET40 (f) ET50



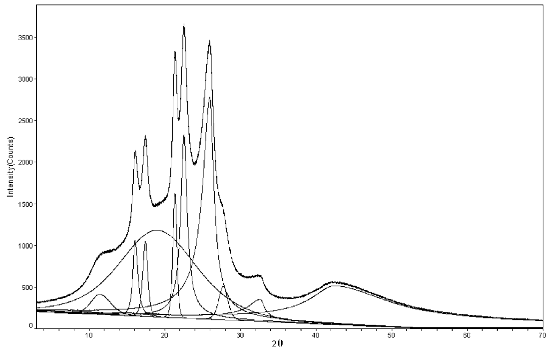
(g) ET60 (h) ET70

Fig. 10. WAXD deconvolution curves for ET copolyesters.



(i) ET80

(j) ET90



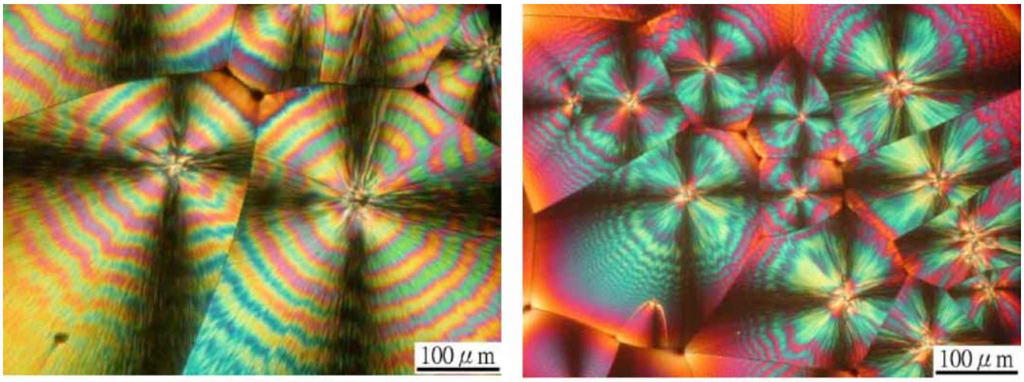
(k) ET100 (PET)

Fig. 10 (*continued*)

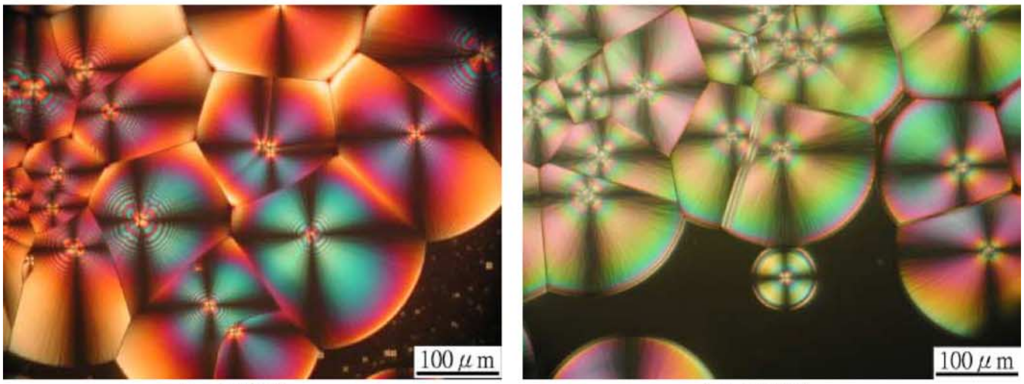
reflections, copolyesters can be grouped into three clusters. In the calculated relative amounts of P_{PDO} between 100 and 60%, such as for ET10, ET20, ET30, ET40, and ET50, the reflections of the copolyesters are generally closely related to that of the PTT (ET0) homopolymer. The PTT backbone chain geometry is maintained to be a host crystal. Here, all of the reflections of ET10 and ET20 are related to the PTT reflections. The reflections of ET30, ET40, and ET50 are related to the PTT reflections, with an additional reflection at ca. 20.72–20.76, which does not relate to the PTT or the PET reflections. Correspondingly, the calculated relative amounts of P_{EG} between 100 and 60%, such as ET80 and ET90, the reflections of both copolyesters are related to that for the PET (ET100) homopolymer. Again the PET backbone chain geometry is maintained as a host crystal. A mixture of reflections were observed from P_{PDO}-rich ET60 and P_{ET}-rich ET70 copolyesters, for which the relative amounts of EG/PDO calculated by ^{13}C NMR were 42.78/57.22 and 52.68/47.32, respectively. It shows six reflections from the WAXD of the P_{PDO}-rich ET60 copolyester, containing four PTT-related reflections, one PET-related reflection, and a 2θ diffraction peak at ca. 20.73. Two reflections, one PET-related reflection and one PTT-related reflection, were separated from the WAXD of the P_{ET}-rich ET70 copolyester.

The supermolecular structure of copolymers was observed in a hot stage polarizing microscope. Fig. 11 shows the spherulitic textures formed on cooling at 10 °C/min from the melt. Generally speaking, ET100, ET90, ET60, ET50, ET40, ET30, ET20, ET10, and ET0 could grow spherulites from the melt. Both banded and non-banded spherulites grow in melt-crystallized copolymer (Fig. 11). Banded spherulites are considered to be attributed to lamellar twisting [36]. It is generally realized that the cause of lamellar twisting is the stress set up during crystallization [34,37]. The Maltese cross can be seen clearly in these polarized photomicrographs. However, under this condition the crystalline morphology of ET70 and ET80 could not be observed using a polarizing microscope. Further study of the supermolecular structure of ET70 and ET80 copolyesters was carried out under isothermal melt-crystallization conditions (Fig. 12). It is evident that crystallites formed at the isothermal temperature of 105 °C for ET80, and at 110 °C for ET70, for 30 min, respectively, although the crystallites of the ET80 copolyester are not very clear on the polarized photomicrograph.

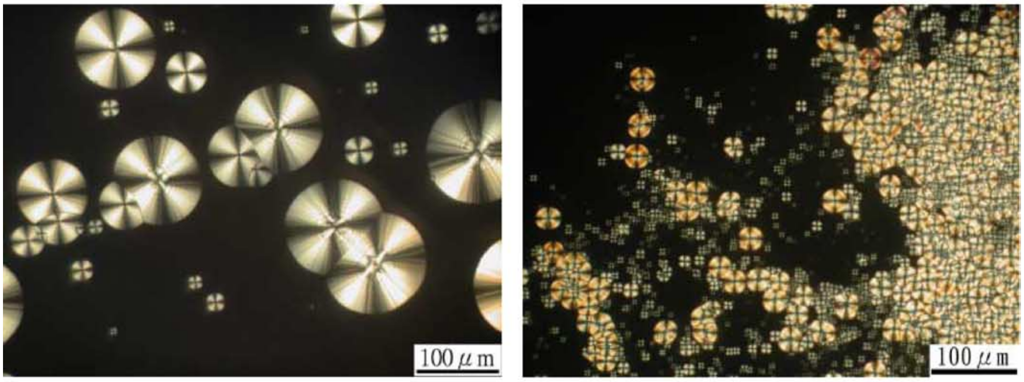
After being etched with chlorophenol, the inner part of the spherulites was observed using a SEM (Fig. 13) [38]. The spherulitic structure of ET100 and ET0 homopolymers is a multilayered dominant lamellae radiating outward from the center of the spherulite (Fig. 13(a) and (b)). A sheet-like lamellar structure is revealed, and it seems to have certain preferred orientations. The lamellae of the stack are almost parallel, and the amorphous component is located in the space between the crystal lamellae. However, the lamellar structures contained in the melt-crystallized homopolymers



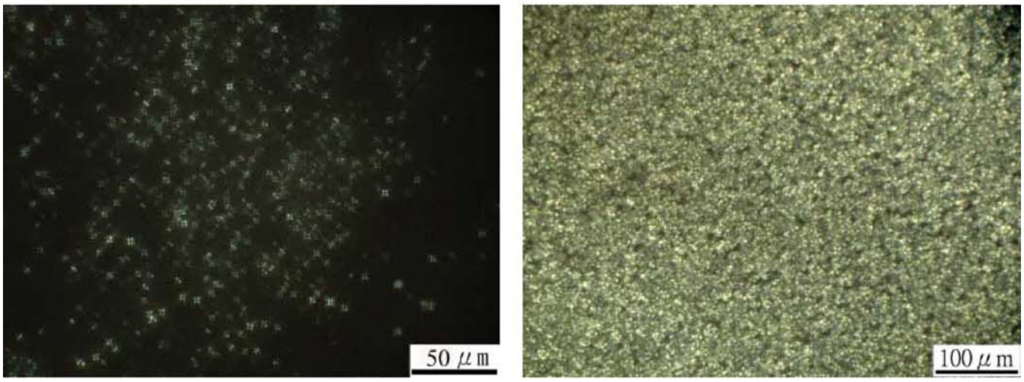
(a)ET0(PTT) (b)ET10



(c) ET20 (d) ET30



(e) ET40 (f) ET50

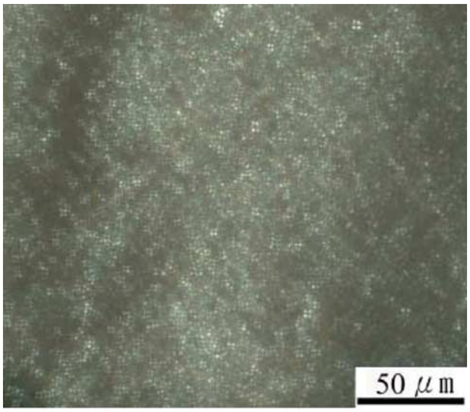


(g) ET60 (h) ET90

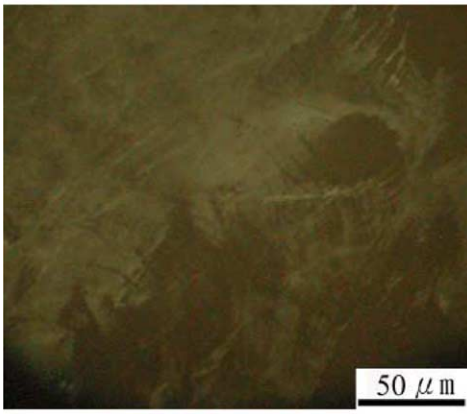
Fig. 11. Polarized photomicrographs of some copolyesters on cooling at 10 °C/min.

(i) ET100(PET)

Fig. 11 (*continued*)



(a) ET70



(b) ET80

Fig. 12. Polarized photomicrographs for ET70 and ET80 copolyesters isothermally crystallized for 30 min at 110 and 105 °C, respectively.

and copolyesters are quite different. The random lamellar structure dominates the spherulite of the copolyesters (Fig. 13(c) and (d)). The multilayer crystal has a central nucleus and consists of stacks of random lamellae growing outward from the center. Regular lamellar stacking is absent in the copolyesters. This indicates that the random distribution of the constitutional repeating unit in the molecular chain disturbs the host crystal formation and the lamellar orientation.

4. Conclusion

A series of poly(ethylene/trimethylene terephthalate) copolyesters were synthesized and characterized using nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR). The difference in monomer reactivity was significant in the polymerization. Results show that 1,3-propanediol reacted faster with terephthalic acid in ET copolyester polymerization than ethylene glycol did. The calculated relative amount of EG/PDO was 52.70/47.30, and the calculated number-average sequence of ETE/ETP/PTP was 26.84/51.69/21.47, when the feed ratio of EG/PDO was 70/30. All of the protons of ET copolyesters resonate at a higher field than those of the homopolymers. This indicates that a third constitutional unit introduced to the homopolymer resulting highly shielded the protons.

Based on the HSPM and WAXD studies there is strong evidence of crystallites forming across the full range of the ET/PDO composition, even though the constitutional repeating unit in the molecular chain is randomly distributed in the copolyester. The WAXD deconvolution curves show that the higher relative amount of constitutional repeating unit in the molecular chain dominates the crystal structure as a host crystal. It must be noted that in the cases of the ET30, ET40, ET50, and ET60 copolyesters, a new 2θ diffraction peak at ca. 20.72–20.76 was deconvoluted. The third constitutional unit incorporated into the host crystal interrupts the ideal crystalline structure and decreases the endothermic melting peak temperature of the copolyester. A minimum endothermic melting peak temperature of the copolyester occurs at the nearly equalized relative amount of EG/PDO in the ET70 copolyester. Mixtures of PET-related and PTT-related reflections were found on the nearly equalized relative amount of EG/PDO of the ET60 and ET70 copolyesters.

The fact that random distribution of the constitutional repeating unit in the molecular chain of ET copolyesters disturbs the host crystal formation and lamellar orientation was verified. Etched samples showed the change of lamellar structure from homopolymer to copolyester. The crystal lamella stack in homopolymers shows a sheet-like lamellar structure with a certain preferred orientation, while a random lamellar structure shows in copolyesters.

Acknowledgements

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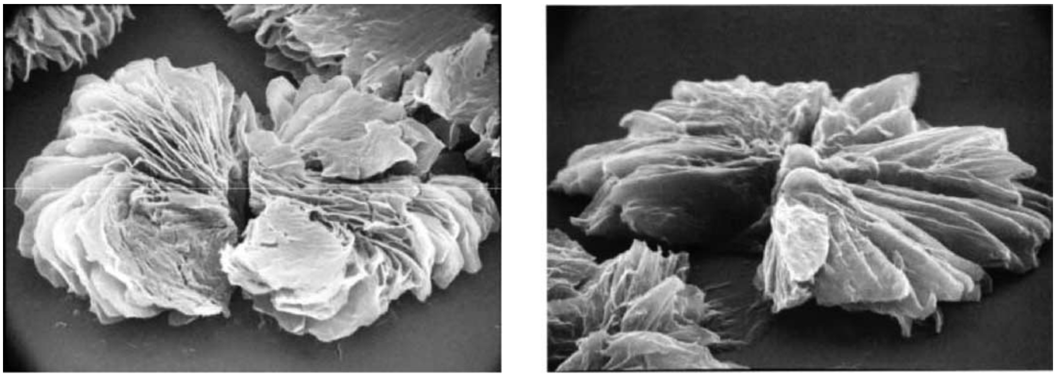
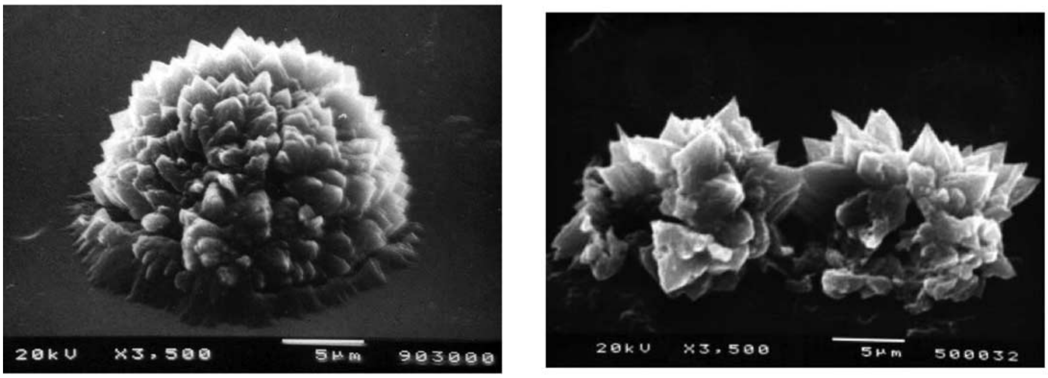


(a) ET0 (PTT) (b) ET100 (PET)



(c) ET10 (d) ET20

Fig. 13. SEM photographs of lamellar structure of copolyesters after being etched with chlorophenol.

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