

## Synthesis and Crystallization Behaviors of Modified PET Copolymers

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**Abstract:** A series of random copolyesters having various compositions were synthesized by bulk copolymerization of bis-hydroxyethyl terephthalate (BHET) with 1,4-cyclohexane dimethanol (CHDM) or dimethyl isophthalate (DMI). CHDM and DMI content was less than 10 wt%. For the synthesized copolyesters, isothermal crystallization rate, melting behavior, and equilibrium temperature were investigated by calorimetry and by Avrami and Hoffman-Weeks equation. Crystalline lattice and morphology were studied by WAXD and SEM. Regardless of the composition, the value of the Avrami exponent was about 3, which indicates that crystallization mechanism of the copolyester was similar to those of PET homopolymer. Incorporation of CHDM or DMI units in PET backbone decreased the crystallization rate of the copolyesters. Surface free energy of copolyesters was evaluated using the newly proposed equation. The value of surface free energy was about  $189 \times 10^{-6} \text{ J/m}^2$  regardless of comonomer contents. This result is in good agreement with that of PET homopolymer.

**Keywords:** Copolyester, Melting behavior, Equilibrium melting temperature, Surface free energy, Crystallization rate

### Introduction

Poly(ethylene terephthalate) (PET), which is a common semicrystalline polymer, is widely used as synthetic fibers, packaging films, bottles for beverage and food because of the excellent thermal and mechanical properties, high chemical resistance, and low gas permeability[1-3]. However, PET has undesirable properties such as poor dyeability, poor processability, and poor adhesion to metals. In general, copolymerization has been frequently used to overcome these undesirable properties, for example, poly(ethylene terephthalate-co-naphthalate)[4], poly(butylene adipate-co-isophthalate)[5], and poly(ethylene terephthalate-co-isophthalate)[6,7], etc. The properties of copolymer can be improved in somewhat extent depending on the amount and dispersity of comonomer units along the polymer backbone.

Patkar and Jabarin[8] investigated the crystallization behavior of PET having different DEG contents (up to 3 mol %/DMT). Their results showed that increasing the DEG content increases the half time of crystallization, indicating a decrease in the crystallization rate. Li *et al.*[6] studied crystallization behavior of poly(ethylene terephthalate-co-isophthalate) by DSC. They reported that the equilibrium melting temperature ( $T_m^0$ ) of copolyesters was decreased with increasing the dimethyl isophthalate (DMI) contents. With the incorporation of DMI, the copolyester could not be crystallized perfectly.

In this work, we synthesized a series of poly(ethylene terephthalate-co-isophthalate) and poly(ethylene terephthalate-co-dimethyl cyclohexane terephthalate) copolyesters using dimethyl isophthalate (DMI), or 1,4-cyclohexane-dimethanol (CHDM). DMI or CHDM were used in the contents of less than 10 wt%, in order to maintain some

properties of PET homopolymer. Melting behavior, crystallization kinetics and morphology of copolyesters were investigated by using DSC, SEM, and WAXD in terms of comonomer compositions.

### Experimental

#### Synthesis and Characterization

Bis-(2-hydroxyethyl) terephthalate (BHET) was obtained from Hyosung Co., Korea. Poly(ethylene terephthalate-co-isophthalate) (PETI, I.V.  $\approx 0.5 \text{ dl/g}$ ) copolyesters and dimethyl isophthalate (DMI) comonomer were supplied from SK Chemical Limited, Korea. Ethylene glycol (EG), antimony trioxide, and 1,4-cyclohexanedimethanol (CHDM) were purchased from Aldrich Chemical Co.. Triphenyl phosphate (TPP) was purchased from Junsei Chemical Co.. All the chemicals were used as received without further purification.

Poly(ethylene terephthalate-co-dimethyl cyclohexane terephthalate)s (PET/DMCT)s of various composition (1, 3, 5, 7 wt%-CHDM) were synthesized by conventional two-step polycondensation reaction.

Compositions of the copolyesters were determined using a  $^1\text{H-NMR}$  spectrometer. Proton NMR was conducted on a Bruker 300 MHz FT-Nuclear Magnetic Resonance Spectroscopy. Sample solutions were prepared using deuterated trifluoro acetic acid as solvent. Intrinsic viscosities (I.V.) of copolyesters were measured from 2-chlorophenol solution at  $25 \pm 0.1^\circ\text{C}$  using Ubbelohde capillary viscometer.

#### Thermal Analysis

The general thermal properties of PET copolyesters were examined using DSC (Perkin Elmer DSC 7). About 10 mg of samples was preheated to  $283^\circ\text{C}$  for 5 min in order to eliminate all crystalline nuclei, and rapidly cooled down to  $20^\circ\text{C}$ . Subsequently, samples were heated up to  $283^\circ\text{C}$  with a

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heating rate of 10°C/min, and melting temperature,  $T_m$ , and crystallization temperature from the glassy state,  $T_{cc}$ , were determined. The molten samples were also cooled slowly with a rate of 10°C/min in order to measure crystallization temperature from the melt,  $T_c$ .

In order to investigate equilibrium melting temperature, isothermally crystallized sample were reheated with a rate of 10°C/min. To investigate the crystallization kinetic, isothermal crystallization was performed at a selected temperature followed by melting at 283°C.

### Morphology

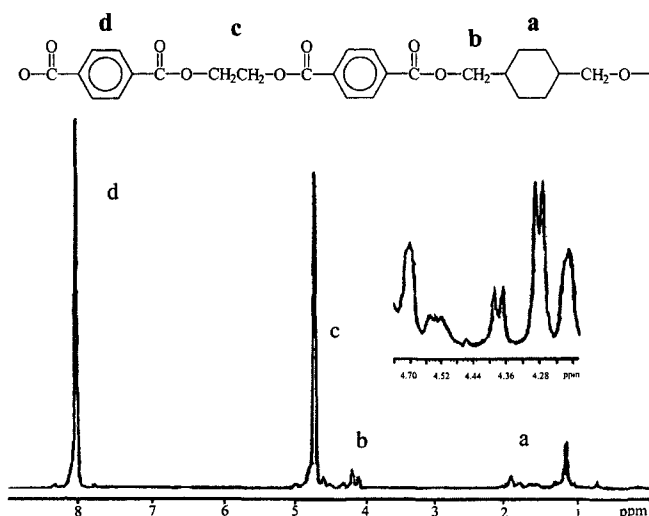
Wide angle X-ray diffraction (WAXD) patterns were taken with Ni-filtered  $\text{CuK}\alpha$  radiation using RAD-C X-ray Diffractometer (Rigaku Denki Co.). The scanning range was from  $2\theta = 0.5^\circ$  to  $40^\circ$ , and scan rate was  $5^\circ/\text{min}$ .

The morphology of spherulite was observed using SEM (Joel JSM 35-CF). Samples crystallized for 24 hours were etched in n-propyl amine and then coated with gold in an automatic sputter.

## Results and Discussion

### Synthesis

In Figure 1, the chemical shifts of a, b protons of CHDM comonomer showed up 1.2 ppm and 4.3 ppm, respectively. Especially, b protons of methylene unit attached cyclohexane unit appeared in two doublet peaks indicating trans- and cis-isomer. The c and d protons of PET showed up 4.47 ppm, 8.12 ppm. In general, diethylene glycol (DEG) is formed in a side reaction under the conditions of synthesis of PET from dimethyl terephthalate and ethylene glycol. Its presence affects many important properties of PET such as crystallization behavior,  $T_m$ , and dyeability, etc. In our study,



**Figure 1.**  $^1\text{H-NMR}$  spectra of poly(ethylene terephthalate-co-dimethyl cyclohexane terephthalate).

**Table 1.**  $M_v$  of PET copolymer

	Wt%	$\eta$ (dl/g)	$M_v$ ( $10^{-4}$ )		Wt%	$\eta$ (dl/g)	$M_v$ ( $10^{-4}$ )
CHDM	1	0.69	2.3	DMI	4	0.49	1.5
	3	0.75	2.6		6	0.53	1.6
	5	0.71	2.4	PET	10	0.55	1.7
	7	0.78	2.9		0	0.66	2.1

the protons of DEG were appeared at 4.13 ppm and 4.61 ppm. But DEG content was constantly less than 2 wt%, at any content of CHDM (DMI comonomer, 1.4 wt% as well).

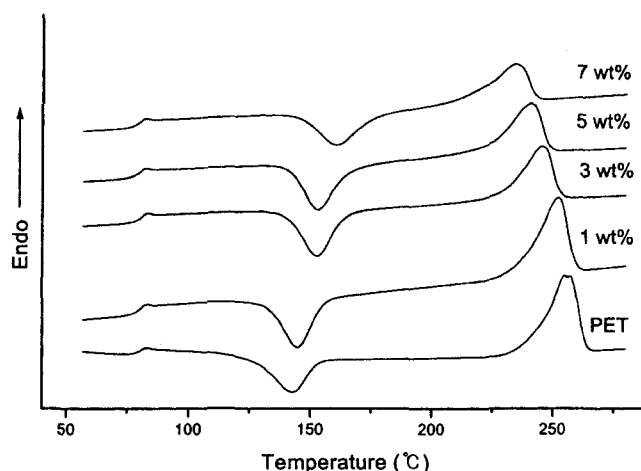
The viscosity average molecular weights ( $M_v$ ) were estimated from the measured intrinsic viscosities ( $\eta$ ) using the Mark-Houwink equation with constants  $\alpha$  and  $k$ [9].

$$[\eta] = 3 \times 10^{-4} M_v^{0.77} \quad (1)$$

The results were listed in Table 1. The resulted  $M_v$  values were in the range of 15000-29000. PET/DMCT should relatively higher  $M_v$  than PET/I.

### Thermal Behavior

The DSC heating thermograms of PET and PET/DMCT were shown in Figure 2. The scanning from the glassy state was performed at a rate of 10°C/min. The melting peak of pure PET was shown at 254°C and that of PET/DMCT moved to lower temperature with increasing CHDM content. The reduction in  $T_m$  may be due to restriction of crystalline growth by DMI and CHDM to regular PET polymer backbone. The peaks of cold crystallization temperatures,  $T_{cc}$ , shifted to higher temperature and became broader and larger as CHDM content increased. It could be suggested that the comonomer component takes a role of the retardation on the crystallization because it restricts the

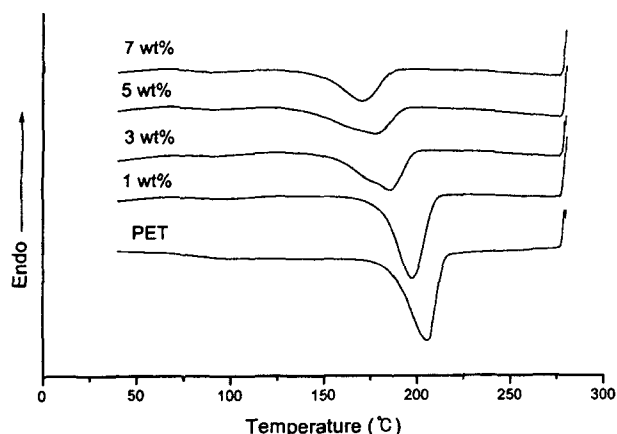


**Figure 2.** DSC heating thermograms of PET and various compositions of poly(ethylene terephthalate-co-dimethyl cyclohexane terephthalate).

mobility of polymer molecules. The degree of supercooling ( $\Delta T = T_m - T_{cc}$ ), describing the thermodynamic driving force of crystallization, decreased as the comonomer composition increased. But the glass transition temperature,  $T_g$ , was constantly shown at 78°C and heats of fusion,  $\Delta H_{cc}$ , were close to 29 J/g. These parameters were not affected by CHDM contents. In general, it has been known that  $T_g$  decreased with increasing comonomer content in Fox equation[6,10]. In this study, however,  $T_g$  were not changed. This result was probably due to a relatively small amount of comonomer below 10 wt%.

Figure 3 showed the crystallization exotherms of copolyesters during cooling scan from the melt at a rate of 10°C/min. The crystallization temperatures,  $T_c$ , shifted to lower temperature and  $\Delta H_c$  of PET/DMCT were remarkably lower than those of pure PET. The exothermic peaks became broader as CHDM content increased. Similar data obtained for a series of PET/I.

The results of DSC thermograms were summarized in Table 2. It suggested that the thermal behavior of PET copolyesters, especially the heat of fusion, were affected by compositions of comonomers. And it could be confirmed the



**Figure 3.** DSC cooling thermograms of PET and poly(ethylene terephthalate-co-dimethyl cyclohexane terephthalate).

**Table 2.** Thermal properties of PET and PET copolymer

		Heating				Cooling		
		$T_g$	$T_{cc}$	$T_m$	$\Delta T$	$\Delta H_{cc}$	$T_c$	$\Delta H_c$
PET		79.2	142	254	112	29.1	205	44.8
C	1	79.1	144	252	107	31.4	197	42.9
H	3	79.4	152	245	92	29.9	185	32.3
D	5	78.7	153	240	87	28.5	177	23.8
M	7	78.9	160	233	73	29	170	22.4
D	4	77.7	146	248	101	29.7	194	40.7
M	6	77.6	150	243	92	29.3	188	37.8
I	10	76.9	168	234	65	31	164	26.1

retardation of crystallization rate by introducing comonomer unit.

### Equilibrium Melting Temperature

A semicrystalline polymer has a wide range of melting temperature according to the crystallization conditions, such as a different crystallization time and temperature. This indicates that many crystals with finite thickness grow in a polymer, so the equilibrium melting temperature  $T_m^0$ , a melting point of crystals with infinite thickness, should be considered as a characteristic of semicrystalline polymer. The equilibrium melting temperature can be experimentally determined by a number of different methods such as a Thompson-Gibbs equation[11], Broadhurst equation[12] and Hoffman-Weeks equation[13,14]. In present study, especially, the equilibrium melting temperature was obtained using the Hoffman-Weeks equation, expressed in equation (2), by reheating isothermally crystallized samples with 10°C/min heating rate.

$$T_m = T_m^0 \left(1 - \frac{1}{\gamma}\right) + \frac{T_c}{\gamma} \quad (2)$$

where  $T_m$  indicates the melting temperature obtained from reheating scan of isothermally crystallized samples with 10°C/min heating rate, and  $\gamma$  is a constant which depends on the lamella thickness. In our study, all crystallized sample showed multiple endotherms during DSC scans. This multiple endothermic behavior was also reported in other works [5,15]. Semicrystalline polyesters showed two or three melting endotherms which were denoted as  $T_m(I)$ ,  $T_m(II)$ , and  $T_m(III)$  normally, depending on crystallization temperature. Righetti studied these melting phenomenon of branched poly (butylene terephthalate)[16] (PBT) and poly(butylene adipate-co-isophthalate)[5] (PBAI). He explained that  $T_m(I)$ , observed at about 5~10°C above crystallization temperature, was the melting of crystallized portions of the amorphous phase,  $T_m(II)$  is that of primary crystal formed at crystallization temperature, and  $T_m(III)$  is that of recrystallized portion during DSC scan. From these consideration,  $T_m(II)$  was regarded as a melting temperature of all samples in our study.

$T_m^0$  can be obtained by the extrapolation of the experimental melting temperature into the  $T_m = T_c$  line as shown in Figure 6 and evaluated results of  $T_m^0$  were given in Table 4.  $T_m^0$  of 3 wt%-PET/CT is about 273°C and 7 wt%-PET/CT is 259°C. PET homopolymer's  $T_m^0$  is 283°C. This reduction of equilibrium melting temperature could be due to the decrease in the perfectness of crystalline as the comonomer content increased. A series of PET/I also showed similar tendency.

### Overall Crystallization Kinetics

The copolymer sample was crystallized isothermally to evaluate the crystallization kinetics using the following

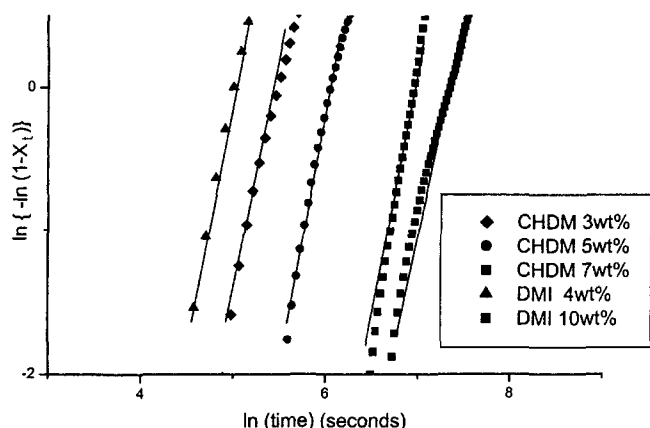


Figure 4. Avrami plot of PET copolymer at 207°C.

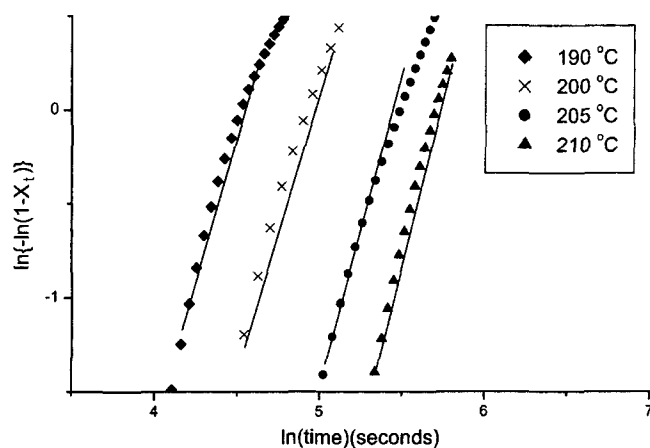


Figure 5. Avrami plot of PET copolymer with 3 wt% CHDM at various temperatures.

modified Avrami's equation (3) suggested by Khanna and Taylor[15].

$$1 - X_t = \exp(-k \cdot t)^n \tag{3}$$

where  $k$  is the overall kinetic constant,  $n$  is the Avrami exponent describing the mechanism of crystalline growth.  $X_t$  is the fraction of crystallized materials at any time  $t$ .

Figures 4 and 5 were shown according to equation (4) in a double-logarithmic form of equation (3).

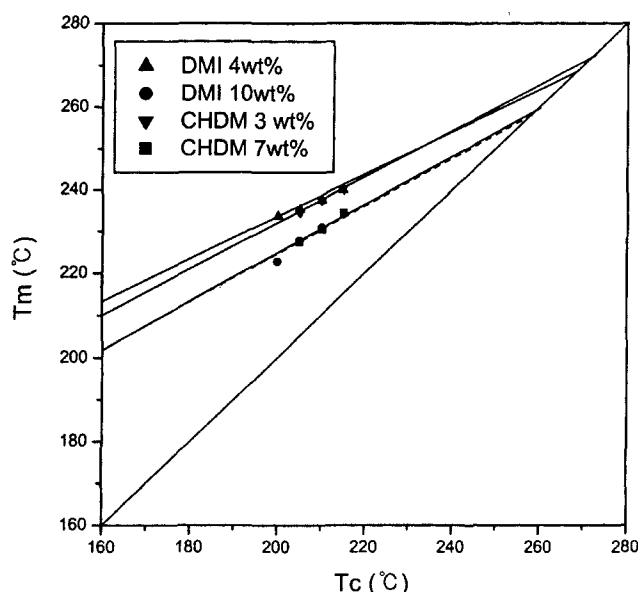


Figure 6. Hoffman-Weeks plot of PET copolymer.

$$\ln[-\ln(1 - X_t)] = n \ln k + n \ln t \tag{4}$$

A plot of  $\ln[-\ln(1 - X_t)]$  vs  $\ln t$  yielded a straight line in which the slope is equal to  $n$  and intercept is equal to  $n \cdot \ln k$ . Figure 4 showed Avrami plot of various compositions of PET copolyesters at 207°C, and Figure 5 was same plot of PET copolyester with 3 wt% CHDM at different temperature. Similar data obtained for all PET copolyesters. The value of  $n$  and  $k$  were listed in Table 3. Avrami plot of all PET copolyesters showed linearity at an early stage. However it showed a little deviation from linearity at the end of crystallization. The deviation from linear slope could be attributed to secondary crystallization. Ismail[17] studied the morphology of crystallized PET at different crystallization time and explained crystallization mechanism; initially, dominant lamella grows, from common axis and splay apart to form an array radiating outwards which was called primary crystallization, and then secondary crystallization began within interstitial regions.

The values of  $n$  for primary crystallization were close to 3 for all the samples, indicating a heterogeneous spherulitic

Table 3. Avrami kinetic parameters (overall rate  $k = (10^{-3})$ )

$T_c$	CHDM 3 wt%			CHDM 7 wt%			DMI 4 wt%			DMI 10 wt%		
	$t_{1/2}(\text{min})$	$n$	$k$	$t_{1/2}$	$n$	$k$	$t_{1/2}$	$n$	$k$	$t_{1/2}$	$n$	$k$
180	0.9	3.1	12.8	2.06	2.9	3.6	0.86	3.1	13.1	3.71	3.1	3.73
190	1.42	3.0	10.1	3.31	2.9	2.68	1.01	3.2	11.8	4.11	3.2	2.49
200	1.99	3.0	7.53	7.75	3.1	1.47	1.69	3.0	8.62	9.34	3.1	1.61
205	3.48	2.9	4.05	15.9	3.2	0.86	2.21	3.0	6.33	12.9	3.0	0.66
210	4.48	3.1	3.31	25.8	3.0	0.58	3.2	2.9	4.1	-	-	-

**Table 4.** Equilibrium melting temperature of PET copolymer

	CHDM 3 wt%	CHDM 7 wt%	DMI 4 wt%	DMI 10 wt%
$T_m^o$ (°C)	272.9	259.1	268.6	258

structure. The fact that the values of  $n$  were similar for all the samples, indicates that the mechanism of isothermal crystallization is not affected by comonomer content. The values of  $k$  reduced and the half time of crystallization,  $t_{1/2}$ , increased with comonomer contents. Frank and Zachman [18] attributed this result to the decrease in degree of supercooling ( $\Delta T = T_m^o - T_{cc}$ ), resulting from  $T_m$  decrease due to comonomer insertion and this is due to the irregularities introduced by comonomer in the PET regular structure [19]. But there are no significant differences between CHDM and DMI in terms of the effect of the chemical structure upon crystallization kinetics.

### Surface Energy

Surface energy was evaluated using the Lauritzen and Hoffman growth theories [20] for crystallization. The Lauritzen and Hoffman theory provided expressions for the linear growth rate ( $G$ ) with which spherulites or axialities grow radially, as given in equation (5).

$$G = G_o \exp(-\Delta E/k_b T_c) \exp(-\Delta G_g^*/k_b T_c) \quad (5)$$

where  $G_o$  is a pre-exponential temperature independent constant,  $\Delta E$  is a activation energy for transport from the isotropic phase to anisotropic phase,  $\Delta G_g^*$  is a the critical change in free energy for secondary nuclei formation,  $T_c$  is a crystallization temperature and  $k_b$  is the Boltzman constant ( $1.38 \times 10^{-23}$  J/K).

In Palys's work [21], the crystallization behavior of PET corresponded to regime II was introduced in the Lauritzen and Hoffman theory, and  $\Delta G_g^*$  is expressed by in equation (6).

$$\Delta G_g^* = 2 b_o \sigma_e T_m^o / \Delta H \Delta T \quad (6)$$

where  $b_o$  is a monolayer thickness,  $\Delta H$  is a heat of fusion, and  $\sigma$ ,  $\sigma_e$  are lateral surface energy and fold surface energy, respectively. For PET, the values of  $\Delta H$  and  $b_o$  are well known as  $1.8 \times 10^8$  J/m<sup>3</sup> and 5.53 Å, respectively [21]. If activation energy for transport of inter-phase in equation (5) is ignored, the measurement of linear growth rate and  $T_m^o$  could yield the value of the product  $\sigma \sigma_e$  by combining equations (5) and (6). The linear growth rate of crystalline polymer can be experimentally determined by polarized light microscopy. In this work, however, diameter of PET and PET copoly-esters spherulite was about 8 μm which was too small to be observed. So, equation (7) was introduced from a relation between overall kinetics rate,  $k$ , from Avrami equation (8) and the nucleation rate,  $N$ , and the linear growth rate,  $G$ , with which spherulite or axialite grows radially, Jabarin's study [8] alike.

$$\ln k = C_o - 4\Delta G_g^*/k_b T_c \quad (7)$$

$$k = \frac{4}{3} \pi N G^3 \quad (8)$$

where  $N$  is a nucleation rate,  $G$  is a linear growth rate and  $C_o$  in equations (7) is a constant which is related to the potentials for nucleation and  $G_o$ .

From equations (6) and (7), we can obtain equation (9).

$$\ln k = C_o - 8b_o \sigma_e T_m^o / k_b T_c \Delta H \Delta T \quad (9)$$

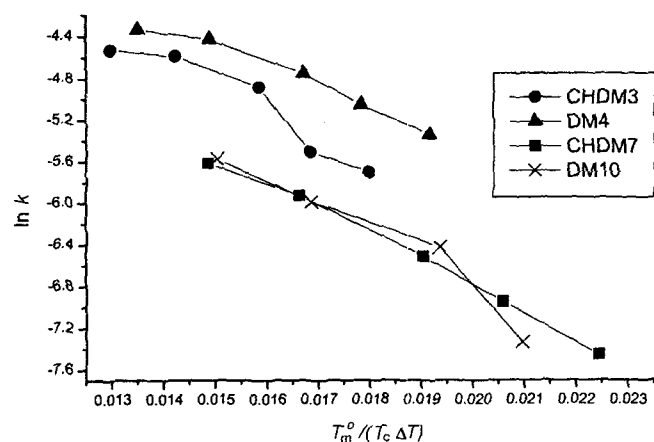
The the product  $\sigma \sigma_e$  of crystalline can be measured from the slope of plotting  $\ln k$  vs  $T_m^o/T_c \Delta T$ . This plot was presented in Figure 7. The slope of all copolyesters is a about  $189 \times 10^{-6}$  J<sup>2</sup>/m<sup>4</sup> regardless of comonomer contents, and this value is a good agreement with Palys' study of PET homopolymer [21]. As  $\sigma_e$  is strongly correlated with the work of chain folding, the obtained results suggest that the presence of comonomer unit in the contents of less than 10 wt% do not affect on the chain folding.

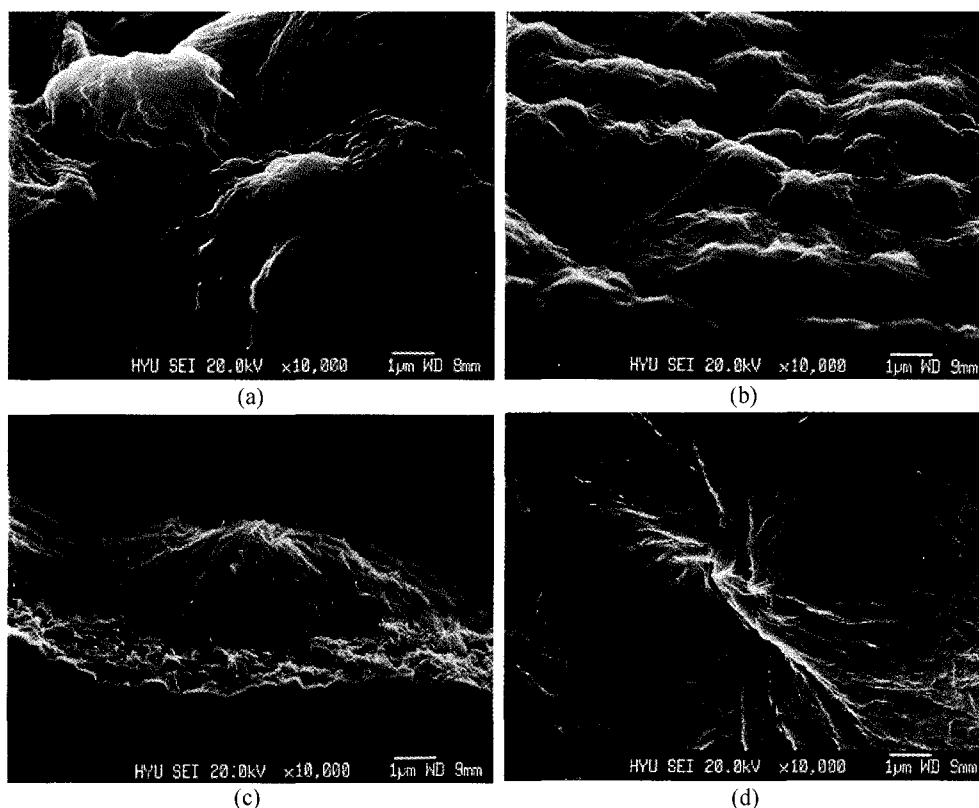
But, the plots of copolyesters containing comonomers less than 5 wt% showed a mild curvature at low temperature. This result is due to the fact that the overall crystallization growth rate was evaluated under the assumption that lamellar crystal grows in a manner of perfect spherulitic forms. The nucleation density increase as the supercooling increases, so that there is the impingement among crystallites at earlier crystallization stage and imperfect spherulites were formed. At that point, the linear crystallization growth was ceased, however overall crystallization could proceed.

### Morphology

All copolyesters and homo PET showed a spherulitic structure as shown in Figure 8, when it was examined by SEM after crystallized from the melt at various temperatures for 24 hours. The impingement among the crystallite was shown in Figure 8-a.

Comparing Figure 8-b with Figure 8-c for the samples

**Figure 7.** Plot for evaluation of surface energy of PET copolymer.



**Figure 8.** SEM micrographs of PET and PET copolymer: (a) Spherulite of PET crystallized at 180°C, (b) Spherulite of PET copolymer containing 4 wt% DIM, crystallized at 200°C, (c) Spherulite of PET copolymer containing 7 wt% CHDM, crystallized at 200°C, (d) Spherulite of PET copolymer containing 7 wt% CHDM, crystallized at 210°C.

crystallized at 200°C for 24 hours, especially, the size of spherulites for the 7 wt% PET/DMCT is bigger than those of 4 wt% PET/I. At the same temperature, 200°C, 7 wt% PET/DMCT should have the lower nucleation density and slower molecular chain motion, so that it could form much bigger spherulites. In the case of Figure 8-c and Figure 8-d for the samples crystallized at different temperature, size of spherulites crystallized at 210°C is bigger than those at 200°C. From the SEM micrograph and WAXD pattern results, it could suggest that crystallization mechanism is not affected by comonomer introduced to polymer backbone, but the size of crystallite is affected by comonomer contents.

### Conclusions

We synthesized a series of poly(ethylene terephthalate-co-isophthalate) and poly(ethylene terephthalate-co-dimethyl cyclohexane terephthalate) copolyesters containing dimethyl isophthalate(DMI) and 1,4-cyclohexane dimethanol(CHDM), respectively. To maintain PET homopolymer properties, DMI and CHDM content was less than 10 wt%. Regardless of the composition, the value of the Avrami exponent was about 3, which indicates that crystallization mechanism of the copolyester was similar to those of PET homopolymer. The

morphology of copolyesters showed spherulitic structure. From the DSC results, it was suggested that the comonomer components act as a retardant against crystallization because it might restrict the movement of molecular chains. Through Avrami and Hoffman-Weeks equation, we measured the surface free energy of copoly-esters. The value of the surface free energy is a about  $189 \times 10^{-6} \text{ J/m}^2$  regardless of comonomer contents, and this value is a good agreement with Palys' results on PET homopolymer. But, the values of  $k$  decreased and the half time of crystallization increased with increasing comonomer content.

### Acknowledgement

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