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랜덤 공중합체의 화학구조가 결정화거동에 미치는 효과

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Effect of Chemical Structure on Crystallization Behavior in Random Copolymers

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요 약 : 에틸렌 테레프탈레이트-1,4-시클로헥실렌 디메틸렌 테레프탈레이트 공중합체, P(ET-CT)의 화학구조가 결정화 거동에 미치는 효과를 DSC 분석을 통하여 조사하였다. 공중합체의 용융온도, 결정화도 및 결정화 속도는 공중합 조성이 증가됨에 따라 감소하였고 34몰%의 CT 조성에서는 결정화가 진행되지 않아서 이들 특성치를 관측할 수 없었다. 이러한 랜덤 공중합체의 결정화 특성을 평균 연쇄에 근거한 임계 결정성 연쇄 길이(the critical crystallizable sequence length)를 통하여 해석할 수 있었다. 34몰%의 CT조성을 갖는 공중합체의 비결정성은, 평균 연쇄 길이가 임계 결정성 연쇄길이보다 짧기 때문인 것으로 설명할 수 있었다.

Abstract : The effects of chemical structure on crystallization behavior in poly(ethylene terephthalate -co- 1,4-cyclohexylene dimethylene terephthalate), P(ET-CT) copolymers were investigated by DSC analysis. The melting temperature, crystallinity and crystallization rate in the copolymers decreased with an increase of the copolymer composition. However, the copolymer of 34 mole % CT was observed not to crystallize. Such crystallization behavior in the random copolymers could be discussed sucessfully with the critical crystallizable sequence length based on the averaged sequence. Non-crystallizability of the copolymer containing 34 mol % CT could be explained with its average sequence length shorter than the critical crystallizable sequence length.

INTRODUCTION

Crystallization behavior of pure polymers has been studied widely. In contrast, little information on the crystallization of copolymers is available. Much less are crystallization studies on copolymer system over the entire range of the copolymer composition.[1~5] A small variation in chemical struc-

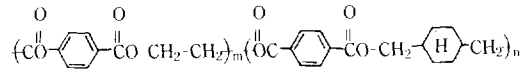
ture, such as the copolymer composition and sequence distribution, brings about considerable changes in crystallization behavior as well as crystal structure in random copolymers. The melting temperature and the crystallinity sharply decrease with increasing the composition of comonomer for the following reasons. The crystallization behavior in random copolymers is controlled by local crystallization due to fractionation of the crystallizable sequences. The short sequences can not be involved in crystallization, whereas the longer crystallizable sequences in major component can crystallize. The shorter is the crystallizable sequences of repeating units, the lower is the temperature needed to induce its crystallization from the molten state. As the temperature is lowered, however, the chain mobility is increasingly restricted, hindering the diffusion of crystallizable sequences to crystallization sites.[6]

Before investigating the effect of chemical structure on crystallization behavior in random copolymer systems, the chemical structure was investigated. According to previous NMR study,[7] poly (ethylene terephthalate -co- 1,4-cyclohexylene dimethylene terephthalate), P(ET-CT) copolymers were characterized as statistically random copolymers, which could be confirmed by 'diad' sequence distribution calculated with ^{13}C NMR spectra.

In this study, the effect of average copolymer sequence length on crystallization behavior of random P(ET-CT) copolymers is investigated from the viewpoint of the crystallizable sequence length over the entire copolymer composition.

EXPERIMENTAL

Samples. Poly(ethylene terephthalate -co- 1,4-cyclohexylene dimethylene terephthalate), P(ET-CT) copolyester samples were used in this study.



All samples were kindly supplied by Eastman Kodak and Sun Kyung Industries. The composition and average sequence lengths calculated from diad sequence distribution were obtained previously with ^1H NMR and ^{13}C NMR spectroscopies,[7] and listed in Table 1.

Samples were dried at 100℃. under vacuum for 24 hours, hot-pressed to form a thin film, and quenched in liquid nitrogen. The isothermally crystallized film samples were obtained by crystallization at 180℃ for 50 minutes.

Measurements. The measurement of thermal properties was made using a DSC(Du Pont 900) at a heating rate of 20℃/min. Temperature calibration was done with indium.

Wide-Angle X-ray Diffractogram(WAXD) was obtained with a diffractor(Rigaku Rad B) at 40 kV and 20 mA. Ni-filtered Cu Kα radiation(the wave length : 0.154 nm) was used.

The degree of crystallinity was determined by X-ray method, evaluating the contributions of crystalline reflections and amorphous halo separately,[8] and it was also confirmed by DSC method.

RESULTS AND DISCUSSION

Fig. 1 shows DSC thermograms for the quenched samples. The melting temperature(T_m) decreases and the cold crystallization temperature (T_{cc}) increases with an increase of the minor component of copolymer. It is interesting to note that

Table 1. The Copolymer Composition and Averaged Sequence Lengths in P(ET-CT) Copolymer Samples, Cited from Ref.[7]

Composition (ET/CT)		Inherent viscosity	Averaged sequence length			
			〈Ln〉e	〈Ln〉c	〈Lw〉e	〈Lw〉c
PET,	100/0	0.74	–	–	–	–
COP-	95/5	0.80	17.7	1.1	29.4	1.1
	80/20	0.65	4.7	1.3	8.4	1.5
	66/34	0.75	3.0	1.5	4.9	2.0
	34/66	0.75	1.6	2.8	2.1	4.5
	20/80	0.75	1.3	4.5	1.6	7.9
PCT,	0/100	0.89	–	–	–	–

* n and w indicate the number-averaged and the weight-averaged.
** e and c indicate ET and CT repeating units.

the peaks of T_m and T_{cc} in COP-(66/34) are not observed during heating process. The enthalpies of cold crystallization and fusion can be obtained from the exothermic and endothermic peak areas, respectively, and its values are shown in Fig. 2. These thermal properties can be discussed on the basis of copolymer sequence length.

The value in Table 1 is plotted again in Fig. 3. The average sequence lengths for both ET and CT units become shorter with an increase of minor copolymer component. The crystallizable sequence length of random copolymer can be statistically interpreted in terms of the average sequence length (⟨L⟩). The shorter is the crystallizable sequence length, the lower are melting temperature and the higher cold crystallization temperature needed to induce its crystallization from the glass state, as shown in Fig. 1. The shortened average sequence length of major component and the increased interference by minor component give rise to an increased free energetic barrier during crystallization process, preventing the major component molecules from rearranging and packing.

According to the X-ray study on P(ET-CT) co-

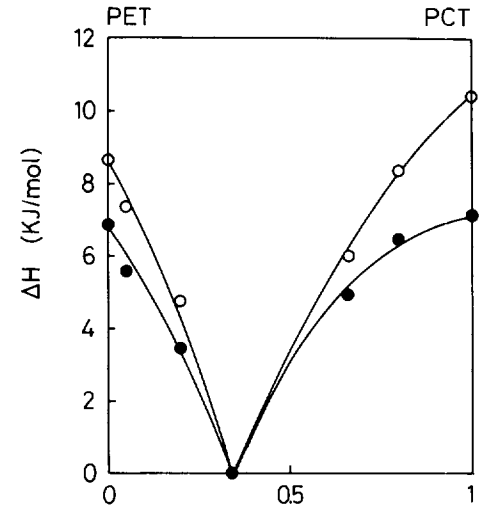


Fig. 2. Plots of enthalpy against the mole fraction of CT unit.(● : cold crystallization, ○ : melting)

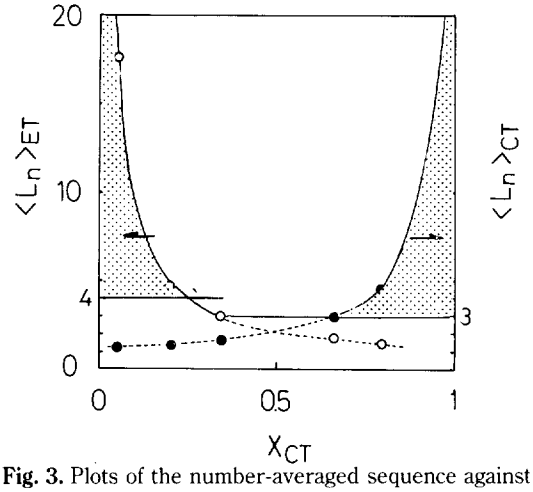


Fig. 3. Plots of the number-averaged sequence against the mole fraction of CT units.(● : ET unit, ○ : CT unit)

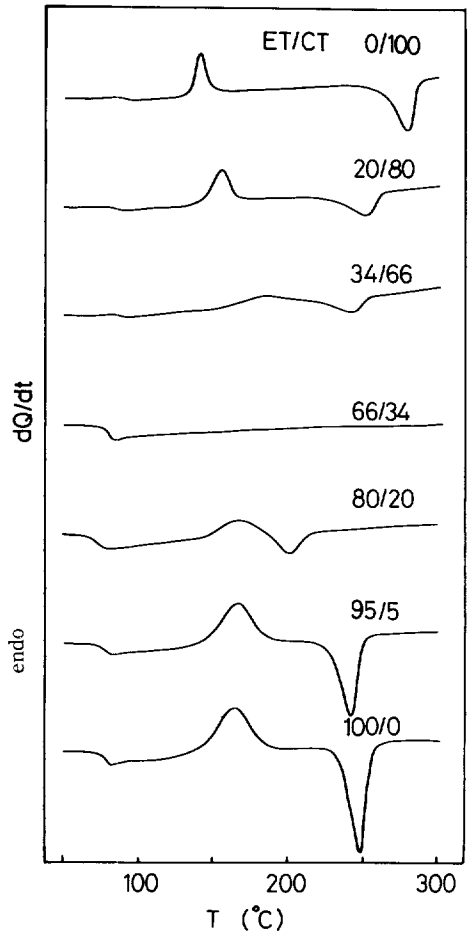


Fig. 1. DSC thermograms for quenched samples.

polymer,[8] the copolymer in the composition range of 0 to 20 mol% CT makes PET crystal, whereas the copolymer in the range of 66 to 100 mol % CT makes PCT crystal. In addition, the critical crystallizable sequence length(ξ_c) of these copolymers were obtained from the critical crystal core size along the chain axis with the assumptions($\xi_c = l_c = L \times X_c = m \times c$, where l_c, L, X_c, m and c indicate the critical crystal core size, long spacing, crystallinity, an integer and repeating unit length, respectively). As the results, four ET units for ET crystal and three CT units for CT crystal were obtained on the base of the number-averaged sequence length.[8] The dotted area in Fig. 3 corresponds to the sequences longer than ξ_c. Comparing two copolymers containing same copolymer sequence length, COP-(66/34) with three ET units is noncrystallizable for the sequence length shorter than ξ_c(= four ET units), whereas COP-(34/66) with three CT units is crystallizable for sufficient sequence length(ξ_c=three CT units). Accordingly, the crystallizability of random copolymers can be discussed successfully with average sequence length. In addition, the ξ_c values based on the weight-averaged sequence length were six ET units for PET crystal and four CT units for PCT crystal.[8]

However, the investigation of isothermal crystallization should be required for more detailed discussion, since cold crystallization process is a non-equilibrium condition. Fig. 4 shows DSC thermograms for the isothermally crystallized samples at 180℃ for 50 minutes that is enough time to reach a saturated(or equilibrium) state of the crystallization. The thermogram of COP-(66/34) is excluded here, since its shape is as almost same as that in Fig. 1, showing neither cold crystallization nor melting peak. No cold crystallization peak is found for all samples and two melting peaks are observed, as seen in Fig. 4. The high melting peak is attributed to the crystal formed by the primary crystallization. In contrast, the low and small melting peak can be associated with melting of the crystal formed by the secondary crystallization.[9~11] The low melting peak in polymers is usually observed

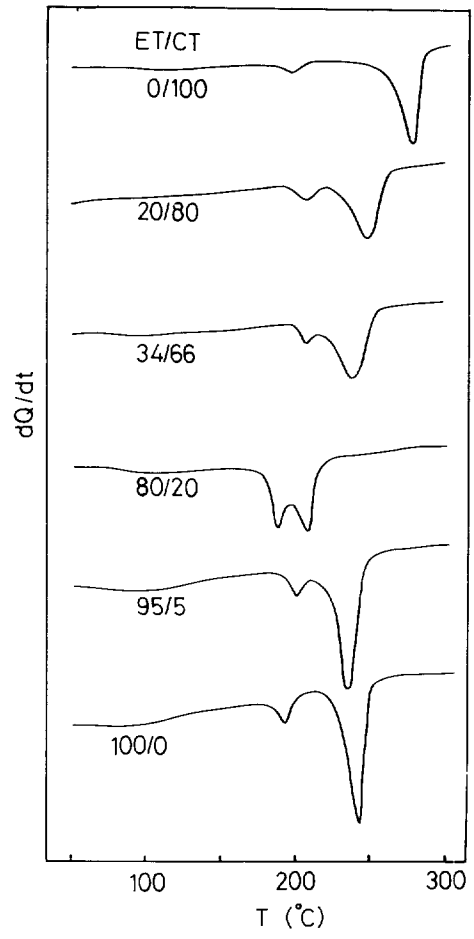


Fig. 4. DSC thermograms for the samples crystallized isothermally at 180℃ for 50 minutes.

at about 10℃ above the isothermal crystallization temperature,[9,10] even though exact interpretation of secondary crystallization behavior still remains unknown. This behavior is usually interpreted as the melting of 'fringed micelle type' crystal[9] or of the crystal formed during crystal perfection process.[11]

Fig. 5 is the plots of the heat of fusion(a), and the crystallinity determined by DSC($X_c = \Delta H/\Delta H^\circ$) and WAXD methods(b), for the samples of Fig. 4. The heat of fusion for the perfect crystal(ΔH°) could be determined by extrapolation to the perfect crystal density of 1.265 g/cm^3 for PCT[12] and 1.515 g/cm^3 for PET.[13] The extrapolated values are found

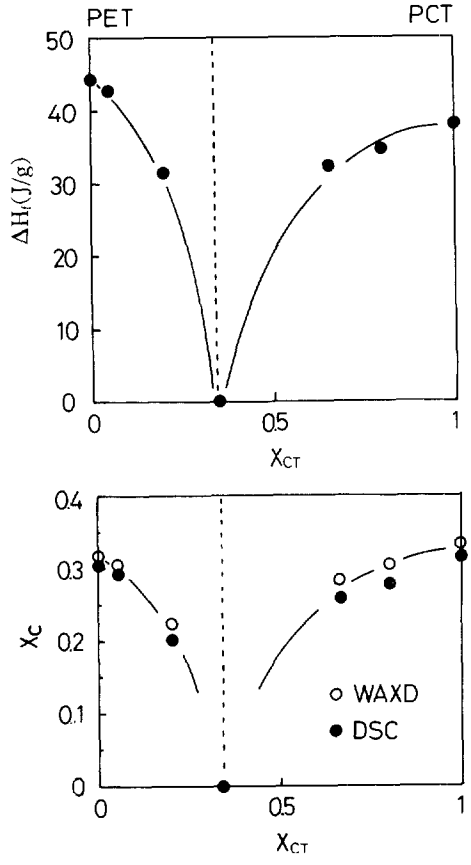


Fig. 5. Plots of the heat of fusion(a), and the crystallinity(b) against the mole fraction of CT unit.

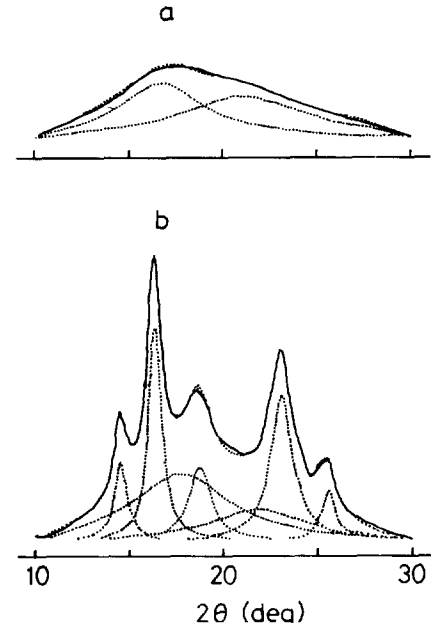


Fig. 6. The separated WAXD curves of PCT. a) amorphous halo, b) crystalline reflections.

to be 27.75 KJ/mol for PCT and 26.9 KJ/mol for PET.[14] In WAXD method, the crystallinity can be obtained from the relative ratio of crystalline peak area to the total area observed.[8] The crystalline peaks and amorphous halo could be separated successfully by a fitting program using a Lorentzian type of diffraction function, as shown in Fig. 6. A good coincidence between two methods can be obtained.

The copolymer composition dependence of the crystallinity is very noticeable. If the content of minor component is higher than about 34 mol %, the copolymer does not crystallize independent of the crystallization method. In general, block and graft copolymers can easily contain crystallizable repeating unit of sufficient sequence length to build up crystallinity. In contrast, random copolymers show sharp reduction in crystallinity with a increase of the content of minor copolymer component.[6] The crystallinity in random P(ET-CT) copolyesters decreases with minor copolymer composition and drops to zero around the composition of 34 mol % CT. Effect of the copolymer composition on crystallization behavior is also found in crystallization kinetics. Fig. 7 shows the reciprocal of the crystallization half time, namely a crystallization rate, which was measured from the exothermic peak at 180℃ in DSC thermogram. COP-(66/34) sample did not crystallize at all.

The crystallinity can also be discussed with the fraction of copolymer sequences. The fraction of sequence with the length of 'm' can be calculated by random copolymer statistics based on a equilibrium theory.[15~17]

$$N_A(m) = P^{m-1}(1-X_A) \quad (1)$$

$$W_A(m) = m \times P^{m-1}(1-X_A)^2 \quad (2)$$

where N_A and W_A indicate the fractions of the number- and the weight-averaged sequence with the length of m, X_A is the mole fraction of A repeating units. In equation (1) and (2), $m \geq 2$.

Fig. 8 is the plots of N(m) for ET and CT units sequences against the sequence length m calculated with equation (1). The dotted area indicates the fraction of copolymer sequences longer than the critical crystallizable sequence length($m \geq 4$ for ET unit, and $m \geq 3$ for CT unit), as in Fig. 3. This area can be regarded as the fraction to build up

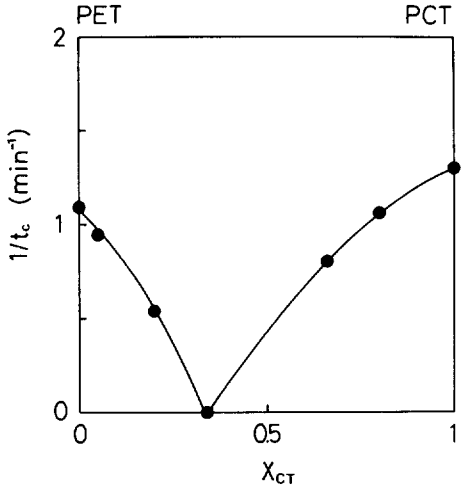


Fig. 7. Plots of the reciprocal of the crystallization half time against the mole fraction of CT unit.

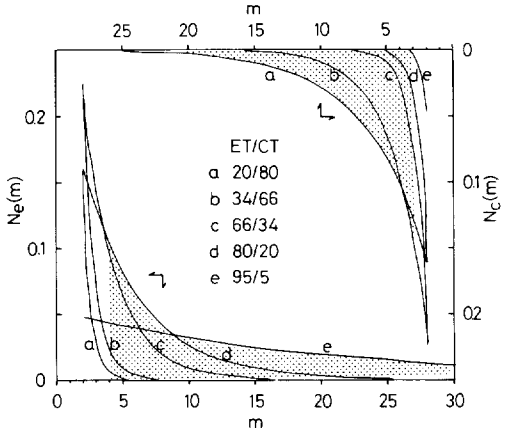


Fig. 8. Plots of N(m) against the length of sequence. (e and c indicate ET and CT units)

the theoretically maximum crystallinity in random copolymers.[15,17] To discuss this fraction, a new parameter needs to be defined for the number- and weight- averaged sequences as follow

$$X_c^\circ(N_A) = \Sigma N_A (m \geq 4 \text{ for ET, } 3 \text{ for CT}) / \Sigma N_A \quad (m \geq 2) \tag{3}$$

$$X_c^\circ(W_A) = \Sigma W_A (m \geq 6 \text{ for CT, } 4 \text{ for CT}) / \Sigma W_A \quad (m \geq 2) \tag{4}$$

Here, X_c° can represent the degree of the maximum or equilibrium crystallinity in random copolymers, assuming all sequences longer than ξ_c could take part in crystallization. In addition, the relative crystallinity of copolymer to that of homopolymer can be calculated with the experimental value of ΔH(copolymer)/ΔH(homopolymer), and it can be compared with the value(X_c°) calculated by equations (3) and (4).

Fig. 9 shows $X_c^\circ(N_A)$, $X_c^\circ(W_A)$ and the values of relative crystallinity calculated from the values of ΔH in Fig. 5-a. In the composition range of 66 to 100 mol % CT, the relative crystallinity can reach the values of equation (4). This means that almost all weight-averaged sequences longer than ξ_c can be included into the crystalline phase and

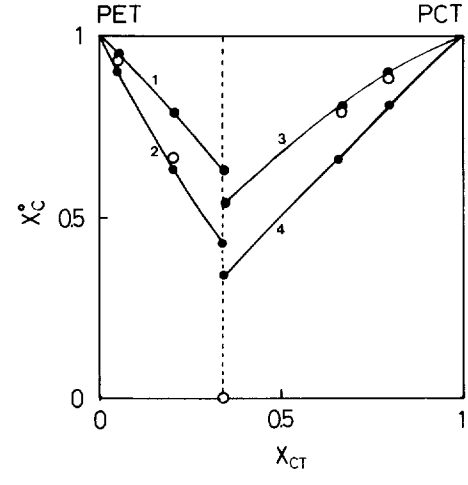


Fig. 9. Plots of X_c° against the mole fraction of CT unit.(1-$X_c^\circ(W_{ET})$, 2-$X_c^\circ(N_{ET})$, 3-$X_c^\circ(W_{CT})$, 4-$X_c^\circ(N_{CT})$, ●-$\Delta H_{co}/\Delta H_{homo}$)

build up the crystallinity upto equilibrium value. According to solid state NMR study,[18] the copolymer in the range of 66 to 100 mol % CT makes isomorphism due to co-crystallization of ET units and thus the contribution of ET sequences to the relative crystallinity can also be considered. On other hand, the relative crystallinity in the range of 0 to 20 mol % CT is lower than the equilibrium crystallinity of equation (4). This can be explained with the fact that CT sequences are almost excluded from PET crystal.[18] However, it is observed that the crystallinity in random copolymers can be associated with the weight-averaged sequence rather than the number-averaged sequence.

CONCLUSION

The effects of chemical structure on crystallization behavior in P(ET-CT) copolymers were investigated by DSC analysis.

In case of the melt-quenched samples, the melting temperature decreases and the cold crystallization temperature increases with an increase of the copolymer composition. The peaks of cold crystallization and melting decrease with the copolymer composition and disappear at the composition of 34 mol % CT.

The crystallinity and isothermal crystallization rate at 180℃ also show similar composition dependence as in cold crystallization behavior. No crystallization of COP-(66/34) could be explained with the average sequence length shorter than the critical crystallizable sequence length.

It is confirmed that the relative crystallinity in random copolymer to its homopolymer is associated with the weight-averaged sequence rather than the number-averaged sequence.

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