Co-crystallization behaviour and melting-point depression in poly(ethylene terephthalate-*co*-1,4-cyclohexylene dimethylene terephthalate) random copolyesters

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The crystallization behaviour of the poly(ethylene terephthalate-*co*-1,4-cyclohexylene dimethylene terephthalate) (P(ET/CT)) random copolyesters is studied by d.s.c. analysis. ET units can crystallize with complete rejection of the CT units from the crystals, whereas CT units can co-crystallize with incorporation of ET units to some extent, resulting in a minimum melting temperature at an intermediate composition of about 30–40 mol% CT. A good linear relation is found between the compositions at which the melting point exhibits a minimum experimentally in various random copolyesters and those at which the cohesive energies for two components estimated by group contribution methods are identical.

(Keywords: random copolymers; copolyesters; co-crystallization)

INTRODUCTION

In the crystallization behaviour of a binary A/B-type random copolymer which consists of both crystalline components, there is the possibility of finding some degree of isomorphism due to co-crystallization between A and B units with similar repeating units. Thus, co-crystallization is found in various polymers including copolyamides[1–6], copolyesters[7–13], vinyl polymers[14–18] and diene copolymers[19]. Co-crystallization requires a similar main-chain conformation between two comonomer segments in the crystal lattice. The co-crystallization behaviour can be divided into three types, depending on the chemical structure and the crystallizability of the A and B comonomeric units.

(i) Crystallization of A or B units takes place either in an A-polymer or a B-polymer crystal with complete rejection of the comonomer units from the crystals, exhibiting the crystal lattice transition from the A-crystal to the B-crystal at some intermediate copolymer composition.

(ii) A units can crystallize with complete rejection of the B units from the crystals, whereas B units can co-crystallize with incorporation of A units to some extent, depending on the copolymer composition. In both (i) and (ii) the melting temperature is dependent on the copolymer composition and exhibits a minimum (or eutectic point) at some intermediate composition at which the crystal lattice transition is usually observed.

(iii) A and B units can co-crystallize into a single crystal structure (copolymer isomorphism) over the full range of copolymer composition, exhibiting a continuous change in the lattice parameters from the A-crystal to the B-crystal and in the melting temperatures without reaching a minimum point.

The crystallization behaviour in random copolymers is controlled by local crystallization due to fractionation of the crystallizable sequences. The short parts of the crystallizable sequences cannot be involved in crystallization but the longer parts are capable of undergoing crystallization. The crystallizability of each comonomer unit may be a function of the crystallizable sequence distribution, the cohesive energy of molecules, the molecular mobility and the surface free energy of the crystal such as the end and lateral crystal surface energies. All of these parameters should be dependent on the copolymer composition. The crystallization behaviour of a random copolymer system is strongly influenced by copolymer sequence distribution. A small variation in the chemical structure brings about considerable changes in the crystallization behaviour. There are a lot of studies on these parameters of crystallization behaviour except from the point of view of cohesive energy of random copolymers. In this paper, the crystallization behaviour of a random copolyester system is studied in terms of thermodynamic equilibrium theory as a function of crystallization temperature over the entire range of copolymer compositions. The minimum melting temperature and the corresponding heat of fusion *versus* the copolymer composition are discussed on the basis of the cohesive energy corresponding to each component polymer.

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Table 1 Copolyester samples and their compositions

Polymer	Copolymer composition (ET/CT) (mol%) in solution	 in crystal
PET	100/0	100/0
P(ET/CT)-1	95/5	100/0
P(ET/CT)-2	80/20	100/0
P(ET/CT)-3	66/34	–
P(ET/CT)-4	34/66	13/87
P(ET/CT)-5	20/80	9/91
PCT	100/0	0/100

EXPERIMENTAL

Samples

The samples used in this study are listed in *Table 1*. The repeating unit of poly(1,4-cyclohexylene dimethylene terephthalate) (PCT) has a similar chemical structure to poly(ethylene terephthalate) (PET) except for the introduction of a cyclohexane ring between the methylene groups[20]. Poly(ethylene terephthalate-*co*-1,4-cyclohexylene dimethylene terephthalate) (P(ET/CT)) is a terephthalic copolyester based on ethylene glycol and 1,4-cyclohexane dimethanol. All samples except P(ET/CT)-2 are commercial products available from Eastman Kodak Company with the trademark of Kodpak or Kodar. P(ET/CT)-2 was kindly supplied by Sun Koung Industry.

The sequence distributions of the P(ET/CT) copolyesters determined by ^{13}C n.m.r. spectra were almost statistically random. The copolymer compositions in solution and in the solid state (crystallized) were analysed by ^{1}H and ^{13}C n.m.r. spectroscopy and are listed in *Table 1*[21,22].

Measurements

The samples were dried at 100°C under vacuum for 24 h, hot-pressed to form thin films and quenched into liquid nitrogen. The samples were isothermally crystallized from melt at various temperatures. The measurements of melting point and heat of fusion were made using a Dupont 910 DSC calorimeter at a heating rate of 20°C min^{-1} with indium as a calibration standard. Density measurements were made at 25°C in a thermostatically controlled density gradient column containing n-heptane and tetrachloromethane.

RESULTS AND DISCUSSION

D.s.c. curves of quenched copolyesters

Figure 1 shows the d.s.c. curves for the quenched samples. For all compositions except 34 mol% CT, a single melting temperature (T_m), a cold crystallization temperature (T_{cc}) and a glass transition temperature (T_g) are found during the heating process in d.s.c. The copolymer with 34 mol% CT shows only T_g, indicating that no crystallization occurred during the heating process. The T_m decreases and the T_{cc} increases with a change in the copolymer composition as shown in *Figure 2*. It is interesting to note that the T_g exhibits a discontinuous change at the composition of about 30 mol% CT. Details of this T_g change with the copolymer composition will be reported in a separate paper. Both T_m and T_{cc} peak areas decrease and disappear at about 30–40 mol% CT, as shown in *Figure 3*.

According to the results of n.m.r. spectroscopy[21,22],

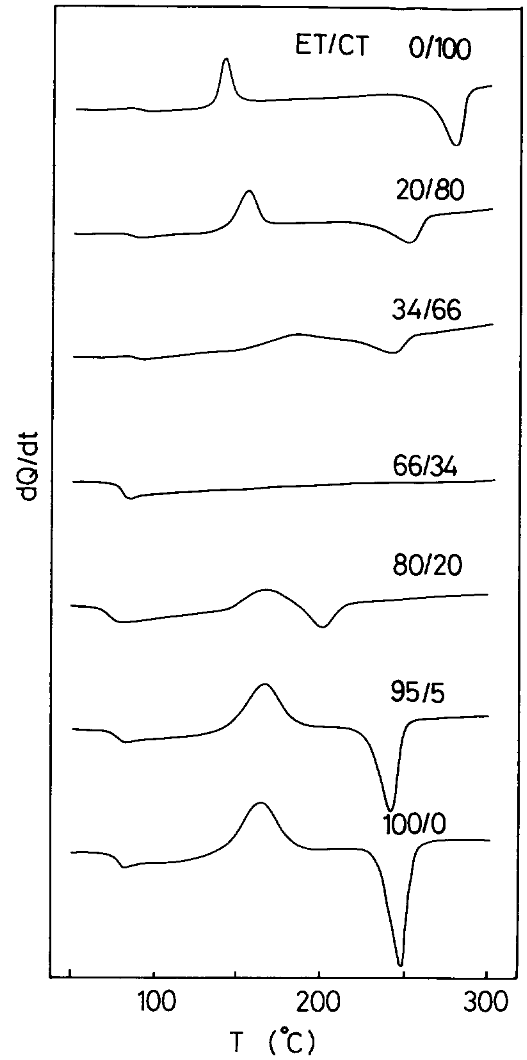

Figure 1 D.s.c. curves for the quenched P(ET/CT) copolyesters

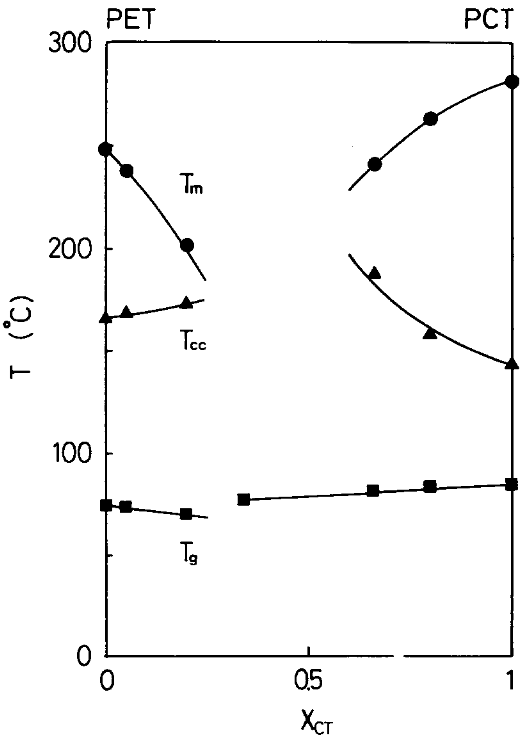

Figure 2 Melting temperature (T_m), crystallization temperature (T_{cc}) and glass transition temperature (T_g) as a function of copolymer composition expressed as CT molar fraction (X_{CT})

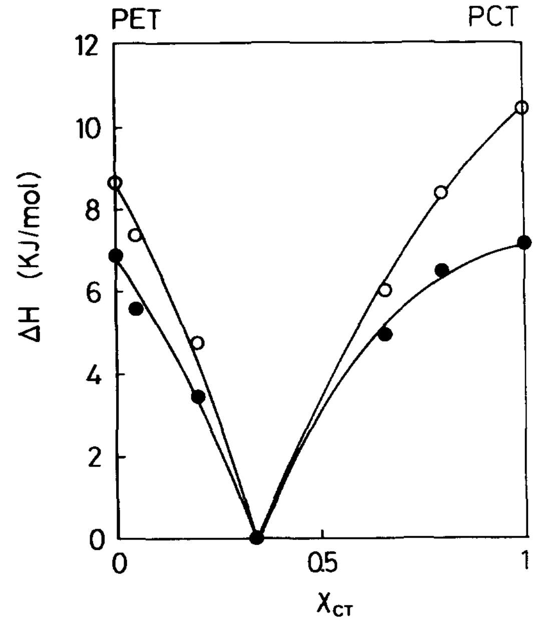

Figure 3 Heat of fusion (○) and heat of crystallization (●) as a function of CT molar fraction (X_{CT})

the crystalline phases in P(ET/CT)-1 and -2 copolymers consist of only the ET component, whereas those in P(ET/CT)-4 and -5 copolymers permit the incorporation of the comonomer units to some extent as seen in *Table 1*. X-ray analysis has also indicated that the crystal lattice dimensions of PCT are distorted by the inclusion of comonomer units but no changes are apparent in the PET lattice[23]. The crystal lattice transition also occurred at about 30 mol% CT. The crystal lattice of PCT can accommodate the repeating unit of PET but not *vice versa*, since the packing density of the PCT crystal[24] is much smaller than that of the PET crystal[25]. Therefore, the co-crystallization between PCT and PET is possible to some extent in the composition region rich in CT units, and minima in plots of T_m and the heat of fusion (ΔH_m) *versus* the copolymer composition are observed, as seen in *Figures 2* and *3*. Detailed discussions on the above thermodynamic properties are necessary on the basis of the equilibrium thermodynamic parameters, such as an equilibrium melting temperature.

Equilibrium melting temperature

Figure 4 shows d.s.c. thermograms for the copolyesters crystallized isothermally at 180°C for 50 min. The cold crystallization peak is not found but two melting peaks are observed. The higher melting peak is attributed to the crystals formed by isothermal crystallization but the lower small peak may be associated with the crystals formed during the cooling process after isothermal crystallization.

In order to determine the equilibrium thermal properties for the copolyesters, the polymer samples were isothermally crystallized at different temperatures. Plots of the heat of fusion against density for the homopolymers of PET and PCT show good linear relations (see *Figure 5*). The heat of fusion for the perfect crystal was determined by extrapolation to the perfect crystalline density of 1.265 g cm^{-3} for PCT[24] and 1.515 g cm^{-3} for PET[25]. The extrapolated values are found to be 27.75 kJ mol^{-1} for PCT and 26.90 kJ mol^{-1} for PET. The linear relationships between the heat of fusion and the density are also extrapolated to the zero heat of fusion so that amorphous densities of 1.190 g cm^{-3} for PCT and 1.335 g cm^{-3} for PET are obtained. These extrapolated values for PET agree very well with the reference data[26].

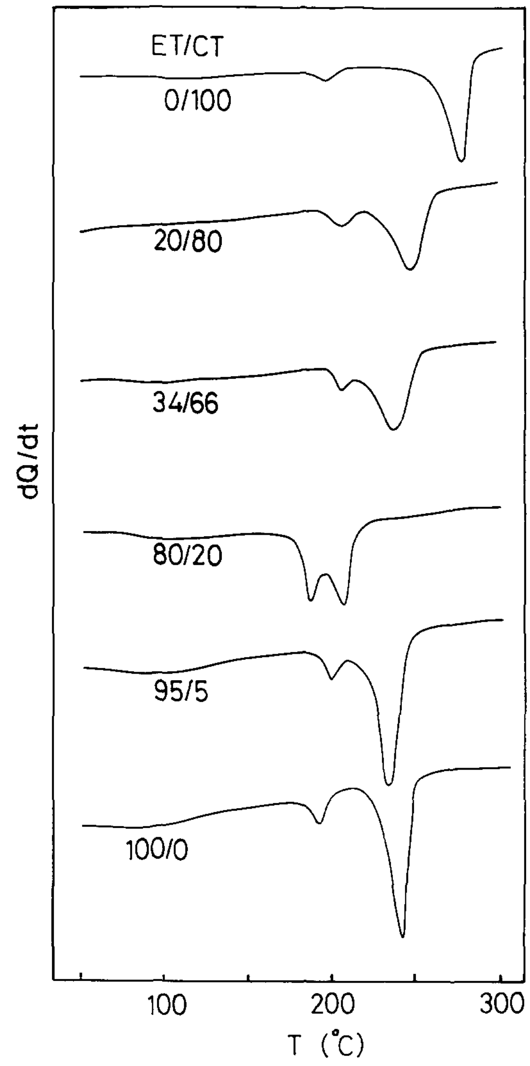

Figure 4 D.s.c. thermograms for P(ET/CT) samples crystallized isothermally at 180°C for 50 min

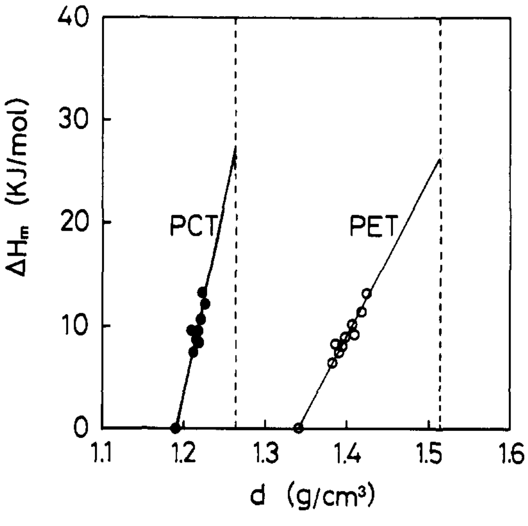

Figure 5 Relationships between heat of fusion (ΔH_m) and density (d) for PET and PCT samples crystallized isothermally at various temperatures

Figure 6 shows the plots of observed melting temperature (T_m) and crystallization temperature (T_c) according to Hoffman–Week plots[27]. The T_m depends on the T_c according to equation (1), which can be assumed to apply to a copolymer system:

$$T_m^\circ - T_m = M(T_m^\circ - T_c) \qquad (1)$$

where T_m° denotes the equilibrium melting temperature of a copolymer crystal of an infinitely large crystal of the corresponding composition. The parameter M lies between zero and unity as a function of crystalline morphology. For example, $M=0$ for a large extended chain crystal, $M=0.5$ for a lamellar crystal and $M=1$ for a small fibrous crystal[27–29]. The extrapolated intercept of the T_m/T_c plot on the line depicting $T_m = T_c$ leads to a value for T_m°. The values of M and T_m°, thus obtained, are shown in *Figures 7* and *8*, respectively, as a function of the copolymer composition. T_m° appears to have a minimum point at about 30 mol% CT. Here, the copolymer with the composition of 34 mol% CT could not be crystallized at all from the molten state at any crystallization temperatures in this study. Very little crystallization, however, occurred under the molecular orientation[30].

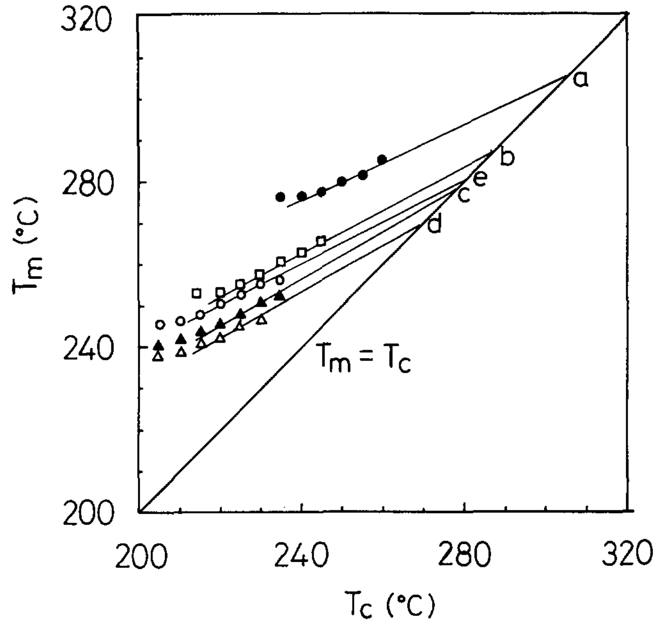

Figure 6 Plots of melting temperature (T_m) against crystallization temperature (T_c) for P(ET/CT) samples: (a) PCT; (b) P(ET/CT)-5; (c) P(ET/CT)-4; (d) P(ET/CT)-1; (e) PET

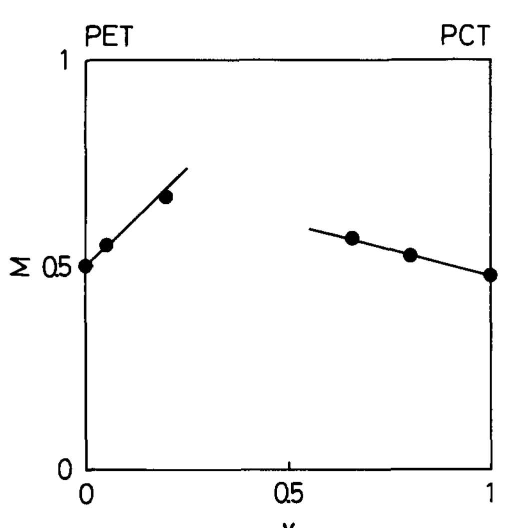

Figure 7 Slopes of M on T_m/T_c plots for P(ET/CT) samples as a function of copolymer composition (X_{CT})

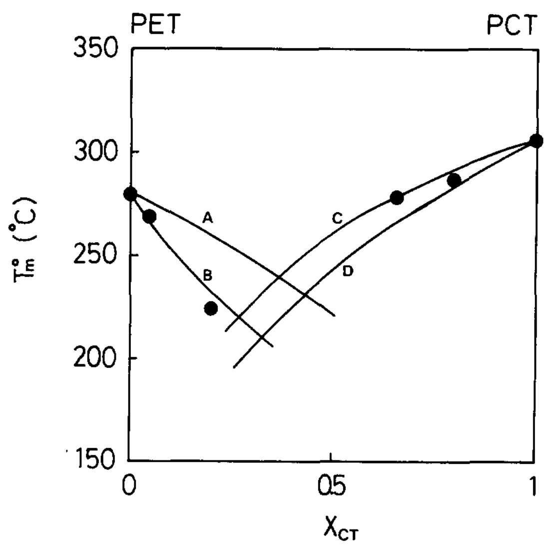

Figure 8 Extrapolated equilibrium melting temperatures (T_m°) for P(ET/CT) samples *versus* copolymer composition (X_{CT}): experimental data, (●); curves A to D are theoretically predicted by Flory (A and D), Baur (B) and Helfand and Lauritzen (C)

The value of M increases with the comonomer content and its composition dependence in the range 80–100 mol% ET is about three times larger than that in the range 66–100 mol% CT. Various factors affect M, such as the ratios of the mature crystallite dimensions (d, l) to those of the initial nucleus (d^*, l^*) (i.e. $m=(l/l^*)$ and $n=(d/d^*)$, where l and d are the crystallite thickness and the lateral dimension, respectively) and the ratio of the surface energies between the crystallite (σ) and the nucleus (σ^*) (i.e. $a=(\sigma_e/\sigma_e^*)$ and $b=(\sigma_s/\sigma_s^*)$, where σ_e and σ_s are the end and the lateral surface free energies, respectively) as expressed by equation (2)[27–29]:

$$M = a/2m + b/n \qquad (2)$$

For the special case of the lamellar crystallite with regularly folded chains, assuming that $a=b=1, m=1$ and $n \gg 1$, M reduces to 0.5, which was originally given by Hoffman and Weeks[27]. In the case of copolymer crystallization, the surface energies and the crystallite dimensions are strongly dependent on the copolymer composition; however, it may be simply assumed that the value of M is considered solely on the basis of the crystallite dimensions. It can be expected in random copolymers that the ratio of the lateral dimensions (n) between the mature crystallite and the initial nucleus becomes smaller with an increase in the comonomer units and then M will be larger than 0.5. Therefore, the results in *Figure 7* indicate that the crystal size of PET will decrease much more than that of PCT as the comonomer component increases.

The melting depression in a random A/B-copolymer system is expressed as a function of the copolymer composition (X) as predicted by Flory[31], Baur[32], Sanchez and Eby[33], Helfand and Lauritzen[34] and many others[35–39]. For example, when the sequences of A units in the random copolymer can be crystallized but the B units are completely excluded from the crystals, the melting depression as proposed by Flory is expressed by equation (3):

$$1/T_m^\circ - 1/T_m^* = -(R/\Delta H_m)\ln X_A \qquad (3)$$

where T_m° and T_m^* are the equilibrium melting temperatures of a random copolymer of molar fraction X_A and the corresponding homopolymer, respectively. ΔH_m is the heat of fusion of a homopolymer and R is the gas constant. Taking into account the effect of the sequence length of crystallizable units which can be crystallized only when their length corresponds to the crystal thickness, a modified exclusion theory as proposed by Baur[32] is expressed by equation (4):

$$1/T_m^\circ - 1/T_m^* = -(R/\Delta H_m)\ln(X_A - 1/\langle L\rangle) \qquad (4)$$

where $\langle L\rangle$ is the average sequence length of crystallizable units, given by $[2X_A(1-X_A)]^{-1}$ for a random copolymer system.

According to the results of n.m.r. spectroscopy[21,22], the CT units are completely excluded from the PET crystals, so that the above exclusion models can be applied to the melting temperature depression for the copolymer in the range 80–100 mol% ET. *Figure 8* shows the equilibrium melting temperatures obtained experimentally as a function of the copolymer composition, and those predicted by the theories of Flory (curve A) and Baur (curve B). The Flory equation gives a smaller melting-temperature depression than that from the experimental data, whereas the Baur equation fits well with the experimental data.

However, the inclusion model of comonomer units in the crystal should be applied to the melting-temperature depression in the region 66–100 mol% CT, since the comonomer ET units are incorporated into the CT crystal phase[21,22]. The PCT lattice became deformed by incorporation of ET units[23] and then the melting point of PCT decreased with the composition. Copolymer melting theories on the basis of the excess free energy associated with the incorporation of comonomer units into the crystal lattice have been proposed by Helfand and Lauritzen[34] and Sanchez and Eby[33]. The Helfand–Lauritzen equation is employed in this study because the excess energy is expressed simply as a function of the copolymer composition:

$$1/T_m^\circ - 1/T_m^* = -(R/\Delta H_m)[\ln X_A + (1-X_A)\exp(-H_{ex}/RT)] \qquad (5)$$

where H_{ex} is the excess free enthalpy due to incorporation of the comonomer units in the crystal lattice. The enthalpy can be calculated by the equilibrium copolymer composition (X_{CB}) of B units in the crystal phase as follows:

$$H_{ex} = -RT\ln[X_A X_{CB}/(1-X_A)(1-X_{CB})] \qquad (6)$$

The value of X_{CB} for the present copolymer system estimated by n.m.r. spectroscopy, as listed in *Table 1*[21,22], is a function of the copolymer composition, resulting in $X_{CB}=0.35(1-X_A)$. Using these relationships, the experimental data are fitted very well by the Helfand–Lauritzen equation (curve C in *Figure 8*), whereas the Flory equation (curve D in *Figure 8*) gives a larger melting-temperature depression than that from the experimental data.

The minimum points in thermodynamic parameters

In a binary A/B random copolymer system, where the A and B components are crystallizable, the copolymer can be crystallized either in an A-homopolymer or a B-homopolymer crystal depending on the copolymer composition, exhibiting a crystal lattice transition at a certain composition. On crystallization of the random copolymer, minima in the melting point and the heat of fusion are found, regardless of whether the comonomer units are completely rejected from the crystals or partially incorporated in the crystal lattice. In addition, the dependence of the maximum crystal growth rate on composition exhibits a minimum[40,41] and the glass transition temperature shows a discontinuous jump[42] at a certain composition. In other words, the crystal lattice transition manifests itself at a minimum point for various physical properties and crystallization behaviour as a function of copolymer composition. When either of the two components (for example, the A-component) begins to crystallize, the other component (the B-component) cannot be crystallized independently; however, B units could possibly be incorporated into the A-crystal phase to some extent. The onset of crystallization of the A-component in preference to the B-component could be caused by energetic interaction between the segments of each component polymer molecule in the molten state prior to crystallization. The cohesive energy is an important property expressing the energetic interaction in the molten state. The cohesive energy (E) corresponding to the A and B components in the random copolymer is assumed to be proportional to the copolymer composition, i.e. $E_A V_A$ and $E_B V_B$, where E_A and E_B are the cohesive energies of the A and B monomeric units corresponding to those of the respective homopolymers and V_A and V_B are the volume fractions of components A and B, respectively. For example, if the cohesive energy corresponding to the A component ($E_A V_A$) is larger than that corresponding to the B component ($E_B V_B$), only A units can be crystallized, condensing the B units into a non-crystallized region, or *vice versa*. When the cohesive energies for the two components are identical ($E_A V_A = E_B V_B$), both components can be crystallized independently into each crystal lattice or co-crystallized into a crystal lattice at the composition given by equation (7):

$$V_A^* = E_B/(E_A+E_B) \qquad (7)$$

Here, the cohesive energy of a polymer can be estimated by group contribution methods[43].

The molar fraction of PCT units, X_{PCT}^*, calculated on the basis of equation (7) is about 39 mol% in the present copolyester system; this value coincides very well with the experimentally observed value of 34 mol% CT at which the melting point and the heat of fusion exhibit a minimum. This idea can be applied to other random copolyester systems, such as poly(ethylene terephthalate-*co*-propylene terephthalate)[8], poly(ethylene terephthalate-*co*-1,4-butylene terephthalate)[8], poly(ethylene terephthalate-*co*-oxybenzoate)[9], poly(3-hydroxy butyrate-*co*-3-hydroxy valerate)[10] and the poly(*n* methylene terephthalate-*co*-ethylene sebacate) series[11] where *n* is the number of methylene groups ranging from 2 to 7 and 10. *Figure 9* shows the relationship between the compositions, X^*, at which the melting point exhibits a minimum experimentally in the random copolyesters and those at which the cohesive energies for two components

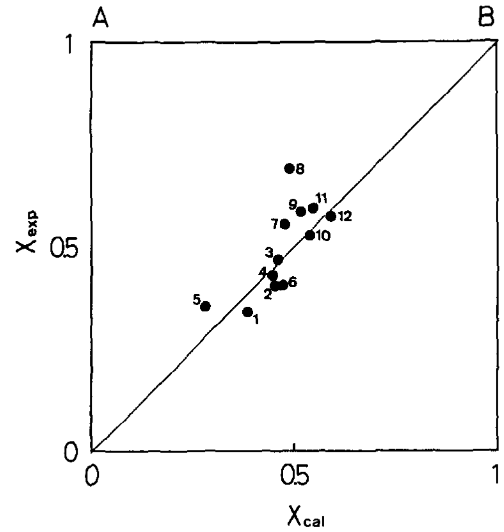

Figure 9 Relationship between the compositions (X_{exp}) at which the melting point shows a minimum experimentally in various random copolyesters and those (X_{cal}) at which the cohesive energies for two components estimated by group contribution methods are identical: (1) poly(ethylene terephthalate-*co*-1,4-cyclohexylene dimethylene terephthalate); (2) poly(ethylene terephthalate-*co*-propylene terephthalate); (3) poly(ethylene terephthalate-*co*-1,4-butylene terephthalate); (4) poly(3-hydroxy butyrate-*co*-3-hydroxy valerate); (5) poly(ethylene terephthalate-*co*-oxybenzoate); (6)–(12) poly(*n* methylene terephthalate-*co*-ethylene sebacate) series where *n* is the number of methylene groups ranging from 2 to 7 and 10, respectively

estimated by group contribution methods are identical. It is interesting to note that a good linear relation is found between the observed and the calculated compositions. This relationship suggests that the cohesive energy corresponding to each component in the random copolymers plays an important role in the crystal lattice transition from one crystal structure to the other.

CONCLUSIONS

The examination of the crystallization behaviour of the poly(ethylene terephthalate-*co*-1,4-cyclohexylene dimethylene terephthalate) (P(ET/CT)) random copolyesters shows that the copolymers rich in ET units form crystals with complete rejection of the CT units, whereas CT units can co-crystallize with ET units to some extent in the composition region rich in CT units. The melting temperatures of these copolymers are depressed with an increase in CT in the compositions and show a minimum at the intermediate composition of about 30–40 mol% CT at which the crystal lattice transition occurred. Among the various crystallization parameters for the random copolymers, the cohesive energy is found to be one of the important factors controlling the crystal lattice transition from one crystal to the other. A good linear relation is found between the compositions at which the melting point shows a minimum experimentally in various random copolyesters and those at which the cohesive energies for two components estimated by group contribution methods are identical.

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