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Multiple melting endotherms from ethylene terephthalate–caprolactone copolyesters

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The melting behaviour of ethylene terephthalate (ET)–caprolactone (CL) random block copolyesters (TCLs) crystallized from the melt were studied by differential scanning calorimetry (d.s.c.). The TCLs with high ET contents showed three melting endotherms. Peaks I and II can be attributed to the melting of crystallites formed during primary and secondary crystallization processes respectively, and peak III is the fusion of crystals recrystallized during the d.s.c. heating scan process. For TCL having relatively lower ET content, another melting endotherm, corresponding to the fusion of crystallites of the CL segments, was observed, which indicated that the segregation occurred during the annealing process because of the non-uniformity of the chemical composition and sequence length distribution of the ET and CL segments in TCL copolyesters.

(Keywords; melting behaviour; copolyester; segregation)

Introduction

A number of polymers crystallized from the melt have been observed to show two or more endotherms in melting experiments[1–6]. Poly(ethylene terephthalate) (PET), which was found to yield multiple melting endotherms, has been extensively studied in the past[6–15]. Generally, after crystallization by annealing the PET at a temperature (T_c) above the glass transition temperature, two endotherms are found on subsequent differential scanning calorimetry (d.s.c.) heating experiments. The lower temperature peak, being strongly dependent on the temperature and time of annealing, was considered as the fusion of crystallites formed at T_c. The higher temperature endotherm, depending upon the scanning rate of heating, is attributed to the fusion of crystals recrystallized and perfected during the heating process in d.s.c. measurement. Another melting endotherm of isothermally crystallized PET was found by Zhou and Clough[15]. They attributed this peak to the fusion of crystallites formed at T_c in the primary crystallization process.

In order to modify the crystallization behaviour of PET, a series of ethylene terephthalate (ET)–caprolactone (CL) random block copolyesters (TCLs) was synthesized; their characterization has been investigated by gel permeation chromatography (g.p.c.), low angle laser light scattering, nuclear magnetic resonance (n.m.r.) spectroscopy, and d.s.c.[16,17]. In the present work, the melting behaviour of synthesized TCL copolyesters with relatively higher ET contents was examined by d.s.c. The results of varying crystallization conditions on the multiple melting peaks in TCLs were obtained.

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Experimental

Materials. The TCLs used in this work were synthesized in our laboratory and purified by precipitation in large amounts of methanol from chloroform solution. Their ET contents, intrinsic viscosities [η] and glass transition temperatures (T_g) are given in *Table 1*. The ET content was determined by n.m.r. spectroscopy as described in ref. 17.

Processing. The TCL samples were sealed in d.s.c. aluminium pans and held at 530 K under nitrogen atmosphere for 5 min to erase the previous thermal history. Then, the sealed pans with molten samples were quenched to the desired temperature in the differential scanning calorimeter or on a hot stage having a temperature controller to make the TCL samples crystallize isothermally for different times. After this process, the annealed samples were quenched to room temperature. The samples were stored in a vacuum oven at 30°C for two days prior to d.s.c. measurement.

Differential scanning calorimetry. The melting curves of the annealed TCL samples were recorded at the desired heating rate under nitrogen atmosphere in the differential scanning calorimeter (Perkin–Elmer DSC-2C). The temperature was calibrated with ultrapure indium.

Wide-angle X-ray diffraction. Wide-angle X-ray diffraction (WAXD) patterns were recorded in the reflection mode using a Rigaku D/max-rA diffractometer. A copper target in conjunction with an Ni–K filter was used for X-ray experiments.

Table 1 Description of synthesized TCL copolyesters

Acronym	ET content[a] (wt%)	ET/CL (mol)	T_g[b] (K)	η[c] (dl g^{-1})
TCL91	91	6:1	327.6	0.6169
TCL82	82	2.7:1	306.0	0.8369
TCL72	72	1.5:1	291.0	0.9554

[a] ET content determined by n.m.r.
[b] T_g determined by d.s.c. at a heating rate of 20 K min^{-1}
[c] η measured in m-cresol at 30°C

ET: $-O-\overset{O}{\overset{\|}{C}}-C_6H_4-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-$

CL: $-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-CH_2-$

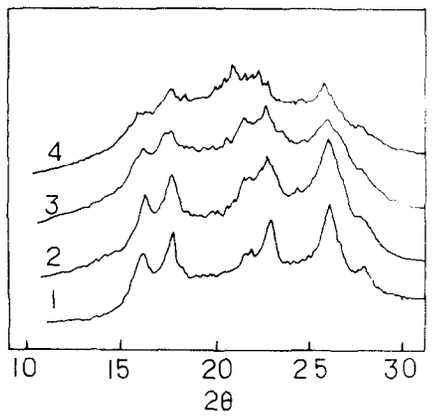

Figure 1 Wide-angle diffraction patterns of PET and TCLs. The specimens were isothermally crystallized at 140°C for 12 h. 1, PET; 2, TCL91; 3, TCL82; 4, TCL72

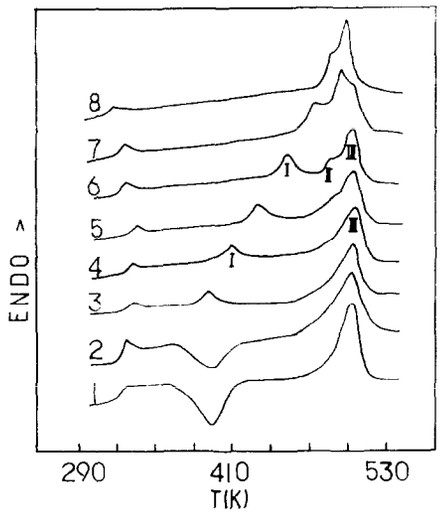

Figure 2 D.s.c. thermograms of TCL91 isothermally crystallized at the indicated temperature for 12 h. 1, 60°C; 2, 80°C; 3, 100°C; 4, 120°C; 5, 140°C; 6, 160°C; 7, 180°C; 8, 200°C

Results and discussion

The WAXD patterns of the PET and TCLs, as given in *Figure 1*, show that the crystalline TCL has the same lattice as the crystal of PET, and the diffraction peaks become less sharp with decreasing ET content. These results indicate that the crystallinity of the TCLs may be attributed to crystallization of the ET segments, and the perfection of the ET crystal was decreased by CL monomeric units in the TCL copolyesters.

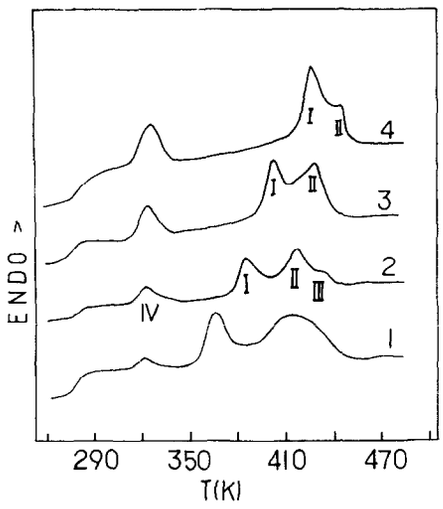

Figure 3 D.s.c. thermograms of TCL72 isothermally crystallized at the indicated temperature for 12 h. 1, 80°C; 2, 100°C; 3, 120°C; 4, 140°C

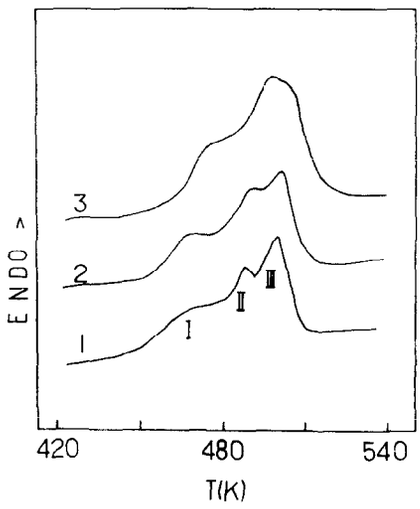

Figure 4 Scanning rate dependence of d.s.c. thermograms of TCL91. The specimens were isothermally crystallized at 170°C for 30 min. 1, 10 K min^{-1}; 2, 20 K min^{-1}; 3, 40 K min^{-1}

The typical d.s.c. thermograms of TCL samples which crystallized isothermally at different temperatures are shown in *Figures 2* and *3*. The peaks are labelled as I, II and III starting from the lowest temperature endotherm. Peak I, which occurs at a temperature about 15 K above T_c, increases in size and moves to higher temperature with increasing annealing temperature. With increasing heating rate, the location and relative area of peak I do not appear to change (*Figure 4*). These results indicate that endotherm I is the fusion of the crystallites formed prior to the d.s.c. scan, rather than the crystallites grown during the period of heating. This peak is similar to endotherm I observed in the annealed PET samples by others[6,15].

Endotherm II was observed in the TCL samples annealed within a certain temperature range. The

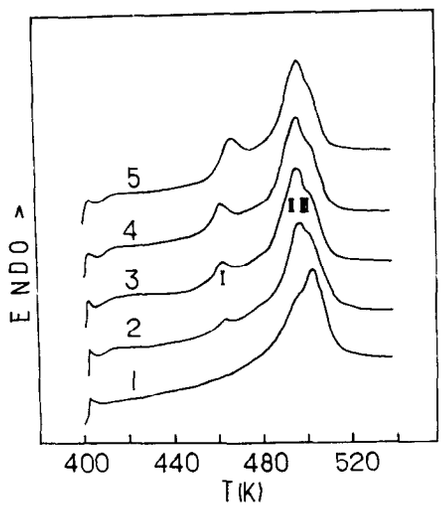

Figure 5 D.s.c. thermograms of TCL91 isothermally crystallized at 180°C for different times. 1, 1 min; 2, 3 min; 3, 5 min; 4, 10 min; 5, 30 min

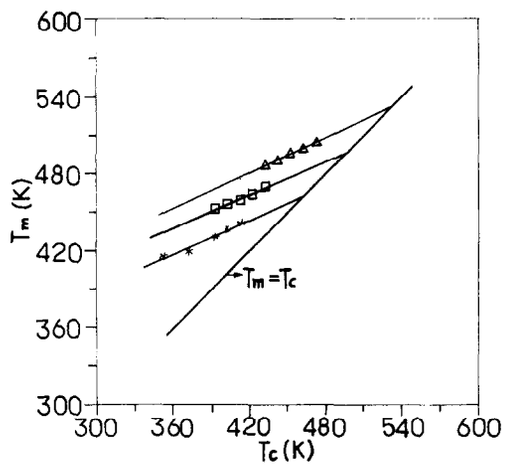

Figure 6 The T_m of peak II *versus* T_c for isothermally crystallized TCLs. △,TCL91; □, TCL82, *, TCL72

temperature and area of this peak increase with increasing T_c. At a relatively higher annealing temperature peaks II and III will merge to an apparent single peak. Heating-rate dependence experiments show that peak II does not appear to change with variation of the scanning rate. *Figure 5* shows thermograms of the TCL91 samples crystallized at a given temperature for different times. Peaks I and II increase in melting temperature and size with increasing annealing time. From these results, we may think that peak II pertains to the fusion of the crystallites originally formed at T_c. In *Figure 5* we also found that peak II appeared at the shortest crystallization time (1 min), prior to the observation of peak I, which is similar to the phenomenon observed by Zhou and Clough[15]. From these results, we may believe that peak II in TCL pertains to the fusion of crystals grown at T_c in a primary crystallization process. Considering peak II as a fusion of the crystallites grown from the primary crystallization process, we can extrapolate the T_m (II) to $T_m = T_c$ to obtain T_m, and retain the values of 532 K, 496 K and 462 K corresponding to the T_m of TCL91, TCL82 and TCL72 respectively (*Figure 6*).

The melting temperature of peak III does not change

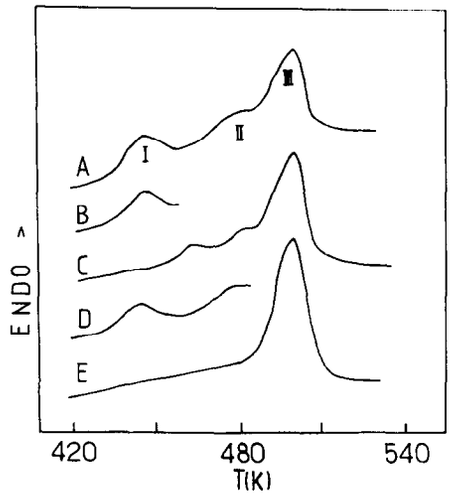

Figure 7 D.s.c. thermograms of TCL91 with different thermal histories. A, Original specimen (isothermally crystallized at 160°C for 12 h); B, original specimen heated to 460 K; C, specimen quenched from process B; D, original specimen heated to 490 K; E, specimen quenched from process D

appreciably with annealing temperature (T_c), and its area decreases with increasing T_c and scanning rate during the d.s.c. experiment (*Figure 3*). After thermal cycles, illustrated in *Figure 7*, the area of the endotherm III evidently increased. It is well understood that this peak in PET relates to the fusion of crystals grown and perfected during the d.s.c. scan itself[7,10,15]. The d.s.c. results of TCL with different ET contents in this work are consistent with this interpretation.

A more complicated melting behaviour was observed for TCL72, as shown in *Figure 2*. Besides the three melting peaks mentioned above, another peak (IV), at a temperature of about 324 K, was observed. The area of this peak increases with increasing annealing temperature and storage time at 30°C. This peak, with a melting temperature similar to that of polycaprolactone, may be attributed to the fusion of crystallites of CL segments in the TCL copolyester molecular chains. This result indicated that microphase separation or segregation was occurring in the TCL copolyesters during the isothermal crystallization process. The non-uniformity of the chemical composition and sequence length distribution of the TCL copolyesters may be the reason for this segregation phenomenon.

Acknowledgement

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References

1 Yeh, J. T. and Runt, J. *J. Polym. Sci., Polym. Phys. Edn* 1989, **27**, 1543
2 Nichols, M. E. and Robertson, R. E. *J. Polym. Sci., Polym. Phys. Edn* 1992, **30**, 755
3 Xenopulos, A. and Wunderlich, B. *J. Polym. Sci., Polym Phys. Edn* 1990, **28**, 2271
4 Cebe, P. and Chung, S. *Polym. Compos.* 1990, **11**, 265
5 Koberstein, J. T. and Galambos, A. F. *Macromolecules* 1992, **25**, 5618
6 Groeninckx, G., Reynaers, H., Borghmans, H. and Smets, G. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**, 1311

7 Lin, S. B. and Koenig J. L. *J. Polym. Sci., Polym. Symp.* 1984, **71,** 121
8 Holdsworth, P. J. and Turner-Jones, A. *Polymer* 1971, **12,** 195
9 Bell, J. P. and Sweet, G. E. *J. Polym. Sci., Polym. Phys. Edn* 1972, **8,** 2141
10 Roberts, R. C. *J. Polym. Sci., Lett.* 1970, **8,** 38
11 Roberts, R. C. *Polymer* 1969, **10,** 113
12 Roberts, R. C. *Polymer* 1969, **10,** 117
13 Fakirov, S., Fischer, E. W., Hoffmann, R. and Schmidt, G. F. *Polymer* 1977, **18,** 1121
14 Alfonso, G. C., Pedemonte, E. and Ponzetti, L. *Polymer* 1979, **20,** 104
15 Zhou, Z and Clough, S. *Polym. Eng. Sci.* 1988, **28,** 65
16 Fang, F. Master thesis, University of Science and Technology of China, 1989
17 Luo, X. and Ma, D. *Acta Polym. Sinica* 1986, **6,** 676