

Double melting behavior of cyclic tris(ethylene terephthalate)

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SUMMARY

Cyclic tris(ethylene terephthalate) (CTET) was separated from oligomeric extract of poly(ethylene terephthalate) by the conventional solvent separation method. The structure of CTET was characterized by differential scanning calorimetry, X-ray diffraction, and scanning electron microscopy. It is shown that the double melting behavior of melt-crystallized CTET is attributed to the morphological change created by heat-treatment. The effect of the morphological change on the crystal structure of CTET was also examined.

INTRODUCTION

Polycondensates contain cyclics as a result of interchange reaction during melt equilibrium(1). Studies on the cyclics, generally low molecular weight oligomers, have been reported mainly for some industrially important polycondensates such as poly(ethylene terephthalate) (PET)(2,3), nylon 6 (4), and others(5). In comparison with other polycondensates, cyclic oligomers of PET detrimentally affect various textile processes. A large amount of works have been done for the PET oligomers, especially cyclic tris(ethylene terephthalate)(CTET), since it is present in greater amounts than any other oligomer component in PET. Various studies of CTET including synthesis, separation from PET, and characterization have been performed in the past. CTET may be prepared by step-wise synthesis or separation from PET and subsequent purification. However, as a means of preparing pure CTET, the separation technique has been widely used, since the synthetic method is time-consuming with low yield. The separation of CTET from oligomeric extract of PET was studied mainly on the basis of solubility difference. For the characterization, high performance liquid chromatography (HPLC), x-ray diffraction (XD) analysis, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) have been employed. It has been known that CTET is highly crystallizable and the structure has been studied by some investigators(6-8). Recently, there has been an attempt by Perovic(6) to elucidate the mechanism of growth and the causes of morphological instabilities of CTET crystals. Although instrumental analyses characterizing the crystal structure of CTET have been performed considerably, there are still some problems in interpreting the results. In the present paper, we report some results obtained by the characterization of double melting phenomenon which appeared on the DSC thermogram and of crystal structure revealed by XD analysis and SEM.

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EXPERIMENTAL

Separation of CTET from PET

200g of finely powdered PET (bright chip, Dong Yang Polyester Co., Korea) was soxhlet extracted for 48 hrs with 500 ml of dioxane. 1ℓ of water was added to the extracted solution to precipitate the product. The whole mass was stored in refrigerator at 0°C for 24 hrs. The precipitated product was filtered, dried, and used to separate CTET by the method proposed by Ito and Okajima(9). The oligomeric extract from dioxane was extracted again with monochlorobenzene (MCB) and recrystallized by slow evaporation of MCB at room temperature (crystalline material 1, CM1). After filtration, CM 1 was dissolved in dimethylformamide (DMF) and recrystallized at room temperature (crystalline material 2, CM2).

Instrumental analyses

The oligomer separation by HPLC was performed on a High Performance Liquid Chromatograph (Waters, USA) equipped with a ultraviolet (UV) detector. Wavelength of UV absorption detector (Model 440) was fixed at 254nm. A μ -Porasil column was used with hexane/dioxane (50/50 v/v) as the mobile phase at a flow rate of 2.0 ml/min. Pure CTET was used for calibration. Thermal analysis was carried out with a Differential Scanning Calorimeter (Perkin Elmer DSC 4, USA) using about 2 to 3 mg samples in a nitrogen atmosphere at a heating rate of 20°C/min. Wide angle x-ray measurements were made on an X-ray Diffractometer (Rigaku Denki DMax IIIA, Japan) with Ni-filtered Cu K α radiation at 35 kV and 20 mA. Scanning electron micrographs were taken on an Akashi ISI-SX 30E (Japan) at an acceleration voltage of 15 kV.

RESULTS AND DISCUSSION

Separation of CTET from PET

HPLC chromatograms of the oligomers extracted with dioxane, CM1, and CM2 are shown in Figs. 1-3. In Fig.1, the most predominant peak (2.19 min) is identified as cyclic trimer, CTET, from calibration run for pure CTET. Other peaks are assigned as cyclic tetramer (2.45 min), pentamer (2.68 min), hexamer (2.86 min), etc. The peak of retention time 1.77 min is due to the solvent used for sample injection, in this case, chloroform. We can find that CM1, which was obtained by recrystallization from MCB, is composed of CTET, cyclic tetramer and traces of other components (Fig.2). Fig.3 shows only one peak, exhibiting that CM2 is pure CTET.

DSC analysis

The DSC thermogram for CM2 showed melting endotherm at 316.2°C, which is known to be the melting temperature of CTET (Fig.4). On the other hand, the DSC thermogram for melt-crystallized CTET, which was produced by quenching the melted CM2, showed double endotherm at 251.9°C and 313.2°C [Fig.5(a)]. A number of polymers including PET crystallized from the melt have yielded multiple endotherms during the DSC melting experiments. As cited in a recent work by Zhou and Clough(10), for the annealed PET, two endotherms are found on the DSC thermogram. It is well known that the lower temperature peak due to fusion of crystallites, which was formed at annealing temperature, is dependent on the temperature and time of annealing. The higher temperature endotherm is attributed to fusion of crystals recrystallized and perfected during the DSC

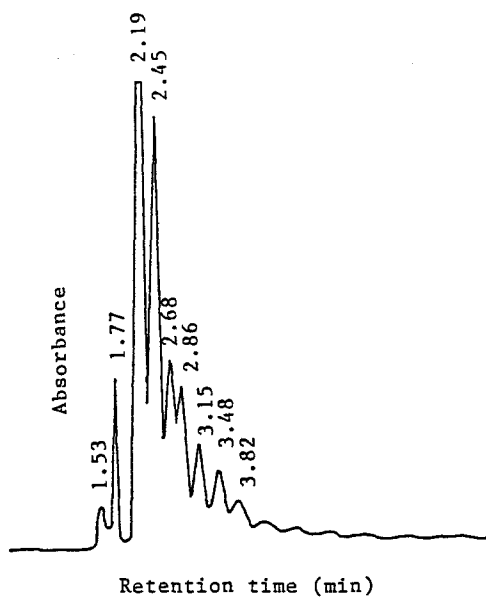


Fig.1. HPLC chromatogram for cyclic oligomers extracted with dioxane.

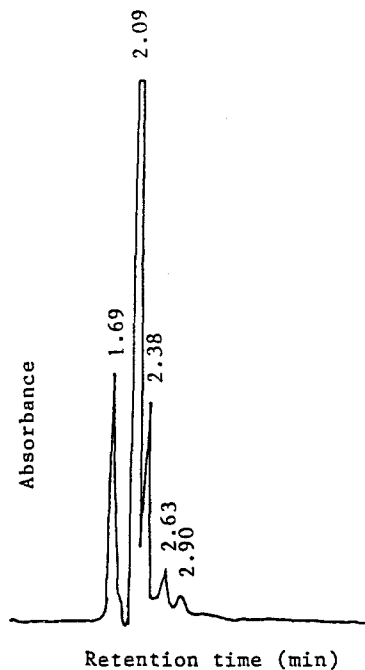


Fig.2. HPLC chromatogram for CM1.

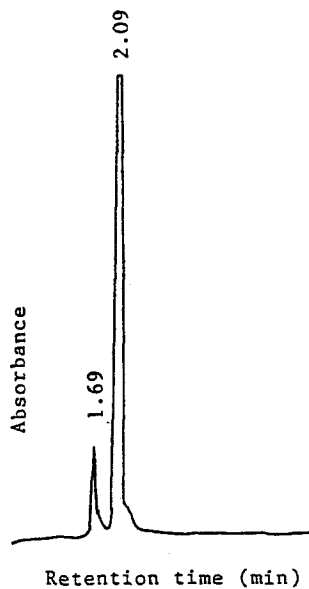


Fig.3. HPLC chromatogram for CM2.

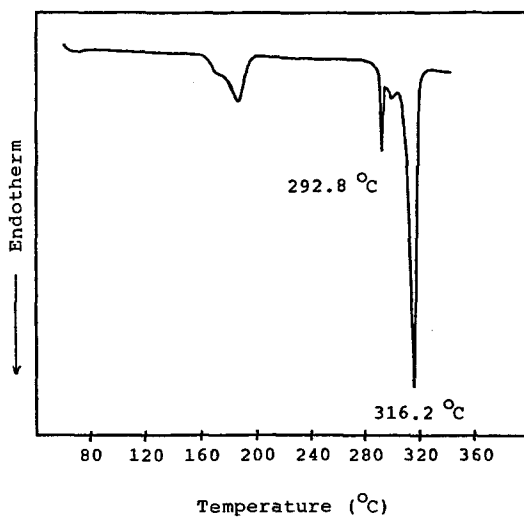


Fig.4. DSC thermogram for CM2.

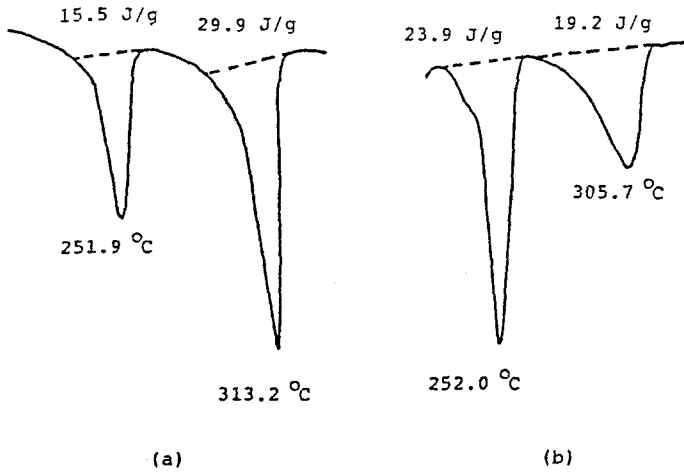


Fig.5. DSC thermograms for melt-crystallized CTET before (a) and after (b) heat-treatment for 1hr at 200°C.

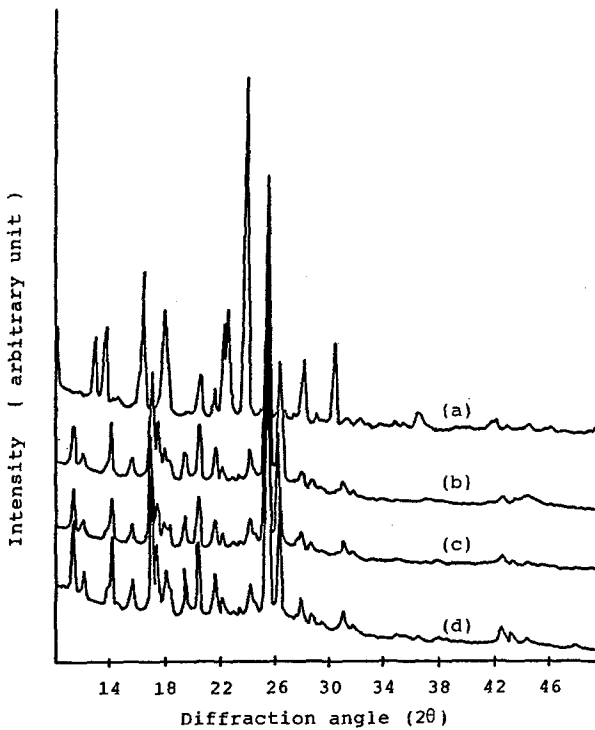


Fig.6. XD curves for CM2 recrystallized in DMF(a) and CTETs, in which CM2 was melt-treated for 3min at 350°C and quenched in liquid nitrogen (b), and (b) was crystallized at 150°C for 30 min (c) and at 200°C for 1hr (d), respectively.

run. However, the origin of double endotherm for the melt-crystallized CTET is explained somewhat differently from that of PET. As Fig.5(b) shows the DSC thermogram for CTET after heat-treatment at 200°C for 1 hr of the melted and quenched sample indicated the shift of the higher temperature endotherm to lower side. Furthermore the heat of fusion of lower temperature endotherm increased with the heat-treatment. This implies that one of the crystal forms grew at the sacrifice of the other during the annealing at 200°C.

XD analysis

Fig.6 shows XD curves for CM2 (a) and CTETs, in which (a) was melted and quenched(b), and crystallized at 150°C for 30 min (c) and 200°C for 1hr (d), respectively. The XD curve for (a) presents a marked contrast to those for (b-d). It is obvious that the crystal structure of CM2 as-crystallized from DMF changes to the other crystal form after melting, quenching, and prolonged heat-treatment. However, we confirmed that though CM2 as-crystallized from DMF was recrystallized from MCB, the XD curve was the same as that of CM2 as-crystallized from DMF. Combining this finding with the results of DSC curves in Fig.5, the double melting behavior of melt-crystallized CTET is considered to be independent of the difference of crystal forms. It may be rather ascribable to the perfectness of the crystal structure. The lattice spacings of CM2 obtained from Fig.6(a) are similar to those of CTET obtained by Ito and Okajima(9) and A type crystal by Binns et al.(7), whereas the crystal structure of melt-crystallized CTET [Fig.6(b-d)] is nearly identical to that of B type by Binns et al.(7).

SEM analysis

Fig.7 shows SEM micrographs of CTET crystals formed under different conditions. The CTET crystal obtained from the DMF solution was an angled pillar - shape (Crystal I) [Fig.7(a)]. When this crystal was melted and then quenched, a grown crystal with smooth basal faces (Crystal II) was formed [Fig.7(b)]. After the heat - treatment of Crystal II at 150°C for 15min, the nearly perfect hexagonal plate-like crystals were newly developed on the basal face [Fig.7(c)]. With the increase of heat-treatment time at a higher temperature (200°C for 1 hr), the formation of cavities in the middle of grown hexagonal crystal faces was observed [Fig.7(d)]. Perovic (6) also showed in a recent work that very pronounced sharp walls were formed at the edges of hexagonal plates by prolonged annealing of the CTET crystals in PET film, and proposed that this effect was caused by two simultaneously occurring processes : supersaturation inhomogeneity in the center of the plates and formation of the kinematic (shock) waves at the edges of the plates. The above results of SEM micrographs now enable us to explain lucidly the double melting behavior of the CTET crystals described in the DSC analysis ; one is due to the crystal remained in the center of hexagonal plates and the other is induced by the crystal newly formed at the edges of the plates. In fact, the section of the latter grew step-wise with increasing heat-treatment time, and this is well reflected in the double melting behavior. DSC thermograms in Fig.5 show that the heat of fusion of the lower temperature peak increases in compensation for the reduction of the higher one. Considering the results of DSC and SEM data, the endotherm at the lower temperature must be attributable to newly formed imperfect crystal fraction at the edges of the hexagonal plates. However, it is quite apparent from the XD analysis results that the crystal fraction formed at the edges has no new crystal structure.

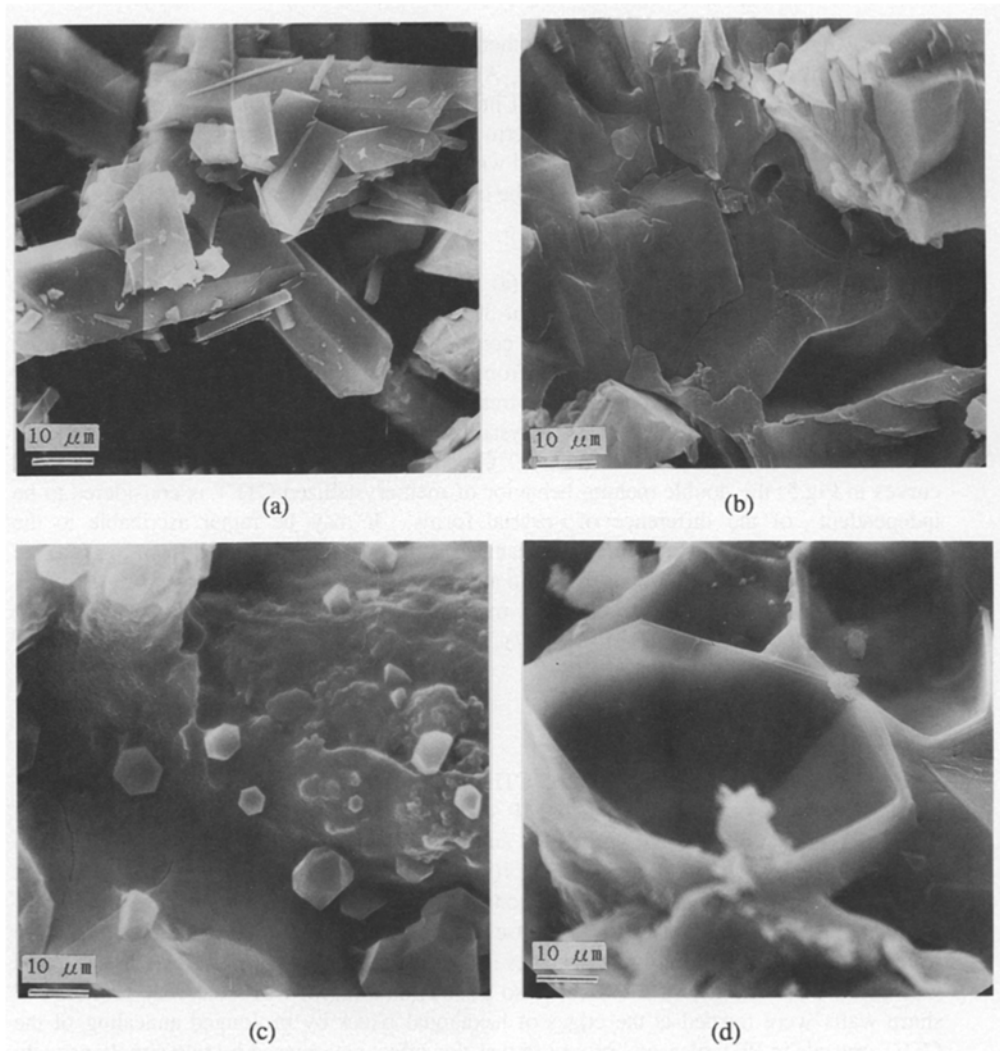


Fig. 7. Scanning electron micrographs of CTET : (a) as-crystallized from DMF (Crystal I), (b) quenched from the melt (Crystal II), (c) heat-treated at 150°C for 15 min, (d) heat-treated at 200°C for 1 hr.

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