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Crystallization of Cyclic Oligomers in Commercial Poly(ethyleneterephthalate) Films

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Summary

The crystallization of cyclic oligomers occurs in commercial films of poly(ethyleneterephthalate) upon annealing the films above 100°C or exposing to solvent vapor. The size of the crystals increase with time and temperature of annealing. The crystals obtained on annealing are in the form of hexagonal prisms whereas they are in the form of cylindrical prisms on exposure to solvent vapor.

Introduction

There have been several structural and morphological studies on poly(ethyleneterephthalate) (PET) fibers due to its importance in the textile industry. Measurement of orientation and crystallinity, and their effect on the mechanical properties and dye diffusion have been reported (HEFFELFINGER and SCHMIDT, 1965; DUMBLETON et al, 1968). While these studies were concerned with the properties of the polymer itself, the influence of diethylene glycol, which is present as a byproduct (HOVENKAMP and MUNTING, 1970) of the synthesis, on the properties of the fibers has been studied (MILITKY et al, 1980). The presence of oligomers in PET fibers has also been recognized (FARROW et al, 1960). NEEDLES et al (1980) found oligomer crystals in the form of platelets, on the surface of the fibers, upon annealing polyester fibers and related their effect on the dyeing properties.

Crystallization of amorphous polymer films upon exposure to organic solvent vapor is a well-known phenomenon. DESAI and WILKES (1974) and MAKAREWICZ and WILKES (1978) reported the crystallinity and spherulitic morphology obtained by treating cold drawn PET with methylene chloride, dioxane, and nitromethane. Most of these studies used initially amorphous PET fibers and the effect of various treatments was then explored. In this study, the effect of annealing and solvent exposure on oligomer crystallization in semicrystalline, oriented, commercial PET films, is reported.

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Experimental

Commercial PET films of 4 and 5 mil thickness were obtained from Dupont Canada Inc. (Mylar 400D and 500D). The films, as determined by x-ray diffraction, were semicrystalline and biaxially oriented. Methylene chloride was used to study the effect of solvent exposure. Generally, a piece of the film was kept, for a specific period of time, over a small beaker containing the solvent, with the assembly enclosed in a wide-mouthed bottle with a screw cap. The setup is admittedly primitive, but the kinetics of solvent diffusion are not reported here.

Scanning electron micrographs were recorded using an ISI Super II SEM and Philips 505 SEM. In order to identify the low molecular weight materials in the film, ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM-250 Fourier transform spectrometer.

Effect of Annealing

Microscopic observation of the annealed PET films showed the presence of prismatic crystals. A scanning electron micrograph of the 5 mil film, annealed at 200°C for 2½ hours is shown in Figure 1.

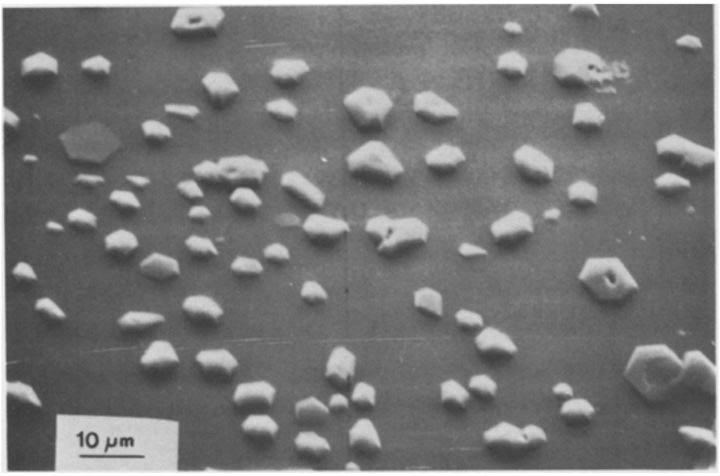

Figure 1: Scanning electron micrograph of 5 mil film, annealed at 200°C for 2½ hrs.

The identity of the crystals was determined by NMR spectroscopy (G.K. HAMER, personal communication). A strip of the annealed 5 mil film (∿3cm x 1cm) was extracted for 24 hrs with 20 mil of methylene chloride in a Soxlet apparatus. The extract was evaporated to dryness and the residue dissolved in 0.5 ml chloroform-d for ^{1}H and ^{13}C NMR analysis.

Subsequent SEM examination of the extracted film showed that the surface crystals produced by heat treatment had been removed by the Soxlet extraction.

The ^{1}H NMR spectrum of the total extract indicated the presence of two components: one, water soluble and the other not. The former was identified to be diethylene glycol by comparison of its ^{1}H and ^{13}C spectra with those of an authentic diethylene glycol sample. From its ^{13}C NMR spectrum, the other component was deduced to have the same basic structure as PET, but unlike PET, was of sufficiently low molecular weight to be soluble in methylene chloride. The presence of only two peaks in the ^{1}H NMR spectrum ruled out the possibility of linear oligomers. Thus, it was identified to be a cyclic oligomer, most probably the trimer (FARROW et al, 1960).

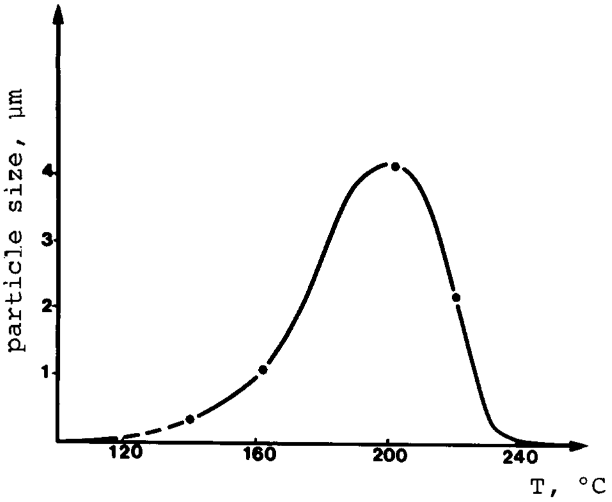

Figure 2: The average size of oligomer crystals in 5 mil film, annealed for 20 min, as a function of temperature.

Since the T_g of the film is 100°C, an attempt was made to determine the average size of the crystals as a function of the annealing temperature, starting slightly above T_g. The 5 mil film was annealed for 20 minutes, at temperatures ranging from 140° to 240°C, at intervals of 20°. The results are shown in Figure 2. The curve shows a maximum at 200°C, and is characteristic of the temperature-dependent particle growth mechanism, involving nucleation and growth. The growth rates of polymers, which is nucleation controlled, have generally been described using the TURNBULL-FISHER (1949) equation, which relates the transport and nucleation rates. The rate of transport or jump rate increases with temperature, whereas the rate of nucleation decreases with increasing temperature. Hence, the growth rate passes through a maximum where the two factors are comparable.

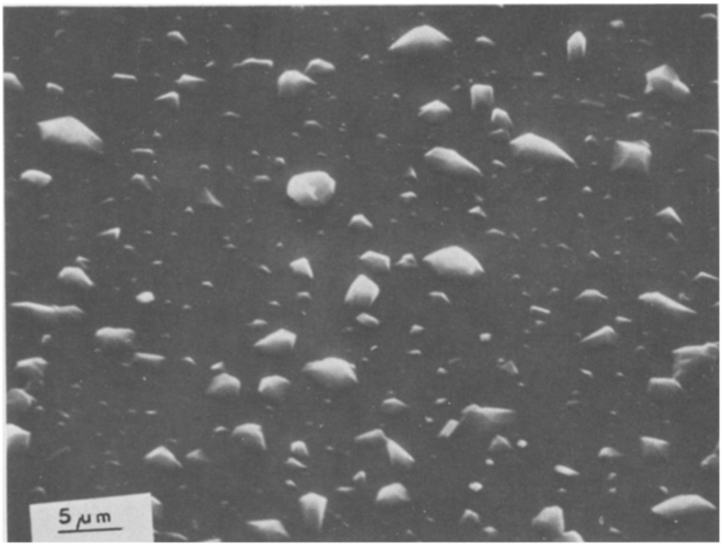

Figure 3: SEM micrograph of 5 mil film annealed at 140°C for 3 days.

Although small crystals of 0.5μ in size are seen with 5 mil film annealed at 140°C, the size of the crystals increase with time. Figure 3 shows a SEM micrograph of the film heated at 140°C for 3 days. Near-hexagonal particles of approximately 4μ are seen, in addition to smaller crystals. Similarly, at 200°C, the size of the crystals doubled as the annealing time is increased from 20 mins. to 2½ hrs.

Figure 4 shows micrographs of crystals from 400D (annealed at 200°C, 2½ hrs. and 22 hrs.), obtained using the Philips 505 SEM. An interesting feature of the micrograph in Figure 4a is the "frills" seen along the edges of the crystal. They correspond to the growing faces of the crystal growth.

Effect of Solvent Exposure

The phenomenon of solvent-induced crystallization of amorphous polymer films is well known. DESAI and WILKES (1974) and MAKAREWICZ and WILKES (1978) reported the growth of spherulites in cold-drawn PET films, upon exposure to methylene chloride, dioxane and nitromethane. Crystllization of bisphenol-A polycarbonate film upon exposure to acetone or carbon tetrachloride vapor is another example (TURSKA and JANECZEK, 1979). When the polymer film is exposed to the solvent vapor above T_g, the diffusion of the solvent increases the segmental mobility of the polymer chains as well as increasing the nucleation probability, thus inducing crystallization to occur. In the case of polymer films containing molecularly dispersed small molecules, exposure to the solvent causes the small molecules to aggregate and crystallize. It was felt that the cyclic trimers which crystallize upon annealing might behave similarly upon exposure to solvent vapor.

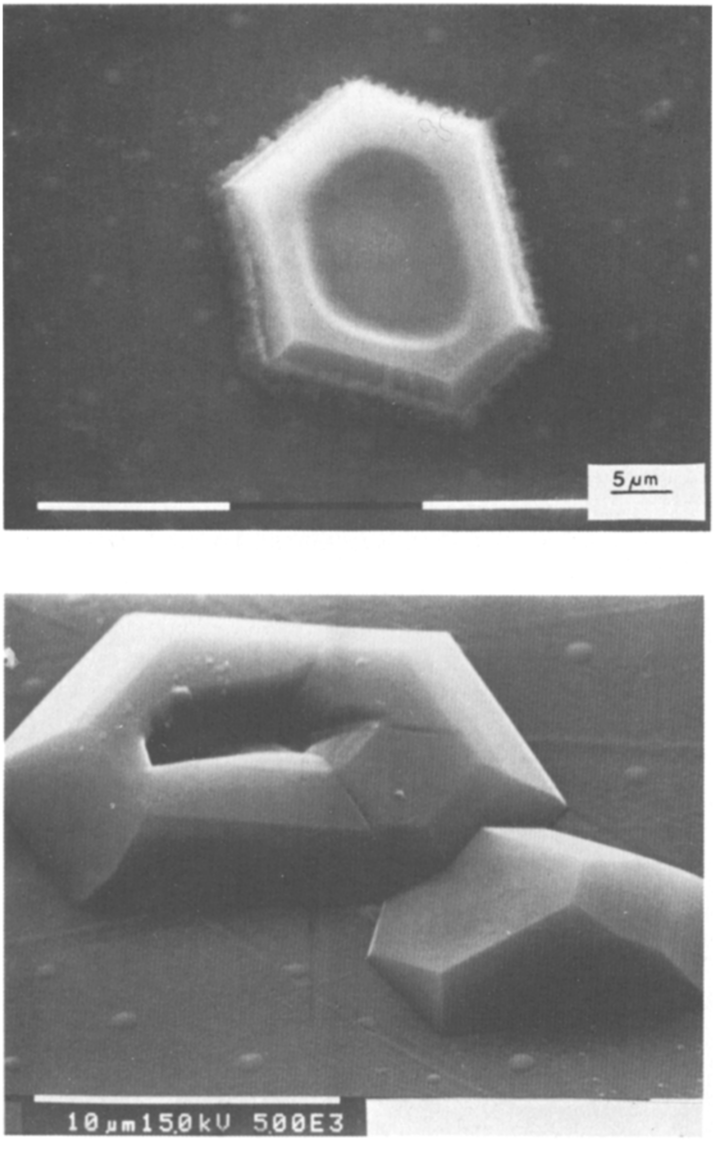

Figure 4: SEM micrograph of the oligomer crystal, from 4 mil film, (a) annealed at 200°C for 2½ hrs, and (b) for 22 hrs.

PET films of 4 and 5 mil thickness were used for exposure to methylene chloride vapor. Figures 5 and 6 show the micrographs of these films after an exposure of six hours to the vapor. It is seen that the crystallization of oligomers has occurred. The crystals are in the form of cylindrical prisms, varying in size from 5 to 30 μm.

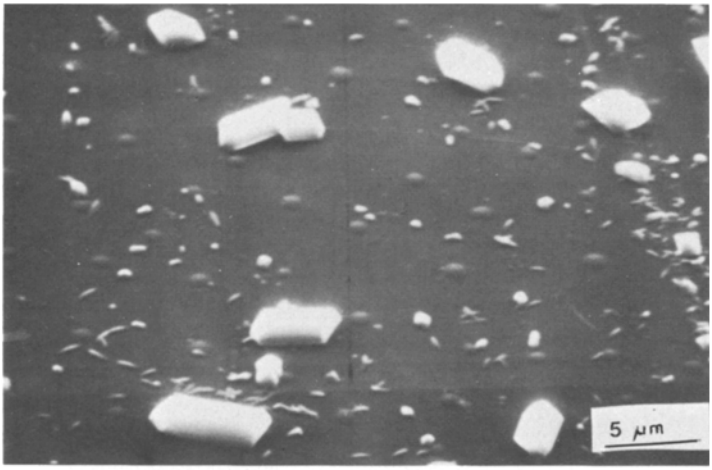

Figure 5: SEM micrographs of 4 mil film upon exposure to solvent vapor for six hrs., showing the presence of oligomer crystals.

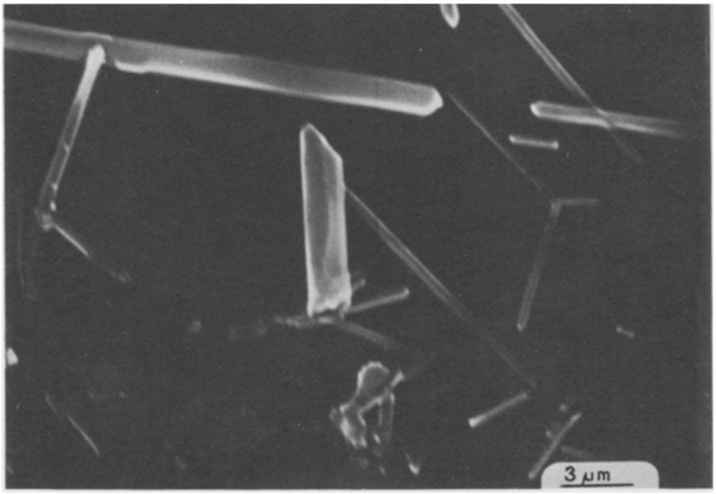

Figure 6: SEM micrographs of 5 mil film exposed to solvent vapor for six hrs., showing the presence of oligomer crystals.

The difference in the shapes of the crystals due to annealing and solvent exposure is interesting, and could be due to the difference in surface energies of the crystal faces between the two cases, the solvent vapor favoring the growth of lateral faces of hexagonal prisms while the annealing treatment favors the growth of basal planes. A detailed analysis of this behavior would require study of the crystal shapes using different solvents and this is not explored here. It is also likely that different conformations of the cyclic trimer molecule contribute to the crystal shape and size. Two conformations are possible (FARROW et al, 1960) for the cyclic trimer: one with the para phenylene groups cis, the methylene groups gauche and the benzene rings in the plane of the molecule. In the other, the para phenylenes are trans, the methylene groups gauche and the benzene rings perpendicular to the plane of the molecule.

Thus it is likely that the shape of the oligomer crystal depends on the conformation of the molecule resulting from the particular treatment: annealing or vapor exposure. The purpose of this report has been to draw attention to the annealing and solvent induced crystallization of cyclic oligomers in PET. A detailed study of the time-dependent and solvent-dependent growth and morphology of the crystals will doubtless add to an understanding of the behavior of these systems.

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