Change of amorphous state of poly(ethylene terephthalate) by heat treatment below the glass transition temperature

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Several papers have demonstrated that structural changes in the amorphous regions of semicrystalline polymers can be produced by heat treatment below the glass transition temperature (T_g). In this paper, we report structural change in the amorphous phase of poly(ethylene terephthalate), heat-treated below and above T_g. The density, the T_g, the endothermic peak at T_g and the relative spectral intensity in the 973 cm^{-1} band (due to the C—O stretching vibration), all increased with heat treatment below T_g, but the specific heat decreased. The stability of the amorphous state was examined by further heat treatment at temperatures above T_g and sufficiently high for crystallization, and it was verified that structural changes in the amorphous regions do not result in acceleration of the rate of crystallization. We therefore suggest that the amorphous region is one phase, rather than two phases consisting of random and regular regions.

INTRODUCTION

There has been increasing interest in the amorphous state of polymers, and a variety of models[1–10] have been reported for this state, including the so-called 'random coil' homogenous structure and a 'ball-like structure' having a certain regularity. However, these models have not been fully elucidated, and no single, acceptable concept of the amorphous phase has yet emerged.

Several papers have reported that the amorphous state of poly(ethylene terephthalate) (PET) can be changed by heat treatment below its glass transition temperature (T_g), and similar changes have been reported in other polymers[6].

This paper describes experiments in which changes in the amorphous state of PET were induced by heat treatment below T_g, and discusses the effect of these changes on crystallization. Our observations are based on thermal, infra-red and density measurements.

EXPERIMENTAL

Sample

A film of PET, 50 μm in thickness, made by Teijin Co. Ltd was used. This film was quite isotropic (as indicated by observations of the film using an Abbé refractometer), and quite amorphous (as indicated by X-ray diffraction). There was no abnormal endothermic peak on a differential scanning calorimeter trace.

Heat treatment below T_g

The T_g was measured at different heating rates using a differential calorimeter (DSC—II type by Perkin—Elmer Co. Ltd), and a temperature of 61°C was obtained after extrapolation to zero heating rate. We hence selected a heat treatment temperature of 59°C.

Samples of film were wrapped with aluminium foil and immersed in a silicone oil bath at 59°C, for between 1 and 200 h to obtain heat-treatment specimens.

Density measurement

The density of each sample was measured at 20°C using a density gradient tube with n-heptane and carbon tetrachloride.

Infra-red absorption measurement

The change in the contribution of the *trans* conformation C—O[11–13] vibration to an absorption band at 973 cm^{-1} was measured using an infra-red spectrophotometer (Hitachi EPI—2). The thickness of each sample was corrected by reference to the 1058 cm^{-1} band.

Thermal measurement

A DSC type II was used for the thermal measurement at a heating rate of 20°C/min, and d.s.c. curves were obtained for each sample after heat treatment below T_g. The samples had weights from 1.3 to 2.0 mg. The T_g of each sample was determined as the point of intersection of the base line of the d.s.c. curve with a line tangential to the maximum slope of the endothermic peak. The endothermic peak area was calculated and converted into units of heat energy by reference to a peak obtained from the heat of fusion of indium.

The specific heat of each sample was obtained relative to sapphire, using the calorimeter.

RESULTS

Figure 1 shows d.s.c. curves of various samples at a heating rate of 20°C/min: *Figure 1*, curve A, shows a sample heat-

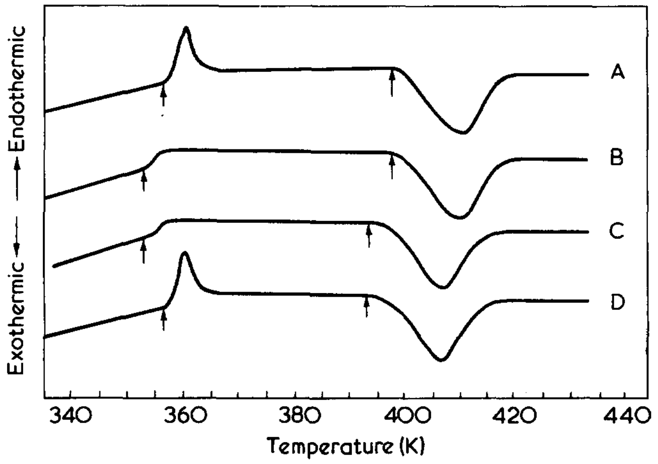

Figure 1 D.s.c. curves at heating rate of 20°C/min: A, heat-treated at 59°C for 50 h; B, untreated; C, heat-treated at 80°C for 50 h; D, heat-treated at 59°C for 50 h after heat-treatment at 80°C for 50 h

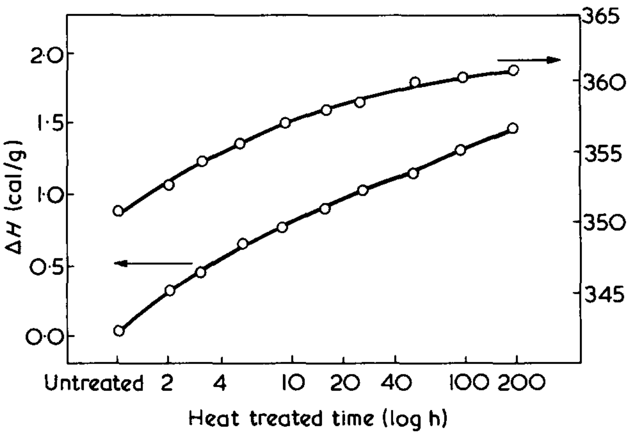

Figure 2 Changes of T_g and of heat capacity of endothermic peak at T_g with time of heat treatment below T_g

treated at 59°C for 50 h and *Figure 1*, curve B, an untreated sample. Their glass transition points were observed near 355K and exothermic peaks due to crystallization near 395K. Changes in T_g, the heat capacity of the endothermic peak at T_g, the starting temperature of cold crystallization, and the exothermic heat capacity due to crystallization, with heat treatment below T_g, will be described below.

In *Figure 2* it is seen that T_g tends to shift to higher temperature and the endothermic heat capacity also increases, as the heat treatment time increases.

The effect of heat treatment time on the temperature of onset of crystallization, and on the exothermic heat capacity due to crystallization, are shown in *Figure 3*. The crystallization temperature remains approximately unchanged as does the exothermic heat capacity.

Figure 4 shows the density and *trans* conformation component of samples, in terms of heat treating time. The *trans* conformation component was obtained from the infra-red absorption spectrum in the band at 973 cm^{-1} attributed to the stretching vibration of C–O *trans* conformation and sensitive to crystallization[11], since the spectral intensity in this band increases with the progress of crystallization. It was observed that the *trans* conformation component decreases with increasing heat treatment time.

Figure 5 shows a specific heat change of samples due to heat treatment. The specific heat tends to decrease with increasing heat treatment time.

From the results mentioned above, it was confirmed that heat treatment below T_g produces changes in the state of the specimens. We further investigated the state of samples given a second heat treatment above T_g. The purpose of this experiment was to find out how long the foregoing state is maintained in time. The result is shown in *Figure 6*. In this experiment, the samples already heat treated at 59°C for 1, 25 and 100 h were further heated at a temperature of 78.5°C (i.e. above T_g) for different treating times. Changes

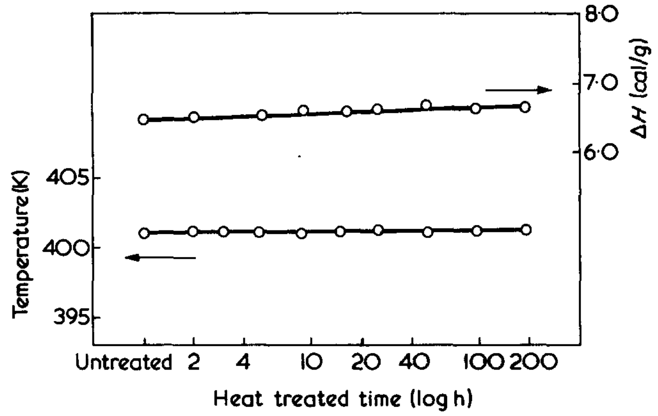

Figure 3 Changes of 'cold' crystallization starting temperature, and of heat capacity of exothermic peak at crystallization temperature, with time of heat treatment below T_g

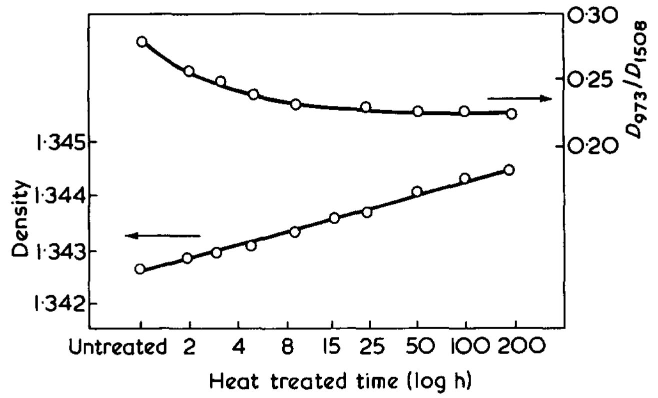

Figure 4 Changes of density and of relative intensity of 973 cm^{-1} band with time of heat treatment below T_g

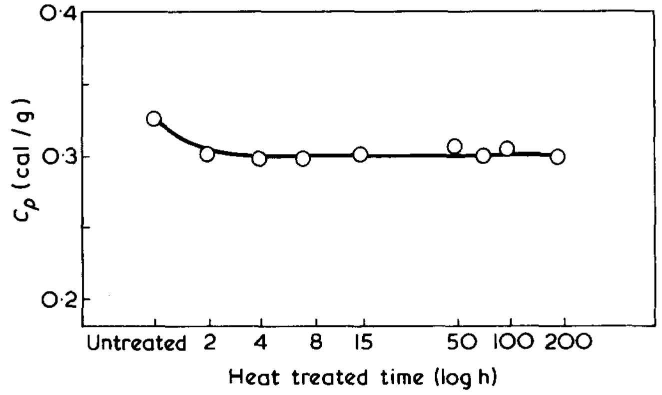

Figure 5 Change of specific heat at 320K with time of heat treatment below T_g

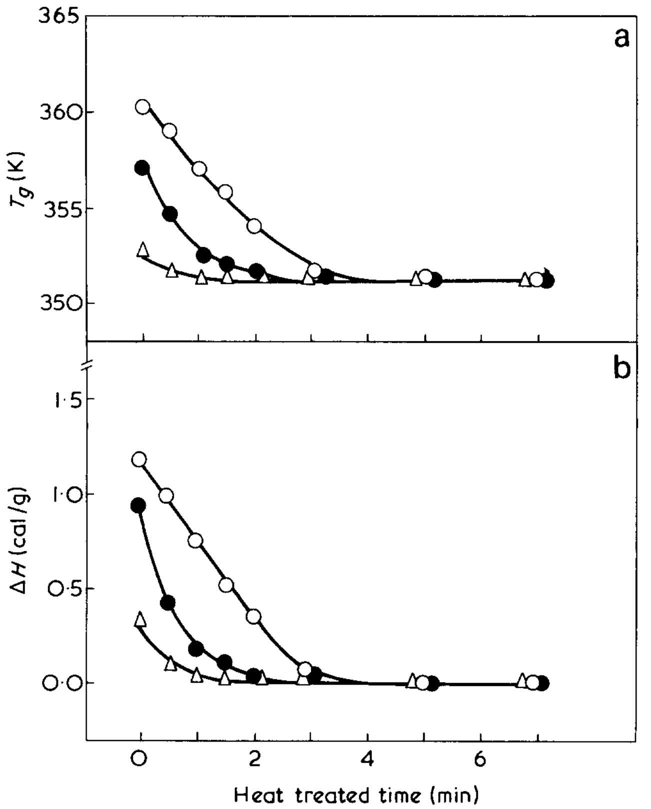

Figure 6 (a) Change of T_g (○, 59°C, 1 h; ●, 59°C, 25 h; △, 59°C, 100 h) (b) change of endothermic peak (○, 59°C, 1 h; ●, 59°C, 25 h; △, 59°C, 100 h) at T_g with time of heat treatment above T_g (78.5°C)

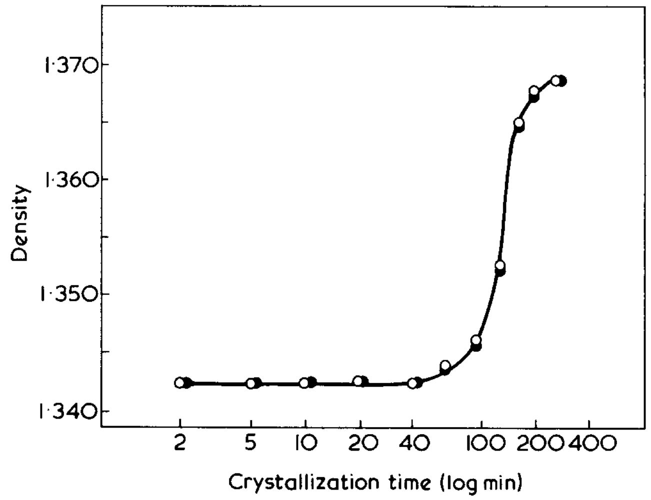

Figure 7 Change of density with time of crystallization at 95°C: ○, untreated; ●, 59°C, 100 h

of T_g and the endothermic heat capacity of each sample were observed. *Figure 6a* shows that the T_g values of the 1 and 100 h treated samples have fallen to the same temperature as the T_g of the untreated sample after heat treatment at 78.5°C for about 1 and 3 min, respectively. The endothermic peaks at T_g also disappeared at nearly the same rate as the reversion of T_g. We can say, therefore, that the state of each sample established by heat treatment below T_g reverts rapidly with further heat treatment above T_g. This fact explains why heat treatment below T_g has no effect on the starting temperature of 'cold' crystallization and exothermic heat capacity as shown in *Figure 3*.

Results on isothermal crystallization (as opposed to crystallization under rising temperature, referred to previously as cold crystallization) are shown in *Figures 7* and *8*. This demonstrates that little difference can be observed between the crystallization behaviours of the untreated and 100 h treated samples. This again would be expected from the rapid disappearance above T_g of any condition induced by treatment below T_g. *Figure 8* shows that the amount of *trans* conformation in the 100 h treated sample is slightly smaller than that of the other samples for about 60 min before the beginning of crystallization.

DISCUSSION

The above results suggest that the increase of the density and the enhancement of the exothermic peak at T_g, with heat treatment below T_g, arise from an improvement in the packing of the molecular chains as a result of heat treatment. This agrees with the explanation given by Wunderlich[14].

The decrease of the amount of *trans* conformation implies an increase in the conformational entropy of the molecular chains as a result of the heat treatment (the free energy of *trans* conformation is less than that of *gauche*). The specific heat of each sample, however, tends to decrease with heat treatment. If it is assumed that this specific heat relates to two factors, concerning intramolecular and intermolecular contributions respectively, the decrease of the specific heat can be attributed to the decrease of the intermolecular contribution factor. This results in a decrease of the intermolecular entropy. It is not clear, however, that the intermolecular entropy decreases by the formation of a specific regular structure in the amorphous region or otherwise a more uniform random structure (i.e. one phase structure) in the amorphous region. Even if a certain regularity appears in the amorphous region, this can neither grow a nucleus of crystal nor accelerate the rate of crystallization, as shown in *Figures 8* and *9*, since the structure formed by the heat treatment below T_g rapidly disappears by heat treatment above T_g.

It has been reported that PET crystallized at a temperature of 80°C has an induction time of about 10^3 min for crystallization[15]. Therefore, it is considered that no crystal is produced by heat treatment at 80°C for 50 h, though nuclei of crystal may be generated. Such conditions will be considered below. No change is observed in density with-

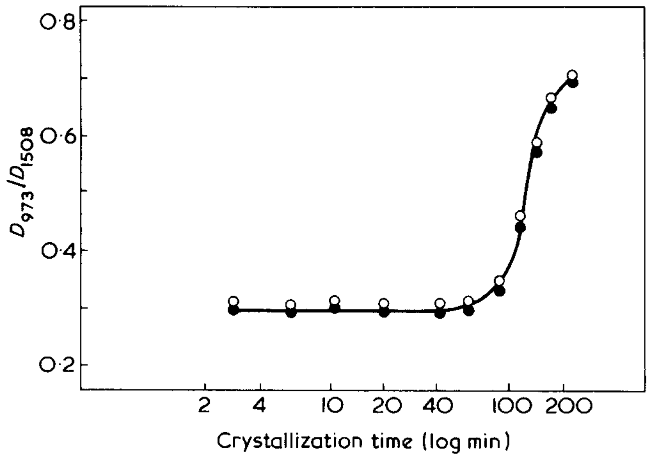

Figure 8 Change of relative intensity of 973 cm^{-1} with time of crystallization at 95°C: ○, untreated; ●, 59°C, 100 h

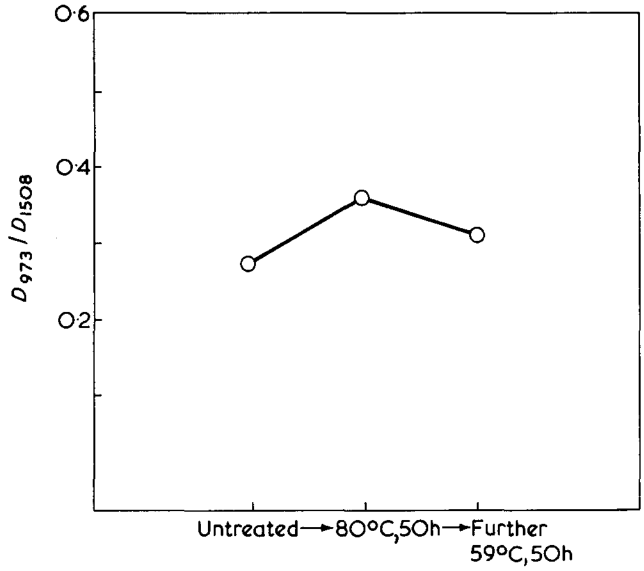

Figure 9 Change of 973 cm^{-1} relative intensity with various heat treatments

in the induction time, as shown in *Figure 7*.

A d.s.c. curve of the sample at a heating rate of 20°C/min is shown in *Figure 1*, curve C. Two facts can be seen from the curve. (a) The starting temperature of 'cold' crystallization is lowered. This fact implies the formation of nuclei by heat treatment at 80°C. (b) T_g remains unchanged and there is no observed endothermic peak at T_g. These facts show that the molecular chains are not compactly packed, even if structures with good regularity (such as nuclei) are formed.

Another d.s.c. curve of the sample previously treated as 80°C for 50 h and further treated at 59°C for 50 h is shown in *Figure 1*, curve D. An endothermic peak of this sample is now observed at T_g, and the starting temperature of cold crystallization remains low. The density of this sample is equal to that of the sample treated only at 59°C for 50 h, but increased compared with that of the sample treated only at 80°C for 50 h.

Figure 9 shows the amount of *trans* conformation for these samples. The density remains unchanged with the treatment at 80°C for 50 h, but the amount of *trans* conformation increases with this treatment. When this sample is further treated below T_g, the amount of *trans* conformation decreases, as shown in *Figure 9*. The sample heat-treated below T_g after heat treatment at 80°C for 50 h has the same state as the sample treated below T_g and contains nuclei of crystal. It is considered that no structure having a regularity such as a crystal nucleus can be produced only by heat treatment below T_g. This follows from a comparison of the d.s.c. curve of this sample with that of the sample treated only below T_g. If a structure in the amorphous region, consisting of two elements (i.e. regular and random regions) is formed by heat treatment below T_g, the corresponding d.s.c. curve would show the same behaviour as that shown in *Figure 1*, curve D.

The molecular chains are thus compactly packed by heat treatment below T_g so that the intermolecular entropy is reduced. This compactly packed state quickly disappears with heat treatment above T_g, and is not capable of producing a nucleus for crystallization. Therefore, it is considered that the structure of the amorphous state may be homogeneous rather than consisting of a mixture of regions having regular and random regions.

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