

Melting Behavior of Poly(ethylene terephthalate) Crystallized and Annealed under Elevated Pressure

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ABSTRACT: For poly(ethylene terephthalate) crystallized and/or annealed under elevated pressure, the melting behavior was studied, using a differential scanning calorimetry technique at atmospheric pressure. The melting point of the sample crystallized from the melt by slow cooling under elevated pressure is lower than that of the sample crystallized at atmospheric pressure, although the former sample has a slightly thicker lamella than the latter one. This implies that the fold surface energy is much larger in the elevated pressure crystallized sample. The atmospheric pressure melting point increases greatly by annealing under elevated pressure. In particular, a remarkable increase in melting point is observed at the early stage of the annealing for the elevated pressure crystallized sample, which may be due mainly to the decrease in fold surface energy in addition to lamella thickening. An electron micrograph of the sample annealed for a long period after the melt crystallization under elevated pressure shows a morphology of a band structure composed of extended-chain-like crystal.

KEY WORDS Poly(ethylene terephthalate) / Elevated Pressure / Crystallization / Annealing / Melting Point / DSC / Morphology /

There are many reports on the study of the structure and thermal properties of certain kinds of polymers crystallized and/or annealed under elevated pressure. For example, with polyethylene,¹ polyamide,^{2,3} polychlorotrifluoroethylene,⁴ and poly(vinylidene fluoride)⁵ crystallized and/or annealed under elevated pressure, their melting points approach equilibrium melting points and extended-chain crystal structures are shown.

In poly(ethylene terephthalate) (PET), there have already been many reports on the study of the crystallization and annealing at atmospheric pressure.⁶⁻⁸ However, there have been no reports on the study of the thermal properties or morphology of PET crystallized and annealed under elevated pressure, because of the difficulties in elevated pressure experiments resulting from the relatively high melting point and sensitive pressure dependence of the melting point of PET.

In the present work, we carried out experiments on crystallization and annealing of PET under elevated pressure using a high-pressure differential thermal analysis (DTA) apparatus having a heater set inside

the high pressure vessel. The melting behavior of the elevated pressure crystallized and annealed sample was examined by a differential scanning calorimetry (DSC) method at atmospheric pressure. The density, wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) were also measured. The morphology was observed using an electron microscope. The microscopic structure of PET crystallized under elevated pressure and the mechanism of the annealing under elevated pressure are discussed in this paper.

EXPERIMENTAL

An unoriented commercial PET (Teijin Tetoron) was used as the original sample. Its molecular weight, calculated from the viscosity,⁹ was about 40000. Its room temperature density was 1.338 g cm⁻³. The original samples were allowed to stand for several hours just above the glass-transition temperature in vacuum to eliminate moisture.

The crystallization and annealing experiments were carried out using high-pressure DTA ap-

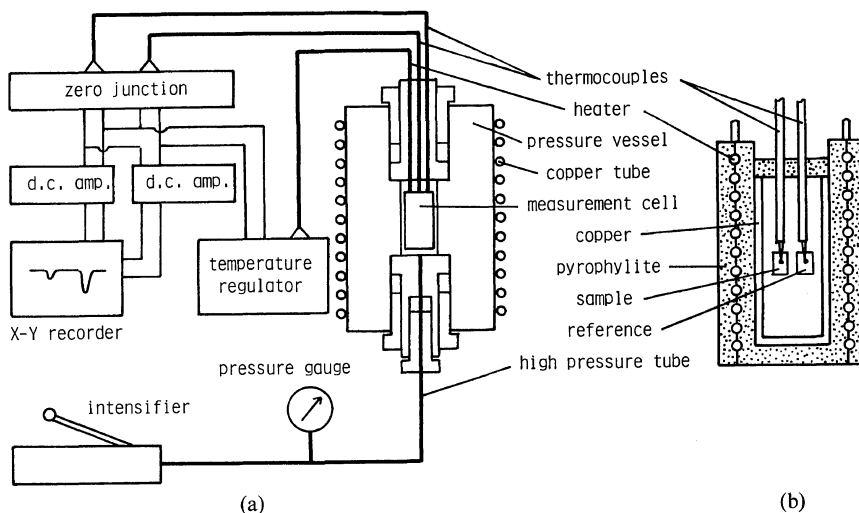


Figure 1. Schematic diagram of (a) the high pressure DTA apparatus and (b) DTA measurement cell.

paratus, whose schematic diagram is shown in Figure 1(a). Its measurement cell is magnified in Figure 1(b). The inner diameter of this high-pressure vessel is 25 mm. This apparatus can be used at temperatures ranging from room temperature to 400°C and in a pressure range from atmospheric pressure to 10000 kg cm⁻². The sample can be heated intensely without a thermal load on the high-pressure vessel and rapidly cooled (about -100°C min⁻¹), since the high-pressure vessel can be cooled by the water running in the copper tube wound round the vessel. The temperature was precisely controlled to within ±0.5°C. The hydrostatic pressure was measured by a Bourdon gauge (Heise) connected to the high-pressure vessel and was controlled to within ±20 kg cm⁻². Silicone oil (10 cs) was used as the pressure transmitting liquid.

First, the original samples were crystallized from the melt at various pressures, from atmospheric pressure to 2000 kg cm⁻². At the same time, for later annealing and isothermal crystallization experiments, pressure dependences of the glass transition, cold crystallization, melting, and melt crystallization peak temperatures were examined. The results are shown in Figure 2. Both the heating and cooling rates of these experiments were 8°C min⁻¹. The increase in each peak temperature per 1000 kg cm⁻² is 22°C for the glass transition and the cold

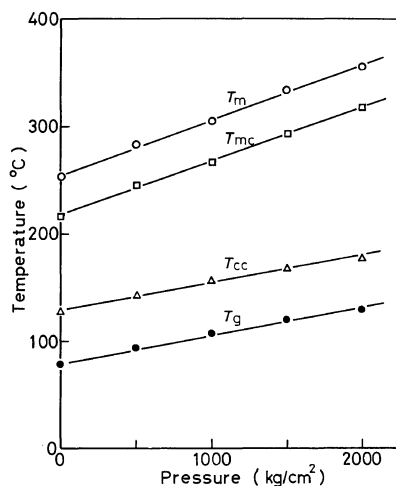


Figure 2. Pressure dependences of the peak temperatures of the glass transition (T_g), the cold crystallization (T_{cc}), the melt crystallization (T_{mc}), and the melting (T_m).

crystallization, 50°C for the melting, and 49°C for the melt crystallization. The observed pressure dependence of the melting peak temperature of PET is higher than that of polyethylene (about 20°C per 1000 kg cm⁻²).¹⁰

Next, the annealing of two kinds of starting

samples was carried out at 2000 kg cm^{-2} . One starting sample was crystallized from the melt at 1500 kg cm^{-2} , and another sample was crystallized from the melt at atmospheric pressure. Cooling rate for each crystallization was 8°C min^{-1} . The annealing experiments were carried out by varying the annealing time and temperature. After annealing, the samples were rapidly cooled (about $-100^\circ\text{C min}^{-1}$) to room temperature. In this study, experiments at pressures exceeding 2000 kg cm^{-2} were not carried out because of the temperature limit of the high-pressure vessel; the melting point temperature at 2000 kg cm^{-2} becomes a very high 355°C , as shown in Figure 2. In order to prevent a thermal degradation occurring at high temperatures, one of the starting samples was crystallized at 1500 kg cm^{-2} rather than at 2000 kg cm^{-2} .

Isothermal crystallization from the melt was also carried out by varying the crystallization time. The crystallization condition was 330°C and 2000 kg cm^{-2} . After the crystallization, the samples were rapidly cooled (about $-100^\circ\text{C min}^{-1}$) to room temperature.

The samples prepared above were examined with respect to thermal properties using a DSC apparatus (Rigaku Denki). The heating rate for each measurement was $10^\circ\text{C min}^{-1}$. The sample weight used was about 15 mg. An electron microscope (Hitachi HS-7D) was used to observe the fracture surfaces of the samples. The density measurement was made by the floating method at 25°C , using a carbon tetrachloride and heptane mixture. Measurements of WAXD and SAXS were carried out with a Ni-filtered $\text{Cu-K}\alpha$ radiation.

RESULTS AND DISCUSSION

Crystallization under Elevated Pressure

For the sample crystallized from the melt by slow cooling under various pressures, DSC thermograms were obtained. The results are shown in Figure 3. The DSC thermogram trace of the sample crystallized under higher pressure shows double melting peaks. Moreover, we noticed that the peak temperature of the lower temperature peak is lower than that of the sample crystallized from the melt at atmospheric pressure.

For the purpose of the assignment of these double melting peaks, it was initially examined by the WAXD to see whether or not another crystal

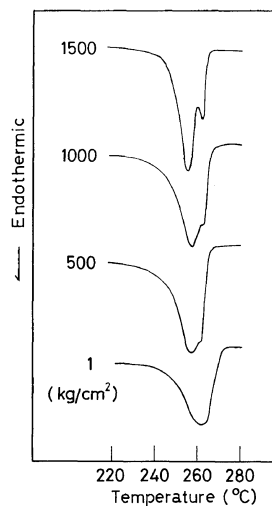


Figure 3. DSC thermograms of the samples crystallized from the melt by slow cooling at various pressures.

structure existed. The sample crystallized under elevated pressure was found to contain only the crystal with the same triclinic structure as observed in the sample crystallized at atmospheric pressure,¹¹ but also that the diffraction lines of the former sample were sharper than those of latter one. Thus, the double melting peaks are not due to the melting of the two kinds of crystals having different structures.

Next, the heating rate effect on the DSC thermogram for the sample crystallized at 1500 kg cm^{-2} was examined and the results are shown in Figure 4. The higher temperature peak becomes larger as the heating rate is reduced. It has already been reported that for the atmospheric pressure crystallized samples,^{12,13} double melting peaks appear in the annealing experiments at atmospheric pressure. The heating rate effect on the thermogram has been examined to make assignment of this peak. Reports on this show that the lower temperature peak becomes small and the higher one becomes large as the heating rate is reduced. The explanation for this is that the lower temperature endotherm results from the melting of the crystal already existing, while the higher one comes from the melting of the crystal formed by simultaneous melting and recrystallization at lower temperatures during the DSC scan. There is enough time for

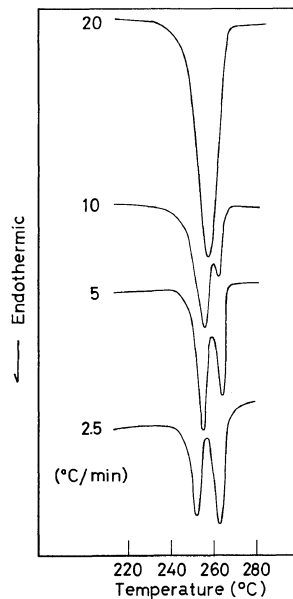


Figure 4. Heating rate effect on the thermograms. The samples were crystallized from the melt by slow cooling at 1500 kg cm^{-2} .

recrystallization when the heating rate is slow. For the sample crystallized under elevated pressure, the origin of the double peaks can be also concluded to come about in the same way, *i.e.*, from the heating rate effect. That is, the lower temperature endotherm is due to the melting of the elevated pressure crystallized material, while the higher one is due to the melting of the melt recrystallized material during the DSC scan.

The reason why the material crystallized under elevated pressure has a lower melting point than that crystallized at atmospheric pressure will be discussed later.

Annealing under Elevated Pressure

The annealing experiments at 335°C and 2000 kg cm^{-2} were carried out for both starting samples crystallized at 1500 kg cm^{-2} and atmospheric pressure. The relation between the annealing time and the DSC melting peak temperature measured at atmospheric pressure is shown in Figure 5. Although it was reported that the melting point of unoriented PET does not increase so much in the case of annealing at atmospheric pressure,^{8,14,15} the

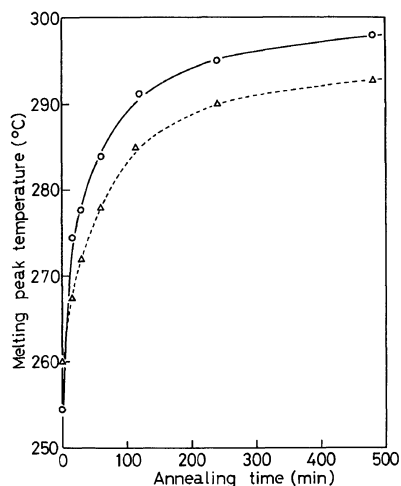


Figure 5. Dependence of the DSC melting peak temperature on the annealing time at 335°C and 2000 kg cm^{-2} . The starting samples were crystallized from the melt at (O) 1500 kg cm^{-2} and (Δ) atmospheric pressure.

drastic rise in melting peak temperature could be observed for both starting samples by annealing under elevated pressure. This phenomenon is particularly remarkable for the starting sample crystallized at 1500 kg cm^{-2} . The largest increase in the melting point observed in this experiment is 43°C , in comparison with the melting point of the starting sample with no annealing process (255°C).

Moreover, it was noticed that an inversion of the melting peak temperatures for both series of the samples takes place at the early stage of annealing. After this inversion, the melting peak temperatures of both series of the samples increase in the same way. This suggests that the increase in the melting peak temperature with annealing time beyond about 15 min is due to the same mechanism, probably "the thickening of lamella," for both annealing series. The lamella thickening was verified by the results of the SAXS measurement.

Next, the effect of annealing temperature was examined, since the annealing temperature of 335°C corresponds to the lower-temperature side midslope and foot of the high-pressure DTA endothermic peak at 2000 kg cm^{-2} for the sample crystallized at 1500 kg cm^{-2} and atmospheric pressure, respectively. Annealing experiments, in which the pressure

and annealing time were fixed, were carried out. The results of the annealing for 60 min at 2000 kg cm^{-2} are shown in Figure 6. It can be seen that the distinct difference in the melting peak temperatures between both series of samples exists even at the lower annealing temperature. This implies that this difference in the melting peak temperature is not merely due to the problem of whether the annealing temperature corresponds to the midslope or foot of the high-pressure DTA endotherms.

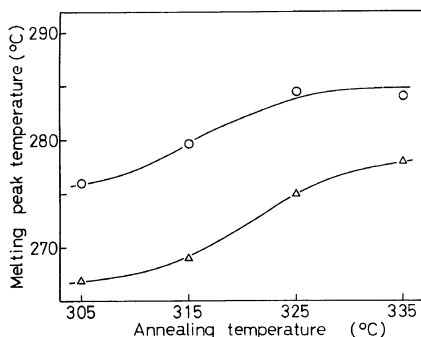


Figure 6. Dependence of the DSC melting peak temperature on the annealing temperature for the samples annealed for 60 min at 2000 kg cm^{-2} . The starting samples were crystallized from the melt at (○) 1500 kg cm^{-2} and (△) atmospheric pressure.

For the study of early stage of annealing, SAXS and density measurements for the two starting samples were carried out. It was found that each starting sample has almost the same long period of about 130 \AA , but that the crystallinity calculated from the density for the sample crystallized at 1500 kg cm^{-2} is higher by 10% than that crystallized at atmospheric pressure. When a model of the alternation of crystalline and amorphous regions is assumed, the mean lamellar thickness of the sample, l , is

$$l = L \cdot X_c \quad (1)$$

where L is the long period measured by SAXS and X_c is the crystallinity.¹⁶ From the eq 1, it is found that the mean lamellar thickness of the sample crystallized at 1500 kg cm^{-2} is slightly thicker than that crystallized at atmospheric pressure. The crystal PET does not become the so-called "thick lamella crystal" in the case of melt crystallization

for a short time under elevated pressure, thus differing from polyethylene.¹

From the above, the lamellar structure of the sample crystallized and annealed under elevated pressure can be discussed. The simplest expression¹⁷ for the melting point of a polymer is,

$$T_m(l) = T_m^\circ (1 - 2\sigma/l \cdot \Delta H) \quad (2)$$

where σ is the fold surface energy of a crystal; l , the lamellar thickness; ΔH , the heat of fusion, and T_m° , the melting point of an infinite perfect crystal. To explain why the sample, crystallized at 1500 kg cm^{-2} , has the lower melting point, it is considered that this sample may have a much larger value of σ in spite of having a slightly thicker lamella. The larger value of the fold surface energy means a high degree of disorder in the fold surface: roughness and strain in the fold surface. At the early stage of annealing under elevated pressure, the great rise in the melting point for this sample may originate mainly in a mechanism such that the fold surface is ordered by annealing. The inversion of the melting point shown in Figure 5 may be due to this mechanism. After that, the increase in the melting points for both starting samples take place by the lamellar thickening mechanism.

For examination of the annealing mechanism mentioned above, other evidence is available, *i.e.*, the data of the isothermal crystallization from the melt at 330°C and 2000 kg cm^{-2} . The DSC melting thermograms (a, b, c) as shown in Figure 7 were obtained for the samples crystallized isothermally from the melt for 60, 120, and 240 min. Three endotherms are seen to exist. The highest-temperature endotherm is due to the melting of the isothermally crystallized material, and the middle one is due to the melting of the material crystallized rapidly from the residual molten material in the process of cooling. The lowest one may be due to the melting of the partially degraded material. It is supposed that the rapidly crystallized material may have a large value of σ . Roberts¹⁵ suggested that the crystallite formed by cooling rapidly from the melt at atmospheric pressure has a large surface energy and hence, a low melting point. The annealing for 15 min at 335°C and 2000 kg cm^{-2} was carried out for the sample crystallized isothermally for 60 min. The DSC thermogram of this sample is shown in Figure 7(d). The middle endotherm becomes very small by annealing for only 15 min, whereas the

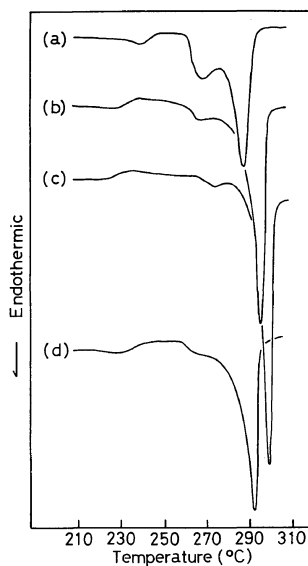


Figure 7. DSC melting thermograms of the samples crystallized isothermally from the melt at 330°C and 2000 kg cm⁻² for various periods; (a) 60 min, (b) 120 min, and (c) 240 min. The curve (d) is the thermogram of the sample annealed for 15 min at 335°C and 2000 kg cm⁻² after isothermal crystallization for 60 min at 330°C and 2000 kg cm⁻².

higher one becomes large. This means that the great increase in the melting point occurs because the disordered fold surface is ordered by the elevated pressure annealing for a short period: if the increase in the melting point resulted from the thickening of lamella, the middle endothermic peak would slightly shift to the higher temperature position by annealing for only 15 min.

Finally, the morphology of the sample annealed at elevated pressure was observed. A typical electron micrograph of a replica of the fracture surface of the sample is shown in Figure 8. This sample was crystallized at 1500 kg cm⁻² at a cooling rate of 8°C min⁻¹ and then annealed for 480 min at 335°C and 2000 kg cm⁻². The micrograph shows the band structure of the thick lamella, though it is not so clear as that of high-pressure crystallized polyethylene.¹⁸ The WAXD pattern of this sample is the same as that of the sample crystallized at atmospheric pressure, but the diffraction lines of this sample are narrower, as shown in Figure 9. The SAXS peak observed for the sample crystallized at

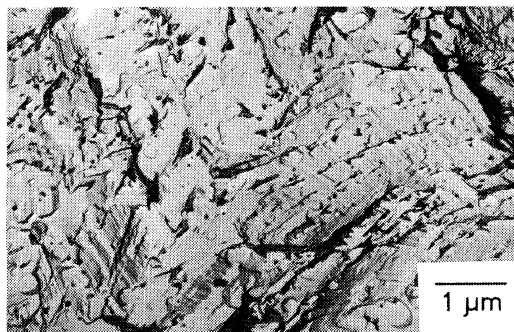


Figure 8. Electron micrograph of the replica of the fracture surface of PET crystallized from the melt at 1500 kg cm⁻² and then annealed for 480 min at 335°C and 2000 kg cm⁻².

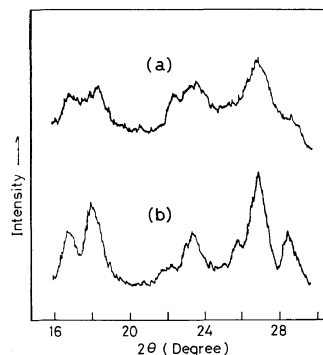


Figure 9. WAXD of (a) the sample crystallized from the melt by slow cooling at atmospheric pressure and (b) the sample of Figure 8.

atmospheric pressure cannot be observed for this sample. In the case of atmospheric pressure annealing, Zachmann *et al.*¹⁹ reported that the long period decreases with annealing time, in contrast to the behavior of other polymers. The density of this sample is 1.451 g cm⁻³ and is very close to that of the perfect crystal (1.455 g cm⁻³) reported by Daubeny *et al.*¹¹ From these results, it can be concluded that the long period of this sample is very long and that the degree of crystallinity is very high.

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REFERENCES

1. B. Wunderlich and T. Arakawa, *J. Polym. Sci., A*, **2**, 3697 (1964).
2. S. Gogolewski and A. J. Pennings, *Polymer*, **18**, 654 (1977).
3. S. Gogolewski and A. J. Pennings, *Polymer*, **18**, 660 (1977).
4. Y. Miyamoto, C. Nakafuku, and T. Takemura, *Polym. J.*, **3**, 120 (1972).
5. K. Matsushige and T. Takemura, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 921 (1978).
6. E. W. Fischer and S. Fakirov, *J. Mater. Sci.*, **11**, 1041 (1976).
7. P. J. Holdsworth and A. Turner-Jones, *Polymer*, **12**, 195 (1971).
8. G. C. Alfonso, E. Pedemonte, and L. Ponzetti, *Polymer*, **20**, 104 (1979).
9. L. D. Moore, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.*, **1**, 234 (1960).
10. M. Yasuniwa, C. Nakafuku, and T. Takemura, *Polym. J.*, **4**, 526 (1973).
11. R. de P. Daubeny, C. W. Bunn, and C. J. Brown, *Proc. R. Soc., London, Ser. A*, **226**, 531 (1954).
12. R. C. Roberts, *J. Polym. Sci., B*, **8**, 381 (1970).
13. M. Ikeda, *Kobunshi Kagaku*, **25**, 87 (1968).
14. S. Fakirov, E. W. Fischer, R. Hoffmann, and G. F. Schmidt, *Polymer*, **18**, 1121 (1977).
15. R. C. Roberts, *Polymer*, **10**, 117 (1969).
16. M. Ikeda, *Kobunshi Kagaku*, **26**, 102 (1969).
17. J. I. Lauritzen and J. D. Hoffmann, *J. Res. Natl. Bur. Stand., A*, **64**, 73 (1960).
18. P. H. Geil, F. R. Anderson, B. Wunderlich, and T. Arakawa, *J. Polym. Sci., A*, **2**, 3707 (1964).
19. H. G. Zachmann and G. F. Schmidt, *Makromol. Chem.*, **52**, 23 (1962).