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Melting point maximum against pressure in poly(4-methyl-pentene-1) crystals

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The melting point maximum against pressure is reported for poly(4-methyl-pentene-1): 270°C at 1.5 kbar. X-ray diffraction at high pressures shows no transformation up to 15 kbar at room temperature; the long-range order in the crystal remains unchanged with pressure while disorder of the first kind increases to cause the increase of the internal energy of the crystal. The origin of the melting point maximum is discussed on the basis of the low packing coefficient of helical polymers with bulky side groups and the long-range order maintained up to the melting point at high pressures. Copyright © 1996 Elsevier Science Ltd.

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Introduction

Isotactic poly(4-methyl-pentene-1) (P4MP1), $-(CH_2-CHCH_2CH(CH_3)_2)_n-$, is an unusual material in that its crystal density ρ_c (0.813) is lower than the amorphous density ρ_a (0.830) at room temperature. The low crystal density is due to the loose packing of helical chains with bulky side groups. With increasing temperature, however, ρ_c becomes larger than ρ_a at 50–100°C, and hence the coefficient of melting point T_m against pressure P is positive at atmospheric pressure as for most materials: $(dT_m/dP) > 0$.

Rastogi *et al.*[1,2] studied P4MP1 by means of high-pressure X-ray diffraction and reported the transformation (amorphization) of the tetragonal phase into a disordered phase at about 2 kbar at room temperature. They also observed at 248°C at a pressure from 1 to 6 kbar. Taking account of the differential thermal analysis (d.t.a.) data reported by Jain *et al.*[3] and Zoller *et al.*[4], they proposed a phase diagram for P4MP1 in which the melting temperature has a maximum between 2 and 4 kbar, yet to be determined.

On the other hand, Ito[5] reported the hydrostatic compression of P4MP1 up to 5 kbar at room temperature and found a decrease in the intensity of X-ray reflections with pressure but did not observe any transformation. On annealing at high temperatures and high pressures, Hasegawa *et al.* reported an unspecified structure[6].

The present paper reports a maximum of the melting point against pressure for P4MP1. In order to reexamine the phase behaviour of P4MP1, X-ray diffraction was conducted at pressures of up to 15 kbar.

Experimental

A small tip of P4MP1 (from Scientific Polymer Product Inc.) was set in a high-pressure cell[7] for d.t.a. to determine the pressure dependence of the melting point; a copper–constantan thermocouple 0.1 mm in diameter was embedded in the specimen to get a large d.t.a. signal. The pressure-transmitting fluid was silicone oil (Toshiba TSF 451). Pressure was measured with a calibrated manganin gauge. The heating rate was $10°C\,min^{-1}$.

For high-pressure X-ray diffraction, a melt-crystallized rod of P4MP1 was drawn in boiling water and annealed at 200°C for 1 h to obtain a *c*-axis oriented specimen. The specimen was cut into a small piece measuring $0.3 \times 0.1 \times 0.1\,mm^3$. The high-pressure cell was of the diamond-anvil type with a stainless steel gasket 0.4 mm thick and a hole 0.4 mm in diameter. The specimen was inserted in the gasket hole, filled with ethanol (pressure-transmitting fluid) together with a graphite tip (pressure calibration reference) and compressed between the diamond anvils. Pressure was measured from the shift of the (0 0 2) spacing of graphite[8]. The X-ray diffraction pattern was recorded on a flat imaging plate (Fuji Imaging Plate, BAS UR, Fuji Photo Film Co., Ltd) with Mo K_α radiation filtered by a zirconium film. The camera length of about 100 mm was determined from the 1 1 1 reflection of silicon. Read-out and data processing of the imaging plates were done with R-AXIS DS2 (Rigaku Corporation, Japan).

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Results and discussion

Pressure dependence of melting point. With increasing pressure, the peak temperature in the d.t.a. curve of P4MP1 increases first, passes through a maximum and decreases (*Figure 1*). *Figure 2* plots the peak temperatures against pressures. As clearly seen in the figure, the existence of the melting point maximum has been found. The melting point has a maximum value of 270°C around 1.5 kbar, while Rastogi *et al.*[1] predicted the maximum around 3 kbar. Jain *et al.*[3] and Zoller *et al.*[4] conducted high-pressure d.t.a. of P4MP1 up to up to 1 kbar and 1.5 kbar, respectively, and hence could not observe the maximum.

As shown in *Figure 1*, the d.t.a. signal on melting decreases with pressure. The decrease is due to that in the heat of fusion ΔH; $\Delta H = \Delta U + P\Delta V$, where ΔU and ΔV are the differences between internal energies and volumes of crystalline and liquid states, respectively. The rate of $P\Delta V$ to ΔH is given by the following equation derived from the Clausius–Clapeyron relation:

$$P\Delta V/\Delta H = (P/T_{\mathrm{m}})\mathrm{d}T_{\mathrm{m}}/\mathrm{d}P \qquad (1)$$

The values of the variables on the right-hand side can be evaluated from the data in *Figure 1*; the ratio increases with pressure in positive value, reaches the maximum around 1 kbar and decreases to negative values through zero at the pressure of the melting point maximum. The absolute value of the ratio is very small: less than 0.05. Thus the decrease in ΔH is mainly attributed to that in ΔU: the increase in the internal energy of the crystal. The origin of the increase in internal energy will be discussed in the next section in the light of pressure-induced disorder in the crystal.

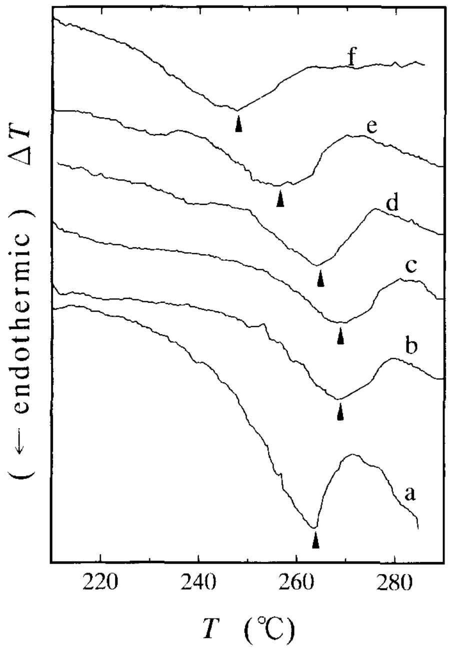

Figure 1 D.t.a. curves of isotactic P4MP1 at several high pressures. The arrows indicate the peak positions. (a) 0.95 kbar; (b) 1.3 kbar; (c) 1.4 kbar; (d) 1.65 kbar; (e) 1.9 kbar; (f) 3.05 kbar

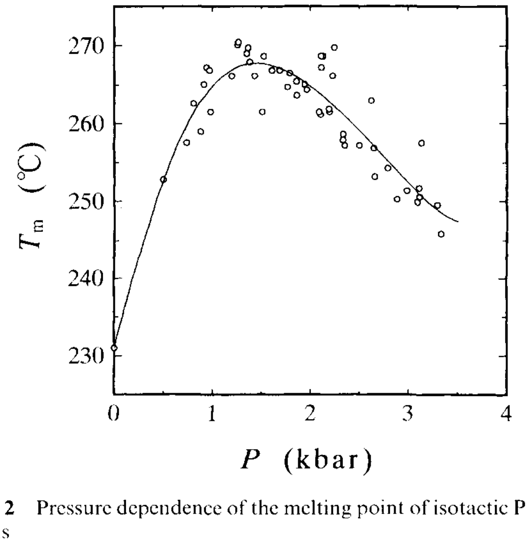

Figure 2 Pressure dependence of the melting point of isotactic P4MP1 crystals

According to the Clausius–Clapeyron relation, a melting point maximum is caused by the change in the sign of the difference between the densities of crystals and liquids at the melting point: the difference $\Delta\rho > 0$ at pressures lower than 1.5 kbar, and $\Delta\rho < 0$ at higher pressures in P4MP1. Since liquids usually have compressibilities higher than those of crystals, $\Delta\rho$ decreases with pressure giving rise to a decrease in the coefficient $\mathrm{d}T_{\mathrm{m}}/\mathrm{d}P$. However, for most materials, the condition $\Delta\rho > 0$ holds at high pressures up to several kbar, and hence a melting point maximum is not observed. The specific features in P4MP1 are not only the low crystal density but also the very low packing coefficient, k, in the crystal[9]. k is the ratio of the volume occupied by the monomers in a unit cell to that of the unit cell: 0.60 for P4MP1, 0.66 for polypropylene and 0.71 for polystyrene. This low value of k in P4MP1 is caused by the bulky side groups, $-CH_2-CH(CH_3)_2$, arranged with the 7_2 helix in the tetragonal phase. The helical order remains unchanged at high pressures. Consequently, with increasing pressure, the value of k (hence the density of the crystal) cannot increase so much as that in the liquid, which has no long-range helical order. Thus the density difference $\Delta\rho$ may change its sign from positive to negative at a certain pressure for materials such as P4MP1 with a low value of k. In conjunction with this consideration, it is important to confirm that the crystal structure remains unchanged with increasing pressure.

X-ray diffraction at high pressure. X-ray reflections from the drawn P4MP1 at atmospheric pressure could be indexed with the tetragonal lattice reported[10]. *Figure 3* shows diffraction patterns under high pressures at room temperature. No new reflections or amorphous haloes other than those of the tetragonal phase are observed up to 15 kbar (*Figures 3a–d*), and hence we conclude that no transformation took place. Further, with increasing temperature under high pressures less than 5 kbar, solid P4MP1 showed the reflections from the tetragonal phase until melting.

The intensities of the tetragonal phase decrease with pressure. When pressure is released, the intensities of the reflections were recovered (*Figure 3d*); the changes in the intensities are reversible with pressure, agreeing with previous results[1]. The disorder caused by pressure therefore is not due to plastic deformation but due to elastic strain, giving rise to fluctuations of the position of chain molecules around the averaged lattice sites to reduce volume. It can be this pressure-induced disorder

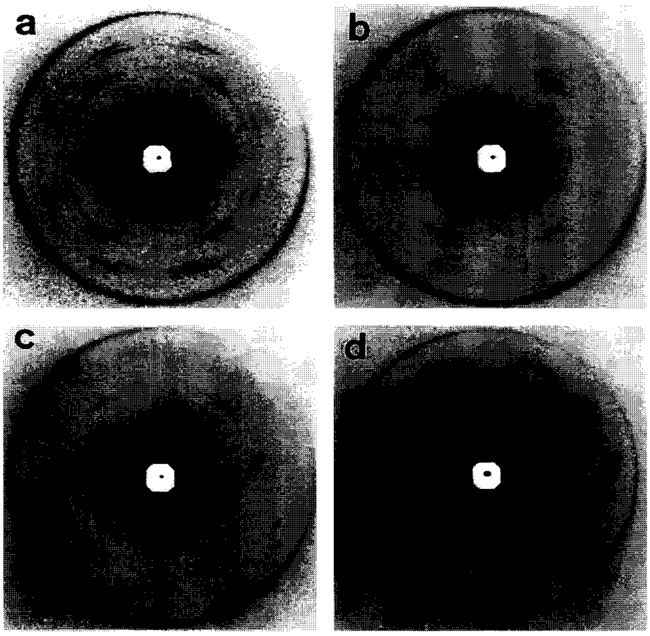

Figure 3 X-ray diffraction patterns (video copies) of drawn specimens at room temperature under high pressures. The outermost Debye ring is the 0 0 2 reflection of graphite for pressure calibration. (a) Atmospheric pressure; (b) 2.0 kbar; (c) 7.7 kbar; (d) pressure released after compression up to 15 kbar

that causes the increase in internal energy of the crystal at the melting point, and accordingly the d.t.a. signals on melting decrease with pressure, as discussed above.

The widths of the reflections hardly changed with pressure. Therefore the long-range order of the crystal remains unchanged, while the disorder of the first kind increases in the crystal with pressure. Since the long-range order in the crystal remains up to the melting point under high pressure, it is to be expected that the crystal density will not increase so much as the liquid density, and hence the melting point maximum may result.

Experimental results are controversial regarding amorphization[1] and disorder of the first kind. A shear stress component promotes pressure-induced transformation[11]. The uniaxial stress in the experiment of Rastogi *et al.*[1] may be larger than that in Ito's experiment[5] and in the present study. The discrepancy in the experimental results among these studies may be attributed to the difference in the uniaxial stress superimposed to hydrostatic pressure.

References

1 Rastogi, S., Newman, M. and Keller, A. *Nature* 1991, **353**, 55
2 Rastogi, S., Newman, M. and Keller, A. *J. Polym. Sci., Polym. Phys. Edn* 1993, **31**, 125
3 Jain, P. C., Wunderlich, B. and Chaubey, D. R. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 2271
4 Zoller, P., Starkweather Jr, H. W. and Jones, G. A. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 1451
5 Ito, T. *Polymer* 1982, **23**, 1412
6 Hasegawa, R., Tanabe, Y., Kobayashi, M., Tadokoro, H., Sawaoka, A. and Kawai, N. *J. Polym. Sci.* 1970, **8**, 1073
7 Asahi, T., Miyamoto, Y., Miyaji, H. and Asai, K. *Polymer* 1982, **23**, 773
8 Miyaji, H. *J. Phys. Soc. Jpn* 1973, **39**, 1346
9 Privalko, V. P. *Polym. J.* 1975, **7**, 202
10 Kusanagi, H., Takase, M., Chatani, Y. and Tadokoro, H. *J. Polym. Sci., Polym. Phys. Edn* 1978, **16**, 131
11 Avilov, V. V. *JETP Lett.* 1983, **37**, 315