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## Thermodynamic anomalies in the pressure-temperature phase diagram of poly-4-methyl pentene-1: Disordering of crystals on cooling

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**Abstract:** We report on some highly unusual phase behavior of general implication for condensed matter in a polymer poly-4-methyl pentene-1. In situ x-ray studies, at the prerequisite pressure and temperature, reveal amorphization in this polymer, passing through a continuously varying sequence of mesomorphic states, at two widely separated temperature regions, the process being reversible. Present findings invoke the possibility of the reentrant, widely separated disordered phases with temperature. Such possibility has arisen for the first time in a single-component system. The pressure-induced disordered phase, obtained at room temperature, converts into crystal with increasing temperature and reverts to a glassy disordered phase on lowering the temperature. Other unexpected findings include a new pressure-induced modification of poly-4-methyl pentene-1, with a one-way entry only. A few aspects of similar features found in other materials are also stated.

**Key words:** Poly-4-methyl pentene-1; phase diagram; pressure; temperature; amorphization

The purpose of this communication is to report some highly unusual observations in a polymer poly-4-methyl pentene-1 (P4MP1), specifically, phase transitions induced by pressure ( $P$ ) and temperature ( $T$ ). Polymer crystallizes in tetragonal phase ( $C_t$ ) on straightforward solidification from the melt. At room temperature and atmospheric pressure crystal density ( $P_c = 813 \text{ kg m}^{-3}$ ) is less than the amorphous density ( $P_A = 830 \text{ kg m}^{-3}$ ), whereas above  $50^\circ\text{C}$ , at atmospheric  $P$ , such an inverted relationship, at room temperature, acquires special significance, as discussed in the following.

Figure 1, shows effect of pressure at room temperature on an oriented film of P4MP1. In situ x-ray observations reveal that on raising  $P$  above a threshold value, crystal reflexions broaden and become diffuse, those close together merge into liquid-pattern-type blobs, while others disappear. Indeed, long-range crystal periodicity is lost, and the system becomes disordered (Figs. 1a—d). The whole sequence is fully reversible with  $P$  (Fig. 1e). The continuous effect of pressure-induced amorphization (denoted as LC, A) is shown as Pathway

1 in Fig. 2. Figs. 1a—d refer to points (i)—(iv) in Fig. 2. At the highest  $P$  ( $\sim 6\text{Kb}$ ) accessible to us, point (v) in Fig. 2, there is virtually an oriented amorphous material.

The above change from order to disorder with increasing  $P$  is consistent with the anomalous density relation  $P_c < P_A$ . In this respect, P4MP1 seems to fall in the same class as water or bismuth where  $P$  causes a decrease in the melting point. However, the presently observed transitions occur about  $220^\circ\text{C}$  below the a.p. melting point and not in the melting region as in the familiar case of water.

To bridge this latter gap we proceeded to examine the effect of  $P$  also in the range of melting temperature ( $T_m$ ), i.e. around  $245\text{—}300^\circ\text{C}$ , along Pathway 2 in Fig. 2.

Experimental findings shown elsewhere [1, 2] clearly demonstrate that on raising the  $P$ , isothermally  $T$  ( $248^\circ\text{C}$ ), from point (vi) to (vii) in Fig. 2, initially  $C_t$  goes into the liquid phase (referred as  $LC'$ ,  $A'$ ). This process is completely reversible. This indicates a decrease in the melting temperature ( $T_m$ ) with  $P$ . Experiments [1, 2] conclusively

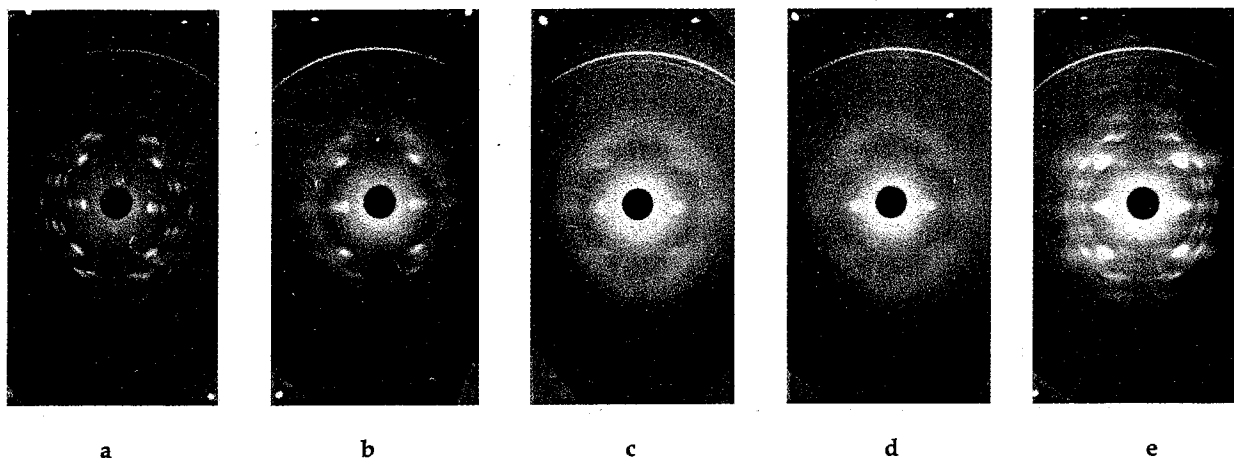


Fig. 1. X-ray diffraction patterns of drawn films of P4MP1 at r.T. recorded in situ at the various pressures: a) 0.24 Kb; b) 2.24 Kb; c) 4.56 Kb; d) 5.36 Kb; e) 0.24 Kb. (a) to (d) correspond to points (i) to (iv) respectively in Fig. 2 with (e) corresponding to a reversal to point (i). The sharp reflexions on the periphery are due to diamond and the rings to a gasket; these serve as useful intensity standards when comparing different members in a sequence

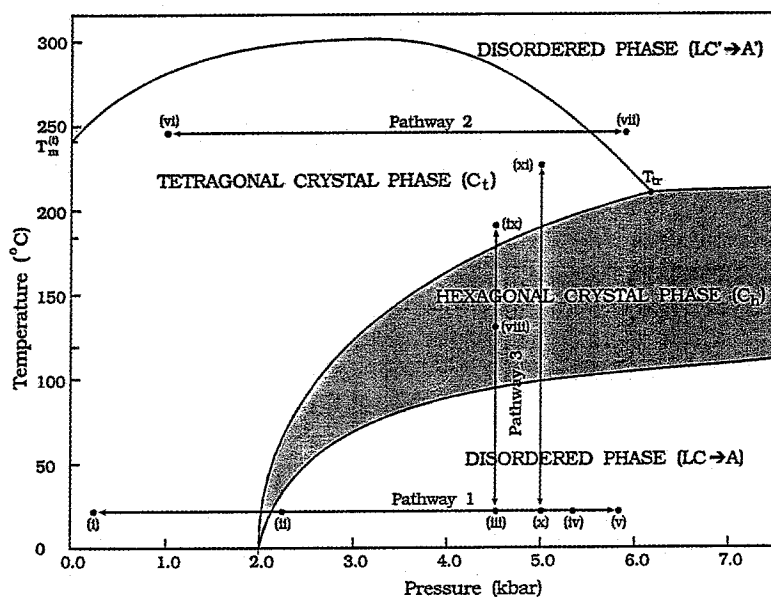


Fig. 2. *P-T* phase diagram of P4MP1. Liquid (amorphous), solid (crystal in tetragonal form) and intermediate (liquid crystal) denoted by *A*, *C<sub>t</sub>* and *LC* respectively. The shaded region encompasses a further (hexagonal) crystal phase

demonstrate that  $T_m$  first rises with  $P$ , reaching a maximum at a certain  $P^1$ , decreasing thereafter on further increase in  $P$ . This is readily explained on the basis that the amorphous (liquid) phase is more compressible than the crystal. This in turn means that, when starting from  $\rho_c > \rho_A$ , the densities will invert at a sufficiently high  $P$ , leading to the condition of  $\rho_c < \rho_A$ .

Two widely separated disordered phases in the different temperature regions on  $T$  axis imply a liquid phase reentry — the first ever anticipated in a single-component system. Such a possibility of reentry is indeed verified along Pathway 3 in Fig. 2.

Experiments [1, 2] along Pathway 3 show that the disordered phase achieved along Pathway 1, (i) to (x), crystallizes in  $C_t$ , on heating from (x) to (xi)

for the fixed  $P$ . Crystalline material  $C_i$  goes back into the disordered phase on lowering the  $T$  from (xi) to (x), suggesting that  $C_i$  has higher entropy compared to that of the disordered phase ( $LC$ ,  $A$ ). To our knowledge, such a process of disordering on cooling has no precedent in any known system.

The shaded region in Fig. 2 corresponds to a new crystalline hexagonal ( $C_h$ ) phase. It may be obtained along Pathway 3, i.e. on raising  $T$  for the fixed  $P$  from (iii) to (viii). On raising  $T$  further, from (viii) to (ix), the  $C_h$  to  $C_i$  transition occurs. Such a solid-to-solid transition is a one-way entry on the  $T$  axis in the  $P$ - $T$  phase diagram, i.e. on cooling from (ix) to (viii) to (iii),  $C_i$  goes directly into the disordered phase (for details see [2]).

The above findings are novel and are the first ever reported for a polymer. Some aspects of this behaviour (like  $P$ -induced amorphization with an inversion in sign of the temperature dependence of  $T_m$  with  $P$ ) have been found or surmised recently in water-ice [3] and silica [4].

Amorphization with  $P$  at room temperature is reported in several materials, such as  $\text{SiO}_2$  (quartz) [5],  $\text{AlPO}_4$  [6–8],  $\text{SnI}_4$  [9],  $\text{LiKSO}_4$  [8],  $\text{Ca(OH)}_2$  [10–13],  $\text{CaAl}_2\text{Si}_2\text{O}_8$  (anorthite) [9] and  $\text{Fe}_2\text{SiO}_4$  (fayalite) [9]. In most of these materials pressure-induced amorphization is irreversible, but in some cases reversibility could also be observed, such as in  $\text{SnI}_4$ ,  $\text{AlPO}_4$ ,  $\text{LiKSO}_4$ ,  $\text{Ca(OH)}_2$ .

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