Unusual pressure-induced phase behavior in crystalline poly-4-methyl-pentene-1

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Unusual Pressure-Induced Phase Behavior in Crystalline Poly-4-methyl-pentene-1

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SYNOPSIS

We report some highly unusual phase behavior, of general implication for condensed matter, on the polymer poly(4-methyl-pentene-1) (P4MP1) induced by changes in pressure and temperature, as observed in situ by x-ray diffraction. Upon increasing pressure beyond a threshold, the polymer, crystalline under ambient conditions, loses its crystalline order isothermally, passing through a continuously varying sequence of mesomorphic states, the process being reversible. This behavior is observed in two widely separated temperature regions, suggesting, for the first time in a single component system, the possibility of reentrant liquid-crystal and amorphous phases. At the upper temperature region (ca. 250°C) there is a consecutive increase and decrease of melting point with pressure. In the lower temperature region (room temperature) the pressure converts the crystal into an amorphous-like glass obviating the need for going through the melt first, and this in a reversible manner. The latter pressure-induced disordered phase converts into crystal on raising the temperature, and reverts to the glassy, disordered phase on lowering the temperature. Some aspects of this behavior have been found quite recently in water-ice and silica but the process of "melting on cooling" has no precedent in any known system. Other unexpected findings include a new pressure-induced modification of P4MP1 with a one-way only entry with temperature, but full reversibility with pressure leading to a triple point in the PT phase diagram. The above highly uncommon results are putting several prevailing preconceptions to test which are being scrutinized. In the course of it some early expectations on general phase behavior, allowing among others for reentrant phases in one component systems, are being invoked as potentially appropriate for certain polymeric systems, if not for condensed matter in general. © 1993 John Wiley & Sons, Inc.

Keywords: poly-4-methyl-pentene-1 • PT phase diagram • amorphization under pressure • disordering on cooling • thermodynamic anomalies

INTRODUCTION

The purpose of this communication, following a preliminary announcement¹ is to report some highly unusual observations on the polymer poly(4-methyl-pentene-1) (P4MP1); specifically, phase transitions induced by changes in pressure and temperature, representing an uncommon class of phase behavior.

Undoubtedly the totality of the unusual effects, as here reported, pertain only to P4MP1, or possibly to such other polymers which have similarly loosely

packed crystal structures (see below). Nevertheless some of the new findings encountered should extend to a much wider range of polymers, and to materials beyond the confines of polymer science. In particular, the issues arising lead back to basic questions in thermodynamics, such as had been raised at the turn of the century: among others, the present paper should serve for their revitalization. In addition, some of our new findings on P4MP1 have parallels in recent works on such inorganic substances as water, silicates, phosphates, and others, thus providing a welcome convergence of hitherto separate inquiries all, so we believe, of potential relevance to the wider subject of phase transitions in condensed matter. Finally, a common ground with some aspects of organization in colloids, is also indicated.

In addition to features pertaining specifically to

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P4MP1, the general issues to be touched upon are as follows: (1) Amorphization of crystalline materials by pressure; (2) phase transformations into and from the glassy state; (3) continuity between amorphous and liquid crystalline phases; (4) reentrant melt (or disordered) phases in single-component systems where the latter includes the unprecedented effect of reversible disordering on cooling together with the concomitant effect of crystallization on heating; (5) the existence of a crystal phase accessible only through one-way entry, and most significantly, (6) the inversion of the pressure coefficient of the melting point with pressure.

Isotactic P4MP1 can exist in several crystal forms, of which only the most commonly occurring tetragonal is fully explored crystallographically. This arises on straightforward solidification from melts and in most, even if not all, precipitations from solution. Here the chains are 7_2 helices forming a tetragonal lattice of 4 chains per cell.^{2,3} The cell parameters are: $a = b = 18.65 \text{ \AA}$, c (chain direction) = $13.76 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$. The rather unusual fourfold coordination of helices has been attributed to the special intermeshing requirement of the side groups,³ the resulting packing being rather open. The calculated (tetragonal) crystal density (ρ_C) at room temperature (RT) is $\rho_C = 0.813$. This is not only low for a polyolefin but lower than that of the corresponding amorphous material (ρ_A), which, as extrapolated to RT (P4MP1 cannot be obtained completely amorphous at RT), yields $\rho_A = 0.830$. This closeness of densities, and in particular the inverted relationship between ρ_C and ρ_A , will acquire special significance in what follows. Some further factual information: the melting point (T_m) of P4MP1 is 245°C under atmospheric pressure (AP). The uncrystallized component is supposed to have a glass transition (T_g) at around 50°C .

A number of other crystal structures for P4MP1 also feature in the literature.⁴⁻⁶ Their origin is usually unspecified (preceding solvent treatments are mostly involved) being known to varying degrees of detail and accuracy, ranging from fairly full specifications,^{5a,5b} to merely broadest outlines.⁶ They will not concern us further here. In this work we shall refer to a further (hexagonal-provisional assignment) structure further below: this is a new structure and not identical to any of the other structures referred in the literature on P4MP1 crystals (see also later).

EXPERIMENTAL

In the present work we are examining the response of P4MP1 to the combined influence of P and T by

in situ recording of x-ray diffraction patterns at specified P and T .

The material of our investigation was isotactic poly-4 methyl pentene-1 (P4MP1) provided kindly by Professor Bassett (Reading) and Dr. Delmas-Patterson (Montréal). Both samples were of the same origin, namely ICI TPX dating from the 1960s. Based on experience in parallel work on crystallization behavior,⁷ we preferred this material to the current commercially available TPX (Mitsui), as by existing evidence it conforms more closely to the expected behavior of pure homopolymer. Molecular weight, by information provided, is $M_w = 200,000$; $M_w/M_n = 4.7$.

For the present work films were prepared by melt pressing and were then oriented by drawing for reasons to be apparent below.

The pressure apparatus enabling the present work is that of Hikosaka and Seto (see ref. 8). The maximum attainable pressure—in the form set up presently—is 6 kbar, and the temperature can be varied between RT and 300°C . Diamond windows used in the pressure cell enable in situ x-ray diffraction investigation, and this at preselected pressures P and temperatures T , and thus the following of phase behavior either isobarically by varying T , or isothermally by varying P . (It is a special feature of this particular apparatus—not shared by most others used in high pressure studies with polymers—that P can be maintained constant in face of volume changes on phase transformation). For x-ray diffraction work a rotating anode generator was used with a Mo target. The diffraction patterns were recorded as flat-plate photographs. They also contain reflections from diamond serving as windows in the pressure cell; such reflections can provide convenient internal standards for both spacing and intensity. The P4MP1 samples were mostly used in the form of oriented films, which provided more reflection rich, and correspondingly better interpretable patterns than a sample with random orientation. Also, the changes in orientation at the various values of P and T provided noteworthy additional information.

In order to convey what we hold as the main issues we shall adopt a selection in the presentation of the sequence of phase transitions. Each of the sequences was corroborated by repeated runs along the same, or closely similar pathways. We were not aware of time dependant effects, at least on the time scale of our experiments, which was 5–10 h per exposure including adjustment times.

First, we shall choose pathways which involve transformations of the tetragonal solid (crystal)

Figure 1. PT phase diagram of poly(4-methyl-pentene-1), (P4MP1) comprising the fully reversibly realizable and transformable phases: liquid (amorphous), solid (crystal in tetragonal form), and intermediate (liquid crystal), denoted by A, C_t , and LC, respectively. There is continuous gradation between LC and A, hence the two are represented collectively as LC-A corresponding to disordered structures as compared to C_t , and are marked as such in the phase diagram: (The arrow (here as in Fig. 9, and in the appropriate text portions) is meant to indicate passage through this gradation). The reversible transition from LC-A to C_t on raising or lowering T involves passing through a broad regime, drawn shaded in the Fig. 1, which encompasses a further (hexagonal) crystal phase C_h , with partially irreversible characteristics to be taken note of further in the more complete phase diagram of Fig. 9. The Roman numerals denote experimental points documented by x-ray diffraction patterns featured as illustrations in this paper. (The gap in the uppermost C_t -L phase line separates measurement range in refs. 9, 10 at low P , from those in present work at high P .)

phase C_t into liquid (amorphous) A or liquid crystal LC phase,⁹ and vice versa—such transformations all being fully reversible. These pathways, and transitions along them, will serve to make our main points and are expressed in the PT phase diagram of Figure 1. Some experimental points, those corresponding to the x-ray diffraction patterns used here for illustration are indicated (denoted by Roman numerals, for corresponding diffraction patterns see captions of Figs. 3–7). The phase demarcation boundaries are drawn through knowledge gained from such diffraction patterns. In spite of obvious gaps, the existence of the novel effects of our present concern should be apparent.

As the work proceeded the intervention of a second solid (crystal) phase, partly in an irreversible manner, became also apparent. While of undoubted interest, we consider this rather as an overlay on

the primary messages we wish to convey. Thus to simplify the presentation, results and pathways involving this second phase are left to a later section of this paper, the relevant, more complete phase diagram containing them being presented at that stage (Fig. 9).

RESULTS

Reversible Effects Involving the C_t Crystal Phase

Figure 2 is a diffraction pattern from an oriented film of P4MP1 at room temperature (ca. 20°C) and at atmospheric pressure (1 bar). It corresponds to the tetragonal crystal form (C_t). This will be our starting point.

Figure 2. X-ray diffraction pattern of drawn film of P4MP1 at atmospheric pressure (AP) and room temperature (RT). This, as all subsequent diffraction patterns, with the exception of Fig. 8, corresponds to the tetragonal crystal phase C_t . Here, as in subsequent oriented diffraction patterns, the draw direction is vertical.

Pathway 1

This will be the sequence of increasing P at 20°C , Figs. 3a–d, showing the corresponding diffraction patterns. As apparent, the crystal reflections broaden, and become diffuse, those close together merge into liquid-pattern type blobs while others disappear. Clearly, long-range crystal periodicity is lost and the system becomes disordered. The whole sequence is fully reversible with P ; in particular, on reducing P , again close to AP, (point i in Fig. 1)

from whichever maximum value, the starting state in Figure 3a is fully regained. Figure 3e shows an example. Thus, each stage seems to correspond to thermodynamic equilibrium at the stated P and T . We shall indicate the underlying reversibility in our notation by arrows in both direction, in what follows. At the highest P (ca. 6 kbar) accessible to us, we have virtually an oriented amorphous material, and indeed, when using an unoriented sample from the start (Fig. 4a) an essentially crystal to amorphous ($C_t \leftrightarrow A$) transformation is indicated (Fig. 4b). From the higher information content of the fiber samples, preferential retention of a certain amount of order in the packing of chains becomes apparent through the greater distinctness and intensity of the diffraction features along the equator (i.e., perpendicular to the fiber axis). At intermediate pressures this has the characteristics of an oriented nematic (or columnar) state among liquid crystals (LC). Thus we have a transition sequence $C_t \leftrightarrow LC \leftrightarrow A$. Above a certain P the sequence of disordering (or ordering on pressure removal) is a continuous one: beyond a threshold of ca. 2 kbar there is no abrupt change from one distinct state to another. This of course prevents us from defining clear boundaries in the phase diagram such as Figure 1. For presentation purposes we shall take LC and A together as a single disordered phase distinct from crystal solid (C_t) and shall keep referring to LC and A collectively. (The precise boundary between the two would

Figure 3. X-ray diffraction patterns of drawn films of P4MP1 at r.T recorded in situ at the various pressures (Pathway 1 in Fig. 1). (a) 0.24 kbar, (b) 2.24 kbar, (c) 4.56 kbar, (d) 5.36 kbar, (e) 0.24 kbar. (a) to (d) correspond to points (i) to (iv), respectively, in Fig. 1, with (e) to a reversal to point (i). The sharp reflections on the periphery here and in Fig. 4–8 are due to diamond and the rings to a gasket. These, amongst others, serve as useful intensity standards when comparing different members in a sequence.

Figure 4. X-ray diffraction patterns of unoriented films of P4MP1 displaying the effect of pressure along Pathway 1. (a) 0.24 kbar, (b) 5.8 kbar. (point (v) in Fig. 1).

be difficult to define structurally, and in any case will depend on the value of P .)

The above change from order to disorder with increasing pressure is consistent with the anomalous density relation $\rho_C < \rho_A$ referred to above. In this respect P4MP1, (as far as each stage in the continuous range of transformations can be regarded as of first order) appears to fall in the same class as water or bismuth, where pressure causes a decrease (as opposed to the usual increase) in the melting point. However, the presently observed transitions occur about 220°C below the AP 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 T_m (i.e., at around 245–300°C in what follows).

T_m as a function of P has been examined calorimetrically previously up to 2 kbar^{9,10,11} which we shall reiterate (as it leads to temperatures close to 300°C, it was beyond the present capabilities of our own diffraction-based pressure technique). The findings in ref. 9 are included as a solid line in Figure 1. As can be seen, T_m increases with P as in most solids. Even so, the T_m vs. P line shows signs of levelling off with P , suggesting the possibility of a change in sign in the T_m vs. P relation at still higher P , a lead which we proceeded to follow up next.

Pathway 2

Here we chose the elevated T , of 248°C which is below the T_m value at the highest pressures reported in the literature, yet just above T_m at atmospheric P , and examined the effect of increasing P at constant T . We found that we could reach the disordered state (LC' or A' taken collectively, by at-

taching a hyphen we reserve the possibility that the two x-ray-wise identical disordered states, namely those around RT and around the much higher T_m , may be different) at sufficiently high P . This is illustrated by Figure 5 where (a) represents the crystalline (C_t) and (b) a disordered state with disordering setting in continuously beyond a threshold P corresponding to the region of intersection of Pathway 2 with the phase demarcation line. The process is reversible, the C_t state is regained on reducing P (Fig. 5c). Here, in contrast to Pathway 1, passage through the LC' or A' region is accompanied by disorientation, in the course of which the initial fiber orientation is largely lost. (In Fig. 5 some loss of orientation is attributable also to heating up while in the C_t state—compare Fig. 5a with Fig. 2. However, we find that such disorientation while in the C_t state, can be prevented by increasing P first and raising T subsequently, in which case the full disorientation occurring in the cycle becomes attributable to passage through the LC' or A' state alone.)

It follows from the above, and from several other experimental series, that at sufficiently high P , dT_m/dP is negative. Accordingly, the T_m vs. P line should have a maximum at some $P \equiv P'$ value. It follows that we have a situation where for $P < P'$ T_m rises with P , as for most substances, and for $P > P'$ it decreases [similarly to the case of water, in this instance with reference to the true (conventional) T_m]. Connection between the melting curve and disorientation has been explored along this pathway. To quote an example: at 250°C on in-

Figure 5. X-ray diffraction patterns of drawn films (partially disoriented at the higher temperatures) of P4MP1 at ca. 248°C at various pressures (Pathway 2 in Fig. 1) (a) 1 kbar, (b) 6 kbar, (c) ca. 0.74 kbar. (a) and (b) correspond to points (vi) and (vii) respectively in Fig. 1 while (c) is a reversal to point (vi).

Figure 6. X-ray diffraction patterns of P4MP1 films displaying the effect of isobaric cooling to r.T at two different pressures (Pathways 3 in Fig. 1). (a) at 4.4 kbar, at a starting temperature of 200°C. Drawn film. (b) as 6(a) after cooling to RT. (a) and 6(b) correspond to points (ix) and (iii) in Fig. 1.

creasing the pressure from 3.2 to 4.0 Kb orientation is lost. This indicates that at 4.0 Kb we are closer to T_m than at 3.2 Kb. For the same temperature of 250°C, orientation is lost on reducing pressure from 3.0 to 2.0 Kb. Again, we infer that we are closer to the melting point at 2.0 Kb, compared with 3.0 Kb, which thus seems to be close to the maximum T_m attainable by application of pressure.

Pathway 3

This pathway, leads to possibly the most remarkable of effects. It consisted of pursuing a pathway such as 2 but without increasing P so far as to melt the sample (i.e., stopping short of the C_t - A' demarcation line in Fig. 1). Here at elevated T and P , while still in the C_t phase, T was lowered to RT isobarically. In such a case, the sample, highly crystalline at the elevated temperature, *loses* order (i.e., changes toward the LC, or A states on *cooling*). The extent of the disordering depends on the value of P : the same decrease in T leads to a more pronounced disorganization for higher P . Figures 6 and 7, show the effect on cooling for two P values. As can be seen, the disordered phase falls into the sequence Figure 3a-d established previously with increasing P at RT (i.e., along Pathway 1). The effect can again be regarded as reversible insofar as the initial crystal state (C_t) at high T is reattained on heating at the same P . However, this thermal cycle producing reversible disordering on cooling and crystallization (in the tetragonal phase) on heating cannot be carried out without the intervention of a further, different crystal phase to be addressed below. Nevertheless, when

focusing on the end states alone, the conditions represented in Figure 1 regarding reversible disordering on cooling and ordering on heating remain upheld.

A further, Pressure-Induced, Crystal Structure

By the experimental evidence quoted so far, from Pathways 1 and 2 we would expect disorder (LC and/or A) in two widely separated temperature regions, one at around 200–250°C, the other at ca. 20°C; in case of a continuous connection between the two regions, this would represent a reentrant disordered phase in terms of T . The existence of such a phase region continuity, however, could not be established, owing to the intervention of a new crystal phase C_h (h stands for hexagonal), to which we now turn.

The x-ray fiber diffraction pattern of the new crystal phase is shown by Figure 8. The cell parameters determined therefrom at RT and AP are: $a = b = 16.88\text{\AA}$, $c = 6.31\text{\AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 60^\circ$. Thus the structure should be hexagonal with the c period consistent with chains in the form of 3_1 helices. The crystal density of this C_h phase is 0.826 which is larger than that of the loosely packed C_t phase, in fact only slightly lower than the amorphous density extrapolated to RT (in view of the latitude in the extrapolation, the two densities can be taken as equal). The reflections and corresponding planes indexed on the basis of the above cell are shown in Table I.

The above C_h phase is different from a previously reported uncommon crystal form, unspecified in terms of full unit cell and symmetry, obtained after treatment at high pressure and elevated temperature.⁶ The fiber period of 6.5Å

Figure 7. See Fig. 6. (a) at 5 kbar at a starting temperature of 220°C. Unoriented film. (b) as 7(a) after cooling to RT. (a) and 7(b) correspond to points (xi) and (x) in Fig. 1.

Figure 8. X-ray diffraction pattern of drawn P4MP1 film in the newly found (hexagonal) crystal phase C_h . It was attained by following Pathway 1 to point (viii) followed by heating.

quoted is consistent with a 3_1 helix but the other reflections in the pattern, while not commented on in ref. 6, are visibly different from ours. A further different crystal pattern, identified as hexagonal, has been noted in solution grown single crystals.⁵ But here also the unit cell with $a = b = 22.17\text{\AA}$ and $c = 6.69\text{\AA}$ is significantly different from our C_h structure.

Our pressure-induced new C_h phase could be obtained along two routes corresponding to two fundamentally different processes: (1) irreversibly (one-way entry) from disordered LC or A phase, by raising T at elevated P , and (2) reversibly from C_t by raising P within an appropriate (elevated) T range. In what follows we describe these two routes with illustrations.

Route 1

As demonstrated earlier in Figure 3, when crystals in the tetragonal phase (point o in Fig. 9) are compressed above a certain threshold value, they transform into the disordered LC or A phase (point a in Figure 9) without any loss of orientation. On raising T at fixed pressure from point a to b in Figure 9, the disordered LC or A phase (at RT) undergoes a phase transition into the crystalline hexagonal phase C_h without any loss of orientation. On further raising the temperature at the same pressure (point b to c in Figure 9), we have a solid (C_h) to solid (C_t) transition. Points b and c in Figure 9 refer to Figure 10 α and 10 β , respectively. Thus we have crystallization on heating in two successive stages, namely into C_h and C_t .

In the above quoted case of Figure 10 α there is no loss in orientation, nevertheless at the lower $P = 0.78\text{ Kb}$ for the

same temperature, orientation may be effected as in Figure 5a. In general, higher temperature is detrimental to retention of orientation, while for a given T higher P favors orientation retention in the P range up to P' and has the opposite effect for $P > P'$.

The tetragonal crystal phase C_t at point c in Figure 9, transforms into the disordered phase on cooling (independent of cooling rate) without passing through the C_h phase. Crystallization on heating and disordering on cooling of C_t crystals, along Pathways 3 in Figure 1, has already been demonstrated in Figures 6 and 7. It follows that the process LC (or A) $\leftrightarrow C_t$ is reversible with T , while C_h is reached only by heating from LC (or A), but not by cooling from C_t , suggesting an unusual one-way entry into the C_h phase. However, C_h is retained, and this without any loss or change in orientation, on passing from b to a, and also further from a to O in Figure 9 (i.e., C_h can be preserved at RT and AP by following this route).¹²

Unlike the C_t phase, the C_h phase does not pass through a phase transformation in response to pressure (within our experimental limits) at RT, whereas on heating, either at atmospheric or elevated pressures, a $C_h \rightarrow C_t$ transition takes place. At AP the temperature for $C_h \rightarrow C_t$ transformation ($T_{h \rightarrow t}$) was identified as 120°C . This being irreversible (namely there is no reversion to C_h on cooling) indicates that the C_h phase is metastable with re-

Table I. X-Ray Diffraction Data on the New (C_h) Crystal Modification

Measured Lattice Spacing ($\text{\AA}$)	Proposed Index	Calculated Lattice Spacing ($\text{\AA}$)	Measured Intensity
14.60	(100)	14.62	mw
8.44	(110)	8.44	ms
7.39	(200)	7.31	s
5.13	(hk0)	unknown	w
4.99	(111)	5.05	s
4.85	(300)	4.87	m
4.75	(201)	4.78	m
4.19	(220)	4.22	mw
4.13	(211)	4.15	mw
3.68	(400)	3.65	w
3.15	(022)	3.16	m
2.07	(103)	2.08	w

Spacings as measured from observable reflections and as calculated for a hexagonal unit cell. $a = b = 16.88\text{\AA}$, $c = 6.30\text{\AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 60^\circ$ together with corresponding intensities. (Reflections corresponding to $9.34\text{\AA}$ and $4.28\text{\AA}$ could also be seen with variable intensities. These we attribute to remnants of the C_t structure and are omitted from the table.)

Figure 9. PT phase diagram as in Fig. 1 including also the new (hexagonal (C_h)) crystal phase and triple point Q. Here the C_h state occupies the same zone which is shown heavily shaded in Fig. 1. There is a fundamental difference as to whether this C_h zone is entered (i) isobarically (by varying T), in which case the entry is only one-way by heating, or (ii) isothermally (by varying P) when the transformation is fully reversible. The lightly shaded area denotes the region where C_h can still exist but is metastable with respect to both P and T .

spect to C_t . This region of metastability (as distinct from the region of one-way entry from the disordered phase) is indicated by light shading in Figure 9. DSC scans passing through ($T_{h \rightarrow t}$) showed that the $C_h \rightarrow C_t$ transition is slightly endothermic.

Figure 10. In situ x-ray diffraction patterns showing irreversible $C_h \rightarrow C_t$ transition on raising temperature range 100–250°C at fixed pressure 3.7 Kb. (α) C_h phase, obtained on raising temperature from a to b. (β) C_t phase, found on raising temperature further, from b to c. a, b, c are care points shown in Fig. 9.

Route 2

In what follows, another route of obtaining the C_h phase is described. At a fixed T' , where $T_{h \rightarrow t} < T' < T_m$ (e.g., point d in Fig. 9), on increasing P sufficiently so as to reach the dark shaded region of the C_h phase in Figure 9 (e.g., d to e in Fig. 9), a solid (C_t) to solid (C_h) phase transition occurs. On releasing the pressure at the same temperature, C_h transforms back into the C_t phase. X-ray patterns are shown in Figure 11 and refer to points d and e, respectively. For the temperature and pressure chosen in the present case, no loss in orientation is observed during this reversible $C_h \leftrightarrow C_t$ transition.

Further similar experiments, namely entering the C_h region isothermally by increasing P , have been performed also at several different temperatures: specifically at $T = 190^\circ\text{C}$, $T = 200^\circ\text{C}$, and $T = 215^\circ\text{C}$, identifying C_h regions at $P = 4.2$ Kb, $P = 5.5$ Kb, and $P = 5.8$ Kb, respectively. This served to provide a broad mapping of the $C_t \rightarrow C_h$ transition region (as along routes such as here denoted as 2, i.e., by varying P) showing that this transition has a positive slope in the PT diagram. Accordingly, this crystal-crystal transition is reversible with P (for

Figure 11. In situ x-ray diffraction showing reversible $C_t \rightarrow C_h$ transition, with increasing pressure, from 0.2–6.0 kb, at the fixed temperature, 185°C. (α) C_t phase, at point d and (β) C_h phase, obtained on raising pressure from d to e; d and e are points shown in Fig. 9.

fixed T but not with T (at fixed P). It follows, among others, that we can obtain C_h at RT and AP along two different pathways. These are (1) (quoted previously). $o \rightarrow a \rightarrow b \rightarrow a \rightarrow o$ and (2) $d \rightarrow e \rightarrow f \rightarrow o$ both referring to Figure 9. C_h has been obtained along both of these pathways in the present work.

The Existence of a Triple Point

By the foregoing results we know that above 3.0 Kbar, T_m of the tetragonal crystal phase decreases with P while the temperature for the $C_h - C_t$ transition (reversible with P but not with T) rises with P throughout. This should lead to an intersection of the $C_h - C_t$ with the $C_t - LC'$ or A' line at a particular P (P_{tr}) and T (T_{tr}) defining a triple point Q in the PT phase diagram of P4MP1.

It follows from the designation of the triple point that the C_t phase cannot exist for P beyond P_{tr} . More specifically, for $P > P_{tr}$, raising T should lead into the LC' or A' phase, and lowering T to crystallization directly into the C_h phase. While the confirmation of the first effect was at the limit of our experimental capability, we could verify the second, namely direct crystallization into C_h . This is illustrated by Figure 12 which shows that on cooling to 180°C at the fixed P of 6.0 Kbar the disordered LC' or A' phase (Fig. 12, α) crystallizes directly into the C_h phase (Fig. 12, β) without passing into the C_t phase, as happens for $P < P_{tr}$. Figure 12, γ shows $C_h \leftrightarrow C_t$ transition on the release of P at fixed T .

Through the above experiment (Fig. 12) the existence of the triple point has thus been verified. Further experiments located it as lying between 5.5 and 6.0 Kbar at approximately 200°C.

DISCUSSION

The Specific Issues

Disordering with increase in pressure is contrary to the behavior of most materials. The best and longest known exceptions are those with inverted densities (i.e., where $\rho_C < \rho_A$) such as water-ice (near 0°C and at AP), Bi and a few others, where T_m decreases with P , for all $P > 0$. In addition, as has been revealed by recent researches, there are a number of compounds where normally $\rho_C > \rho_A$, which become “amorphized” on application of pressure beyond a certain, usually substantial threshold P (several to 100-s Kbars) at temperatures which can extend substantially below the atmospheric melting temperature. Such are SiO_2 (quartz),¹³ $AlPO_4$,^{14–16} SnI_4 , $LiKSO_4$, $Ca(OH)_2$,¹⁷ $CaAl_2Si_2O_8$ (anorthite), and Fe_2SiO_4 (fayalite),¹⁸ and even elements such as Ba, Se, Te, and C. While most of the changes in this latter class of materials were found to be irreversible, in some cases reversibility could also be observed [SnI_4 , $AlPO_4$, $LiKSO_4$, $Ca(OH)_2$], where in the case of $AlPO_4$ also the initial crystal orientation was regained¹⁶ (memory glass).

In the P4MP1 polymer we have both of the above class of effects, namely that where $\rho_C < \rho_A$, and where (at least initially) $\rho_C > \rho_A$, at two widely separated temperature ranges: one at ca. 20°C, the other in the region of conventional melting, namely at 200–250°C. As at ca. 20°C $\rho_C < \rho_A$, for this lower temperature of amorphization the preconditions seem similar to those for ordinary melting of ice,

Figure 12. In situ x-ray diffraction patterns illustrating the existence of a triple point in the P - T phase diagram, Fig. 9, and $C_h \rightarrow C_t$ transition on releasing the pressure from 6.0 k–1.5 kb at the fixed temperature 160°C. (α) shows (LC' (or A') phase at 6.0 kb, 248°C, (β) C_h , obtained on cooling from 248°C to 160°C, at the same $P = 6$ kb, (γ) C_t after releasing the pressure, from 6.0–1.5 kb, at 160°C.

the phase transitions in both systems being reversible. However, at this point the similarity ends. Namely, with P4MP1, amorphization sets in only beyond a certain threshold pressure ($P \approx 2$ Kbar) and the disordered state is expected to be a glass. The second, high temperature region of transformation bears a closer resemblance to conventional melting, hence the "amorphized" material here is expected to be closer to what is conventionally considered as a liquid. However, it is known that in this region at AP, for P4MP1, $\rho_C > \rho_A$; i.e., that the densities invert on heating from RT up to the melting point. In terms of this inversion of density with the application of pressure, this second, high-temperature region of amorphization is therefore a closer analog to effects recently observed in the class of simple materials such as SiO_2 , AlPO_4 , etc. mentioned above. Again, the effect in P4MP1 is fully reversible.

Taking the effect at high T (200–250°C) first, we recall that here T_m first rises with P , reaching a maximum at P' , then decreases on further increase in P . This is readily explicable 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 $\rho_C < \rho_A$. It follows from the Clausius–Clapeyron relation

$$\frac{dT_m}{dP} = \frac{T\Delta V}{\Delta H}$$

(ΔV = change in volume, ΔH = change in heat content) that as long as $\rho_C > \rho_A$, $dT_m/dP > 0$, i.e., T_m will rise with P . When ρ_A exceeds ρ_C we have $\rho_C < \rho_A$, hence, $dT_m/dP < 0$ with T_m falling with P . This should account for the shape of the T_m vs. P curve such as that drawn schematically in Figure 13a. It follows that at a given T below T_m at AP (i.e., in the solid, crystal state) isothermal application of pressure should lead to a disordered phase (liquid along route (1), amorphous along route (2)), as denoted in Fig. 13a) when intersecting the downward sloping branch of the T_m vs. P curve (Fig. 13a). This clearly accounts for "amorphization" in our high-temperature range (Fig. 5). The same explanation already has been suggested for the "amorphization" of silica.¹³ In that case the temperature of the experiment was 27°C [i.e., very much below

Figure 13. (a) Explanation of liquification-amorphization by pressure in terms of PT phase diagrams. "Normal" solid with $\rho_C > \rho_A$ at atmospheric pressure. In view of higher compressibility of the liquid/amorphous phase, as compared to the crystal, dT_m/dP could become negative beyond a certain $P(P')$, where T_m would pass through a maximum. The liquid/amorphous state could then be achieved isothermally by applying pressure to the solid. Two routes are indicated: (1) above T_g leading to a disordered phase which is a liquid, and (2) below T_g , where it leads to amorphous material of solid consistency ("amorphous solid" "or glass"). Anticipated rise of T_g with P , not indicated by the diagram, would also raise the demarcation temperature between "liquification" (1) and "amorphization" (2). (b) The same construction as in (a), but for a system where $\rho_C < \rho_A$ at atmospheric pressure (e.g., water), thus without a positive section of the T_m vs. P curve. Here, (as also for Fig. 13a) the T_m vs. P curve need not be that for the lowest free energy throughout the whole PT range indicated: namely other stable crystal phases may intervene. In the latter case the curve shown here will be an extrapolation of the phase line corresponding to the stable state near atmospheric pressures. (e.g. for ordinary ice which melts at 0°C).

the conventional melting zone (ca. 3000°C)] hence, by the above argumentation (Fig. 13a) requiring very high P for the above mentioned intersecting of the downwards branch of the T_m vs. P line; in fact 250 kbar was found experimentally. There, in contrast to our P4MP1, the T_m vs. P curve is unknown and the turning over from a positive to negative slope with P is merely postulated. Independently, the same explanation has been proposed for the recently studied behavior of water-ice systems at -196°C where amorphization of hexagonal ice was reported at P ca. 10 Kbar.^{18,19} This differs from our P4MP1 case (and from the proposed explanation for SiO_2) only insofar that with water-ice $dT_m/dP < 0$ throughout as from 1 bar (ice melts under pressure anyway) and the T_m vs. P curve (always with negative slope) is being extrapolated through various ice modifications down to -196°C , where it is intersected along an isothermal pathway with increasing P to produce the amorphization of hexagonal ice (Fig. 13b). It is to be noted that the amorphizations of both SiO_2 and ice (at -196°C) are irreversible, in contrast to the reversibility in our P4MP1.

In the above respect (i.e., change in sign of dT_m/dP with P), we are dealing with a fundamental behavior pattern of matter in broadest generality, for which P4MP1 now provides a conclusive example. Preliminary experiment indicates the beginnings of the same effect with isotactic polystyrene at the upper P limit of our experimentation. The case of SiO_2 , and water-ice, together with other materials quoted above, demonstrates that the validity of this argumentation extends beyond polymers, possibly to all materials. In fact this had been foreseen by Tammann, together with much else, as a thermodynamic necessity as early as 1903 (see further below).^{20,21}

The amorphization of P4MP1 in the lower temperature range, RT, falls in a different category. In view of $\rho_C < \rho_A$ at RT *ab initio*, the above argumentation (based on inversion of densities with P) is both unnecessary and inappropriate. In any event, the onset of amorphization occurs at much too low P for it to be attributable to intersecting the negative branch of the T_m vs. P line as extrapolated to 20°C on the basis of Figure 13a. The disordered phase must therefore be reentrant in terms of T with the possibly surprising consequence that at a sufficiently high P it should be obtainable on *lowering* of T . As is apparent from our experiment, this striking effect has in fact been observed (Figs. 6, 7).

At this point one may enquire about the continuity between the two disordered phase regions observed at high and low temperatures (as in Fig. 9).

In our case, passing from one region to the other in a continuous manner (i.e., circumnavigating the intruding crystal region) however, is frustrated by the intervention of an additional crystal phase, the C_h phase in Figure 9 as described in the Experimental section. Under these conditions the thermodynamic identity or otherwise of the two classes of disordered phase (LC and LC' in its various gradations, A and A') remains unverifiable. The observed reversibility itself strongly points to the fact that equilibrium conditions pertain, even if recognizing that this need not be an absolute criterion.²²

In addition to the unusual, if not extraordinary effect of reversible disordering on cooling, together with the associated ordering on heating, some further unusual effects need highlighting. Such is the broad nature of the transition which comprises the new intervening crystal phase (C_h), accessible by one-way entry only with T , but reversibly with P . We shall return to some fundamental implications below. Here we merely read off the straightforward message of the experiment, that C_i cannot transform to any other crystalline state, it can only disorder, while C_h rather transforms to a crystalline state than disorders. Further, C_h only forms from the disordered state when under pressure; intriguingly by heating only when $P < P_{tr}$, but both by cooling and heating when $P > P_{tr}$ (the latter, i.e., by heating, while self-evident, still requires verification).

Other unusual effects, which will be listed without any attempt at explanation, include the continuity between decreasing stages of order from what, by diffraction criteria, could be classified as liquid crystal (LC) to completely random [amorphous, (A)], following the first sudden loss of crystalline order at some threshold pressure. This continuous gradation of change in order with P within the combined LC and A (and LC' and A') regimes has to our knowledge no counterpart in other kind of condensed matter. As at each stage *all* material seems to be involved the unavoidable inhomogeneity of molecular lengths is unlikely to provide an explanation. Consequently, the gradual nature of the changes has to be regarded as a genuine property of matter.

Further, there is the issue of changes involving the glassy state. These are of two kinds: transformation of crystals into the glassy state, and transformations from the glassy state into crystals, the latter arising where the crystal to liquid (or liquid crystal) transformation is reversible below what by normal expectation should be the glass transition. Authors of the papers on SiO_2 and on water-ice consider the amorphization observed by them below T_g

as unprecedented and of far reaching implications. The same applies to the low-temperature transformation in our polymer, to which we now give the same emphasis. Our case, however, is even more unusual because, while in ice and silicates the transformation was found irreversible, (the material stayed glassy amorphous on removal of P) in our case there was complete reversibility (Fig. 3e). If the question of how phase transformation can take place into the glassy state appears puzzling, then reversal into the crystalline state from the glass (if indeed the material with a certain amount of LC characteristics is a glass at these high P -s) is even more so!²²

However, there is a wider issue overlying it all: namely, what is the relation of the particular states in question to the PT phase diagram of the corresponding materials? Specifically, are the observed states, and transformations to and from these states interpretable through equilibrium phase diagrams? By addressing these issues we do not wish to imply that the states in question, as we are observing them, have actually attained their state of maximum stability, hence are in ultimate equilibrium; we merely wish to make sure that by considering them as such we would remain within the validity of the basic laws. It is to these wider fundamental questions, arising from the present results, that we turn in what follows.

General Considerations

In the above connection the central point to consider is the feasibility of disordering (and even melting) on cooling as a thermodynamically definable process and the consequent reality of reentrant disordered phases in PT phase diagrams of *single* component system. Issues relating to the glassy state then follow as sequels.

Disordering on cooling implies crystal with entropy higher than that of the disordered state (amorphous or melt) of the same substance. This at first sight may seem to violate the deeply ingrained notion that the higher degree of order implicit in a crystal necessarily implies lower entropy. In what follows we shall attempt to dispel such notions. For this, first we shall refer to actual systems known from experience in a different field of specialization (colloids) to be followed by reinvoking some long standing, but largely bypassed, basic early considerations on phase relations.

First it needs recalling that order, as defined by geometry, need not be synonymous with order as defined by thermodynamics, (or rather by the un-

derlying statistical mechanics). For this there are well documented and theoretically well founded examples, and precedents. Such are, e.g., regular lattices of spherical colloidal lattices where the entropy of the crystal is higher than that of the corresponding disordered arrangement of the particles at the same concentration.²⁴ This situation is due to the increase in correlational possibilities within the lattice which more than compensates for the loss of configurational freedom associated with the fixing of the centers of gravity of the particles to geometrically defined lattice sites. In view of the fact that no heat effect is involved ($\Delta H = 0$, "hard sphere" approximation) here this increase in entropy is in fact the driving force for "crystallization." Also, the well known case of self alignment of rigid rods is basically a similar entropy driven ordering of elongated bodies, in this case from the isotropic to the nematic state.²⁵

For polymers with loosely packed crystal structures, as compared to their denser, configurationally hindered melts or glasses, the above possibility (i.e., higher overall entropy in the geometrically more ordered phase) may pertain, a situation which may arise at sufficient pressure when $P > P'$ at least deserve consideration. Of course in contrast to ideal hard bodies, in the case of molecular ordering heat effects will never be negligible, and competition between ΔH and ΔS will always pertain ($H \equiv$ enthalpy, $S \equiv$ entropy). However, in principle there can be an inversion of sign not only for ΔS (argued above), but also for ΔH when passing from one phase to another which would create a situation such as that currently observed with our polymer.

It is this situation which was foreseen by Tamman in his generalized treatment of phase diagrams.^{20,21} As the source books may not be readily accessible the essentials will here be reiterated. The basic underlying motivation (as expressed in the conclusion of ref. 20) was the realization that there can be no critical point for a system of crystal-liquid. This means that if we could follow a phase line in the PT phase diagram to arbitrarily high T and P , such a line would either have to go on to infinity, or alternatively, would have to curve back on itself. It is this latter alternative considered by Tamman, but to our knowledge not taken note of since, which would give rise to reentrant phases, even in a single component system, irrespective of whether such a stage is accessible to us in practice. Specifically, such turning over (i.e., maxima in terms of T or P in the phase lines) can be quantitatively located through what Tamman terms, "neutral lines" to be briefly outlined.

Figure 14. Stages in the Tamman construction of a "full" PT phase diagram through utilization of "neutral lines." (a) Volume (V) vs. pressure for liquid (V') and crystal (V'') as an example of a scalar property that may cross over for the two states. (b) The "neutral line" for V ($\Delta V = 0$) and its intersection with the phase line (S-S, see text) in the PT plane. (c) The "neutral line" for heat content (R), where $\Delta R = 0$ (Tamman's notation) and its intersection with the phase line (S-S). (d) A crystal-liquid/amorphous phase diagram derivable through (b) and (c) which in the absence of other phases intervening, would be a closed loop enclosing the crystalline state. (e) A situation similar to (d) but with vapor-liquid phase line intersecting the liquid-crystal phase line with a continuous pathway between liquid and (equilibrium) "amorphous solid" indicated by dashed line (see text). From Tamman and Mehl²¹ based on the German original by Tamman.²⁰ (Some retouching of curves and lettering by present authors).

Following Tamman, take volume (V) and consider it as functions of P and T . In view of the higher compressibility and thermal expansion of the liquid compared to the crystal the V vs. P . and V vs. T curves will cross (irrespective of whether this is achievable in practice in terms of facilities or time scale). Figure 14a, depicts this situation for V vs. P . When plotting V vertically with respect to the plane of the paper, we have two VPT surfaces, one for liquid and one for crystal which intersect along a line where V for liquid and crystal are equal, hence in a phase transformation $\Delta V = 0$. Projection of this line on the PT plane is a "neutral line" for V ($\Delta V = 0$ in Fig. 14b). The point of intersection of this "neutral line" with the crystal-liquid phase line (S-S in Fig. 14b) corresponds to a maximum in the T_m vs. P curve (i.e., to the P where dT_m/dP changes sign). The relevance of this representation to our own experimental material will by now be self-evident (compare with Figs. 1 and 9).

Tamman then proceeds to construct a similar neutral line for the change in heat content on phase transformation. (R in his notation), leading, by an argument analogous to the one above, to a neutral line with an ensuing maximum of the phase line S-S in terms of P (i.e., to a point where $dT_m/dP = \infty$ (Fig. 14c). Asserting a theorem that for crystal and liquid, neutral lines for different properties cannot coincide then, if at least two such neutral lines exist, a reentry in phase lines must follow. Thus, if no other phase intervenes, the phase line will meet up with itself forming a closed loop (Fig. 14d) or meet one of the coordinates (i.e., at $P = 0$ or $T = 0$). Or alternately, it will join up with other phase lines (e.g., vapor-liquid as represented by Figure 14e). It will be apparent that at least the fully reversible features of our own system are embodied by this general scheme. Thus by Tamman's thermodynamic argument (which we see no ground to question) our present findings are consistent with expectations from general phase behavior of matter, even if some features may, by past experience, appear highly uncommon or even unprecedented.

Tamman denotes the disordered phase at high temperature as "liquid" and that at low temperature as "amorphous solid" (Fig. 14e). This distinction is not based on thermodynamics, but merely on consistency. By present language "amorphous solid" would signify "glass". It is then a further matter that in current usage the term "glass" is being associated with a nonequilibrium state. It is essential to realise that from the thermodynamic point of view this need not be necessarily so. In principle at least a glass could approach equilibrium, satisfying the Tamman criterion of an equilibrium "amorphous solid", (which of

course by the criterion of consistency will be a glass *a fortiori*). Whether in an actual situation the glass is in true equilibrium or still somewhat above it, will not affect the principle of this type of phase construction, merely the quantitative location of the phase line itself, a point of only secondary concern to us at this stage of broad-brush mapping of uncommon phase behavior. Even so, we recognize the possibly profound implications of the above considerations for ongoing thoughts and related terminology in the study of glasses and for such conceptual issues as e.g. the Kauzmann paradox.

Tamman himself was well aware of the fact that most of the situations embodied by his generalized phase diagrams were beyond the experience of his day. He attributed this to conditions not realizable at the time. Taking known thermodynamic parameters, and their variation with P and T for specific substances, he carried out extrapolations, to P and T ranges beyond what was accessible at the time, thus constructing "full" phase diagrams, utilizing amongst others the conception of "neutral lines". For example, for benzophenone he obtains a flat-based reentrant loop truncated by both the T and P coordinates, that is with flat bases of $P = 0$ and $T = 0$, respectively.²⁰ (It would be interesting to follow up how far such predictions have stood the test of time!). Tamman knew that realization of the "full" phase diagrams would, in most cases, require conditions which are extreme in terms of P and T .²⁶ This point has been taken up later by Vogel (p. 49 of ref. 29) expecting such extreme conditions to be pertinent in outer space and within the earth interior where thus the Tamman considerations would be expected to apply. References to geological and extra terrestrial relevance were also made in the recent works on water-ice^{18,19} and silica,¹¹ without, however, any apparent awareness of the long standing Tamman precedent. It now appears that in view of the new findings on a polymer such, so far geological and extraterrestrial, conditions may have become accessible closer to laboratory circumstances.

CONCLUSIONS

The PT phase diagram of poly-4-methyl-pentene-1 displays a wealth of unusual effects. Some of these are undoubtedly specific to this polymer in which the density of the crystal is lower than that of the amorphous solid (as extrapolated to room temperature), but others are likely to reflect more general behavior of matter even beyond the confines of

polymers. The latter include the inversion of sign in the Clausius-Clapeyron equation with pressure; phase transitions involving the glassy state, including cases of reversibility; and, above all, disordering (formation of liquid crystal and amorphous states) on cooling indicative, among other things, of the existence of reentrant disordered phases with temperature. Search for thermodynamic justification of such effects (which imply, among others, crystal entropy which exceeds that of the liquid) leads to precedents and parallels in the self organization of colloidal hard bodies and to the revisiting of some basic considerations about phase diagrams in the early literature that has now fallen into oblivion. Revitalization of the latter, as prompted by the present, highly definitive experimental material may well open up new perspectives in the phase behavior of condensed matter in general with polymers as test materials particularly suited for this purpose. The new findings and the approach they generate may have practical outlets insofar as they point to states of materials not accessible previously, and to processes for bringing them into being, with properties which are unforeseeable at present. As far as the polymer field is concerned, the new findings on P4MP1 call for extension of such work to other polymers, and to the possible design of new polymers, such as would or could respond in a positive way to the presently developed experimentation. Returning from the general to the specific, the present findings provide much new information about P4MP1 itself, both of interest in its own right, and calling for renewed attention to this particular polymeric substance.

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REFERENCES AND NOTES

1. S. Rastogi, M. Newman, and A. Keller, *Nature*, **353**, 55 (1991).

2. G. Natta, P. Corradini, and I. W. Bassi, *R. C. Acad. Lincei*, **19**, 404 (1955).
3. F. C. Frank, A. Keller, and A. O'Connor, *Phil. Mag.*, **4**, 200 (1959).
4. M. Takayanagi and N. Kawasaki, *J. Macromol. Sci. Phys.*, **B4**, 741 (1967).
5. (a) G. Charlet and G. Delmas, *Polymer*, **25**, 1619 (1984); *Ibid* 1613. (b) G. Charlet and G. Delmas, *Polymer*, **25**, 1613 (1984).
6. R. Hasegawa, Y. Tanabe, M. Kobayashi, H. Tadokoro, A. Sowoka, and N. Kawai, *J. Polym. Sci.*, **8**, 1073 (1970).
7. M. Newman, Ph.D. thesis, Bristol University, to be submitted.
8. M. Hikosaka and T. Seto, *Jpn. J. Appl. Phys.*, **21**, L332-L334 (1982).
9. The designation of LC is based on the nature of the diffraction pattern alone, in as far as it does not display the full three-dimensional positional correlation appropriate to crystal proper.
10. P. C. Jain, B. Wunderlich, and D. R. Chaubey, *J. Polym. Sci. Polym. Phys. Ed.*, **15**, 2271-2275 (1977).
11. P. Zoller, H. W. Starkweather Jr., and G. A. Jones, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 1451-1458 (1986).
12. Hasegawa et al.⁶ have also obtained their new phase of unspecified symmetry, having a similar *c* spacing to our *C_h* phase, along this route by raising pressure to 4.5 Kb at 220°C. Since their x-ray work was confined to RT and AP only changes which are irreversible with *T* and *P* could have been detected. However, as stated earlier, their new phase of largely unspecified crystal structure is not identical to our *C_h* phase.
13. R. J. Hemley, A. P. Jephcoat, H. K. Mao, L. C. Ming, and M. H. Manghnani, *Nature*, **334**, 52-54 (1988).
14. A. Jayaraman, D. L. Wood, and R. G. Maines, *Phys. Rev.*, **B35**, 8316-8321 (1987).
15. Q. Williams and R. Jeanloz, *Science*, **239**, 902-905 (1988).
16. M. B. Kruger and R. Jeanloz, *Science*, **249**, 647-649 (1990).
17. Y. Fujii, M. Kowaka, and A. Onodera, *J. Phys. C.*, **18**, 789-797 (1985); S. Sugai, *ibid*, 799-808 (1985); F. E. A. Melo, V. E. Lemos, F. Cerdeira, J. Mendes Filho, *J. Phys. Rev.*, **B35**, 3633-3636 (1987); H. Sankaran, S. K. Sikka, S. M. Sharma, R. Chidambaram, *Ibid*, **B38**, 170-173 (1988).
18. O. Mishima, L. D. Calvert, and E. Whalley, *Nature*, **310**, 393-395 (1984); *Nature*, **314**, 76-78 (1985).
19. R. J. Hemley, L. C. Chen, and H. K. Mao, *Nature*, **338**, 638-640 (1989).
20. G. Tamman, *Kristallisieren und Schmelzen*, Verlag Johann Ambrosius Barth, Leipzig, 1903.
21. G. Tamman and R. F. Mehl, *The States of Aggregation*, Van Nostrand Co., New York, 1925.
22. Retention of orientation may seem to mitigate against true equilibrium. Yet in polymers preservation of orientation memory is a common feature due to delayed chain relaxation in the highly viscous, but by all other criteria, fully amorphous state, and thus need not represent a significant enough departure from the truly random state to warrant the invoking of an altogether different nonequilibrium situation such as dynamic instabilities or frustrated solid-state transitions as is done for analogous effects in some small molecular substances (e.g., AlPO_4).^{16,17} Even so, such possibilities should not be excluded altogether.
23. The same issue is being currently addressed in connection with the so called "memory glasses" of which AlPO_4 is a prime example.¹⁶ Here, as already referred to, explanations are being thought of along specific structures in the glasses concerned, and through the dynamics of atomic motions therein, specific to those small-molecule materials. Their relevance, if any, to polymers with permanent, covalently bonded chains would require separate consideration.
24. M. J. Baus, *J. Stat. Phys.*, **48**, 1129-1146 (1987).
25. L. Onsager, *Ann. N.Y. Acad. Sci.*, **51**, 627 (1949).
26. Perhaps not coincidentally, we encountered an example of a small-phase reentry (with *T*) in an un-referenced phase diagram of carbon in a standard textbook (p. 376 of ref. 26). To our knowledge this is the sole example so far of such an effect in a single-component system; [there are of course numerous others in systems of two or more components (see, e.g., ref. 28)].
27. M. W. Zemansky, *Heat and Thermodynamics*, 5th ed. McGraw-Hill, New York, 1968.
28. J. E. Ricci, *The Phase Rule and Heterogeneous Equilibrium*, Dover Publications Inc., London, 1966.
29. R. Vogel, *Die Heterogene Gleichgewichte*, 2nd ed., Akademische Verlagsgesellschaft, Leipzig, 1959.

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