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Non-linear changes in the specific volume of the amorphous phase of poly(4-methyl-1-pentene); Kauzmann curves, inverse melting, fragility

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Abstract

The existence of a re-entrant phase at high temperature and high pressure has been reported for a polymer, poly(4-methyl-1-pentene), recently [Rastogi S, Newman M, Keller A. Nature 1991;55:353; Rastogi S, Newman M, Keller A. J Polym Sci, Phys Ed 1993;31B:125; Rastogi S, Höhne GWH, Keller A. Macromolecules 1999;32:8909; Greer AL. Nature (News Views) 2000;404:134; Van Ruth NJL, Rastogi S. Macromolecules 2004;37:8191 [1–5]]. In a similar manner to the general phase behaviour proposed by Tammann in 1903 [Tammann G. Kristallisieren und Schmelzen; 1903; Metzger and Wittig Leipzig [6]], a re-entrant region exists where the entropy of a crystal is greater than that of its liquid. The existence of a crystal having entropy greater than its corresponding liquid is in contradiction to the Kauzmann paradox [Kauzmann W. Chem Rev 1948;43:219 [7]]. Here, we show how by careful study of its origin, a re-entrant phase can exist without invoking a paradox. Tammann ascribes the origin of the re-entrant behaviour, depicted in a pressure–temperature diagram, to the existence of a line where the difference in specific volume between the liquid and the crystal is zero ($\Delta V = 0$ line) and another line where the difference in enthalpy between liquid and crystal is zero ($\Delta H = 0$ line). Here, we provide direct experimental evidence for the existence of this $\Delta V = 0$ line for the first time. The experimental observations also show the presence of a second $\Delta V = 0$ line at lower temperatures. This second $\Delta V = 0$ line has an essential role in resolving the apparent entropy crisis [Debenedetti PG, Stillinger FH. Nature 2001;410:259 [8]] in the re-entrant region of the pressure–temperature phase diagram, through a relationship between the specific volume and the entropy. These two $\Delta V = 0$ lines, when combined with the melting and glass transition temperature, describe the shape of the pressure–temperature phase diagram of this polymer.

Keywords: Kauzmann curve; Shrinkage; Isotherm

1. Introduction

One of the main advantages of polymers over more conventional materials such as metal and wood, besides their low cost and low density, is their easy processability due to the fact that most polymers can be processed via the melt. One of the most important processing methods is injection moulding; in this process the polymer is melted in an extruder and pumped into a mould at high pressure. As the polymer cools and solidifies it shrinks and backpressure has to be applied to keep the mould filled completely. The shrinkage will be especially large in semi-crystalline polymers because solidification involves crystallisation during which the volume of the material generally decreases dramatically (an exception to this is, for example, water, which expands when it crystallises into ice). Because of this shrinkage, internal stresses build up in the material limiting the precision and complexity of the moulding products that can be fabricated.

Unfortunately, there are no polymers available that behave like water in the sense that they expand upon crystallisation (at least, not at atmospheric pressure). There are, however, polymers for which the crystal density can be lower than the amorphous density. For the poly-olefin isotactic poly(4-methyl-1-pentene) it is known that the crystal density is lower than the amorphous density at room temperature and atmospheric pressure below 50 °C [2]. At the crystallisation temperature, however, the crystal density is higher than the amorphous or liquid density and thus the polymer crystallises in a conventional fashion.

The remarkable behaviour of these polymers under pressure has been studied. The *p-T* phase diagram of isotactic poly(4-methyl-1-pentene), or P4MP1, is shown in

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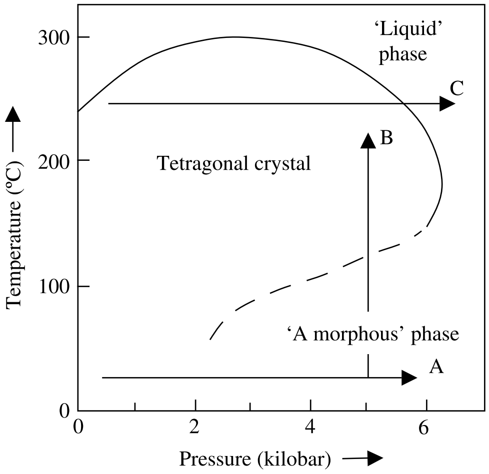

Fig. 1. Schematic pressure–temperature phase diagram of poly-4-methyl-1-pentene derived from the experimental observations reported elsewhere (Refs. [1–4]). For simplicity behaviour of tetragonal phase has been considered. Arrows in the phase diagram represents pathways along which the experiments have been performed.

Fig. 1 [1–4]. The crystalline phase of P4MP1 normally contains helical chains with seven monomer units per two helical turns and these helices are packed in a tetragonal lattice with unit cell parameters $a = b = 18.66$ Å, $c = 13.80$ Å.

According to the Clapeyron equation,

$$\frac{dT_m}{dp} = \frac{T \cdot \Delta_{fus} V}{\Delta_{fus} H}$$

A 'normal' liquid has a greater volume than its corresponding crystalline form. As is evident in Fig. 1, the melting point increases initially with pressure, i.e. dT_m/dp and the specific volume change upon melting, ΔV, are positive. As pressure is increased further, the melting point passes through a maximum at which dT_m/dp and $\Delta V = 0$. Beyond this, the melting temperature starts to decrease with increasing pressure and dT_m/dp is negative. The material will now expand upon crystallisation (in a similar manner to water forming ice at atmospheric pressure), i.e. ΔV is negative. For an isothermal experiment along line C (Fig. 1), the crystalline P4MP1 melts upon increasing pressure at high pressures (~6 kbar). However, at room temperature along line A, the crystalline phase disorders at a much lower pressure (~2 kbar). This re-entrant behaviour is very similar to the general phase behaviour predicted by Tammann in 1903.

1.1. Tammann's phase diagram

The transition line between solid and melt (i.e. the locus of T_m with p) generally has a positive dT_m/dp slope, which means that the melting point rises with increasing pressure. It was speculated by Tammann [6], however, that due to the greater compressibility of the liquid, at elevated pressures a liquid may have the same volume as the crystal, i.e. there should be a line for which $\Delta V = 0$. Above this pressure the sign of the slope dT_m/dp would become negative and the melting temperature will decrease with increasing pressure (as we have observed in P4MP1). Tammann also suggested that on increasing pressure further, at a certain point when $\Delta H = \Delta S = 0$ and thus $dT_m/dp = \infty$, the melt-line would invert and continue towards lower pressures. Only the liquid phase would exist above this pressure. He drew this conclusion in order to avoid a critical point at which the enthalpies of the crystal and the melt would be identical, unlike the critical point, which exists at the equilibrium of a fluid and its vapour. Tammann explained this re-entrant behaviour of the melt-line by the existence of a line where ΔV between the amorphous and crystalline phases is zero, and another line where the enthalpy difference ΔH is zero. The concept of such 'neutral' lines arises from the

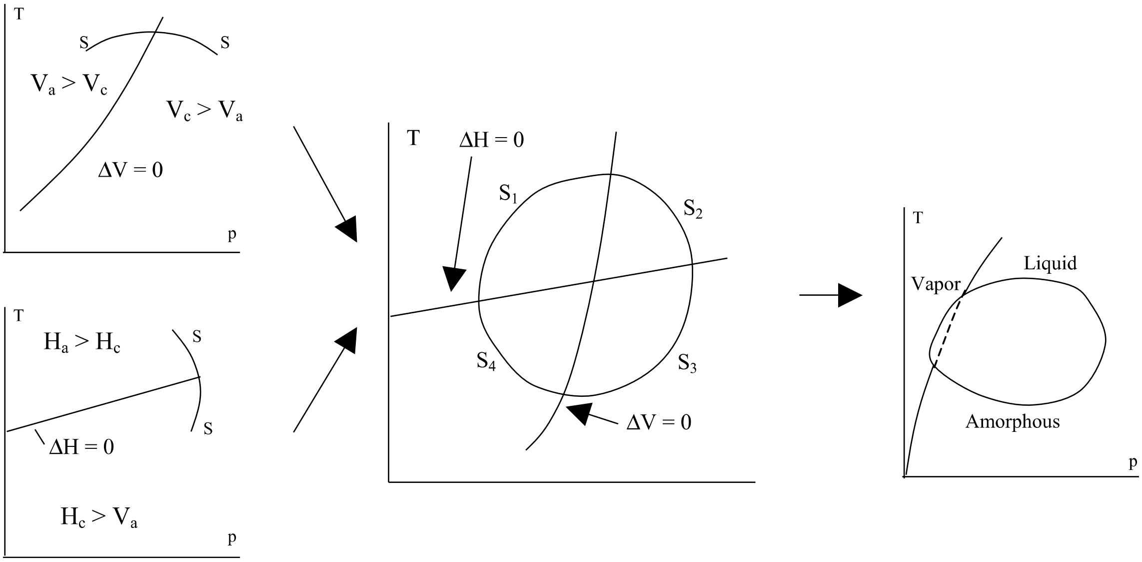

Fig. 2. Tammann's re-entrant phase diagram from Ref. [6]. Neutral lines, $\Delta V = 0$ and $\Delta H = 0$, drawn in the phase diagram are the origin of the re-entrant phase behaviour. The phase diagram is divided into four regions, where S_1 shows increase in melting temperature with pressure, S_2 inversion in density i.e. crystal density becomes lower than the liquid, S_3 and S_4 are the regions where crystal entropy exceeds the amorphous phase.

observation that the expansion coefficient, α, and the heat capacity, C_p, of the liquid are greater than those of the crystal. Due to the lack of experimental evidence the existence of these neutral lines, $\Delta V=0$ and $\Delta H=0$, in Tammann's phase diagram is still a subject of discussion. Moreover, regions S_3 and S_4 in Fig. 2 suggest that the entropy of the crystal will be larger than that of the amorphous. The Kauzmann paradox, discussed in Section 1.2, contradicts such a possibility.

1.2. Kauzmann's paradox and the glass transition

Kauzmann [7], like Tammann, proposed that the intersection of the specific volume and the enthalpy with decreasing temperature (essential for the validity of the previously mentioned general phase diagram) would lead to a higher specific volume and enthalpy for the crystal. According to Kauzmann this would lead to a paradox situation. The Clausius–Clapeyron equation represents the change in entropy upon melting:

$$\frac{dp}{dT}=\frac{\Delta S_m}{\Delta V_m}$$

According to this equation the entropy difference will invert in a phase diagram like the one suggested by Tammann, and the entropy of the crystal will be greater than that of the liquid (or amorphous). If the entropy of the liquid and the crystal are extrapolated to $T=0$ K, the entropy of the crystal will become zero and the entropy of the liquid/amorphous will be negative, which is a violation of the third law of thermodynamics, hence a paradox situation arises. To resolve this paradox, a transition will occur that will prevent the volume, enthalpy and entropy of the crystal and liquid from intersecting. This transition is the glass transition, which occurs ideally at, but practically above, the Kauzmann temperature. This is visualised in Fig. 3(b).

The Kauzmann paradox is an important phenomenon in most thermodynamic concepts to explain the glass transition. Although it is based on an extrapolation over a large temperature range, which makes it rather controversial, the Kauzmann temperature, T_k, is often regarded as the true glass transition temperature.

Theories concerning the glass transition can be divided into two categories; thermodynamic ones view the observed glass transition as a kinetically controlled manifestation of an underlying transition, and non-thermodynamic ones, which consider the glass transition as a purely dynamic singularity.

The entropy viewpoint, an example of a thermodynamic theory, of the glass transition is closely connected to the Kauzmann paradox. It considers the glass transition as a true second order phase transition of the liquid to the glass, which results in the glass having the same entropy as the crystal if crystallisation would have occurred just before vitrification. This ideal glass transition temperature is the same as the Kauzmann temperature. In practice the glass transition occurs at a higher temperature than the true glass transition (it is well known that the glass transition temperature increases with increasing cooling rate, which illustrates the fact that the glass transition is kinetically driven) and the glass has higher entropy than the corresponding crystal. This viewpoint is in agreement with the Vogel–Tammann–Fulcher (VTF) equation, which correlates viscosity of the liquid with temperature using T_0, which is thought to be the ideal glass transition temperature.

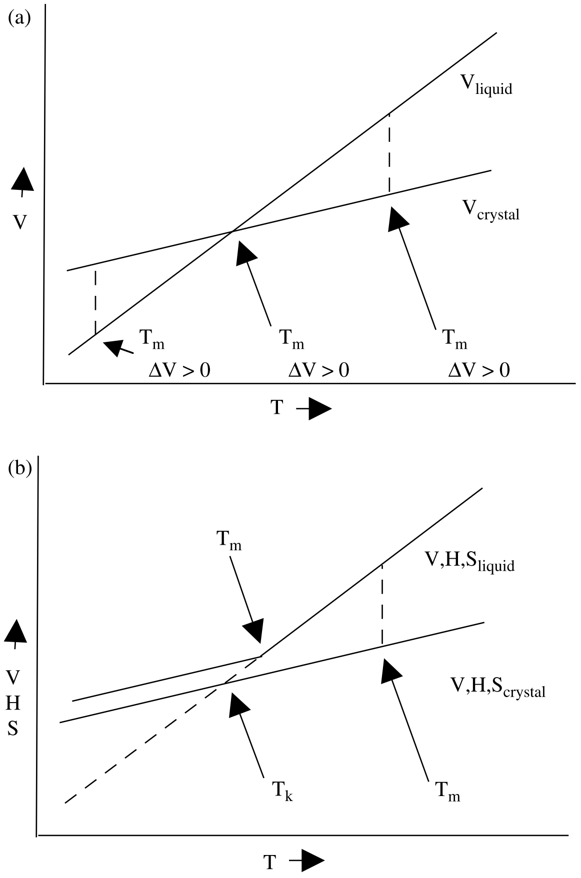

Fig. 3. (a) Intersection of the liquid and crystal specific volume lines in a *V–T* diagram. Three possible melting points depicting differences in the volume changes are represented in the figure. (b) Shows variation in liquid line on intervention of T_g. In the diagram, T_k represents the Kauzmann temperature.

$$\eta=B\times\exp\left(\frac{A}{T-T_0}\right)$$

The free volume viewpoint, also a thermodynamic theory, uses an ideal glass transition temperature as well, although this ideal glass transition temperature is not directly related to the Kauzmann temperature. The free volume viewpoint is in agreement with the Williams–Lendel–Ferry (WLF) equation for the temperature dependence of the viscosity, which is similar to the previously mentioned VTF equation.

$$\log_{10}\frac{\eta(T)}{\eta(T_g)}=\frac{-C_1(T-T_g)}{C_2+T-T_g}$$

The dynamic viewpoint does not make use of an ideal glass transition temperature and does not consider the glass transition to be a thermodynamic transition.

2. Experimental methods to determine Tammann's $\Delta V=0$ line

From Tammann's phase diagram it is evident that the inversion in melting temperature with increasing pressure invokes the existence of $\Delta V=0$ line in the *p-T* phase diagram. The co-existence of the crystalline and amorphous phase in the semi-crystalline polymer allows direct measurement of the difference in specific volume. For example, using small-angle X-ray scattering (SAXS), the difference in specific volume can be determined. Simultaneous data collection of wide-angle X-ray scattering (WAXS) provides information regarding possible phase transitions. Synchrotron radiation combined with high-pressure equipment [3] provides the possibility to perform simultaneous time resolved SAXS/WAXS studies as a function of both pressure and temperature. The evolution of the difference in specific volume is determined in both isothermal and isobaric experiments in the pressure–temperature phase diagram. Information thus obtained will provide further information in rather complicated *p-T* phase diagram of P4MP1.

2.1. Methods

2.1.1. Materials used

The P4MP1 used throughout this study, unless noted otherwise, was supplied by Scientific Polymer Products®, the melting point of this grade is 235 °C, the weight-average molecular weight is 650 kg/mol and the polydispersity is 4.7.

2.1.2. X-ray scattering

Small-angle X-ray scattering experiments, combined with simultaneous wide-angle X-ray scattering experiments, were performed at beamline ID02, European Synchrotron Radiation Facility (ESRF), Grenoble, France (wavelength = 0.999 Å). The sample detector distance for the SAXS measurements could be varied between 1.5 and 10 m. The WAXS detector covered part of the two-dimensional scattering pattern. Both SAXS and WAXS data were converted from two-dimensional images to one-dimensional patterns by using FIT2D software supplied by the ESRF.

The SAXS intensity is proportional to the difference in electron density between the two phases [9], which in this case is proportional to the density difference and thus the difference in specific volume. Simultaneous WAXS was used to detect any phase transitions during the measurement. During all the experiments reported here no occurrence of the hexagonal phase was detected. To vary pressure and temperature, a diamond window pressure cell was used with a temperature range of 30–300 °C and a pressure range of 0–500 MPa [1].

2.2. Experimental validation of the $\Delta V=0$ line

A series of simultaneous SAXS/WAXS experiments are performed above and below the glass transition temperature in order to follow any changes in the specific volume of the crystalline and amorphous phases with pressure. Fig. 4 shows

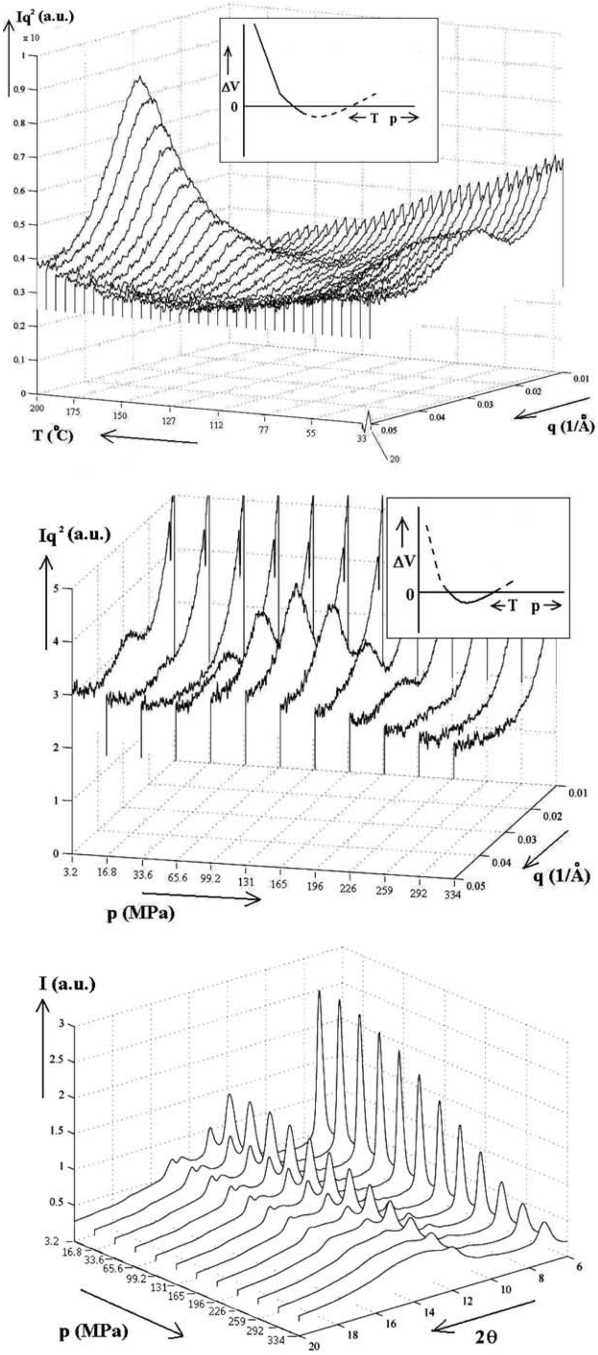

Fig. 4. Time resolved X-ray diffraction patterns recorded at elevated pressures and temperatures. The figure shows evolution of SAXS patterns (a) on decreasing temperature at fixed pressure 32 MPa and (b) increasing pressure at fixed temperature 100 °C. The simultaneously recorded WAXD pattern is shown in (c). The scattered intensity at small angle is proportional to the difference in specific volume between the crystalline and amorphous phase in the semi-crystalline polymer. The variation in specific volume difference in isobaric and isothermal conditions, with decreasing temperature and increasing pressure, respectively, is shown in the inlay of the figures. The solid part of the line corresponds to the data presented in the figure; the dashed part of the line refers to data obtained from another set of experiments. From these figures two $\Delta V=0$ points, one in the lower pressure region and the other in the higher pressure region, can be determined, along with a ΔV maximum positioned between the two $\Delta V=0$ points. The scattering vector q refers to the scattering angle. The z-axis refers to the Lorentz corrected intensity. The simultaneously recorded WAXD pattern shows onset in the loss of crystallinity above 259 MPa.

SAXS data recorded in-situ during isothermal and isobaric experiments. Fig. 4(a) shows the variation in intensity on cooling at a fixed pressure of 32 MPa. From this figure it is evident that the intensity decreases sharply during the initial stages of cooling, followed by a more gradual decrease towards a minimum. Upon further decrease of temperature a subsequent increase of intensity is observed. The simultaneously recorded WAXS patterns show no structural changes. From the variation in SAXS intensity, the variation in specific volume difference is obtained, the observed minimum in intensity corresponding to a $\Delta V = 0$ point. A schematic representation is shown in the inlay; the continuous part refers to the experimental data and the dashed part to a series of similar isobaric experiments at different constant pressures.

Fig. 4(b) shows the variation of intensity with increasing pressure at 100 °C. From this figure it is evident that initially the intensity decreases to zero (at $p = 33.6$ MPa), followed by an increase towards a maximum (at $p = 131$ MPa). On increasing pressure further a second decrease in intensity is observed. The inlay shows a schematic representation of the variation of specific volume difference, as observed in Fig. 4(b). The simultaneously recorded WAXS data, Fig. 4(c), shows no structural changes below 226 MPa, however, above 259 MPa the anticipated phase transition from crystalline tetragonal to amorphous is observed [1–3].

From a series of similar experiments, under isobaric and isothermal conditions, it is concluded that the influence of increasing pressure or decreasing temperature results in the same variation of specific volume difference. From the combined set of experiments, four distinct features related to the specific volume difference relevant in the pressure–temperature phase diagram are assigned. The distinct features are: an initial sharp gradient of the ΔV line, a $\Delta V = 0$ point, a maximum in ΔV and a second minimum in ΔV as a function of increasing pressure or decreasing temperature.

The understanding of the origin of the observed second ΔV minimum requires consideration of the anticipated phase transition (from crystalline tetragonal to amorphous) at low temperature and elevated pressure [2]. From simultaneous WAXS studies it is evident that as the SAXS intensity approaches zero, the phase transition takes place. A closer look at the data suggests that the phase transition from crystalline tetragonal to amorphous phase occurs just before the SAXS intensity approaches zero, i.e. before the $\Delta V = 0$ point is reached in the phase diagram. Moreover, the observed ΔV maximum is located at much lower pressure than the phase transition. To define a minimum a decrease in intensity should be followed by an increase. The absence in the difference of electron density fluctuations in the amorphous phase, because of the phase transition at low pressure, explains why no return of SAXS intensity is observed. From this it is concluded that the second ΔV minimum is a second $\Delta V = 0$ point.

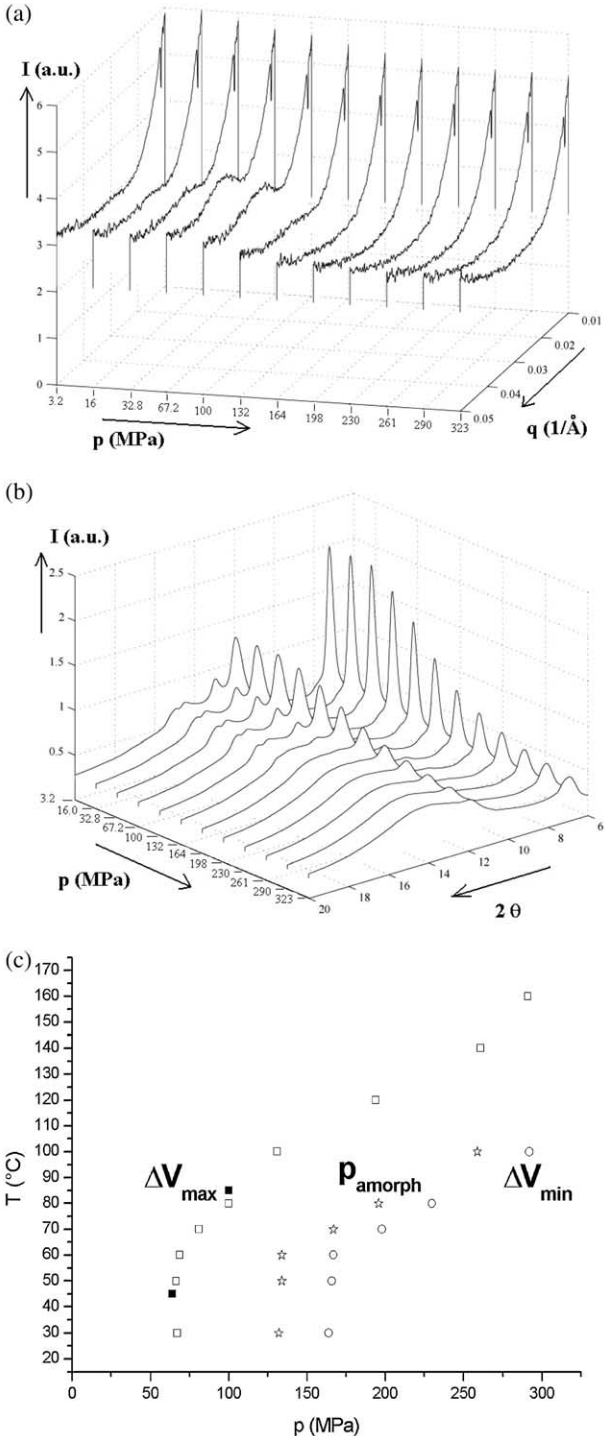

Fig. 5. The existence of ΔV minimum in the p-T phase diagram. (a) and (b) Show SAXS and WAXD patterns, respectively, recorded simultaneously at fixed temperature 50 °C. SAXS pattern show a maximum in intensity at 66.4 MPa. After this maximum the intensity decreases to a minimum. Beyond 164 MPa the SAXS intensity does not return and a minimum can be observed. This can be explained due to onset in the loss of crystallinity above132 MPa (see (b)). Figure (c) represents the amorphisation pressure p_{amorph} with the $\Delta V_{\max}$ and $\Delta V_{\min}$, the amorphisation pressure is located below the $\Delta V_{\min}$ pressure.

Fig. 5 shows a series of SAXS/WAXS experiments performed isothermally at 30 °C, i.e. below the glass transition temperature for P4MP1 at atmospheric pressure. Since at atmospheric pressure and 30 °C, the densities of the crystalline and amorphous phases in P4MP1 are rather similar, no intensity in SAXS is observed. With increasing pressure, close to 67.2 MPa, a maximum in electron density difference occurs while the corresponding WAXS pattern remains the same. However, on increasing pressure further, close to 132 MPa, a sudden disappearance of several reflections in the WAXS pattern is observed, which suggests a sudden structural change or phase transition. Simultaneous SAXS patterns also show the sudden drop in intensity, which converges to near zero at 164 MPa. These observations are in accordance with the earlier reported solid-state amorphisation under these conditions. On comparing Fig. 5(a) and (b) with Fig. 4(b) and (c), it is evident that above the glass transition temperature, the phase transition from the crystalline to the amorphous phase occurs at higher pressures. It may be also noted that the first $\Delta V=0$ point is absent in the samples that are subjected to pressure below the glass transition temperature as may be anticipated because of the equivalent density between crystalline and amorphous phases below T_g. Fig. 5(c) shows ΔV_{max}, first and second $\Delta V=0$ points, and the pressure required for amorphisation, p_{amorph}, at different pressures and temperatures. These data are obtained from a series of experiments performed under various isothermal and isobaric conditions. Fig. 5(c) conclusively demonstrates that pressure required for phase transition is always slightly higher than $\Delta V=0$ line. Moreover, the ΔV_{max} line exists at much lower pressures than p_{amorph}. Below 60 °C (i.e. below T_g at atmospheric pressure for semi-crystalline iP4MP1) the first $\Delta V=0$ points do not exist and the ΔV_{max}, p_{amorph}, the second $\Delta V=0$ points are independent of pressure and temperature.

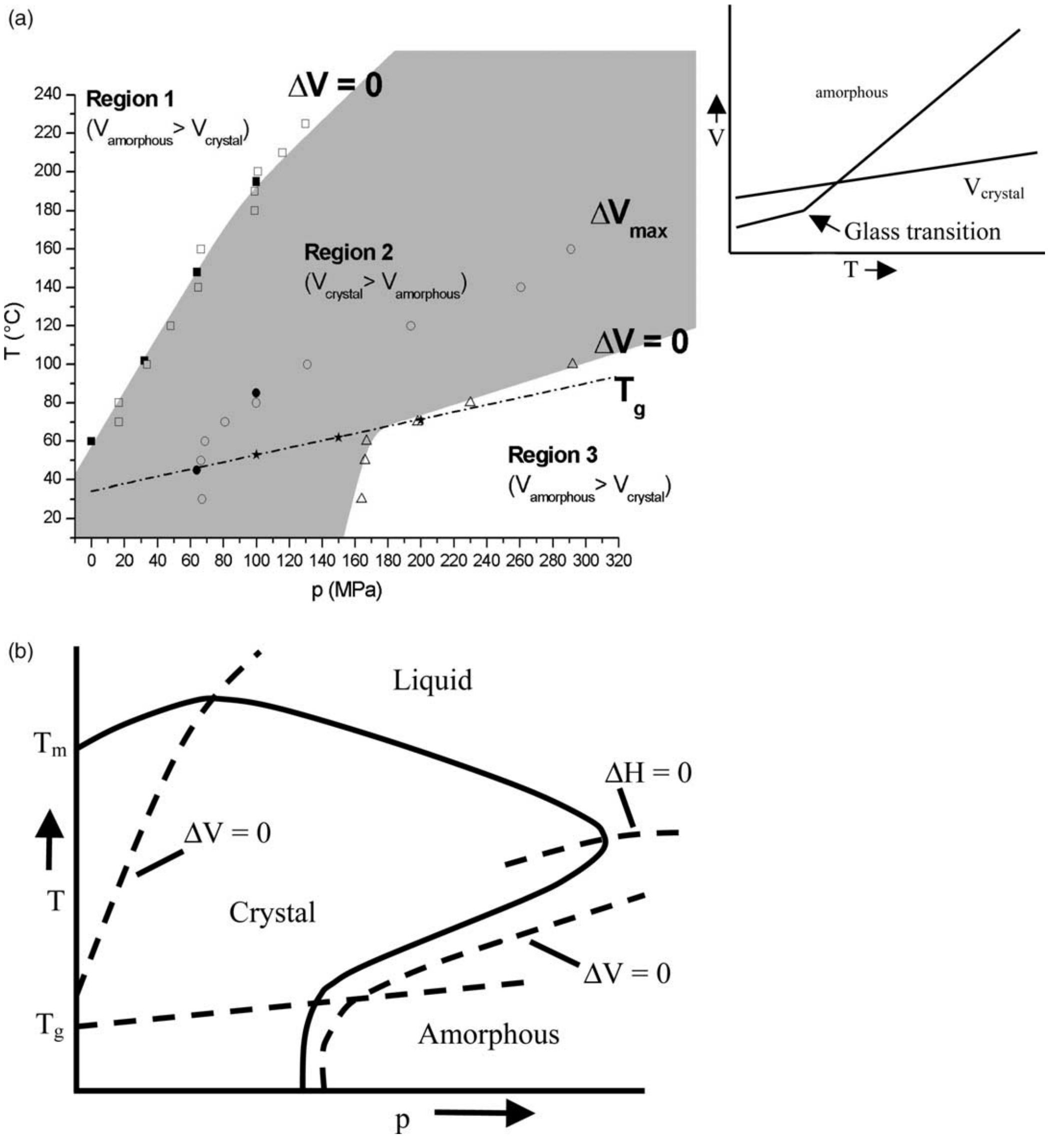

Fig. 6. From a series of experiments similar to those shown in Figs. 4 and 5, (a) summarises the obtained $\Delta V=0$ and ΔV_{max} points in a *p-T* diagram. Open symbols refer to isothermal measurements, closed symbols to isobaric measurements, the stars are measured glass transition temperatures. The two resultant $\Delta V=0$ lines divide the *p-T* diagram into three regions; regions 1 and 3 correspond to the normal specific volume difference relationship where $V_{amorphous}$ is greater than $V_{crystal}$, the shaded region 2 corresponds to the unusual specific volume difference relationship where $V_{crystal}$ is greater than $V_{amorphous}$. Within region 2, which is bounded by the two $\Delta V=0$ lines, the ΔV_{max} line is located. The V_g line, obtained from PVT measurements, is shown in this figure. The influence of the glass transition on the trajectory of the second $\Delta V=0$ line and the ΔV_{max} line is evident. A schematic *p-T* phase diagram is presented in (b); the two obtained $\Delta V=0$ lines, shown as the dashed lines, govern the trajectory of the phase transition line, shown as a continuous line, in both the normal and re-entrant region of the phase diagram. At the re-entrant point the phase transition line intersects with the anticipated $\Delta H=0$ line, shown as a dash-dot line.

2.3. The $\Delta V=0$ lines and the phase behaviour of P4MP1

Fig. 6(a) summarises the distinct features, the two $\Delta V=0$ points and the ΔV maximum, for the complete set of isobaric and isothermal experiments similar to those described in Figs. 4 and 5. The figure also includes a glass transition line, based on pressure–volume–temperature measurements that have been performed by us. The obtained line is in accordance with the earlier reported data [3]. The influence of the glass transition on the slope of the ΔV maximum line and the second $\Delta V=0$ line is evident from the figure. An explanation for this change in slope is provided by the decrease of the difference between the expansion coefficients of the crystal and the amorphous below the glass transition temperature, as shown in the inlay. When changes in the specific volume difference are combined with phase transition data obtained from simultaneous WAXS studies and previous work [3], the schematic phase diagram, shown in Fig. 6(b), is obtained. Considering the differences in specific volume, the phase diagram is divided into three regions. Region 1, positioned to the left of the first $\Delta V=0$ line in the phase diagram, shows a positive dT_m/dp slope, corresponding to a greater specific volume of the liquid than the crystal, according to the Clapeyron equation. Region 2, positioned between the two $\Delta V=0$ lines, shows a negative dT_m/dp slope, corresponding to a greater specific volume of the crystal than the liquid. The slope dT_m/dp becomes positive after the inversion of the enthalpy difference. Considering the Clapeyron equation the specific volume of the crystal will remain greater than that of the liquid. Region 3 is positioned below the second $\Delta V=0$ line. The phase transition line cannot intersect with the $\Delta V=0$ line and enter region 3, because of the positive slope of the second $\Delta V=0$ line. If the intersection were to take place, dT_m/dp would have to be zero, according to the Clapeyron equation. Thus, the second $\Delta V=0$ line governs the trajectory of the phase transition line in the re-entrant region of the phase diagram.

From Fig. 6(b) the re-entrant behaviour of the crystalline phase is evident. The re-entrant point in the phase diagram is defined as the point where dT_m/dp is infinite. At this point, considering the Clapeyron equation, both ΔH and ΔS are equal to zero. Below this point in the p-T diagram, in the re-entrant region, ΔH and ΔS are negative at the phase transition line. The Kauzmann paradox defines a transition temperature (T_K) to be the temperature at which ΔS is equal to zero [8,10] The experimental observations are that in this polymer T_K is higher than the experimentally observed T_g in the re-entrant region of the phase diagram. A possible explanation for the unusual observation, where the entropy of the crystal is greater than that of the liquid, is provided on consideration of the vibrational entropy contribution (S_{vib}) [11,12] a point to which we will address further in the liquid fragility section of this paper.

2.4. Circumvention of the tetragonal phase: a route to obtain the glassy polymer

Considering the re-entrant nature of the phase diagram of P4MP1 with a high-pressure inversion point, it should be

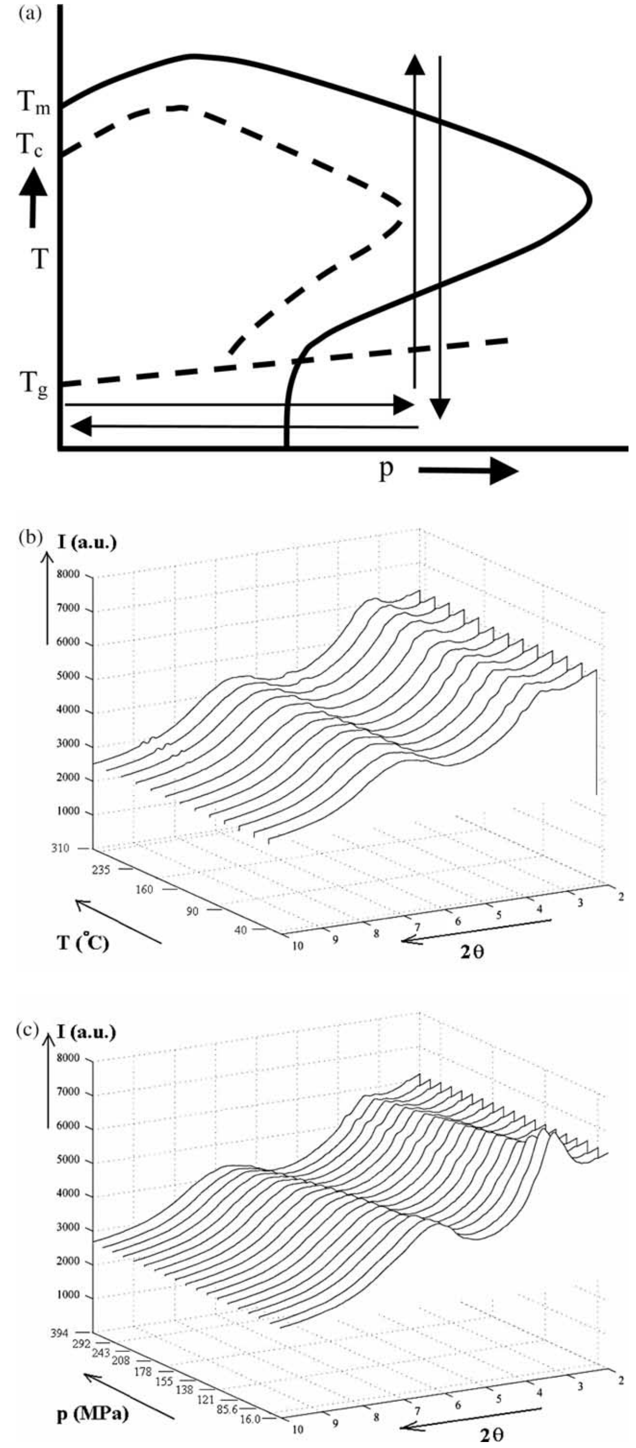

Fig. 7. A route to obtain glassy P4MP1 by circumvention of the tetragonal phase. (a) Schematic depiction of the high-pressure cycle to obtain amorphous P4MP1. The propose crystallization curve lies well inside the melt-line curve. The crystallization curve does not continue below the glass transition temperature, where crystallization is hindered by kinetics. (b) WAXD patterns during cooling at 400 MPa from 310 to 35 °C. A trace of hexagonal phase can be observed through the shoulder at the inner halo at $2\Theta=4$. No tetragonal modification can be observed. (c) WAXD pattern during releasing pressure at 30 °C. An almost completely amorphous sample is obtained.

possible to circumvent the tetragonal phase by cooling at high pressure. This possible route in the phase diagram can be used to obtain an amorphous sample at room temperature, if no other crystal modification intervenes. Since the material is below its glass transition temperature (35 °C) at room temperature (25 °C), it should remain amorphous also when the pressure is released. The pressure requirement for circumventing the melt-line of the tetragonal phase is outside the experimental pressure limit of the pressure cell used. However, the crystallisation line in the phase diagram will exist below the melt-line, as polymers require undercooling for crystallisation. This 'high-pressure cycle' is depicted in Fig. 7. This kinetically driven crystallisation process allows the possibility to obtain amorphous phase on cooling from melt at high pressures.

The presence of any crystallinity during the cycle can be detected by WAXS. According to the phase diagram of P4MP1, as presented in Fig. 1, the hexagonal phase will be encountered during this high-pressure cycle. The experimental observations are that appearance of this phase can be prevented by fast cooling, i.e. at cooling rates >100 °C/min.

The WAXS results for the high-pressure cycle are shown in Fig. 7(b) on cooling at high pressure and Fig. 7(c) during releasing pressure at room temperature. From these results it is concluded that the material remains almost amorphous; though a small shoulder appears on the inner halo, which can be associated to the hexagonal crystal modification [1–3].

These results conclusively demonstrate that the tetragonal phase can be avoided completely by cooling at high pressure, as predicted from the phase diagram. Considering the rapidity with which P4MP1 crystallizes at atmospheric pressure, where the amorphous phase cannot be obtained on cooling quickly, these observations are rather unique. The results also show that upon releasing pressure, and thus returning to ambient conditions, no crystallinity appears. This is contrary to what is observed during pressure-induced amorphisation, where the crystallinity returns after the pressure is released. This implies that there is a difference between the amorphous state at high pressure when it is obtained through a high-pressure cycle or through pressure induced amorphisation. This can be explained by the fact that the pressure induced amorphisation occurs below the glass transition temperature, where the polymer chains cannot move sufficiently to reach the fully random state from the ordered crystalline state although the side groups, which are much shorter than the main chain, can disorder into a random state more easily than the main chain. The presence of this main chain ordering will allow the material to return to its crystalline state when the pressure is released, whereas the amorphous material obtained through the high-pressure cycle cannot crystallise below the glass transition temperature due to the lack of mobility.

2.5. Non-linear variation in the specific volume of the amorphous phase: the origin of the second $\Delta V=0$ line

From the SAXS/WAXS results presented in this paper and summarised in Figs. 4 and 5 it is concluded that a second $\Delta V=0$ line exists at a lower temperature than the first $\Delta V=0$ line, and a $\Delta V_{\max}$ line lies between the two $\Delta V=0$ lines, Fig. 6 (depicted in Fig. 8a). It is apparent that the first $\Delta V=0$ line is the neutral line as suggested by Tammann. The other two lines, $\Delta V_{\max}$ and the second $\Delta V=0$ line, cannot be explained by means of the general phase diagram suggested by Tammann. This highly unusual behaviour in specific volume difference must be explained by specific volume anomalies in the amorphous and crystalline phases. Since the specific volume of the crystal does not show any non-linearity with varying pressure or temperature, as traced by WAXS, the specific volume anomaly is attributed to the amorphous phase. The specific volumes of the amorphous and the crystal are plotted separately, shown schematically in Fig. 8b. A kink in the volume change of the amorphous phase is due to a high order transition that was observed by Rånby et al. [13] in the liquid of atactic P4MP1 at 130 °C and atmospheric pressure, which is schematically depicted in Fig. 8c. This transition can account

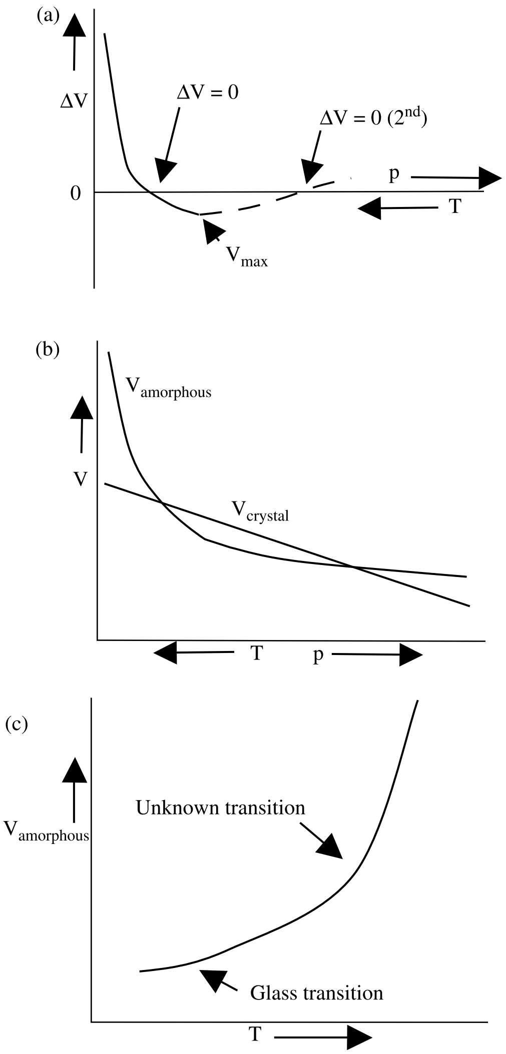

Fig. 8. Non-linear changes in the specific volume of the amorphous phase of P4MP1. (a) Represents ΔV as a function of temperature and pressure, where pressure increasing left to right and temperature right to left. (b) Changes in the specific volume of the amorphous and crystal as a function of temperature or pressure. (c) The glass transition and unknown transition anticipated by Rånby (Ref. [13]) are shown in the schematic diagram of the amorphous P4MP1. Kink in the (a and b) represent the unknown transition.

for the sudden fast rise in the specific volume difference at high temperature. Non-linear changes in the specific volume account for the non-linear variation in SAXS intensity. From SAXS measurements at atmospheric pressure, a sudden fast increase in intensity is noticed around 130 °C, termed as an unknown transition in schematic drawing of the Fig. 8c. With increasing pressure this transition temperature increases, for example, at 32 MPa, it is approximately 160 °C (see Fig. 4). The increase in this transition temperature with pressure is faster than changes in the $\Delta V=0$ line in the p-T phase diagram.

Studies performed on a series of other polymers, such as syndiotactic polystyrene [14], syndiotactic poly(para-methyl)-styrene [15] and poly(di-ethyl)siloxane, also show unusual features in their phase diagrams similar to those observed in P4MP1. These results suggest that by controlling the molecular architecture of the polymer with respect to the side-group, a non-linearity in the specific volume behaviour of the liquid can be generated, which, in combination with a high specific volume of the crystal, allows the existence of re-entrant behaviour. This non-linear behaviour of the liquid is not restricted to the specific volume; preliminary results show a large deviation of the viscosity dependency on temperature of P4MP1 from normal liquids, perhaps similar to the concepts proposed for fragile liquids [16,17]. The rheological behaviour of P4MP1 is discussed later at the end of the paper.

2.6. The second $\Delta V=0$ line and its influence on the re-entrant nature of the phase diagram

Here, we need to recapitulate some essential points concerning the second $\Delta V=0$ line once again. The second $\Delta V=0$ point cannot be established solely from SAXS data, Figs. 4 and 5, because the intensity does not increase after the proposed minimum at high pressures. To resolve this issue, simultaneous WAXS experiments, which provide information about the crystal modification of the polymer, have been analysed. The WAXS patterns show the amorphisation of the P4MP1. If the pressure at which the onset of amorphisation occurs is defined as the pressure where the crystallinity tends to decrease, and this onset-amorphisation is included in the phase diagram, Fig. 5(c) is obtained. From this figure it is evident that the amorphisation pressure follows the second minimum exactly, which is unlikely to be a coincidence. Since there will be no crystalline phase left at higher pressures, there will be no electron density difference to be measured. This explains why the SAXS intensity does not return at high pressures, and thus it is obvious to associate the second minimum in SAXS patterns to the second $\Delta V=0$ line. The Clapeyron equation states that when $\Delta V=0$, $\mathrm{d}T/\mathrm{d}p=0$ also. This second $\Delta V=0$ line is positioned in the S_3 region of the general phase diagram of Tammann (Fig. 2). Since both the phase transition line and the $\Delta V=0$ line have a positive slope and the phase transition line is positioned above the $\Delta V=0$ line, the phase transition line can never cross the $\Delta V=0$ line, because its slope would have to become zero, which is not observed experimentally. This result implies that the position of the two $\Delta V=0$ lines dominate the shape of the phase diagram of the tetragonal phase of P4MP1, since the first $\Delta V=0$ line determines the existence and position of the inversion point of the melt-line, and the second $\Delta V=0$ line determines the shape of the phase transition line in the low-temperature region (see Fig. 6).

Since these two $\Delta V=0$ lines should be an intrinsic property of the polymer, independent of the grade used, the amorphisation pressures in the low-temperature region of the phase diagram will be the same independent of the grade. However, different grades will show different phase behaviour in the high temperature, melting region of the phase diagram, because of the different melting point.

Fig. 6 illustrates the role of the T_g line in the p-T diagram. From the figure it is evident that the second $\Delta V=0$ line bends sharply as it crosses the T_g line and continues approximately vertically downwards with decreasing temperature. The explanation why this sharp bend occurs is provided in the inlay of Fig. 6. Since upon crossing the glass transition temperature, the difference in expansion coefficient between the amorphous and crystalline phase decreases, it can be concluded that the specific volume difference between the amorphous and the crystalline phase will stay approximately constant on cooling below the glass transition temperature. This means that the $\Delta V=0$ line will stay at approximately the same pressure once the temperature is below the glass transition temperature. This also means that the specific volume of the crystal will become smaller than that of the amorphous again at low temperatures, shown by the second intersection point at high p (low T) in the Fig. 8b.

2.7. Non-linearity in the specific volume: resolution of the entropy crisis

In an earlier work, Gibbs and DiMarzio [18] considered the difference in the vibrational entropy between the liquid and crystal to be negligible. Since the configurational (or conformational) entropy of the ideal crystal is zero, the entropy difference between the liquid and crystal was taken to be solely the configurational (or conformational) entropy (S_{conf}) of the liquid. In comparison with inorganic molecules, the conformational entropy is likely to be of more relevance than the configurational entropy in polymers. Recent work [19], taking water as an example, has shown that the vibrational entropy contribution is dependent upon the specific volume. This means that a significant difference in vibrational entropy between the liquid and crystal can occur when a difference in the specific volume is present. In region 2 of the phase diagram shown in Fig. 6, the specific volume of the crystal is greater than that of the liquid, which means that the vibrational entropy contribution in the crystal will be greater than that in the liquid. On decreasing temperature, and entering the re-entrant region of the phase diagram, the configurational (or conformational) entropy contribution of the liquid will decrease, and a situation will occur where the vibrational entropy of the crystal will exceed the sum of the vibrational and configurational (or conformational) entropies of the liquid. Thus, the origin of the apparent entropy crisis in the re-entrant region is the unusual specific volume difference between the crystal and the liquid. The apparent entropy crisis [8] is resolved when the difference in specific volume between the liquid and the crystal returns to normal, as occurs in region 3 of the phase diagram, shown in Fig. 6(a). These experimental findings show that the Kauzmann paradox, and therefore the entropy viewpoint of the glass transition [10], does not apply to this polymer. The linear extrapolation of the entropy of the liquid to absolute zero temperature, in which the Kauzmann paradox is based [7], is shown to be non-general. The non-linearity of the entropy of the liquid at low temperature is caused by the non-linear variation of the specific volume difference between the liquid and crystal (shown in the inlay of the Figs. 4 and 5, and more specifically in Fig. 8) with pressure or temperature. Since the WAXS results show no non-linearity for the specific volume of the crystal, the non-linearity in specific volume difference is attributed to the non-linearity of the specific volume of the liquid.

2.8. Fragility in the polymer melt

In the thermodynamic theories available for the explanation of the glass transition temperature, the entropy viewpoint is not applicable to P4MP1, for the reasons given in Section 2.7. The free volume viewpoint, which is also a thermodynamic theory, and shows an agreement with the WLF equation for the temperature dependence of the viscosity and is similar to VTF equation, may provide further insight.

We all know that with decreasing temperature glass-forming liquids become increasingly viscous, until a temperature is reached where they fail to flow on an experimental time-scale. The general consensus is that at the glass transition temperature, T_g, the viscosity reaches a value of 10 Pa s [12], the approach to this large viscosity being strongly dependent on the liquid. When displayed as an Arrhenius plot of log(viscosity) versus inverse temperature $1/T$, some liquids (such as silica) show a steady, linear increase, while others display a much steeper dependence on $1/T$ as illustrated elsewhere [16,17,20] and summarized schematically in the Fig. 9(a). The liquids that follow the Arrhenius behaviour are termed ‘strong’ liquids, and the others ‘fragile’. This range of behaviour is implicit in the VTF (or WLF) form, observed to describe the T dependence of viscosity (as well as diffusivity and relaxation times) in many glass-formers. The VTF equation may be expressed as:

$$\eta = \eta_o \exp\left(\frac{T_0}{K_{\mathrm{VTF}}(T - T_0)}\right)$$

where T_0 is the temperature of the apparent divergence in viscosity, and K_{VTF} is a material-specific parameter quantifying the kinetic fragility; more fragile liquids have larger K_{VFT} values. This behaviour of viscosity correlates with the jump in heat capacity at the glass transition—the more fragile the liquid, the sharper and bigger the jump. Rationalization of this correlation comes from the Adam–Gibbs relationship, which predicts a dependence of the viscosity on the configurational entropy S_c of the liquid.

Considering the non-linear changes in the specific volume of the amorphous phase and the anticipated unusual entropy variations in the re-entrant region of the phase diagram, P4MP1 is expected to show ‘fragile’ liquid behaviour. To test such a possibility rheological studies are performed on atactic, non-crystallizing P4MP1 in the melt state. What follows is a brief overview of the experimental observations and their implications.

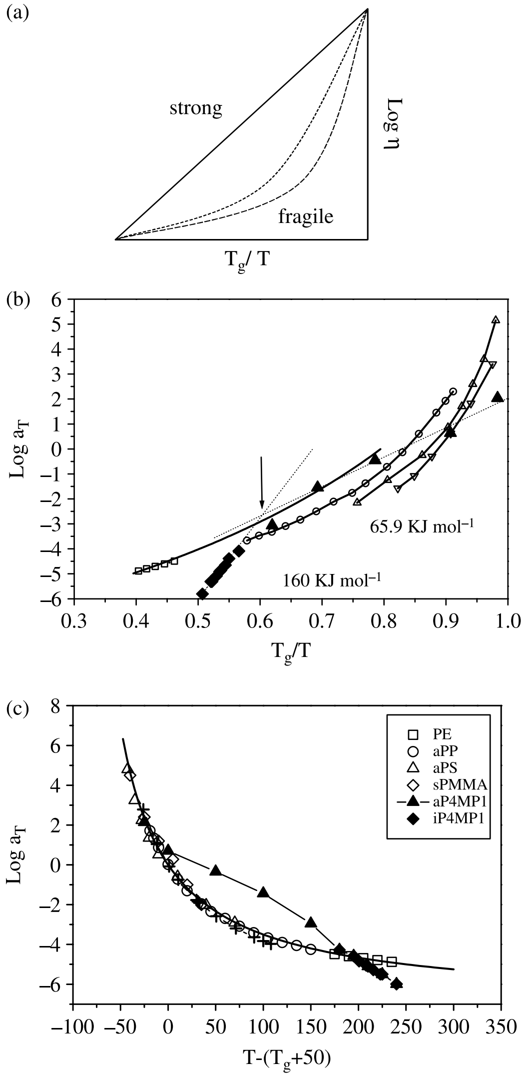

Fig. 9. Variation in the viscosity of the supercooled liquids. (a) Schematic diagram showing distinction between liquids following arrhenius (strong) and non-arrhenius (fragile) like behaviour. (b) A plot showing the temperature dependence of amorphous materials. Conventional materials for example PE, PP, PS or PMMA show a similar behaviour as temperature approaches to T_g. In the case of amorphous P4MP1 this picture seems not to hold and a clear transition from fragile to strong behaviour is seen around $T_g/T=0.6$. This observation is in agreement with the unknown transition anticipated at 130 °C (Fig. 8). The higher flow activation energy of P4MP1, compared to the other polymers referred in the figure, is due to the chain rigidity. (c) The non-arrhenius like behaviour of P4MP1 (compared to the other polymers) become evident when temperature is normalized. Symbols in Fig. 9b represent the polymers mentioned in the inlay of Fig. 9c.

Fig. 9(b) shows the temperature dependence of the viscoelastic properties of the amorphous P4MP1 sample. Similar to other semi-crystalline and amorphous polymers, a characteristic Arrhenius law is observed for P4MP1 in the high temperature range. However, P4MP1 shows a sudden breakup of the Arrhenius dependence around 130 °C (close to the unknown transition temperature predicted by Rånby (see ref 13)) and lower temperatures, thus suggesting fragility in its liquid state. The different behaviour of the P4MP1 samples is clearer when the temperature shift factors are plotted at a constant distance from T_g for various materials. Values of a_T and T_g have been collected from the literature for typical amorphous and semi-crystalline materials. At this point we would only like to state that rheological data on P4MP1shows distinct differences with the other conventional semi-crystalline or amorphous polymers. A detailed publication on the rheological aspects of P4MP1 is under preparation.

3. Conclusions

1. From the SAXS results the existence and position of the $\Delta V=0$ neutral line, as suggested by Tammann, is concluded. This $\Delta V=0$ line is likely to be an intrinsic property of the polymer P4MP1, independent of tacticity, molar mass or molar mass distribution. This means that decreasing the melting point of P4MP1 will result in lowering the pressure at which the melt-line inverts.
2. From the combination of SAXS and WAXS the existence of the second, high-pressure $\Delta V=0$ line is concluded. By the Clapeyron equation, the dominance of the second $\Delta V=0$ line in defining the shape of the p-T phase diagram in the high-pressure/low-temperature region (the re-entrant region) is revealed.
3. The glass transition temperature shows a strong influence on the trajectory of the second $\Delta V=0$ line, and thus also on the p-T phase diagram in the re-entrant region. Combined with the ability to circumvent the tetragonal phase by application of a high-pressure cycle, these results put aside all doubts about the circular nature of the tetragonal crystal phase of P4MP1, and also provide an explanation for the exact shape of the p-T phase diagram.
4. The only parameter missing to complete the entire general phase diagram, as suggested by Tammann, is the $\Delta H=0$ neutral line. Although the $\Delta H=0$ line cannot be measured directly, its existence can be concluded indirectly by application of the Clapeyron equation on the observed phase transition line.
5. The existence of a liquid above its glass transition temperature with lower entropy than the crystal is concluded from these results. Also, it is shown how this entropy crisis, or Kauzmann paradox, can be resolved. This means that the Kauzmann temperature, T_K, is higher than the observed glass transition temperature in at least some regions of the phase diagram. The only other known examples in which a Kauzmann temperature can be observed experimentally are the helium isotopes He [3] and He [4] (at 0.3 and 0.8 K, respectively). Quantum effects dominate the properties of these isotopes, however, which sets this example apart from the case of P4MP1.
6. The implication that the Kauzmann paradox does not apply to P4MP1 is that the Kauzmann temperature T_K is not the same as the ideal glass transition temperature. The results for other bulky side-group polymers, like syndiotactic polystyrene and syndiotactic poly(*para*-methyl)styrene, which show some similar characteristics to P4MP1, indicate that this behaviour is not restricted to one polymer. This raises the question of whether the connection between the Kauzmann temperature and the ideal glass transition is valid for polymers in general, since the vibrational entropy seems to play an important role.
7. The results strongly suggest that the difference in specific volume has a great influence on the difference in vibrational entropy contribution. Earlier considerations reported in the literature do not take into account the difference in the vibrational entropy contribution.
8. Experimental results, reported in ref [21], clearly demonstrate that the melt-line inversion leads to an expansion upon crystallisation, similar to water/ice at atmospheric pressure. The pressure at which this melt-line inversion occurs is shown to be directly related to the $\Delta V=0$ line. These findings are of practical significance since they provide a pathway to obtain materials, which do not contract upon crystallisation during processing.

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