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Pressure-Induced Amorphization and Disordering on Cooling in Semi-Crystalline Polymers: Calorimetric Evidence for Inverse Melting in One Component System

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SUMMARY: We report some unusual phase behaviour, of general implication for condensed matter, on the polymer poly-4-methyl pentene-1 (P4MP1) induced by changes in pressure (*P*) and temperature (*T*), as observed by in-situ X-ray diffraction and high pressure DSC. Upon increasing pressure beyond a threshold value, the polymer, crystalline at ambient conditions, looses its crystalline order isothermally. The process is reversible. This behaviour is observed in two widely separated temperature regions, one below the glass transition temperature (< 50°C) and one close to the melting temperature (250°C), thus showing solid state amorphization and inversion in the melting temperature with increasing pressure. This further suggests inverse melting, i.e. re-entrant of the two widely separated liquid and amorphous phases along the T-axis at fixed *P*. This is confirmed experimentally as disordering in the crystalline structure on cooling. The inverse melting in P4MP1 raises the possibility of exothermic melting and endothermic crystallization as anticipated by Tammann (1903), see reference 1. The anticipated exothermic melting and endothermic crystallization is confirmed experimentally in the one component system P4MP1. We are observing similar features in a range of polymers.

Introduction

Crystals of the polyolefin poly-4-methyl pentene-1 (P4MP1) normally contain helical chains with seven monomers for every two helical turns (7_2 helix). These helices form a tetragonal lattice with four chains per unit cell. The unit cell parameters are a=b=18.65Å, c(chain direction)=13.67Å and α=β=γ=90°. The rather unusual fourfold co-ordination of helices has been attributed to the intermeshing requirements of the side groups, resulting in rather open packing. The calculated (tetragonal) crystal density (ρ_c) at room temperature is 0.813g/cm^3; this is not only low for a polyolefin but is also lower than the density of the corresponding amorphous state (ρ_a), 0.830g/cm^3 at the room temperature. The significance of this similarity in densities and in particular the inverted relationship between ρ_c and ρ_a is of

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interest. Above the glass transition temperature (T_g), the usual density relationship exists. The melting temperature (T_m) and T_g of semi-crystalline P4MP1 are 245°C and (approximately) 50°C, respectively.

Experiments

The effect of P and T on the phase behaviour is investigated experimentally by in-situ X-rays and Raman spectroscopy using a piston cylinder type pressure cell. The maximum pressure attainable is 6kbar, and the temperature could be varied between room temperature to 300°C. For the X-ray diffraction studies synchrotron radiation available at beamline ID11/BL2 at ESRF, Grenoble, and a rotating anode generator with Mo target were used. The diffraction patterns were recorded using Princeton CCD detector or flat plate camera. The recorded patterns contain reflections from the diamond windows, which provide convenient internal standards for both spacing and intensity. The samples were mostly in the form of oriented films, the diffraction patterns from them have more information to convey than those of randomly oriented samples. The calorimetric measurements were carried out using a high pressure differential calorimeter cell (HP-DSC) constructed at the University of Ulm. The high pressure cell (which can be connected to a commercial power compensated DSC) allows measurements in the T region from room temperature to 330°C at P-s up to 5.5kbar.

Results

In this paper, results from selected pathways through the pressure-temperature phase diagram which involve transformations between the tetragonal solid (crystal) phase (C_t) and the liquid or amorphous phase are presented. These pathways are indicated in the p-T phase diagram of Figure 1. The phase boundaries are deduced by the X-ray diffraction patterns and high pressure DSC [2,3,4].

Experimental observations by high pressure DSC have been summarised in Figure 1b. Except along pathway 1 all other points shown in the figure are endothermic. It has to be noted that the experimental observations made by high pressure DSC show a good resemblance with the observations made by in-situ X-rays as summarised in Figure 1a.

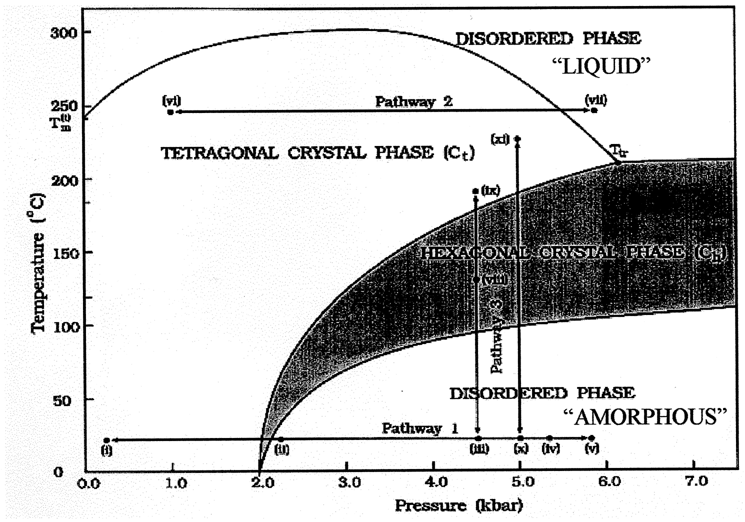


Figure 1a. *p-T* phase diagram of P4MP1 showing the phases between which fully reversible transformations occur: Liquid, Amorphous and Crystal ((C_t) and (C_h)). Roman numerals denote experimental points documented by X-ray diffraction patterns. The reversible transition from Amorphous to C_t on raising or lowering *T* involves passing through a broad regime (shaded) which encompasses a new (hexagonal) crystal phase, C_h. This phase may be encountered on heating along pathway 3. A transition from C_h to C_t occurs on further heating. In contrast to cooling at fixed P, C_t goes directly in the disordered phase. All transitions along pathways 1,2 and 3 have been confirmed by high pressure DSC as shown later in Figure 1b.

Pathway 1:Increasing P isothermally below the T_g, "Solid State Amorphization": exothermic melting

Figure 2 shows the X-ray diffraction patterns as observed on increasing pressure at room temperature along pathway 1 (Fig.1a), i.e. below the glass transition temperature. It has to be noted that on increasing pressure, above the threshold value of 2kbar, Fig. 2b, the sharp reflections get diffuse and those close together merge into one. Further changes beyond 2kbar are gradual, Figs. 2c and 2d, while on releasing the pressure the initial C_t state is regained with some modification as shown in Fig. 2e. At the highest accessible pressure the sample is essentially the oriented amorphous phase. In such oriented samples, retention of a certain amount of order in the packing of chains becomes apparent from the greater distinctness and intensity of the diffraction features along the equator (perpendicular to the orientation direction). High pressure DSC shows an exothermic peak at 2kbar on increasing pressure below the T_g (Fig.1b, pathway 1). The heat evolved during the process is approximately 0.9J/g, thus indicating that the entropy of the crystal is lower than the disordered (amorphous) phase.

This change from order to disorder with increasing pressure, is consistent with the anomalous density relationship ($\rho_c < \rho_a$) below the T_g. In this respect P4MP1 seems to fall in the same class as water and several other materials, of which pressure causes a decrease in the T_m, but here the change occurs at a temperature ~ 220°C below the T_m at atmospheric pressure. What follows are the experimental observations along pathway 2 in the Fig.1.

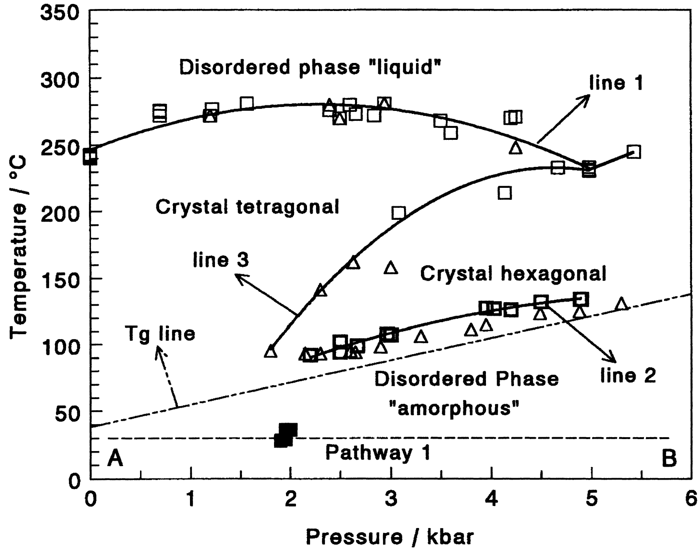


Figure 1b: p-T phase diagram of P4MP1 as obtained by DSC. Open symbols represent peak positions of endotherms, filled symbols (■) correspond to exotherm along pathway 1. Open squares (□) refer to endotherms obtained on first heating at fixed pressure, whereas open triangles (Δ) refer to endotherms obtained on reheating the sample cooled from the melt. For details see references 3,4 and 5.

Pathway 2: Increasing P at constant T=248°C. Inversion in the Clausius-Clapeyron Equation

Our experimental observations by in-situ X-ray studies, Fig.3, are that on increasing pressure beyond 3kbar isothermally, the initially C_t phase (Fig.3a, fibre order is lost because of high temperature) transforms into liquid (Fig.3b), while on releasing the pressure the initial crystalline state is regained (Fig.3c). A series of similar experiments along pathway 2 (fig.1a) indicates that a maximum in the melting temperature around 2.8kbar exists. Beyond 2.8kbar, an inversion in the Clausius-Clapeyron equation sets in. Experimental observations made by high pressure DSC further confirms the inversion in Clausius-Clapeyron equation above 2.8kbar, see line 1 in Fig. 1b. It follows from the results that below 2.8kbar, $dT_m/dP > 0$, $\rho_c > \rho_a$ and above 2.8kbar, $dT_m/dP < 0$, therefore $\rho_c < \rho_a$. Thus, we have an unique situation of inversion in density relationship with increasing pressure at the melting temperature. This seems to arise due to the greater compressibility of the liquid phase than the crystalline phase. The inversion in the Clausius-Clapeyron equation and solid state amorphization with increasing pressure at two widely separated temperature regions suggests the possibility of a re-entrant of Liquid and Amorphous phases as shown in Fig.1. Such a possibility has been investigated along pathway 3 in the *p*-*T* phase diagram, Fig.1a.

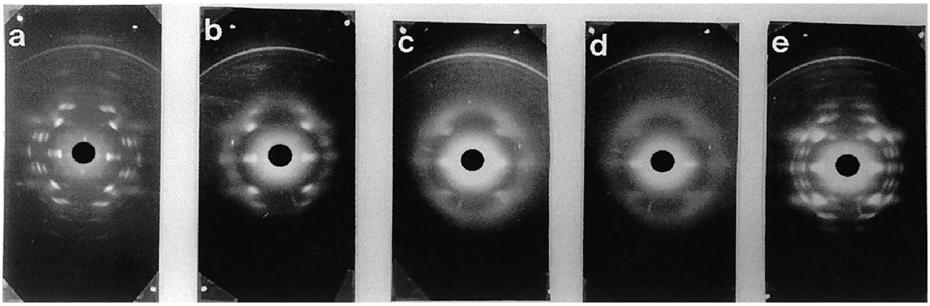


Figure 2: X-ray diffraction patterns of drawn films of P4MP1 at room temperature recorded in-situ at pressures of (pathway 1 in Fig.1), *a)*, 0.24kbar, *b)*, 2.24kbar, *c)*, 4.56kbar, *d)*, 5.36kbar, *e)*, 0.24kbar. The sharp reflections on the periphery here and in subsequent figures are due to the diamonds; the rings arise from a gasket. These reflections serve as intensity standards when comparing different photographs in a sequence.

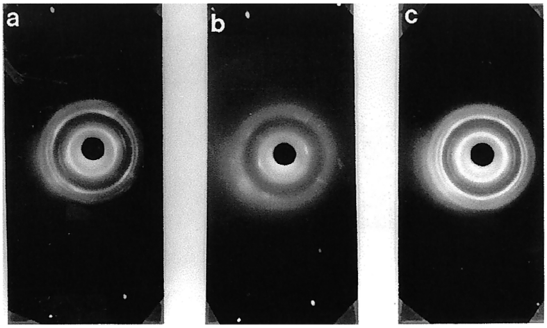


Figure 3: X-ray diffraction patterns of drawn films at higher temperatures (partially disoriented on heating) of P4MP1 at ~248°C at pressures of *a)*, 1kbar; *b)*, 6kbar; *c)*, 0.7kbar (pathway 2 in Fig.1).

Pathway 3: Disordering on cooling and crystallization on heating (isobarically); Endothermic crystallization

In a series of X-ray experiments performed along pathway 3 in Fig.1a we observed that on cooling the C_t phase (Fig.4a) looses its long range order and transforms into the disordered amorphous phase (Fig.4b). The extent of the disordering depends on the pressure: the same decrease in T leads to a more pronounced disorganization for higher P.

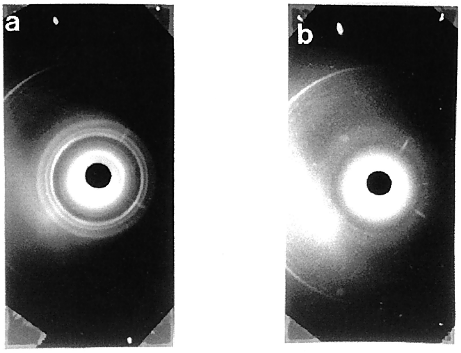
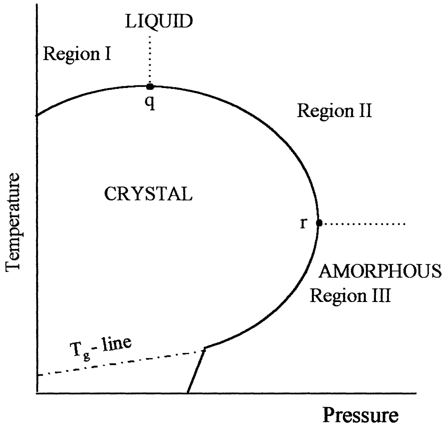


Figure 4: X-ray diffraction patterns showing disordering on cooling. *a*, 5kbar at 220°C and *b*, after cooling to room temperature isobarically at 5kbar. *b* has been exposed for longer time than *a*, in purpose.

On heating the disordered amorphous phase, obtained either on cooling (along pathway 3) or by increasing P (along pathway 1), transforms into a new crystalline phase C_h. This phase transformation in *p-T* phase diagram results into an endotherm, line 2 in Fig.1b. These experiments suggest that under the specified conditions, crystallization proceeds via absorption of heat. On heating further the C_h phase transforms into the usual C_t phase, again seen as an endotherm, line 3 in Fig.1b. The C_h phase is entrant only on heating not on cooling. Detailed high pressure DSC investigations suggest that disordered (amorphous) to C_h transition occurs just above the T_g line (Fig. 1b). While the hexagonal region is of interest in its own right but for the purpose of our present considerations it is an extraneous complication.

Out of the numerous results shown above, two sets of results are most unusual and need to be lifted out separately. First, is the exotherm at 2kbar obtained along pathway 1 in Fig. 1b. The heat evolved though small in magnitude is reproducible and corresponds to the onset of disordering as identified by X-ray diffraction Fig. 2. It follows that the pressure induced disordering, “solid state amorphization”, is a first order transition and this through an exotherm, which is in manner appropriate to a re-entrant amorphous phase i.e. exothermic melting. The second set of thermograms corresponds to the isobaric crossing of line 2 (Fig.1b) which gives rise to a clear identifiable endotherm corresponding to crystallization on heating from the disordered amorphous phase. At first sight an endothermic peak accompanying ordering from disorder may seem anomalous. Nevertheless, as it requires an increase in entropy it is consistent with the exothermic melting along the pathway 1. By X-ray evidence we would expect an exotherm on isobaric cooling when traversing line 2, i.e. along pathway 3 in Fig. 1a. This we did not observe by DSC. We are attributing this to likelihood that the heat evolution, small in any event, is too widely spread out in terms of T to produce a detectable signal. Yet that such a phase change, together with an associated heat evolution, has taken place is supported by the appearance of the endotherm on subsequent heating, which by X-ray evidence corresponds to crystallization shown by symbol (Δ), around line 2 in Fig.1b.



Region I : $dT_m/dP = T.\Delta V / \Delta H > 0$; $\Delta V = V_{liquid} - V_{crystal} > 0$; $\Delta H > 0$; $\Delta S > 0$

Region II : $dT_m/dP = T.\Delta V / \Delta H < 0$; $\Delta V < 0$; $\Delta H > 0$; $\Delta S > 0$

Region III: $dT_m/dP = T.\Delta V / \Delta H > 0$; $\Delta V = V_{amorphous} - V_{crystal} < 0$; $\Delta H < 0$; $\Delta S < 0$

Figure 5: Simplified *p*-*T* phase diagram with its thermodynamic implications. Melt phase has been subdivided into LIQUID and AMORPHOUS, here we have followed Tammann. For detail see reference 3.

By omitting the crystal-crystal boundary line, i.e. the intervening C_h phase, the overall *p*-*T* phase diagram, as obtained by the combined X-ray diffraction and calorimetric investigation (Figs. 1a and 1b), can be represented schematically as in Fig.5 also including the line for T_g.

Fig. 5 has been subdivided into Regions I, II and III separated by the extreme values denoted by q and r along the *p-T* phase lines. In Region I, dT_m/dP is positive displaying the conventional behaviour. The changing over into Region II, where T_m decreases with increasing *P*, is provoked by the change in sign of ΔV in the Clausius-Clapeyron equation, while that from Region II into Region III by a change in sign of ΔH which, in the present case of equilibrium, involves also a change in sign of ΔS. Throughout Region III, the melt phase (irrespective whether a liquid or an amorphous solid) is re-entrant implying 'inverse melting'. Even if the intervening additional crystal phase (C_h region as shown in Fig.1) has prevented us from passing continuously from the conventional melt (liquid) into the re-entrant melt region (amorphous), the thermodynamic relations we observed here - including the exothermic amorphization and the endothermic crystallization for the first time ever in a single component system - and expressed in the text portion of Fig.5 are fully consistent.

Conclusions

In addition to the thermodynamic generality as envisaged for the first time by Tammann in 1903, the findings described in this paper are highlighting the unusual behaviour that can be displayed by some polymeric systems, including solid state amorphization by pressure an issue with wider potential in the science and application of materials (see references quoted in reference 2).

References

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