Journal of Molecular Liquids 200 (2014) 28–31

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Structurally different amorphous solids of isotactic poly(4-methyl-1-pentene) and an apparently press-working-induced amorphization

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A R T I C L E I N F O

Article history:
Received 3 December 2013
Received in revised form 20 August 2014
Accepted 22 August 2014
Available online 4 September 2014

Keywords:
Polyamorphism
High pressure
Polymer melt
First sharp diffraction peak
Intermediate range order

A B S T R A C T

We have done press working of isotactic poly(4-methyl-1-pentene) (P4MP1) and carried out X-ray diffraction measurements of the pressed sheet at atmospheric pressure. The result shows an apparently pressure-induced amorphization, although the result will be partly due to the pressure gradient in the sample in the compression process. Separately from this measurement, we quenched the melted state of this polymer at atmospheric pressure and obtained an amorphous solid, and measured its X-ray diffraction at room temperature. Although the diffraction spectrum of this amorphous sample partially contained crystalline Bragg peaks, we found a difference between the diffraction spectra of quenched and pressed amorphous samples at the first peak height, which mirrors the difference between the diffraction spectra of low-density and high-density melt of the same polymer. We also suggest from the diffraction results that the crystalline state at room temperature contains high-density amorphous parts rather than low-density amorphous parts.

1. Introduction

Crystalline polymorphs are well known and studied extensively so far. Recently there has been a considerable interest in “polyamorphism”, which is a concept that there are different structures even in amorphous or liquid systems. Well-known examples are amorphous–amorphous transition in ice [1] and liquid–liquid transition in phosphorus (P) [2,3]. Also, there seem to be many other examples [4], such as seen in molecular liquids [5].

Pressure-induced amorphization means that a crystal changes to an amorphous solid by applying pressure. This phenomenon is firstly observed in ice [6], and then in SiO_2, GeO_2, SnI_4 [7], and other materials, and interestingly it is suggested that many of these cause amorphous-amorphous [8–10] or liquid-liquid transitions or structural changes [11]. The reason is simply that pressure-induced amorphization has roots in the negative slope of the melting curve.

If a melting curve shows a negative slope as a function of pressure, there will be a pressure-induced melting at high temperatures (as seen in ice), whereas pressure-induced amorphization may occur in low temperatures, as schematically shown in Fig. 1. This is what is seen for ice [12]. In Fig. 1, a melting curve maximum is assumed in a low-pressure region, since the melting curve is normally supposed to have a positive slope because the density of a liquid state is, in many cases, lower than that of its crystalline state. In what follows, we describe the meaning of this melting curve maximum.

The melting curve of P has a kink at around 1 GPa [13]. However, the kink used to be regarded as a smooth maximum [1,14] as shown in Fig. 2. Since 1967, a relation between melting curve maxima and structural changes in liquids has been theoretically suggested by use of Bragg–Williams and quasichemical approximations [15,16]. The suggestion is rather natural because if a liquid can be transformed into a crystal by pressure (point A in Fig. 2), and then by continuing to increase the pressure transformed back into liquid (point B), it is reasonable to conclude that the low and high pressure liquids are different. In other words, given that ΔS is always positive on melting, the Clausius–Clapeyron relation $dP/dT = \Delta S/\Delta V$ results in a volume expansion on melting at point A and contraction at B, meaning that there would be a large change of density as a function of pressure in the liquid state. For liquid phosphorus, in fact, a liquid–liquid phase transition was found at the high-temperature side of what was thought to be a melting curve maximum at that time [2].

It is suggested that such density anomaly is not necessary for the presence of low-density and high-density liquids [17]. However, to look for polyamorphism in polymers, melting curve maxima serve as convenient marks to find good candidates. We chose to look at isotactic poly(4-methyl-1-pentene) (P4MP1) (Fig. 3) because (i) it is reported that there is a melting curve maximum as a function of pressure [18], and (ii) at lower temperatures (i.e., at room temperature in this case), pressure-induced amorphization was also reported [18]. We may also note that a change from a “strong” liquid to a “fragile” liquid as a

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http://dx.doi.org/10.1016/j.molliq.2014.08.037
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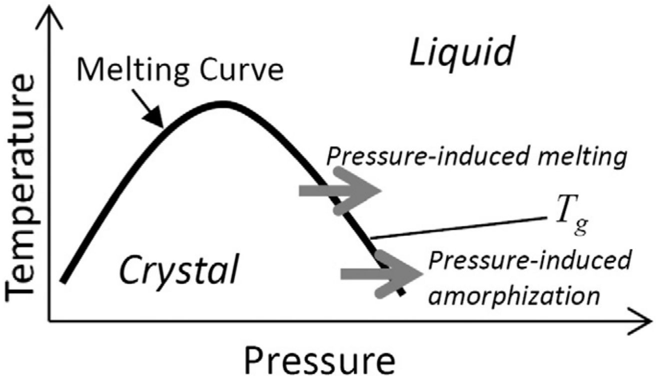

Fig. 1. Schematic picture of pressure-induced melting and amorphization [12]. T_g indicates the glass transition temperature.

function of temperature was reported, although the authors compare the melted states of different tacticities [19].

We thus chose to look at isotactic P4MP1 and found a pressure-induced structural change in its melted state, as we reported in Ref. [20]. We described above the reasons for the choice of this polymer, but as to the point (ii) above, another work reports the absence of such pressure-induced amorphization [21]. We may also note that the past work [20] showed a reversible pressure-induced amorphization, that is, the amorphous sample crystallizes again when the pressure is released. To clarify these points, we pressed P4MP1 and carried out X-ray diffraction measurements as follows.

2. Experimental

We aimed to study the pressure-induced amorphization. Besides compression, we handled samples at atmospheric pressure. We quickly compressed isotactic P4MP1 purchased from Scientific Polymer Product, Inc. with an ENERPAC NRR-3150 hydraulic press using a P-84N hand pump. In the compression process, the load was increased up to 250 kgf/cm^2, kept for 2 min and quickly released. A sample was compressed, being just sandwiched by pistons without a holder or cylinder as shown in Fig. 4. Hence the pressure anisotropy in the sample should be large. The pressure of the central part of the sample largely depends on the rigidity and viscosity of the surrounding part of the sample and these conditions are expected to vary with the compression process. Thus we could not estimate the absolute pressure of the sample at the compression.

The size of the pressed sample was approximately 15 mm in diameter and 0.3 mm in thickness but it always showed cracks at the edge. Large differences in pressure are expected between the central and edge parts of the sample. To avoid detecting the influence of such differences, we took the central part only and cut it as shown in Fig. 4. A typical size of the sample was approximately 15 × 1 × 0.3 mm^3. Because the compression was uniaxial, we irradiated the pressed surface (Fig. 4, a) and the cut surface (Fig. 4, b) by incident X-ray in the diffraction measurements.

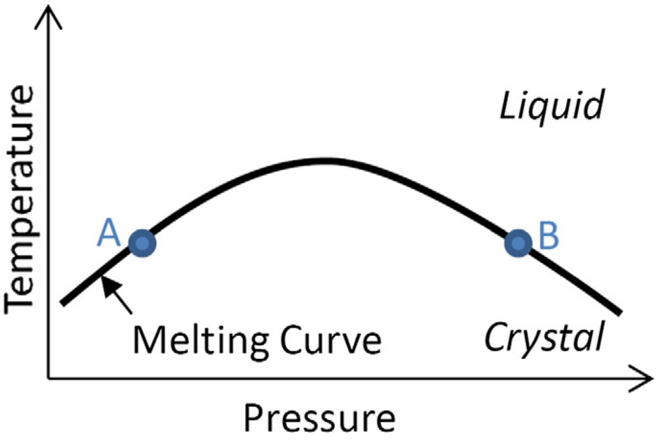

Fig. 2. Schematic picture of a melting-curve maximum in a pressure–temperature phase diagram.

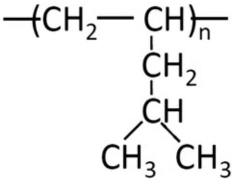

Fig. 3. Molecular structure of P4MP1.

For comparison with the pressure induced amorphous sample, we prepared a melt-quenched low-density amorphous sample at atmospheric pressure. The sample was put on a stainless-steel sheet of 0.1 mm thickness to facilitate handling. It was heated up to 260 °C (the melting point is 235 °C), kept for 5 min and quenched into ice water at 0 °C. We treated the sample in N$_2$ atmosphere to avoid oxidation. To measure the as-received crystalline sample, we prepared a slab of the sample by cooling the melt at 260 °C slowly.

X-ray diffraction measurements were carried out using Cu Kα radiation generated by Rigaku Gaigerflex. The 2-θ/θ diffractometer of Bragg–Brentano geometry was used. During the measurements, the room temperature was kept at 19 °C to prevent the sample from crystallization since the glass transition temperature is approximately 30 °C at atmospheric pressure [19]. However crystallization during a scan was observed. Fig. 5 shows X-ray diffraction spectra of a quenched amorphous sample. A gray thick line denotes a result of the first quick scan. There appear several Bragg peaks in the spectrum. This means that the sample was initially contaminated by crystals due to a slow cooling rate. However, partial crystallization certainly occurs during the scan and Bragg peaks in the second scan become large as indicated by a red thin line in Fig. 5. The spectrum of the first quick scan is noisier than that of the second one at a normal speed. For the low density amorphous sample, there is a shoulder at the lower-angle side of the Bragg peak at around 9°, which implies that a broad amorphous peak exists at around 9.3–9.4°. Although we prepared an amorphous sample quenched into dry ice (with ethanol) at −72 °C, a problem of crystalline contamination was not resolved. On the other hand, a pressure-induced amorphous sample is stable and a sign of crystallization was not observed during the measurements.

3. Results and discussions

Fig. 6 shows the diffraction spectra of crystalline (the black thin line), pressed (the blue thick line and the red dotted line), and quenched (the gray thickest line, the same spectrum shown in Fig. 5) samples. The difference between the blue thick and the red dotted lines is the direction of the incident beam as we mentioned above (Fig. 4). Here the intensity is plotted in log scale because the diffraction intensities of amorphous samples are very weak compared to crystalline Bragg diffraction. For comparison, the spectra are normalized at a broad maximum from 12 to 27°. The diffraction spectrum of the crystalline sample shows that it contains some amorphous parts, and this is a character commonly seen in crystalline polymers. We may note in passing that the first peak position is observed at around 0.6 Å^{-1} for this polymer in the melted state at around 280 °C in our previous work [20] whereas it is observed at around 0.67 Å^{-1} in amorphous solids at room temperature in this work. The inter-chain distance increases with increasing temperature and the first peak is assigned to the inter-chain (i.e., backbone–backbone) correlation [20]. Hence the shift of the first peak position is