

Pressure-induced structural change of intermediate-range order in a polymer melt

Pressure-induced liquid-liquid phase transitions have attracted much attention. These are transitions between two liquids with different macroscopic properties such as density, viscosity, and entropy, and different microscopic structures. Similar transitions in crystalline and, more recently, amorphous solids have been a focus of study so far, but the discovery that it is possible to have such pressure driven transitions in liquids is novel, and has posed some interesting technological and theoretical problems. The existence of a first-order transition of liquid phosphorous (*l*-P) is now well known [1]. In the low-pressure range, *l*-P is a P₄ molecular liquid, in which the molecules have a tetrahedral structure, but at high pressures, approximately 1 GPa, its structure and properties change as it polymerizes. The transition is first-order, and takes place in the liquid state near the kink of the melting curve in the pressure-temperature phase diagram.

This kink of the melting curve has been considered to be a smooth maximum [1], as schematically shown in Fig. 1(a). If a liquid can be transformed into a crystal by the application of pressure at point A in Fig. 1(a), and then by continuing to increase the pressure transformed back into a liquid at B, it is reasonable to conclude that the low- and high-pressure liquids are different, either simply because the liquid is more compressible or because it has a completely different structure. Indeed, some studies indicate that any material that has the maxima in the melting curve in the pressure-temperature plane is likely to have a pressure-induced liquid-liquid transformation [2]; although the transformations will usually be continuous and not first-order.

If there are similar liquid-liquid transformations

in polymer melts, they will take place at much lower temperatures and pressures than in liquids such as *l*-P, since the polymer molecules have high degrees of freedom and flexibility with interactions mostly involving weak forces, such as intermolecular or configurational forces. This would make such a phenomenon much easier to access than in *l*-P, water, or other liquids currently known to have pressure-induced structural changes. Although there have been studies on so-called liquid-liquid transitions in polymers [3], most of the studies have focused on a certain type of transition, which is intrinsically related to changes not in static structure but in relaxation phenomena. These changes occur in a variety of glass forming polymers, and presumably in any other glass forming systems, at relatively low temperatures of approximately 1.2 times the glass transition temperature T_g . To investigate changes in a static structure, measurements as a function of pressure are preferable because applying pressure can alter interatomic potentials more directly.

The aim of our study [4] is thus to carry out an *in situ* search for a liquid-liquid transformation in a polymer melt by the path shown in Fig. 1(a). A good candidate material is isotactic poly(4-methyl-1-pentene) (P4MP1) (Fig. 1(b)), which has a maximum in the melting curve. High-pressure *in situ* X-ray diffraction measurements were conducted at constant temperatures at the beamline **BL10XU**.

Figure 2(a) shows the pressure dependence of X-ray diffraction patterns of the P4MP1 melt at 280°C. The intensity of the peak at approximately 0.6 Å⁻¹, which we call the first sharp diffraction peak (FSDP), shows a remarkable decrease with pressure, as does the ratio of the intensities of the FSDP to the second peak (Fig. 2(b)). This kind of change observed in the FSDP shows a structural change in intermediate-range order, which is a structural order intermediate between short-range discrete chemical bonds and long-range crystalline lattices. Figure 2(b) shows the change in the slope (pressure dependence) at 0.5 and 0.7 kbar at 280°C and 290°C, respectively. This change in slope was also observed for the pressure dependence of the position of the FSDP [4]. We have also performed measurements of specific volume. The result shows high compressibility at low pressures, and we found an increase in the bulk modulus at a certain pressure for each temperature, which indicates the second-order transition [4]. Thus we observed changes in the pressure dependence of the microscopic structure as well as that of the macroscopic density.

In polymers, the FSDP is usually assigned

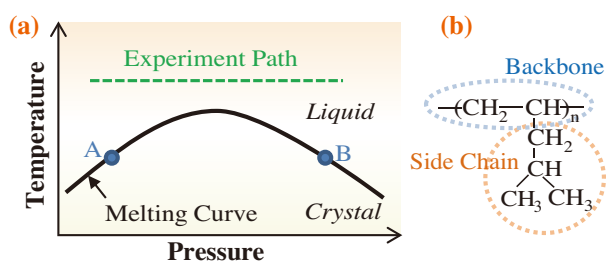


Fig. 1. (a) Maximum of melting curve in pressure-temperature phase diagram. We conducted high-pressure *in situ* X-ray diffraction measurements at constant temperatures as shown by the broken line. (b) Molecular structure of P4MP1.

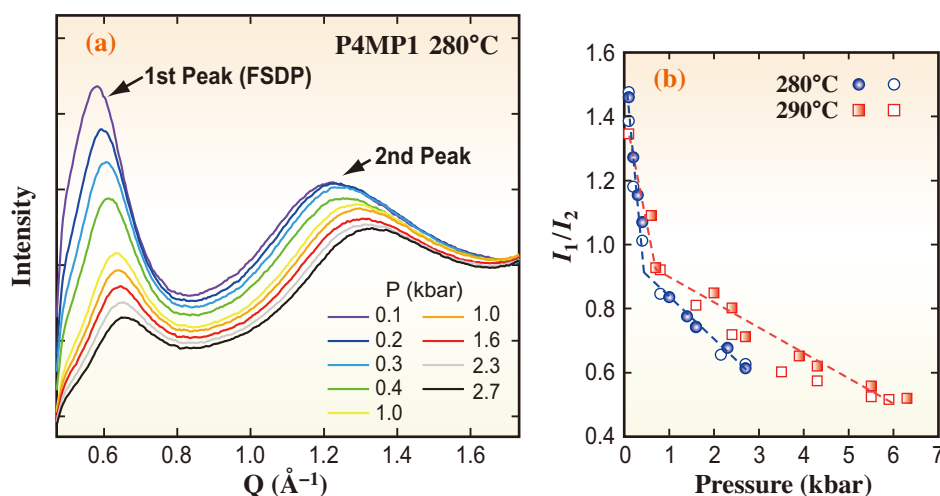


Fig. 2. (a) X-ray diffraction patterns of P4MP1 melt at 280°C. (b) Pressure dependence of the ratio of the intensities of the FSDP (I_1) to that of the second peak (I_2). Filled symbols show the data obtained under increasing pressure and open symbols under decreasing pressure. Broken lines are guides for the eyes.

to backbone-backbone correlation [5]. This is a correlation of dense backbones surrounding voids that are sparsely filled by the bulky side chains (Fig. 1(b) and Fig. 3(a)). Given that the origin of the FSDP is related to the correlation between backbones (Fig. 3(a)), we can assume that the rapid decrease in the intensity of the FSDP with pressure (Fig. 2) indicates a disordering of backbone-backbone correlations, and the shift to higher momentum transfers (Fig. 2 (a)) indicates a reduction of the void spaces between backbones. That is, the high compressibility we observe in the low-density melt is due to compaction

of the void space, which suppresses the backbone-backbone correlations (Figs. 3(a) and 3(b)).

In this study, we found evidence of the liquid-liquid transition (or continuous but sharp transformation) in P4MP1, which is characterized by a change in intermediate-range order. The finding that such a large change occurs in P4MP1 at easily accessible pressures is noteworthy, and originates from the nature of the loosely packed structure of the polymer with a bulky side chain. This and the moderate pressures and temperatures at which these phenomena occur open up the intriguing possibility of using liquid-liquid transitions as an industrial process to control the physical properties of plastics.

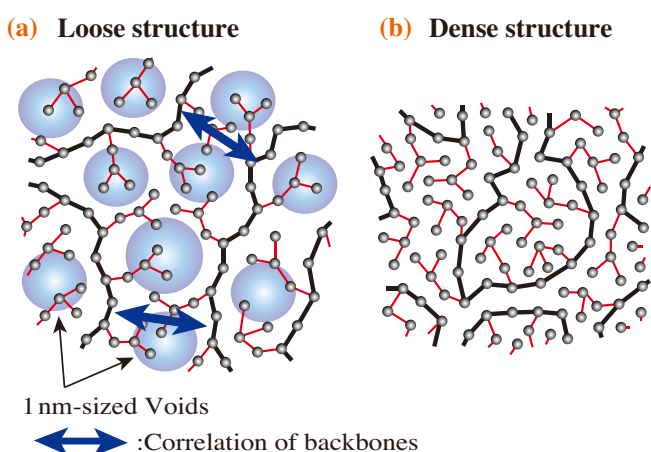


Fig. 3. Schematics of possible structures of P4MP1 melt. (a) Low-density melt and (b) high-density melt. Small spheres indicate carbon atoms, and thick black and thin red lines indicate the main and side chains, respectively. Blue arrows indicate correlations between backbones (main chains) and large blue circles indicate void spaces, both of which would cause the intermediate range order.

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