Macromolecules
COMMUNICATION TO THE EDITOR

Macromolecules **2010**, *43*, 2115–2117 **2115**
DOI: 10.1021/ma902662d

Molecular Aggregation Structures of Polyimide Films at Very High Pressure Analyzed by Synchrotron Wide-Angle X-ray Diffraction

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Received December 2, 2009
Revised Manuscript Received January 24, 2010

Introduction. Polyimides (PIs) are well-known high-performance engineering plastics exhibiting outstanding properties.[1] PIs have been used in a wide range of high-tech fields and also attracted much interest as a new class of thermally stable electronic and optical materials.[2-4] The aggregation structures of PIs have been investigated because they significantly influence the various properties of PI films, such as their thermal, mechanical, and optical properties.[5,6]

The molecular aggregation structures of PI chains have been investigated using wide-angle X-ray diffraction (WAXD).[7-14] For instance, Russell et al. reported that the aggregation structures of PMDA/ODA films ranged from amorphous structures to ordered crystalline structures depending on the film thickness and preparation conditions.[8] In general, PI films do not exhibit definitive crystalline diffraction peaks, which indicates the absence of large domains with three-dimensional positional order. Hence, the ordered domains with mesomorphic order between crystalline and amorphous phase in the film can be interpreted as liquid-crystalline-like (LC-like) ordered domains.

PIs have been frequently used in applications in which they encounter high pressures (> 1 GPa) such as shock compression and explosive applications.[15] X-ray diffraction patterns of conventional polymers have been measured under high pressure to examine the compression effects on their physical properties,[16-21] whereas the pressure-induced variations in WAXD patterns of PIs have never been examined. In this Communication, we examined the variations in the aggregation structures of PI chains in the ordered domains, which were generated at high pressures up to 8 GPa, using the synchrotron-radiation WAXD technique.

Experimental Section. The PI films of *s*-BPDA/PDA and PMDA/ODA (product name: Upilex-S and Kapton-V; thickness: ca. 25 μm; Figure 1) were kindly supplied by Ube Industries, Ltd. and DuPont-Toray Co., Ltd., respectively. A PMDA/DCHM film with a 20 μm thickness was prepared at our laboratory using equimolar amounts of pyromellitic dianhydride (PMDA) and 4,4′-diaminodicyclohexylmethane (DCHM). Because the proportion of *trans*−*trans* isomer of DCHM was estimated to be 94% by the ^{1}H NMR spectrum, most of the PMDA/DCHM chains should have an extended *trans*−*trans* configuration (Supporting Information).

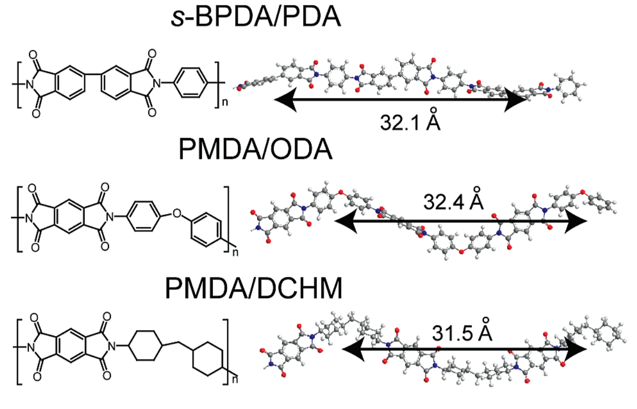

Figure 1. Molecular structure of PIs, optimized geometries of PI trimers, and the value of the calculated length of one pitch consisting of two repeating units obtained by DFT calculations at the level of [B3LYP/6-311G(d)].

The pressure experiment was carried out with a diamond anvil cell (DAC) using silicone oil as the pressure medium and ruby photoluminescence as the pressure calibration method.[22] Because the size of the sample chamber was only 230 μm in diameter, the transmission X-ray diffraction measurements were performed with a BL40B2 beamline at the Japan Synchrotron Radiation Research Institute (SPring-8) using an image plate as the detector. The wavelengths (λ) of the X-ray were 0.7 Å for *s*-BPDA/PDA and 0.8 Å for PMDA/ODA and PMDA/DCHM. The diffraction peaks assignable to silicone oil and diamond anvil cell were removed from the diffraction patterns by subtracting a reference pattern measured without a sample.

Results and Discussion. Figure 2 shows the pressure-induced variations in the diffraction patterns of three PI films. Figure 3a,b shows the variations in strain (ε) of each peak observed in Figure 2. Strain is defined as $\varepsilon_{(hkl)} = \Delta d/d_{0,(hkl)}$, where $d_{0,(hkl)}$ is the *d*-spacing of the (*hkl*) plane at 0 GPa and Δd the variation in *d*-spacing at high pressures. First, *s*-BPDA/PDA having a pseudo-rigid-rod molecular structure was reported to form a crystalline structure based on the orthorhombic unit cell.[11] At 0 GPa, this PI exhibits a (004) peak at $q = 7.9$ nm^{-1} and a (110) peak at 12.7 nm^{-1}. The former peak represents the periodic structure along the PI chains (*c*-axis), and the latter peak represents the intermolecular ordering of the PI chain packing (*a*- and *b*-axes), which are perpendicular to the PI chains. Second, PMDA/ODA exhibits a peak at $q = 4.0$ nm^{-1} at 0 GPa. This peak was indexed as a (002) peak, which represents half the value of the length of a curved structure consisting of two repeating units (L) corresponding to the periodic structure along the PI chains.[7] Third, PMDA/DCHM exhibits a sharp peak at $q =$ 3.9 nm^{-1} and a broad peak at 12.4 nm^{-1} at 0 GPa. Since half of the calculated L value ($d = 15.7$ Å, see Figure 1) is close to the *d*-spacing estimated from the peak at 3.9 nm^{-1} (16.1 Å), the former peak can be indexed as (002). Although no diffraction peaks assignable to the crystalline region were observed in PMDA/DCHM, the bandwidth of the scattering at 12.4 nm^{-1} is much narrower than those of amorphous halos.[8] Thereby, this peak can be characterized as the scattering representing the PI chain packing (ch-pack) in the mesomorphic order region interpreted as LC-like

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ordered domains. This peak is partly overlapped by an amorphous halo.

The *d*-spacing of the (004) peak, *d*(004), of *s*-BPDA/PDA was gradually decreased by 0.7% from 0 to 6 GPa, which is mainly caused by shrinkage of the skeletal structure because this PI has a pseudo-rigid-rod structure without bent linkages. The higher frequency shifts of IR vibrational modes in poly(methyl methacrylate) (PMMA) and polycarbonate induced by high pressure (~5 GPa) were also attributed to the decrease in bond lengths by Covington et al.[18,19] In the case of PMDA/ODA, which has a bent diphenyl ether linkage, it should be noted that the value of *d*(002) was not decreased but increased by 0.3% by applying pressure up to 0.4 GPa. The compression stress induced by pressure can be concentrated at the ether linkage in the main chain, and thus a widening of the C−O−C angle leads to a stretch of the pitch consisting of two repeating units (see Figure 1). At further elevated pressures up to 6 GPa, the value of *d*(002) was, in turn, decreased by 1.0%, which is mainly attributable to shrinkage of the skeletal structure, similar to *s*-BPDA/PDA. In contrast, the value of *d*(002) of semialiphatic PMDA/DCHM significantly decreased by 5.3% from 0 to 6 GPa. The slope of variation gradually decreased above 2 GPa. Christian et al. reported the effective conversion of halogenated cyclohexanes from the equatorial to the axial forms by applying pressure.[23] Thus, such a significant decrease in the values of *d*(002) could be accompanied by the conformational changes occurring at the $-CH_2-$ linkage or the cyclohexane structures in the diamine moiety.

By applying pressure up to 6 GPa, the values of *d*(110) of *s*-BPDA/PDA and *d*(ch-pack) of PMDA/DCHM significantly decreased by 11 and 14%, respectively (see Figure 3b). The variations in ε of these peaks were much larger than those along the PI chains (00*l*). This clearly indicates that the periodic structures along the interchain distances possess much larger compressibility compared with the periodic length along the main chains. Figure 3c depicts the variations in the linear compressibilities (κ) for the diffraction peak of (110) (κ_{110}) of *s*-BPDA/PDA and that for the peak of ch-pack ($\kappa_{\text{ch-pack}}$) of PMDA/DCHM. The κ values were estimated as the numerical first derivatives of strain with respect to pressure ($\kappa = \partial\varepsilon/\partial P$). The values of $\kappa_{\text{ch-pack}}$ were significantly larger than those of κ_{110} below 2 GPa. This indicates that the semialiphatic PMDA/DCHM contains larger amounts of interchain free volume in the LC-like ordered regions, and the free volume is more compressible below 2 GPa. In contrast, the fully aromatic *s*-BPDA/PDA contains smaller amounts of compressible free volume in their ordered region. Furthermore, the trend of a significant decrease in $\kappa_{\text{ch-pack}}$, which represents the loose chain packing of PMDA/DCHM, was completed at around 2 GPa, and the pressure dependences of $\kappa_{\text{ch-pack}}$ and κ_{110} got close to each other above this pressure. This suggests that the easily compressible free volume of PMDA/DCHM almost disappeared at 2 GPa, and both PIs demonstrate similar compressibility at higher pressures. A similar phenomenon was observed in the variations of the free volume of PMMA and polycarbonate at high pressures.[18,19]

Figure 4 displays the pressure dependence of the κ_{110} values of four semicrystalline polymers having orthorhombic unit cells.[24] The κ_{110} of *s*-BPDA/PDA at 0 GPa is much smaller than those of other polymers. Since the compressibility of polymer crystals decreases by increasing packing density,[24] *s*-BPDA/PDA has inherently very dense interchain packing at atmospheric pressure. This is attributable to the dense packing of pseudo-rigid-rod PI chains reinforced by electrostatic interactions due to the high polarity of aromatic and imide rings. In addition, note that

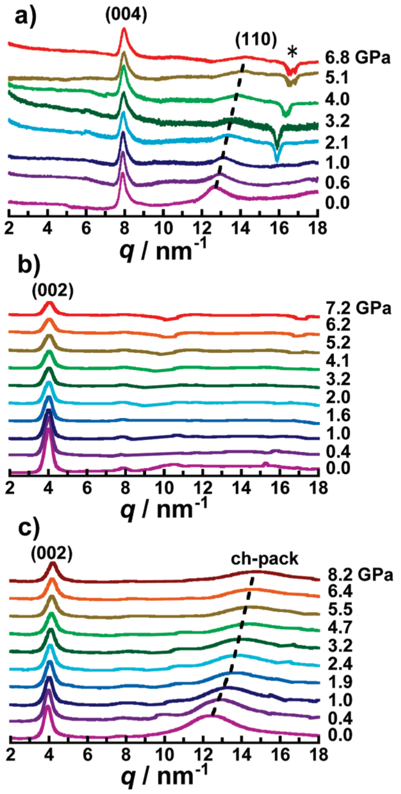

Figure 2. Variations in the X-ray scattering patterns for (a) *s*-BPDA/PDA, (b) PMDA/ODA, and (c) PMDA/DCHM PI films by applying pressure. The negative peaks indicated with asterisks (*) arise from nonperfect spectral subtraction of the pressure medium (silicone oil).

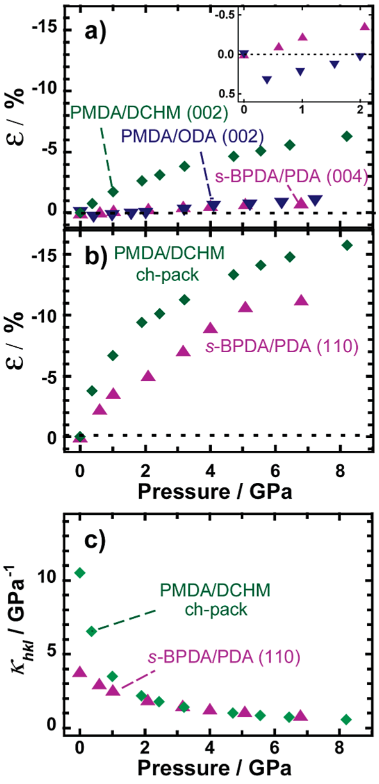

Figure 3. Variations in the strains (ε) of (a) (00*l*) and (b) chain packing peaks by applying pressure. The inset shows a magnified representation at around 1 GPa. (c) Variations in the linear compressibilities (κ) along the (110) plane of *s*-BPDA/PDA and the ch-pack of PMDA/DCHM.

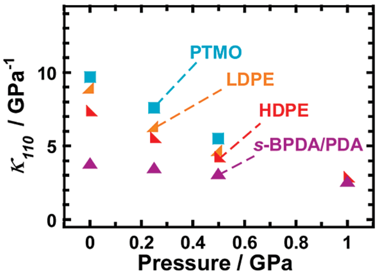

Figure 4. Variations in the linear compressibilities along the (110) plane of *s*-BPDA/PDA (this work), poly(tetramethylene oxide) (PTMO), and low/high-density polyethylene (LDPE/HDPE) orthorhombic crystals.[24]

the κ_{110} values of *s*-BPDA/PDA and the other polymer crystals get close to each other at 1 GPa. This indicates that the compressible volumes in these polymer crystals almost disappeared at this pressure.

Conclusion. The wide-angle X-ray diffraction patterns of three kinds of fully aromatic and semialiphatic polyimides (PIs) were measured under high pressure up to 8 GPa using a diamond anvil cell. For *s*-BPDA/PDA having a pseudo-rod-like structure, the *d*(004) value was slightly decreased due to the shrinkage of bond lengths under high pressure, whereas the *d*(002) of PMDA/ODA having an ether linkage in the main chain increased up to 0.4 GPa, which should have originated from the bond angle change at the ether group. The *d*(002) of PMDA/DCHM having a methylene linkage and two cyclohexane rings in the main chain was significantly decreased, which should have been due to the structural change in the flexible diamine moiety. The variations in *d*(110) of *s*-BPDA/PDA and *d*(ch-pack) of PMDA/DCHM at higher pressures were significantly larger than those of *d*(00*l*) in both PIs, which indicates that the interchain distances are much more compressible than the periodic length along the PI chains. Semialiphatic PMDA/DCHM exhibited a significant decrease in *d*(ch-pack) below 2 GPa, which is attributable to an appreciable decrease in the interchain free volume. In contrast, *s*-BPDA/PDA showed a much smaller decrease in the interchain distance (*d*(110)), which is due to the highly ordered packing structure of the PI chains.

Acknowledgment. The synchrotron radiation experiments were performed with a BL40B2 beamline with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2008B-1434, 2009A-1348). The authors thank Kei Hirose and Ryosuke Sinmyo at the Department of Earth and Planetary Sciences, Tokyo Institute of Technology, for advice on diamond anvil cell. We also thank Kazuyuki Horie at JASRI for helpful discussions.

Supporting Information Available: Experimental details (synthetic procedures and synchrotron radiation) and transmission X-ray scattering patterns at atmospheric pressure. This material is available free of charge via the Internet at http://pubs.acs.org.

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