PS-9

DIFFERENCE IN STRUCTURAL CHANGES BETWEEN POLYIMIDES CONTAINING AMIDE AND ESTER LINKAGES INDUCED BY VERY HIGH PRESSURE

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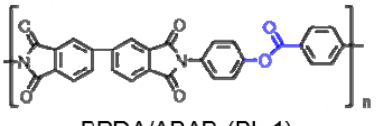
Intoroduction

Polyimides (PI) are widely known as high-performance engineering plastics exhibiting high thermal stability, mechanical strength, and good flexibility. The aggregation structures of PIs exert significant influences on physical properties, such as density, refractive index, thermal expansion, and thermal conductivity. These properties can be enhanced by applying high pressure due to the formation of dense aggregation structures induced by high pressure. Recently, relationships between the aggregation structures and the optical properties of PIs having different chemical structures were investigated by wide-angle X-ray diffraction (WAXD) and UV/vis absorption spectroscopy under very high pressure up to 8 GPa.[1] In those studies, similar dependence of the aggregation structure on pressure was observed irrespective of the chemical structure. However, inter-chain interactions and the local conformations of PIs should affect the aggregation structure under high pressure. Thereby, we focused on amide linkage in PI chains, which has unique characters such as hydrogen bond (H-bond) and planar conformation. In this study, structural changes were investigated for two analogous PIs, *i.e.* one with an amide linkage and another with an ester linkage in the backbone, by using UV/visible absorption and FT-IR spectroscopies (Fig. 1).

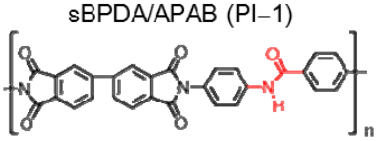
Figure 1. Schematic illustration of change in the aggregation structure under very high pressure.

Experimental

The molecular structure of the PIs used in this study is shown in Fig 2. A diamond anvil cell (DAC) with 600 μm diamond culets was used to apply high pressure up to 8 GPa to the PIs (Fig. 3). The pressure inside the sample chamber of the DAC was measured by the standard ruby fluorescence technique. The UV/visible absorption spectra of the films loaded in a DAC at elevated pressures were measured with multichannel CCD spectrometer in the range of 200–950 nm, using a Xe lamp as a light source and a silicone oil as the pressure medium. The infrared absorption spectra of the films in the DAC were measured by an IRT-3000 infrared microscope (JASCO Co., Ltd.), using KBr as the pressure medium.



sBPDA/APAB (PI–1)



sBPDA/DABA (PI–2)

Figure 2. Molecular structure of PI-1 and PI-2.

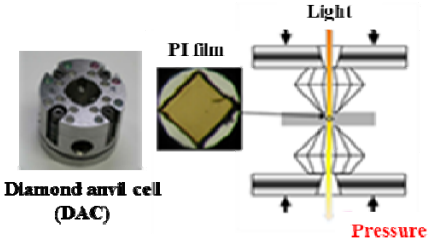


Figure 3. Optical microscope image of the DAC and a PI film in DAC and schematic presentation of a cross-section of DAC.

Results & Discussion

The UV/vis absorption spectra of *s*BPDA/APAB (PI-1) and *s*BPDA/DABA (PI-2) under very high

pressure are shown in Fig. 4. Pressure-induced bathochromic shifts are observed. The shift indicates that inter-chain distances decrease with pressure, because the band gap decrease with increasing van der Waals interactions which depend on an inter-chain distance. The wavelengths at the point that the intensity is 1.0, λ_{OD1}, shifted to longer wavelengths with pressure. The values of λ_{OD1} are plotted against pressure (Fig. 5). The change rates (slope) of λ_{OD1} in lower pressure region are larger than that in higher pressure region. This result implies that free volume mainly decreases in lower pressure region. The inflection point of the slope for PI-1 was lower than that for PI-2.

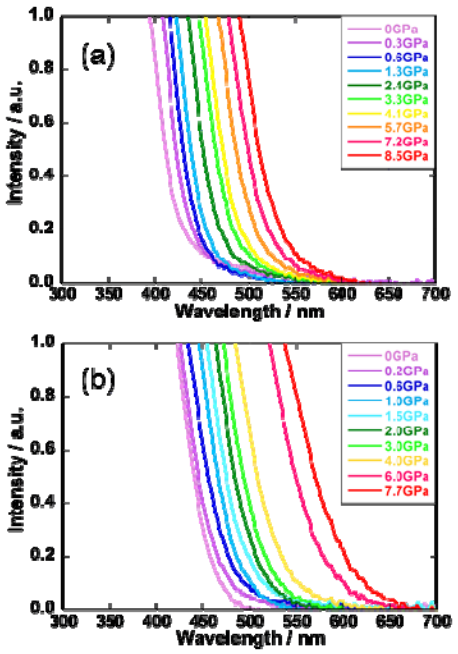


Figure 4. Pressure dependence of UV/visible absorption spectra of (a) PI-1 and (b) PI-2.

The IR spectra of PI-1 and PI-2 were measured under very high pressure and clear shifts of the band peaks were observed. In general, the peak shifts of IR-band to higher wavenumber are caused by increasing in binding constants (*k*) of the covalent bonds. The peak shifts of C–N stretching vibration bands of PIs are plotted against pressure (Fig. 6). The peak shifts are almost zero at lower pressure region, while they increase at higher pressure region. This result implies the large distortion of the C–N bonds in the backbones is induced in high pressure region, while little distortion is induced at low pressure region. In this measurement, the peak-shift of PI-1 drastically changes at lower pressure than that of PI-2 does, similarly to the result of UV/vis absorption measurement.

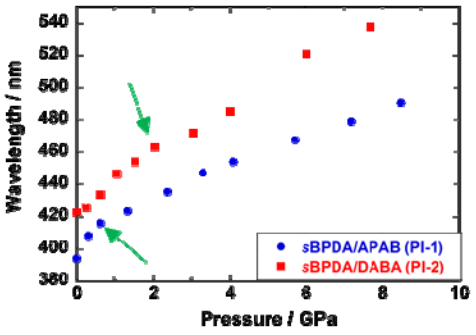


Figure 5. Pressure-induced shifts of the UV/vis absorption wavelengths where intensity is 1.0; PI-1 (blue) and PI-2 (red).

Above two spectroscopic results indicate that the amide linkage tend to suppress the pressure-induced structural changes in both the inter-chain distance scale (the aggregation structure) and the intra-chain distance scale (the backbone distortion), while the ester linkage resulted in a similar pressure-dependence to the other PIs without an amide linkage.[1]

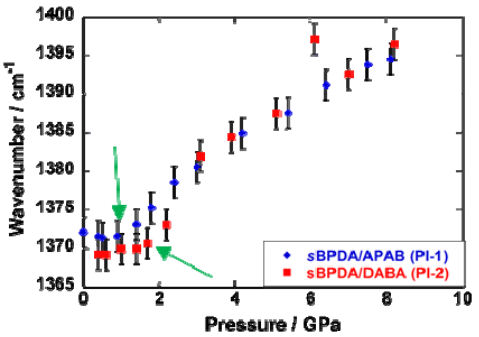


Figure 6. Peak shifts of C–N stretching vibration bands of PI-1 and PI-2 with pressure.

In this study, pressure induced structural changes of two similar PIs with amide or ester linkages were investigated by UV/vis and IR spectroscopic method. It is concluded that the amide group shows an effect to suppress the changes of aggregation structures and backbone distortion induced by pressure thorough the unique characteristics such as the H-bond and the coplanar nature.

References:

1. K. Takizawa, J. Wakita, S. Azami, S.Ando, *Macromolecules,* 2011, **44**, 349. *ibid*. 2012, **45**, 4764. *ibid*. 2014, **47**, 3951.