



Characteristic changes in the structures and properties of polyimides induced by very high pressures up to 8 GPa

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Abstract

Various in situ measurement techniques have been applied to investigate changes in the three-dimensional structures and the properties of fully aromatic polymers (mainly aromatic polyimides: PIs) generated at very high pressures up to 8 GPa. In particular, significant changes occurred in the ordered structures, aggregation states, electronic structures, and intermolecular interactions in the repeating units of the PI molecular chains and were observed by applying pressure with a high-pressure optical cell (up to 0.4 GPa, ca. 4000 atm) or a diamond anvil cell (DAC, up to 8.0 GPa, ca. 80,000 atm). In addition, the structural changes in the PI molecular chain repeating units and interchain distances induced by the ultrahigh pressures were observed with wide-angle X-ray diffraction, and they were compared and contrasted with optical absorption, fluorescent and phosphorescent emission spectra, infrared absorption spectra, and refractive indexes observed under the same conditions. These findings obtained at very high pressures provide molecular design guidelines for new PI materials with novel optical, electronic, and thermal functionalities that are not easy to achieve under ambient conditions.

Introduction

Among heat-resistant, tough and flexible superengineered polymers, aromatic polyimides (PIs) have been widely used in a variety of high-tech industries with aerospace, electric, electronic, and optical applications owing to their high thermal and chemical stabilities, radiation resistance, and mechanical strengths [1–3]. In addition, semialiphatic polyimides (Al-PIs) have recently been developed to produce electronic and optical materials owing to their high optical transparencies within the ultraviolet (UV)/visible region, low refractive indices, low dielectric constants, and photoluminescence properties [4–7].

The polymer chains of aromatic PIs, which withstand the harshest operating environments, have donor-acceptor structures consisting of alternating “acid anhydride” and “diamine” moieties that act as electron acceptors and electron donors, respectively. The intramolecular and

intermolecular charge-transfer (CT) interactions of the PI chains are one reason why the physical properties of the PIs change depending on the electron-donating properties of the diamines, the electron-accepting properties of the dianhydrides, and the aggregation state of the PI chains. Therefore, investigations of the relationships between the ordered structures, aggregation states, local motions of molecular chains, and intermolecular interactions are essential for understanding the photonic, electronic, and thermophysical properties of the PIs and to improve their functionality and performance.

The application of high pressures to aromatic polymers changes their three-dimensional structures and aggregation states, which cause anisotropic compression and expansion and significantly impacts their optical, dielectric, and thermal properties. After Bridgman (Nobel Prize in Physics, 1946) developed the essential techniques for high-pressure devices, Merrill-Bassett [8] developed diamond anvil cells (DACs) based on the high-pressure anvil cell devices conceived by Drickamer [9]. Although several review papers have been published on the use of high pressure techniques and their applications to inorganic condensed matter, only one comprehensive review has been published, by Knaapila and Guha, on high pressure studies of π -conjugated polymers [10]. Guha and coworkers [11, 12] observed significant redshifts in the absorption and photoluminescence

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Fig. 1 Chemical structures of typical aromatic and semialiphatic polyimides (PIs)

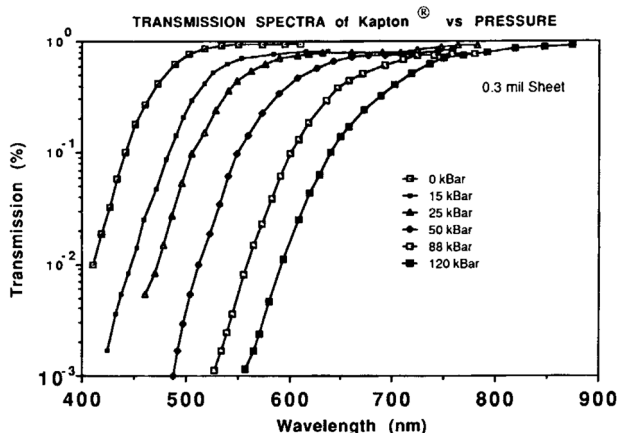
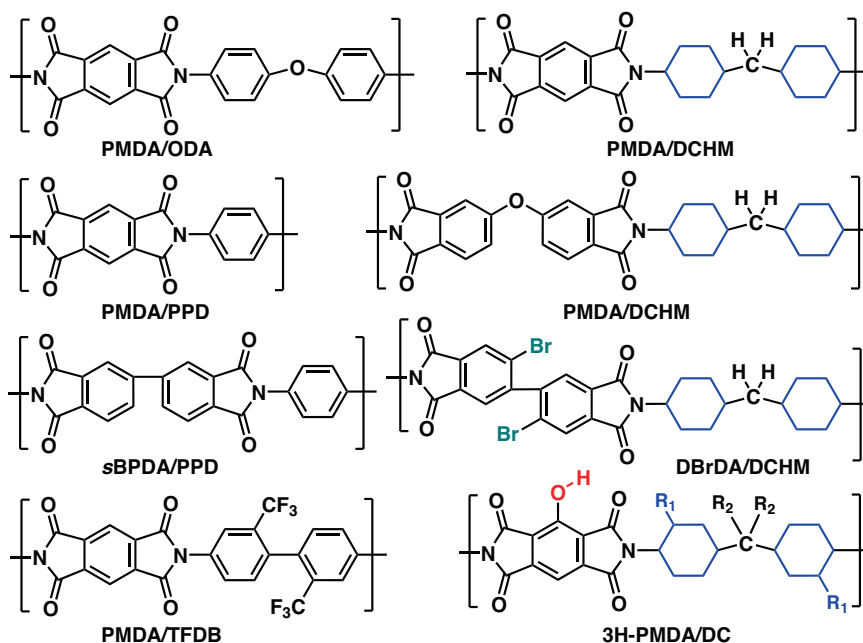


Fig. 2 Transmission spectra of the Kapton film measured as a function of pressure at room temperature [13]. Copyright 1988 John Wiley & Sons

(PL) peaks for ladder-type poly(para phenylene) at elevated pressures (0.1 MPa to 7.3 GPa) in addition to broadening of the individual vibronic structures. At lower pressures, a sharp change was observed in the PL energies owing to planarization of the polymer chains.

Spectroscopic changes in polyimides induced by ultrahigh pressures

In 1988, Erskine and coworkers [13] reported the optical absorption spectra of Kapton (PMDA/ODA) PI films (Fig. 1) at elevated pressures, as shown in Fig. 2, which was part of a pioneering work investigating the high pressure

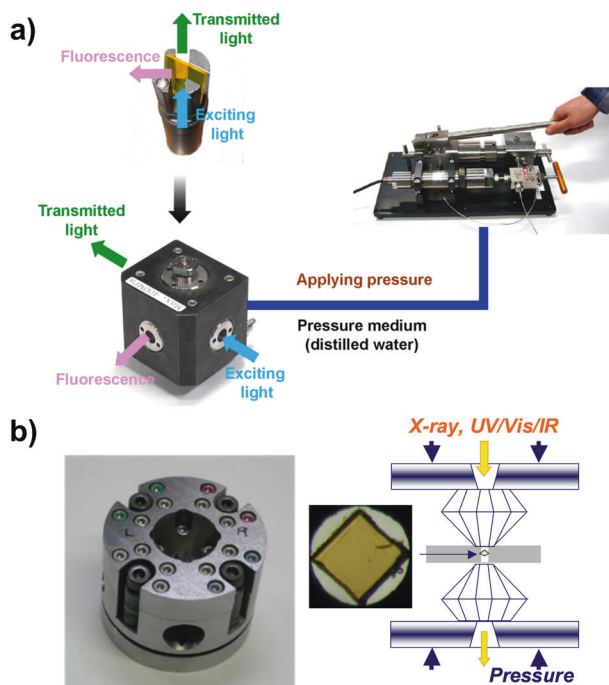


Fig. 3 Photograph and schematic view of (a) a high-pressure cell and a hand pump generating pressures of up to 400 MPa (0.4 GPa) [14]. (b) Photo and schematic view of a type of DAC generating pressures up to 8 GPa

changes occurring in the optical properties and electronic states of fully aromatic polymers. They concluded that the significant pressure-induced redshifts of the absorption band edge were understandable in terms of intermolecular CT transitions between the imide and diphenyl ether portions of the PI backbones.

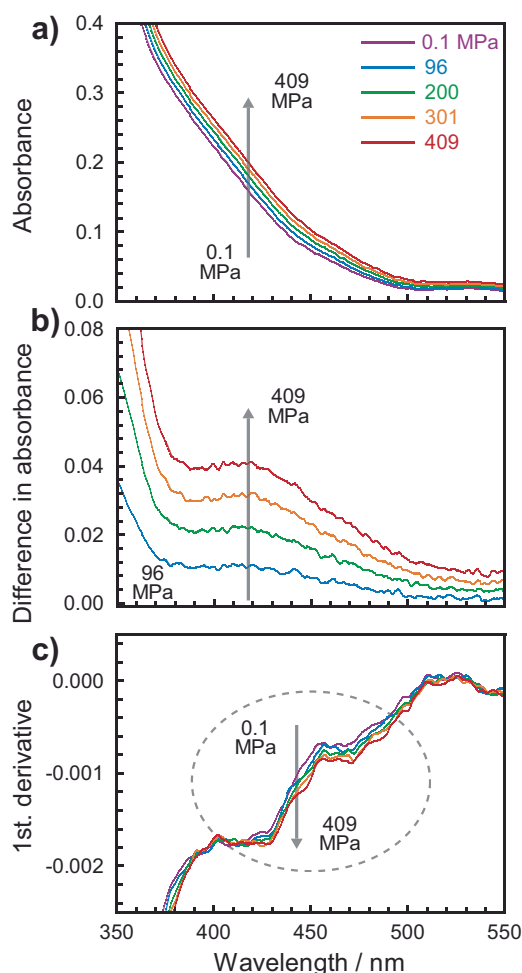


Fig. 4 Pressure dependence of the (a) optical absorption spectra, (b) absorption differential spectra, and (c) first derivative spectra for a PMDA/ODA thin film [14]. Copyright 2009 American Chemical Society

After two decades, Wakita and Ando et al. [14] observed changes occurring in the optical absorption spectra of thin film PMDA/ODA PI at pressures up to 400 MPa by using a custom-built hydrostatic pressure optical cell and a hand pump (Fig. 3). As shown in Fig. 4, a pressure-induced increases in absorbance were observed for the CT absorption bands of PMDA/ODA and PMDA/TFDB (Fig. 1) PIs in the visible region, which indicated that the bands were assignable to intermolecular CT transitions. A pressure-induced redshift with increasing spectral bandwidth was also observed for a locally excited (LE) absorption band in the UV region for a semialiphatic *s*BPDA/DCHM (Fig. 1), which was related to an increase in van der Waals interactions arising from reduced intermolecular distances. In contrast, a pressure-induced bathochromic shift without an increase in absorbance was observed for the CT band of *s*BPDA/PPD (Fig. 1), which indicated that this band was assignable to an intramolecular CT transition. It should be noted that these pressure-induced changes can be utilized to

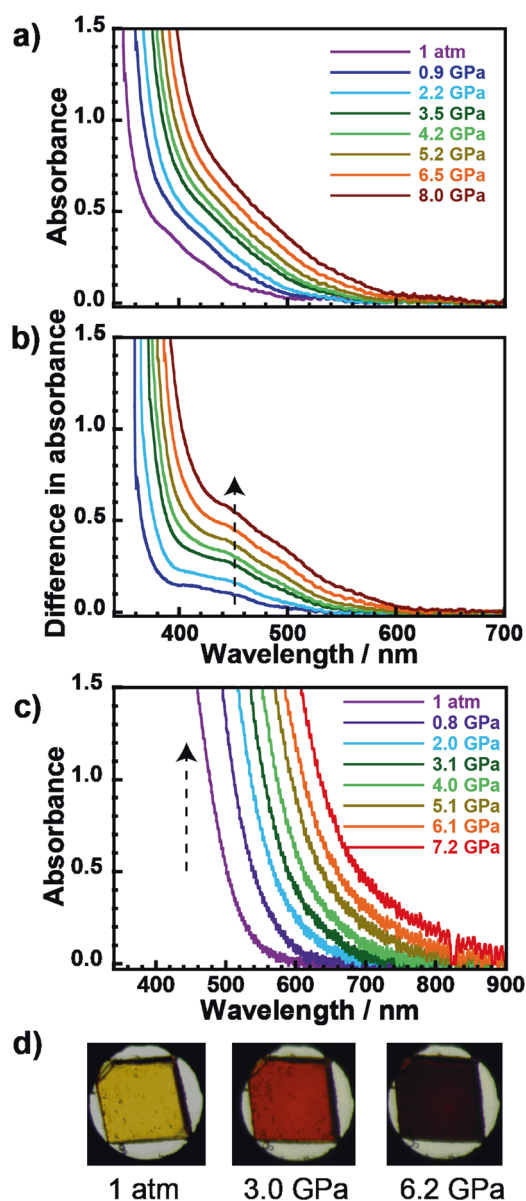


Fig. 5 Pressure dependence of the (a) UV/visible absorption spectra and (b) absorption differential spectra for a PMDA/ODA thin film. (c) Pressure dependence of the UV/visible absorption spectra for PMDA/ODA thick film. (d) Pressure-induced variations in the color of a PMDA/ODA thick film [15]. Copyright 2011 American Chemical Society

characterize the absorption bands seen at longer wavelengths for PIs.

Subsequently, Takizawa and Ando et al. [15] observed changes occurring in the optical absorption spectra of thin films of PMDA/ODA, PMDA/DCHM, and *s*BPDA/PPD PIs at pressures of up to 8 GPa by using a custom-built diamond anvil cell (DAC, Fig. 3). Pressure-induced redshifts were observed for the LE absorption bands of PIs, which were related to enhanced van der Waals interactions caused by the reduced interchain distances. Note that the intensity of the CT absorption band for *s*BPDA/PPD PI was

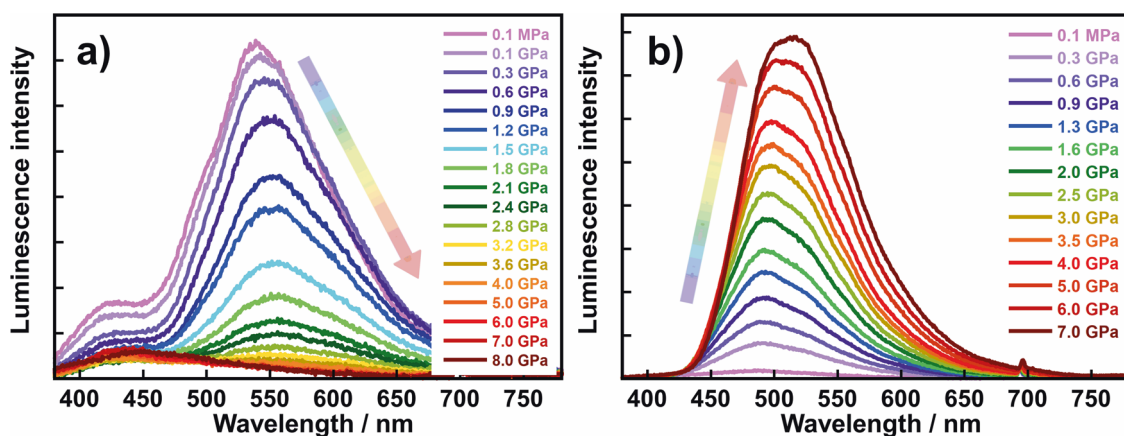


Fig. 6 Pressure dependence of the photoluminescent spectra for thin films of (a) DBrDA/DCHM and (b) DBrDA-MC dispersed in PMMA [26]

not increased but was reduced at up to 0.3 GPa, indicating that conformational changes affected the intramolecular CT interactions. In contrast, the CT absorptions of PMDA/ODA and PMDA/DCHM PIs were effectively enhanced by increasing the pressure, as shown in Fig. 5 which was caused by enhancement of the intermolecular CT interactions. Note that apparent densifications in color from pale yellow through reddish brown to blackish brown were observed for these fully aromatic PIs.

The spectroscopic measurements made under high pressure were extended to include fluorescence (FL) and phosphorescence (PH) emission spectra. In 2009, Wakita and Ando [6] proposed a molecular design concept for thermally stable and highly fluorescent PIs as follows: (1) alicyclic diamines and (2) aromatic dianhydrides with flexible linkages and extended conjugation were used, and a series of highly fluorescent PIs was developed by using aromatic dianhydrides, such as *s*BPDA, ODA, 1,4-bis(3,4-dicarboxytrifluorophenoxy)tetrafluorobenzene dianhydride (10FEDA), and alicyclic diamines such as DCHM (Fig. 1). Takizawa and Ando et al. [16] reported that the FL intensity of a 10FEDA/DCHM PI film imidized at 220 °C was significantly reduced by applying pressures up to 1 GPa, which was due to an appreciable reduction in the interchain free volume. In contrast, a PI film imidized at 300 °C, which exhibited weaker fluorescence, demonstrated a much smaller reduction in fluorescence intensity below 1 GPa. These differences in pressure dependence obviously reflected the degrees of PI chain packing resulting at different temperatures. Furthermore, Kanosue and Ando et al. [17, 18] synthesized highly phosphorescent PIs by utilizing the heavy atom effects of bromine and iodine atoms. As shown in Fig. 6a, the intensity of the green PH peak of DBrDA/DCHM, for which intersystem crossing was enhanced by bromine, was significantly attenuated by pressures up to 8 GPa, and this analysis provided information on the photophysical processes occurring in the excited

state, especially intermolecular exciton energy transfer [16]. In contrast, the PH intensity of the model compound (MC) of DBrDA/DCHM dispersed in PMMA markedly increased at pressures up to 7 GPa (Fig. 6b). This was considered to be a ‘pressure-induced phosphorescence enhancement’ caused by suppression of the vibrational motion by pressure because localized vibrations are another cause of exciton energy dissipation in the triplet state.

Takizawa, Wakita, and Ando et al. [15, 19–21] measured wide-angle X-ray diffraction (WAXD) patterns of fully aromatic and semialiphatic PIs under high pressures up to 8 GPa. For the *s*BPDA/PPD PI, the $d(004)$ spacing along the *c*-axis was slightly decreased due to shrinkage of the bond lengths under high pressure (figure is not shown) [19], whereas the $d(002)$ spacing of PMDA/ODA surprisingly increased at pressures up to 0.4 GPa, which originated from bond angle changes at the ether groups. (Fig. 7) [20]. In contrast, the $d(002)$ spacing of PMDA/DCHM was significantly decreased, which was due to structural changes involving the flexible diamine moieties. The changes in the $d(110)$ spacing of *s*BPDA/PPD and the $d(\text{ch-pack})$ spacing of PMDA/DCHM at higher pressures were significantly larger than those of the $d(001)$ spacings in both PIs, which indicated that the interchain distances were much more compressible than the periodic lengths along the PI chains.

A similar trend was also observed for colorless transparent semiaromatic PIs developed to intentionally suppress the CT interactions inherent in PIs, but the correlations with ordered/aggregated structures were not clear due to their low crystallinities. Therefore, the pressure dependence of absorption peaks for the PI molecular chain direction (C–N stretching vibration) and for the interchain direction (C=O asymmetric stretching vibration) were combined in microscopic FT-IR measurements performed under high pressure [19]. The former showed a clear inflection point at 2 GPa and the latter at 1 GPa, which suggested that in the low pressure range (<1 GPa), the free volumes of the easily

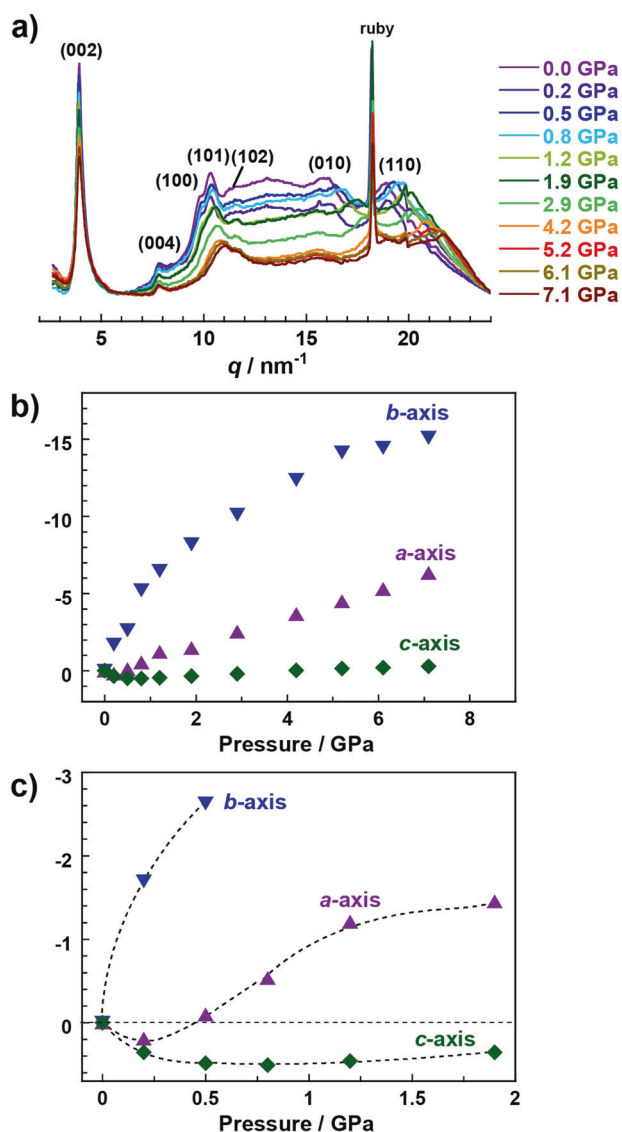


Fig. 7 Variations in (a) the X-ray diffraction patterns and (b) the strains along the *a*-, *b*-, and *c*-axes for a PMDA/ODA PI powder as a function of applied pressure. (c) Magnified representations of the strains induced at lower pressures [20]. Copyright 2014 American Chemical Society

compressible molecular chains were first reduced, followed by compressive stress mainly along the side chains at pressures up to 2 GPa; beyond that, strong compressive stress was applied in the molecular chain direction, resulting in significant structural changes in the bond lengths and bond angles of the PI molecular chains. Interestingly, the physical properties of the PIs exhibited inflection points at approximately 1–2 GPa, almost independent of the PI molecular structure, which was universally observed.

Fujiwara and Ando et al. [22] investigated the relationships between the photoexcitation dynamics and the structures of semialiphatic PIs by using ultrafast fluorescence emission spectroscopy at pressures of up to 4 GPa. The 3HPMDA-PI

films exhibited prominent fluorescence with extremely large Stokes shifts exceeding $10,000\text{ cm}^{-1}$ due to excited-state intramolecular proton transfer (ESIPT). 3HPMDA-PI films showed fluorescence peaks at shorter wavelengths originating from the closely packed aggregated PI chains, and the fluorescence occurred through Förster resonance energy transfer (FRET) from an isolated enol to aggregates. The efficiency of the FRET and the emission intensity of the aggregated forms were substantially increased by applying pressures up to 1 GPa due to effective compression of the interchain free volume and additional gradually increased even more at higher pressures owing to structural and/or conformational changes in the main chains (Fig. 8).

In addition, Fujiwara and Ando et al. [23] discussed the lattice deformations resulting from increases in the pressure or temperature of a rigid-rod PMDA/PPD PI prepared by a hydrothermal synthesis, which were enhanced by increases in the weight density of the lattice. As shown in Fig. 9, this unique behavior was caused by suppression of the lattice deformation by means of “*misfit strain*”, which is induced by a mismatch of the interchain distances between the crystalline and noncrystalline domains. With lattice compression under high pressures, interchain compression was suppressed with a decrease in the crystallinity and/or an increase in the number of PI chains penetrating the interfaces between the crystalline and noncrystalline domains. This was caused by enhancement of the misfit strain in the crystalline lattice. In contrast, the lattice strain along the main-chain direction increased with increases in the volume fractions of the compressible space near the PI chain ends included in the crystalline domains.

Furthermore, Ueda, Higashihara, and Ando et al. [24] developed various PIs with high refractive indexes ($n > 1.8$) and low birefringences (Δn) that were used in the micro-optical elements in electronic devices. Since the average refractive indexes (n_{av}) of polymers are almost proportional to their densities, the n_{av} values of PIs should be increased at higher pressures. Anisotropic Brillouin scattering was measured for an sBPDA/PPD film in a DAC, and it was found that n increased by 0.12 and Δn decreased by half when a pressure of 2 GPa was applied [25]. The increase in n_{av} corresponded to an increase in density of 11.3%, which was consistent with the volume compression ratios determined with WAXD measurements. However, as with other physical properties, the high refractive indexes generated at higher pressures were not easily fixed because the material quickly returned to its prepressurized state after depressurization.

Conclusion

A variety of in situ spectroscopic and diffraction techniques have been used to observe characteristic changes occurring

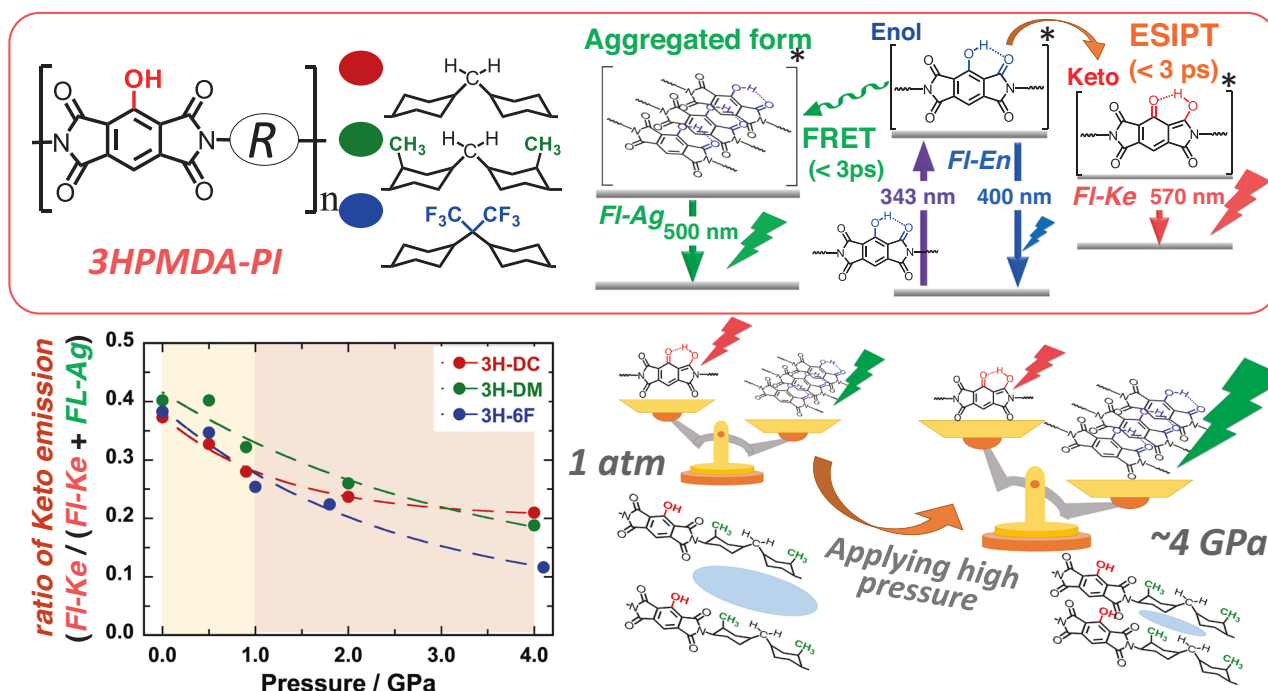


Fig. 8 Schematic representation of the excitation and emission mechanism for a 3H-PMDA/DC PI films and pressure-induced variations in the amplitude ratio of ESIPT emission (FI-Ke) to aggregation state emission (FI-Ag) [22]. Copyright 2021 American Chemical Society

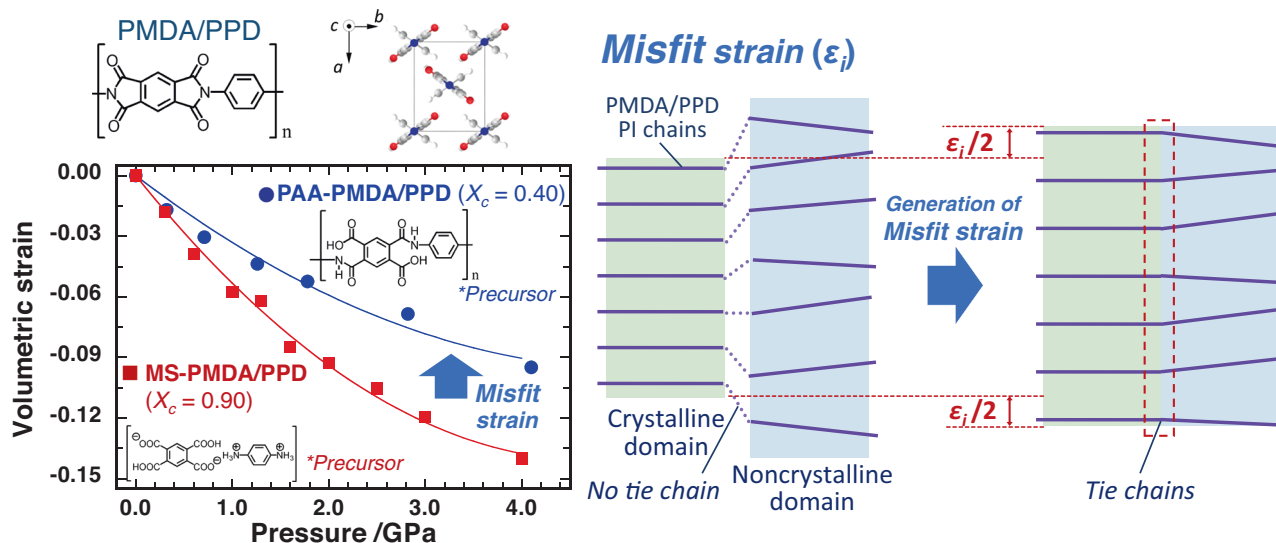


Fig. 9 Schematic two-phase models for semicrystalline PMDA/PPD PI powders with induction of misfit strain in the crystalline lattice [23]. Copyright 2021 American Chemical Society

in the structures and physical properties of aromatic/semi-aliphatic polyimides (PIs) under very high pressures by using a high-pressure optical cell (up to 4,000 atm) or a diamond anvil cell (DAC, up to 80,000 atm). The anisotropic changes in the ordered structures, aggregation states, electronic structures, and local motions of PIs resulting from the applied pressures have been observed, and the effects of compression on the intermolecular interactions and

photophysical processes have been evaluated. For instance, the structural changes occurring in the repeat units of the PI chains and the intermolecular distances caused by high pressures were observed with wide-angle X-ray diffraction and newly developed spectroscopic systems. High pressures also suppress molecular motions, deform molecular structures (bond lengths, bond angles, dihedral angles), and enhance intra- and intermolecular interactions. High-

pressure experiments have allowed us to explore the relationships among the stereochemical/aggregation structures, electronic states, and optical, thermal, and dielectric properties for the development of functional PIs.

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Compliance with ethical standards

Conflict of interest The author declares no competing interests.

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