



Effects of UV Crosslinking under High Temperature on the Refractive Indices and Aggregation Structures of Benzophenone-containing Polyimides

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For controlling the optical and thermal properties of photo-sensitive benzophenone (BP)-containing polyimides (PIs), an attempt was made to fix the dense polymer chain packing induced by high pressure using intermolecular crosslinking reactions. The effects of temperature and pressure during UV irradiation on the reaction rates of photo-crosslinking and refractive indices were evaluated. After UV irradiation at ambient temperature and pressure, refractive indices of the PIs increased due to the densification of chain packing. The degree of crosslinking was further increased with increasing the irradiation temperature. The PI films irradiated at 400 MPa exhibited higher refractive indices than those irradiated at 0.1 MPa, despite the nearly identical reaction rates. The fluorescence intensities of the PIs irradiated at 400 MPa showed smaller dependence on the pressure than those irradiated at 0.1 MPa, which indicates that the dense chain packing formed under high pressures was partially and effectively fixed by UV irradiation. The increase in refractive indices of the PIs irradiated at elevated pressures is attributable to the densification of aggregation structures, which was controllable by pressure under UV irradiation.

Keyword: Polyimide, Intermolecular crosslinking, High pressure, Refractive index, Aggregation structure

1. Introduction

Polyimides (PI) are super-engineering plastics exhibiting high thermal and chemical stability, flame retardancy, radiation resistance, high mechanical strengths, and good flexibility [1]. They have been widely used in aerospace, electric, electronic, and optical/photonic applications.

The optical and thermal properties of polymers are closely related to their aggregation structures which can be controlled by pressure and temperature [2–4]. For instance, the density, the refractive index, and the thermal conductivity of polymers can be enhanced by applying pressure, which is due to the dense chain packing formed under high pressure [5–8]. However, in many cases, the aggregation structures and the enhanced properties of polymers are reverted to their original states after depressurization. Thereby, it is required

to fix the dense chain packing to maintain their unique optical and thermal properties induced by high pressure. Although the number of reports to fix the chain packing by pressure is limited, photo-crosslinking has been used to fix the orientations of liquid crystalline molecules [9-10].

Benzophenone (BP)-containing PIs are well-known photo-sensitive aromatic polymers [11]. Their photo-crosslinking mechanism has been explained as follows [12]: a BP moiety in the triplet-state formed by UV excitation undergoes hydrogen abstraction from the spatially adjacent benzyl-position of the diamine moiety, and successively forms a radical couple to yield a inter-molecular crosslink. It has been reported that the reaction rate of crosslinking is significantly enhanced at elevated temperatures [13].

For PIs which emit fluorescence after UV

excitation, the fluorescent intensity is a sensitive property reflecting the aggregation structures of the PIs [14,15]. Although benzophenone (BP) itself shows a weak fluorescence, the products generated by UV-irradiation of BP and the model compounds of BP-containing PIs exhibit strong fluorescence [16,17]. Therefore, to evaluate the aggregation structures of BP-containing PIs, it would be useful to compare the variations of fluorescent intensities of cross-linked PIs irradiated at atmospheric and elevated pressures.

In this study, we attempted to fix the dense chain packing of BP-containing PIs formed under high temperature (80°C) and pressure (400 MPa) by using inter-molecular cross-linking reactions caused by UV irradiation. The reaction rates of photo-crosslinking were quantitatively evaluated by FT-IR spectra measured before and after the UV irradiation. Further, the effects of temperature and pressure during UV irradiation of BP-containing PIs on their crosslinking rates, refractive indices, and aggregation structures of PIs were examined.

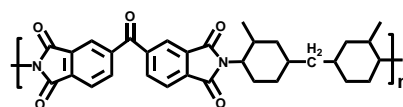
2. Experimental

2.1. Materials

3,3',4,4'-Benzophenone-tetracarboxylic dianhydride (BTDA), purchased from Kanto Chemical Co. Inc., was recrystallized from acetic anhydride followed by sublimation under reduced pressure. 4,4'-Methylene-bis(2-methylcyclohexyl amine) (DMDHM), purchased from Aldrich, was purified by distillation under reduced pressure. *N,O*-Bis-(trimethylsilyl) trifluoroacetamide (99+%, BSTFA) and *N,N*-dimethylacetamide (anhydrous, DMAc), purchased from Aldrich, were used without further purification.

2.2. Preparation of polyimide (PI) films

The molecular structures of PIs used in this study are shown in Scheme 1. The precursor of BTTA-DMDHM, poly(amic acid)silylester (PASE), was prepared by the *in situ* silylation method [18]. First, DMDHM was dissolved in DMAc, and 1.05 molar amount of BSTFA were slowly added to the solution to form *N*-silylated alicyclic diamine. This silylation reaction can avoid salt formation between unreacted amino (-NH₂) and carboxyl (-COOH) groups at the amic acid moiety. Then, equimolar amount of dianhydride was added to the solution. The PASE solution thus prepared were stirred with an ice bath for 2h followed by stirring at ambient temperature for 24h. The PI films were prepared via spin-coating of PASE precursor



Scheme 1 BTDA-DMDHM polyimide.

solutions onto Si substrates, followed by drying at 70°C for 1h and thermal imidization at 250°C under a nitrogen atmosphere.

2.3. UV irradiation under high pressure.

PI films were irradiated with a UV LED light ($\lambda=350$ nm, Hamamatsu Photonics) under various irradiation conditions. First, PI films were irradiated at r.t. and atmospheric pressure in air to evaluate the reaction rates of photo-crosslinking. Then, other PI films were irradiated at r.t. and 80°C and at 0.1 MPa and 400 MPa using a custom-built hydrostatic pressure optical cell manufactured by TERAMECS co., Ltd. The inside pressure up to 400 MPa was generated by a hand-pump using distilled water as a pressure medium.

2.4. Measurements

The reaction rates of photo-crosslinking were analyzed by Fourier transform infrared (FT-IR) absorption spectra. Firstly, FT-IR spectra were obtained with a JASCO FT/IR-4200 using Mercury Cadmium Telluride (MCT) detector to measure the reaction rates during UV irradiation. Then, FT-IR spectra were obtained with a Thermo-Nicolet AVATAR-320 FT-IR spectrometer to measure reaction rates of thick films. The refractive indices of PI films whose thickness were controlled between 8–11 μm were measured using a prism coupler (Metricron, model PC-2010) at a wavelength of 1324 nm for the in-plane (n_{TE}) and out-of-plane (n_{TM}) polarizations. The average refractive indices were estimated according to eq.1

$$n_{av} = \sqrt{(2n_{\text{TE}}^2 + n_{\text{TM}}^2)/3} \quad (1)$$

The fluorescent excitation/emission spectra of crosslinked PI films were obtained with a Hitachi F-4500 fluorescent spectrophotometer equipped with a Hamamatsu R928 photomultiplier. The spectra were measured under various pressures using the custom-built hydrostatic pressure optical cell. A 'front-face setup' was adopted to reduce self-absorption of fluorescence. Fluorescent emission spectra were measured with excitation at peak wavelengths (λ_{ex}) in the excitation spectra. In contrast, excitation spectra were measured by monitoring the fluorescence intensities at peak wavelengths (λ_{em}) of the emission spectra.

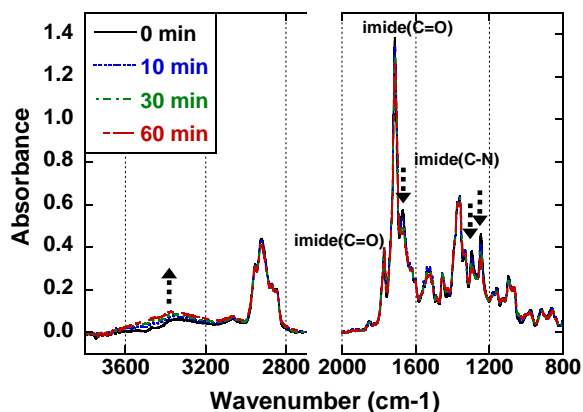
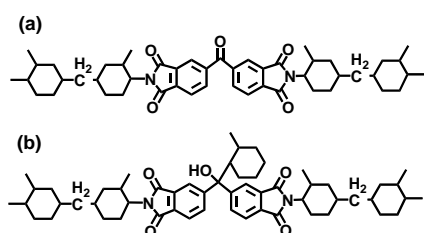


Fig.1 FT-IR spectra of BTDA-DMDHM PI measured during UV irradiation.



Scheme 2 Model compounds for (a) pristine PI and (b) UV-irradiated PI.

2.5. Quantum Chemical Calculation

The density functional theory (DFT) with the three-parameter Becke-style hybrid functional (B3LYP) [19] was adopted for calculating the electronic structures and spectroscopic properties of PIs. The 6-311G(d) basis set was used for the geometry optimizations and the calculation of IR spectra for imide model compounds. The calculated wavenumbers were scaled down by multiplying by a factor of 0.98 for correcting the vibrational anharmonicity, basis set truncation, and neglected part of electron correlation. The molecular polarizabilities were calculated using the 6-311++G(d,p) basis set. All calculations were performed with the Gaussian-09 B.01 program package installed in the Global Scientific Information and Computing Center (GSIC), Tokyo Institute of Technology.

3. Results and Discussion

3.1. Reaction rate of photo-crosslinking

Several methods have been proposed to evaluate the degree of crosslinking of polymers [13, 20]. In this study, reaction rates of photo-crosslinking, as represented by degrees of conversion, were estimated from variations in the FT-IR spectra [21]. Fig.1 shows the IR spectra measured during UV irradiation at r.t. and 0.1 MPa. The absorbance at three absorption peaks (1670,

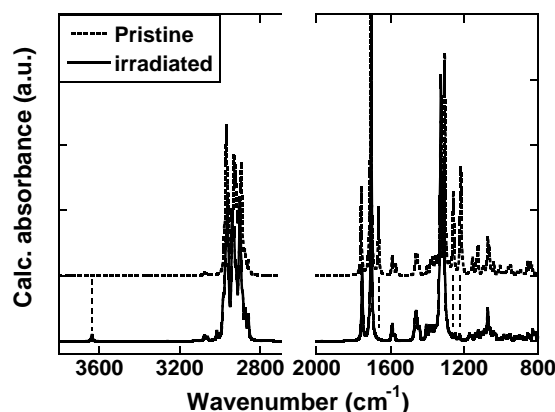


Fig.2 Calculated IR spectra of model compounds.

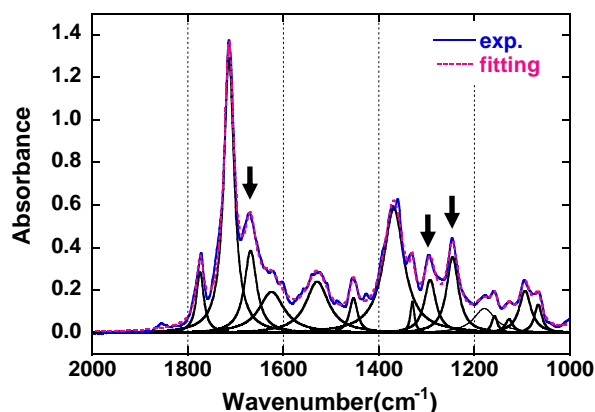


Fig.3 FT-IR spectrum of BTDA-DMDHM PI with fitted Lorentzian functions.

1293, 1246 cm^{-1}) were significantly decreased with UV irradiation, whereas the absorbance around 3450 cm^{-1} was increased. Fig.2. shows the calculated IR spectra of model compounds of the pristine and irradiated BP-containing PIs (Scheme 2). The spectra indicate that the three absorption peaks assignable to the carbonyl of BP-moiety (1707, 1305, 1259 cm^{-1}) disappeared and one peak assignable to hydroxyl group (3637 cm^{-1}) appeared after UV irradiation. These results coincide well with the experimental spectra (Fig.1). Therefore, the reaction rate of photo-crosslinking could be estimated from decrease and increase in absorbance of the peaks attributable to the BP-moiety. In this study, all the spectra were fitted using Lorentzian functions prior to estimate the crosslinking rates (Fig.3). Fig.4 shows the UV irradiation time dependence of the degree of conversion estimated from the three IR peaks. Very close UV-duration dependences were obtained for the peaks, which confirm the reliability of the method used for estimating the degrees of conversion. Due to the difficulties to estimate the exact absorbance near strong absorption peaks for thick films, the degrees of conversion were

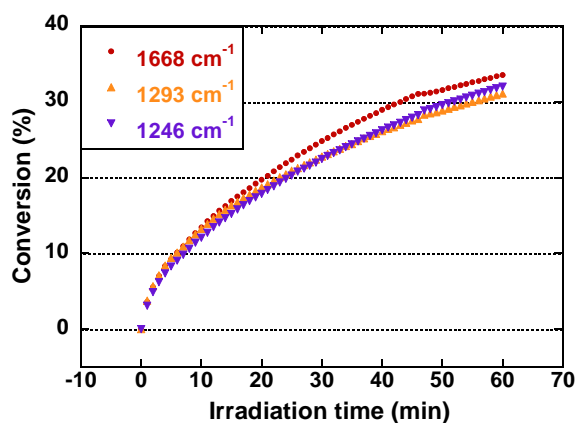


Fig.4 Relationship between conversion rates and UV-irradiation time.

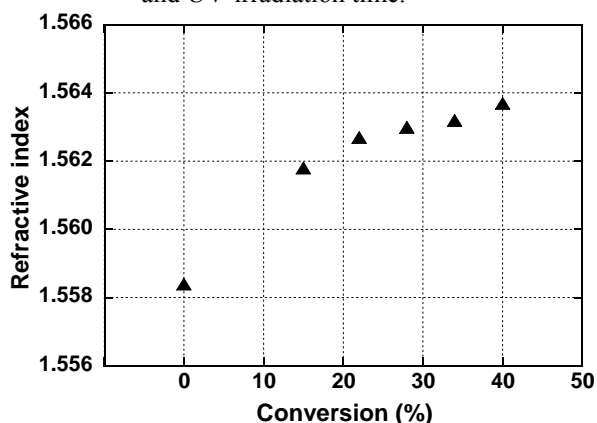
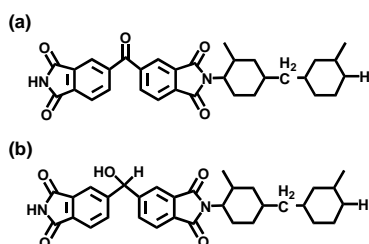


Fig.5 Relationship between conversion rates and refractive indices of PIs irradiated at r.t.

estimated from the absorption peak at 1293 cm^{-1} .

3.2. Effect of UV irradiation at room temp. and atmospheric pressure on refractive indices

Fig.5 shows the relationship between the degree of conversion and the refractive indices of the UV-irradiated PIs. The refractive indices increased with increasing the conversion. It has been reported that both the density and refractive indices of polymers can be increased by crosslinking reactions [22]. In general, the relationship between the refractive indices (n_{av}) of polymers and the molecular packing coefficient (K_p), which reflects the aggregation structure, is expressed by the



Scheme 3 Model compounds used for calculation of molecular polarizabilities for (a) pristine PI and (b) UV-irradiated PI.

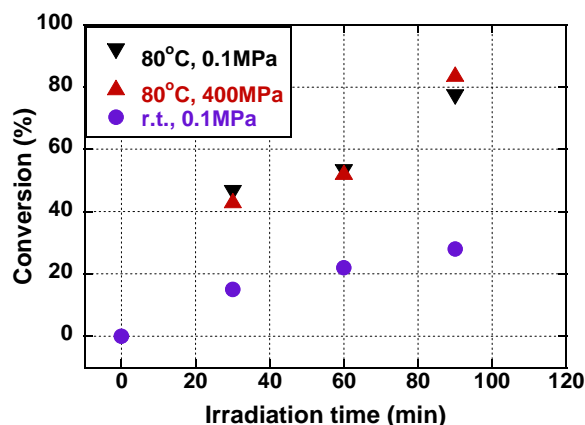


Fig.6 Effect of temperature and pressure during UV irradiation on the conversion rates.

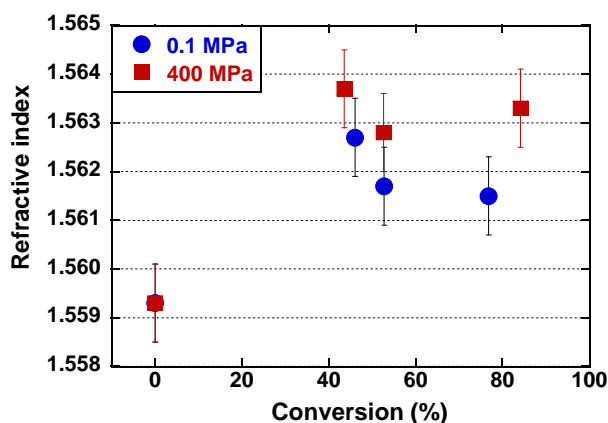


Fig.7 Effect of pressure during UV irradiation on the refractive indices of PIs.

Lorentz-Lorenz equation (eq.2).

$$\frac{n_{av}^2 - 1}{n_{av}^2 + 2} = \frac{4\pi}{3} \cdot K_p \cdot \frac{\alpha}{V_{vdw}} \quad (2)$$

where V_{vdw} is the van der Waals volume of the repeating unit, and α is the average molecular polarizability. This indicates that the refractive index is closely related to the aggregation structure (K_p) and polarizability (α). To evaluate the effects of structural changes caused by crosslinking reactions on the polarizability of PIs, the polarizability of model compounds (Scheme 3) were calculated using DFT method. When the K_p value is assumed as 0.60, the calculated refractive indices for the models of (a) pristine PI and (b) crosslinked PI at 800 nm are 1.5464 and 1.5454, respectively. This supports that the polarizability of pristine PI is not be significantly affected by UV crosslinking. Therefore, the increase in refractive indices of the PIs caused by photo-crosslinking should be originated from an increase in K_p .

3.3. Effect of crosslinking under high temperature and pressure on refractive indices

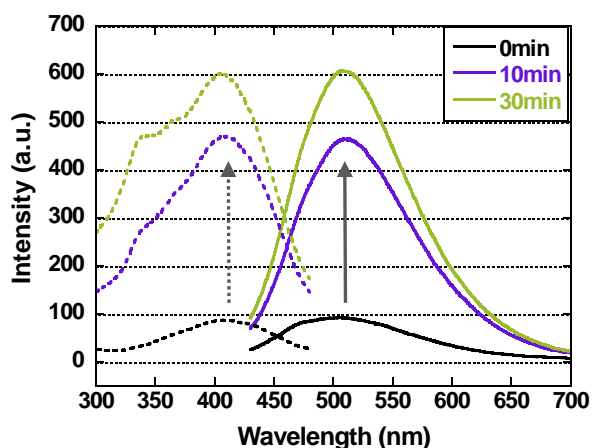


Fig.8 Excitation (dotted line) and emission (solid line) spectra of BTDA-DMDHM during UV irradiation ($\lambda_{\text{ex}}=405\text{nm}$, $\lambda_{\text{em}}=507\text{nm}$).

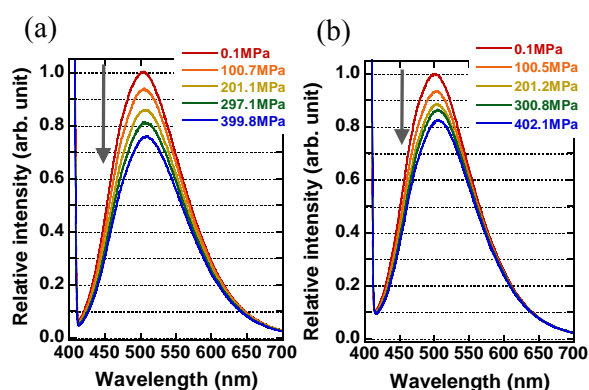


Fig.9 Fluorescent spectra of irradiated PIs measured at various pressures. ($\lambda_{\text{ex}}=397\text{nm}$) (a) irradiated at 0.1MPa and (b) at 400 MPa.

Fig.6 shows the relationships between the irradiation time and the degree of conversion of the PIs irradiated at different temperatures and pressures. The conversion was significantly influenced by the temperature, which agrees with a previous study [13]. In contrast, pressure did not give apparent influence on the conversion. Higuchi et al. suggested that the photo-crosslinking of BP-containing PIs is dominated by local motions of PI main chains [13]. The limited effect of pressure on the conversion indicates that the local chain motions in BP-containing PIs were not considerably suppressed up to 400 MPa.

Fig.7 shows the relationships between the conversions and the refractive indices of the PIs irradiated at 80°C under different pressures (0.1 and 400 MPa). The PIs irradiated at high pressure ($\text{PI}_{400\text{MPa}}$) exhibit higher refractive indices than those irradiated at atmospheric pressure ($\text{PI}_{0.1\text{MPa}}$), whereas the conversion rates are almost the same. Thereby, the increase in refractive index should be caused by an increase in K_p . In other words, since $\text{PI}_{400\text{MPa}}$ possesses more dense chain packing than

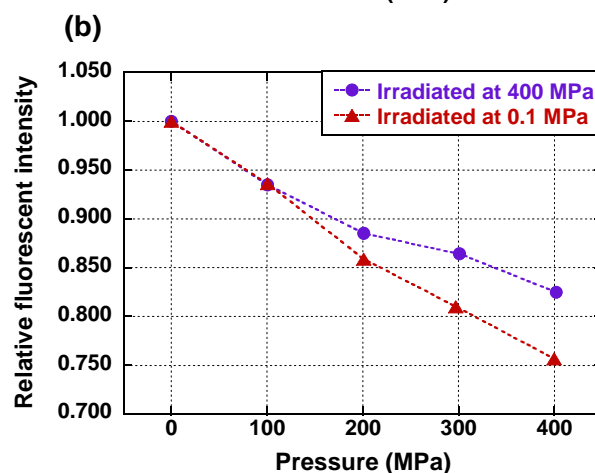
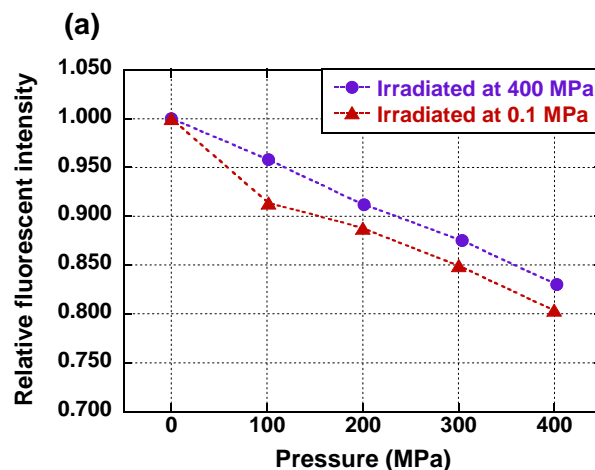


Fig.10 Fluorescent intensities of PIs measured at various pressures during (a) pressurization and (b) depressurization processes.

$\text{PI}_{0.1\text{MPa}}$, the former shows a higher refractive index than the latter. Comparing with the refractive indices of PMMA measured at 0.1 and 400 MPa [23], the difference in refractive indices between $\text{PI}_{0.1\text{MPa}}$ and $\text{PI}_{400\text{MPa}}$ is much smaller. This is explainable by two hypotheses as follows. Firstly, the pressure effects on the aggregation structures of PIs are smaller than those of PMMA because PIs have more dense chain packing at ambient conditions. Secondly, the dense packing of PIs formed at elevated pressure was not entirely fixed by UV-crosslinking. The aggregation structures of PIs were partially fixed, but most of them were reverted to the original states after depressurization.

3.4. Estimation of aggregation structure of PIs irradiated at different pressures.

Fig.8 shows the variations in fluorescent excitation/emission spectra of BTDA-DMDHM PI caused by UV irradiation. Although the un-irradiated pristine PI showed very weak

fluorescence, the fluorescent intensity was significantly increased by UV irradiation, in which the emission is attributable to crosslinked PIs.

Fig.9 shows the variations in the fluorescent spectra of PIs irradiated at 80°C for 30 min under different pressures. The spectral feature and the λ_{em} of the PI irradiated at 400 MPa (PI_{400MPa}) coincide well with those irradiated at 0.1 MPa (PI_{0.1MPa}). The fluorescence intensities of both PIs were significantly reduced with increasing the pressure. This reduction was caused by non-radiative deactivation due to the densification of aggregation structures, which is effectively enhanced by decrease in distance among polymer chains.

Fig.10 shows the variations in the fluorescent intensities of PI_{0.1MPa} and PI_{400MPa} at 500 nm measured at elevated pressures. PI_{0.1MPa} shows a larger pressure dependence of fluorescent intensities than PI_{400MPa} under the same pressurization and depressurization processes. Comparing with the aggregation structures with loose chain packing in the PI irradiated at 0.1 MPa, those of the PIs with dense chain packing irradiated at 400 MPa shows apparently smaller variations by pressure. This indicates the changes in the aggregation structures in the latter PI are smaller, which means that PI_{400MPa} possesses more dense chain packing than PI_{0.1MPa}. In conclusion, the dense chain packing of PIs formed at elevated pressure was partially and effectively fixed by UV crosslinking, which is reflected on the increase in refractive indices and the smaller pressure dependence of the fluorescent intensities.

4. Conclusion

For controlling the optical properties of photo-sensitive PIs, the aggregation structures of BP-containing PIs with dense chain packing was effectively fixed by UV crosslinking under high temperature and pressure. The photo-crosslinking rates were quantitatively evaluated from the variations in FT-IR spectra. The refractive indices of the crosslinked PIs increased with increasing the degree of conversion because the crosslinked PIs have more dense chain packing than the pristine PI. The reaction rates of the photo-crosslinked PIs irradiated at high pressure was almost the same as that irradiated at atmospheric pressure. Therefore, the pressure effect on the conversion was negligible. In contrast, the conversion of PIs irradiated at high temperature were significantly higher than those of PIs at ambient temperature. Therefore, the UV irradiation temperature is more

influential to conversion than the pressure. The refractive indices of the PIs irradiated under high pressure were higher than those irradiated at atmospheric pressure. Further, the pressure dependence of fluorescent intensities of the former was smaller than that of the latter. As a result of fixation of the dense chain packing formed by UV crosslinking at elevated pressures, the PIs irradiated at high temp. and pressure possess more dense chain packing with high refractive indices.

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