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Promotion of Thermal Imidization of Semi-Aliphatic Polyimide Precursors by Incorporation of Polyethylene Glycol and Their Modified Solid Structures

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Thermal imidization reaction of semi-aliphatic poly(amic acid)s (PAAs) prepared from four different semi-aliphatic dianhydrides and 2,2’-bis(trifluoromethyl)-4,4’-diaminobiphenyl (TFDB) was effectively promoted by adding a low-Mw polyethylene glycol (PEG) into the PAAs solutions. The noticeable reduction of imidization temperature is attributable to the plasticizing effects of PEG on the PAA chains. The molecular motions of PAA chains are maintained at elevated temperatures owing to the high decomposition and evaporation temperatures of PEG. Moreover, birefringence and refractive index measurement revealed that more isotropic chain-orientation and dense molecular packing were formed in the PI films cured with PEG. The modified solid structures lead to the better physical properties especially for optical and photonic applications.

Keywords: semi-aliphatic polyimide / poly(ethylene glycol) / degree of imidization / chain mobility / refractive index / birefringence

1. Introduction

Polyimides (PIs) have been widely used in many industrial fields, such as aerospace, electric, electronic, and optical applications, due to their out-standing thermal stability, chemical and radiation resistance, flame retardancy, mechanical strength, good flexibility, and excellent dielectric properties. In particular, insulating polymeric films with low dielectric constants are one of the key materials in semiconductor industry [1]. Due to their rigid main chain structures, PIs generally exhibit very low solubility to organic solvents, high glass transition temperature (T_g), and high thermal degradation temperatures (T_d). Thereby, PI is generally processed from a soluble precursor, poly(amic acid) (PAA), which can be converted to PI via thermal curing up to 300–400 °C. Although nearly perfect imidization is preferable for exerting the inherent physical properties of PIs, conventional curing processes at lower temperatures (< 230 °C) is usually incomplete. However, high temperature processes over 250 °C are frequently unfavorable for semi-conductor components, multi-layer wiring, insulating layers, and production facilities of electronic circuit boards. Therefore, there has been a strong demand for new processes to provide high degrees of imidization (φ_i) for PAAs at lower temperatures (preferably < 250 °C).

For enhancing the imidization reaction and lowering the imidization temperatures, 2,6-dimetylpipelidine, *p*-hydroxybenzoic acid, 1,4-diazabicyclo[2.2.2]-octane, and 1,8-diazabicyclo-[5.4.0]undec-7-ene have been used as catalysts [2−4], though residues of these catalysis cause unfavorable effects on the circuits and components. On the other hand, enhanced molecular motion at elevated temperatures is advantageous for promoting the thermal imidization of PAAs [5]. Thereby, lowering of T_g

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of PAA by introducing flexible linkages in the main chains is promising to enhance φ_i at lower temperatures. It was reported that the T_g of PIs can be lowered by incorporating flexible components via copolymerization or blending of PAAs. For instance, the imidization of a conventional PI almost completed at 180 °C by copolymerizing with poly(dimethylsiloxane) (PDMS) [6]. In addition, blending of polyurethane (PU), which acted as a plasticizer of a fluorinated PI (6FDA/ODA) having flexible and rotatable linkages, significantly reduced the imidization temperature [7, 8]. However, in the former case, a high content of PDMS component is required to improve the mobility of PI, and in the latter case, control of micro phase separation in blends of PU and PAAs is a formidable task. Thereby, imidization promoters which possess high compatibility with PAAs and can enhance the φ_i of PIs with small amounts are highly preferable. Recently, one of the present authors reported that the φ_i of a fully aromatic PI prepared from pyromellitic dianhydride and 4,4'-diaminodiphenyl ether (PMDA/ODA) was effectively enhanced by introducing PEG to its PAA solution [8]. This effect was attributed to the lowering of the apparent T_g of PAA chains based on the van der Waals interactions between PAA, PEG, and residual solvent, in which the chain mobility of the PAA was significantly enhanced during imidization. Moreover, it is advantageous that PEG can be thermally decomposed and evaporated after curing of PI.

A low dielectric constant is an indispensable property for polymeric insulating materials usable for electronic circuit boards [1]. For this application, fully aromatic PIs are not the best materials due to their dielectric constant ($\varepsilon \approx 3.5$). Instead, semi-aliphatic PIs are good alternatives due to their low ε and good film-forming property as well as good optical properties [9−11]. In particular, PIs derived from aliphatic dianhydrides have been explored for this application. However, the dehydrating cyclization of the aliphatic dianhydride moieties of PAAs, *i.e.* imidization reaction, are complicated and not efficient due to their structural isomerism and large steric hindrance. Thereby, the φ_i of such semi-aliphatic PIs are frequently difficult to increase at lower temperature [12, 13].

In this study, the effects of a PEG additive as plasticizer and imidization promoter for semi-aliphatic PIs applicable to low dielectric insulators were investigated. The final curing temperature dependences of φ_i were quantitatively examined by FT-IR absorption spectra for four kinds of semi-aliphatic PIs (Fig. 1a) as well as two kinds of aromatic PIs (Fig. 1b) as the references. The degrees of in-plane orientation and molecular packing of PI chains were also quantitatively estimated via optical measurements, *i.e.* average refractive indices (n_{av}) and in-plane/out-of-plane birefringence (Δn).

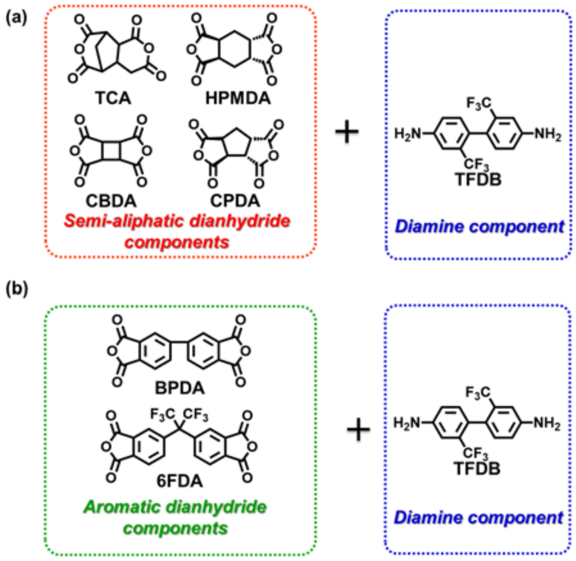

Fig. 1 Synthetic procedures for (a) semi-aliphatic and (b) fully aromatic polyimides (PIs). A fluorinated diamine (TFDB) was used as the common diamine.

2. Experimental

2.1. Materials and synthesis

2,3,5-Tricarboxycyclopentyl acetic dianhydride (TCA), 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA), trans-1,2,3,4-cyclopentane-tetracarboxylic dianhydride (CPDA), and 1,2,4,5-cyclohexanetetracarboxylic dianhydride (HPMDA) were kindly supplied by JSR Co., Ltd. and used as received. 3,3',4,4'-Bispheyltetracarboxylic dianhydride (BPDA) purchased by Wako Chemical was dried in vacuo at 180 °C for 8 h before use. Hexafluoroisopropylidene-2,2-bisphthalic-anhydride (6FDA) and 2,2'-bis(trifluoromethyl)-4,4'-diamino-biphenyl (TFDB) supplied by Central Glass Co., Ltd. were dried in vacuo at 80 °C for 2 h. Phthalic anhydride (PA) purchased by Kanto Chemical Co., Ltd was sublimated in vacuo before use. *N*,*N*-Dimethylacetamide (DMAc, 99%, anhydrous) purchased from Sigma-Aldrich was used as received. Low molecular weight polyethylene glycol (PEG, M_w= 600) purchased from Wako chemical was used as received.

An imide model compound TF-PA was synthesized from PA and TFDB. PA and TFDB, mixed with 2:1 molar ratio, were dissolved in anhydrous propionic acid (b.p. 141 °C), followed by refluxing for 6 h. After cooling to room temperature, the precipitate was filtered and washed by water and ethanol several times, followed by drying under reduced pressure.

DMAc solutions of PAAs, which are precursors of PIs, were prepared by addition polymerization of equimolar amounts of a dianhydride and a diamine. PAA/PEG blend solution was prepared by adding a variable amount of PEG to a PAA solution and stirring at room temperature for 1h. PAA and PAA/PEG blend solutions were spin-coated onto silicon wafers, followed by prebaking at 70 °C for 1 h, and stepwise thermal curing at 180 °C for 30 min, 230 °C for 30 min and 300 °C for 30 min. All the preparation and thermal curing procedures were conducted under nitrogen atmosphere. In this study, the PIs derived from 6FDA, BPDA, TCA, CBDA, CPDA, HPMDA as dianhydrides and TFDB as a diamine are abbreviated as 6F-PI, BP-PI, TC- PI, CB-PI, CP-PI, and HP-PI, respectively.

2.2. Measurements

Fourier transfer infrared (FT-IR) spectra of PI films coated on 0.52 mm-thick Si substrates were recorded by FT-IR spectrophotometer (JASCO 4200) by the transmission mode. In-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of PI films formed on Si substrates were measured by a prism coupler (Metricon, PC-2010) at a wavelength 1310 nm. Average refractive index (n_{av}) of PI films was estimated as $n_{\mathrm{av}} = (2n_{\mathrm{TE}} + n_{\mathrm{TM}})/3$, and in-plane/out-of-plane birefringence Δn was estimated as a difference between n_{TE} and n_{TM}. The film thickness was adjusted between 10 and 30 μm. Thermal mechanical analysis (TMA) was conducted using a Shimadzu TM-5000 analyzer at a heating rate of 10 °C min^{-1} with a fixed load of 1.5 g. The thermal degradation behaviors of PEG and semi-aliphatic PIs with/without PEG were investigated by thermogravimetric analysis (TGA, Shimadzu, DTG-60) at a heating rate of 5 °C min^{-1} up to 500 °C under nitrogen flow. Each semi-aliphatic PI sample was thermally annealed for 30 min at 110 °C prior to measurement to remove absorbed water.

3. Results and Discussion

3.1. T_g and in-plane CTE of PIs

The coefficients of thermal expansions in the in-plane direction (CTEs) and the T_gs of the PI films measured by TMA are summarized in Table 1. Among the semi-aliphatic PIs (HP-PI, CP-PI and CB-PI), CB-PI showed the highest T_g (374 °C). The dianhydride moieties of HP- and CP-PIs are more flexible or asymmetric than that of CB-PI, which lowers their T_gs. Among them, the T_g of TC-PI was the lowest (280 °C). Although it was reported that thermal degradation of a fully imidized semi-aliphatic PI prepared from TCA and 4,4'-diaminodiphenyl ether (TCA/ODA) was not observed up to 400 °C [13], a weight loss was readily observed at around 240 °C for a TC-PI film cured at 230 °C. As described below, this weight loss is attributable to the imidization reaction of residual PAA component due to its low φ_i. TCA dianhydride is hardly cyclized owing to its large steric hindrance and asymmetric structure, as discussed in the next section. It is likely that the T_g of fully imidized TC-PI is higher than 280 °C. For fully aromatic PIs, 6F-PI showed a higher T_g than BP-PI, which is due to the steric hindrance and rotational barrier around the hexafluoroisopropylidene ($-C(CF_3)_2-$) group in 6FDA.

As shown in Table 1, HP-PI, 6F-PI and TC-PI exhibited large CTEs, indicating that these PIs do not tend to orient along the film-plane due to their steric and bulky structures of the dianhydride moieties. On the other hand, CB-PI and BP-PI showed smaller CTEs than the other PIs, which is attributable to their planar and rigid structures of the dianhydride moieties, which facilitates in-plane orientation of the PI chains.

Table 1 Thermal properties of PI films cured at 230 ºC

Polyimide	T_g (ºC)^a	CTE^b (ppm/K)
CB-PI	374	23.6
HP-PI	364	65.4
6F-PI	343	50.9
CP-PI	342	45.0
BP-PI	335	18.7
TC-PI	280	88.3

^{a}Measured by TMA, ^{b}Measured at 130−180°C.

3.2. Thermal imidization of semi-aliphatic PI

The FT-IR spectra of PI films cured at 300 °C are shown in Fig. 2. The absorption bands at 1720 cm^{-1} (orange) and 1680 cm^{-1} (green) are assigned to the C=O symmetric and asymmetric stretching vibrations of imide ring, respectively. The band at 1480 cm^{-1} (yellow) is assigned to the C=C

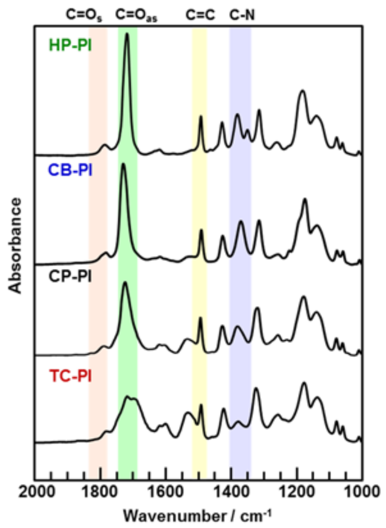

Fig. 2 FT-IR spectra of a series of semi-aliphatic PI films after curing at 300 °C. The characteristic absorption bands are marked in colors with signal assignments (top).

stretching of benzene rings, and that at 1380 cm^{-1} (purple) is assigned of the C–N stretching between the imide and phenyl rings. Firstly, from the comparison of the FT-IR spectra, the absorbance of C=O asymmetric and C–N stretching vibrations were decreased in the order of HP-PI > CB-PI > CP-PI > TC-PI. In particular, the C=O symmetric and C–N stretching vibrations of TC-PI was hardly observed. Since the amide group is located far from the carboxyl groups as shown in Fig. 3a, the cyclization of TC-PAA is fairly difficult. In a similar way, CP-PAA is also difficult to cyclize due to the large distance between the carboxyl and amide groups as shown in Fig. 3b. Thereby, the dehydration reaction of CP-PAA possibly gives a bent and irregular 'CP-PAA/PI' structure instead of CP-PI. In the case of CB-PI, the cyclobutane skeleton is rigid, and the steric strain at the imide-rings of CB-PI could be larger than that of HP-PI (Fig. 3c). Hence, the φ_i of CB-PI might be lower than that of HP-PI. As explained above, the characters of imidization reactions in the semi-aliphatic PIs are closely related to the structural rigidity and the relative spatial positional relation between –COOH and –NHCO– at the amide acid moieties. This is significantly influenced by the structural isomerism of the aliphatic dianhydride, and this is the key factor for enhancing the φ_i of semi-aliphatic PIs.

3.3. Enhancement of imidization reactions by introduction of PEG to PAA

As described above, addition of PEG to PAA solutions was reported to be effective to reduce the apparent T_gs of aromatic PAAs by enhancement of molecular mobility [8]. Hence, a low-M_w PEG was added to DMAc solutions of semi-aliphatic PAAs to enhance their φ_i values even at lower curing temperatures (230 °C and lower).

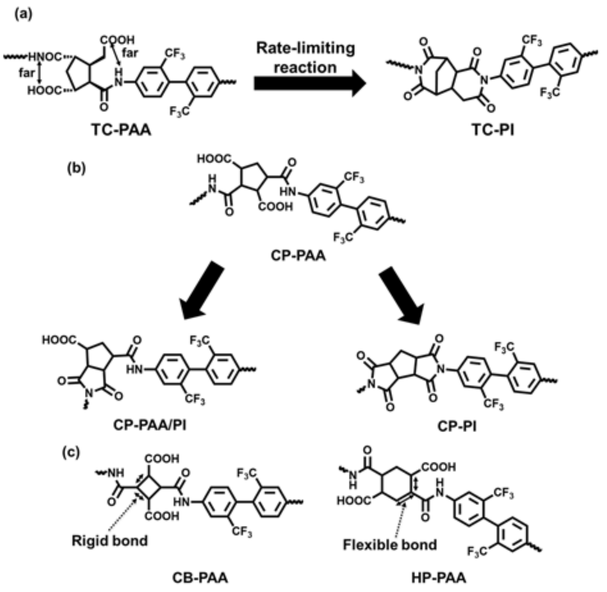

Fig. 3 Chemical structure of semi-aliphatic PAAs and PI. (a) TC-PAA and TC-PI, (b) CP-PAA, 2 types of isomers, and (c) CB-PAA and HP-PAA. A bent and irregular structure (CP-PAA/PI) is possibly formed in CP-PI. Steric strain exerted around the ring structures of TC-, CP- and CB-PAA should be a main cause for the low imidization ratios in these PIs.

Firstly, in order to evaluate the φ_i of PAAs and PIs, the FT-IR spectra of 6F-PI were compared with that of a model compound (TF-PA) which can be easily imidized and used as a reference of φ_i=100 %. Fig. 4 shows the FT-IR spectra of 6F-PI cured at 300 °C for 30 min with and without PEG, and that of TF-PA. Both intensities of symmetric (1780 cm^{-1}) and asymmetric C=O (1720 cm^{-1}) stretching, and C–N stretching vibrations (1380 cm^{-1}) at imide rings were similar to those of 6F-PI cured at 300 °C with PEG and TF-PA. Thus, it can be assumed that the φ_i of each PI was ca. 100 % after curing at 300 °C for 30 min with 25 wt% PEG content. The value of φ_i after thermal curing was estimated by the following formula.

$$\varphi_i\ (\%) = \frac{\dfrac{Abs(1380\ cm^{-1})}{Abs(1490\ cm^{-1})} - \dfrac{Abs(1380\ cm^{-1})_{r.t.}}{Abs(1490\ cm^{-1})_{r.t.}}}{\dfrac{Abs(1380\ cm^{-1})_{final}}{Abs(1490\ cm^{-1})_{final}} - \dfrac{Abs(1380\ cm^{-1})_{r.t.}}{Abs(1490\ cm^{-1})_{r.t.}}} \times 100$$

where $Abs\ (x)$ is the absorption intensity at x cm^{-1} at a given temperature, $Abs\ (x)_{final}$ and $Abs\ (x)_{r.t.}$ are the absorption intensities at x cm^{-1} after thermal curing at 300 °C for 30 min containing a 25 wt% PEG and that at room temperature, respectively.

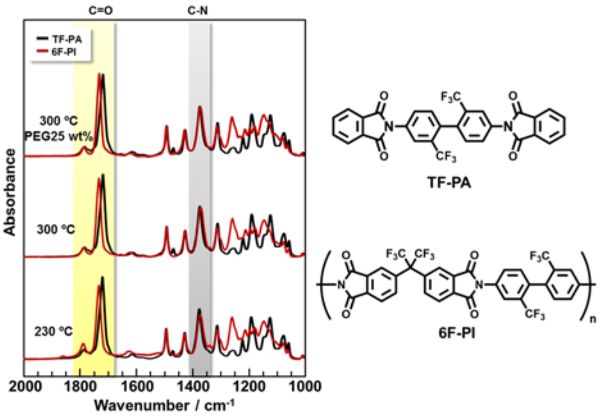

Fig. 4 FT-IR spectra of 6F-PI (Red) and TF-PA model compound (black) imidized under three conditions. The yellow and gray bands correspond to the absorptions of C=O and C−N stretching, respectively.

The above formula utilizes the intensity of C−N stretching vibration (1380 cm^{-1}) at the imide group against that of C=C stretching vibration (1490 cm^{-1}) of benzene rings. The latter band can be used as the standard owing to its insensitivity to the extent of imidization.

The promoting effects of PEG on imidization are clearly seen in the temperature dependence of φ_i presented in Fig. 5. Firstly, the imidization of 6F-PAA almost completed at 230 °C with a 5 wt% PEG content while the φ_i of neat 6F-PI without PEG was only 85 %. This result coincides well as the previous report [8]. According to the literature [5], enhancement of flexibility in the polymer chain is effective to lower the barrier of the molecular motion which facilitates imidization reaction. Thereby, this promoting effect is attributable to an increase in the molecular motion by PEG additive. Compared with HP-PI, the φ_i of CB-PI was hardly increased with a low PEG content, as seen in Figs. 5b and 5c. The structural flexibility and mobility at the carboxyl and amide groups is restricted and not enhanced due to the rigid PI chain skeleton. The evolution of φ_i of CP-PI was almost the same as that of CB-PI. Though, the φ_i of CP-PI was significantly increased at 300 °C with a 25 wt% PEG content. Considering the reaction mechanism, CP-PAA is possibly to form a bent and irregular CP-PAA/PI structure as depicted in Fig. 3b. However, by adding a PEG, this side reaction could be suppressed by lowering the effective activation energy of the forward reaction. On the other hand, the variation in φ_i of TC-PI is remarkably different, which is more analogous to an exponential behavior. It was reported that the φ_i of a semi-aliphatic PI derived from TCA and 4,4’-methylenedianiline (TCA/MDA) was lower than those of the other semi-aliphatic and aromatic PIs on account of difference in the imide ring strain energy [12]. Thus, the imidization rate of TC-PAA is much slower than those of the other semi-aliphatic PIs owing to the large strain at the imide ring.

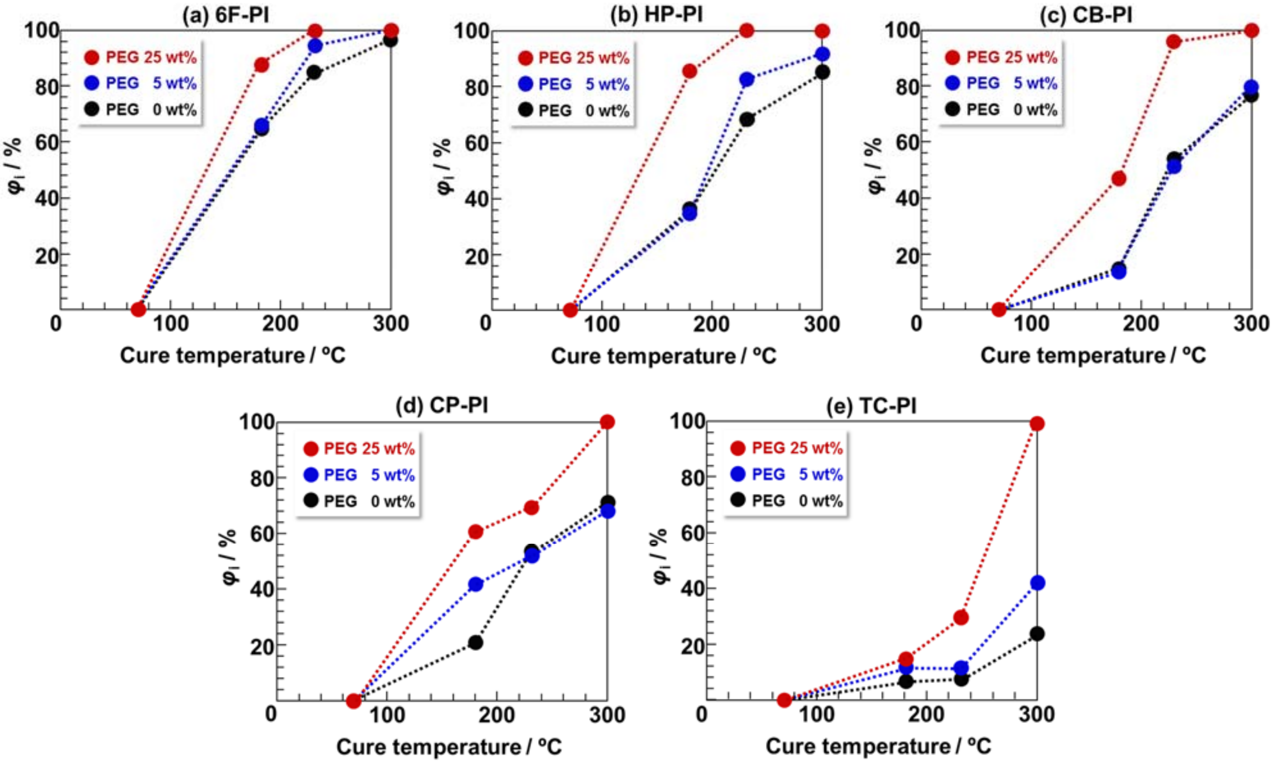

Fig. 5 Curing temperature dependences of the degree of imidization (φ_i) for five kinds of PIs.

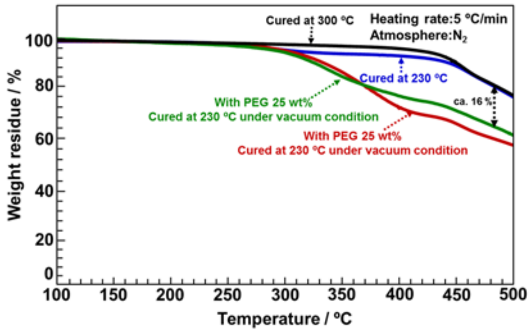

Fig. 6 TGA curves of CB-PI films with and without PEG thermally cured at 230 °C and 300 °C.

3.4. Residual PEG in semi-aliphatic PI films cured at 230 °C

For estimating the residual contents of PEG in the cured CB-PI film, TGA analysis was performed as shown in Fig. 6. Firstly, it was confirmed that a CB-PI film cured at 230 °C showed a slight weight loss at 250 °C. Since this was not observed for the films cured at 300 °C, the weight loss is attributable to the dehydration reaction of residual PAA parts. Furthermore, for a CB-PI film containing PEG, a significant weight loss was observed between 250 and 450 °C, which corresponds to the dehydration of PAA parts and the degradation of PEG. Based on the TGA of neat PEG, PEG itself degrades or evaporates between 150 and 250 °C. Nevertheless, the thermolysis rate of PEG is much slower in CB-PI film, which is attributable to the strong intermolecular interactions of CB-PI film with PEG. The residual amounts of PEG were estimated by comparison of the reduced weights of CB-PI cured at 230 °C with and without PEG. The residual amounts of PEG (23 wt%) in CB-PI film indicates that the residual PEG dissolved in CB-PI film was hardly removed at this temperature. In the case of copolymerization of PDMS with a PI, although a 40 wt% PDMS content was required to lower the T_g of the copolymer [6], the PEG content was smaller than the PDMS content. In the blend of PU and PAAs, clear micro phase separation was observed [7], while it was not observed in the semi-aliphatic PI films containing PEG. Moreover, the residual amount of PEG in a CB-PI film cured at 230 °C under vacuum condition was smaller than that cured in nitrogen atmosphere. Hence, larger amount of PEG can be removed from semi-aliphatic PI films after long-time curing under vacuum condition. Based on these results, it was revealed that a low-Mw PEG is a remarkable imidization promotor for semi-aliphatic PIs.

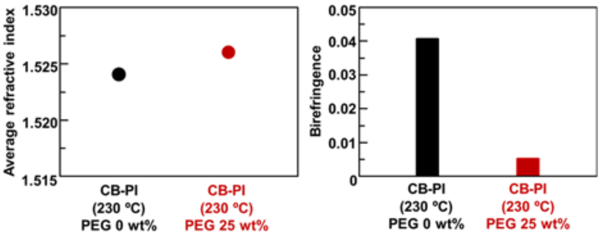

Fig. 7 Average refractive indices (left) and birefringence (right) of CB-PI cured at 230 ºC with and without PEG.

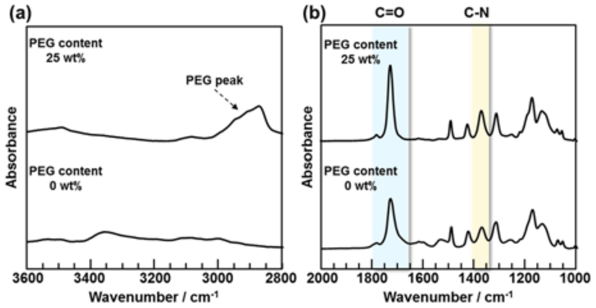

Fig. 8 FT-IR spectra of CB-PI prepared with and without PEG. (a) 2800-3600 cm^{-1}, (b) 1000-2000 cm^{-1}. The thermal curing temperature was 230 ºC. The blue and yellow bands correspond to the absorption band assigned to C=O stretching vibration and C-N stretching vibration, respectively.

3.5. Relationship between the refractive indices and the degrees of imidization of PIs

The excellent physical properties of PIs originate from the dense molecular aggregation,

Table 2. Refractive indices and degree of imidization of PIs cured at different temperatures and additives.

Polyimide	Curing temp. (°C)	PEG content (wt%)	n_{TE}	n_{TM}	n_{av}	Δn	φ_i (%)
CB-PI	230	0	1.537	1.496	1.524	0.041	55
		25	1.528	1.522	1.526	0.006	96
CP-PI	230	0	1.528	1.501	1.524	0.023	56
		25	1.519	1.514	1.518	0.005	71
6F-PI	350	0	1.518	1.510	1.515	0.008	100
		25	1.520	1.510	1.517	0.011	100
BP-PI	350	0	1.610	1.566	1.596	0.045	98
		25	1.615	1.577	1.602	0.038	100

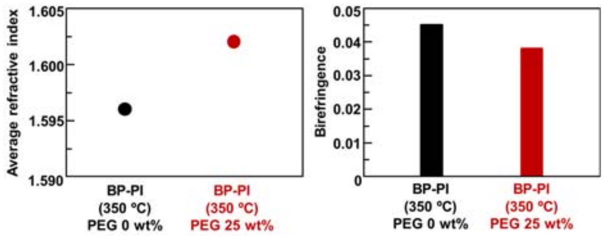

Fig. 9 Average refractive indices (left) and birefringence (right) of BP-PI thermally cured at 350 ºC with and without PEG.

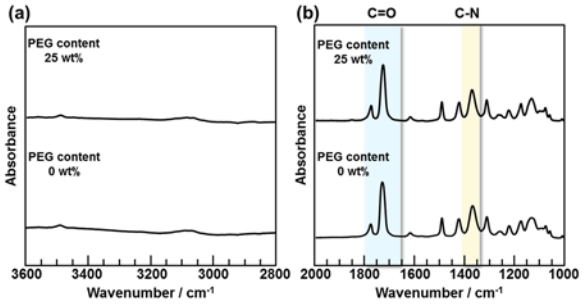

Fig. 10 FT-IR spectra of BP-PI films prepared with and without PEG. (a) 2800-3600 cm^{-1}, (b) 1000-2000 cm^{-1}. The highest curing temperature was 350 ºC. The blue and yellow bands correspond to the absorption bands assigned to C=O stretching and C-N stretching vibrations, respectively.

local ordered structures, and entire orientation of main chains [14−16]. Since the average refractive indices n_{av} and in-plane/out-of-plane birefringence Δn of PIs are closely related to the molecular aggregation and in-plane orientation [17−20], these structures can be estimated by measuring the polarization-dependent refractive indices of PI films. The values of n_{av} and Δn for CB-PI thermally cured at 230 °C with and without PEG were shown in Figs. 7 and 8. The φ_{i} values and refractive indices of the PI films are listed in Table 2. Homogeneous films were obtained both for CB-PI and CP-PI, and the measurements and analysis were successfully conducted. For CB-PI, the n_{av}s of the films thermally cured at 230 °C with and without PEG were almost the same. Since the refractive index of PEG is lower than those of semi-aliphatic PIs [21], the n_{av}s of PI films containing PEG should be lower than those of pristine PI films. Though, the n_{av}s of PI films are related with, not only the aggregation state, but also the linear polarizability of the molecular structure [22]. For the CB-PI film, the cured PI chains should have a larger polarizability due to the progress of imidization (φ_{i} : 55→96%). However, the n_{av}s of both the films become nearly the same due to the trade-off between the inclusion of PEG, which lowers the n_{av}, and the enhancement of φ_{i}, which increases the n_{av}. In contrast, the n_{av} of CP-PI film cured at 230 ºC with PEG was slightly lower than that without PEG. Since the φ_{i} of CP-PI was not sufficiently promoted with PEG (φ_{i} : 56→71%), the inclusion of residual PEG was strongly reflected on the n_{av} of the film.

Moreover, the birefringence (Δn) of CB-PI and CP-PI were significantly reduced with the incorporation of 25 wt% of PEG by 86 and 80 % respectively, indicating that the PI chains in the obtained films were much more isotropically oriented. It is obvious that PEG additive disordered the in-plane orientation of PI chains, which is the most striking feature of the inclusion of PEG into PAA. The drastic reduction in Δn is very beneficial for optical applications such as waveguides and flexible substrates for flat panel displays.

As described above and in section 3.4, when semi-aliphatic PIs were thermally cured at 230°C under nitrogen, it is obvious that a certain part of PEG remained in the PI system, which is mainly caused by the low curing temperature. Thereby, thermal curing over 300 °C is required to remove all the residual PEG from the semi-aliphatic PI films. However, thermal curing of semi-aliphatic PIs at very high temperature leads to thermal degradation of the aliphatic skeleton. Actually, in the TGA curves of CB-PI and CP-PI cured at 230 and 300 °C, slight weight losses were observed around 350 °C. In contrast, fully aromatic PIs, 6F-PI and BP-PI, exhibited significantly high thermal degradation temperatures due to the lack of aliphatic structures [23, 24].

The experimental values of n_{av} and Δn and the FT-IR spectra of a BP-PI film cured at 350 °C with and without PEG are shown in Figs. 9 and 10. No peak assignable to PEG was observed in the FT-IR spectra, and the estimated values of φ_{i} are almost the same for both the films, indicating that residual PEG was fully removed after curing at 350 °C. However, it should be noted that, the n_{av} was increased and Δn was slightly decreased in the BP-PI film cured with PEG, and a similar trend was observed for 6F-PI as well (Table 2).

The increase in n_{av} caused by the addition of PEG can be discussed from a viewpoint of enhancing the PI chain mobility during curing. DMAc solvent (bp: 165 °C) in PAA solutions evaporates at elevated temperatures with the progress of drying and thermal curing of PIs. The molecular mobility of PAA and PI chains are gradually and steadily restricted with evaporation of the solvent and progress of imidization. In the case of PAA solution containing PEG, the molecular mobility can be maintained even at elevated temperatures because PEG molecules, which are miscible with PAA chains, acts as a residual solvent, having high boiling temperature, in the films and facilitates not only imidization but also formation of more isotropic chain orientation with dense molecular packing. Accordingly, the PI films become denser with high n_{av} and more isotropic orientation with small Δn. Actually, the density of PI is significantly affected by the amount of residual solvent [25]. The change in n_{av} caused by PEG for BP-PI was more significant than that for 6F-PI. Since the PIs having rigid and linear structures possess relatively high packing coefficients [22], this difference reflects the denser packing ability of BP-PI. In contrast, a dense packing is inherently difficult to be formed in 6F-PI containing a large free volume owing to its spatially steric structure.

Consequently, the addition of PEG is a very facile and effective method, not only for enhancing the φ_i of semi-aliphatic PIs at lower temperatures, but also for increasing the n_{av} and lowering the Δn both for the semi-aliphatic and fully aromatic PIs. Since all the PI films prepared in this study are transparent and almost colorless, the structural changes caused by the incorporation of PEG endows highly advanced performance with the PI films applicable to optical and photonic applications.

Conclusion

The degree of thermal imidization (φ_i) was successfully and significantly increased for a series of semi-aliphatic polyimides (PIs) at relatively lower temperatures (~230 °C) by incorporation of low-Mw polyethylene glycol (PEG) into their precursor (PAA) solutions. In addition, some PEG-added semi-aliphatic and fully aromatic PI films demonstrated more isotropic chain orientation and dense molecular packing as expressed by higher average refractive indices (n_{av}) and reduced birefringence (Δn). These properties are attributable to the relatively dense aggregation and more isotropic orientation of PI chains with the aid of enhanced chain mobility facilitated by PEG molecules during thermal curing. We can conclude that the addition of PEG is very facile and effective way to enhance not only the φ_i but also the structural morphology, which enables precise control of the physical properties of the PIs.

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