Absorption, Fluorescence, and Thermal Properties of Transparent Polyimides Based on Cyclobutanetetracarboxylic Dianhydride

Qinghua LI, Kazuyuki HORIE, and Rikio YOKOTA*

*The University of Tokyo, Graduate School of Engineering, Department of Chemistry
and Biotechnology, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
* Institute of Space and Astronautical Science, 3-1-1 Yoshinodai,
Sagamihara, Kanagawa 229-8510, Japan*

ABSTRACT: Ultraviolet/visible absorption spectra and fluorescence spectra of transparent polyimides derived from 1,2 : 3,4-cyclobutanetetracarboxylic dianhydride (CBDA) with an aromatic diamine, 4,4'-diaminodiphenylmethane (DPM), a fluorinated diamine, 2,2-bis(4-diaminodiphenyl)hexafluoropropane (6FdA), and an alicyclic diamine, 4,4'-diaminodicyclohexylmethane (DCHM) were investigated, compared with their model compounds. Both monomer and excimer fluorescence were observed in concentrated CH_2Cl_2 solution of model compounds, suggesting head to tail intermolecular overlap structures at the excited state. All polyimide films derived from CBDA showed high transparency in the visible region, i.e., no absorption tail was found above 375 nm. Especially, PI(CBDA/DCHM) showed the highest transparent property with almost no absorption above 310 nm. Absorption shoulders at 235 nm of PI(CBDA/DPM) and PI(CBDA/6FdA) are due to the absorption of phenylene groups in the diamine moieties. The fluorescence spectra of all polyimide films studied showed the existence of ground-state complexes. Their excitation wavelength dependence would be due to the existence of various conformations of packing structure. The glass transition temperatures, T_g, of these polyimides based on CBDA lie in the region of 277°C to 360°C. These polyimides have decomposition temperatures around 450°C under deaerated conditions.
    KEY WORDS   Transparency / Polyimides / Alicyclic Dianhydride / Fluorescence / Excitation Wavelength Dependence / Packing Structure / Glass Transition Temperature /

Polyimides (PI), one of typical high-performance materials, have been widely used as electrical insulators, coatings, adhesives, substrates for flexible printed circuits, because of their superior thermal, mechanical properties and low dielectric constants.[1] In general, PI are prepared by a two-step process; first, diamines react with dianhydrides in aprotic polar solvents at room temperature to give poly(amide acid)s (PAA), the precursor of polyimides; secondly, PAA are converted to PI by either thermal or chemical imidization. Recently, New PI with various functional groups which show high solvent solubility,[2-4] high photosensitivity,[5-9] photo-conductivity,[10-12] have been actively investigated. Although polyimides have been widely used in micro-electronics and the aerospace industry, their apparent color from yellow to brown has limited their application in optical communication and liquid crystal display devices.

Kotov et al.[13] attributed the coloration of polyimide films mainly to the intermolecular charge-transfer (CT) complexes formed owing to molecular aggregation between PI chains in solid states. In order to obtain a transparent polyimide, the most important point is to eliminate the inter- and/or intramolecular CT formation in usual aromatic polyimides, where aromatic moieties from diamine act as electron donors and the imide moieties act as electron acceptors. PI derived from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropanedianhydride (6FDA),[14-18] are well known to be very transparent. In recent years, Jin et al.[19-21] reported that PI prepared from an alicyclic diamine, 4,4'-diaminodicyclohexylmethane (DCHM), show good transparency, photochemical and dielectric properties as well as good thermal stability. In our previous paper,[22] ultraviolet/visible (UV-Vis) absorption and fluorescence spectra

were investigated for transparent PI, PI(6FDA/DCHM) and PI(6FDA/PDA), prepared from fluorinated dianhydride, 6FDA, with an alicyclic diamine, DCHM, as well as with p-phenylenediamine (PDA). Both PI(6FDA/DCHM) and PI(6FDA/PDA) showed high transparency in the visible region, where no absorption band above 370 nm was found. The reason is that, by introducing 6FDA and/or DCHM to the polyimide main chain, the bulky substituent group $-C(CF_3)_2-$ prevents molecular packing in polyimide films, resulting in weakened inter-molecular CT. Meanwhile, a weak electron donating property of the alicyclic diamine, DCHM, prevented the occurrence of both inter- and intramolecular charge transfer in polyimide films.

PI prepared from alicyclic dianhydride, 1,2 : 3,4-cyclobutanetetracarboxylic dianhydride (CBDA) are also attracting much interest. Nakanishi et al.[23] first prepared polyimides from CBDA with hexamethylenediamine or p,p'-diaminodiphenylmethane. Moore et al.[7] reported that polyimide, PI(CBDA/ODA), prepared from CBDA and oxydianiline (ODA) showed intrinsic photosensivity which could be used for positive photoimaging. Ohkita et al.[24] examined photocleavage reactions of model compounds having cyclobutane rings in the main chain, and reached the conclusion that the cyclobutane ring in the polyimides is photocleaved via the excited intramolecular CT where the aromatic moieties act as electron donors and imide rings act as electron acceptors. Although the PI derived from CBDA are used as a liquid crystal (LC) alignment layer,[25,26] their transparency, fluorescence, and thermal properties have not been investigated or reported yet.

In the present study, transparent polyimides based on CBDA with an aromatic diamine, 4,4'-diaminodiphenylmethane (DPM), a fluorinated diamine, 2,2-bis(4-

diaminodiphenyl)hexafluoropropane (6FdA), and an alicyclic diamine, DCHM, were prepared and their spectroscopic and thermal properties are studied. Their UV-Vis and fluorescence spectra as well as those of their model compounds give an insight into the micro-structures of the polyimide films based on CBDA.

EXPERIMENTAL

Materials

CBDA was kindly supplied by Nissan Chem. Co., and used without further purification. The reagent grade DPM and 6FdA were recrystallized from ethanol and dried under vacuum at 50°C for 24 h. DCHM was obtained from Wako Chemical and used without further purification. Succinic anhydride (SA) was recrystallized in distilled acetic anhydride, and dried at 50°C under vacuum for 24 h. Succinimide (SI) and N-methylsuccini-mide (MSI) were recrystallized in benzene. Aniline (A) was used for reaction with SA to prepare N-phenyl-succinimide (PSI).

Solvent used for the preparation of PAA and their model compounds was N,N-dimethylacetamide (DMAc) which was distilled before use and stored with a molecular sieve. Spectroscopic grade dichloromethane (CH_2Cl_2) was used for measuring the UV-Vis absorption spectra of model compounds.

Preparation of Poly(amide acid)s (PAA) and Polyimides (PI)

PAA were prepared following the usual procedure[27] using a 100 ml three neck round-bottom flask fitted with a mechanical stirrer, nitrogen inlet and a drying tube. A typical procedure is as follows: DCHM (1.034 g, 5.0 mmol) was dissolved in DMAc (18 ml) under nitrogen. CBDA (0.996 g, 5.0 mmol) was then added and the mixture was kept stirred at 0°C for 1 h. The mixture was continuously stirred for 24 h at room temperature to produce a viscous and homogeneous PAA solution.

The resulting PAA(CBDA/DCHM) was cast on a glass plate, and dried under vacuum at room temperature for 6 h. The film was peeled off the glass plate, and dried again under vacuum at 50°C for 24 h. The PAA film was heated stepwise at 160°C, 200°C, and 240°C for 1 h, respectively. The almost complete conversion of the PAA to the corresponding PI was ascertained by IR spectra. The films of other polyimides such as PI(CBDA/6FdA), PI(CBDA/DPM) were prepared by the same procedure as for PI(CBDA/DCHM). These films were used for measurement of fluorescence and thermal properties. The limiting viscosity numbers, $[\eta]$, of the PAAs are 0.47 dl g^{-1} for PAA(CBDA/DCHM), 0.64 dl g^{-1} for PAA-(CBDA/DPM), and 0.53 dl g^{-1} for PAA(CBDA/6FdA) which were measured in DMAc at 30°C. The chemical structures of polyimides are illustrated in Scheme 1.

Preparation of a Model Compound

A model compound, PSI, was prepared by reacting SA (1.035 g, 10.35 mmol) with A (0.94 ml, 10.35 mmol) in DMAc (18 ml) at room temperature under nitrogen atmosphere for 5 h. Then 4.2 ml pyridine and 3.2 ml acetic anhydride were dropped into the reaction solution, and the solution was kept stirred at 60°C under nitrogen
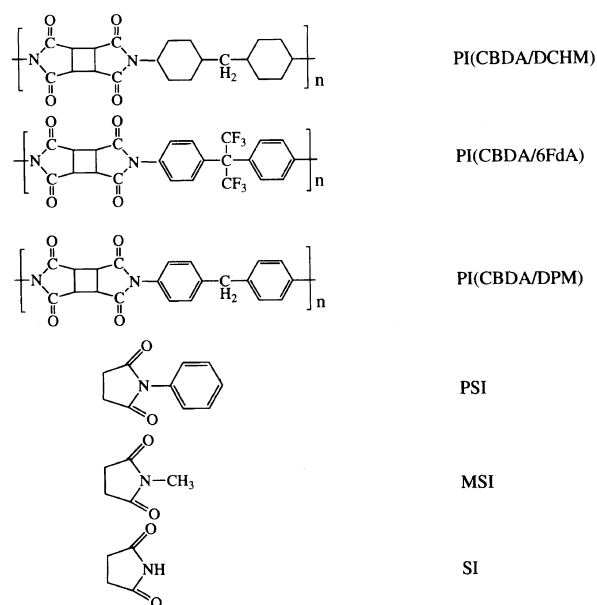
Scheme 1. Structures of transparent polyimides and model compounds.

atmosphere overnight. After the reaction was completed, DMAc was evaporated under reduced pressure at 60°C, and a light yellow crystal was obtained. After recrystal-lization in benzene, and filtration, a white crystal was obtained, which was dried under vacuum at 50°C over-night. The crystal was ascertained to be PSI by IR spectrum and melting point (153—154°C).

Measurement of UV-Vis and Fluorescence Spectra

UV-Vis absorption spectra were measured with a JASCO V-570 UV/VIS/NIR spectrophotometer for PIs and PAAs on quartz wafers. The samples were spin-coated from 2.5% DMAc solutions of PAAs on quartz wafers, then dried under vacuum for 24 h, and heated to imidization with the same conditions as for the peeled films. Absorption intensity was normalized with the film thickness measured with a topographically measured optical/laser microscope. Fluorescence spectra were measured with a fluorescence spectrophotometer (Hi-tachi Model 850) for films peeled off the glass plates. No photodegradation was observed in the present experi-mental conditions. The UV-Vis and fluorescence spectra of model compounds were measured in CH_2Cl_2 solution.

Measurement of Thermogravimetry (TG), Thermo-mechanical Analysis (TMA), and Differential Scanning Calorimetry (DSC)

The thermal characteristics of the polyimides were measured with TG, TMA, and DSC. TG was measured with a Thermal Analysis Instruments 2050 thermogravi-metric analyzer at a heating rate of 10°C min^{-1} under nitrogen atmosphere up to 600°C. TMA was carried out with a Rigaku Thermoflex TAS 200 thermomechanical analyzer. A 14 mm × 3 mm ribbon shape sample was mounted between two chucks in the TMA equipment, and the distance between them was recorded under a fixed load (5 g for PI(CBDA/6FdA) and PI(CBDA/ DCHM), 10 g for PI(CBDA/DPM)) with increasing temperature (10°C min^{-1}) under nitrogen atmosphere. DSC was carried out with a Thermal Analysis Instru-
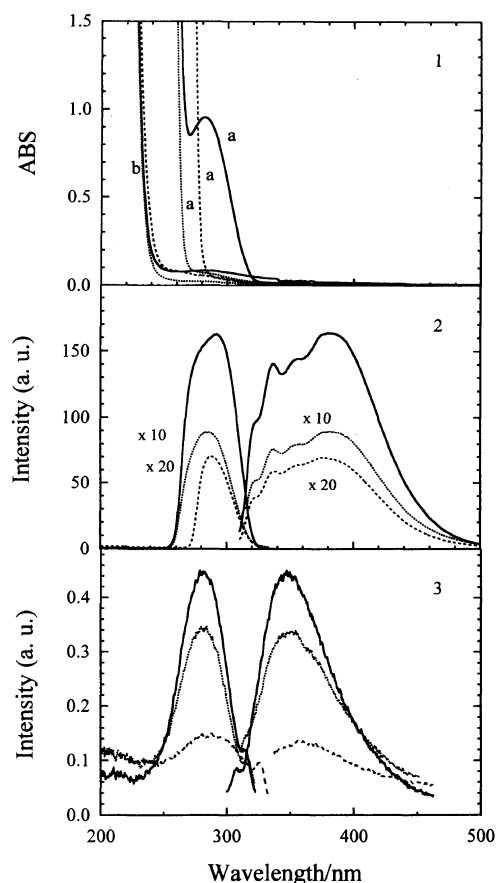
Figure 1. UV and fluorescence spectra of model compounds in CH₂Cl₂ solution. (1) UV absorption spectra in 9.3×10^{-2} M (a) and 9.3×10^{-5} M (b) solutions: ———, SI; ------, MSI; ---, PSI. (2) fluorescence spectra in 9.3×10^{-2} M solution: left, excitation spectra monitored at 380 nm; right, emission spectra excited at 290 nm; ———, SI; ------, MSI; ---, PSI. (3) fluorescence spectra in 9.3×10^{-5} M solution: left, excitation spectra monitored at about 350 nm; right, emission spectra excited at 280 nm (SI); 285 nm (MSI); and 300 nm (PSI); ———, SI; ------, MSI; ---, PSI.

ments 2010 differential scanning calorimeter with a heating rate of $20°C \, min^{-1}$ under nitrogen atmosphere up to 350°C.

RESULTS AND DISCUSSION

UV-Vis and Fluorescence Spectra of Model Compounds

In order to elucidate the aggregate state of solid transparent polyimides, their model compounds; SI, MSI, and PSI, were used in this study. Figure 1.1 shows the ultraviolet/visible (UV-Vis) absorption spectra of model compounds at 9.3×10^{-2} M and 9.3×10^{-5} M CH₂Cl₂ solutions. For SI, an absorption peak was observed at 290 nm, with the molar extinction coefficient, ε, of about $100 \, M^{-1} cm^{-1}$, which lies in the region of $n-\pi^*$ transition. So we can assign this absorption peak to $n-\pi^*$ transition of imide carbonyl group. When the solution concentration was diluted, no absorption peak was found. For MSI and PSI, no absorption peak was found in concentrated (9.3×10^{-2} M) or diluted (9.3×10^{-5} M) solutions.

Figures 1.2 and 1.3 show the fluorescence excitation and emission spectra of model compounds in 9.3×10^{-2} M and 9.3×10^{-5} M CH₂Cl₂ solutions, respectively. As it can be seen in the concentrated solutions,

Table I. Emission and excitation peak wavelengths of model compounds

Model compounds	Emission peak wavelength/nm Monomer	Emission peak wavelength/nm Excimer	Excitation peak wavelength/nm
Succinimide (SI)	348	382	280—290
N-Methylsuccinimide (MSI)	350	383	285
N-Phenylsuccinimide (PSI)	354	377	289

SI gives broad emission spectra from 300 nm to 500 nm, with peaks at around 330 nm, 360 nm, 380 nm. The excitation spectra monitored at 330 nm (not shown in the figure) and 380 nm show a same peak at around 290 nm similar to that of the absorption spectrum in Figure 1.1. In the dilute solution (9.3×10^{-5} M), the emission peak of SI is found at 355 nm, which can be assigned as monomer emission of SI molecules. When monitored at 350 nm, the excitation peak is found at 280 nm, almost at the same wavelength as in the concentrated solution in Figure 1.2. The observation of a similar excitation peak for fluorescence at 380 nm in the concentrated solution and that at 355 nm in the diluted solution suggests that the emission at 380 nm in Figure 1.2 is due to the excimer formation between SI molecules at the excited state. Fluorescence spectra of MSI and PSI also show excimer emission at around 380 nm and monomer emission around 355 nm. The emission and excitation peak wavelengths of these three model compounds are summarized in Table I.

As are shown in Table I, the excimer spectra of SI, MSI, PSI appear at about the same wavelength. Consequently, we can presume that the excimer emission are due to the head-to-tail overlap of two imide rings, since no effect of steric hindrance of the N-substituent groups was observed. The fluorescence intensity of SI, MSI, and PSI in the concentrated solution decreases markedly from SI to MSI and PSI. The electron donating property of the N-substituents changes in the order of phenyl group > methyl group > -H. The imide ring has an electron accepting property though SI has no aromatic ring. So it is supposed that at the excitation state of PSI and MSI, intra- or intermolecular CT occurs, resulting in increase in non-radiative deactivation of the excitation state.[28]

UV-Vis Absorption Spectra of Films

Figure 2a shows the UV-Vis absorption spectra of thin films of PI(CBDA/DPM), PI(CBDA/6FdA), and PI(CBDA/DCHM), which are normalized with a film thickness of 0.3 μm. Spectra of both PI(CBDA/DPM) and PI(CBDA/6FdA) have no absorption band above 375 nm, and that of PI(CBDA/DCHM) has almost no absorption band above 310 nm, which means all polyimides derived from alicyclic dianhydride CBDA together with PI(CBDA/DPM), PI(CBDA/6FdA), and PI(CBDA/DCHM) show highly transparent properties in the visible region. This is due to the weak electron accepting property of the alicyclic imide moieties originating from CBDA, which weakens the intra- or intermolecular charge transfer that occurs in the conventional aromatic polyimides. Above 300 nm, weak
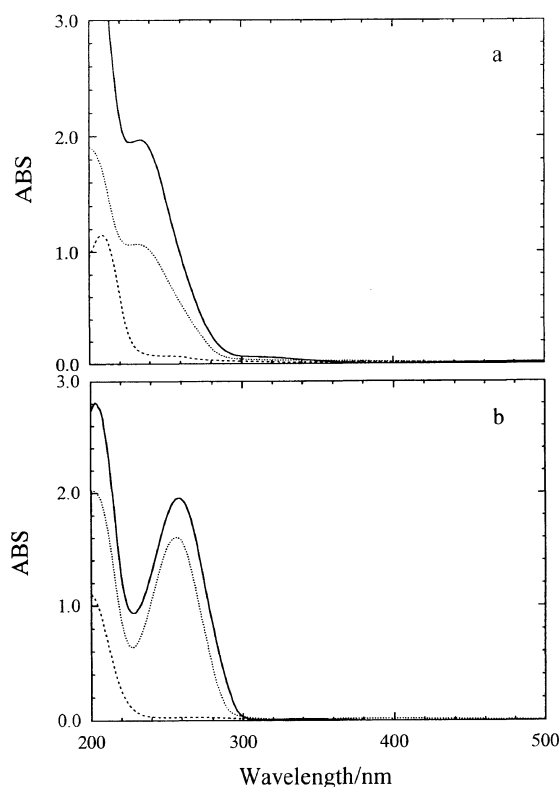
Figure 2. UV absorption spectra of polyimides (a) and poly(amide acid)s (b) thin films of *ca.* 0.3 μm thick, (CBDA/DPM) ——, (CBDA/6FdA) ------, and (CBDA/DCHM) ---.

absorption tails in PI(CBDA/DPM) and PI(CBDA/6FdA) are observed. The absorption tail of PI(CBDA/DPM) is bigger than that of PI(CBDA/6FdA). Weak ground-state charge transfer complex based on weak electron accepting property of CBDA may thus be formed in both PI(CBDA/DPM) and PI(CBDA/6FdA) films. Moreover, a bulky substituent group $-C(CF_3)_2-$ exists in 6FdA, tight molecular packing in PI(CBDA/6FdA) would be prevented, thus resulting in weak intermolecular interaction.

PI(CBDA/DPM) and PI(CBDA/6FdA) have absorption peaks at 236 nm and 235 nm, respectively, almost at the same wavelength. This suggests that these peaks are due to the absorption of phenylene groups of the diamine moieties, as the dianhydride belongs to alicyclic compounds. The difference in absorption intensity between PI(CBDA/DPM) and PI(CBDA/6FdA) may be explained by different electron attracting properties of the substituents for phenylene groups. The 6FdA, which has a bulky substituent group $-C(CF_3)_2-$ between two phenylene groups, would reduce the electron density of the phenylene groups, owing to the strong electron negativity of fluorine atoms.

As can be seen in Figure 2a, PI(CBDA/DCHM) has an absorption peak at 210 nm, and shows almost no absorption above 310 nm, which exhibits extremely transparent property in almost all UV-Vis regions. This can be explained by the weak electron donating property of alicyclic diamine, DCHM,[29] and the weak electron accepting property of alicyclic dianhydride, CBDA, resulting in elimination of intra- and intermolecular charge transfer formation.

The UV-Vis absorption spectra of thin films (*ca.*

0.3 μm) of PAA(CBDA/DPM), PAA(CBDA/6FdA), and PAA(CBDA/DCHM) are shown in Figure 2b. Comparing to the absorption spectra of PI(CBDA/DPM) in Figure 2a, PAA(CBDA/DPM) shows an absorption peak at 260 nm, while PI(CBDA/DPM) shows an absorption peak at 236 nm, which means a blue shift of 24 nm when the poly(amide acid) is imidized to the polyimide. Sung *et al.*[30] studied the UV spectra of a model imide derived from 1,5-diaminonaphthalene (DAN) and phthalic anhydride, and found a blue shift of spectra when the amide acid was converted to an imide. In the present study, we used an alicyclic dianhydride, CBDA, which has no absorption in UV-Vis region. Thus, the absorption peak of 236 nm is due to the absorption of the diamine moiety in PI(CBDA/DPM). In PAA partial contribution of enolization of amide bond[31] ($-C(OH)=N-$) would extend the delocalization of electrons, which results in a red shift of the absorption spectra of PAA(CBDA/DPM). Another reason for the blue shift when the poly(amide acid) is converted to the polyimide is that the electron donating property of amide bond is bigger than imide bond, which increases the $n-\pi$ conjugation between amide nitrogen and phenyl group in PAA(CBDA/DPM). The absorption above 300 nm for PI(CBDA/DPM) is bigger than for PAA(CBDA/DPM). After imidization by 160°C, 200°C, and 240°C for 1 h each, molecular aggregation of PI(CBDA/DPM) is improved, compared to PAA(CBDA/DPM), resulting in increase in intermolecular CT formation.

The blue shift of absorption peak after imidization was also found in PI(CBDA/6FdA) and PAA(CBDA/6FdA) films. A reduction of absorption intensity of PI(CBDA/6FdA) was also observed. No distinct difference in absorption tails was found between these films.

Both CBDA and DCHM are alicyclic compounds, thus PI(CBDA/DCHM) shows absorption peak only at 210 nm which corresponds to the absorption of imide rings. The small red shift of PI(CBDA/DCHM) compared to PAA(CBDA/DCHM) is due to the formation of imide rings.

Fluorescence Spectra of Polyimide Films

Fluorescence spectroscopy is usually used for investigating the microstructures or aggregate structures of polymers,[32-35] because it is very sensitive to changes of microenvironments of chromophore moieties in polymer matrices. Figure 3 shows the fluorescence spectra of PI(CBDA/DCHM) film with a thickness of 50 μm. When excited at 324 nm, an emission peak is observed at 424 nm. When excited at 370 nm, 390 nm, 410 nm, 430 nm, 450 nm, 470 nm, respectively, red shifts of emission peaks from 430 nm to 524 nm are observed, showing marked excitation wavelength dependence of the emission peak. No monomer fluorescence was found which appeared in the fluorescence spectra of model compounds.

The marked excitation wavelength dependence has also been observed in the fluorescence spectra of 6FDA-containing polyimides, PI(6FDA/DCHM) and PI(6FDA/PDA),[22] as well as in those of paracrystalline solid of a liquid crystalline aromatic polyester.[34] This is a special phenomenon in transparent polyimide films, compared to the fluorescence of conventional aromatic polyimides.[33,36,37] Frank *et al.*[36,37] investigated the
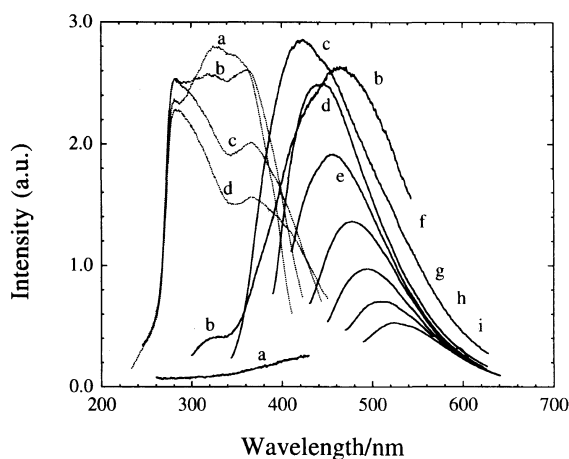
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Figure 3. Fluorescence spectra of PI(CBDA/DCHM) film (50 μm thick) imidized at 160°C, 200°C, and 240°C. ———: emission spectra excited at (a) 240 nm, (b) 280 nm, (c) 324 nm, (d) 370 nm, (e) 390 nm, (f) 410 nm, (g) 430 nm, (h) 450 nm, and (i) 470 nm, respectively; ------: excitation spectra monitored at (a) 424 nm, (b) 450 nm, (c) 480 nm, and (d) 500 nm, respectively.

Figure 4. Fluorescence spectra of PI(CBDA/DCHM) film (50 μm thick) imidized at 160°C, and 200°C. ———: emission spectra excited at (a) 240 nm, (b) 280 nm, (c) 324 nm, (d) 350 nm, (e) 370 nm, (f) 390 nm, (g) 410 nm, (h) 430 nm, and (i) 450 nm, respectively; ------: excitation spectra monitored at (a) 427 nm, (b) 450 nm, (c) 480 nm, and (d) 500 nm, respectively.

degree of cure of PI(PMDA/ODA) film with fluorescence spectroscopy where PMDA denotes pyromellitic dianhydride, and reported that fluorescence intensity increased with increasing cure temperature. They assigned their emission spectra to the emission of charge transfer complex in the excited state which was formed between excited pyromellitimide moiety as an electron acceptor and diphenyl ether moiety as an electron donor. Hasegawa et al.[33] reported that in PI(BPDA/PDA) derived from biphenyltetracarboxylic dianhydride (BPDA) and PDA, annealing induces not only increase in emission intensity at 525 nm but also the appearance of a new emission spectra at 540 nm, which they assigned to emission of a ground-state intermolecular CT complex and considered this is due to increase in degree of molecular packing resulting from annealing. Hasegawa et al.[33] found a red shift of the emission peak after another thermal annealing, possibly be due to the appearance of another packing structure. However the excitation wavelength dependence of fluorescence in a same sample as is shown in Figure 3 was not observed for PI(BPDA/PDA). Thus we suggest that this excitation wavelength dependence of emission spectra is a specific phenomenon to the present polyimide films. In Figure 3 two excitation peaks are observed for the PI(CBDA/ DCHM) film, one is at 324 nm, the other is at 370 nm. Strong fluorescence excitation occurs at 280—300 nm, but sudden decrease at shorter wavelengths than 280 nm would be a ghost due to increase in absorbance of the thick (50 μm) film. The shapes of the excitation spectra are different from that of the UV spectrum in Figure 2 and those of excitation spectra of the model compounds in Figures 1. Thus we presume that ground-state complexes with various energy levels exist in the PI(CBDA/ DCHM) film. When the film was irradiated by UV light, the ground-state complexes were excited to their excited states and emit at various wavelengths. We are not sure if energy transfer in the excited states occurs between the excited ground-state complexes. But we probably had better interpret the emission spectra to the direct emission from excited ground-state complexes, since the energy
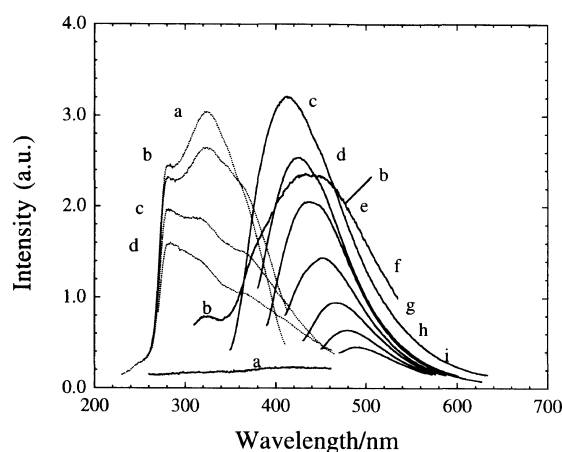
difference between the ground and excited states of each complex is not monodisperse in amorphous solids and the red shift of the emission peak occurs regularly according to the shift of excitation wavelength.

It is of great interest that, when PI(CBDA/DCHM) film was excited at 280 nm, its emission peak was found at a longer wavelength ((b) in Figure 3) apart from those for other excitation-wavelength-dependent emission spectra. However, when PI(CBDA/DCHM) film was imidized at 160°C and 200°C for 1 h each, the emission spectrum excited at 280 nm showed a peak at 436 nm (Figure 4) and became within the profiles of other excitation-wavelength-dependent emission spectra. The shift in emission peak is noticed only for the spectra excited at 280 nm where the monomeric imide moiety can be excited. This shift of emission peak excited at 280 nm with increasing imidization temperature suggests that the excited energy transfer from the excited singlet state of the monomeric imide moiety to a ground-state complex in PI(CBDA/DCHM) becomes a dominant process and the energy level and conformation of the complex to which energy transfer occurs differ by changing the imidization conditions. A minor peak observed at 322 nm for the emission excited at 280 nm in Figures 3 and 4 would correspond to monomer fluorescence of the imide moiety in PI(CBDA/DCHM). As CBDA and DCHM both are alicyclic compounds having configurational and conformational isomers, the micro-structures of the complexes in PI(CBDA/DCHM) would be complicated and of various types.

In conventional aromatic polyimides, two kinds of packing structures are proposed,[38] "preferred layer packing" (PLP) in which the imide moieties of neighboring chains are aligned in a face-to-face fashion and "mixed layer packing". Proponents of the latter often argue that charge transfer forces are significant and give rise to a packing arrangement whereby the imide ring of one chain and the (amine) phenyl ring of another chain adopt a coplanar "sandwich" conformation.

In the present case of PI(CBDA/DCHM), the cyclo-butanediimide moiety is a mixture of two configurational
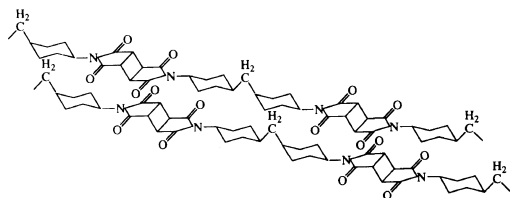
Figure 5. An example of the packing structures in PI(CBDA/DCHM) film.

Figure 6. Fluorescence spectra of PI(CBDA/DPM) film (50 μm thick), ——: emission spectra excited at (a) 250 nm, (b) 310 nm, (c) 350 nm, (d) 370 nm, (e) 390 nm, (f) 410 nm, (g) 430 nm, and (h) 450 nm, respectively; ------: excitation spectra monitored at (a) 449 nm, (b) 500 nm, and (c) 550 nm, respectively.

Figure 7. Fluorescence spectra of PI(CBDA/6FdA) film (50 μm thick), ——: emission spectra excited at (a) 280 nm, (b) 300 nm, (c) 310 nm, (d) 328 nm, (e) 350 nm, (f) 370 nm, (g) 390 nm, (h) 410 nm, (i) 430 nm, and (j) 450 nm, respectively; ------: excitation spectra monitored at (a) 405 nm, (b) 450 nm, and (c) 500 nm, respectively.

isomers; *trans*-diimide and *cis*-diimide. DCHM[19] is also a mixture of *trans–trans*, *trans–cis*, and *cis–cis* isomers as to the 1,4-disubstituted cyclohexane moiety. The observation of excimer fluorescence at the same wavelength for three model compounds (Figure 1) suggests that the head-to-tail overlap is favorable to the intermolecular dimer interaction between alicyclic imide moieties. Fluorescence spectra (Figures 3 and 4) show the existence of intermolecular ground-state complexes of various energy levels. As DCHM shows weak electron donating property and CBDA shows weak electron attracting property, very weak intermolecular CT might also occur in the excited state. By considering these results, the packing arrangement of PI(CBDA/DCHM) may be proposed as a mixed layer packing with the head-to-tail stacking of imide ring of one polymer backbone with that of another polymer backbone. An example of the local packing structure is shown in Figure 5. As both CBDA and DCHM have configurational and conformational isomers, coplanar packing is very difficult, and the conformation is suggested to include various non-coplanar packing structure due to various degrees of constraint formation. As is shown in UV spectra in Figure 2, the ground-state interaction is very weak, this kind of weak interaction would be strengthened at excited state because of the increased donating property of DCHM and accepting property of CBDA at the excited state. The existence of two peaks in fluoresecence excitation spectra at 324 nm and 370 nm and increase in the proportion of the peak at 370 nm by the annealing at higher imidization temperature (240°C) in Figure 3 compared to the case in Figure 4 would be attributed to increase in more stable packing structure in PI(CBDA/DCHM) by annealing probably with a partial contribution of CT nature.

Excitation wavelength dependence is also observed in emission spectra of PI(CBDA/DPM) and PI(CBDA/6FdA) films, as shown in Figures 6 and 7 respectively. The packing structures of PI(CBDA/DPM) and PI(CBDA/6FdA) films are suggested to be similar to that of PI(CBDA/DCHM). In PI(CBDA/DPM), the fluorescence emission intensity decreased compared to that of PI(CBDA/ DCHM), as well as a red shift of the peak by 25 nm, owing to the increase in CT contribution because of the strong electron donating property of DPM. On the other hand, in PI(CBDA/6FdA), emission intensity is almost the same as that of PI(CBDA/ DCHM). A bulky $-C(CF_3)_2-$ group in 6FdA moiety, together with the large electron negativity of fluorine atom, would reduce the electron donating property of 6FdA compared to that of DPM. The packing structure of PI(CBDA/6FdA) is thought to be less ordered compared to PI(CBDA/DPM) due to the steric constraint
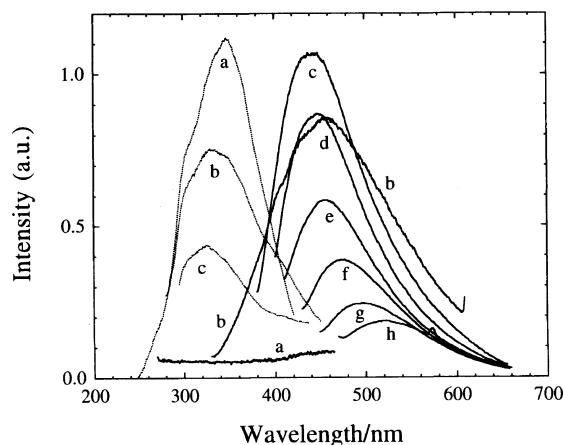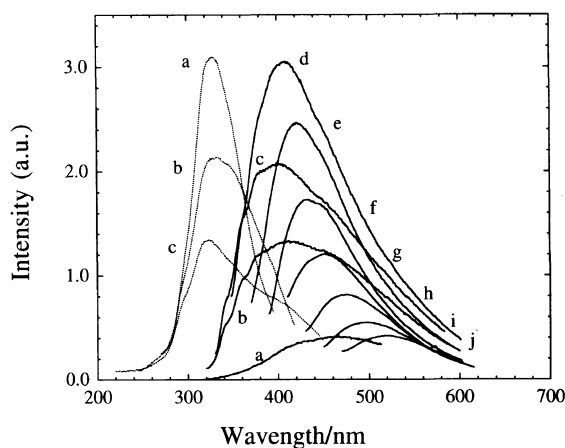
resulting from the bulky $-C(CF_3)_2-$ group, and would be similar to that of PI(CBDA/DCHM). Both PI-(CBDA/6FdA) and PI(CBDA/DPM) show one peak in their excitation spectra in Figures 6 and 7, when they are monitored at different wavelengths. PI(CBDA/6FdA) and PI(CBDA/DPM) are supposed to form ground-state complexes with the head-to-tail stacking of imide rings in polymer backbones, where the contribution of charge transfer should also be considered because CBDA moiety acts as an electron acceptor, and 6FdA or DPM moiety acts as an electron donor.

Thermal Properties of CBDA-Containing PI

Figure 8 shows TG curves of PI(CBDA/DPM), PI-(CBDA/6FdA), and PI(CBDA/DCHM) films. PI(CBDA/DPM), PI(CBDA/6FdA), and PI(CBDA/DCHM) exhibited little weight loss from room temperature up to 440°C. Above 440°C, PI(CBDA/DCHM) loses weight rapidly, and shows remaining weight of about 30% after heating to 500°C, as a fully alicyclic polyimide. PI-(CBDA/6FdA) shows decomposition at 441°C, and
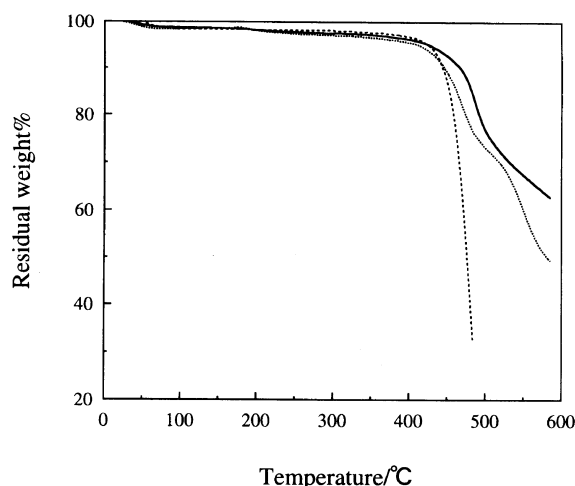
Figure 8. TG curves of PI(CBDA/DPM) ——, PI(CBDA/6FdA) ------, and PI(CBDA/DCHM) ——— in N_2 with a heating rate of 10°C min⁻¹.
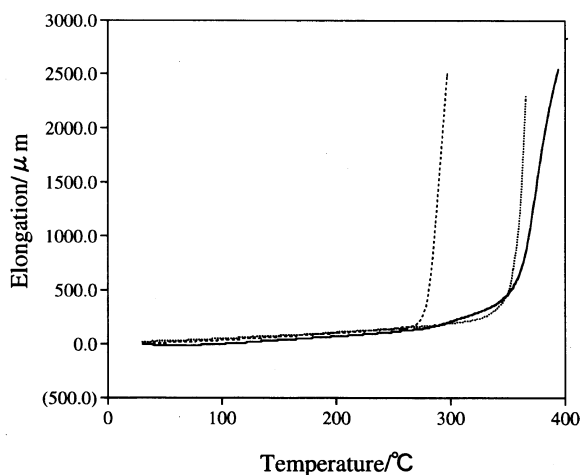
Figure 9. TMA curves of PI(CBDA/DPM) ——, PI(CBDA/6FdA) ------, and PI(CBDA/DCHM) ——— in N_2 with a heating rate of 10°C min⁻¹, and under a fixed load 5 g for PI(CBDA/DCHM) and PI(CBDA/6FdA), 10 g for PI(CBDA/DPM).

then the slope becomes less steep at about 500°C. The decomposition at 441°C is due to the decomposition of the moiety of CBDA, and the second change at 530°C would be due to the moiety of 6FdA which has a bulky group $-C(CF_3)_2-$. The remaining weight of PI(CBDA/6FdA) is about 50% after heating to 600°C. PI(CBDA/DPM) loses weight quickly above 454°C, and shows a remaining weight about 60% after heating to 600°C. From the above data, we conclude that the decomposition is primarily due to decomposition of the alicyclic moiety.

The TMA curves of PI(CBDA/DPM), PI(CBDA/6FdA), and PI(CBDA/DCHM) films are shown in Figure 9. We obtained tough films of these polyimides by cooling under vacuum from the imidization temperature. In the case of PI(CBDA/6FdA), a tough film was obtained after imidization at 160°C, 200°C, 240°C, and 300°C for 1 h each, which was used for TMA measurements. The films were elongated gradually with increasing temperature until their glass transition temperature, T_g, is reached, where the films were elongated rapidly towards infinite. The glass transition temperature of PI(CBDA/DPM),

Table II. Summary of thermal properties of PI(CBDA/DPM), PI(CBDA/6FdA), and PI(CBDA/DCHM)

Sample	$T_d/°C$ by TG	$T_g/°C$ by TMA
PI(CBDA/DPM)	454	360
PI(CBDA/6FdA)	441	349
PI(CBDA/DCHM)	440	277

PI(CBDA/6FdA), and PI(CBDA/DCHM) obtained from TMA curves are 360°C, 349°C, and 277°C, respectively. Compared to a conventional aromatic polyimide, e.g., PI(PMDA/DPM) with $T_g = 336°C$ by TMA,[19] the introduction of alicyclic dianhydride CBDA into the polyimide main chains, did not change the T_g values so much. PI(CBDA/DPM) and PI(CBDA/6FdA) show essentially the same thermomechanical behavior under heating, whereas PI(CBDA/DCHM) shows T_g at a lower temperature, suggesting that the introduction of alicyclic DCHM, having trans–trans, trans–cis, and cis–cis isomers to the polyimide backbone affects the thermomechanical behavior of the polyimides owing to the existence of various non-coplanar packing structure.

The thermal properties of PI(CBDA/DPM), PI(CBDA/6FdA), and PI(CBDA/DCHM) measured with TG and TMA are summarized in Table II. These polyimides are thermally stable up to 440—450°C under the deaerated conditions and the stability is influenced by CBDA moiety. PI(CBDA/DPM) and PI(CBDA/6FdA) have very high T_g similar to conventional aromatic polyimides, while PI(CBDA/DCHM) shows its T_g at 277°C.

DSC curves of these three polyimides films showed no substantial exotherms or endotherms in the temperature range of 50—350°C.

CONCLUSIONS

Transparent polyimides derived from CBDA with DPM, 6FdA, or DCHM were successfully prepared. Their UV-Vis absorption and fluorescence spectra were investigated, compared with model compounds. All polyimides based on CBDA showed high transparency in visible region and no absorption was found above 375 nm. Especially, PI(CBDA/DCHM) showed the highest transparency without almost any absorption above 310 nm. The absorption at 235 nm of PI(CBDA/DPM) and PI(CBDA/6FdA) was assigned to that of the phenylene group in diamine moieties. The fluorescence of all polyimides studied is attributed mainly to the excited ground-state complex. Excitation wavelength dependence of fluorescence peaks was observed, due to various conformation of packing structure. From the measurement of TMA and TG, PI prepared from CBDA show very high glass transition temperature, T_g, in the region of 277—360°C, and decomposition temperature around 450°C. Thus, we conclude that introduction alicyclic dianhydride CBDA to the polyimides chains can prevent the formation of both inter- and intramolecular CT without reducing their thermal properties compared to corresponding aromatic polyimides.

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