

Absorption and Fluorescence Spectra and Thermal Properties of a Novel Transparent Polyimide PI(6FDA/DCHM)

Qinghua Li, Kazuyuki Horie, Rikio Yokota[‡]

The University of Tokyo, Graduate School of Engineering, Department of Chemistry and Biotechnology, 7-3-1 Hongo, Bunkyo-Ku, Tokyo 113, Japan

[‡]Institute of Space and Astronautical Science, 3-1-1 Yoshinodai, Sagami-hara, Kanagawa 229, Japan

Introduction

Ultraviolet-visible absorption spectra, fluorescence spectra and thermal properties of PI(6FDA/DCHM) were investigated compared to aromatic polyimides derived from 6FDA. PI(6FDA/DCHM) showed higher transparency than PI(6FDA/PDA) in the ultraviolet-visible region. Inter- and intramolecular charge transfers were weakened by introducing fluorinated dianhydride, 6FDA, and alicyclic dicyclohexyldiamine, DCHM, in polyimide main chains. Excitation-wavelength dependence was found in the fluorescence spectra, which suggests inhomogeneous, less-ordered aggregation in polyimide films including 6FDA or DCHM. PI(6FDA/DCHM) had glass transition temperature, T_g of about 250°C, as the same as PI(6FDA/PDA), from the TMA measurements, which proved that thermal stability of polyimides was not reduced by introducing the alicyclic group.

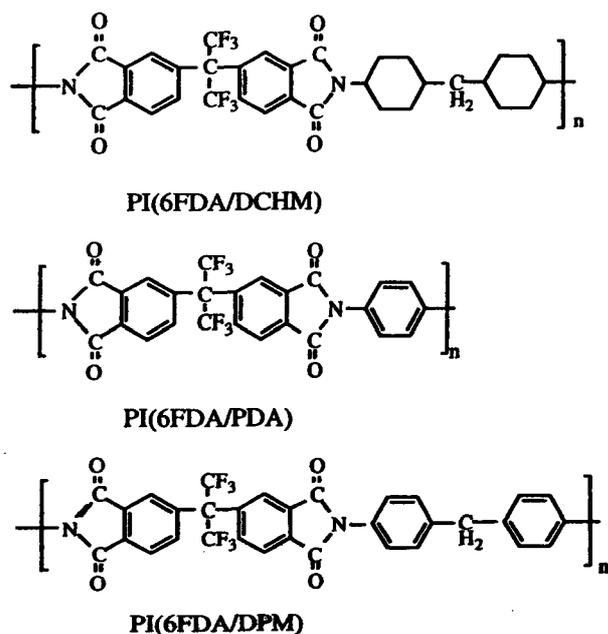
Experiments

DCHM was dissolved in an aprotic solvent, DMAc, in a dry three-necked, 100 ml round-bottom flask fitted with a mechanical stirrer, a nitrogen inlet and drying tube. A stoichiometric amount of dianhydride, 6FDA, was added. The solution was allowed to stir for 24 h until the solution became homogeneous and viscous owing to the formation of a poly(amide acid) (PAA).

The resulting PAA(6FDA/DCHM) was cast on a glass plate, and dried under vacuum at room temperature for 5 h, then 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 1h respectively. The almost complete conversion of the PAA to polyimide, PI(6FDA/DCHM), was ascertained by IR spectra. The polyimides, PI(6FDA/PDA) and PI(6FDA/DPM), were prepared in a similar procedure. The limited viscosity numbers, $[\eta]$, of these PAAs were measured to be 0.46 dL/g for PAA(6FDA/DCHM), 0.45 dL/g for PAA(6FDA/PDA), and 0.45 dL/g for PAA(6FDA/DPM) in DMAc at 30°C. The chemical structures of polyimides investigated are illustrated in Scheme 1.

UV-vis spectra were measured with a Jasco V-570UV/vis/NIR spectrophotometer. Fluorescence spectra were measured with a fluorescence spectrophotometer (Hitachi Model 850).

The thermal characteristics of the polyimides were measured with DSC, TG and TMA. DSC was carried out with a Thermal Analysis Instruments 2010



Scheme 1. The chemical structure of polyimides

DCHM), and aromatic polyimide, PI(6FDA/PDA), which are normalized with a film thickness of 0.6 μm . As it can be seen, both spectra of PI(6FDA/DCHM) and PI(6FDA/PDA) have no absorption band above 370 nm, which means that both PI(6FDA/DCHM) and PI(6FDA/PDA) are highly transparent in the visible region. The bulky group $-\text{C}(\text{CF}_3)_2-$ prevents molecular packing in the polyimides films, thus resulting in weak intermolecular interaction, which exists between diamine moiety as an electronic donor and diimide moiety as an electronic acceptor. It is interesting to note that the absorption spectrum of PI(6FDA/DCHM) shows a very small platform region from 260 nm to 300 nm. On the other hand, PI(6FDA/PDA) shows a shoulder absorption at 260 nm, which is similar to that for kapton type aromatic polyimide, attributed to the intramolecular charge transfer by Lafemina et al.¹ and Kan et al.² The very weak intramolecular charge transfer of PI(6FDA/DCHM), compared with PI(6FDA/PDA), can be explained to be due to the weak electron donating property of DCHM³ compared with PDA. The absorption intensity for PI(6FDA/DCHM) above 300 nm is weaker than that for PI(6FDA/PDA), showing that intermolecular charge transfer in PI(6FDA/DCHM) is very weak even if it was formed, compared with that for PI(6FDA/PDA).

From the above, we could arrive the conclusion that the introduction of 6FDA into polyimide chains would weaken the intermolecular charge transfer due to the steric hindrance.⁴ On the other hand, the weak electron donating property of DCHM would reduce not only intermolecular charge transfer but also intramolecular charge transfer. Thus, by introducing 6FDA and DCHM into

differential scanning calorimeter under nitrogen atmosphere at a heating rate of 10°C/min. TG was measured with a Thermal Analysis Instruments 2050 thermogravimetric analyzer with a heating rate of 20°C/min under nitrogen atmosphere up to 800°C. TMA was carried out with a Rigaku Thermoflex TAS 200 thermomechanical analyzer under a fixed load (10 g) with increasing temperature (10°C/min) under nitrogen atmosphere.

Results and Discussion

Figure 1 shows the UV-vis absorption spectra of thin films of the alicyclic polyimide, PI(6FDA/

polyimide chain, a very transparent polyimide film was obtained.

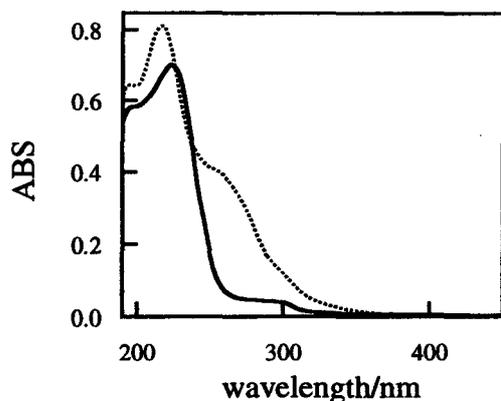


Figure 1. The UV absorption spectra of PI(6FDA/DCHM) (—) and PI(6FDA/PDA) (.....) thin film of 0.6 μm .

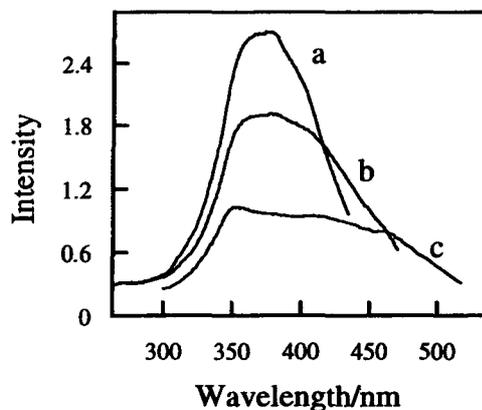


Figure 3. The fluorescence excitation spectra of PI(6FDA/DCHM) monitored at (a) 466 nm, (b) 500 nm, (c) 550 nm, respectively.

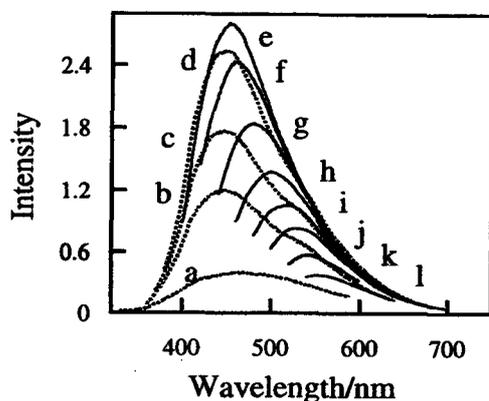


Figure 2. The fluorescence spectra of PI(6FDA/DCHM) (20 μm), excited at (a) 300 nm, (b) 330 nm, (c) 340 nm, (d) 350 nm (.....), (e) 373 nm, (f) 390 nm, (g) 410 nm, (h) 430 nm, (i) 450 nm, (j) 470 nm, (k) 490 nm, (l) 510 nm (—).

Figure 2 shows the fluorescence spectra of PI(6FDA/DCHM) film excited at various wavelengths. When the film was excited at 300 to 350 nm, the emission peak was found at 450 nm. When the film was excited in longer excitation wavelength region from 373 nm to 510 nm, the fluorescence peak red shifted from 466 nm to 560 nm. No monomer fluorescence was found when the film was excited at 230 nm to 250 nm. The very strong excitation wavelength dependence shows that there exist various ground-state interaction complexes in the PI(6FDA/DCHM) film. Evans³ studied the charge-transfer

spectra involving saturated hydrocarbons and concluded that cyclohexane showed weak electron-donating property. Thus, we might presume this kind of ground-state complex as charge-transfer complex between 6FDA moiety as an electron acceptor and diamine moiety as an electron donor. As DCHM has configurational and conformatinal isomers and 6FDA has large steric hindrance, the aggregation structure of PI(6FDA/DCHM) would not be so ordered as usual aromatic polyimides are, thus resulting in the existence of interaction with various energy levels in PI(6FDA/DCHM) film. A marked excitation-wavelength dependence has also been observed for the fluorescence spectra of paracrystalline solid of a liquid-crystalline aromatic polyester.⁵ The excitation spectra of PI(6FDA/DCHM) film monitored at various wavelengths are shown in Figure 3. The appearance of excitation spectra are different according to the different monitor wavelengths. This also proves that there are various kinds of ground-state

interactions in the PI(6FDA/DCHM) film.

The excitation-wavelength dependence is also observed in the PI(6FDA/PDA) film, but the fluorescence intensity decreases rapidly due to the charge-transfer nature of the excited state. The intermolecular and intramolecular charge transfers usually formed in aromatic polyimide films are thought to be weakened by the bulky group $-C(CF_3)_2-$ in 6FDA and/or the weak electronic donating property of DCHM.

The TMA curves of PI(6FDA/DCHM) and PI(6FDA/PDA) films are shown in

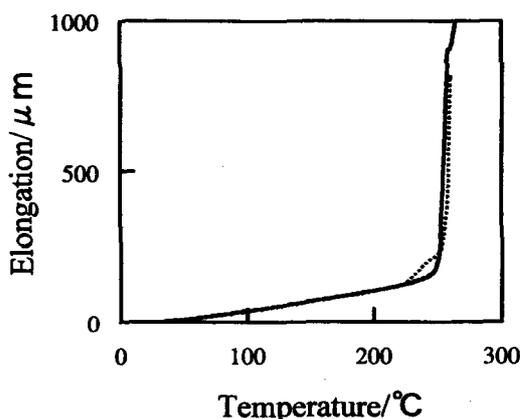


Figure 4. The TMA curves of PI(6FDA/DCHM) (—) and PI(6FDA/PDA) (.....) in N₂ with a heating rate of 10°C/min.

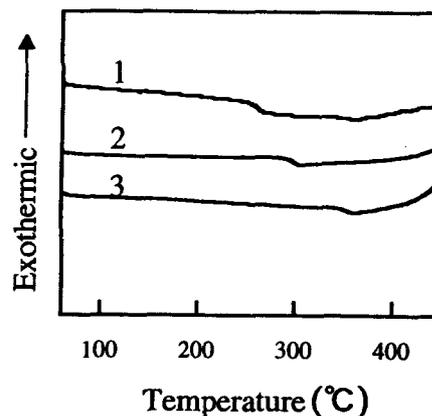


Figure 5. The DSC curves of PI(6FDA/DCHM) (1), PI(6FDA/DPM) (2) and PI(6FDA/PDA) (3) in N₂ with a heating rate of 10°C/min.

Figure 4. The films were elongated gradually with increasing temperature until their glass transition temperatures, T_g , where the films were elongated rapidly towards infinite. The glass transition temperature of PI(6FDA/DCHM) and PI(6FDA/PDA) obtained from TMA curves are 251°C and 252°C, respectively. The T_g value of the alicyclic polyimide prepared from 6FDA is not very different from that of the aromatic polyimide with the same skeleton structure and shows similar thermomechanical behavior under heating.

The DSC curves of PI(6FDA/DCHM), PI(6FDA/DPM) and PI(6FDA/PDA) are shown in Figure 5. For PI(6FDA/DCHM), endothermic peak shift for glass transition was observed at 260°C, and no endothermic or exothermic peak was found until 440°C. Above 440°C the curve drifted rapidly, which is due to the chemical degradation of the polyimide. PI(6FDA/DPM) used for comparing its thermal properties with PI(6FDA/DCHM) showed a glass transition at 292°C. For PI(6FDA/PDA) the glass transition temperature was found at 350°C, and the drift was observed at about 440°C.

Figure 6 shows the TG curves of PI(6FDA/DCHM), PI(6FDA/DPM) and PI(6FDA/PDA) films. PI(6FDA/DCHM), PI(6FDA/DPM) and PI(6FDA/PDA) exhibited no weight loss from room temperature up to 460°C. Above 460°C, PI(6FDA/DCHM) loses its weight rapidly and finds no remaining weight at last. In contrast, PI(6FDA/DPM) and PI(6FDA/PDA) become to lose their weight at

526°C and 541°C, respectively, and show a remaining weight of about 50%. This can be explained by the fact that alicyclic chains would suffer decomposition under heating above 460°C, while the aromatic chains carbonize under these conditions.

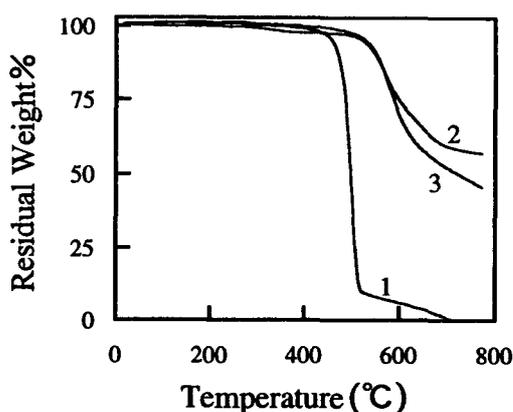


Figure 6. The TGA curves of PI(6FDA/DCHM) (1), PI(6FDA/DPM) (2) and PI(6FDA/PDA) (3) in N₂ with a heating rate of 20°C/min.

Conclusions

A novel transparent polyimide derived from 6FDA with alicyclic DCHM was prepared. Ultraviolet-visible absorption and fluorescence spectra were studied compared with aromatic polyimides derived from 6FDA. PI(6FDA/DCHM) show higher transparency than PI(6FDA/PDA) in ultraviolet-visible region. The introduction of 6FDA into the polyimide main chains weakened the intermolecular charge transfer, and the introduction of alicyclic diamine, DCHM, to the polyimide main chains, both inter-

and intramolecular charge transfer were weakened. The marked excitation-wavelength dependence of their fluorescence spectra was attributed to the heterogeneity of their less ordered structure. Furthermore, the thermal properties of PI(6FDA/DCHM) were also discussed. PI(6FDA/DCHM) is thermally stable compared to PI(6FDA/PDA) with the T_g of above 250°C. From the TMA measurements, the thermomechanical property of the alicyclic polyimide is similar to the corresponding aromatic polyimides. So we conclude that the introduction of 6FDA and the alicyclic diamine to the polyimides chains can prevent the formation of inter- and intramolecular charge transfer without reducing the thermal properties compared to corresponding aromatic polyimides.

References

1. J. P. Lafemina, G. Arjavalingham and G. Hougham, *J. Chem. Phys.* **90**, 5154 (1989).
2. L. Kan and K. C. Kao, *J. Chem. Phys.*, **98**, 3445 (1993).
3. D. F. Evans, *J. Amer. Chem. Soc.*, **849**, 4229 (1957).
4. A. K. St. Clair and T. L. St. Clair, *Polym. Mater. Sci. Eng.*, **51**, 62 (1984).
5. H. W. Huang, K. Horie, T. Yamashita, S. Machida, M. Sone, M. Tokita, J. Watanabe and Y. Maeda, *Macromolecules*, **29**, 3485 (1996).