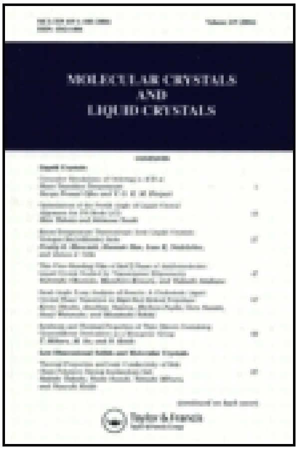

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Photoluminescences from Aromatic Polyimides in Thin Films: Effects of Precursor Origin and Imidization History

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Poly(*p*-phenylene biphenyltetracarboximide) and poly(4,4'-oxydiphenylene pyromellitimide) in thin films were prepared from their poly(amic acid)s (PAA's) and poly(amic diethyl ester)s (PAE's), respectively, through thermal imidizations over 300-415°C. The photoluminescence characteristic, molecular orientation, and density of these polyimides were dependent strongly on the precursor origin as well as the imidization history. Higher temperature imidization produced higher density and molecular in-plane orientation in the resultant polyimide film, regardless of the precursor origin. However, as the imidization temperature increased, the fluorescence intensity in the films from the PAA's increased, whereas that in the films from the PAE's decreased. These indicate that PAE's lead quite different morphologies and molecular conformations in the resultant polyimide films, compared to the PAA's.

Keywords: polyimides, imidization, excitation, fluorescence, birefringence, density, molecular ordering

INTRODUCTION

Aromatic polyimides are widely used in the microelectronic industry because of their excellent properties and easy processability[1]. The representative polyimides, poly(*p*-phenylene biphenyltetracarboximide) (BPDA-PDA) and poly(4,4'-oxydiphenylene pyromellitimide) (PMDA-ODA), are insoluble and intractable, so that they are always processed in soluble precursor forms and then followed by imidization[1]. One type of soluble precursors is poly(amic acid) (PAA), which is easily synthesized by the polycondensation of dianhydride and diamine[1]-[5]. Another type of soluble precursors is poly(amic diethyl ester) (PAE), which is hydrolytically stable[1],[2],[4].. The imidization behavior of PAE is known to be quite different from that of PAA[4]. The difference in the imidization kinetics may lead to different morphological structures and properties in the resultant polyimides[3]-[5].

In this study, PMDA-ODA and BPDA-PDA polyimides prepared from both types of precursors have been examined by fluorescence spectrophotometry. In addition, density and birefringence were measured.

EXPERIMENTAL

For BPDA-PDA and PMDA-ODA, PAA and PAE precursors were synthesized in *N*-methyl-2-pyrrolidone (NMP), respectively, as the synthetic methods described in the literature[2]-[5]. The intrinsic viscosity [η] measured in NMP at 25°C was 0.69 *dl*/g for BPDA-PDA PAA, 0.85 *dl*/g for BPDA-PDA PAE, 0.60 *dl*/g for PMDA-ODA PAA, and 0.80 *dl*/g for PMDA-ODA PAE.

The precursor solutions were spin-coated onto glass slides and softbaked at 80°C for 1 h, followed by imidization under a nitrogen gas flow through various imidization protocols: i) 300°C/30 min; ii) 300°C/30 min and 350°C/ 30 min; iii) 300°C/30 min, 350°C/30 min, and 400°C/30 min; iv) 300°C/30 min, 350°C/30 min, 400°C/30 min, and 415°C/30 min. Here, a ramping rate of each step was 5.0 K/min. The imidized films were taken off from the substrates with the aid of deionized water, followed by drying in vacuum at room temperature for 2 days. The thickness of the films was ca. 10 μm. For the polyimide films, density (ρ) was determined at 30°C using a calibrated density gradient column filled with tetrachloromethane/cyclohexane mixtures. Out-of-plane birefringence (Δ) was measured by a prism coupling technique[3]. Photoluminescence characteristics were examined at room temperature using a Simadzu RF-500 spectrophotometer. Each film was excited in a front-face arrangement in order to minimize the self-absorption. For both excitation and emission monochromators, bandpasses were 2 nm, respectively. All excitations were conducted at 486 nm.

RESULTS AND DISCUSSION

For films imidized at various temperatures from the precursors, PAA's and PAE's, the measured densities (ρ's) and birefringences (Δ's) are listed inTable I.

TABLE I Densities and birefringences of films imidized at various temperatures from PAA and PAE precursors

Precursor	T_i^a	ρ^b	Δ^c	Precursor	T_i	ρ	Δ
PMDA-ODA PAA	300	1.448	0.0593	PMDA-ODA PAE	300	1.434	0.0500
	350	1.448	0.0620		350	1.442	0.0614
	400	1.456	0.0642		400	1.457	0.0748
	415	1.457	0.0642		415	1.457	0.0855
BPDA-PDA PAA	300	1.476	0.2177	BPDA-PDA PAE	300	1.465	0.1465
	350	1.481	0.2330		350	1.473	0.2038
	400	1.483	0.2413		400	1.475	0.2425
	415	1.483	0.2426		415	1.481	0.2462

[a] Final imidization temperature. [b] Density (g/cm^3). [c] Birefringence.

Overall, higher temperature imidization produced higher density and birefringence in the resultant polyimide film, regardless of the precursor origins. However, these properties show a dependency to the precursor origin and imidization history. For PMDA-ODA polyimide films imidized at <400°C, the PAE produced relatively lower ρ's than the PAA, whereas for those imidized at 400-415°C, both the PAE and the PAE produced comparable ρ's. For the films imidized at <350°C, the PAE gave lower Δ's than the PAA, whereas for those at 350-415°C, the PAE caused higher Δ's than the PAA. For BPDA-PDA polyimide films, the PAE always produced lower ρ's than the PAA. The Δ's in the films imidized at <400°C from the PAE were lower than those in the films from the PAA. For the films imidized only at 400-415°C, the PAE produced slightly higher Δ's than the PAA.

Fluorescence measurements were performed for the PMDA-ODA and BPDA-PDA films. The results are shown in Figure 1. For the films imidized from the PAA's, the fluorescence spectra were enhanced in intensity as the imidization temperature increased. These are consistent with the results reported previously by several research groups[6]-[8]. However, the films imidized from the PAE precursors showed quite different fluorescence emission behaviors. That is, for those from the PAE's, the fluorescence spectra were declined in intensity as the imidization temperature increased (see Figures 1 and 2). In addition, the fluorescence spectra were broadened with increasing imidization temperature. Only the PMDA-ODA film imidized at 350°C exhibited a relatively higher fluorescence emission than that prepared at 300°C.

In general, fluorescence emissions of aromatic polyimides are known to be due to the formation of charge transfer (CT) complexes, which can be provided

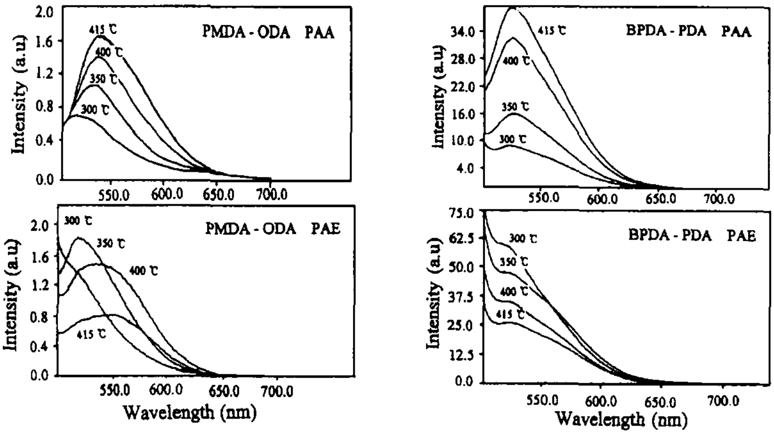

FIGURE 1 Emission spectra excited at 486 nm for PMDA-ODA and BPDA-PDA films imidized at various temperatures from their precursors. The denoted temperatures are the final imidization temperatures.

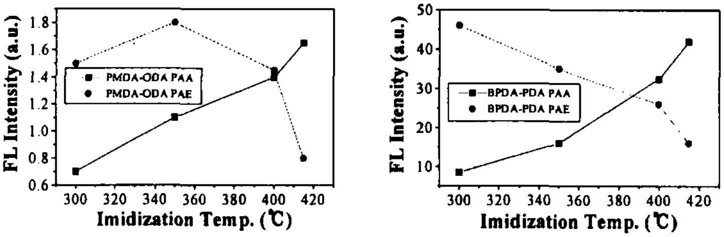

FIGURE 2 Variations of intensities at the maximum emissions in Figure 1 for PMDA-ODA and BPDA-PDA films imidized at various temperatures from their precursors.

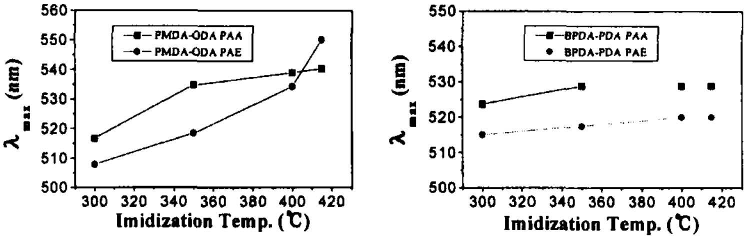

FIGURE 3 Variations of wavelengths (λ_{max}'s) at the maximum emissions in Figure 1 for PMDA-ODA and BPDA-PDA films imidized at various temperatures from their precursors.

by intermolecular interactions and/or by intramolecuar interactions[6]-[12]. In particular, these fluorescence spectra over the range of 500-700 nm are known to result mainly from the intermolecular CT fluorescence emissions which are caused by light absorption due to chemical structural units in the polymer backbones[6]-[8]. The increase of fluorescence emission in intensity has been reported to be due to an increase in the population of locally ordered coplanar state associated with the increase in the imidization temperature[8]-[10].

Therefore, the results indicate that as imidization temperature increases, the population of locally ordered coplanar state with the intermolecular CT complex increases in the films from the PAA precursors, but decreases in the films from the PAE's. However, as shown in Figure 2, for the PMDA-ODA films except one imidized at 415°C, the PAE provided relatively higher fluorescence intensity than the PAA, indicating that the PAE generated relatively higher population of locally ordered coplanar state in the film than the PAA. A similar trend was observed in the BPDA-PDA film. For the films imidized at <400°C, the PAE gave higher fluorescence intensity than the PAA, whereas for the films imidized at ≥400°C, the PAA produced higher fluorescence intensity than the PAE.

The fluorescence emissions were shifted into the red light region as the imidization temperature increased, regardless of the precursor origins, as shown in Figures 1 and 3. The red-shift was apparently much higher in the PMDA-ODA polyimide than the BPDA-PDA polyimide. The red-shift is known to be due to the intermolecular ordering as well as the conformational change of polyimide chains coincident with varying imidization condition[8]-[10]: Higher both intermolecular ordering and coplanarity between the aromatic imide ring of dianhydride unit and the phenyl ring of diamine unit give larger red-shift. With this fact, for the PMDA-ODA with an inherently less intermolecular ordering, both the intermolecular ordering and coplanarization are improved siginificantly by increasing imidization temperature, whereas for the BPDA-PDA with a high molecular order, they are improved slightly.

CONCLUSION

For both PMDA-ODA and BPDA-PDA polyimides prepared from their PAA and PAE precursors, respectively, the higher temperature imidization produced the higher density as well as the higher molecular in-plane orientation in the resultant polyimide films. However, the photoluminescence characteristics, molecular orientation and density of these polyimides were dependent strongly on the precursor origin as well as the imidization history. In particular, the fluorescence emissions in the polyimide films prepared from the PAE precursors were quite different from those of the films from the PAA's: That is, as the imidization temperature increased, the fluorescence intensities decreased in the films from the PAE's, whereas those increased in the films prepared from PAA's. These indicate that the PAE's lead quite different morphologies and molecular conformations in the resultant polyimide films, compared to the corresponding PAA's. The differences in the morphological structures and molecular conformations might be caused by a large difference between the imidization kinetics of the two different types of precursors as well as a difference between the bulkinesses of side groups in the precursors.

Acknowledgments

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References

[1.] M. K. Ghosh and K. L. Mittal, *Polyimides: Fundamentals and Applications* (Marcel Dekker, New York, 1996).

[2.] M. Ree, K. Kim, S. H. Woo, and H. Chang, *J. Appl. Phys.*, **81**, 698 (1997).

[3.] Y. Kim, M. Ree, T. Chang, C. S. Ha, T. L. Nunes, and J.S. Lin, *J. Polym. Sci.: Part B: Polym. Phys. Ed.*, **33**, 2075 (1995).

[4.] K. Kim, J. H. Ryou, Y. Kim, M. Ree and T. Chang, *Polymer Bulln.*, **34**, 219 (1995).

[5.] M. Ree, S. Swanson, and W. Volksen, *Polymer*, **34**, 1423 (1993).

[6.] E. D. Wachsman and C. W. Frank, *Polymer*, **29**, 1191 (1988).

[7.] M. Hasegawa, Y. Shindo, T. Sugimura, S. Ohshima, K. Horie, M. Kochi, R. Yokota, and I. Mita, *J. Polym. Sci.: Part B: Polym. Phys.*, **31**, 1617 (1993).

[8.] M. Hasegawa, H. Arai, I. Mita, and R. Yokota, *Polymer J.*, **22**, 875 (1990).

[9.] H. Ishita, S. T. Wellinghoff, E. Baer, and J. L. Koenig, *Macromolecules*, **13**, 826 (1980).

[10.] J.-W. Yu and C. S. P. Sung, *Macromolecules*, **30**, 1845 (1997).

[11.] B. V. Kotov, T. A. Gordina, V. S. Voishchev, O. V. Kolninor, and A. N. Pravednikov, *Polym. Sci. U.S.S.R.*, **19**, 711 (1977).

[12.] J. M. Salley, T. Miwa, and C. W. Frank, *Mater. Res. Soc. Symp. Proc.*, **227**, 117 (1991).