Notes

Imidization Study by Charge Transfer Fluorescence

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Introduction

Aromatic polyimides exhibit a weak but distinct fluorescence spectra due to the formation of charge transfer (CT) complexes, which can be formed by intermolecular interactions[2−4] and/or by intramolecular interactions.[5−7] The CT fluorescence in aromatic polyimides has been known for quite some time, and many studies have been reported on the interactions[8] and aggregations of solid polyimides.[9,10] Even though the fluorescence techniques showed potential for the imidization study, only one attempt was reported by Hasegawa et al.[10] to correlate CT fluorescence with the extent of imidization. However, since in their study the CT fluorescence emission intensity from polyimide around 490−530 nm when excited at 350 nm decreased in the early stage up to 60% of imide formation, followed by some increase because of aggregation, there was no one-to-one correlation between CT fluorescence intensity and the extent of imidization. Recently, we have found CT fluorescence from polyamic acid at a longer emission wavelength (∼650 nm), and the corresponding CT fluorescence excitation spectra changed continuously throughout imidization with decreasing intensity and red shift. In this note, we describe this CT fluorescence behavior from polyamic acid as a method to characterize the extent of imidization.

Experimental Section

1,2,4,5-Benzenetetracarboxylic anhydride (PMDA) and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) were recrystallized and vacuum-dried before use. A sublimed and zone-refined 4,4′-diaminodiphenyl ether (ODA) and 1,4-phenylenediamine (PDA) were used as received. Spectrophotometric grade 1-methyl-2-pyrroldinone (NMP) was dried over molecular sieves and vacuum-distilled.

A polyamic acid (PAA) stock solution was prepared by slowly adding an equimolar amount of dianhydride to the 10 wt % diamine solution in NMP, followed by stirring for 6 h at room temperature. PAA films were prepared by casting on a quartz plate using a blade (thickness set to 60 μm), followed by drying at 85 °C for 30 min. Stepwise imidization conditions were used for all the experiments by heating the films for 20 min at 130 °C, followed by 20 min at 150 °C and 20 min at 180 °C.

The fluorescence spectra were taken using a Perkin-Elmer LS50 b luminescence spectrometer. For the determination of percent imidization, a Nicolet FT-IR spectrometer was employed to monitor imide carbonyl formation. Since thickness changes result in different rates of imidization under identical imidization conditions,[11] all the samples had the same thickness.

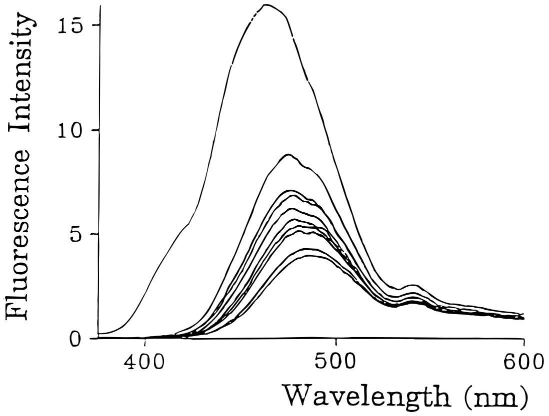

Figure 1. Fluorescence excitation spectra of PAA(PMDA/ODA) emitted at 650 nm (from top to bottom): (0, 5, 10, and 20 min at 130 °C; 5, 10, 15, and 20 min at 150 °C; 5 and 10 min at 180 °C.

Table 1. Peak Positions in Fluorescence Excitation Spectra of Three Polyamic Acids (PAA) and Polyimides (PI)

	flourescence excitation, nm		
	PAA	PI	$\Delta\lambda$
PMDA/ODA	463	487	24
BTDA/ODA	447	483.5	36.5
BTDA/PDA	461	483	22

Result and Discussion

The CT fluorescence following use of a previously reported excitation wavelength[10] (340−380 nm) was studied first. The polyimide (PI) from PMDA/ODA film when excited at 380 nm showed double emission peaks at 462 and 501 nm. The general trend of initially decreasing intensity followed by some increase was consistent with the findings of Hasegawa et al.[10] This result is also expected from the result of Ishida et al.,[5] which described a pyromellitimide CT peak located at 378 nm in its UV−visible absorption spectrum.

We also found fluorescence at a much longer wavelength. Fluorescence emission spectra of PAA (PMDA/ODA) film when excited at 490 nm showed a peak maximum around 660 nm. Figure 1 shows the corresponding fluorescence excitation spectra for PAA from PMDA/ODA, with a main peak changing from 463 to 487 nm as a fuction of cure time. To confirm that this fluorescence originated from a CT, a solution study was performed. To a PMDA (1×10^{-3} M) solution in NMP, an equimolar ODA solution in NMP was added. Fluorescence excitation spectra (emitted at 650 nm) were recorded as a function of time after mixing these two solutions. The fluorescence excitation intensity at 578 nm increased linearly with time. This fluorescence excitation peak was absent in each component, but as soon as the two components were mixed, the 538 nm excitation peak appeared, which is characteristic of the

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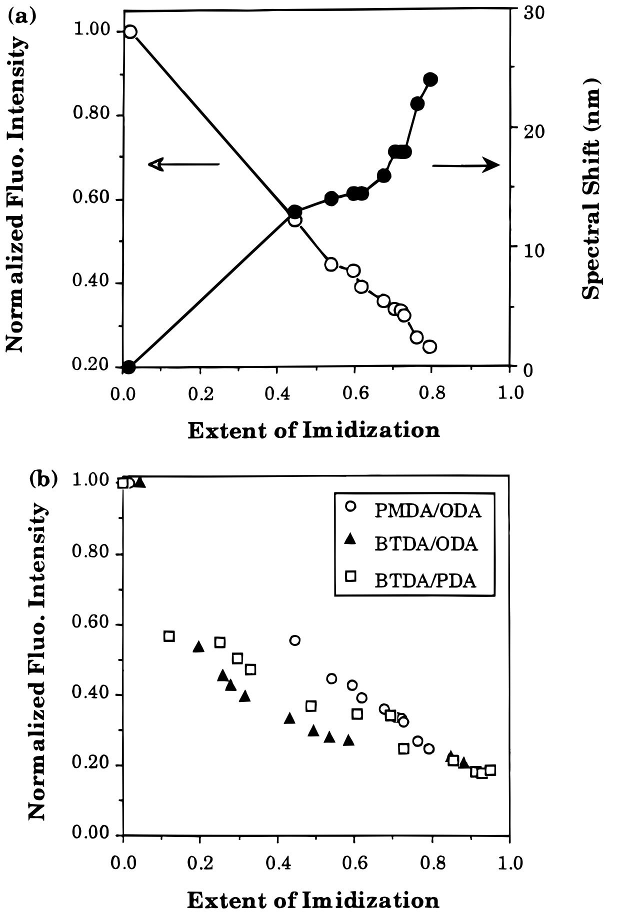

Figure 2. (a) Correlation plot for PMDA/ODA [normalized intensity change at excitation maxima (463–487 nm) (○) and spectral shift (●)]. (b) Comparison of the correlation plot for PMDA/ODA, BTDA/ODA, and BTDA/PDA. Normalized fluorescence intensity was at excitation maxima corresponding to each polyimide.

CT complex. The CT excitation position in solution is quite different from that in film. Since it is known that CT fluorescence spectra show a strong polarity dependency,[8] this difference may be due to the presence of solvent.

We have also investigated other polyimides made from different moieties such as BTDA/ODA and BTDA/PDA. These polymers exhibited similar trends such as decreased intensity and red shifts in their main peaks, as a function of cure time, as summarized in Table 1. It may be that the main CT peak observed in this study is due to trimer because the fluorescence maxima occurred at longer wavelengths than the maxima for dimer CT fluorescence described in several reports.[7–10] The small peak at 540 nm in Figure 1 may also be related to CT, but its origin is not well-known.

The symmetrical stretching band of imide carbonyl near 1778 cm^{-1} in FT-IR was used for the determination of the extent of imidization while the aromatic vibration at 1015 cm^{-1} was used as an internal standard. A correlation plot was established by combining spectral shift or normalized fluorescence intensity changes of excitation spectra (for emission at 650 nm) and the extent of imidization as shown in Figure 2. The normalized intensity decreased faster in the order of PMDA/ODA < BTDA/PDA < BTDA/ODA. The rigidity of these three systems is the reverse order of the intensity.[12] The fluorescence intensity is decreased with the progress of imidization, because the orientation required for CT complexation is reduced as a result of conformation change to form imide moiety from amic acid.[9]

In summary, charge transfer fluorescence was observed in aromatic polyamic acids and polyimides with the shorter wavelength CT fluorescence related to the polyimide state. The longer wavelength CT fluorescence excitation spectrum showed a steady bathochromic shift and decrease in intensity with increasing imidization. A rigid polyimide showed a slower fluorescence intensity decrease than a flexible polyimide.

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