Features of Fluorescence Spectra of Polyethylene 2,6-Naphthalate Films

I. Ouchi,[1] I. Nakai,[2] M. Ono,[3] S. Kimura[4]

[1]Faculty of Engineering, Tokushima Bunri University, Shido, Kagawa 769-2193, Japan
[2]Faculty of Engineering, Tottori University, Koyama, Tottori 680-8552, Japan
[3]Teijin–DuPont Films Japan Limited, Ampachi, Gifu 503-0123, Japan
[4]Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

ABSTRACT: The characteristics of the fluorescence spectra of polyethylene 2,6-naphthalate (PEN) films were compared with those of poly(ethylene terephthalate) (PET). The fluorescence spectra of PEN films were found, by photoselection, to consist of two components, one peaking at 425 nm and the other at 445 nm, with their emission transition moments perpendicular to each other. The integrated excitation spectra of the PEN films were much more intense than those of PET. After the resolution of the integrated excitation spectra of PEN, most, but not all, of their component peaks corresponded to those of the absorption spectra. On the basis of this fact together with previous data on photodegradation, the spectral component peaking at 445 nm originated, at least partly, from traces of photochemical products generated by exposure during the measurements. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 114–121, 2007

Key words: films; fluorescence; photochemistry; polyesters

INTRODUCTION

Because of the similarities in the molecular structures, polyethylene 2,6-naphthalate (PEN)
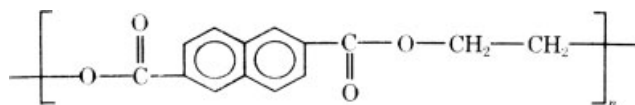
has often been studied with poly(ethylene terephthalate) (PET) for a long time.[1] As films, these polyesters are endowed with excellent practical properties; therefore, their comparison has attracted much scientific and technological attention.[2,3] They are transparent in the visible region but absorb light strongly in the ultraviolet region, in which the absorption and emission spectra extend toward longer wavelengths in PEN than in PET.[2,4] The electron-beam-excited fluorescence of PET and PEN was first observed by Phillips and Schug,[4] who attributed the main broad fluorescence band of a PEN film peaking around 430 nm to excimers. Thermally stimulated chemiluminescence was observed in PEN when it was heated to 80–140°C.[5]

Upon prolonged exposure to light at the absorption edge, PET and PEN films were slightly colored around 310 and 382 nm, respectively, whereas the effects of photodegradation and the evolution of fluorescence were different for PET and PEN.[6] The fluorescence of PEN was examined in films and solutions, together with its monomer, dimethyl 2,6-naphthalate (DMN), as in the case of PET.[7,8] The fluorescence peak at about 380–390 nm in a PEN solution was assigned to monomer fluorescence because of its coincidence with that of DMN, whereas the broad peak around 420–430 nm in a PEN film was maintained to be excimer fluorescence because the excitation spectrum monitored at 430 nm coincided with that for the monomer fluorescence of a solution.[8–10] Fluorescence and excitation spectra of poly(ethylene terephthalate-co-2,6-naphthalate) copolymers with less than 4 mol % DMN were studied; in this way, the energy transfer in the copolymers and their photodegradation were discussed.[11] Comparing with that of PET, which emits two species of fluorescence, the fluorescence of PEN seems to be normal, forming a mirror image against the absorption spectra and following Kasha's law.[12]

The absorption spectra of PEN have appeared in some of the publications mentioned previously[5,8] and in some other publications.[13,14] On the basis of the reflection measurements and the Kramers–Kronig conversion, absorption spectra of oriented films of PEN and PET from the vacuum ultraviolet region to the visible region have been described.[15]

There have been numerous studies of the absorption and emission of PET. Major features of the

absorption spectra of PET films have been clarified in much more detail than those of PEN;[15–17] this is particularly true for the analysis of the first absorption bands peaking at 290–300 nm.[16] Molecular orbital calculations for PET correspond fairly well to experimental values.[16,17] Faint absorptions found at 340–360 nm have been recognized for a long time,[10,16] but their origins were not uncovered until our recent fluorescence study.[18]

In the fluorescence of a PET film, a weak emission at 330–340 nm, which is caused by excitation at wavelengths shorter than 320 nm, is intrinsic fluorescence from the lowest excited state of PET molecules, whereas the origin of the more intense fluorescence peaking at 380 nm, which occurs by the excitation of wavelengths longer than 320 nm, has been controversial for a long time.[19] Most researchers have asserted that the latter originates in dimers because of the dependence of the intensity on the concentration in a solution.[19] However, the fluorescence shape and intensity of PET depend very much on the thickness of the film; that is, the intrinsic fluorescence peaking at 330–340 nm, generated by short-wavelength excitation, is dominant in thin films and solutions, whereas the trap fluorescence peaking at 480 nm is overwhelming in thick films.[20] This phenomenon has been confirmed experimentally and explained by an elementary calculation of the thickness dependence of the fluorescence intensity, without the assumption of dimer absorption.[18] Furthermore, possible effects of polymerization catalysts on fluorescence have been investigated with different catalyst systems. After the resolution of the fluorescence spectra, the peak position of each component is independent of the catalyst systems, whereas the fluorescence intensity of PET films is sensitive to minute local structures such as defects and catalyst residues.[18] The integrated excitation spectra have been resolved; in this way, a hidden $n \rightarrow \pi^*$ transition has been identified at 323 nm, together with peaks at 338, 354, and 370 nm. These peaks of the components correspond to the aforementioned faint absorptions at 338 and 354 nm. It has been concluded that the trap fluorescence peaking at 380 nm arises from $n \rightarrow \pi^*$ transitions assisted by phonon energy in a similar way as in the indirect transitions in the absorption process of semiconductors.[18]

In this article, a reexamination of the florescence of PEN films is intended to improve our level of understanding of PEN films by providing additional knowledge about its features. First, after reviewing the absorption and fluorescence spectra of PEN films, we consider the polarized fluorescence spectra of PEN. Second, we examine integrated excitation spectra to view the large difference from PET and to examine the nature of the fluorescence. Third, we discuss the possible effects from photochemical reactions.

EXPERIMENTAL

Undrawn, uniaxially drawn, and biaxially drawn PET and PEN films of various thicknesses (mostly 60–100 μm), without additives, were prepared at the Film Research Laboratory of Teijin–DuPont Films (Ampachi, Japan). Actual sample pieces were taken from the central part of the web. The quality of the webs, such as the surface roughness, was alike for PET and PEN.

Transmission measurements were made with a UV2400PC double-beam spectrophotometer (Shimadzu). Fluorescence measurements were performed with an RF 5300PC fluorescence spectrometer (Shimadzu, Kyoto, Japan) with a xenon lamp as a light source at a viewing angle of 90°. A Jusco (Tokyo, Japan) spectrophotometer consisting of two monochromators with a halogen light source was also used with a 90° viewing angle. Three-dimensional (3D) fluorescence measurements were taken with a Hitachi (Tokyo, Japan) FD-4500 fluorescence spectrometer.

The integrated excitation spectra were measured with synchrotron radiation at the BL-1B of the UVSOR at the Institute for Molecular Science, at which a Seya–Namioka spectrometer with three-type gratings was equipped. In these experiments, a G-3 grating of 600 lines/mm was used for the wavelength range between 50 and 650 nm. Cut samples of 10–15 mm² were screwed between a copper frame and a holder,
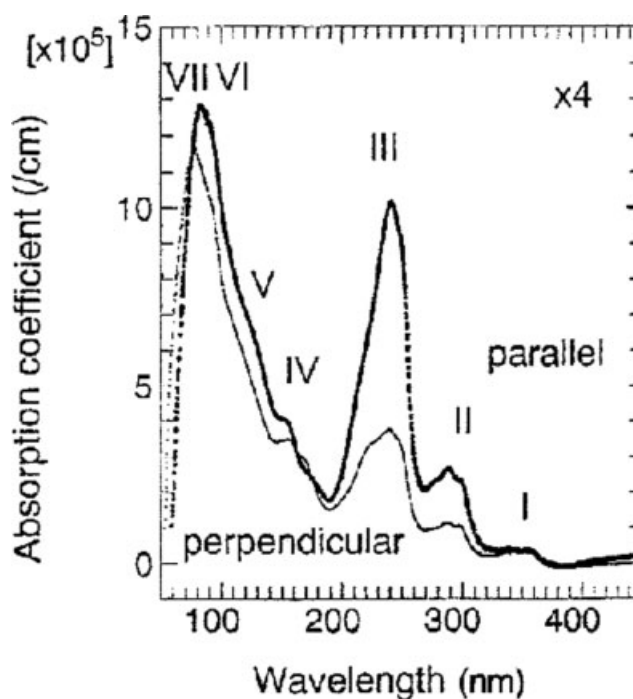

Figure 1 Absorption spectra of a uniaxially drawn (4×) PEN film, converted from the reflection spectra with the Kramers–Kronig conversion and the Fresnel formula.[21] *Parallel* and *perpendicular* indicate that the draw direction of the film is parallel or perpendicular, respectively, to the electric vector of the incidence beam.

which was 160 mm long and 36 mm wide and carried nine circular holes 10 mm in diameter. Each sample film kept the original draw direction, either horizontal or vertical, after setting. After being mounted, the sample films were usually kept *in vacuo* overnight. The holder plate was able to rotate around the axis vertically to the horizontal plane; an incidence angle of 12.5° was usually employed, instead of zero, for a technical reason. A photomultiplier was set at the position of 25° with the incidence beam for reflection measurements and at about 60° for integral excitation measurements. The exit slit width was set at 0.1 mm for both types of measurements. Here, the integrated excitation spectra were spectra taken without a filter or a monochromator for emitted light. That is, only excitation light was monochromatized by the spectrometer; therefore, the detected light was the sum of all the emissions of various wavelengths emitted from the sample and received by the detector. The contribution of strayed light to the luminescence was correctable by the subtraction of the fluorescence intensity observed with a Pyrex glass before the sample; the amount of this correction was less than 1%, except at the wave-

lengths shorter than 100 nm, and usually was neglected. Ordinary fluorescence and excitation spectra were obtainable by the placement of a Yve–Jobin (France) MIC monochromator outside the vacuum chamber and by an increase in the width of the exit slit of the Seya–Namioka monochromator to 0.5 mm.

RESULTS AND DISCUSSION

Absorption and fluorescence spectra of the PEN films

The absorption spectra of uniaxially drawn PEN films are shown in Figure 1; these were obtained from the reflection spectra of the films with the Kramers–Kronig relation and the Fresnel formula.[15,21] The spectral features are rather similar to those of PET, except for the fact that the three major ultraviolet absorption bands (I–III) of PEN are shifted toward longer wavelengths than those of PET. An example of a 3D fluorescence spectrograph of PEN films is shown in Figure 2; the fluorescence spectra of PEN films consist of a broad band with a peak around 430 nm, indicating
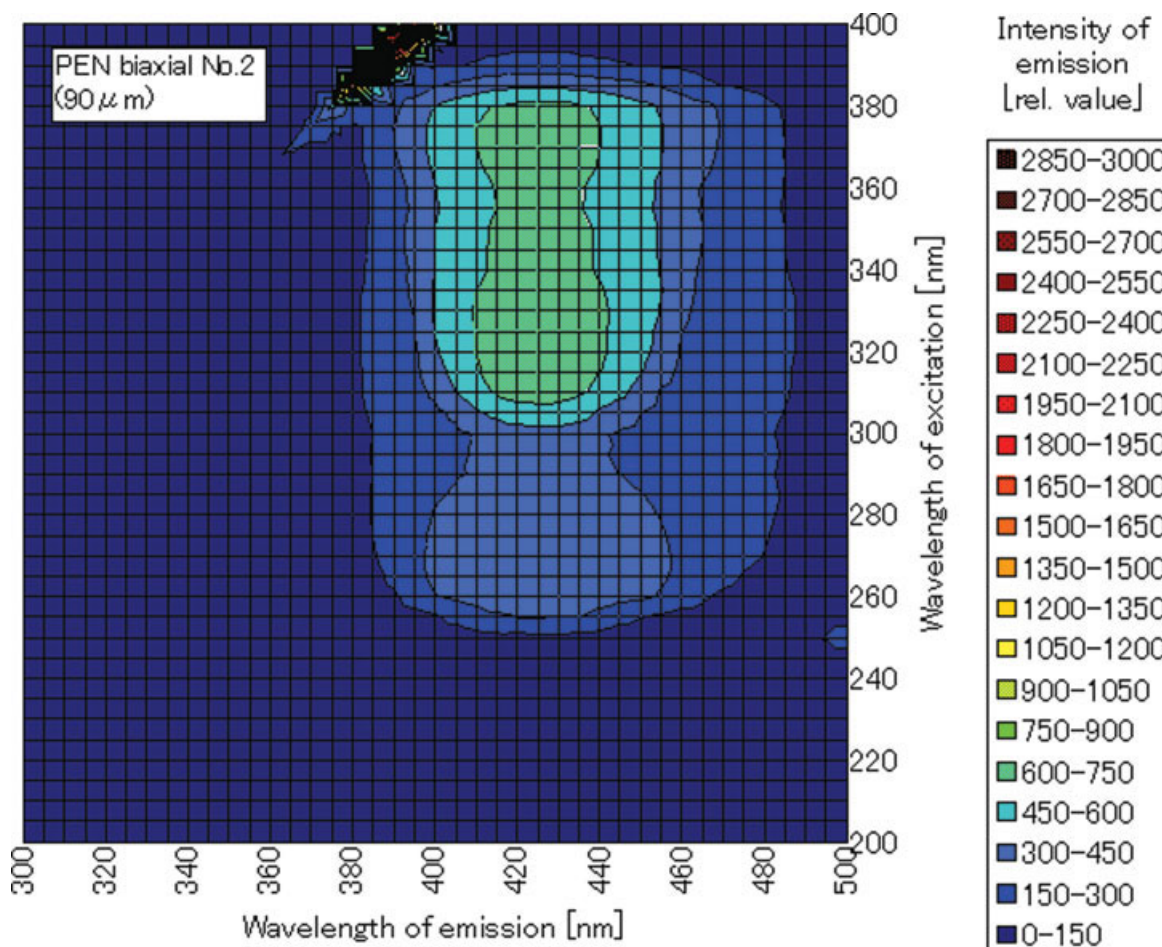

Figure 2 3D fluorescence spectra of a biaxially drawn PEN film 90 μm thick. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
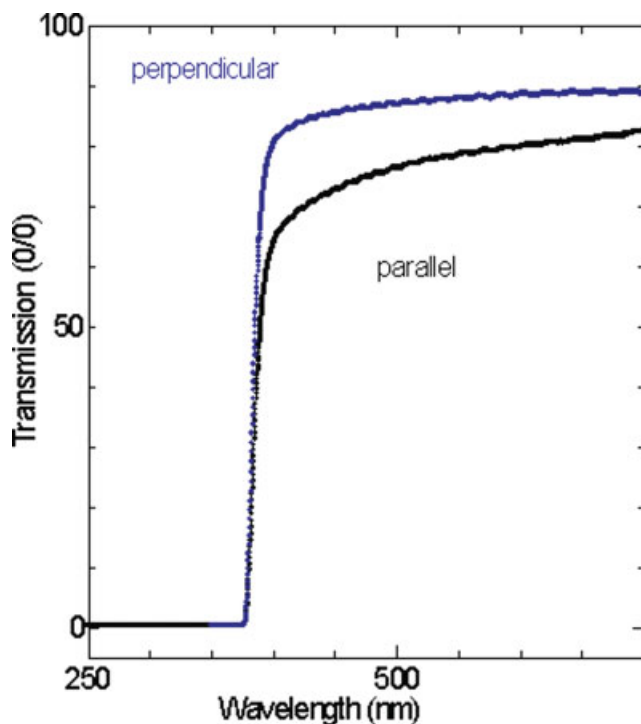
Figure 3 Transmission spectra of a uniaxially drawn (4×) PEN film.

typical characteristics of excimer fluorescence. Their spectral shapes and peak positions are alike for excitations at any responsive wavelength; that is, excited molecules, including those excited to the higher energy levels, give emissions from the excimer level via the lowest excited level. Transmission spectra are depicted in Figure 3; there is no additional faint absorption in the tail, so there is little possibility of the complex emission behavior found in PET, in which intrinsic fluorescence and trap-related fluorescence appear.[18]

Polarized fluorescence spectra of various PEN films are illustrated in Figure 4; H (or V) signifies that the electric vector of the exciting light is horizontal (or vertical), and h (or v) indicates that the electric vector for the emitted light is horizontal (or vertical). As shown in Figure 4(b) [or Fig. 4(c)], the film samples were mounted with the draw axis horizontal (or vertical). From all these figures, each broad emission band is judged to be composed of two components having a v peak at about 425 nm and an h peak at about 445 nm. That is, regardless of the state (isotropic or not), some PEN molecules absorb H or V light of a certain wavelength (λ_1) and emit fluorescence having a vertical electric vector and a peak wavelength of 425 nm, whereas some other molecules absorb light of an H or V nature of a different wavelength (λ_2) and emit fluorescence of a horizontal electric vector at 445 nm. Because this phenomenon is found in isotropic undrawn films

and, more distinctly, in uniaxially drawn films, it may be interpreted as photoselection.[22]

This interpretation seems to be plausible because the same results were obtained even when unpolarized light was illuminated onto the films. However, to have this happen, there must be two excited levels in PEN excimers, corresponding to the emission peaks of 425 and 445 nm, each with a different polarity. Naphthalene has three absorption bands corresponding to those of PEN. The second band of naphthalene at 280 nm is B_{2u} and is short-axis-polarized but is mixed with a long-axis-polarized component; furthermore, its first band at 305 nm is B_{3u} and is long-axis-polarized but, if resolved by linear dichroism, consists of many vibrational components of mixed polarization.[23] The first absorption band of PEN has not been examined in as much detail as that of PET or naphthalene. Moreover, the intramolecular excimers of PEN and related model compounds have been extensively explored,[9,24–26] whereas detailed knowledge of the excimer states in solid PEN is not available at the present. Hence, the identification of the character of the excimer fluorescence peaks at 425 and 445 nm would be difficult without some more clear evidence and theoretical treatments.

In the previous argument, we assume that PEN is the only existing species. If so, an undrawn PEN film, which is isotropic and amorphous, must emit fluorescence with an intensity relation of $I_h^H = I_v^H$ in this apparatus setting with a viewing angle of $90°$.[27] In actuality, however, there is a difference between I_h^H and I_v^H, in both the peak positions and intensities, as shown in Figure 4(a–d). A part of this difference must be due to the vertical and horizontal spectral imbalance of the receiving monochromator, which is difficult to measure, but a majority of it must arise from the true difference between I_h^H and I_v^H rather than the apparatus origin. Hence, the fluorescence of PEN films consists of at least two components, a component generating a polarized peak at about 425 nm and another at 445 nm. Therefore, there should be a possibility that a new material would be generated photochemically during the fluorescence measurements, although it has not been identified directly. This possibility is further discussed in another section.

Integrated excitation spectra

Integrated excitation spectra of PEN and PET are compared in Figure 5, and there is a big difference between them. Except for the trap fluorescence at longer wavelengths, almost all the intrinsic fluorescence of PET is covered by the background, whereas in the PEN films, the fluorescence emitted from any energy level is quite intense, in agreement with the features found in the 3D fluorescence spectra.
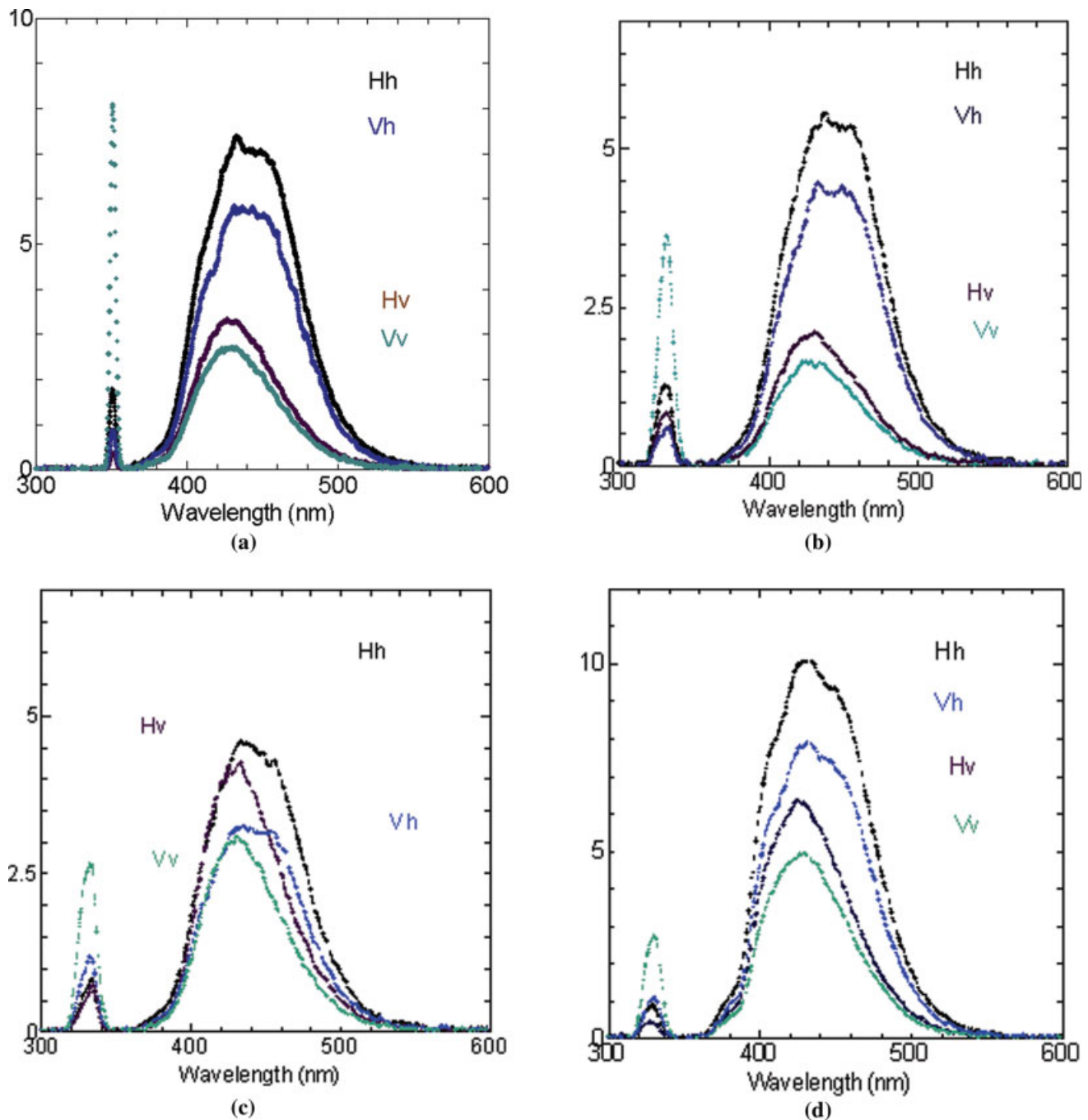
Figure 4 Polarized fluorescence spectra (uncorrected) of PEN films excited at 330 nm (no filter to cut the strayed incidence beam was used): (a) an undrawn PEN film, (b) a uniaxially drawn PEN film (3×) that was mounted so that the draw axis would be horizontal, (c) a uniaxially drawn PEN film (3×) that was mounted so that the draw axis would be vertical to the horizontal plane, and (d) a biaxially drawn PEN film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The integrated excitation spectra of PEN look complicated at a glance and do not seem to have a good correspondence with the absorption coefficients. However, after curve resolution, they seem to be related loosely, as illustrated in Figure 6.

In the integrated excitation, fluorescence intensity I_{int} is the sum of all the differential fluorescence intensities dI_f of wavelength λ_f emitted from each volume element at the depth of x from the surface to the rear:

$$I_{int} = \int_{\lambda} d\lambda_f \int_0^D dI_f(\lambda_f, \lambda_e, x)dx \qquad (1)$$

This is proportional to the intensity of the excitation beam (I_0) and the quantum efficiency (m) at the exci-
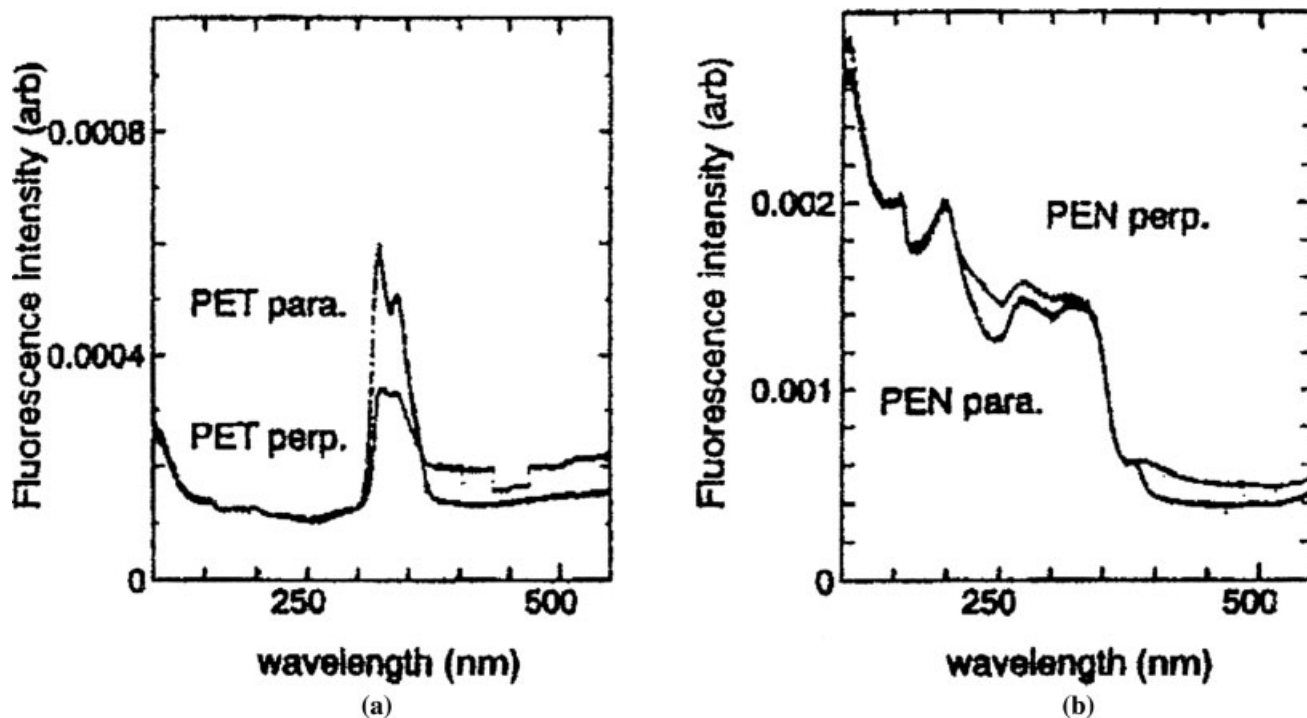
Figure 5 Integrated excitation spectra of uniaxially drawn (3×) films of (a) PET and (b) PEN, whose draw axes were horizontal.

tation wavelength (λ_e) and is affected by film thickness D and geometric constant C. Considering the refractive angle (θ_e) of the incidence ray and incidence angle (θ_f) of the emission light from the volume element (dx) onto the inner surface of the film and summing up the emission arising from the volume element at $x = 0$ to D, we obtain

$$I_{int} = \int_\lambda CI_0m(\lambda_e)\{\alpha_e/([\alpha_e/\cos\theta_e] + [\alpha_f/\cos\theta_f])\}$$
$$\{1 - \exp -([\alpha_e/\cos\theta_e] + [\alpha_f/\cos\theta_f])D\}d\lambda_f \quad (2)$$

where α_e and α_f are the absorption coefficients of the excitation and emission light, respectively. For simplicity, the contribution of the reflection from the rear surface is neglected. Because there is no extra faint absorption in the tail of the first absorption band in the PEN films as found in PET, α_f is always much smaller than α_e and can be neglected; hence

$$I_{int} \propto C'I_0m(\lambda_e)\{1 - \exp -([\alpha_e/\cos\theta_e]D)\} \quad (3)$$

Therefore, the intensity of the integrated excitation spectra is determined by the quantum efficiency for the excitation wavelength [$m(\lambda_e)$] and by the product of α_e and D. By the differentiation of I_{int} by λ_e, if $m(\lambda_e)$ is constant, the peak positions of I_{int} will coincide with those of α_e; therefore, the integration excitation spectra would look like absorption spectra.

The measured spectra of the integrated excitation were resolved into the same number of components

as the absorption peaks, assuming a Gaussian-like shape as $\sum_i I_i \exp -\{(x - \lambda_i)/\sigma_i\}^2$, where I_i is the intensity, λ_i is the peak position, and σ_i is the half-width of the ith component. We first performed the calculation by putting the wavelength of each absorption peak, found in previous literature,[15] into λ_i and by assuming width σ_i according to the read-
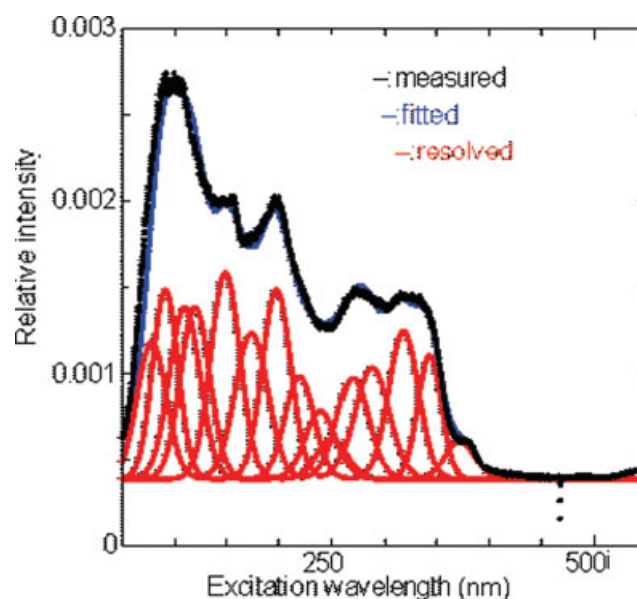

Figure 6 Resolved integrated excitation spectra of the PEN film shown in Figure 5. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ings of Figure 1; then, we repeated this, altering λ_i and σ_i, until the best fitting was made. As a result, the correspondence of the peak positions of absorption and excitation can be found in Table I.

There seems to be a one-to-one correspondence between the absorption peaks and integrated excitation peaks, except for an extra-strong component in the valley region of the third and fourth absorption bands. Also, the intensity of the component peaks is rather flat at shorter wavelengths than the third absorption band.

In the first absorption band, the absorption coefficient is approximately 3000 cm^{-1}. Hence, as much as 5% of the incident light penetrates the film more deeply than 10 μm from the surface, contributing to I_{int}. However, at wavelengths shorter than the second absorption band, I_{int} must be almost constant because of the large value of α, as long as the quantum efficiency [$m(\alpha_e)$] does not change much. If this explanation applies to the general appearance depicted in Figure 5, a strong extra component peak at 198 nm and relatively weak component peaks at 220–250 nm in the third absorption band would signify that $m(\alpha_e)$ is variable, and there would be the possibility of a different species of molecules other than PEN. We discuss this possibility in the next section.

Effects of the photochemical reactions

In the early stages of the semicommercialization of PEN films, the photodegradation of PEN films was investigated.[6] It was demonstrated that PET films were slightly colored upon exposure to light of the wavelength of 310 nm, which led to chain scission, whereas PEN films were colored at 382 nm and subject to insolubilization together with chain scission. Because of the coloration, photodegradation occurred only at the surface in PEN, and the effect did not propagate into the interior of the film. These reactions accompanied a change in the fluorescence. In PEN films, after 24 h of exposure to a high-pressure mercury lamp, the fluorescence peak decreased in height by approximately 40%, and its peak position shifted from 430 to 445 nm, whereas in PET, the fluorescence peaks decreased in intensity at 370–410 nm, and a new band at 480 nm increased to three times the original peak height at 480 nm after 24 h.[6]

In comparison with the previously described old photoexposure experiments, the exposure time was shorter by more than an order of magnitude and did not give rise to any coloration in the fluorescence measurements, if the exposure intensity was set aside. Nevertheless, there is a possibility that very slight photochemical reactions may proceed during the measurements. The conjecture, made in the last section, that the exposure to synchrotron radiation during the integrated excitation measurements may have caused the

TABLE I
Correspondence of the Peak Wavelengths of the Absorption and Integral Excitation of a Uniaxially Drawn (3×) PEN Film

		First absorption band			Second absorption band			Third absorption band				Fourth absorption band		Fifth absorption band	
Absorption	Peak position (nm)	358	341	326	299	288	278	250	240	220		170	155	123	110
	Absorbance (cm^{-1})	3000			26,000			103,000				40,000		70,000	
Excitation	Peak position (nm)	372	343	318	—	288	270	250	240	218	198	174	149	120	110
	Relative intensity	23	72	86	—	65	59	24	40	60	110	80	120	100	100

change in the dependence of $m(\alpha_e)$ on λ_e, because of a possible generation of new photochemical products, is consistent with this old observation. The second interpretation of the polarized fluorescence spectra described in the section before last also confirms this, although more careful experiments, after thorough characterization of the receiving monochromator, might be desired if this is only a reason or a partial cause.

CONCLUSIONS

Fluorescence spectra of PEN films have a broad band peaking at 430–440 nm that originates in the excimers. According to the polarized fluorescence spectrometry, the spectra are composed of two components: one having a peak at 425 nm and one at 445 nm. After the resolution of the integrated excitation spectra, the emission quantum efficiency likely depends on the wavelength. Taking account of our old experiments on photodegradation, we believe that the fluorescence component peak at 445 nm probably arises, at least partly, from exposure during the measurements.

References

1. Hill, R.; Walker, E. E. J Polym Sci 1948, 3, 609.
2. Ouchi, I.; Aoki, H.; Shimotsuma, S., Asai, T.; Hosoi, M. Proc Jpn Congr Mater Res 1974, 17, 217.
3. Ouchi, I. Rep Prog Polym Phys Jpn 2000, 43, 771.
4. Phillips, D. H.; Schug, J. C. J Chem Phys 1969, 50, 3297.
5. Richards, R. R.; Rogowski, R. S. J Polym Sci Polym Phys Ed 1974, 12, 89.
6. Ouchi, I.; Hosoi, M.; Matsumoto, F. J Appl Polym Sci 1976, 20, 1983.
7. Allen, N. S.; McKellar, J. F. J Appl Polym Sci 1978, 22, 2085.
8. Chen, S.; Bai, F.; Qian, R. Sci Sin 1981, 24, 639.
9. Mendicutti, F.; Patel, B.; Mattice, W. Polymer 1990, 31, 453.
10. Hashimoto, H.; Hasegawa, M.; Horie, K.; Yamashita, T.; Ushiki, H.; Mita, I. J Polym Sci Part B: Polym Phys 1993, 31, 1187.
11. Cheung, P.-S. R.; Roberts, C. W.; Wagener, K. B. J Appl Polym Sci 1979, 24, 1809.
12. Ouchi, I.; Miyamura, R.; Sakaguchi, M.; Hosaka, S.; Kitagawa, M. Polym Adv Technol 1999, 10, 195.
13. Ouchi, I. Rep Prog Polym Phys Jpn 1979, 22, 437.
14. Niino, H.; Yabe, A.; Nagano, S.; Miki, T. Appl Phys Lett 1989, 22, 2159.
15. Ouchi, I.; Nakai, I.; Kamada, M. Nucl Instrum Methods Phys Res Sect B 2003, 199, 270.
16. Ouchi, I. Polym J 1983, 15, 225 and references therein.
17. LaFemina, J. P.; Avjaralingam, G. J Phys Chem 1991, 95, 984.
18. Ouchi, I.; Naki, I.; Ono, M.; Kimura, S. Jpn J Appl Phys 2004, 43, 8107.
19. Hemkar, D. J.; Frank, C. W.; Thomas, J. W. Polymer 1988, 29, 437 and references therein.
20. Chen, L.; Jin, X.; Du, J.; Qian, R. Makromol Chem 1991, 192, 1399.
21. Ouchi, I. Kobunshi Kako (in Japanese) 2002, 51, 393.
22. Albrecht, A. C. J Mol Spectrosc 1961, 6, 84.
23. Davidsson, A.; Norden, B. Chem Phys Lett 1974, 28, 221.
24. Mendicuti, F.; Saiz, E.; Mattice, W. L. Polymer 1992, 33, 4908.
25. Bravo, J.; Mendicuti, F.; Mattice, E. L. J Polym Sci Part B: Polym Phys 1994, 32, 1511.
26. Martin, O.; Mendicuti, F.; Saiz, E.; Mattice, W. L. J Polym Sci Part B: Polym Phys 1999, 37, 253.
27. Cehelnik, E. D.; Mielenz, K. D.; Velapoldi, R. A. J Res Natl Bur Stand Sect A 1975, 79, 1.