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Microenvironments in poly(1,4-butylene terephthalate) solids revealed by fluorescence spectroscopy

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Abstract

The relationship between the fluorescence behavior and crystallinity of poly(1,4-butylene terephthalate) (PBT) films, prepared by a spin-casting method, was investigated. Throughout the fluorescence measurements of PBT thin films having different crystallinities, the main-chain phenylene fluorescence near 320 nm and that near 365 nm were assigned to monomer fluorescence mainly from crystalline regions and excimer fluorescence from amorphous regions, respectively. It was found that the ratio of the fluorescence intensity at 320 nm to that at 365 nm can be an effective indicator of PBT crystallinity. The present work should provide a quick and nondestructive method for determining the crystallinity of PBT factory products.

Keywords: Amorphous; Crystallinity; Fluorescence techniques

1. Introduction

Fluorescence spectroscopy is growing remarkably as a powerful and effective tool to study the physical and chemical behaviors of macromolecules [1–5]. Because fluorescence techniques are not only highly sensitive but also nondestructive, they are useful for monitoring real-time changes in the formation of very small amounts of products and/or changes in the microenvironment. Thus far, however, fluorescence properties of material polymers have not always been clarified so extensively. We therefore undertook studies on the luminescence of material polymers that have aromatic groups in their main chain [6–10].

Aromatic polyesters such as poly(ethylene terephthalate) (PET) and poly(1,4-butylene terephthalate) (PBT) have quite important applications as engineering plastics. PET has a fluorescent phenylene moiety in the main chain showing its fluorescence peak at 330–340 nm in fluid solution, but thick PET films showing fluorescence with fine structures at 369 and 387 nm have been assigned to the phenylene ground-state dimer [11–14], which has an absorption peak at 336 nm. However, the intrinsic luminescence of PET films was not well characterized until we studied PET films prepared by a spin-casting method, which provides the most reproducible conditions to prepare films [8–10]. Finally we found that PET fluorescence consists of two fluorescent components in addition to the ground-state dimer: one with a peak near 330 nm coming out from the main-chain phenylene groups in the crystalline region and the other at longer wavelengths from the phenylene in the amorphous region [8,9].

Relative to the number of studies on PET solids, only a few reports have been published on the fluorescence of PBT solids. Dellinger and Roberts reported that 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) solution of commercial PBT solids displayed a structureless fluorescence with a peak at 324 nm when they were excited at a 290-nm absorption peak wavelength of PBT; however, when excited at 340 nm the PBT chips showed emission maxima at 400, 420, and 460 nm [15]. Those authors assigned the 460-nm emission to the fluorescence of 2-hydroxyterephthalic acid. Hennecke et al. concluded that the rest of the PBT fluorescence resulting from the excitation at 340 nm was due to a ground-state dimer formed between two phenylene moieties in an amorphous region [16]. On the other hand, Takai et al. reported that PBT commercial films showed an unresolved band at 335 nm and a structureless broad band centered at

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370 nm when they were excited at an absorption peak wavelength of PBT [17]. Takai et al. did not observe fluorescence of the ground-state dimer and assigned the fluorescence with a peak at 370 nm to a singlet excimer. The differences among these observations of PBT fluorescence are attributable to the conditions in which the films were prepared, such as film thicknesses, impurities, crystallinities and so on.

In this paper, we report on the fluorescence properties of PBT films prepared by a spin-casting method. This preparation method provides the most reproducible condition to prepare films; thus we can expect systematic measurements of the intrinsic fluorescence of PBT films. In order to ascertain that the PBT films show other fluorescence such as excimer in addition to dimer emissions, we investigate in the present paper the fluorescence behaviors of the PBT films by systematically changing the casting temperatures, which should influence the crystallinity of PBT solids. Our main aim in the present paper is to assign the fluorescence of PBT films and to get the information to support that the fluorescence of phenylene moieties of aromatic polyester solids can be an effective indicator of their crystallinities.

2. Experimental

2.1. Film preparation

The PBT sample used in the present study was purchased from Aldrich Co. ($M_v = 38,000$). Because no difference of fluorescence behavior was observed between both the samples as received and the ones purified by repeated dissolution and precipitation, we used the PBT sample without any purification. The PBT films for the fluorescence measurements were prepared on quartz disks by using a spin-casting method from a 1% solution of 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) or chloroform (CF)–trifluoroacetic acid (TFA) mixed solvents with different fractions,

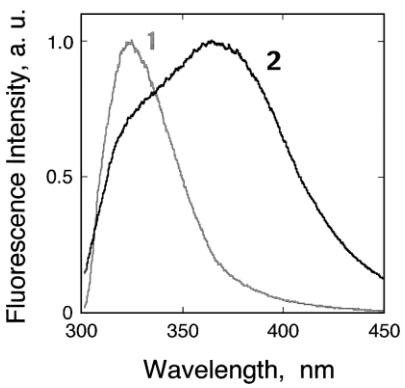

Fig. 1. Fluorescence spectra of PBT in HFP solution (1) and PBT thin film cast on a quartz disk (2). Both spectra are normalized to the peak. The excitation wavelength is 290 nm.

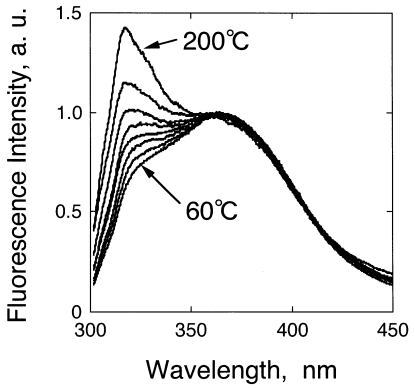

Fig. 2. Cast temperature (T_{cast}) dependence of fluorescence spectra of PBT films prepared using a spin-casting method from a HFP solution (normalized to the peak near 365 nm). T_{cast} of the films are 60, 80, 100, 120, 140, 160, 180 and 200 °C, and the spectra are shown in this order from the lower to the upper at 320 nm. The excitation wavelength is 290 nm.

and dried by extensive pumping under vacuum for more than three days at a constant casting temperature (T_{cast}). After the influx of dry nitrogen gas into the oven, the films were quickly transferred into a vacuum desiccator and quenched to room temperature under vacuum. More than four films were prepared to ascertain the reproducibility. The films were left on the quartz disks for ease of handling during subsequent measurements. The thickness of the PET films prepared under the same method were 350–400 nm [10]. The PBT films for determining weight percentage crystallinity were prepared by using the same spin-casting method on glass disks of 10-cm diameter from a 1% HFP solution.

2.2. Weight percentage crystallinity and fluorescence measurements

The density of PBT films was measured by a pycnometer with xylene and carbon tetrachloride as media. The weight percentage crystallinity was calculated by assuming the densities of the crystal and amorphous region to be 1.396 (α-forms) [18] and 1.282 g/cm^3 [19], respectively [20].

UV absorption spectra were measured on a Shimadzu UV-2200. Fluorescence spectra, fluorescence excitation spectra, and fluorescence polarization spectra were measured at 25 °C on a Hitachi F-4500 spectrofluorometer. Films on quartz disks were set at 45° to the exciting beam. Excitation was at 290 nm. The values of anisotropy were determined by a Hitachi automatic polarizer: the values were determined by averaging the values for 300 s at 320 and 325 nm for PBT in a crystal region, and 365 and 370 nm for PBT in an amorphous region. In order to ascertain the values, the measurements were repeated three times for one film.

3. Results and discussion

3.1. Fluorescence behavior of PBT thin films reflecting crystalline and amorphous regions

Fig. 1 shows the fluorescence spectra of PBT in HFP solution (1) and PBT thin film cast on a quartz disk (2). The two spectra are quite different from each other, and their peak wavelengths are 325 and 365 nm, respectively. The former figure (1) is identical with the spectrum of PBT in HFP by Dellinger and Roberts [15], while the latter (2) is similar to the spectrum of PBT thin film by Takai et al. [17]. Although the 365-nm peak is too red-shifted for fluorescence of phenylene moiety, the excitation spectra for these fluorescences show that all of them are of intrinsic fluorescence from the main-chain phenylene group of PBT.

Next we measured the fluorescence spectra of PBT thin films whose casting temperatures, T_{cast}, were from 60 to 200 °C (Fig. 2). The aim of this measurement was to observe whether or not PBT fluorescence changes with its crystallinity, because PBT films prepared at different T_{cast} have different crystallinities. Each spectrum shown in Fig. 2 was obtained by averaging the spectra of four different films cast at the same T_{cast}, although all four spectra were identical with one another. All the spectra were normalized to the maximum of the fluorescence component of the longer-wavelength. Fig. 2 shows that (i) there are two fluorescence components: the peak wavelength of one component is around 320 nm and that of the other is 365 ± 2 nm; (ii) the shorter-wavelength component increases with an increase in T_{cast}, while the component of longer-wavelength decreases. With regard to (ii), Fig. 3 compares the raw fluorescence intensities of PBT films cast at 40 and 200 °C. Since the two films have nearly the same thickness (400 nm) and then nearly the same concentration of PBT, the increase of the shorter-wavelength component was found to correspond with the decrease of the longer-wavelength component.

Because (I) the excitation spectra for the fluorescence between 320 and 400 nm of all samples were almost identical with one another and with the absorption spectrum

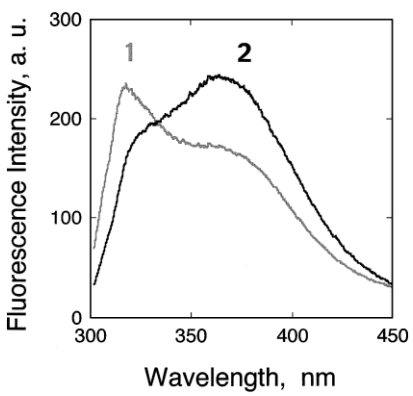

Fig. 3. Fluorescence spectra of PBT thin film cast at 200 °C (1) and cast at 40 °C (2). The excitation wavelength is 290 nm.

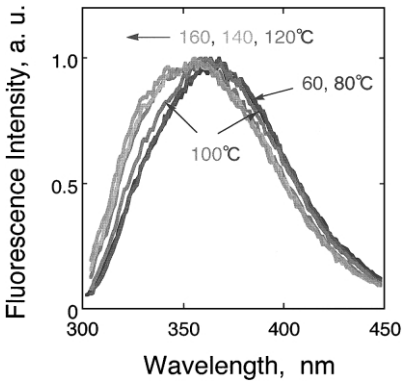

Fig. 4. Cast temperature (T_{cast}) dependence of fluorescence spectra of PET films prepared using a spin-casting method from a chloroform–trifluoroacetic acid (9:1, v/v) solution (normalized to the peak). The excitation wavelength is 292 nm.

of PBT solution and (II) the peak wavelength is constant, the fluorescence component of longer-wavelength can be assigned to an excimer. Thus, the change observed in Fig. 2 indicate that the ratio of monomer and excimer fluorescence of PBT phenylene groups depends on crystallinity of PBT solids.

The reason why the PBT fluorescences at 320 nm, monomer fluorescence, and at 365 nm, excimer fluorescence, reflect a crystal region and an amorphous region, respectively, is explicable if we consider the distance between two phenylene moieties. The analysis of X-ray diffraction of the PBT crystal region demonstrated that any phenylene group should be separated from other phenylene and carbonyl groups by more than 0.47 nm [21,23,24]. This means that the π-electron of the phenylene groups should be isolated from the π-electrons of the others. Thus, any longer-wavelength fluorescent component should never be observed from a crystal region and the phenylene fluorescence in the crystal region should be identical to that in a fluid solution.

On the other hand, some phenylene moieties in the amorphous region can be within a distance of 0.35 nm from a phenylene or carbonyl group. Here the π-electron of the phenylene groups can overlap and interact with the π-electron of other phenylene groups and/or carbonyl groups. If the interaction can take place in the excited state, an excimer or exciplex can be formed; if they interact strongly in the ground state, a ground-state dimer or a charge-transfer complex can be formed [25]. In the case of PBT thin films, the formation of an excimer between two main-chain phenylene rings is most probable.

We have already reported the fluorescence behavior of PET thin films cast on quartz disks [8–10]: there are two emissive components whose peaks are near 330 nm and at longer wavelengths than 370 nm. However, in the case of the PET thin films prepared by the same method, the fluorescence spectrum did not appear to be induced by the spectral overlap of the longer-wavelength component having a constant peak wavelength with phenylene

monomeric fluorescence; rather, it appeared to be induced by the gradual shift of the total spectrum with a change in T_{cast} (Fig. 4). Thus, we hesitated to assign the longer-wavelength component of PET thin films as an excimer whose peak should be constant, and rather assigned it to the red-shifted fluorescence of either phenylene group or phenylene exciplex due to interactions involving some contributions of charge-transfer stabilization among phenylene and carbonyl groups and/or phenylene groups [8]. Actually the excitation spectra of PET thin films were found to have one vibrational peak of 310 nm according to the intensity change of the longer-wavelength component.

The difference of the longer-wavelength fluorescent components between PET and PBT thin films is considered to be due to the length of alkyl chain. The distance between two carbon atoms of carbonyl of one terephthalate moiety is 0.59 nm while that between two carbon atoms of carbonyl of adjacent terephthalate moieties is 0.57 nm in the case of PET. Thus, if two PET chains are close to each other, one terephthalate group in a PET chain could overlap with some parts of π-electron orbitals of another terephthalate group in another PET chain. Here ethylene chain is so short that the terephthalate group could interact locally with the part of carbonyl groups in the ground state, which would induce charge-transfer stabilization among phenylene and carbonyl groups. Therefore, the feature of the PET longer-wavelength fluorescent component is assumed to be different from an excimer. However, in the case of PBT, since (i) the butylene chain can isolate each π-electrons of terephthalate moieties and (ii) the glass transition temperature of PBT is 304 K [26], which is lower than T_{cast}, the location of terephthalate moiety can be settled down in the stable configuration possible to form an excimer. In any rate, the longer-wavelength fluorescent component is assumed to be produced by the interaction between two terephthalate moieties in amorphous region.

As described in Section 1, the shorter-wavelength component of PET thin films is established to be mainly from the phenylene moiety in the crystal region, while the longer-wavelength component is from the phenylene moiety in the amorphous region. We reported that the ratio of the two fluorescence intensities can be an effective indicator of PET crystallinity [10]. The results for the PBT thin films

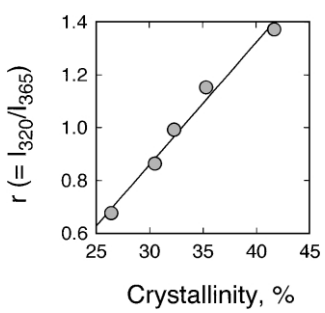

Fig. 5. Relationship between weight percentage crystallinity obtained by measuring density of PBT thin films and its r value.

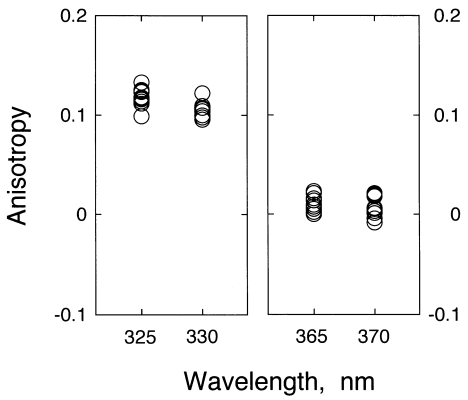

Fig. 6. Fluorescence anisotropic values of PBT thin films at room temperature obtained by excitation at 290 nm. Ten samples were used to determine the anisotropic values of shorter-wavelength fluorescence (325- and 330-nm) and another 10 for longer-wavelength fluorescence (365- and 370-nm).

also suggest that the fluorescence behavior of PBT thin films could be related to their crystallinity. Taking into account a slight shift between PBT and PET, we chose the ratio of the fluorescence intensity at 320 nm, I_{320}, to that at 365 nm, I_{365}.

$$r = I_{320}/I_{365} \quad (1)$$

Fig. 5 shows the relationship between the weight percentage crystallinity, determined by measuring the density of PBT thin films, and their fluorescence intensity ratio, r. The value of r was found to change linearly with crystallinity: the coefficient of determination is 0.98. Although I_{320} consists of monomeric fluorescence from both crystal and amorphous regions, Fig. 5 shows that r can be a quite effective indicator of the crystallinity of PBT thin films as well as that of PET thin films.

The assignment of PBT phenylene fluorescence can be ascertained by the measurements of fluorescence anisotropy. In general, when a chromophore is excited by polarized light, the emission of the chromophore will be observed to be polarized if (I) the molecular motion of the chromophore is slow enough and (II) energy transfer and/or energy migration do not take place. Thus the measurements of the emission anisotropy yield information on molecular motions and/or energy transportation. The fluorescence anisotropy is defined as

$$\text{anisotropy} = (I_p - GI_v)/(I_p + 2GI_v) \quad (2)$$

where I_p and I_v denote the measured intensities when the observing polarizer is parallel and perpendicular, respectively, to the direction of the polarized excitation, and G is a machine constant. When the motion of a chromophore is fast enough or excitation energy can hop among molecules, the anisotropy of the emission falls to zero.

We measured the anisotropy of two fluorescence components of PBT thin films at room temperature. In order to determine the anisotropic values of the shorter-wavelength component, namely a monomeric fluorescence, 10 PBT films with relatively high crystallinities were

measured. On the other hand, the anisotropic values of the longer-wavelength component, namely an excimer fluorescence, were determined by measuring 10 PBT films cast at lower T_{cast} with low crystallinities. Fig. 6 shows that (i) the anisotropic values are quite reproducible, (ii) the values for phenylene fluorescence in the crystalline region are 0.11 ± 0.02, and (iii) the values for phenylene fluorescence in the amorphous region are 0.01 ± 0.02.

Phenylene groups of PBT solids are assumed to be fixed both in crystalline and amorphous regions. Thus, the reason why the anisotropy values were close to zero and the fluorescence was almost depolarized is due to the singlet energy migration among phenylene groups: it can be described by the theory developed by Förster [27,28] and Galanin [29]. The rate constant for singlet energy migration is expressed as a function of the distance between the donor and the acceptor together with the molecular orientation factor. In the crystalline region of PBT solids, the three-dimensional location of each phenylene group is strictly arranged, so even if the distance is within 0.5 nm, the energy migration does not appear to take place so much: fluorescence anisotropy of phenyl group in plastic film at 77 K, which shows the inherent value, is 0.13 [30]. Conversely, in the amorphous region of PBT solids, phenylene groups are disordered and some of them are situated adequately for excitation energy to transport between them. In conclusion, the results of fluorescence depolarization are considered to support our claim that the fluorescence near 320 nm is from a crystalline region and that near 365 nm is from an amorphous region.

3.2. Fluorescence behavior of PBT films prepared from fluid solution where PBT is not well dissolved

We prepared the thin films by using a spin-casting method from a 1% PBT of mixed solvents of trifluoroacetic acid (TFA) and chloroform (CF). The TFA ⊣ CF (9:1, v/v) solution of PBT was transparent and appeared to be uniform. However, the fluorescence spectra of PBT thin films prepared from the mixed solution did not agree with each other, as shown in Fig. 7. Even though the films were from the same volume of the same solution, they had neither the same fluorescence intensity nor the same fluorescence shape. Since all of the films prepared from HFP solution had identical fluorescence, this dispersion would be attributable to the imperfect solubility of PBT in the mixed solution. Fig. 8 shows the dependence of r on the fraction of mixed solvents from which solution the PBT films were prepared. The r values of PBT films from HFP solutions were almost identical with one another and quite low, which means that the crystallinity was low. However, the r values of PBT films from mixed solutions of TFA and CF were different from one another and higher than the r value of PBT films prepared from HFP solution, meaning that the crystallinity was high but not uniform. The results shown in Figs. 7 and 8 are reasonable if we consider that some portion of the PBT crystal could not be solved in the mixed solution of TFA and CF and therefore remained in crystal form even in thin films. Consequently, the fluorescence behaviors of these PBT films are perfectly coherent with our conclusion that the r value can be an effective indicator of PBT crystallinity.

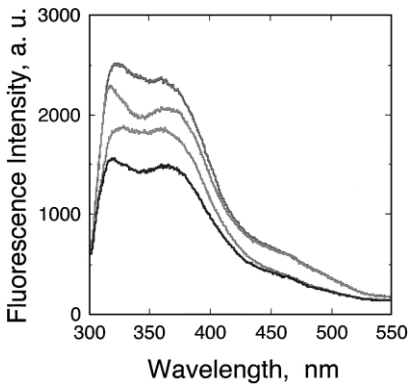

Fig. 7. Fluorescence spectra of PBT thin films prepared using a spin-casting method from a chloroform–trifluoroacetic acid (1:9, v/v) solution. The excitation wavelength is 290 nm.

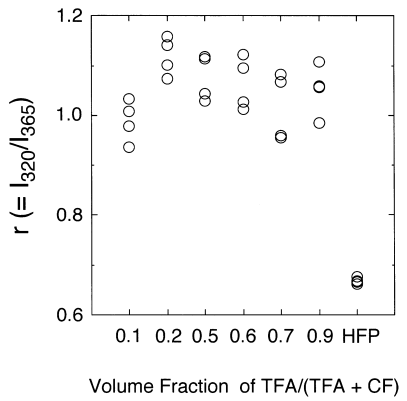

Fig. 8. r values of PBT thin films prepared from a 1% PBT of mixed solvents of trifluoroacetic acid (TFA) and chloroform (CF). Four films were measured for each solution with a different fraction of TFA and CF. The r values of four PBT films prepared from HFP solution served as a reference. The excitation wavelength is 290 nm.

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