S0032-3861(96)00208-X

Polymer Vol. 37 No. 16, pp. 3553–3558, 1996

0032-3861/96/$15.00+0.00

Microenvironments in poly(ethylene terephthalate) film revealed by means of fluorescence measurements

Hideyuki Itagaki*, Yumiko Inagaki and Noritaka Kobayashi
Department of Chemistry, Faculty of Education, Shizuoka University, 836 Ohya, Shizuoka 422, Japan
(Received 3 August 1995; revised 6 December 1995)

The fluorescence behaviour of poly(ethylene terephthalate) (PET) films prepared by using a spin-casting method was measured. The wavelength of the fluorescence peak was found to be dependent on the casting temperature, T_{cast}. This fluorescence is neither from a ground state dimer nor from an excimer. It is the red-shifted fluorescence of either the phenylene group or the phenylene exciplex due to interactions involving some contributions of charge-transfer stabilization among phenylene and carbonyl groups and/or phenylene groups. Both d.s.c. and i.r. measurements clearly showed that the fluorescence reflects whether the main-chain phenylene ring of PET is in the crystal region or in the amorphous region. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(ethylene terephthalate); fluorescence spectroscopy; crystallinity; amorphous)

INTRODUCTION

The luminescent probe method has been widely known to be a useful tool to investigate microstructures and motions of polymer molecules[1–5]. Since the use of the luminescent method guarantees high sensitivity, it could be employed for monitoring small chemical and physical changes in material products. However, we have come to realize through an extensive literature survey that the characterization of fluorescence properties of luminescent material polymers has focused on a very few polymers such as polystyrene and polyvinylcarbazole. Thus we started with the investigation of the luminescence of the material polymers such as polycarbonate[6,7].

Poly(ethylene terephthalate) (PET) is used extensively in the fibre and packaging industries. PET has a fluorescent phenylene moiety in the main chain showing its fluorescence peak at 330–340 nm in fluid solution. However, the intrinsic luminescence of PET films has been less well characterized. The emission at longer wavelengths (~380 nm) was first reported by Phillips and Schug[8], who suggested that it originated from either the triplet state or a tightly-bound excimer. Padhye and Tamhane[9] established that the emission with a peak at 365 nm is not the phosphorescence but the fluorescence from a structure located in amorphous PET by the measurement of PET films at 77 K. Takai *et al.*[10,11] assigned the fluorescence with a peak at 375 nm to a singlet excimer, while Allen and McKellar[12] attributed the fluorescence with a peak at 392 nm to the ground state dimer. Finally the existence of the ground state dimer appears to be established by several authors[13–16]: the ground state dimer of PET films shows the fluorescence and absorption spectra with fine structures (absorption peak at 340 nm and fluorescence peak at 390 nm). However, all the fluorescence data of the PET films are not always explicable, because (1) all the films showing the dimer fluorescence are thick enough, (2) the fluorescence spectra of PET films reported so far are not identical with one another, and (3) the intensity of the fluorescence at longer wavelengths is by far larger than that assumed, even if energy transfer plays an important role. The difference could be induced by the conditions to prepare films. In fact, the fluorescence behaviour of PET films has been reported to depend on whether the fluorescence is from the amorphous region or from the crystal region[9,14,15,17,18].

In this paper, we report on the fluorescence properties of PET films prepared by using a spin-casting method. This preparation method provides most reproducible conditions to prepare films and thus we can expect the systematic measurements of the intrinsic fluorescence of PET films. In order to ascertain that the PET films show other fluorescence such as excimer in addition to dimer emission, we investigate in the present paper the fluorescence behaviour of the PET films by changing systematically the casting temperatures that influence the crystallinity.

EXPERIMENTAL

Film preparation

The poly(ethylene terephthalate) (PET) sample used in the present study was purchased from Aldrich Co. (inherent viscosity = 0.59) and purified by repeated dissolution and precipitation. The PET films for the fluorescence measurements were prepared on quartz disks by using a spin-casting method from a 1% solution of chloroform–trifluoroacetic acid (9:1 v/v), and dried

---

* To whom correspondence should be addressed

by extensive pumping under vacuum for more than 3 days at a constant cast 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 five films were prepared to ascertain the reproducibility. The films were left on the quartz disks for ease of handling during subsequent measurements. The PET films for d.s.c. and i.r. measurements were prepared by using the same spin-casting method on glass disks of 10-cm diameter from a 5% solution and on KBr disks from a 1% solution, respectively.

We also prepared the PET films cast on glass plates by dropping a 1% solution of chloroform–trifluoroacetic acid (9 : 1 v/v). The films were removed from the casting plates after preliminary drying for a day or a few days at room temperature and then dried by extensive pumping under vacuum at a T_{cast}. This method is called a stationary casting method.

Fluorescence, differential scanning calorimetry, infrared absorption measurements

Fluorescence spectra, fluorescence excitation spectra and fluorescence polarization spectra were measured on a Hitachi F-4500 spectrofluorometer at *ca.* 25°C. In order to avoid photodegradation of the PET films, the exposure of films to the light was kept to a minimum: the bandpass of the excitation light is narrow (2.5 nm) and the scanning speed for the fluorescence is fast (2400 nm min^{-1} between 300 and 500 nm, except the fluorescence depolarization measurements, against 10–20 nm around the peak wavelength at 60 nm min^{-1}). The emission decreases with the number of sequential runs of the fluorescence spectrum for the same PET film. However, the decrease is only 3% even for the 15th measurements with no spectral change. Films on quartz disks were set at 45° to the exciting beam. Fluorescence measurements for the concentrated solutions of PET were carried out in a 1-mm (optical path length) quartz cell set at 45° to the exciting beam. D.s.c. measurements were performed on a Perkin–Elmer DSC7. The instrument was calibrated to within ±0.5 K using indium and octadecane for the low-temperature region and using indium and zinc for the higher-temperature region. All data were taken using a scan rate of 20°C min^{-1}. I.r. absorption spectra were measured on a Perkin–Elmer 1720X *FT*i.r. spectrophotometer with resolution of 2 cm^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows concentration dependence of fluorescence spectra of PET in aerated chloroform–trifluoroacetic acid (9 : 1 v/v). The peak wavelength is around 330 nm and is identical with the values reported. Since all the spectra perfectly agree with one another, no excimer of PET is observed in this solution. No spectral change is observed when the fraction of trifluoroacetic acid in mixed solvent is changed from 5% to 20%.

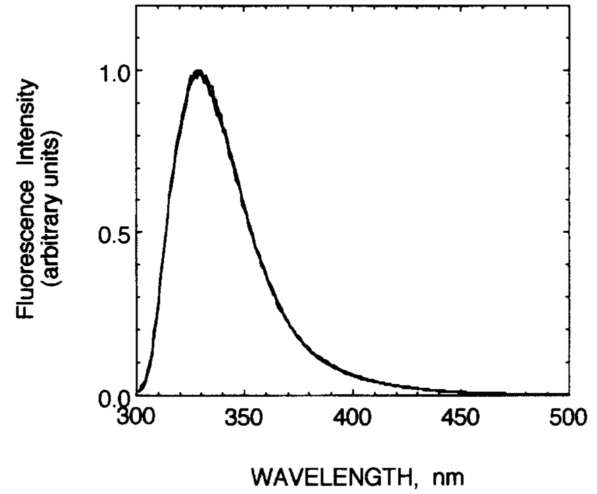

Figure 1 Concentration dependence of PET fluorescence spectra in chloroform–trifluoroacetic acid (9 : 1 v/v) at 25°C: the concentration is 10, 5, 3, and 1% (wt/wt) together with the dilute solution (optical density is 0.05): excitation wavelength is 292 nm. The spectra are normalized at the peak

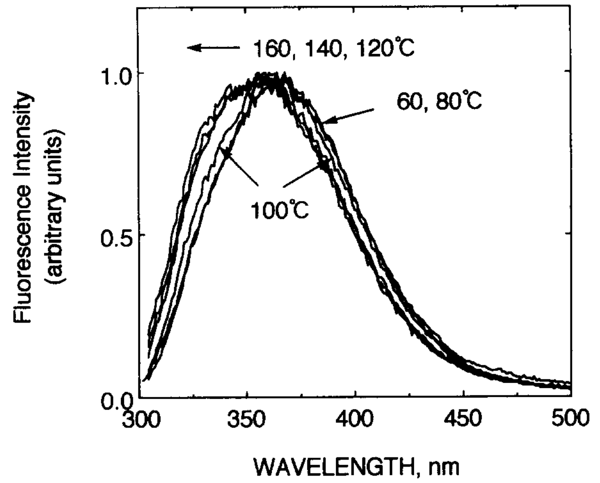

Figure 2 Cast temperature (T_{cast}) dependence of fluorescence spectra of PET films prepared using a spin-casting method from a chloroform–trifluoroacetic acid (9 : 1 v/v) solution (normalized at the peak): excitation wavelength is 292 nm

Figure 2 displays the fluorescence spectra of PET films prepared by a spin-casting method at several casting temperatures, T_{cast}. The results are summarized as follows: (1) the peak wavelengths of all the fluorescence spectra are by far longer than the peak wavelength of PET fluorescence in fluid solution (330 nm), (2) the fluorescence peak is blue-shifted with an increase in T_{cast}, and (3) the dimer fluorescence with fine structure around 390 nm[12–16] is undetectable or neglected. No spectral change is observed for the PET films prepared from the solution where the fraction of trifluoroacetic acid is changed from 5% to 20%.

Figure 3 shows the T_{cast} dependence of the fluorescence excitation spectra at the fluorescence peak wavelength: almost all spectra are perfectly identical with one another except a small change around 303 nm for the films cast at higher temperatures than 130°C. Consequently the fluorescence excitation spectra at 330–400 nm of any films are almost identical with one another and with the absorption spectrum of PET solution.

The above results suggest that the fluorescence of PET films at longer wavelengths is not from a dimer, a charge-transfer complex, or an excimer. Since the fluorescence excitation spectra show that the monomeric phenylene moiety directly absorbs photons, we can deny the possibility of a ground-state dimer and a charge-transfer

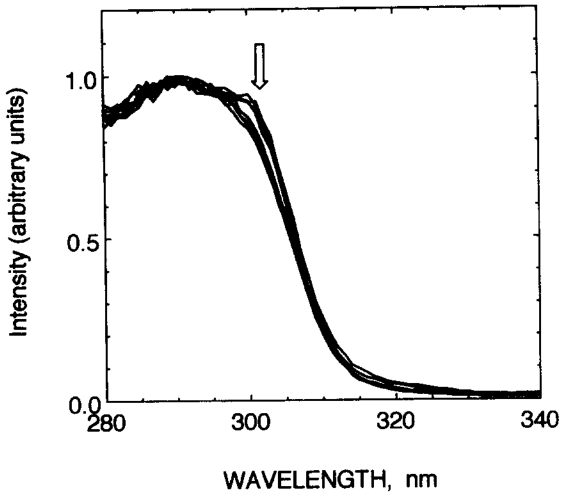

Figure 3 Cast temperature (T_{cast}) dependence of fluorescence excitation spectra of PET films prepared using a spin-casting method from a chloroform–trifluoroacetic acid (9 : 1 v/v) solution (normalized at the peak): emission wavelength of each spectrum is each peak. Arrow shows the vibrational band near 303 nm. The spectra with low intensities at 303 nm are those of 40, 60, 80, 100, and 120°C. Other spectra are 140, 160, and 180°C

complex. In fact, this fluorescence is completely different from the fluorescence of the PET ground-state dimer that has been already reported (absorption peak at 340 nm and fluorescence peak at 390 nm)[12-16].

In relation to dimer fluorescence, we measured the fluorescence of the PET films prepared by using a stationary casting method (explained in Experimental). The fluorescence behaviour is not so dependent on T_{cast}: fluorescence peak of the films whose T_{cast} is 40–160°C is 355–360 nm. The most remarkable difference of the films prepared using a stationary casting method from those using a spin-casting method is that their fluorescence excitation spectra demonstrate the existence of the dimer fluorescence as shown in the previous papers[12-16]. It means that the portion of the ground-state dimer is so small that its fluorescence is not detectable in a thinner film prepared by using a spin-casting method.

Next we would like to give negative comments about the possibility of excimer fluorescence. First, the change in *Figure 2* does not appear to be induced by the spectral overlap of an excimer emission whose peak should be constant, but it rather appears to be the gradual shift of the total spectrum with a change in T_{cast}. Second, no excimer is observed at all in concentrated PET solution (*Figure 1*).

Therefore the fluorescence shown in *Figure 2* would be assigned to the phenylene fluorescence of PET films instead of dimer and excimer fluorescence, and it shifts reflecting the circumstance of the phenylene moieties. We suppose that the interactions among phenylene groups and/or phenylene and carbonyl groups play an important role in the stabilization of the excited monomer state of phenylene moiety. Thus, we tried to examine polarity effect on fluorescence spectra of a monomer model compound using various solvents. Dibenzyl terephthalate (DBT) is employed as a monomer model in order to reflect the surroundings with phenylene moieties being abundant. *Figure 4* clearly shows that the peak wavelength of DBT fluorescence is red-shifted with an increase in polarity of solvent. Consequently, the distribution of electron density of terephthaloyl group is found to be sensitive to polarity.

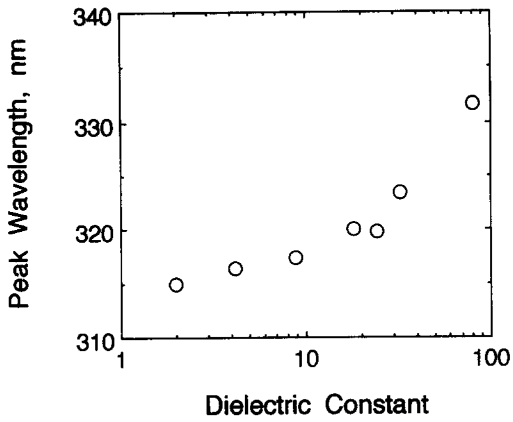

Figure 4 Polarity dependence of fluorescence peak wavelength of DBT, a model compound of PET, in various solvents. The solvents used are cyclohexane (dielectric constant = 2.0), diethyl ether (4.2), dichloromethane (8.9), 2-propanol (18.3), ethanol (24.3), methanol (32.6), and water (80.2): excitation wavelength is 260 nm

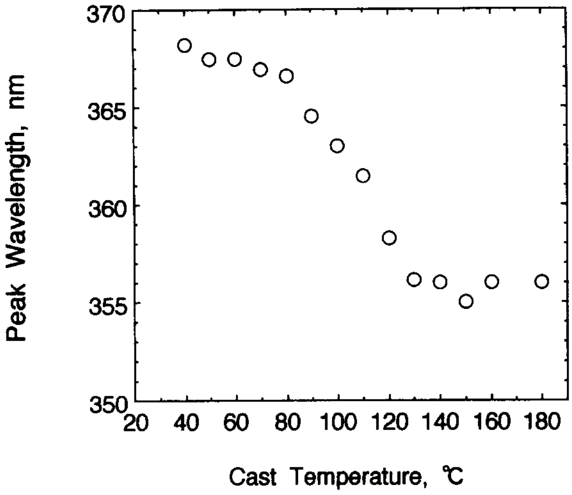

Figure 5 Cast temperature (T_{cast}) dependence of fluorescence peak wavelength of PET films prepared using a spin-casting method from a chloroform–trifluoroacetic acid (9 : 1 v/v) solution: excitation wavelength is 292 nm

Here one might suppose that the fluorescence of PET films should be assigned to a kind of exciplex since it is induced not unimolecularly but by the interaction among terephthaloyl groups: in general, fluorescence peak of an exciplex can change with polarity instead of an excimer. Although we cannot abandon the possibility of an exciplex, we think that the interaction among terephthaloyl groups is not so strong to form strict bimolecular complex such as an exciplex, but that it influences the excited state of phenylene moiety. At any rate, we can say that interaction involving some contributions of charge-transfer stabilization are induced among phenylene and carbonyl groups and/or phenylene groups. In conclusion, the fluorescence of PET films at longer wavelengths is from the phenylene group, whether it is monomeric or exciplex, in a local polar region where it is induced by the interaction among terephthaloyl moieties.

Figure 5 shows the casting temperature dependence of fluorescence peak wavelength of PET films prepared by a spin-casting method. Each wavelength value is obtained

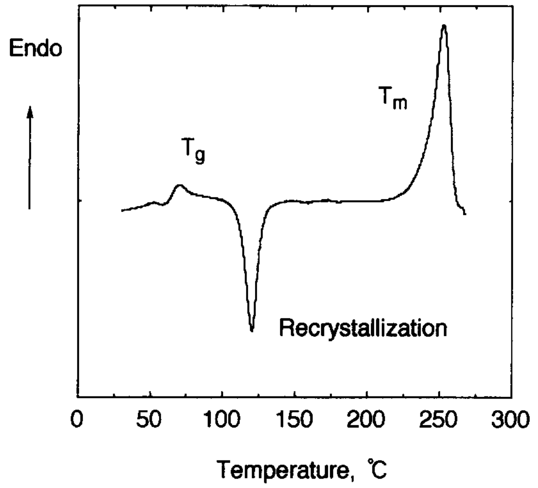

Figure 6 Typical d.s.c. heating curve for PET films prepared using a spin-casting method: a scan rate is 20°C min^{-1}

Table 1 Thermal properties of the PET films prepared by using a spin-coating method obtained from d.s.c. thermograms (scan rate: 20°C min^{-1}): T_{RC} and T_m are the peak temperatures of recrystallization and melting, respectively. S_{RC} and S_m are the areas of recrystallization exotherm and melting endotherm. The ratio, S_{RC}/S_m, shows the relative amorphous content of the PET films

Cast temperature (°C)	T_{RC} (°C)	T_m (°C)	S_{RC}/S_m (%)
50	127	253	17
60	123	253	16
80	129	254	14
100	(113)	257	2.4
120	(114)	253	3.0
150	—[a]	254	[a]

[a] Undetectable

by averaging more than five data. The peak shift is not so remarkable below 80°C and above 130°C, while a large shift is observed between 80 and 130°C: there is a point of inflection near 100°C.

The thermal features of PET films are already well known: the glass transition at 70–80°C (amorphous, 67°C; crystalline, 81°C), the recrystallization at 120–130°C, and the melting at 250–265°C. The above fluorescence behaviour is found to be closely related to the thermal behaviour such as glass transition and recrystallization. Therefore we can assume that the phenylene fluorescence is dependent on its location, which is in the crystalline or amorphous region.

The d.s.c. scans were made on each of the PET films prepared in order to estimate relative amounts of amorphous and crystalline regions. *Figure 6* gives a typical heating curve of a PET film. The recrystallization exothermic peak area, S_{RC}, is proportional to the increase in crystalline content due to the thermal recrystallization process: the larger area shows a larger portion of the amorphous region. The area of a melting endotherm, S_m, is proportional to the total crystalline content including the recrystallized content during the d.s.c. scans. Therefore, the relative amorphous content of each PET film can be obtained to be the ratio of S_{RC} to S_m. *Table 1* summarizes the relative amorphous contents of PET films prepared at several casting temperatures together with temperatures of recrystallization and melting. *Table 1* clearly supports the fact that the amorphous content is high for the films cast below 80°C while it is low for the films cast above 120°C. Thus, the fluorescence shift observed in *Figure 2* is related to the amorphous content of the film.

Table 2 The cast temperature dependence of the intensity ratio of the 1370 cm^{-1} band to the 1265 cm^{-1} of the PET films prepared using a spin-coating method

Cast temperature (°C)	Intensity ratio of 1370 cm^{-1} band to 1265 cm^{-1} band
40	20
60	15
80	15
100	14
130	13
150	11
170	11

The i.r. absorption spectra also give information on the amorphous content of PET film. The intensity of the absorption band at 1370 cm^{-1}, which is assigned to CH_2 deformation vibration, is reported to decrease with increasing crystallinities in PET solids[19,20]. We prepared PET films cast on KBr disks by using the same spin-casting method and measured their i.r. absorption. The thickness of each film appears to be different and change intensities of absorption bands. Thus, we used the strong 1265 cm^{-1} band, being assigned to ester stretching, as an internal standard, since it is not influenced by the crystallinity. *Table 2* shows the T_{cast} dependence of the intensity ratio of the 1370 cm^{-1} band to 1265 cm^{-1} band. It is quite qualitative, but it shows the same T_{cast} dependence of the amorphous content of the film as the d.s.c. data do in *Table 1*. Interestingly, the fluorescence peaks of the PET films cast on KBr disks were ascertained to be identical with those of the PET films cast on quartz disks.

In summary, the amorphous contents of the PET films, which are prepared by using a spin-casting method from the chloroform–trifluoroacetic acid (9 : 1 v/v), are dependent on the casting temperatures, T_{cast}: it is high below the glass transition temperature, T_g, near 80°C, decreases greatly between T_g and 130°C which is about the end temperature of the recrystallization process, and is kept to a low and constant value above 130°C. The fluorescence behaviour of the prepared PET films perfectly reflects the contents of amorphous and crystalline regions: the fluorescence with longer wavelength corresponds to the phenylene moiety in the amorphous region, while that with shorter wavelength corresponds to that in the crystalline region. The fluorescence of the phenylene moiety in the amorphous region is supposed to shift depending on the change in its surroundings such as the polarity.

Generally speaking, the spin-casting method gives uniform films with quite low crystallinity. The use of trifluoroacetic acid as a solvent also appears to induce the increase in amorphous content. We compared the fluorescence behaviour of the PET films prepared differently with the above results: the different preparation method from the same solution and the same spin-casting method using a different solvent.

As described above, we measured the prepared PET films by using a stationary-casting method. The peaks are around 355 nm, which corresponds to the value for

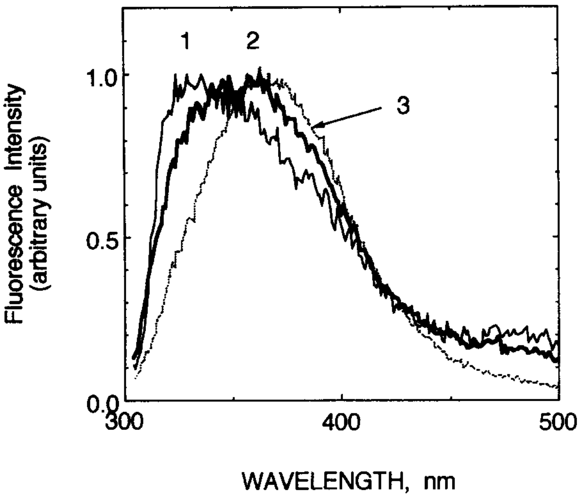

Figure 7 Fluorescence spectra of PET films prepared using a spin-casting method from a DMSO solution (normalized at the peak) (1: cast at 180°C, 2 (heavy line): cast at 60°C) together with the film from a chloroform–trifluoroacetic acid (9:1 v/v) solution (3: cast at 60°C): excitation wavelength is 292 nm

the films with the highest crystallinity of all those prepared by a spin-casting method. The result suggests that the maximum crystallinity is dependent on the chain conformation of PET molecules in condensed solution.

Again we prepared the PET films by using a spin-casting method from a 1% hot solution of dimethyl sulfoxide (DMSO). Since PET is not very soluble in DMSO at room temperature, the appearance of the films is not too good: it looks like a lot of very small particles dispersed in almost transparent films. *Figure 7* shows the fluorescence spectrum of the PET film from a DMSO solution. The spectrum is explicable if the fluorescence near 330 nm is from the crystalline region and that near 350 nm is from the amorphous region.

The cause for the fluorescence of PET films shifts according to the degree of amorphous content and is assumed to be induced by the interaction among the phenylene moieties and/or among phenylene and carbonyl groups. In the crystalline region the phenylene groups are located far from one another[21]. Thus, there is no large interaction among isolated phenylene moieties and the fluorescence is around 330 nm. However, some phenylene moieties are within the distance in which they interact with one another and/or with carbonyl groups in the amorphous region: the interaction could induce resonance of π electrons and/or charge-transfer, and then the red-shifted fluorescence appears due to this stabilization. We assume that a small portion of the chromophores in such resonance can form the ground state dimer, but that its total amount can be neglected in the thin films prepared by using a spin-coating method.

With regard to it, fluorescence polarization was measured for all the PET films. The fluorescence anisotropy, r, is defined as

$$r = (I_p - I_v)/(I_p + 2I_v)$$

where the 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. In general, the anisotropy of the emission falls to zero when motion of a chromophore is fast enough or excitation energy can hop among molecules because of their short separation. The values of anisotropy of the PET films at *ca.* 25°C are summarized in *Table 3*. The results show that the anisotropy is nearly zero for the films cast below T_g, while it increases with an increase in T_{cast}, i.e. the crystallinity. Because the phenylene group in the crystalline region is isolated and fixed, the anisotropy must be larger than that in the amorphous region. The result shown in *Table 3* is considered to support the above assumption.

Table 3 Cast temperature dependence of anisotropy of PET films prepared by using a spin-coating method

Cast temperature (°C)	Wavelength range	Anisotropy
40	(360–370 nm)	0.004 ± 0.003
50		0.004 ± 0.003
60		0.010 ± 0.003
70		0.012 ± 0.004
80		0.010 ± 0.004
90		0.02 ± 0.01
120	(350–360 nm)	0.03 ± 0.01
130		0.03 ± 0.01
150		0.04 ± 0.01
170		0.05 ± 0.01

SUMMARY

The present paper shows that the fluorescence of the phenylene moiety is red-shifted in the amorphous region of PET films. This shift is considered to be induced by interactions involving some contributions of charge-transfer stabilization among phenylene groups and/or phenylene and carbonyl groups. We have demonstrated that the phenylene fluorescence can probe the relative amorphous content of the PET films by means of the reproducible method to prepare uniform films using the spin-casting method and being dried under vacuum at a constant casting temperature: this preparation method gives more reproducible crystallinity than the stationary casting method. The fluorescence whose peak is near 330 nm corresponds to that of the phenylene groups in the crystalline region, while that at longer wavelengths corresponds to the main-chain phenylene in the amorphous region. Thus, the T_{cast} dependence of the PET fluorescence is induced by the change in the amorphous content, since the content depends on T_{cast}.

The above result also suggests that the dynamic process of recrystallization can be detected by monitoring the fluorescence of the main-chain phenylene group of PET film. This trial will be published elsewhere in the future.

ACKNOWLEDGEMENT

We wish to express our sincere gratitude to Dr Chie Sawatari of Shizuoka University for her useful suggestion and discussion.

REFERENCES

1 Guillet, J. E. 'Polymer Photophysics and Photochemistry', Cambridge University Press, Cambridge, 1985
2 Winnik, M. A. (Ed.) 'Photophysical and Photochemical Tools in Polymer Science (Conformation, Dynamics, Morphology)', NATO ASI Series, Reidel, Dordrecht, 1986

3 Horie, K. and Mita, I. *Adv. Polym. Sci.* 1989, **89**, 77

4 Itagaki, H. and Mita, I. in 'Degradation and Stabilization of Polymers 2' (Ed. H. H. G. Jellinek), Elsevier, Amsterdam, 1989, Ch. 2, p. 45

5 Itagaki, H., Horie, K. and Mita, I. *Prog. Polym. Sci.* 1990, **15**, 361

6 Itagaki, H. *J. Photopolym. Sci. Tech.* 1993, **6**, 101

7 Itagaki, H. and Umeda, Y. *Polymer* 1995, **36**, 29

8 Phillips, D. H. and Schug, J. C. *J. Chem. Phys.* 1969, **50**, 3297

9 Padhye, M. R. and Tamhane, P. S. *Angew. Makromol. Chem.* 1978, **69**, 33

10 Takai, Y., Mizutani, T. and Ieda, M. *Jpn. J. Appl. Phys.* 1978, **17**, 651

11 Takai, Y., Mori, K., Mizutani, T. and Ieda, M. *J. Polym. Sci. Polym. Phys. Ed.* 1978, **16**, 1861

12 Allen, N. S. and McKeller, J. F. *Makromol. Chem.* 1978, **179**, 523

13 Hennecke, M., Kud, A., Kurz, K. and Fuhrmann, J. *Colloid Polym. Sci.* 1987, **265**, 674

14 Hennecke, M. and Fuhrmann, J. *Makromol. Chem. Makromol. Symp.* 1986, **5**, 181

15 Hemker, D. J., Frank, C. W. and Thomas, J. W. *Polymer* 1988, **29**, 437

16 Sonnenschein, M. F. and Roland, C. M. *Polymer* 1990, **31**, 2023

17 Cao, T., Magonov, S. N. and Qian, R. *Polymer Comm.* 1988, **29**, 43

18 Clauss, B. and Salem, D. R. *Polymer* 1992, **33**, 3193

19 Yamamoto, Y., Sangen, O. and Kishimoto, Y. *Himeji Kogyou Daigaku Kenkyuu Houkoku* 1972, **25A**, 90

20 Lin, S. -B. and Koenig, J. L. *J. Polym. Sci. Polym. Phys. Ed.* 1983, **21**, 2067

21 Daubeny, R. DeP. and Bunn, C. W. *Proc. Roy. Soc.* 1954, **A226**, 531