Aggregation of pyrene in poly(alkyl methacrylate) films revealed by time-resolved total internal reflection fluorescence spectroscopy

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Fluorescence spectra and decay curves of pyrene in poly(alkyl methacrylate) (methyl, *n*-propyl, isobutyl and cyclohexyl) films cast on sapphire substrates were measured under total internal reflection and normal excitation conditions, and were compared with each other. On the basis of the intensity ratio of the excimer to the monomer fluorescence and the fluorescence decay curve under the normal condition, the degree of pyrene aggregation in these films is discussed in terms of the solubility parameter, chain flexibility and hydrophobicity of the host polymers. Both the difference in the degree of pyrene aggregation and the difference in micropolarity around pyrene molecules between the vicinity of the sapphire/polymer interface and the bulk were found to be quite common for these polymer films cast on sapphire plates, and are discussed in terms of the interaction between substrate surface and polymers. The effect of tacticity of poly(methyl methacrylate) on the degree of the pyrene aggregation and the effect of labelling with pyrene were also investigated.

(Keywords: pyrene; aggregation; excimer)

INTRODUCTION

Surfaces and interfaces, as parts of polymer systems, have received much attention in science and technology. In particular, the dynamics, structure and chemical interaction in the surface or interface layers is of great importance, because of their characteristic properties, functions and reactivities for surface modification. Interactions between the polymer and the surface/interface can induce a change of conformation and orientation, affecting the distribution of free volume, local concentration of dopant or impurity molecules, and mutual association of polymers.

Powerful tools for surface and interface studies are techniques such as electron spectroscopy for chemical analysis and secondary ion mass spectrometry; however, they require vacuum conditions or result in destruction of the sample. Optical spectroscopy can also be used for such studies. Attenuated total reflection infra-red spectroscopy and total internal reflection (t.i.r.) Raman spectroscopy have been applied to the study of various kinds of polymer systems[1–3]. However, these methods cannot directly provide electronic and dynamic information on interface and surface layers of polymer systems. To obtain such information, time-resolved t.i.r. fluorescence spectroscopy is recognized to be a promising method. This spectroscopy has been developed for examining a bilayer film of *p*-bis(2-(5-phenylene oxazolyl)benzene)- and *N*-ethylcarbazole-doped polystyrene films[4,5] and applied to vacuum-deposited films[6], ablated polymer films[7], pyrene-doped poly(methyl methacrylate) (PMMA)[8], pyrene-doped segmented poly(urethane urea) (SPUU)[9], and pyrene-doped poly(*p*-hydroxystyrene) films[10]. Furthermore, this time-resolved spectroscopy was applied to investigate the properties of fluorescent molecules at a solid/solution interface. Fukumura and Hayashi combined this spectroscopy with fluorescence anisotropy and studied the dynamic behaviour of adsorbed protein on various polymer surfaces[11]. Rumbles *et al.*[12] investigated the photophysical properties of fluorescent molecules at a fused silica/solution interface and elucidated that the properties of the adsorbed layer are different from those of the bulk solution. This spectroscopy has recently been reviewed[13].

For pyrene-doped PMMA films, we elucidated that micropolarity around pyrene molecules in the vicinity of the sapphire/polymer interface is higher than that of the bulk, and that an aggregate state of pyrene is different between the vicinity of the interface and the bulk[8].

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To clarify the latter phenomenon, measurement of fluorescence decay curves was indispensable. That is, considering both the steady-state fluorescence spectrum and the fluorescence decay curves, we were able to distinguish two kinds of pyrene aggregates: a dimer that forms an excimer upon excitation, and pyrene aggregates that are responsible for fluorescence quenching. We elucidated the difference in the distribution of these aggregates between the interface and bulk layers.

Molecularly doped polymer films, such as pyrene-doped PMMA films, are used widely for elucidating fluorescence properties, excitation energy migration as well as transfer and charge transport mechanisms[14-18]. Most of these studies have been performed on the assumption that dopant molecules are distributed homogeneously in polymer films. Hence information on differences in fluorescence dynamics between the interface and bulk layers, which has been revealed for the first time experimentally by means of this spectroscopy, was quite novel and could not be obtained by other spectroscopic methods.

In this work, to obtain more information on the difference in the pyrene aggregation between the interface and bulk layers, we investigated fluorescence properties of pyrene-doped poly(alkyl methacrylate) films, pyrene-doped stereoregular PMMA films, and pyrene-labelled PMMA films by means of time-resolved t.i.r. fluorescence spectroscopy. In the labelled polymer films, pyrenyl chromophores are expected to be distributed homogeneously.

EXPERIMENTAL

Pyrene (Aldrich) was zone-refined or chromatographed on silica gel using *n*-hexane for elution. Chromatographed pyrene was sublimed under vacuum. The following poly(alkyl methacrylate) derivatives were used as host matrices: atactic methyl (aPMMA), isotactic methyl (iPMMA), syndiotactic methyl (sPMMA), *n*-propyl (PnPMA), isobutyl (PiBMA) and cyclohexyl (PCHMA). Host polymers were purified by two reprecipitations. Pyrene-labelled aPMMA and sPMMA were synthesized by radical and Ziegler–Natta copolymerization, respectively, of methyl methacrylate and 1-pyrenylmethyl methacrylate. The properties of these polymers were reported previously[19]. Solvents were purified by the usual methods.

Sapphire was used as an internal reflection element ($n_1 = 1.81$ at 310 nm). Polymer films were cast on sapphire plates from toluene solution containing poly(alkyl methacrylate) and a known amount of pyrene at room temperature and dried *in vacuo* for more than 8 h. Pyrene-labelled PMMA films were cast from a dichloromethane solution. PMMA films used for elucidating the effect of tacticity were also cast from a dichloromethane solution. The thickness of these films was ca. 10 μm. The refractive index (n), the glass transition temperature (T_g), the density (ρ), and solubility parameter (δ) and molecular weight per monomer unit of the polymers are listed in *Table 1*.

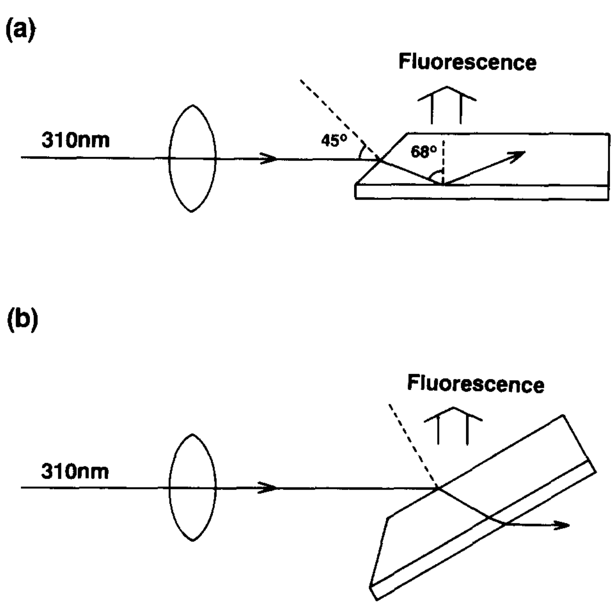

Figure 1 Schematic diagram of set-up for fluorescence measurement. (a) Total internal reflection (t.i.r.) condition; incident angle (θ) = 68°. (b) Normal excitation condition

Table 1 Refractive index (n), glass transition temperature (T_g), density (ρ), solubility parameter (δ), molecular weight per monomer unit (MW) and penetration depth (d_p for $\theta = 68°$) of poly(alkyl methacrylate)s

Polymer	n	T_g (°C)	ρ (g cm^{-3})	δ (cal$^{1/2}$ cm$^{-3/2}$)	MW	d_p (nm)
PMMA	1.53	105	1.19	9.25	100.12	35.7
PnPMA	1.52	35	1.08	8.80	128.17	34.6
PiBMA	1.52	53	1.05	8.53	142.19	34.6
PCHMA	1.55	83	1.10	8.90	168.23	38.2

A schematic diagram for the measurement set-up is shown in *Figure 1*. Fluorescence spectra and decay curves were measured under t.i.r. and normal conditions, and were compared with each other. Under the t.i.r. condition, the effective thickness of the interface layer was calculated by the following equations:

$$I = I_0 \exp(-2\gamma z)$$

$$\gamma = (2\pi n_1/\lambda)[\sin^2\theta - (n_2/n_1)^2]^{0.5}$$

where z is the depth from the interface, I and I_0 are intensities of the excitation light at the interface and at the depth z, respectively, θ is an incident angle of the beam, λ is its wavelength (310 nm), and n_1 and n_2 are the refractive indices of the sapphire and polymers, respectively. The depth (d_p) where the intensity of the evanescent light becomes $1/e$ of that at the polymer/sapphire interface is calculated for the present experimental condition ($\theta = 68°$) and is also listed in *Table 1*.

Fluorescence spectra and rise curves, as well as decay curves, were measured with an apparatus reported previously[8]. Spectra were not corrected for the detector sensitivity.

RESULTS AND DISCUSSION

Micropolarity around pyrene molecules in poly(alkyl methacrylate) films

Fluorescence spectra of PMMA and PCHMA films doped with a low concentration of pyrene are shown in *Figure 2*. These spectra were normalized at the third vibronic band of the pyrene monomer fluorescence. We notice that the fluorescence intensity ratio of the first (0–0) to the third (0–2) vibronic bands (I_1/I_3) is larger

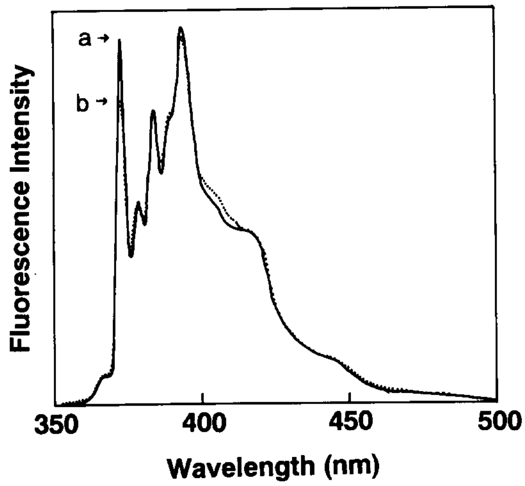

Figure 2 Normalized fluorescence spectra of (a) PMMA and (b) PCHMA films doped with low concentration of pyrene under the normal condition. Concentration: 2.2×10^{-3} mol/MMA unit mol for PMMA and 3.4×10^{-3} mol/CHMA unit mol for PCHMA

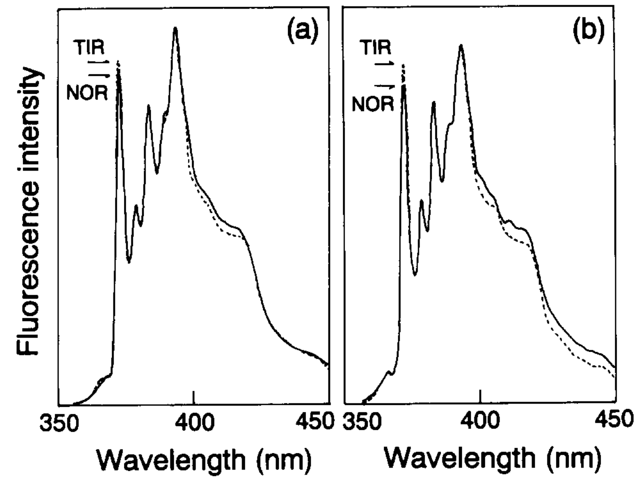

Figure 3 Normalized fluorescence spectra of (a) PnPMA and (b) PiBMA films doped with low concentration of pyrene under normal and t.i.r conditions. Concentration: 3.6×10^{-3} mol/nPMA unit mol for PnPMA and 3.1×10^{-3} mol/iBMA unit mol for PiBMA

for PMMA than for PCHMA. The value of this ratio decreased in the following order: PMMA > PnPMA > PiBMA > PCHMA. The intensity ratio of pyrene molecules has been used as a probe for polarity of surronding environments[20-22]. Hence the present results show that the micropolarity around pyrene molecules decreases in the order of PMMA > PnPMA > PiBMA > PCHMA. For PMMA, we suggested that the micropolarity is due to carbonyl groups of PMMA[8]. Considering the chemical structure of these polymers, this order indicates that, when the pyrene concentration is low, pyrene molecules in these films are located at a position which is liable to be influenced by the carbonyl groups of poly(alkyl methacrylate)s.

Figure 3 shows fluorescence spectra of PnPMA and PiBMA films doped with a low concentration of pyrene under the normal and t.i.r. conditions. The ratio I_1/I_3 under the t.i.r. condition is larger than that under the normal condition. This phenomenon was also observed for PMMA and PCHMA. For PMMA, we have suggested that the micropolarity around pyrene molecules in the vicinity of the sapphire/polymer interface is higher than that in the bulk layer[8]. These results indicate that the difference in the micropolarity around pyrene molecules between the interface and bulk layers is quite common for these polymers.

Pyrene aggregation in poly(alkyl methacrylate) films

Before discussing the difference in pyrene aggregation between the vicinity of the polymer/sapphire interface and the bulk, we describe the pyrene aggregation in polymer films (bulk layer). That is, results measured under the normal condition are discussed. *Figure 4* shows normalized fluorescence spectra of poly(alkyl methacrylate) films doped with the same concentration of pyrene (0.59 M). This pyrene concentration corresponds to an average distance of 14 Å between pyrene molecules, assuming that pyrene molecules are uniformly dispersed in polymer films. The fluorescence spectra of these films consist of red-shifted broad excimer and structured monomer fluorescence. The intensity ratio of the excimer to the monomer fluorescence (I_E/I_M) depends upon the polymer matrix, and the ratio decreases in the following order: PnPMA > PiBMA > aPMMA > PCHMA. Monomer fluorescence decay curves measured at 374 nm are non-exponential, and the larger the value of I_E/I_M shown by the polymer, the more rapidly the polymer decays (*Figure 5*). The excimer fluorescence decay curves measured at 520 nm were also non-exponential and showed the same tendency as the monomer decay curves.

Avis and Porter[17] reported the presence of both excimer-forming molecules (dimer whose geometry is close to the excimer configuration) and non-fluorescent dimers which are responsible for quenching the monomer and excimer fluorescence in PMMA films. These were proposed on the basis of the following observations.

(1) The excitation spectrum of the excimer fluorescence band is different from that of the monomer fluorescence.

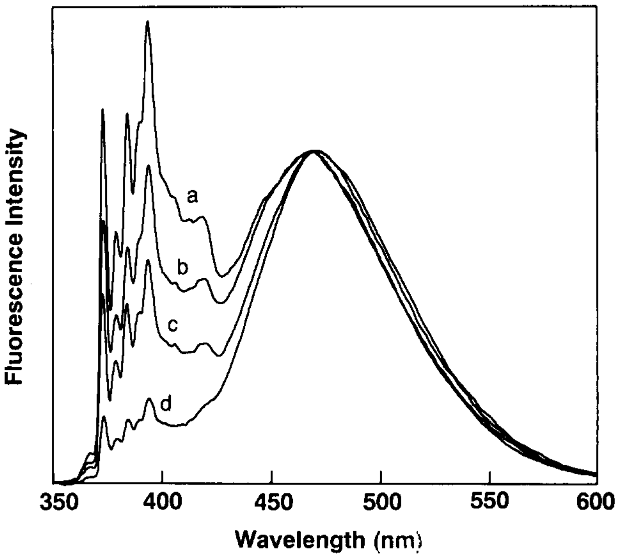

Figure 4 Normalized fluorescence spectra of poly(alkyl methacrylate) films doped with pyrene under the normal condition; concentration 0.59 M. Polymer: (a) PCHMA, (b) aPMMA, (c) PiBMA and (d) PnPMA

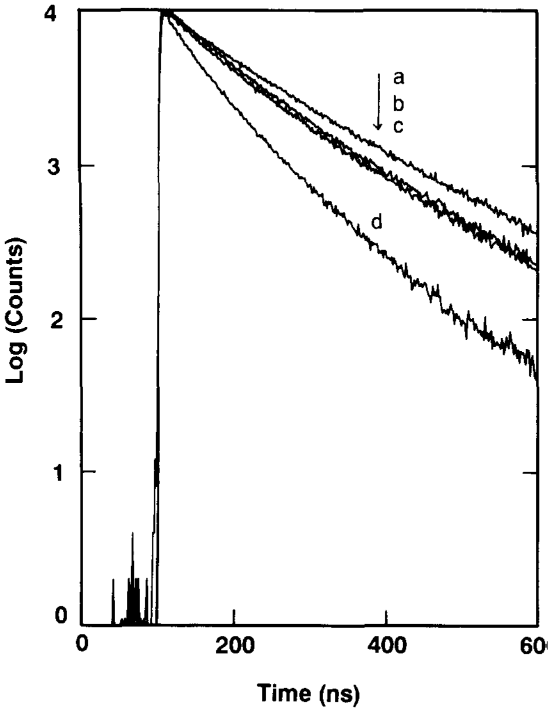

Figure 5 Monomer fluorescence decay curves of poly(alkyl methacrylate) films doped with pyrene under the normal condition; monitoring wavelength 374 nm; concentration 0.59 M. Polymer: (a) PCHMA, (b) aPMMA, (c) PiBMA and (d) PnPMA

(2) An increase in the pyrene concentration leads to both a decrease in the monomer fluorescence intensity and an increase in the excimer fluorescence intensity, and its further increment accelerates not only the monomer fluorescence decay but also that of the excimer. The latter phenomenon was interpreted by energy transfer from the excited state monomer and the excimer to non-fluorescent dimers formed by further increment in the pyrene concentration.

(3) The excimer and the excited state monomer undergo relaxation processes almost independently.

Although further investigation of the photophysical properties of pyrene-doped PMMA films may be needed, we continue our discussion on the assumption that the same situation holds for the present pyrene-doped poly(alkyl methacrylate) films as for the PMMA system reported by Avis and Porter. Thus, the present results on the I_E/I_M value and the fluorescence decay curve show that concentration of both the excimer-forming dimer and the non-fluorescent dimer leading to fluorescence quenching decreases in the following order: PnPMA > PiBMA > aPMMA > PCHMA, despite the same pyrene concentration. That is, the degree of dispersion of pyrene molecules in poly(alkyl methacrylate) films becomes higher in the order of PnPMA < PiBMA < aPMMA < PCHMA.

Recently, Kosbar and Frank[18] have investigated the distribution of pyrene molecules in novolac polymer films which were spin-cast from various solvents. They reported that the minimum value of I_E/I_M was observed when using a casting solvent with a solubility parameter similar to that of the novolac resin and pyrene. Further, the minimum value of I_E/I_M was observed when using a casting solvent with a dipole moment similar to that of the novolac resin. The degree of pyrene aggregation depended upon interaction between the polymer and the casting solvent. The solubility parameter of pyrene is estimated to be 10.6 $\mathrm{cal}^{1/2}\ \mathrm{cm}^{-3/2}$ from its heat of vaporization[18]. This value is larger than the solubility parameter of poly(alkyl methacrylate)s used in the present experiment (*Table 1*). Hence the order (PnPMA < PiBMA < aPMMA < PCHMA) does not correlate with the difference in the solubility parameter between pyrene and the polymers (*Figure 6*). Moreover, although the minimum value of I_E/I_M is observed for PCHMA ($\delta = 8.90$) with the same solubility parameter as the casting solvent, toluene ($\delta = 8.90$), no correlation of I_E/I_M with the solubility parameter of the casting solvent is found (*Figure 6*). Since the carbonyl group is the origin of the dipole moment of poly(alkyl methacrylate), the dipole moment is considered to be almost the same for these polymers. Moreover, since a common casting solvent was used for all samples, the present situation is different from the case of the novolac resin.

Loutfy[23] investigated the fluorescence yield of poly(alkyl methacrylate) films doped with *p*-(*N*,*N*-dialylamino)-benzylidene malononitriles, which is a fluorescent molecule probing the rigidity of the environment. The fluorescence yield decreased in the order of PMMA > PnPMA > PiBMA, and does not relate to the glass transition temperature of the polymers; consequently local flexibility of chain or segments around the probe molecule in these polymer films was considered to be in the order of PiBMA > PnPMA > PMMA. The present result does not correlate with this order.

Adopting the $1/e$ decay time ($\tau_{1/e}$) of the fluorescence as a measure for the fluorescence decay, we plotted both $\tau_{1/e}$ and I_E/I_M against molecular weight per monomer unit of polymers (*Figure 7*). Except for PMMA, I_E/I_M decreases with an increase in the molecular weight per monomer unit, and $\tau_{1/e}$ increases. The increase in the molecular weight of monomer unit for these polymers is due to the alkyl group of the side chains. Since both alkyl groups and pyrene molecules are hydrophobic, hydrophobic interaction between these seems to determine

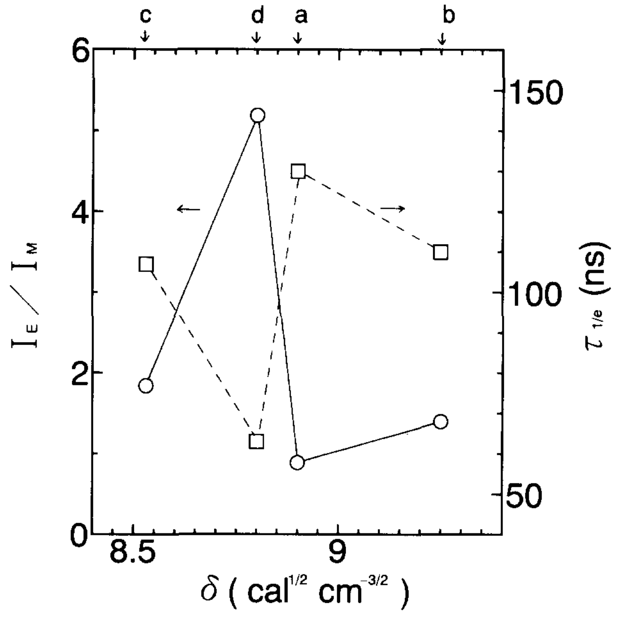

Figure 6 Plots of I_E/I_M and $\tau_{1/e}$ of the monomer fluorescence *versus* the solubility parameter of the polymer. (a) PCHMA, (b) aPMMA, (c) PiBMA and (d) PnPMA

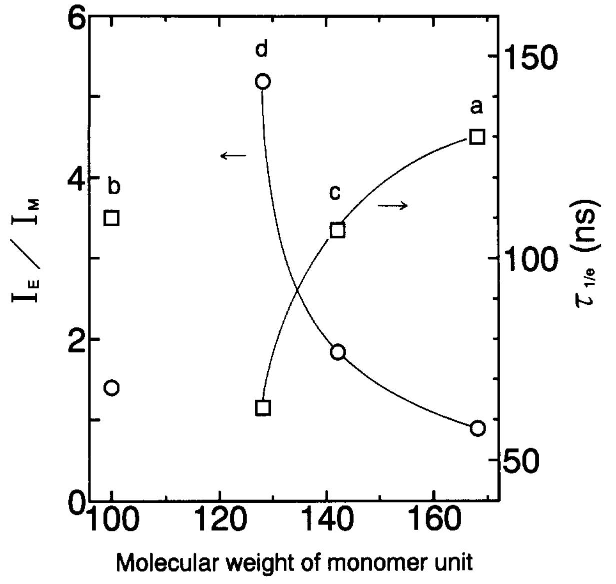

Figure 7 Plots of I_E/I_M and $\tau_{1/e}$ *versus* the molecular weight per monomer unit of the polymer. (a) PCHMA, (b) aPMMA, (c) PiBMA and (d) PnPMA

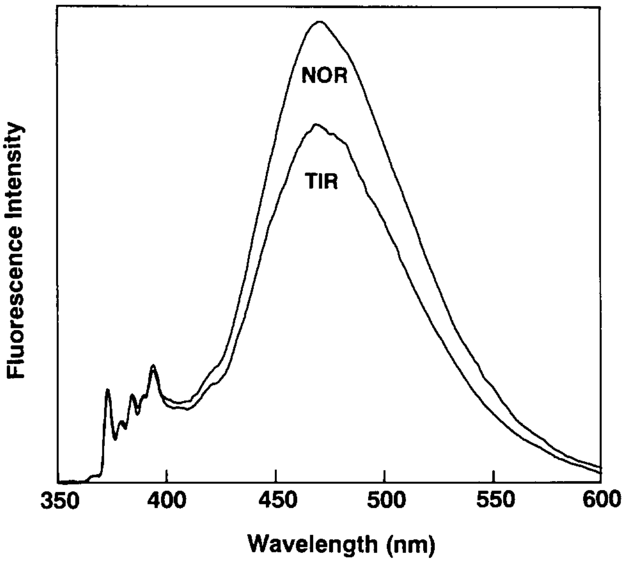

Figure 8 Fluorescence spectra of PnPMA film doped with pyrene under the t.i.r. and normal conditions. Concentration 0.59 M

the degree of dispersion of pyrene molecules in poly(alkyl methacrylate) films. Since the alkyl chain of PMMA is short compared with other poly(alkyl methacylate)s, other factors seem to influence the aggregation of pyrene molecules in PMMA films.

Comparison of aggregation state of pyrene molecules between interface and bulk layers

With regard to comparison of the micropolarity around pyrene molecules between the interface and bulk layers, we described, on the basis of I_1/I_3 for dilute samples (*Figure 3*), that the micropolarity in the interface layer is higher than that in the bulk layer.

As a typical example, fluorescence spectra of PnPMA films doped with a high concentration of pyrene (0.59 M) under the normal and t.i.r. conditions are shown in *Figure 8*. These spectra were normalized at the third vibronic band (0–2) of the monomer fluorescence. Here we notice that I_E/I_M under the normal condition is larger than that under the t.i.r. condition. This difference was also observed for all polymers used, and we have reported in detail the behaviour for PMMA. This result suggests that the concentration of excimer-forming pairs in the interface layer is lower than that in the bulk layer. Hence, if excimer formation is related to the excitation energy migration between pyrene molecules and excimer-forming pairs, it predicts that the decay time of the monomer fluorescence under the t.i.r. condition is larger than that under the normal condition. As shown in *Figure 9*, however, the monomer fluorescence decay under the t.i.r. condition is faster than that under the normal condition, which is in contrast to the prediction from I_E/I_M. Moreover, the excimer fluorescence also showed fast decay under the t.i.r. condition compared with the normal condition. The same result as the PnPMA system was observed for all polymers used. As described above, Avis and Porter[17] proposed the presence of non-fluorescent dimers leading to quenching of both the monomer and excimer fluorescence. The presence of the dimers is characteristic of PMMA films doped with a high concentration of pyrene. In the present experimental conditions, the pyrene concentration is high, and quenching of both the excited-state monomer and excimer takes place efficiently in the interface layer. Hence, the present result indicates that both the excited-state monomer and excimer near the interface are more efficiently quenched by the non-fluorescent dimers compared to those in the bulk. That is, the aggregation state of pyrene molecules in the interface layer differs from that in the bulk layer in the following way: in the interface layer the concentration of the excimer-forming dimer is lower, and the concentration of the non-fluorescent dimer, which is responsible for the fluorescence quenching, is higher compared with the bulk.

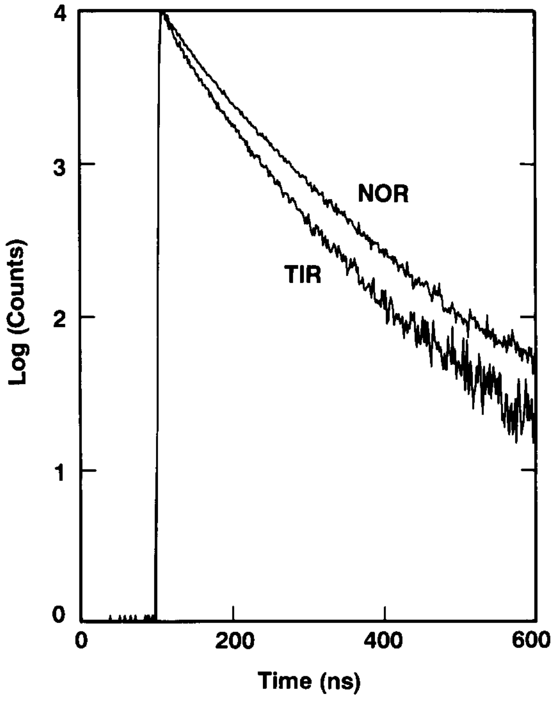

Figure 9 Monomer fluorescence decay curves of PnPMA film doped with pyrene under the t.i.r. and normal conditions. Monitoring wavelength 374 nm; concentration 0.59 M

As a measure of the difference in the aggregation state between the interface and bulk layers, the following values were adopted:

$$\Delta(I_E/I_M) = \{(I_E/I_M)_{NOR} - (I_E/I_M)_{TIR}\}/(I_E/I_M)_{NOR} \times 100\%$$

$$\Delta(\tau_{1/e}) = \{(\tau_{1/e})_{NOR} - (\tau_{1/e})_{TIR}\}/(\tau_{1/e})_{NOR} \times 100\%$$

Figure 10 shows relations between $(I_E/I_M)_{NOR}$ and $\Delta(I_E/I_M)$ and between $(\tau_{1/e})_{NOR}$ and $\Delta(\tau_{1/e})$. We notice that the difference between the interface and bulk layers becomes small in poly(alkyl methacrylate) films, where pyrene molecules tend to disperse homogeneously in films. One possible interpretation for this phenomenon is that, as described above, the hydrophobic interaction between polymers and pyrene molecules results in homogeneous dispersion of pyrene molecules. Since the sapphire surface is hydrophilic, the interface layer of polymer films is likely to be affected by the hydrophilic property of the sapphire surface. This situation results in the difference in dispersive behaviour of pyrene molecules between the interface and bulk layers.

Influence of tacticity on pyrene aggregation

The difference in the fluorescence behaviour between the interface and bulk layers was compared among aPMMA, iPMMA and sPMMA, and the results concerning pyrene aggregation are listed in *Table 2*. The same difference as observed in the aPMMA system is observed between t.i.r. and normal conditions irrespective of the tacticity. The I_1/I_3 ratio of the monomer fluorescence, which reflects the micropolarity around pyrene molecules, is also listed in *Table 2*. The largest value of the I_1/I_3 ratio among the polymers used is for iPMMA, indicating that the micropolarity around pyrene molecules in iPMMA films is large compared with the other polymers. Since the carbonyl group of PMMA is the origin of the micropolarity[8], the present result can be understood on the assumption that the degree of orientation of carbonyl groups towards pyrene is higher for iPMMA films than for aPMMA and sPMMA films.

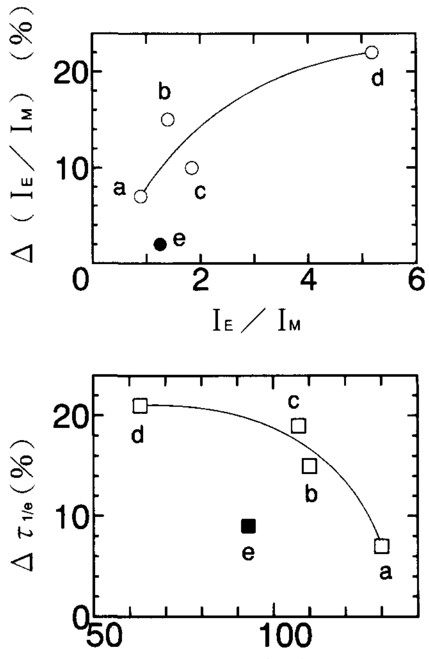

Figure 10 Dependence of $\Delta(I_E/I_M)$ and $\Delta(\tau_{1/e})$ on the fluorescence intensity ratio (I_E/I_M) and the $1/e$ decay time $(\tau_{1/e})$ under the normal condition. Values of $\Delta(I_E/I_M)$ and $\Delta(\tau_{1/e})$ are calculated by the equations in the text, and indicate the difference in the values between the interface and bulk layers. Polymer: (a) PCHMA, (b) aPMMA, (c) PiBMA, (d) PnPMA and (e) iPMMA

For the normal condition, the I_E/I_M ratio for aPMMA is large and the $\tau_{1/e}$ value is small compared with stereoregular polymers. This means that pyrene molecules in aPMMA films are liable to form both the excimer-forming dimer and the non-fluorescent dimer leading to fluorescence quenching, compared with those in the stereoregular polymers. In other words, formation of the pyrene aggregation is disturbed by the stereoregularity, and hence pyrene molecules in the stereoregular PMMA films are dispersed more homogeneously compared with those in aPMMA films.

The difference in the values between t.i.r. and normal conditions for iPMMA is relatively small. This is consistent with the observation that the difference in pyrene aggregation between both layers becomes small in poly(alkyl methacrylate) films, where pyrene molecules tend to disperse homogeneously. The present results indicate that, in the case of PMMA, the influence of polymer tacticity on the pyrene aggregation is important compared with the influence of the interface.

PMMA labelled with pyrene

Fluorescence spectra of aPMMA labelled with 1.0 mol% pyrene and sPMMA labelled with 0.5 mol% pyrene are shown in *Figure 11*. The spectra are normalized at the 0–2 vibrational band of the monomer fluorescence. Assuming that pyrenyl chromophores are homogeneously distributed in polymer films, the average distance between pyrenyl chromophores is calculated to be 24 and 30 Å for the former and latter films, respectively. Very weak excimer fluorescence is observed for aPMMA labelled with 1.0 mol% pyrene, and its intensity ratio to the monomer fluorescence (I_E/I_M) is the same under both conditions. This suggests that the difference in the pyrene aggregation between the interface and bulk layers does not exist for the labelled polymer system, which is quite different from the dopant system. These results are consistent with the novolac system reported by Kosbar and Frank[18]. That is, the dependence of I_E/I_M on spin-casting solvent for novolac labelled with pyrene was much smaller than that for the dopant system.

Table 2 Effect of stereoregularity on I_1/I_3, I_E/I_M and $\tau_{1/e}$

Polymer	I_1/I_3		I_E/I_M		$\tau_{1/e}$		$\Delta(I_1/I_3)$	$\Delta(I_E/I_M)$	$\Delta\tau_{1/e}$
	normal	t.i.r.	normal	t.i.r.	normal	t.i.r.	(%)	(%)	(%)
aPMMA	1.10	1.16	0.97	0.80	125	119	5.5	17.5	4.8
sPMMA	1.12	1.17	0.88	0.76	142	132	4.5	13.6	7.0
iPMMA	1.19	1.22	0.85	0.80	131	124	2.2	5.9	5.3

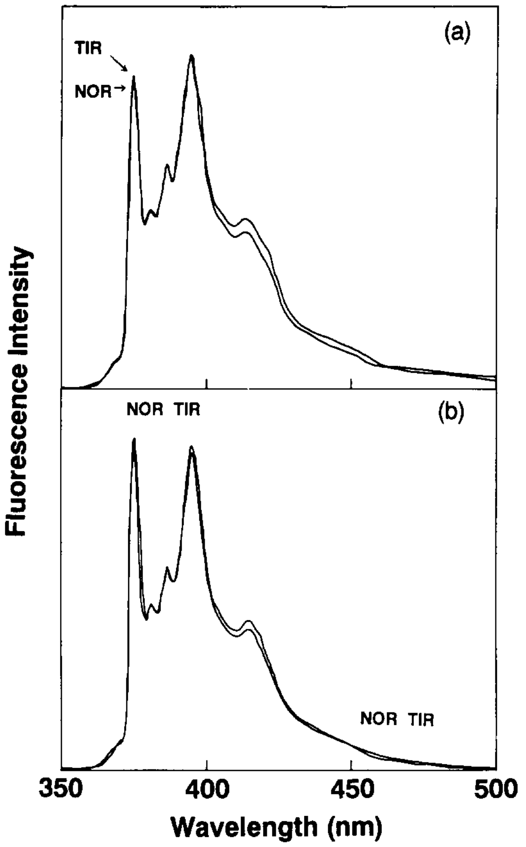

Figure 11 Fluorescence spectra of (a) aPMMA film labelled with 1.0 mol% pyrene and (b) sPMMA film labelled with 0.5 mol% pyrene under the t.i.r. and normal conditions

We observe a small difference in I_1/I_3 for aPMMA, but not for sPMMA. This is consistent with the above-mentioned result; the difference between the interface and bulk layers is smaller for stereoregular polymer than for aPMMA.

Decay curves of the monomer fluorescence were measured at 377 nm. The $\tau_{1/e}$ value for polymers labelled with pyrene was smaller under the t.i.r. condition (164 ns) than under the normal condition (174 and 178 ns). Since the excimer fluorescence is not observed for pyrene-labelled sPMMA, it is difficult to interpret the difference in the $\tau_{1/e}$ value between the interface and bulk layers by considering non-fluorescent dimers. The monomer fluorescent decay of pyrene is known to decrease when the polarity of the solvent is increased. For dilute pyrene-doped SPUU system, the smaller value of $\tau_{1/e}$ under the t.i.r. condition compared with the normal condition was interpreted by the difference in the polarity between the interface and bulk layers[9]. For PMMA films doped with a low concentration of pyrene, as reported previously[8], the difference in I_1/I_3 between the bulk and interface layers corresponds to the difference in $\tau_{1/e}$. For pyrene-labelled sPMMA, however, we do not observe the difference in I_1/I_3. Although we cannot at present give a clear explanation for the difference in $\tau_{1/e}$ of the monomer fluorescence, it is probably due to the difference in conformation of the syndiotactic polymer chain labelled with pyrene between the interface and bulk layers. The difference is induced by the interaction between the polymer and the sapphire during the casting process. The present results indicate that the difference in the fluorescence behaviour between the interface and bulk layers exists even in polymers labelled with chromophores.

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