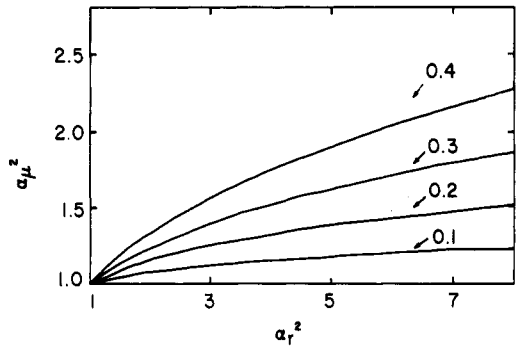

Figure 6. α_μ^2 vs. α_r^2 when $\alpha_\mu^2 = (\alpha_r^2)^a$ and a = 0.1, 0.2, 0.3, and 0.4.

α_μ^2 either remains finite or approaches infinity more slowly than does α_r^2.

With the aid of two figures, we now contrast the information conveyed by eq 3 and 4. Figure 5 depicts $(\alpha_\mu^2 - 1)/(\alpha_r^2 - 1)$ as a function of α_r^2 when α_μ^2 is given by eq 3 with a of 0.1, 0.2, 0.3, or 0.4. Certain real chains with large n can be expected to have a in this range, as shown in Table III. All four curves in Figure 5 have zero as their limit as α_r^2 becomes infinite. Since α_r^2 increases without limit as n becomes infinite, all four curves are in harmony with eq 4 if x is zero. In Figure 6, α_μ^2 is shown as a function of α_r^2 for the same four values of a. In graphic fashion, Figures 5 and 6 show that α_μ^2 can *increase without limit* as α_r^2 increases, even though the limit for $(\alpha_\mu^2 - 1)/(\alpha_r^2 - 1)$ may be zero. In the event that a is negative, α_μ^2 will decrease as α_r^2 increases, but the chain will still obey the limit specified in eq 4 if x is zero.

Racemic Chains. The Introduction describes a simple model chain for which $\alpha_\mu^2 < 1 < \alpha_r^2$. Let the model chain define the xy plane when all internal bonds occupy trans states. Then the dipole moment vectors associated with the bonds are perpendicular to this plane, and they alternate in direction as one proceeds along the chain. There is a perfect cancellation of the dipole moment vectors for adjacent bonds. The polar side chains occur on alternate sides of the plane defined by the backbone when a racemic PVB, PVC, or PClS chain adopts a configuration in which all bonds occupy trans states. However, the three racemic vinyl polymers have $1 < \alpha_\mu^2 < \alpha_r^2$ rather than $\alpha_\mu^2 < 1 < \alpha_r^2$. Racemic PVB, PVC, and PClS chains have a behavior different from the simple model chain. The dipole moment vector for each polar side chain in the racemic vinyl polymers has a component that lies in the plant of the fully extended chain. All of the components in the plane of the backbone are parallel when gauche placements are absent. It is the parallel alignment of the in-plane components in the fully extended racemic vinyl polymers that is responsible for $1 < \alpha_\mu^2 < \alpha_r^2$.

The mean square dipole moment for some, but not all, vinyl polymers should be solvent-dependent. The absence of a useful theory that relates α_μ^2 to α_r^2 makes it difficult to obtain $\langle\mu^2\rangle_0$ from a measured $\langle\mu^2\rangle$.

Acknowledgment. We thank Professor Mansfield for kindly providing a preprint of ref 12. This research was performed with support from National Science Foundation Grant DMR 83-15547.

Registry No. PVB (homopolymer), 25951-54-6; PVC (homopolymer), 9002-86-2; PClS (homopolymer), 24991-47-7.

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Dilute Solution Properties of a Polystyrene–Poly(methyl methacrylate) Graft Copolymer Studied by Emission Probe Techniques. 2.[1] Rotational Relaxation Time of the Graft Copolymer by Fluorescence Polarization Measurement

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ABSTRACT: Dynamic properties of polystyrene (PS)–poly(methyl methacrylate) (PMMA) graft copolymer in dilute solution were studied by means of fluorescence emission probe techniques; a fluorene unit (Fl) is introduced as an energy donor at an appropriate number in the backbone PS chain by copolymerization with 2-vinylfluorene, and a pyrene unit (Py) is introduced as an acceptor at the end of the PMMA chain grafted from Fl. Energy transfer from Fl to Py within the graft copolymer was strongly suggested from the excitation spectra and fluorescence polarized spectra. The micelle formation of PS–PMMA graft copolymer in binary mixed solvents was demonstrated by the effect of polymer chain conformation on the efficiency of the energy transfer from Fl to Py and is discussed on the basis of the data of the rotational relaxation time ρ around the Py located at the end of the grafted PMMA chain; ρ was obtained by the fluorescence polarized spectra and the lifetime of Py. It was revealed that ρ was increased from 10^{-9} to 10^{-7} s, corresponding to the transition phenomena for the formation of the PS–PMMA graft copolymer micelle.

Introduction

Aggregation phenomena of block or graft copolymers in solution have become of interest in recent years because aggregation processes affect the morphology of the polymer films that are formed from solvent casting.[3-7] Furthermore, block and graft copolymers have the ability to activate a

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surface and are often used as compatibilizers for polymer blending.[8-11] It is important to investigate from various points of view the effect of addition of block or graft copolymers on surface stabilization.

We have been studying aggregation processes of graft copolymers in dilute solution with the fluorescence emission probe technique.[1] It is known that block and graft copolymers form a micelle in solvents when one polymer component is soluble and the other component is not.[12] These phenomena have been investigated by viscometry, light scattering, and so on.[13-19] These techniques provide rather macroscopic and static information about the micelle formation. On the other hand, the fluorescence emission probe technique has rather microscopic and dynamic character; it utilizes the information from the fluorescence emission spectra of probes incorporated into the polymer. The spectra are sensitive to the change of the environment around the probes; i.e., the change of the conformation of the polymer and the chain dynamics are reflected by the change in spectra.[20-38] In this paper, we have measured the rotational relaxation time ρ around the grafted chain ending of polystyrene–poly(methyl methacrylate) (PS–PMMA) graft copolymers and investigated the dynamics of the micelle formed by PS–PMMA graft copolymers. Fluorescence polarization is a useful analytical tool for studying the Brownian motion of molecules in solution.[39,40] The fluorescence emission probes are incorporated into the PS–PMMA graft copolymer; the polymer backbone is labeled by fluorene units (Fl), and grafted PMMA chain endings are labeled by pyrene units (Py). ρ was determined by measuring the fluorescence polarization and the lifetime of Py.

Experimental Section

Materials. The preparation of the backbone PS containing an appropriate number of 2-vinylfluorene (2VFl) is described elsewhere;[1] the copolymerized 2VFl unit was found to be 1 mol % by the electronic absorption spectrum,[1] and this corresponds to 4.5 units of 2VFl units per backbone PS. Molecular weight and its distribution on the backbone PS were found to be M_w = 330 000 and M_w/M_n = 1.55, respectively, by GPC (Toyo Soda HLC-802 UR) using monodisperse polystyrene as a standard. The PS–PMMA graft copolymer was prepared and purified according to the previous method.[1] The Py unit was incorporated at the living PMMA ending by the reaction with 1-(bromomethyl)pyrene at −78 °C. The weight fraction of the PS was determined to be 29% by ^{1}H NMR. The number of PMMA branches of the PS–PMMA graft copolymer was determined by electronic absorption spectrum for the end-labeled Py assuming that the extinction coefficient of the Py is the same as that of pyrene; the number of Py was determined as 0.72, i.e., the number of PMMA branches is around unity. Spectrograde tetrahydrofuran (THF), acetonitrile (AN), and cyclohexane (CH) were used without purification for fluorescence spectral measurements.

Fluorescence Measurement. The emission spectra were recorded by exciting at 270 or 280 nm in a similar manner to that described elsewhere.[1] Excitation spectra were measured by monitoring the fluorescence emission maximum of Fl and Py.

Fluorescence Polarization. The measurements were carried out by a differential spectrofluorimeter (Shimadzu RF-503 A) fitted with polarizing film. With the incident beam polarized vertically, polarization (P) should ideally be given by[41]

$$P = (I_{vv} - I_{vh})/(I_{vv} + I_{vh})$$

where I_{vv} and I_{vh} stand for the measured fluorescence with the analyzers vertically and horizontally oriented, respectively. However, the emission must pass through a monochromator whose grating imposes a degree of polarization. Thus, a grating correction factor (G) must be taken into consideration. With $G = I_{hv}/I_{hh}$, the polarization is then obtained from the formula

$$P = (I_{vv} - GI_{vh})/(I_{vv} + GI_{vh})$$

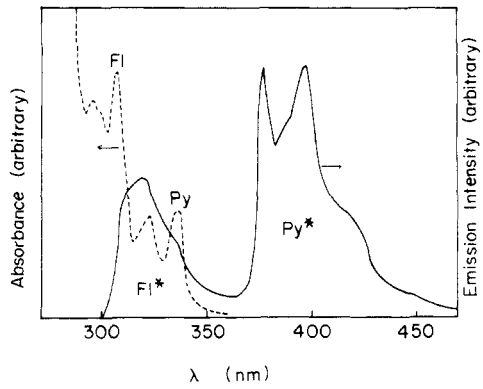

Figure 1. Electronic absorption and fluorescence emission spectra (excited at 280 nm) for PS–PMMA graft copolymer containing fluorene (Fl) in backbone PS and pyrene (Py) at grafted PMMA ending in aerated THF solution.

where I_{hv} and I_{hh} are the measured fluorescence intensities with the analyzers vertically and horizontally oriented using horizontally polarized light.

Fluorescence Lifetime. The sample solution was excited at secondary harmonic wavelength (347 nm) of Rb laser pulse (694 nm) with a half width of 18 ns (Nippon Denki SLG 2009). The fluorescence decay from Py (378 nm) was detected by a photomultiplier, amplified, fed into a dual-beam oscilloscope (Sony-Tektronix 7844), and then analyzed.

Results and Discussion

Energy Transfer in the Dilute Solution of the PS–PMMA Graft Copolymer. The PS–PMMA graft copolymer contains two fluorescing probes, Fl in the backbone PS and Py at the grafted PMMA end. The absorption spectrum and fluorescence emission spectrum excited at 280 nm for the PS–PMMA graft copolymer are shown in Figure 1; Fl in the copolymer exhibits absorption maxima at 307 and 292 nm and emission maximum at 320 nm, and Py shows absorption maxima at 340 and 330 nm and emission maxima at 396 and 378 nm. These spectral features are similar to those of monomer model compounds, fluorene and pyrene, respectively.[42]

The main process dominating the ratio of emission intensity of Py to that of Fl (I_{Py}/I_{Fl}) must be attributable to reaction 1 as we discussed in the previous paper.[1] In

$$Fl^* + Py \rightarrow Fl + Py^* \quad (1)$$

Figure 1, the fluorescence emission spectrum of Fl (energy donor) strongly overlaps the absorption spectrum of Py (acceptor), and in such a case, nonradiative energy transfer, the so-called Förster type, may take place.[43] The efficiency E of this energy transfer depends mainly upon R, which is the distance between the donor and the acceptor groups,

$$E = R_0^6/(R_0^6 + R^6) \quad (2)$$

where R_0 is the donor–acceptor separation distance where 50% of energy transfer takes place.[44] The R_0 between Fl and Py in the PS–PMMA graft copolymer was estimated to be about 37 Å.[1] The efficiency of energy transfer from Fl to Py, which is represented by I_{Py}/I_{Fl}, depends upon the R. Furthermore, the efficiency could be affected significantly by a density of the acceptor Py around the donor Fl. If a multimolecular micelle of the PS–PMMA graft copolymer is formed, the density of Py in the active sphere around Fl becomes higher, leading to the increase in I_{Py}/I_{Fl}. In our experiments, the binary mixed solvents consisting of various compositions of tetrahydrofuran (THF; a good solvent for both PS and PMMA) and acetonitrile (AN; a nonsolvent for PS) or of THF and cyclohexane (CH; a nonsolvent for PMMA) are used as solvents.

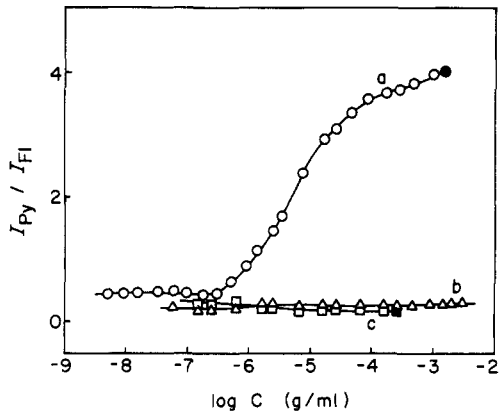

Figure 2. Dependence of the fluorescence ratio I_{Py}/I_{Fl} upon the concentration of PS–PMMA graft copolymer. Compositions of the binary mixed solvents: (a) 100% acetonitrile (AN); (b) 100% THF; (c) cyclohexane (CH):THF = 1:1 (in volume). (●) and (■) represent compositions in which the copolymer is insoluble.

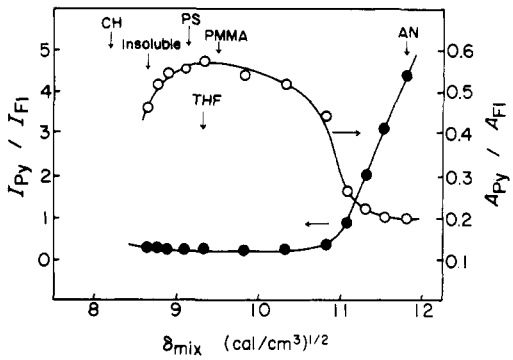

Figure 3. Plots of I_{Py}/I_{Fl} and A_{Py}/A_{Fl} (intensities of excitation spectra) for PS–PMMA graft copolymer in binary mixed solvents (CH–THF and THF–AN) vs. δ_{mix}. Copolymer concentration: 1.01 × 10^{-4} g/mL.

As seen from Figure 2, I_{Py}/I_{Fl} increases with an increase in concentration of the PS–PMMA graft copolymer in poor solvent (100% AN; (a) in Figure 2). It has been confirmed in our previous paper[1] by means of the emission probe technique and low-angle light scattering that such an increase of I_{Py}/I_{Fl} can be correlated with the micelle formation of the PS–PMMA graft copolymers. From an inspection of two tangential lines drawn at low-concentration region (10^{-6}–10^{-5}) and higher concentration region (10^{-5}–10^{-3} g/mL), a critical micelle concentration (CMC) for the PS–PMMA graft copolymer in 100% AN can be estimated to be 2.1 × 10^{-5} g/mL.

Figure 3 shows the dependence of I_{Py}/I_{Fl} upon the solubility parameters δ_{mix} for the binary mixed CH–THF and THF–AN solvents;[45] δ_{mix} for PS and PMMA are 9.1 and 9.5, respectively,[46] and those for AN, THF, and CH are 11.80, 9.32, and 8.18 (cal/cm^3)$^{1/2}$, respectively.[47] When the solubility parameter for the polymer is close to that for the solvent, the solubility becomes higher. In Figure 3, I_{Py}/I_{Fl} increases with increasing δ_{mix} where the content of AN increases in an AN–THF mixture. Thus, it is suggested that multimolecular micelle with a large degree of the association would be formed at such a higher δ_{mix}. In our previous paper,[1] it was suggested that I_{Py}/I_{Fl} reflects the degree of aggregation of the micelle at concentrations above the CMC. In such a micelle, the backbone PS, which is insoluble in AN, could be surrounded and stabilized by the branched PMMA chains, which are soluble in AN. On the other hand, I_{Py}/I_{Fl} shows no change at lower δ_{mix} as in a 1:1 CH–THF mixture ((c) in Figure 2), where δ_{mix} is 8.75 (cal/cm^3)$^{1/2}$. This phenomenon is understood by

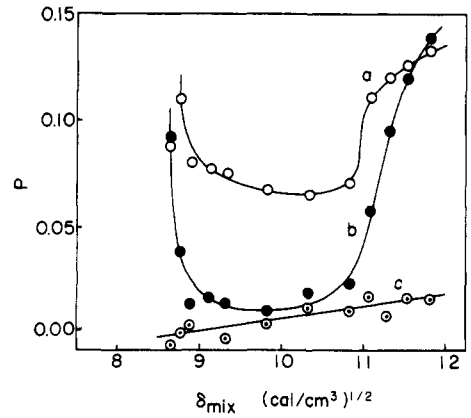

Figure 4. Plots of degree of polarization vs. δ_{mix} for PS–PMMA graft copolymer at concentration of 1.01 × 10^{-4} g/mL: (a) degree of polarization of Fl measured at 320 nm (excitation with 270 nm); (b) that of Py measured at 400 nm (excitation with 340 nm); (c) that of Py measured at 400 nm but excited at 270 nm.

considering the composition of the PS–PMMA graft copolymer used here; the PS–PMMA graft copolymer consists of a small amount of PS (29 mol %). Therefore, it is expected that the minor component PS cannot surround the major component PMMA and stabilize the major component PMMA which is insoluble in CH.

In Figure 3, the data observed with excitation spectra for Py and Fl are also plotted against δ_{mix}, where A_{Py} and A_{Fl} are the intensities of the excitation spectra observed at 340 and 270 nm (the absorption maxima of Py and Fl), respectively. Fluorescence emission intensities were monitored for both Py and Fl at 378 nm. The change in A_{Py}/A_{Fl} shown in Figure 3 is reflected by the change in the efficiency of energy transfer from Fl to Py. If energy transfer expressed by eq 1 is taking place, the fluorescence from Py should be observed by excitation at the absorption band of Fl. The decrease in A_{Py}/A_{Fl} observed at higher δ_{mix} values suggests the increase in the energy transfer from Fl to Py in the micelle. All the emission experiments described above were conducted in aerated solution. In order to discuss the effect of oxygen, I_{Py}/I_{Fl} and A_{Py}/I_{Fl} were also measured in degassed solution; dependencies of them upon δ_{mix} were similar both in aerated (Figure 3) and degassed solutions. These results suggest that I_{Py}/I_{Fl} and A_{Py}/A_{Fl} are dominantly controlled by the efficiency of the energy transfer from Fl to Py but not by the efficiency of the diffusion of oxygen and its quenching.

Fluorescence Polarization and Lifetime Measurements and Determination of Rotational Relaxation Time. Plots of degree of polarization vs. δ_{mix} for the PS–PMMA graft copolymer are shown in Figure 4; in this figure, curve a shows the degree of polarization of Fl measured at 320 nm (excitation with 270 nm), (b) that of Py measured at 400 nm (excitation with 340 nm), and (c) that of Py measured at 400 nm but excited at 270 nm. The concentration of the PS–PMMA graft copolymer was kept constant at 1 × 10^{-4} g/mL, where multimolecular micelle is formed.[1] The feature of (c) plotted in Figure 4 is quite different from those of (a) and (b); this could be explained by the energy transfer from Fl to Py. By the energy transfer, the excited state of Fl bound in the backbone PS excited by incident polarized light (270 nm), whose electronic dipole oscillators are oriented, is transferred to Py, whose oscillators are nearly random. Therefore, the degree of polarization of Py becomes smaller over a wide range of δ_{mix} because many excited states of Py are formed from Fl* and the oscillators are almost oriented randomly.[48-50] On the other hand, when 340 nm is used as an incident polarized light ((b) in Figure 4), the energy transfer from

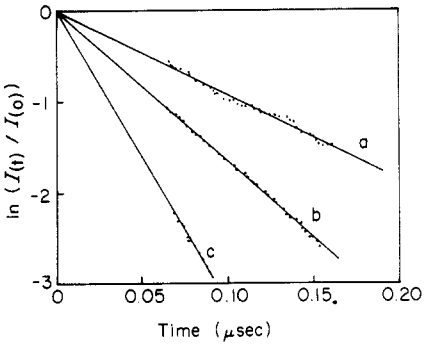

Figure 5. First-order plots for fluorescence decay of Py incorporated into PS–PMMA graft copolymer: (a) 100% AN; (b) AN:THF = 8:2 (in volume); (c) 100% THF.

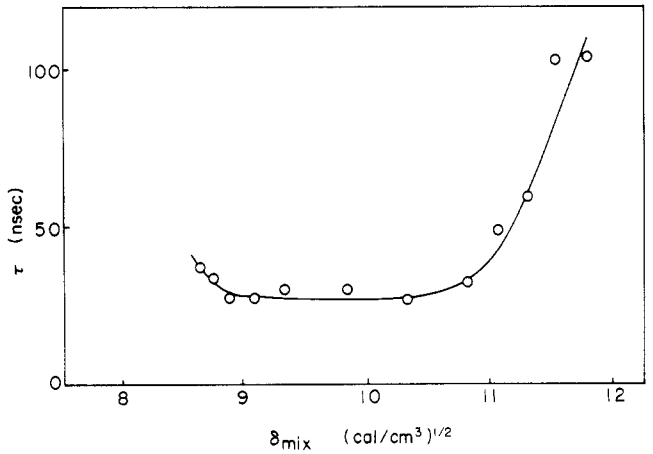

Figure 6. Fluorescence lifetime τ vs. solubility parameter δ_{mix} for binary mixed AN–THF and CH–THF solvents. Concentrations of PS–PMMA graft copolymer and Py are 1.01×10^{-4} g/mL and 4.48×10^{-4} M, respectively.

Fl to Py cannot take place because Fl has no absorption band at this wavelength. Thus, these processes are expressed as

$$\mathrm{Fl} \xrightarrow{270\ \mathrm{nm}} \mathrm{Fl}^* \rightarrow \mathrm{Fl} + h\nu\ (320\ \mathrm{nm}) \tag{3}$$

$$\mathrm{Py} \xrightarrow{340\ \mathrm{nm}} \mathrm{Py}^* \rightarrow \mathrm{Py} + h\nu\ (400\ \mathrm{nm}) \tag{4}$$

$$\mathrm{Fl} \xrightarrow{270\ \mathrm{nm}} \mathrm{Fl}^* \xrightarrow{+\mathrm{Py}} \mathrm{Py}^* + \mathrm{Fl}$$
$$\mathrm{Py}^* \rightarrow \mathrm{Py} + h\nu\ (400\ \mathrm{nm}) \tag{5}$$

where eq 3, 4, and 5 correspond to (a), (b), and (c) plotted in Figure 4, respectively.

When energy-transfer process is absent, the degree of polarization is expressed by the equation[39-40]

$$P/P_0 = 1/[1 + k(\tau/\rho)] \tag{6}$$

where P_0 is the degree of polarization at infinity ($P_0 = 0.5$ at random orientation of electronic dipole oscillations), ρ the rotational relaxation time, τ the lifetime of the excited state, and k a constant ($k = 3 - P_0$) when the incident beam is vertically polarized. From eq 6, it is apparent that the degree of polarization becomes larger when the lifetime of the excited state becomes shorter. It is shown in Figure 4 that the degree of polarization of Fl is larger than that of Py because the fluorescence lifetime of Fl ((a) in Figure 4) is shorter than that of Py ((b) in Figure 4). When the emission probe is bound covalently to the polymer chain, the rotational relaxation time ρ reflects the Brownian motion of the polymer chain segment around the probe.

To determine ρ of Py, the fluorescence lifetime for Py was measured. Figure 5 shows the first-order plots for the

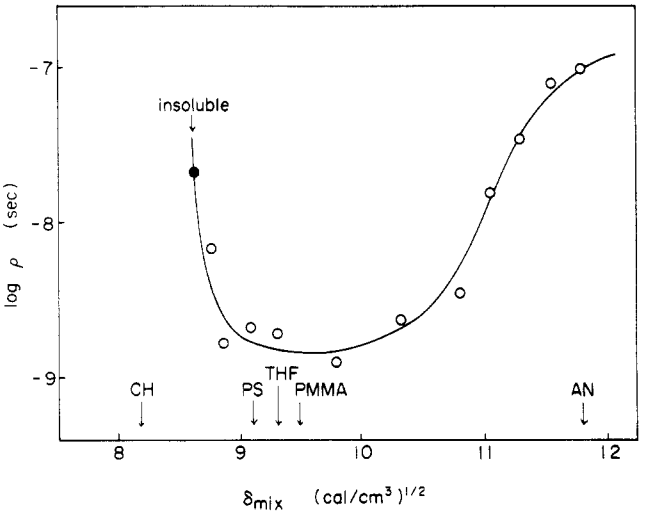

Figure 7. Rotational relaxation time ρ vs. solubility parameter δ_{mix} for PS–PMMA graft copolymer. Concentrations of the copolymer and Py are 1.01×10^{-4} g/mL and 4.48×10^{-4} M, respectively.

Table I
Lifetime (τ) and Rotational Relaxation Time (ρ) of Pyrene Located at the Grafted PMMA Chain Ending of PS–PMMA Graft Copolymer

solvent compsn	δ_{mix}, (cal/cm^3)$^{1/2}$	τ, ns	p^a	ρ,[b] s
100% AN	11.80	105	0.1404	1.02×10^{-7}
AN:THF = 9:1	11.55	104	0.1203	8.27×10^{-8}
AN:THF = 8:2	11.30	59.9	0.0945	3.49×10^{-8}
AN:THF = 7:3	11.06	49.9	0.0571	1.61×10^{-8}
AN:THF = 6:4	10.81	32.7	0.0215	3.68×10^{-9}
AN:THF = 4:6	10.31	27.0	0.0172	2.41×10^{-9}
AN:THF = 2:8	9.82	30.1	0.0085	1.30×10^{-9}
100% THF	9.32	30.1	0.0125	1.93×10^{-9}
CH:THF = 2:8	9.09	27.3	0.0147	2.07×10^{-9}
CH:THF = 4:6	8.86	27.5	0.0117	1.65×10^{-9}
CH:THF = 1:1	8.75	33.6	0.0380	6.91×10^{-9}
CH:THF = 6:4	8.64	37.0	0.0922	2.09×10^{-8}

[a] Measured at 400 nm (excited at 340 nm). [b] [PS–PMMA] = 1.01×10^{-4} g/mL and [Py] = 4.48×10^{-7} g/mL.

emission decay of Py in various binary mixed solvents. The fluorescence lifetime is plotted against the solubility parameter δ_{mix} in Figure 6, and the estimated rotational relaxation times found by using eq 6 are plotted in Figure 7. These δ_{mix}, τ, p and ρ values are summarized in Table I. Judging from the results plotted in Figures 3 and 6, the fluorescence lifetime τ becomes longer when a large micelle is formed. Considering the diffusion coefficient of oxygen and the quenching efficiency for the fluorescence of Py, it is understood that when the multimolecular micelle is formed, Py located at the grafted PMMA ending is surrounded by the polymer chains, leading to the decrease of the diffusion of oxygen, and that the efficiency of quenching for the excited state of Py is decreased and the lifetime of Py is increased. Such an effect becomes larger at a higher degree of aggregation of the PS–PMMA graft copolymer. Rotational relaxation time ρ also shows a dependence upon the solubility parameter δ_{mix}. In a good solvent for the copolymer, such as THF, ρ is of the order of 10^{-9} s, and this time scale corresponds to the rotational motion of the Py molecule at the ending of the grafted PMMA chain.[51] In a poor solvent such as AN where micelle is formed, ρ is of the order of 10^{-7} s, and this time scale corresponds to the micro-Brownian motion of the polymer chain segment over a wide range or to the rota-

tional motion of the entire polymer chain.[52] These results suggest that in a micelle state the motion of the polymer chain segment is rather inhibited. In Figure 7, it is shown that the motion of the polymer chain is highly decreased (ρ is highly increased) at a higher degree of aggregation of micelle in poorer solvent systems. In spite of good solubility of the grafted PMMA chain for AN, the motion of the PMMA chain is suppressed in AN-rich solution. It is, therefore, suggested that the PS chain core, which is insoluble to AN, is stabilized by a tightly surrounding grafted PMMA chain. In Figure 7, ρ for the insoluble state is shown, and its value is smaller than that of micelle state in 100% AN. It is somewhat surprising that the motion of the polymer chain segment is inhibited more strongly at the micelle state than at the insoluble state.

Registry No. (PS)·(PMMA) (copolymer), 25034-86-0.

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