Intramolecular Excimer Formation of the Copolymers Based on Methylphenylsiloxane and Dimethylsiloxane Units in Solution

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Emission quantum yields have been determined for a homopolymer poly(methylphenylsiloxane) and copolymers poly(dimethylsioxane-*co*-methylphenylsiloxane)s with different methylphenylsiloxane (MePhSiO) contents, together with 3,5-diphenyloctamethytetrasiloxane and 3,5,7-triphenylnonamethylpentasiloxane used as the model compounds, in dilute solvent at different temperatures. Dependence of the monomer and excimer fluorescence quantum yields on the MePhSiO content and temperature has been analyzed. Composition and temperature dependence of the spectral data are well interpreted in terms of the superposition of the photophysical properties originating from each $-(Me_2SiO)-(MePhSiO)_n-(Me_2SiO)-$ segment in a copolymer chain. It is inferred from the analyses that the mean binding energy of the excimer of the copolymers does not depend significantly on the MePhSiO content.

Introduction

Phenylsiloxane-based polysiloxanes are not only novel silicones with a variety of possible applications, but also interesting polymers from the photophysical viewpoint.[1−5] It is known that oligomers and polymers containing methylphenylsiloxane (MePhSiO) units exhibit both the monomer and excimer fluorescence through an interaction between the phenyl chromophores and that the intensity ratio of these emission depends on the molar fraction of MePhSiO unit in the copolymers.[6−13]

Horta et al. have measured fluorescence spectra and decay of a homopolymer, poly(methylphenylsiloxane), and copolymers, poly(methylphenylsiloxane-*co*-dimethylsiloxane) with three different compositions at different temperatures in dilute organic solvents.[8,11] The intensity ratio of the excimer to monomer fluorescence of the copolymer shows linear Arrhenius plots (i.e., the logarithmic plots of the intensity ratio against the reciprocal of the absolute temperature, $1/T$) with a positive or a negative slope depending on the MePhSiO content of the copolymer. However, the excimer and monomer fluorescence intensities plotted separately against $1/T$ give double linear plots with break points, which has been ascribed to a transition temperature. On the bases of the decay data, using the kinetic scheme including the monomer, excimer, ground-state dimer and excited monomer, they concluded that there is coexistence of ground-state preformed excimers and rotational excimers in high molecular weight poly(methylphenylsiloxane)s and that in the low molecular weight poly(methylphenylsiloxane-*co*-dimethylsiloxane)s long-range excimers are considered to coexist beside the two types of excimers.[8,11]

Although a number of studies have been carried out for the photophysics of methylphenylsiloxane-based copolymers and homopolymer, no information is available as to the photophysical properties observed upon the systematic change of the copolymer composition. In the present study we have determined the emission quantum yields of well-defined copolymers, poly-

TABLE 1: Characterization of Poly(dimethylsiloxane-*co*-methylphenylsiloxane)s Used in the Present Study

MePhSiO content[a]					
(mol %)	(weight %)	abs[b]	M_n	M_w	M_w/M_n
4.0	7.1	0.15	17260	30350	1.76
20.8	32.5	0.67	18840	30720	1.62
29.8	43.8	0.91	19900	35610	1.78
40.2	55.3	1.20	14990	29970	1.99
47.7	62.6	1.28	14060	23600	1.67
56.9	70.8	1.50	14230	23230	1.63
68.0	79.6	1.70	13640	22090	1.62
89.4	93.9	2.09	15650	27910	1.78
100.0	100.0	2.13	13560	23500	1.73

[a] Estimated from H[1]MNR. [b] Absorbance per g/L at 264 nm in THF.

(dimethylsioxane-*co*-methylphenylsiloxane), with different MePhSiO contents in a dilute organic solvent at different temperatures, together with those of 3,5-diphenyloctamethytetrasiloxane ($Me_3SiO(MePhSiO)_2SiMe_3$) and 3,5,7-triphenylnonamethylpentasiloxane ($Me_3SiO(MePhSiO)_3SiMe_3$) used as the model compounds. Dependence of the monomer and excimer fluorescence yields on the MePhSiO content and temperature has been analyzed. We provide an interpretation which is somewhat different from that reported in previous works. It is shown that there is almost no interaction between the unit structures $-(Me_2SiO)-(MePhSiO)_n-(Me2SiO)-$ in the temperature range employed in the present study. Composition and temperature dependence of the spectral data are well interpreted in terms of the superposition of the emission properties originating from each unit structure $-(Me_2SiO)-(MePhSiO)_n-(Me2SiO)-$ in a copolymer chain. It is shown that the apparent mean binding energy of the excimer in the absence of the unit structure $-(Me_2SiO)-(MePhSiO)-(Me2SiO)-$ does not depend significantly on the MePhSiO content of the copolymer.

Experimental Section

The copolymers were synthesized from octamethylcyclotetrasiloxane and trimethyltriphenylcyclotrisiloxane in tetrahydro-

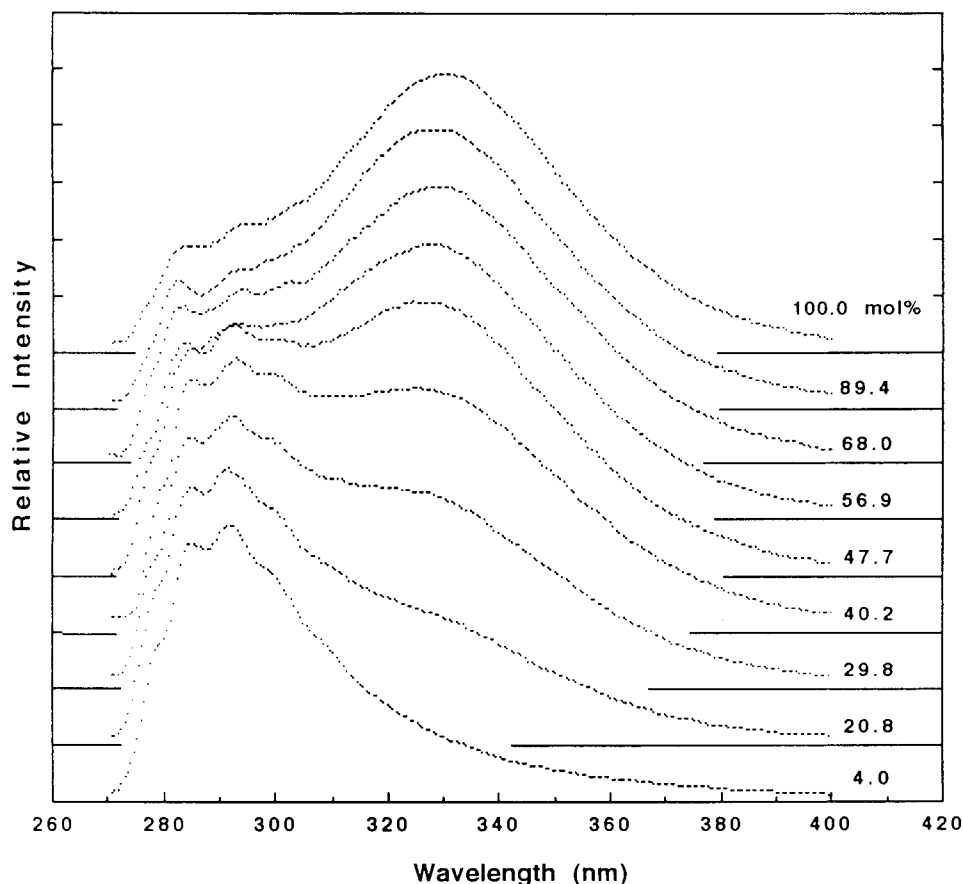* Corresponding author. E-mail: titoh@fc.miyazaki-med.ac.jp.

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Figure 1. Emission spectra of poly(dimethylsiloxane-*co*-methylphenylsiloxane)s with different MePhSiO contents (mol %) in THF at 30 °C.

furan (THF) at 150 °C through an ionic polymerization using $KOSi(CH_3)_3$ as an initiator, and then treated with trimethyl-chlorosilane. The MePhSiO contents were evaluated from the H^1NMR spectra as well as from the UV optical density in THF. The properties of the copolymers used in the present study are summarized in Table 1. 3,5-Diphenyloctamethytetrasiloxane ($Me_3SiO(MePhSiO)_2SiMe_3$) and 3,5,7-triphenylnonamethylpen-tasiloxane ($Me_3SiO(MePhSiO)_3SiMe_3$) obtained from Gelest, Inc., PA, were distilled in vacuo before use.

The average molecular weights were measured with a Kratos Model Spectroflow 400 GPC, using toluene as the eluent and polystyrenes as the calibration standards. H^1NMR spectra were measured with a Brucker 300 Hz spectrometer. Emission and excitation spectra were obtained with a Hitachi 650-10CS or a JOBIN YVON-SPEX Fluorolog-3 Model 21SS fluorescence spectrophotometer and the absorption spectra were measured with a Hitachi Model 2000-20 spectrophotometer. The temper-ature of the samples in a 10-mm square quartz cell was controlled by a thermostated cell holder in which water was circulating. Raman peaks from the solvent (THF) were sub-tracted from the observed emission spectra. Monomer and excimer fluorescence spectra were separated assuming that the fluorescence spectrum of the sample with the MePhSiO content of 4.0 mol % consists almost of the monomer fluorescence (see Figure 2). The absorbance of the sample solutions at 264 nm was always kept near 0.1, which corresponds to the concentra-tion near 0.08–0.03 g/L, so that possible intermolecular excimer formation can be neglected. It was confirmed that the corrected excitation spectra of the observed emission agreed well with the corresponding absorption spectra for all the samples investigated. The fluorescence quantum yields were evaluated by comparing the corrected fluorescence spectra of the copoly-mers with that of quinine in 0.1 N sulfuric acid with the same
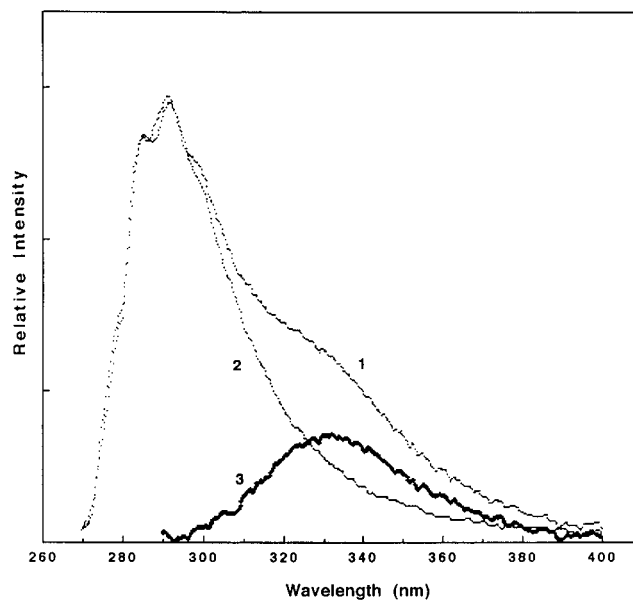

Figure 2. Emission spectra of poly(dimethylsiloxane-*co*-methylphe-nylsiloxane)s with the MePhSiO contents of 20.8 (1) and 4.0 mol % (2) in THF at 30 °C, and the excimer fluorescence spectrum (3) obtained by subtracting the spectrum 2 from 1. Spectra 1 and 2 are normalized to a common magnitude.

absorbance as a standard, assuming that the fluorescence quantum yield of the latter is 0.55.[14] That is, the integrated emission intensity devided by the absorbance for each siloxane sample was compared with the same quantity of the standard sample using the same excitation wavelength. Digital data were analyzed with a Macintosh Quadra 650 computer loaded with a super PC memory and a Macintosh G3 computer.
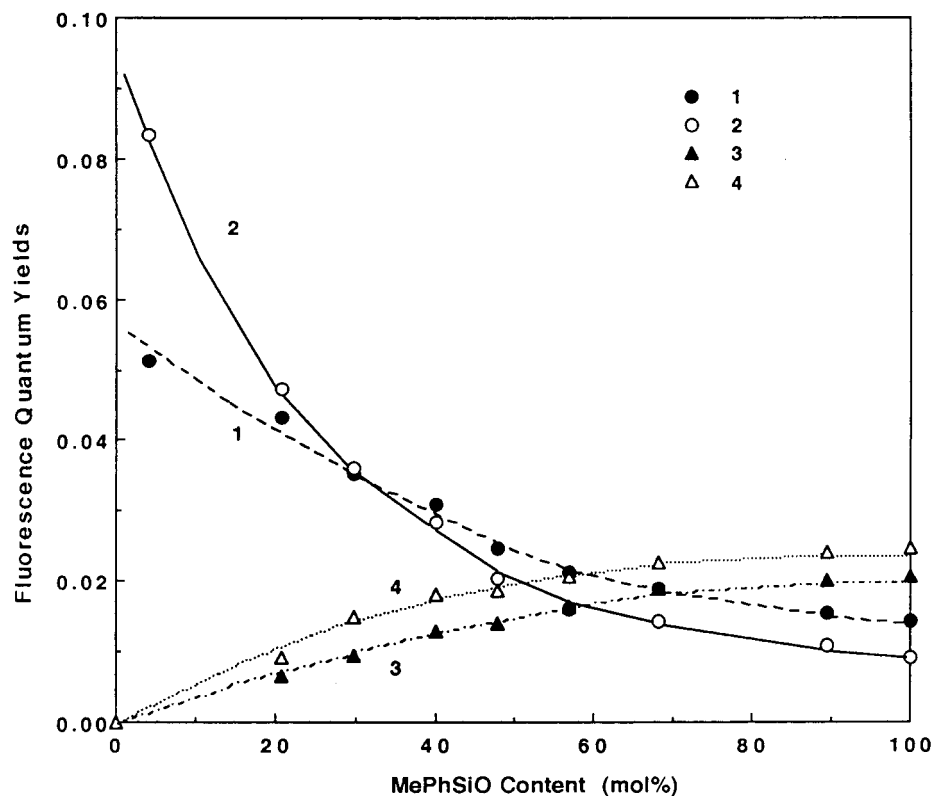
Figure 3. Quantum yields of the monomer Φ_M (1 and 2) and excimer fluorescence Φ_E (3 and 4) plotted as a function of the MePhSiO content for poly(dimethylsiloxane-*co*-methylphenylsiloxane)s in THF at 9 (2 and 4) and 30 °C (1 and 3).
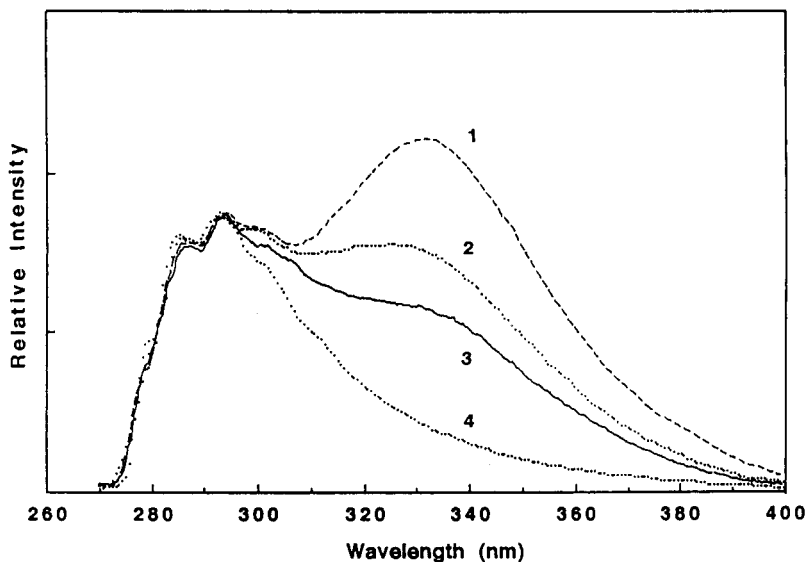

Figure 4. Emission spectra of poly(dimethylsiloxane-*co*-methylphenylsiloxane) with the MePhSiO content of 40.2 mol % (1, 2 and 3) in THF at different temperatures: 1, 7 °C; 2, 30 °C and 3, 54 °C. Spectrum 4 is the emission spectrum of the copolymer with the MePhSiO content of 4.0 mol % in THF at 30 °C, which is supposed to be consist almost of the monomer fluorescence. All the spectra are normalized to a common magnitude.

Results

Figure 1 shows the emission spectra of poly(methylphenyl-siloxane-*co*-dimethylsiloxane)s with different MePhSiO contents in THF measured at 30 °C. The absorption spectral features are found to be almost independent of the MePhSiO content. The structured emission centered at 290 nm is the monomer fluorescence which exhibits a reasonable mirror-image relationship with the absorption spectrum, while the broad emission centered at around 330 nm is the excimer fluorescence. It is seen in Figure 1 that the intensity ratio of the monomer to excimer fluorescence decreases with increasing the MePhSiO

content. Although the emission spectrum of the copolymer with the MePhSiO content of 20.8 mol % at near room temperature can be regarded as consisting mostly of the monomer fluorescence, there remains a small contribution from the excimer fluorescence. Assuming that the emission of the copolymer with the MePhSiO content of 4.0 mol % consists almost of the monomer fluorescence, all the measured spectra were separated into the monomer and excimer fluorescence spectra (Figure 2).

Figure 3 shows the fluorescence quantum yields of the copolymers plotted as a function of the MePhSiO content at two different temperatures. One can see clearly that the
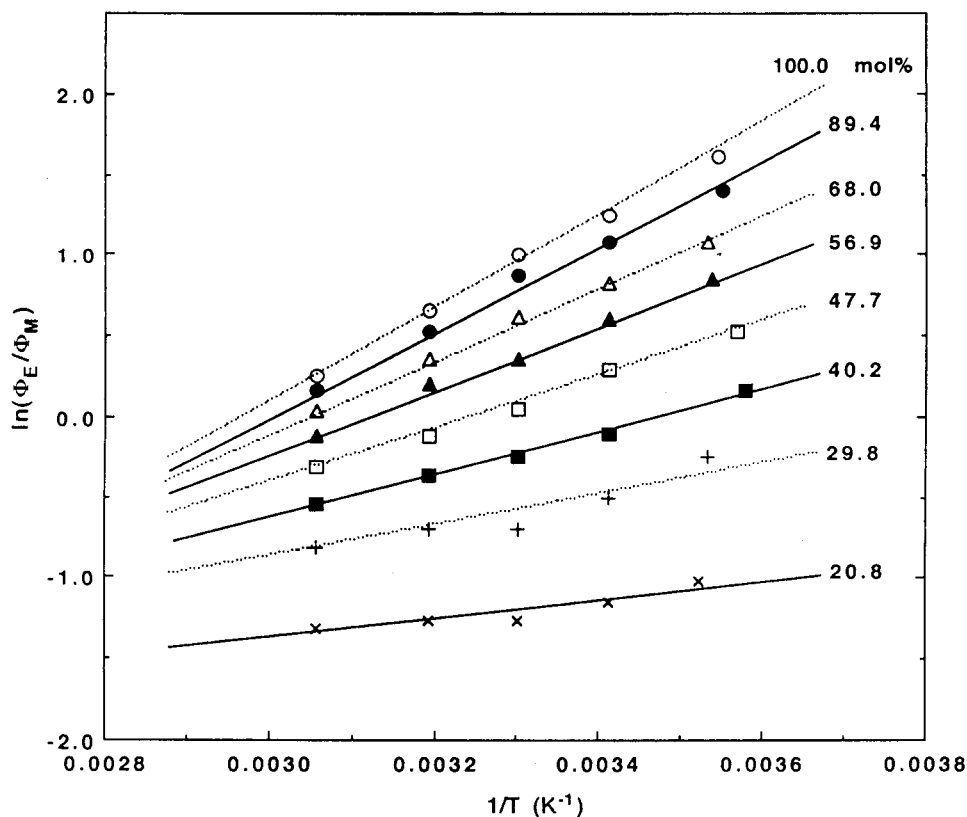
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Figure 5. Logarithmic values of the excimer-to-monomer-fluorescence quantum yield ratio, $\ln(\Phi_E/\Phi_M)$, plotted against $1/T$ for poly(dimethylsiloxane-*co*-methylphenylsiloxane)s with different MePhSiO contents in THF.

monomer-fluorescence quantum yield (Φ_M) decreases monotonically with increasing the MePhSiO content, while the quantum yield of excimer fluorescence (Φ_E) increases from zero to approach a plateau. Further, the prominent feature upon the increase of temperature is, in one hand, the decrease of Φ_M for the low MePhSiO-content copolymers and, on the other hand, the increase of Φ_M for the high MePhSiO-content copolymers.

In Figure 4 we show the emission spectra of poly(diphenyl-siloxane-*co*-dimethylsiloxane)s with the MePhSiO content of 40.2 mol % at different temperatures in THF. It is seen that the intensity of the excimer fluorescence relative to the monomer fluorescence increases with decreasing the temperature. Similar emission spectral change with varying the temperature is observed also for the copolymers with other MePhSiO contents. Temperature dependence of the excimer/monomer fluorescence quantum yield ratio, Φ_E/Φ_M, is shown in Figure 5. It is seen that the ratio Φ_E/Φ_M increases with decreasing temperature. As will be explained later in detail, the apparent binding energy of the excimer, ΔE_{app}, which will be shown to have no appreciable physical meaning, can be obtained from the logarithmic plots of Φ_E/Φ_M versus reciprocal of the absolute temperature ($1/T$). With further decrease of the temperature below about −20 °C the ratio, Φ_E/Φ_M, decreases. Since the behavior of the fluorescence yields in low temperature region is not relating directly to the biding energy of the excimer, we only discuss the temperature dependence of the fluorescence yields at higher temperatures, where the ratio, Φ_E/Φ_M, decreases with increasing temperature. As is seen in Figure 5, the slope of the plots seems to vary systematically depending on the MePhSiO content, indicating formally that the ΔE_{app} value changes with MePhSiO content in the copolymers. Discussion on these observations follows.
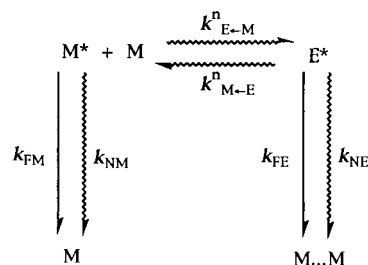

Figure 6. Schematic showing the relaxation processes in each unit structure $-(CH_3PhSiO)_n-$ in a copolymer chain.

Discussion

The rigorous analysis for the stationary kinetics based on the fluorescence properties of methylphenylsiloxane-based copolymers requires the information on the distribution of the polymer structures, such as $-MPM-$, $-MP_2M-$, $-MP_3M-$, ..., $-MP_nM-$, with P and M denoting MePhSiO and Me$_2$SiO units, respectively.[15−18] To analyze the observed quantum yield behavior, the conventional kinetic scheme shown in Figure 6 was applied to each structure, $-MP_nM-$ ($n = 1, 2, 3,...$).[15] In this scheme, $k^n_{E\leftarrow M}$ and $k^n_{M\leftarrow E}$ are, respectively, the rate constants for formation and dissociation of the excimer relating to each structure $-P_nM-$ in the polymer chain. The former rate constant contains implicitly the efficiency of the energy migration in each $-MP_nM-$ structure. k_{FM} and k_{NM} are, respectively, the radiative and nonradiative rate constants of the monomer, and k_{FE} and k_{NE} are those for the excimer; these are assumed to be almost independent of n. If we know the fraction of the sequences of the MePhSiO units MP$_n$M, $F(n)$ ($\Sigma_n F(n) = 1$), for the copolymer with the MePhSiO content, f_P ($0 \leq f_P \leq 100$ mol %), the observed fluorescence quantum yields will be given by

$$\Phi_M(f_P) = \Sigma_n[F(n)\phi^n_M] \tag{1a}$$

$$\Phi_E(f_P) = \Sigma_n[F(n)\phi^n_E] \tag{1b}$$

where

$$\phi^n_M = k_{FM}/\xi^n \tag{2a}$$

$$\phi^n_E = [k_{FE}k^n_{E\leftarrow M}/(k_{FE} + k_{NE} + k^n_{M\leftarrow E})]/\xi^n \tag{2b}$$

with $\xi^n = k_{FM} + k_{NM} + k^n_{E\leftarrow M} - k^n_{M\leftarrow E}[k^n_{E\leftarrow M}/(k_{FE} + k_{NE} + k^n_{M\leftarrow E})]$.[19,20] It follows from eqs 1a and 1b that

$$\Phi_E(f_P)(k_{FE} + k_{NE})/k_{FE} + \Phi_M(f_P)(k_{FM} + k_{NM})/k_{FM} =$$
$$\Sigma_n F(n) = 1 \tag{3}$$

where $k_{FM}/(k_{FM} + k_{NM})$ corresponds to the value for $\Phi_M(f_P)$ at $f_P \rightarrow 0$ mol % (denoted by ϕ^1_M), which stands for the monomer fluorescence yield for the isolated unit structure $-MPM-$ in the copolymer.[19] The values for ϕ^1_M obtained by extrapolation of the plots in Figure 3 to $f_P = 0$ mol % are 0.055 and 0.089 at 30 and 9 °C, respectively. On the other hand, the precise value for $k_{FE}/(k_{FE} + k_{NE})$ (denoted by ϕ_E) is not available, but it is expected to be close to the Φ_E value of a homoplymer, poly-(methylphenylsiloxane), which is 0.025 at 30 °C. Substituting in eq 3 the ϕ^1_M values already obtained and the fluorescence quantum yields, Φ_E and Φ_M, of poly(methylphenylsiloxane), we estimated the ϕ_E values to be 0.027 and 0.028, respectively, at 9 and 30 °C. Equation 3 is then rewritten by the form

$$\Phi_E(f_P)/\phi_E + \Phi_M(f_P)/\phi^1_M = 1 \tag{4}$$

The values for $\Phi_M(f_P)/\phi^1_M + \Phi_E(f_P)/\phi_E$ are plotted against f_P in Figure 7. The obtained plots are almost unity irrespective of f_P as is expected from eq 4. It follows from the present analysis that, to a first approximation, there is almost no interaction between the unit structures $-MP_nM-$ so far as the temperature range employed in the present experiment is concerned.

The information on the fraction $F(n)$ is essential for the clarification of the temperature dependence of the fluorescence properties. To evaluate the values for $F(n)$, we utilized the following approximate forms corresponding to eq 1, parts a and b.

$$\Phi_M \cong \phi^1_M \times F(1) + \phi^2_M \times F(2) + \phi^m_M \times \Sigma_{n\geq 3} F(n), \tag{5a}$$

$$\Phi_E \cong \phi^1_E \times F(1) + \phi^2_E \times F(2) + \phi^m_E \times \Sigma_{n\geq 3} F(n), \tag{5b}$$

$$F(1) + F(2) + \Sigma_{n\geq 3} F(n) = 1 \tag{5c}$$

where ϕ^m_M and ϕ^m_E are, respectively, the monomer and excimer fluorescence quantum yields of the unit structure $-MP_nM-$ averaged over $F(n)$ with $n \geq 3$. The Φ_M value obtained by extrapolation of the plots of Φ_M in Figure 3 to $f_P = 0$ mol %, which stands for the monomer fluorescence yield of the isolated unit structure $-MPM-$ in a copolymer chain, was used as the value for ϕ^1_M. Obviously $\phi^1_E = 0.0$, since the excimer formation cannot be expected for the unit structure $-MPM-$. The fluorescence quantum yields of $Me_3SiO(MePhSiO)_2SiMe_3$ in THF were used as the values for ϕ^2_M and ϕ^2_E. We have estimated also the values for ϕ^3_M and ϕ^3_E for the sake of comparison, referring to the fluorescence quantum yields of $Me_3SiO(MePhSiO)_3SiMe_3$ in THF. The fluorescence quantum yields of the unit structures, ϕ^n_M and ϕ^n_E, thus obtained at two different temperatures are shown in Figure 8. The values for ϕ^3_M and
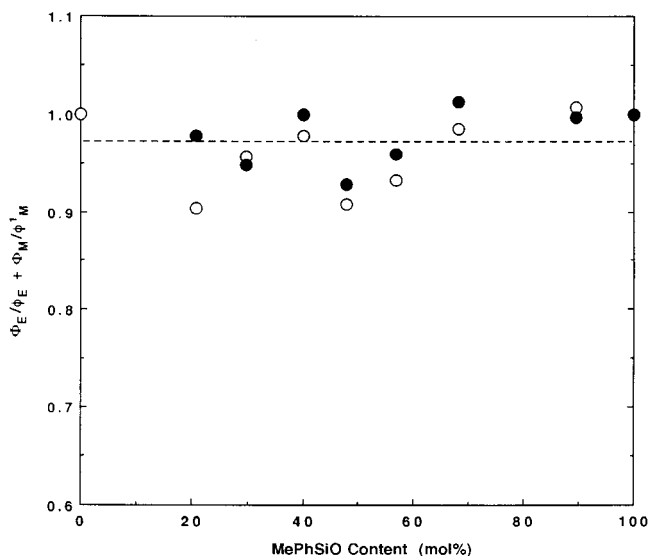
Figure 7. Values for $\Phi_M/\phi^1_M + \Phi_E/\phi_E$ plotted against the MePhSiO content for poly(dimethylsiloxane-*co*-methylphenylsiloxane)s in THF at 9 (open circles) and 30 °C (closed circles). The average value of the plots is indicated by a broken line.
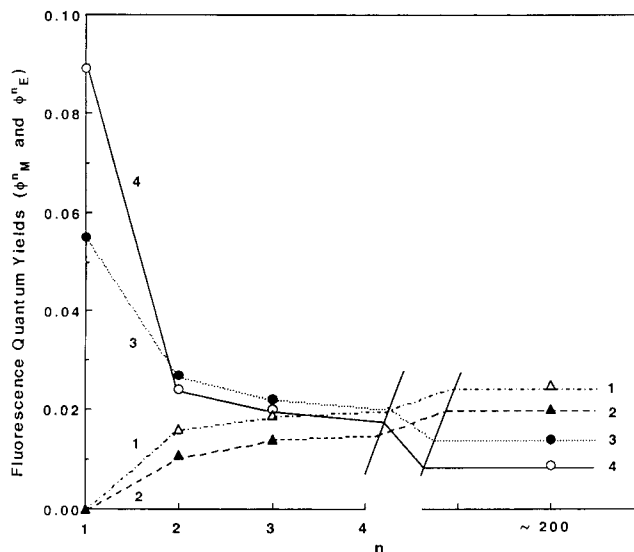
Figure 8. The excimer (1 and 2) and monomer (3 and 4) fluorescence quantum yields, ϕ^n_E and ϕ^n_M, for the unit structures, $Me_3SiO-(MePhSiO)_nSiMe_3$ with $n = 1, 2, 3,$ and ~200, obtained at 9 °C (1 and 4) and 30 °C (2 and 3).

ϕ^3_E are found to be close to those for ϕ^2_M and ϕ^2_E, respectively, as well as to the Φ_M and Φ_E values of the high MePhSiO-content copolymers. This presumably indicates that no abrupt change is expected for the ϕ^n_M and ϕ^n_E values upon further increase of n ($n > 3$). Thus, we have treated the values for ϕ^m_M and ϕ^m_E as parameters varying in the ranges $0.020 > \phi^m_M > 0.009$ and $0.025 > \phi^m_E > 0.019$ at 9 °C, and $0.022 > \phi m_M > 0.014$ and $0.021 > \phi^m_E > 0.014$ at 30 °C. In Figure 9, parts a and b, we show the values for $F(1)$, $F(2)$, and $\Sigma_{n\geq 3}F(n)$ obtained by solving the linear eq 5, parts a–c, using the best-fit parameters for ϕ^m_M and ϕ^m_E. Under the present approximation, both of the $F(1)$ and $F(2)$ values obtained at two different temperatures are found to be in reasonable agreement to each other. It is seen that $F(1)$ decreases rapidly with increasing f_P, while $F(2)$ shows a maximum at f_P near 50 mol %. The fraction of the structure $-MPM-$, $F(1)$, is found to be about 0.3 for the copolymer with f_P near 30 mol %, and decrease down to ~0.1 for that containing 50 mol % MePhSiO. Thus, $F(1)$ is

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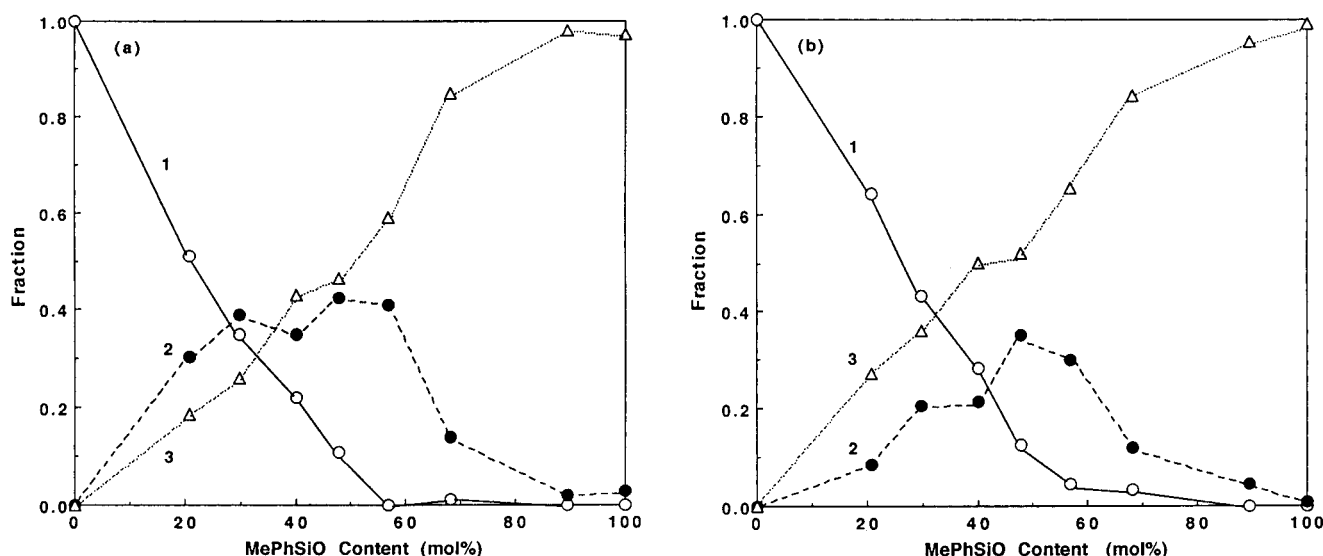*J. Phys. Chem. B, Vol. 106, No. 9, 2002* **2201**

Figure 9. Fractions, $F(1)$ (1), $F(2)$ (2), and $\Sigma_{n \geq 3} F(n)$ (3), obtained by solving the linear eq 5, parts a−c, for poly(dimethylsiloxane-*co*-methylphenylsiloxane)s with different MePhSiO contents in THF at 9 °C (a) and 30 °C (b).
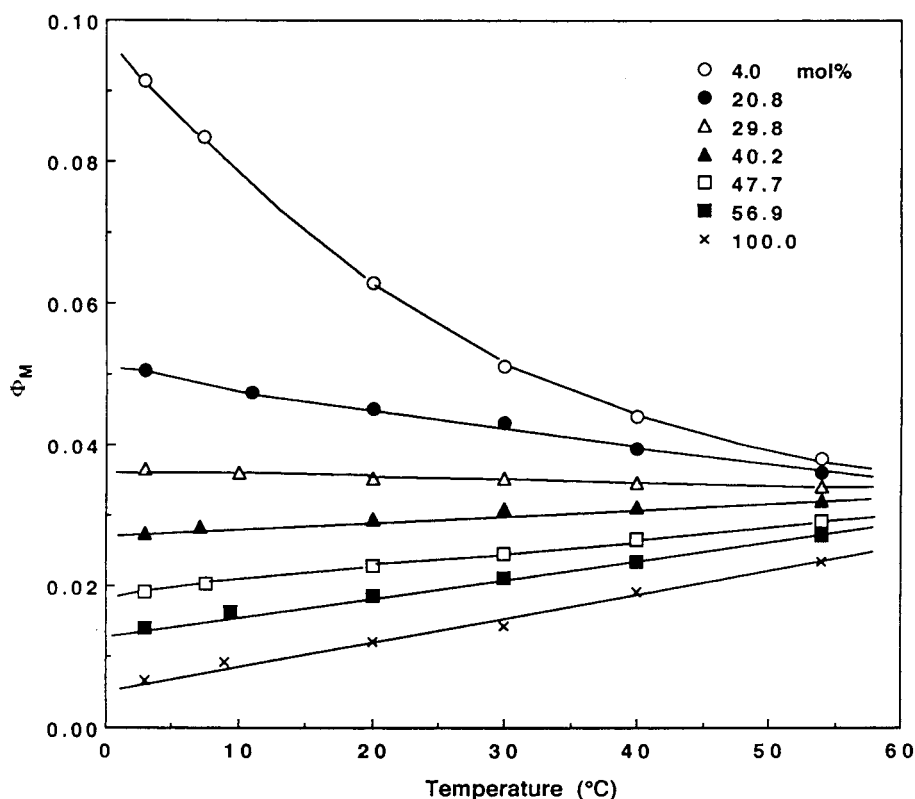

Figure 10. Values for Φ_M plotted against the temperature for poly(dimethylsiloxane-*co*-methylphenylsiloxane)s with different MePhSiO contents in THF.

comparatively large for low PhMeSiO content copolymers and small for high PhMeSiO content copolymers. This is consistent in part with the ^{29}Si NMR data that the siloxane copolymer with 9.5 mol % PhMeSiO units contains as much as 79% −MPM− triads.[13]

It is recognized from the plots in Figure 9 that the temperature dependence of Φ_M for the low MePhSiO-content copolymers is dominated mainly by an isolated −MPM− structure, while that for the high MePhSiO-content copolymers is relating mainly to the excimer formation process in the −MPnM− structures with $n \geq 2$. Therefore, two different behaviors are expected for Φ_M depending on f_P, when the temperature is changed. This is most clearly seen when the value for Φ_M alone is plotted as

a function of temperature for the copolymers with different MePhSiO contents. As is seen in Figure 10, the Φ_M value for the low MePhSiO-content copolymers decreases, while that for the high MePhSiO-content copolymers increases with increasing temperature. The variation of Φ_M with temperature for the low MePhSiO-content copolymers is most probably dominated by the temperature-dependent nonradiative process in an isolated −MPM− structure. It follows from these observations that although the temperature dependence of Φ_M for the high MePhSiO-content copolymers is controlled by the biding energy for the excimer formation in the structure −MP$_n$M− with $n \geq$ 2, that for the low MePhSiO-content copolymers is dominated

mainly by temperature-dependent nonradiative process of the unit structure $-$MPM$-$.

As was shown in Figure 5, the quantum yield ratio of the excimer to monomer fluorescence decreases with increasing temperature in the range from 0 to 60 °C. We have tentatively evaluated the apparent binding energies of the excimer, ΔE_{app}, by plotting the logarithmic value of Φ_E/Φ_M against $1/T$.[21] The value for ΔE_{app} is found to increase from 1.2 up to 5.0 kcal/mol with increasing f_P from 20.8 to 100 mol % (see the slopes of the plots in Figure 5). For the sake of comparison, we have evaluated also the excimer binding energies, ΔE, of the model compounds, $Me_3SiO(MePhSiO)_2SiMe_3$ and $Me_3SiO(MePhSiO)_3$-$SiMe_3$, in THF, on the basis of the temperature dependence of Φ_E/Φ_M. The values for ΔE of the former and the latter compounds are found to be 4.2 and 3.9 kcal/mol, respectively. These values are comparatively close to each other and to the ΔE_{app} value obtained for high MePhSiO-content copolymers (4$-$5 kcal/mol) as well as for a homopolymer, $(MePhSiO)_n$ (5.0 kcal/mol).

To eliminate the contribution from the monomer fluorescence of the unit structure $-$MPM$-$ which shows no excimer emission, we have plotted the logarithmic value of $\Phi_E(T)/[\Phi_M(T) - F(1)\phi^1_M(T)]$ versus $1/T$, instead of that of $\Phi_E(T)/\Phi_M(T)$ versus $1/T$. The energy obtained from the new plots corresponds to the apparent binding energy in the absence of the unit structure $-$MPM$-$. The apparent binding energy thus obtained is found to increase only slightly from near 4.0 up to 5.0 kcal/mol with increasing f_P, although the quantum yield ratio for raw data, $\Phi_E(T)/\Phi_M(T)$, measured as a function of temperature provides a significant increase of the apparent binding energy with increasing f_P (see Figure 5). This may indicate that the mean binding energy of the excimer in the present copolymer system does not depend significantly on the MePhSiO content.

Conclusions

We have determined the monomer and excimer fluorescence quantum yields of well-defined poly(dimethylsioxane-*co*-methylphenylsiloxane)s with different MePhSiO contents, together with those of 3,5-diphenyloctamethytetrasiloxane and 3,5,7-triphenylnonamethylpentasiloxane used as the model compounds, in THF at different temperatures. The fluorescence quantum yields of the copolymers are correlated with sum of those of the sequences of the structures $-(CH_3)_2SiO-(CH_3-(C_6H_5)SiO)_n-(CH_3)_2SiO-$ with $n = 1, 2, 3,...$. It is inferred from the analyses that, after eliminating the contribution of the monomer fluorescence from the unit structure $-(CH_3)_2SiO-CH_3(C_6H_5)SiO-(CH_3)_2SiO-$ which shows no excimer fluorescence, the mean binding energy of the excimer does not depend significantly on the MePhSiO content of the copolymer.

References and Notes

(1) Stark, O. F.; Falender J. R.; Wright, A. P. Silicones. In *Comprehensive Organometallic Compounds*; Wilkins; G. F., Stone, G. A., Abel, E. W., Ed.; 1982; Vol. 2, pp 305$-$363 and references therein.

(2) Warrick, E. L. *Ind. Eng. Chem.*, **1955**, *47*, 2388.

(3) Miller, A. A. *Ind. Eng. Chem. Prod. Res. Dev.* **1964**, *3*, 252.

(4) Morita, M.; Imamura, S.; Tanaka, A.; Tamamura, T. *J. Electrochem. Soc*. **1984**, *131*, 2402.

(5) Burkhard, C. A.; Winslow, E. H. *J. Am. Chem. Soc.* **1950**, *72*, 3276.

(6) Hamanishi, K.; Shizuka, H. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3007.

(7) Salom, C.; Horta, A.; Hernandes-Fuentes, I.; Pierola, I. F. *Macromolecules* **1987**, *20*, 696.

(8) Macanita, A. L.; Pierola, I. F.; Horta, A. *Macromolecules* **1991**, *24*, 1293.

(9) Salom, C.; Semlyen, J. A.; Clarson, S.; Hernandez-Fuentes, I.; Macanita, A. L.; Horta, A.; Pierola, I. F. *Macromolecules* **1991**, *24*, 6827.

(10) Macanita, A. L.; Danesh, P.; Peral, F.; Horta, A.; Pierola, I. F. *J. Phys. Chem.* **1994**, *98*, 6548.

(11) Salom, C.; Hernandes-Fuentes, I.; Pierola, I. F.; Horta, A. *Macromolecules* **1989**, *22*, 1874.

(12) Dias, F. B.; Lima, J. C.; Macanita, A. L.; Horta A.; Pierola, I. F. *J. Phys. Chem. A* **2000**, *104*, 17.

(13) Macanita, A. L.; Horta, A.; Pierola, I. F. *Macromolecules* **1994**, *27*, 3797.

(14) Melhuish, W. H. *J. Phys. Chem.* **1961**, *65,* 229.

(15) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, UK, 1985.

(16) Bokobza, L.; Jasse, B.; Monnerie, L. *Eur. Polym. J.* **1977**, *13*, 921.

(17) Reid, R. F.; Soutar, I. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 231.

(18) Reid, R. F.; Soutar, I. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 457.

(19) Itoh, T.; Yang, M. H.; Chou, C. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3593.

(20) Itoh, T. *Chem. Rev.* **1995**, *95,* 2351.

(21) Itoh, T. *Macromolecules* **1997**, *30*, 6999.