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Photophysical Studies of Molecular Mobility in Polymer Films and Bulk Polymers. 3. Dynamic Excimer Formation of Pyrene in Bulk PDMS

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ABSTRACT: Molecular mobility in polymer films and bulk polymers has been determined by measuring the excimer formation of pyrene. Excimer formation of pyrene in polystyrene and epoxy film was not observed at pyrene concentrations ≤0.1 M. This indicates a very low mobility of the probe molecules in the above polymer films. However, excimers in high yield were formed dynamically in bulk poly(dimethylsiloxanes) (PDMS). The rate constants of excimer formation in PDMS (1–2.5 × 10^6 cP) are 7.1 × 10^9–9.2 × 10^8 M^{-1} s^{-1}. The rate constants are larger than those in squalane, the room-temperature viscosity of which is only 35.4 cP. Viscosity changes induced by various molecular weights of PDMS and by various temperatures impose different effects on the mobility of pyrene molecules. The data are explained by concepts of macroviscosity, microviscosity, the basic structure of the polymer matrix and by free-volume theory. It is found that the natural logarithm of the diffusion rate constant is proportional to the density of polymer in studies with linear PDMS.

Introduction

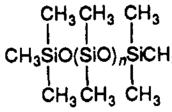
Recent years have seen a great application of photophysical and photochemical methods to the study of diffusion or the movement of molecules in polymer matrices.[1,2] Laser photolysis studies using $T_n \leftarrow T_1$ absorption in glassy and elastomeric polymers have shown that the oxygen-quenching rate constants of the excited triplet in polymers are of the order 10^6–10^9 M^{-1} s^{-1}, which are much higher than those expected from the bulk macroviscosity of the film.[3] Of immediate interest is the diffusion of other molecules that are larger than oxygen in highly viscous polymer film or bulk polymers. In previous papers of this series, the quenching of pyrene fluorescence by phthalic anhydride was studied in bulk poly(dimethylsiloxanes) (PDMS) and in PDMS films;[4] these systems possess the highest oxygen permeability amongst known polymers. Free rotation of methyl groups about Si–O and Si–C bonds, a unique structural feature of PDMS, enhances solute diffusion in these polymers over a viscosity range from 1 to 2.5 × 10^6 cP (molecular weight 2.3 × 10^2–4.2 × 10^5).

Intramolecular excimer formation of various dichromophoric probes dispersed in different elastomers has been used to gain information about the amplitude of the motion performed by the probes in the systems. Dichoromophores used by Monnerie and co-workers are 10,10′-diphenylbis(9-anthrylmethyl) oxide, *meso*-di-*N*-carbazolylpentane, and *meso*-bis[1-(2-pyrenyl)ethyl] ether, where two chromophoric groups are separated by a propyl chain. Intramolecular excimers are formed on rotation of chromophores about the C–C bonds of the propyl linkage to achieve a sandwichlike overlap. The above studies focused on the effect of temperature, and the experimental data were compared with calculations from the WLF equation by using the free-volume concept.[6-8] Studies showed the importance of chemical structure of the polymer matrix on the intramolecular excimer formation and that the probes mobility depends on the fractional free volume obtained by changing either temperature or pressure.

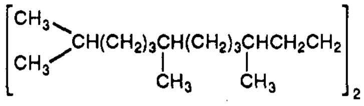
The present report on excimer formation of pyrene in PDMS is a part of photophysical studies of molecular mobility in polymer films and bulk polymers and includes a wider range of viscosities of PDMS than in other studies.[5-8] Pyrene, the probe used in these studies, has a longer lifetime (~400 ns) than that used in other studies.[6-8] Quantitative data on the lateral diffusion of pyrene were produced from the kinetics of intermolecular excimer formation. The effects of viscosity via change in molecular weight and change in temperature on excimer formation rates are compared. Finally the relationships between the free volume, the density, and the diffusion rates are discussed.

Experimental Section

Materials. Poly(dimethylsiloxanes) terminated with trimethylsiloxy groups, PDMS


$$CH_3\overset{CH_3}{\underset{CH_3}{Si}}O(\overset{CH_3}{\underset{CH_3}{Si}}O)_n\overset{CH_3}{\underset{CH_3}{Si}}CH_3$$

with viscosities from 1 to 2.6 × 10^6 cP were purchased from Petrarch System Co. The molecular weights of the samples ranged from 2.37 × 10^2 to 4.23 × 10^5. Squalane (Aldrich)



was purified by chromatography on an alumina column; pyrene (Aldrich) was purified by chromatography on a silica column.

Pyrene was incorporated into the polymer by dilution of 1 × 10^{-2} M stock solutions in methyl ethyl ketone. Each sample was then vortex-mixed and dried. Highly viscous samples (6 × 10^4–2.5 × 10^6 cP) were cast down onto a Mylar film and dried in a vacuum oven at 30 °C for 8 h. Polystyrene and epoxy films were prepared as previously stated.[3] All samples were nitrogen bubbled or placed under vacuum to remove oxygen prior to use.

Measurement. Pyrene-containing samples were irradiated with a PRA LN-100 nitrogen laser (λ = 337.1 nm, pulse width = 0.3 ns, energy = 50 μJ). The light output of the monochromator was monitored at 400 nm for monomer emission and 480 nm for excimer emission by a Hamamatsu R 1644 microchannel plate PMT with a response of 0.2 ns. The signal from this tube was captured by a Tektronix 7912 AD multitransient digitizer.

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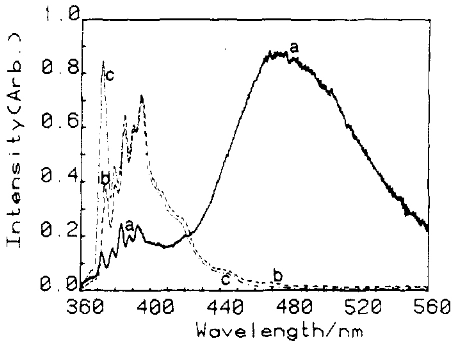


Figure 1. Emission spectra of 0.01 M pyrene fluorescence (a) in poly(dimethylsiloxane) (PDMS; 50 cP) (—), (b) in polystyrene (- - -), and (c) in epoxy film (- · -).

Steady-state fluorescence spectra were measured on a Perkin-Elmer MPF 44B spectrofluorimeter; UV absorption spectra were measured with a Perkin-Elmer 552 spectrophotometer.

Diffusion coefficients of pyrene, D, were calculated by using the measured rate constants of excimer formation, k_1, the interaction radius of the pyrene, r, and the Smoluchowski equation

$$k_1 = 4\pi N(2r)(2D)/1000 = 16\pi NrD/1000 = 1.05 \times 10^{15} D \qquad (1)$$

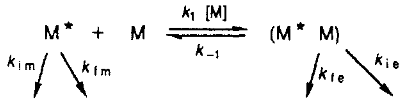
where N is Avogadro's number and r is equal to 3.46 Å.[9] In this simple Smoluchowski equation, the transient terms are disregarded.

Results and Discussion

Dynamic Excimer Formation of Pyrene in Bulk PDMS. The fluorescence spectra of 10 mM pyrene in PDMS of 50 cP, in polystyrene, and in epoxy film are given in parts a–c of Figure 1, respectively. The spectrum in PDMS exhibits a strong, broad, structureless band of the excimer of pyrene at 475 nm; the yield of the excimer is high. Comparison of spectrum a with b and c in Figure 1 reveals a very low efficiency of excimer formation in glassy polystyrene and epoxy films due to the low mobility of the probe molecules. Excimer formation in polystyrene was reported by using a very high concentration of pyrene (>0.3 M).[10] Such a high concentration of pyrene may plasticize the polystyrene film and increase the mobility of the probe. On the other hand, the high concentration may also form dimers or cause a clustering formation of pyrene in the polymer matrix.

Formation of the excimer by migration of two pyrene molecules or by dimer (or by clustering) static formation of the pyrene could be distinguished by measuring the time-dependent emission of pyrene excimer at 480 nm. For dynamic formation, the emission intensity at 480 nm should increase with time, while for dimer (or a cluster) formation the emission maximum intensity should be observed immediately following the laser excitation pulse. Figure 2 shows a typical decay curve of 5 mM pyrene fluorescence monitored at 480 nm, indicating the dynamic nature of the excimer formation in PDMS.

The mechanism shown in kinetic eq 2 has been used to describe the intermolecular excimer formation[11]



(2)

where k_{fm} and k_{fe} are the rate constants of fluorescence decay from the excited monomer and excimer and k_{im} and k_{ie} are the rate constants of nonradiative decay from the excited monomer and excimer, respectively; k_1 and k_{-1} are the rate constants for excimer formation and dissociation, respectively. From this scheme, the time dependences of the fluorescence intensity of monomer, $I_m(t)$, and excimer, $I_e(t)$, are expressed as

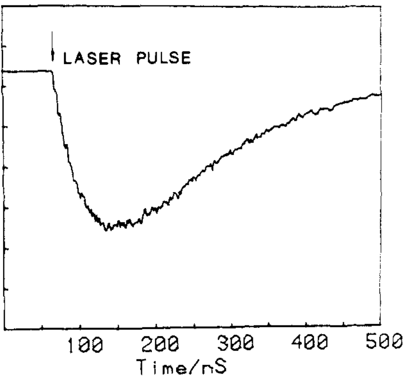


Figure 2. Typical time-dependent profile of 5 mM pyrene fluorescence in PDMS monitored at 480 nm.

$$I_m(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) \qquad (3)$$

$$I_e(t) = A_3[\exp(-\lambda_1 t) - \exp(-\lambda_2 t)] \qquad (4)$$

where

$$\lambda_{1,2} = (1/2)[X + Y \mp \{(Y - X)^2 + 4k_1k_{-1}[\mathrm{M}]\}^{1/2}]$$

$$X = k_1[\mathrm{M}] + k_{im} + k_{fm} \qquad Y = k_{-1} + k_{ie} + k_{fe}$$

$$A_1 = k_{fm}(\lambda_2 - X)/(\lambda_2 - \lambda_1) \qquad A_2 = k_{fm}(X - \lambda_1)/(\lambda_2 - \lambda_1)$$

$$A_3 = k_{fe}k_1[\mathrm{M}]/(\lambda_2 - \lambda_1)$$

In some circumstances, $k_{-1} \ll k_1[\mathrm{M}]$; then the dissociation of excimer to form excited monomer can be ignored. Consequently, eq 3 can be simplified to a single-exponential decay

$$I_m(t) = A_1 \exp(-\lambda_1 t) \qquad (5)$$

Furthermore, the rate of excimer formation k_1 can be determined by the slope of observed rate λ_1 versus concentration of pyrene, due to $A_2 = 0$ and $\lambda_1 = X = k_1[\mathrm{M}] + k_{im} + k_{fm}$ or $\lambda_1 = k_1[\mathrm{M}] + k_0$ where k_0 is the rate in the absence of excimer. λ_1 obtained from $I_m(t)$ monitored at 400 nm is compared with that determined from $I_e(t)$ monitored from 480 nm. However, the data handling via eq 5 is much simpler and much more accurate than that via eqs 3 and 4. The k_1 data in Table I for PDMS of 7-10^6 cP and squalane were determined via eq 5. A similar method for data handling has been reported for excimer formation of pyrene in polymer colloid particles by Winnik[12] and for intramolecular excimer formation of 10,10′-diphenylbis(anthrylmethyl) oxide in cyclic PDMS and polybutadienes by Monnerie.[6-8] In the present studies, the single-exponential decay curves were actually observed at 400 nm in the studied PDMS system from 7 to 2.5 × 10^6 cP and also in squalane (35.4 cP). Figure 3 shows the decay curves of pyrene fluorescence (3 mM) monitored at 400 nm in PDMS of 1, 7, 50, 500, and 1 × 10^6 cP and in squalane at 20 °C. The curves of ln (intensity) vs t are linear, indicating monoexponential decay in the above systems except for PDMS of 1 cP. The plots of λ_1, the observed first-order rate constants, vs concentration of pyrene are also linear for the above systems and are shown in Figure 4. The decay curves monitored at 400 nm in PDMS of 1 cP are monoexponential only at low temperature. When the temperature is above −25 °C, the decay curves are no longer single exponential (shown in Figure 5) and k_{-1} cannot be ignored. Under this condition, the simplified data handling (eq

Table I
Rate Constants of Excimer Formation of Pyrene k_1, in Bulk PDMS and Squalene at 20 °C

$\eta_{20\ °C}$,[a] cP	MW[a]	DP[b]	k_1, $\times 10^9$ $M^{-1}\ s^{-1}$	density	coeff of thermal expansion, $\times 10^{-4}$
1	2.37×10^2	1.0	7.05	0.818	13.4
7	9.50×10^2	10.6	3.08	0.930	11.0
10	1.25×10^3	14.7	2.51	0.935	10.8
20	2.00×10^3	24.8	1.97	0.950	10.7
50	3.78×10^3	48.8	1.78	0.960	10.6
5×10^2	1.73×10^4	231.3	1.60	0.971	9.3
5×10^3	4.94×10^4	664.6	1.21	0.973	9.3
6×10^4	1.17×10^5	1577	1.10	0.976	9.2
6×10^5	2.60×10^5	3407	1.05	0.978	9.2
1×10^6	3.08×10^5	4155	0.98	0.978	9.2
2.5×10^6	4.23×10^5	5707	0.92	0.978	9.2
35.4[c]	4.23×10^2		0.58		

[a] Viscosity at 20 °C, molecular weight of PDMS (MW), density, and coefficient of thermal expansion were taken from: *Silicon Compounds Register and Review*; Petrarch Systems Co., 1987. [b] Degree of polymerization calculated from the molecular weight of the polymer, segment, and terminator by the equation

$$DP = (MW - 162.18)/74.09.$$

[c] In squalane.

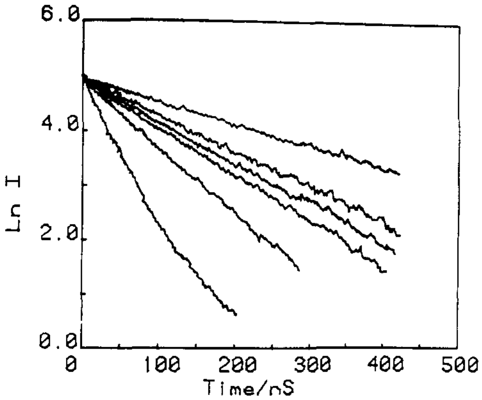


Figure 3. Decay curve of ln (intensity) vs t of 3 mM pyrene fluorescence monitored at 400 nm in PDMS of 1, 7, 50, 500, and 1×10^6 cP and in squalane (35.4 cP) at 20 °C. (Curves are labeled bottom to top.)

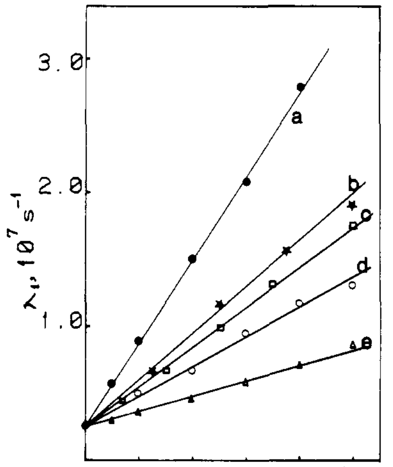


Figure 4. Plots of λ_1, the observed first-order rate constants, versus concentration of pyrene in PDMS (a–d) and in squalane (e): viscosity (cP) = 7 (●), 50 (★), 500 (□), 1×10^6 (○), and 35.4 (△).

5) cannot be used, and k_1 should be determined by using eqs 3 and 4 as shown by Birks.[11] The rate of excimer formation in PDMS of 1 cP at 20 °C was determined as $7.05 \times 10^9\ M^{-1}\ s^{-1}$, which is in agreement with the reported data in cyclohexane ($6.7 \times 10^9\ M^{-1}\ s^{-1}$) and in 95% EtOH ($7.0 \times 10^9\ M^{-1}\ s^{-1}$).[11]

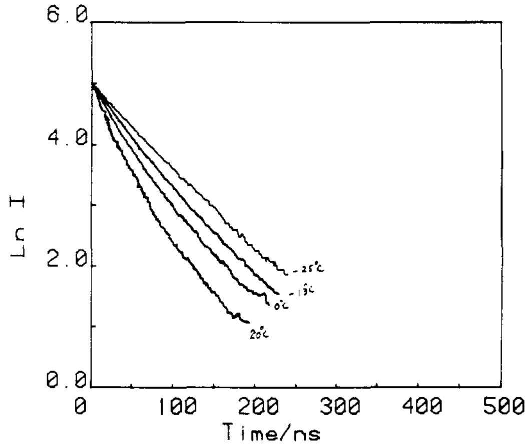


Figure 5. Decay curve of ln (intensity) vs t of 5 mM pyrene fluorescence monitored at 400 nm in PDMS of 1 cP at various temperatures.

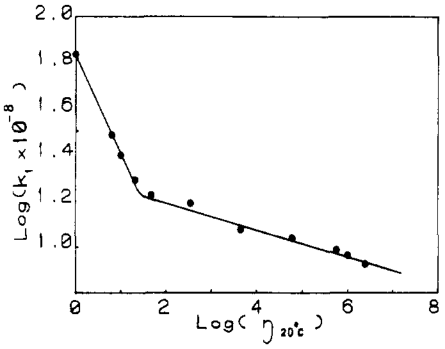


Figure 6. Relationship between the rate constant of excimer formation of pyrene and viscosity of PDMS at 20 °C.

Effect of Viscosity via Variation of Molecular Weight. In order to investigate the effect of viscosity (via change in molecular weight) on the movement of reactant molecules, experiments were done in PDMS with molecular weights from 2.3×10^2 to 4.23×10^5, which produces a viscosity range from 1 to 2.5×10^6 cP at room temperature, 20 °C. Excimer formation rates together with viscosities, molecular weights, densities, coefficient of thermal expansion, and the calculated degree of polymerization of PDMS and squalane are collected in Table I. With Stokes theory, the diffusion-controlled rate constant is proportional to the reciprocal of solvent viscosity; i.e., $k \propto \eta^{-1}$. Large discrepancies in the above concept exist in many systems, especially in more viscous solvents. Recent studies[9] on the quenching of pyrene fluorescence by nitro compounds in a series of hydrocarbons from heptane to squalane (viscosity from 0.41 to 35.4 cP) showed that $k_q \propto \eta^{-0.5}$. In the present studies, the rate constant of pyrene excimer formation is reduced 5-fold as the viscosity of bulk PDMS is increased from 1 to 50 cP; i.e., $k_1 \propto \eta^{-0.4}$, which is close to the earlier finding in alkanes where $k_q \propto \eta^{-0.5}$. However, in PDMS at viscosities greater than 50 cP, the decrease in the rate constant is very small compared to the increase in viscosity. The data plotted in Figure 6 as log k_1 versus log η exhibit a transition point at η = 50 cP, or molecular weight = 3.78×10^3. The slope is equal to 0.42 when η < 50 cP; the slope is less than 0.1 when η > 50 cP; $k_1 \propto \eta^{-0.05}$. This transition point is a critical condition of molecular weight. Below this point the excimer formation rate is dependent on the molecular weight, actually the lin-

Table II
Diffusion Coefficients of Pyrene in PDMS and Squalane

system	$\eta_{20\,°\mathrm{C}}$, cP	D_{Stokes},[a] cm^2 s^{-1}	D_{exptl}[b] × 10^6, cm^2 s^{-1}
PDMS	1	9.3×10^{-6}	6.71
PDMS	7	1.3×10^{-6}	2.93
PDMS	10	9.3×10^{-7}	2.39
PDMS	20	4.7×10^{-7}	1.88
PDMS	50	1.8×10^{-7}	1.70
PDMS	5×10^2	1.8×10^{-8}	1.50
PDMS	5×10^3	1.8×10^{-9}	1.15
PDMS	6×10^4	1.5×10^{-10}	1.05
PDMS	6×10^5	1.5×10^{-11}	1.00
PDMS	1×10^6	9.3×10^{-12}	0.93
PDMS	2.5×10^6	3.7×10^{-12}	0.87
squalane	35.4	2.6×10^{-7}	0.55

[a] D_{Stokes} is calculated from Stokes–Sutherland equation, $D = kT/4\pi\eta r$, which is derived from Stokes law in the case of a moving particle smaller than the solvent molecules. Since $k = 1.38 \times 10^{-16}$ erg·K^{-1}, $r = 3.46$ Å, then $D = 9.3 \times 10^{-6}/\eta$. [b] D_{exptl} is calculated from experimental rate constants of excimer formation, k_1, and by the Smoluchowski equation ($D = 0.9423 \times 10^{-15} k_1$).

ear macromolecular chain length; beyond this point the rate is nearly independent of chain length. Therefore, this property is related to the basic chemical structure of the polymer segment and the packing of the macromolecular chain in the bulk.

The sharp break in the rate constant with increasing viscosity or degree of polymerization, (DP), is also exhibited by the density and the coefficient of thermal expansion of these materials (Table I). These data are quite in accord with a large influence of polymer free volume on the solute diffusion. It is pertinent to note that PDMS tends to exhibit cyclization at low DP, a feature that could explain the sharp break in the properties of these compounds with increased DP.[13]

Table II lists the diffusion coefficient of pyrene in bulk PDMS and squalane. D_{exptl} is the diffusion coefficient calculated from the experimental rate constants of excimer formation by eq 1. D_{Stokes} is the diffusion constant calculated from the solvent viscosity and the solute size by the Stokes–Sutherland equation[14,15]

$$D = kT/4\pi\eta r \tag{6}$$

which is normally used if the molecular dimensions of the solute are smaller than those of the solvent. It can be seen that Stokes law is not applicable either in PDMS or squalane and that D_{Stokes} is smaller than D_{exptl}. In the more viscous PDMS at higher molecular weight the deviation is larger (up to 10^6). Fujita[16] and Frisch[17] have related the diffusion constant, D, of a solute to the solvent viscosity via an expression of the form

$$\ln D = C - (v^*/v_{\mathrm{v}}) \ln \eta \tag{7}$$

where C is a constant and v^* and v_{v} refer to the minimum hole size for the jump process of diffusion of small molecules and viscous flow of solvent molecules, respectively. That the ratio v^*/v_{v} will be less than unity in viscous liquids and in bulk polymers indicates that D varies inversely with a power less than 1, of solvent viscosity, in agreement with the present data and the earlier data of Olea and Thomas.[9]

From the view of the macro- and microviscosity,[4,5,18,24] the macroviscosity of the solvent coincides with gross movement of the complete solvent molecule, but the microviscosity or the local viscosity is derived from the motion of a portion of the molecule, i.e., a segmental or side-group movement. Increasing the degree of polymerization or molecular weight increases the macroviscosity rather than the microviscosity. The microviscosity can be estimated from measurement of the degree of polarization of 2-methylanthracene fluorescence.[4,19] Such measurements show that the microviscosity in the highest molecular weight PDMS is less than 10 cP, while the macroviscosity is equal to 2.5×10^6 cP. The comparatively long Si–O and Si–C bonds reduce steric conflict, i.e., hindrance between methyl groups on neighboring silicon atoms, which facilitates freedom of rotation of methyl group about the Si–O and Si–C bonds. This unique structural feature leads to a significant free volume in bulk PDMS. This also can be seen from the very low glass transition temperature, T_{g} (150 K), and a larger value of the thermal expansion coefficient, α_{f} ($13\text{–}10 \times 10^{-4}$) than other polymers ($<6 \times 10^{-4}$), since $f_{\mathrm{T}} = f_{\mathrm{g}} + \alpha_{\mathrm{f}}(T - T_{\mathrm{g}})$, where f_{T} and f_{g} is the free-volume fraction at temperature T and T_{g}, respectively.[21] It is suggested that the free-volume fraction is related to microviscosity in a polymer matrix. The polymer with the larger free volume has the lower microviscosity. The diffusion of small molecules such as pyrene does not require the movement of the whole solvent macromolecule. Segmental stretching or rotation of side groups gives rise to solvent holes that are sufficient for solute diffusion. Changing the basic segment structure changes the microenvironment and the diffusion rate of solutes in PDMS solvent; similar effects are not noted in hydrocarbon squalane, in polystyrene, or in epoxy resin.

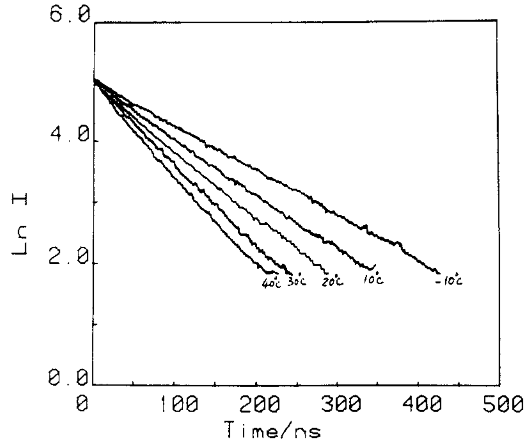


Figure 7. Decay of 5 mM pyrene fluorescence monitored at 400 nm in 50 cP poly(dimethylsiloxane) at various temperatures.

Effects of Temperature-Induced Viscosity Changes. Figure 7 shows the fluorescence time-dependent profiles of 5 mM pyrene monitored at 400 nm in PDMS ($\eta_{20\,°\mathrm{C}} = 50$ cP) at various temperatures. A marked increase in decay rate of pyrene fluorescence was observed on increasing the temperature from −12 to +40 °C. The viscosities and the measured rate constants of excimer formation in the above system from −12 to +40 °C are presented in Table III. A change in temperature from −12 to +40 °C produced a total viscosity variation of 4-fold and a k_1 variation of 5-fold. Although at −12 °C the viscosity of PDMS studied is 116.1 cP, the k_1 value at this temperature is even smaller than that in 2.5×10^6 cP of PDMS at 20 °C. Temperature effects in other PDMS's (5×10^3 cP, 1×10^6 cP at 20 °C) and in squalane were also tested, and similar temperature effects on the rate constant of excimer formation were observed. A comparison of Tables I and III indicates the different effects of viscosity on the excimer formation rate induced via variation in temperature and molecular weight. From the concept of macroviscosity and microviscosity, the data show that temperature changes both the macroviscosity and microviscosity to the same extent.

Table III
Dependence of Rate Constants of Excimer Formation on Changes of Viscosity via Temperature Variation in PDMS (η = 50 cP at 20 °C)

T, °C	η_T, cP	k_0,[b] ×10^6 s^{-1}	k_1,[c] ×10^9 M^{-1} s^{-1}
-12	116.1	2.10	0.80
-10	109.5	2.11	0.83
-6	97.6	2.12	0.88
-2	87.3	2.13	0.94
0	82.7	2.20	1.01
6	70.6	2.22	1.24
10	63.7	2.32	1.31
15	56.3	2.26	1.45
20	50.0	2.30	1.78
25	44.6	2.32	2.13
30	39.9	2.35	2.28
35	35.8	2.39	2.46
40	32.2	2.43	2.71

[a] Viscosity at T (°C) calculated from the equation

$$\eta_T = Ae^{E_\eta/RT} \qquad E_\eta = 16.7\ \mathrm{kJ{\cdot}M^{-1}}\,{}^{20}$$

[b] The decay rates in the absence of excimer, $k_0 = k_{im} + k_{fm}$. [c] The excimer formation rate, k_1.

The earlier data[4] indicate that if the ratio of activation energy of reaction to viscous flow (E_a/E_η) is ≥1, then the slope of ln k_q vs ln (T/η) is unity; if $E_a/E_\eta < 1$, then the slope is less than 1. The former case corresponds to Stokes law and the latter to a non-Stokes condition; the smaller E_a/E_η leads to greater deviations from Stokes law. The data of the present paper are in agreement with the above conclusion. The Arrhenius plots of ln k_1 versus ln (T/η) and ln k_1 vs $10^3/T$ for PDMS of 50 cP were reasonably linear over the full temperature range studied. The activation energies of excimer formation in PDMS of 50 cP were then obtained as 16.2 kJ·M^{-1}, which is close to that of viscous flow, 16.7 kJ·M^{-1}.[20] The slope of ln k_1 vs ln (T/η) is 0.93, which is close to unity.

According to the free-volume theory, the temperature effect on diffusion and relaxation processes should follow the WLF equation

$$\log A_T = -\frac{C_1^g(T - T_g)}{C_2^g + (T - T_g)} = \log \frac{\tau_T}{\tau_g} \tag{8}$$

where A_T is the shift factor and C_1^g and C_2^g are two constants at the glass transition temperature depending on the chemical structure of the polymer matrix. τ_T and τ_g are the correlation times at temperature T and T_g, respectively. T_g is the glass transition temperature. τ is defined as the reciprocal of the rate constant of the excimer formation, of this process. From eq 8 and the definition of τ, eq 9[22] would hold. The plot of ln k_1 vs $10^3/T$, calculated from eq 9, is shown in Figure 8 as a broken curve; the values of C_1^g (6.1), C_2^g (69.0), and T_g (150 K) are given by Ferry.[21] As seen in Figure 8, the slope of the calculated plot is consistent with the experimental one in DPMS of 5 × 10^3 and 1 × 10^6 cP within the studied temperature range (-20 to +40 °C). In the case of 50 cP PDMS, the fitting is only good in the low-temperature range. The slope of the experimental plot of 50 cP is higher than the calculated curve at temperatures above 10 °C. This particular PDMS is located at the transition point of plot of log k_1 vs log η. Studies of the temperature effect again show that PDMS of 50 cP possesses both simple liquid and polymer properties and mostly resembles simple liquids at temperatures above 10 °C. This also corresponds to the data shown in Table I.

$$\begin{aligned} \ln k_1 &= (-\log \tau_T)/\ln e + \text{constant} \\ &= \frac{C_1^g(T - T_g)}{C_2^g + T - T_g} + \text{constant} \end{aligned} \tag{9}$$

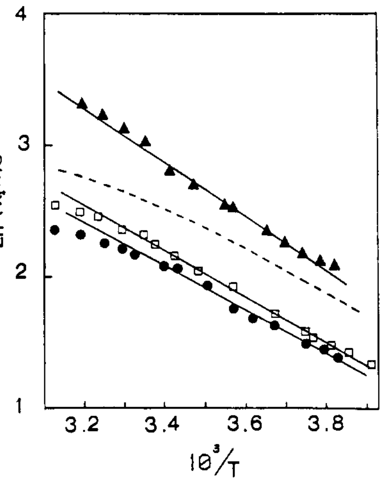


Figure 8. Plots of ln k_1 vs $10^3/T$, for pyrene excimer formation in PDMS: $\eta_{20\,°C}$ (cP) = 50 (▲), 5 × 10^3 (□), 1 × 10^6 (●). The broken curve represents the plot calculated from the WLF equation (eq 9).

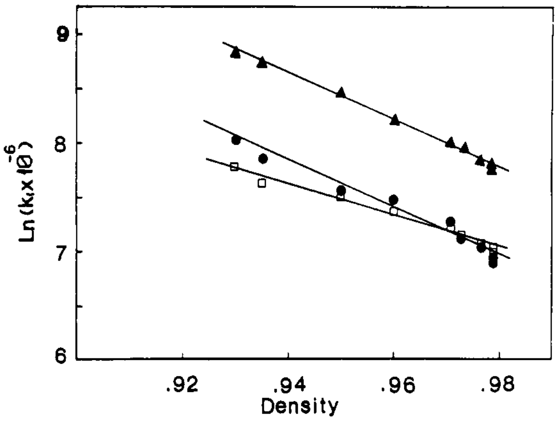


Figure 9. Relationship between the natural logarithm of the diffusion rate constant, ln k, and the density of PDMS. Diffusion processes are as follows: excimer formation of pyrene (●) and quenching of excited pyrene by phthalic anhydride (▲) and by nitrododecanoic acid (□).

Free Volume and Density. Figure 9 shows the relationship between the diffusion-controlled rate constants and densities of poly(dimethylsiloxanes). The diffusion processes included excimer formation of pyrene, quenching of excited singlet pyrene by phthalic anhydride, and quenching by nitrododecanoic acid. Plots of ln k vs density are nearly linear and

$$\ln k = c - a(\text{density}) \tag{10}$$

where c is the intercept and a is the absolute slope value. Studies in 1 cP of dimethylsiloxane are an exception, simply due to the fact that this compound is not a polymer (DP = 1). Increasing the degree of polymerization increases the density of polymer but has little effect above DP = 50.

According to the Cohen and Turnbull theory and the Smoluchowski equation, the relationship between free volume, V_f, of polymer and the diffusion rate, k, should follow

$$\ln k = c' - (a'/V_f) \tag{11}$$

where c' and a' are the constants for a given diffusion process.[23,4]

Table IV
Effect of Percentage of Phenyl Groups[a] on Quenching of Pyrene Fluorescence[b]

phenyl, %	density	T_g,[c] °C	k_q, M^{-1} s^{-1}
0	0.97	−118	3.13×10^9
4–6	0.98	−84	2.30×10^9
18–21	1.05	−75	7.33×10^8
45–55	1.15	−37	$\ll 10^7$

[a] In dimethyldiphenylsiloxane copolymer. [b] Quenching by phthalic anhydride. [c] The glass transition temperature of polymer was measured by the change of phosphorescence intensity of bromopyrene incorporated in polymer with temperature.

Table V
Effect of Length of Alkyl Groups[a] on Quenching of Pyrene Fluorescence[b]

alkyl	density	T_g,[c] °C	k_q, M^{-1} s^{-1}
methyl	0.97	−118	3.13×10^9
hexyl	0.91	−86	1.08×10^9
octyl	0.91	−66	5.0×10^8
octadecyl	0.89	+39	$\ll 10^7$

[a] In poly(methylalkylsiloxanes). [b] Quenching by phthalic anhydride. [c] See Table IV.

With eqs 10 and 11, the following relationship between the free volume and the density of PDMS is obtained

$$1/V_f = c'' + a''(\text{density}) \qquad (12)$$

where $c'' = (c' - c)/a'$ and $a'' = a/a'$. Equation 12 illustrates that the free volume is inversely and linearly proportional to the density of the studied PDMS.

The above relationship between the free-volume density and the diffusion rate constants indicates that tighter packing of the polymer chains gives rise to a smaller free volume and to a restricted molecular mobility of small molecules in the polymer matrices.

However, the above relationship (eqs 10 and 12) is not applicable on changing the basic polymer structure, for example, introducing phenyl groups into the PDMS or replacing a methyl group with longer chain alkyl moieties. Table IV shows that increasing the percentage of phenyl content in PDMS increases the glass transition temperature T_g, and reduces the quenching rate constant of pyrene fluorescence by phthalic anhydride. The reaction rate becomes too small ($k \ll 10^7$ M^{-1} s^{-1}) to measure when the phenyl content in PDMS is above 45–55%. Similar phenomena were observed in poly(methyloctadecylsiloxanes) (shown in Table V). Although the density of this polymer is smaller than that of poly(dimethylsiloxanes), the long alkyl groups introduce rigidity into the polymer chains similar to the effect of phenyl groups. The longer alkyl groups are more efficient in increasing T_g and in reducing the quenching rate. It is suggested that the diffusion of small molecules in the polymer is hindered due to the loss of free rotation of alkyl groups about the Si–O chain. From the point of view of free-volume theory, increasing the glass transition temperature reduces the free volume at room temperature; therefore, the movement of small molecules in polymer is restricted.

Conclusion. This study shows that pyrene molecules diffuse to form excimers dynamically in poly(dimethylsiloxanes) but not in epoxy resin or polystyrene. Compared with simple liquids, the dissociation of excimer pyrene in PDMS is not efficient, and monoexponential decays of excited monomer pyrene were observed.

The relationship between excimer formation rate and macroviscosity is consistent with earlier data for the quenching of excited pyrene by phthalic anhydride.[4] Increasing the degree of polymerization of PDMS has little effect on the free volume of microviscosity above the critical transition molecular weight. This transition occurs with PDMS of 50 cP where the degree of polymerization is close to 50. However, variation of the temperature changes both macroviscosity and microviscosity to the same extent. It is suggested that free volume is related to the microviscosity of the polymer matrices. In linear PDMS, the free volume is inversely and linearly proportional to the density of the polymer. Replacement of the methyl group with phenyl groups or longer chain alkyl groups in PDMS imposes a restriction on the rotation of the side groups about the polymer chain and decreases the diffusion of small molecules in polymer.

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