

Excimer fluorescence technique for study of polymer-segment mobility: applications to pyrene-labelled poly(methyl methacrylate) and poly(methyl acrylate) in solution[†]

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An excimer fluorescence technique for the study of polymer-segment mobility has been developed and applied to pyrene-labelled poly(methyl methacrylate) and poly(methyl acrylate) polymers in solution. The results of the study have been interpreted in terms of Kramers' theory for the crossing of a potential barrier by a particle embedded in a viscous medium. The results show that the internal viscosity has a solvent-independent part and lead to an estimate of the dimensionless internal viscosity parameter introduced by Cerf.

(Keywords: fluorescence spectroscopy; internal viscosity; Kramer's theory; polymer segment mobility; poly(methyl methacrylate); pyrene excimer)

INTRODUCTION

Although the concept of internal viscosity was introduced by Kuhn¹ almost 40 years ago, there remains some uncertainty about the dependence of the internal viscosity on the solvent viscosity. While it is acknowledged^{2,3} that the internal viscosity coefficient is proportional to the solvent viscosity η for small values of the solvent viscosity (less than 1 cP) and also, practically, for large values of the solvent viscosity (larger than 15 cP), there is no agreement on whether the internal viscosity has a solvent-independent part in the intermediate range of the solvent viscosity. In an effort to clarify the concept of internal viscosity, we investigated the segmental motions of two pyrene-labelled poly(methyl methacrylate) polymers and a pyrene-labelled poly(methyl acrylate) polymer in solution.

A technique was adopted based on excimer fluorescence. This technique has been used by Goldenberg and coworkers⁴ to study the rates of conformational transitions of small molecules. However, to our knowledge, the technique has not been applied to the study of polymer-segment motions in solution.

An excimer is formed by the association of an excited molecule with another molecule in its ground state⁵. Such an excimer is characterized by a broad structureless fluorescence which is shifted to longer wavelengths compared to the fluorescence spectrum of the isolated molecule. Excimer formation may also take place by intramolecular processes in polymers which have excimer-forming groups covalently attached to the repeating units. For example, excimer fluorescence has been observed in dilute solutions of polymers such as polystyrene, poly(vinyl naphthalene) and poly(1-naphthyl methacrylate)⁶⁻⁸.

At a low enough temperature in a solution of small excimer-forming species, the extent of excimer formation depends on the rate constant for the diffusion-controlled reaction of an excited monomer and a monomer in the ground state to form an excimer. If the excimer-forming species are covalently attached to a polymer chain, this

rate constant will in addition depend on the polymer-segment mobility. Therefore, we can learn about the polymer-segment mobility by measuring the excimer fluorescence of polymers carrying excimer-forming groups. In the Results and Discussion section of this paper, we shall describe in more quantitative terms the technique outlined above and illustrate the use of this technique to study the polymer-segment mobility.

EXPERIMENTAL

Copolymers

Two random copolymers (see Figure 1) of 1-pyrenylmethyl methacrylate (π MMA) and methyl methacrylate (MMA) were prepared by free-radical polymerization in benzene at 60°C with the use of azobisisobutyronitrile as a catalyst⁹. The mole fractions of pyrenylmethyl methacrylate in the copolymers as determined by u.v. absorption spectroscopy were 0.057 and 0.032, respectively. Similarly, a random copolymer of methyl acrylate and 1-pyrenylmethyl acrylate was prepared by free-radical polymerization. The mole fraction of 1-pyrenylmethyl acrylate in this copolymer was 0.030.

Solvents

Ethyl acetate (Burdick and Jackson Laboratories, 'Distilled in Glass')* was used without further purification. Glycerol tripropionate was found to have an acid content of 2×10^{-6} equivalent per gram and was purified according to the following procedures. A 350 cm³ portion of glycerol tripropionate was washed twice with 20% aqueous K₂CO₃ and thrice with water. The volatile components were distilled away from the washed liquid at room temperature and reduced pressure whereupon the

* Certain commercial equipment, instruments or materials are identified in this paper in order to specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment is necessarily the best available for the purpose

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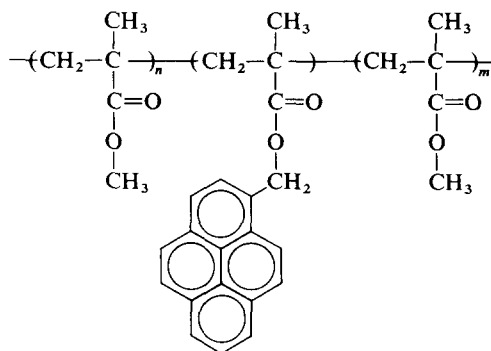


Figure 1 Chemical structure of the copolymer of 1-pyrenylmethyl methacrylate and methyl methacrylate

Table 1 Densities and viscosities of ethyl acetate-glycerol tripropionate mixtures at 22.0°C

Weight per cent glycerol tripropionate	Density (g cm ⁻³)	Viscosity (cP)
0.0	0.8982	0.440
7.5	0.9109	0.496
14.4	0.9227	0.558
20.6	0.9334	0.626
43.8	0.9730	1.030
50.0	0.9835	—
54.1	0.9915	1.338
64.0	1.010	1.810
91.4	1.063	5.340
100.0	1.080	—

washed liquid became clear. The washed liquid was then dried over molecular sieves (Linde 4A) *in vacuo*, filtered, and distilled away, the distillate was collected at ~173°C/20 mm until 75% of the liquid was collected. The distillate was further purified by distilling *in vacuo* with the use of a 6 inch Vigreux column.

Densimetry

The densities of the purified glycerol tripropionate and a 1:1 by weight mixture of glycerol tripropionate and ethyl acetate were determined at 22.0°C with a calibrated pycnometer. The density of ethyl acetate at 22.0°C was interpolated from densities at 20°C and 25°C¹⁰. The densities of other mixtures of ethyl acetate and glycerol tripropionate were estimated by linear interpolation.

Viscometry

The viscosity of ethyl acetate at 22.0°C was interpolated from viscosities at 15.0°C and 25.0°C¹⁰. The kinematic viscosities of some mixtures of ethyl acetate and glycerol tripropionate were determined at 22.0°C with Cannon-Ubbelohde viscometers. The results are given in Table 1. The viscosities of other mixtures were estimated graphically from the plot of the square root of viscosity against the weight fraction of glycerol-tri-propionate.

Refractive indices

The refractive index of ethyl acetate at 22.0°C was interpolated from the indices for 20.0°C and 25.0°C¹⁰. The refractive index of glycerol tripropionate was estimated from the value of 1.43175 at 19°C¹¹ and the temperature coefficient of $-0.00049/^\circ\text{C}$ for ethyl acetate and propyl formate¹⁰. The refractive indices of ethyl acetate-glycerol tripropionate mixtures were calculated with the use of Gladstone-Dale formula¹².

Fluorescence measurements

Uncorrected fluorescence spectra were taken on a spectrofluorimeter equipped with a thermostatically controlled sample holder as well as a reference detector to correct for variation in the lamp intensity. The concentrations of the π MMA-MMA copolymer in solutions were 5×10^{-6} g cm⁻³ with optical density of 0.1. All solutions were degassed by repeated freeze-pump-thaw cycles. All the spectra were taken with an excitation wavelength of 343 nm and the bandpasses of 10 nm and 5 nm for the excitation monochromator and the emission monochromator, respectively.

RESULTS AND DISCUSSION

Kinetics of excimer fluorescence

The fluorescence spectrum of the copolymer of pyrenylmethyl methacrylate and methyl methacrylate (hereafter referred to as π MMA-MMA copolymer) in ethyl acetate at 22.0°C is shown in Figure 2. The spectrum, exhibiting a structured violet fluorescence emission band with a maximum at 377 nm, and a broad structureless blue fluorescence with a maximum at 480 nm, is similar to the fluorescence spectra of concentrated pyrene solutions⁵. The structured band is due to the emission from excited, isolated pyrenyl groups, hereafter referred to as monomers while the structureless band is due to the emission from pyrenyl excimers, hereafter referred to as excimers.

The fluorescence characteristics of the π MMA-MMA copolymer in solution will be treated with a kinetic analysis developed by Stevens and Ban in their study of

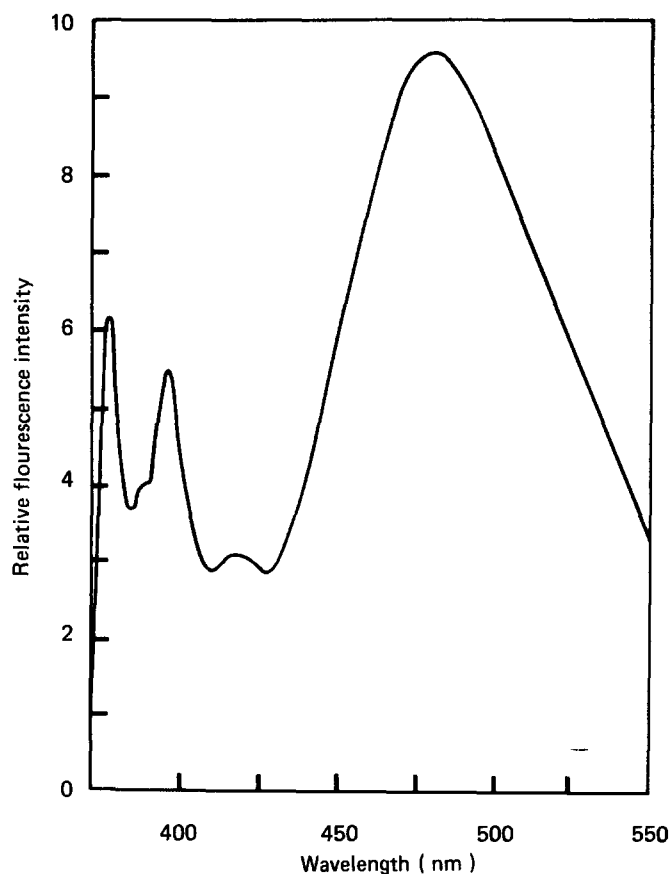
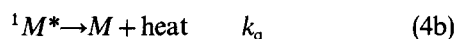
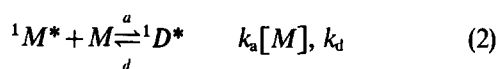


Figure 2 Uncorrected fluorescence spectrum of the π MMA-MMA copolymer in ethyl acetate at 22.0°C. The excitation wavelength was 343 nm

intermolecular excimers formed by substituted naphthalenes¹³. We consider the following processes:



Here, ${}^1M^*$, ${}^1D^*$ and M stand for excited monomers, excimers and ground-state monomers; $h\nu_M$ and $h\nu_D$ represent monomer fluorescence and excimer fluorescence; and the symbols beside the processes are for the rate constants. Under photostationary conditions,

$$d[{}^1D^*]/dt = 0 = k_a[M][{}^1M^*] - (k_d + k_{TD} + k_Q)[{}^1D^*]$$

Rearrangement gives:

$$\frac{[{}^1D^*]}{[{}^1M^*]} = \frac{k_a[M]}{k_d + k_Q + k_{TD}} \quad (5)$$

We define F_D to be the fluorescence intensity of the excimers at 480 nm where only the excimers fluoresce and note that $F_D = C_D k_{TD} [{}^1D^*]$. The constant C_D contains an instrument sensitivity factor and another factor which converts the intensity at a given wavelength into total integrated efficiency; neither of these factors is necessary for our purpose. Then, after similarly defining F_M at 377 nm for the monomers, we have:

$$\frac{F_D}{F_M} = \left(\frac{C_D}{C_M} \right) \left(\frac{k_{TD}}{k_{TM}} \right) \left(\frac{k_a[M]}{k_d + k_Q + k_{TD}} \right) \quad (6)$$

For intramolecular excimer formation from pyrenyl groups attached to a polymer chain, $[M]$ is proportional to the probability that other pyrenyl groups are within some volume element about a given pyrenyl group. In our study, we have changed the solvent viscosity by changing the composition of the mixed solvent of ethyl acetate and glycerol tripropionate. Since these two solvents have similar chemical structures, we shall assume that solvent viscosity has been changed without modifying polymer conformations significantly, and we shall treat $[M]$ as a constant. Further, since for excimer fluorescence from concentrated pyrene solutions (k_{TD}/k_{TM}) has been observed to be independent of the solvent and the temperature⁵ equation (6) simplifies to:

$$F_D/F_M = ck_a/(k_d + k_Q + k_{TD}) \quad (7)$$

where c is a constant.

We now consider the relative importance of the terms in the denominator. Forster¹⁴⁻¹⁶ has found that up to about 60°C the dissociation rate constant, k_d , of the pyrene excimer is small compared to the transition rate k_{TD} . Similarly, for the π MMA-MMA copolymer in ethyl acetate, Figure 3 shows that the relative amount of excimer fluorescence increases as the temperature is

increased in the range 22°C to 70°C. This increase in excimer fluorescence implies that we have not approached the region where dissociation competes with excimer fluorescence. Thus, here again k_d is negligible compared to k_{TD} and we have:

$$F_D/F_M = ck_a/(k_Q + k_{TD}) \quad (8)$$

Figure 4 shows part of the fluorescence spectra of the π MMA-MMA copolymer in ethyl acetate-glycerol tripropionate mixtures at 22.0°C. These spectra have an isoemissive point at 440 nm. The presence of an isoemissive point implies^{17,18} that the quantum efficiency of excimer fluorescence:

$$q_D = k_{TD}/(k_Q + k_{TD}) \quad (9)$$

has not changed with the solvent viscosity. Therefore, equation (8) simplifies to:

$$F_D/F_M = Ck_a/k_{TD} \quad (10)$$

where C is a constant.

Birks and Alwattar¹⁹ have shown that for the pyrene excimer in solution k_{TD} obeys the relation:

$$k_{TD} = n^2 k_{TD}^\circ \quad (11)$$

where n is the refractive index of the solvent and k_{TD}° is independent of the solvent and the temperature. Combining equations (10) and (11), we obtain:

$$F_D/F_M = Ck_a/(n^2 k_{TD}^\circ) \quad (12)$$

Thus, $F_M/(n^2 F_D)$ is proportional to $1/k_a$.

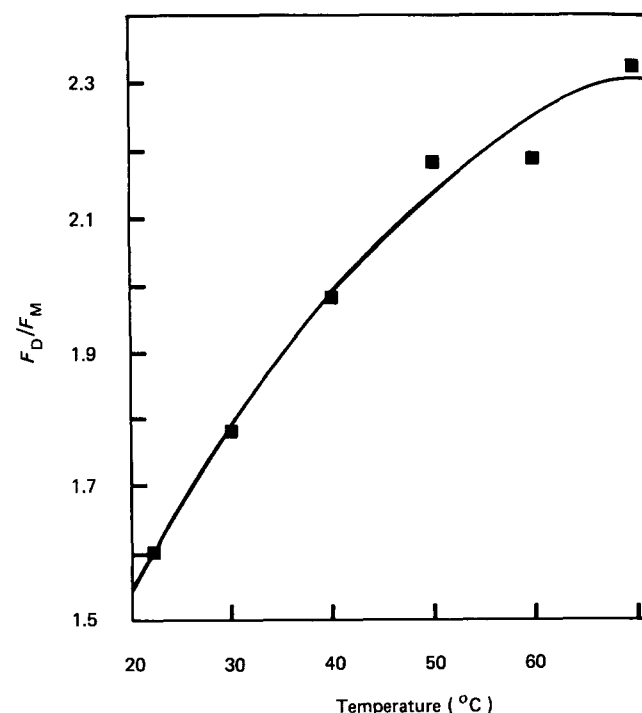


Figure 3 Temperature dependence of the ratio F_D/F_M for the π MMA-MMA copolymer in ethyl acetate. F_D and F_M are the fluorescence intensities at 480 nm and 377 nm, respectively. The excitation wavelength was 343 nm

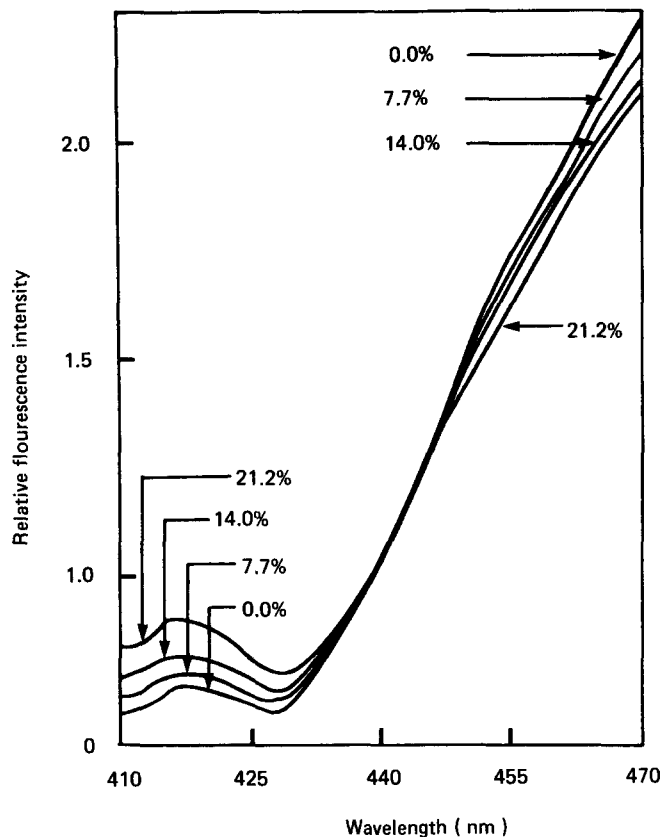


Figure 4 Fluorescence spectra of the π MMA-MMA copolymer in ethyl acetate-glycerol tripropionate mixtures. Curve labels: below 440 nm, from bottom, 0.0, 7.7, 14.0 and 21.2 weight per cent glycerol tripropionate; above 440 nm, from top, 0.0, 7.7, 14.0 and 21.2 weight per cent glycerol tripropionate

Table 2 Viscosities, refractive indices and monomer-excimer fluorescence intensity ratios of the π MMA-MMA copolymer in ethyl acetate-glycerol tripropionate mixture at 22.0°C

Weight per cent glycerol tripropionate	η Viscosity (cP)	n Refractive index	$\frac{F_M n_0^2}{F_D n^2}$	$\frac{F_D n^2 \eta}{F_M n_0}$
0.0	0.440	1.3714	0.57	0.77
7.7	0.497	1.3757	0.64	0.78
14.0	0.554	1.3793	0.70	0.80
21.2	0.634	1.3833	0.76	0.84
44.0	1.037	1.3960	0.89	1.16
44.0	1.037	1.3960	0.90	1.15
57.9	1.488	1.4042	1.12	1.33
64.5	1.842	1.4082	1.16	1.59
64.5	1.842	1.4082	1.12	1.64
76.8	3.00	1.4159	1.38	2.16
76.8	3.00	1.4159	1.34	2.24
84.4	4.07	1.4204	1.48	2.75
91.0	5.26	1.4245	1.66	3.17
91.0	5.26	1.4245	1.63	3.24

Polymer-segment mobility

Equation (12) allows us to study from steady-state measurements the effect of solvent viscosity on k_a , the rate constant for the diffusion-controlled association of an excited pyrenyl group and a ground-state pyrenyl group to form a pyrenyl excimer. We first point out that for the π MMA-MMA copolymer solutions of the concentration chosen for the measurements, pyrenyl excimers are for-

med by intramolecular association of pyrenyl groups attached to a polymer chain, and not by intermolecular association. This statement is supported by the observation that a sixfold increase of the copolymer concentration in ethyl acetate from the chosen concentration of $5 \times 10^{-6} \text{ g cm}^{-3}$ does not change the ratio F_D/F_M . Furthermore, since the pyrenyl groups are covalently attached to an isolated polymer chain and must diffuse toward each other under the restriction of the polymer chain, k_a must be a measure of polymer-segment mobility, just as the rotational correlation time of the spin label covalently attached to a polymer chain has been shown to reflect polymer-segment mobility²⁰.

Table 2 gives, for the π MMA-MMA copolymer in ethyl acetate-glycerol tripropionate mixtures at 22.0°C, the solvent viscosities (η) the refractive indices (n), the ratios $(F_M n_0^2)/(F_D n^2)$ and $(F_D n^2 \eta)/(F_M n_0)$, where n_0 is the refractive index of ethyl acetate. Figure 5 is a plot of $(F_M n_0^2)/(F_D n^2)$ as a function of η .

To discuss the results given in Table 2 and Figure 5, we shall use Kramers' theory²¹ for the crossing of a potential barrier by a particle embedded in a viscous medium. Kramers' theory gives the probability P per unit time that a particle crosses the potential barrier in terms of m and z , the mass and friction coefficient of the moving particle, ω_A and ω_C , the circular vibration frequencies corresponding to the curvatures of the potential in the initial state and at

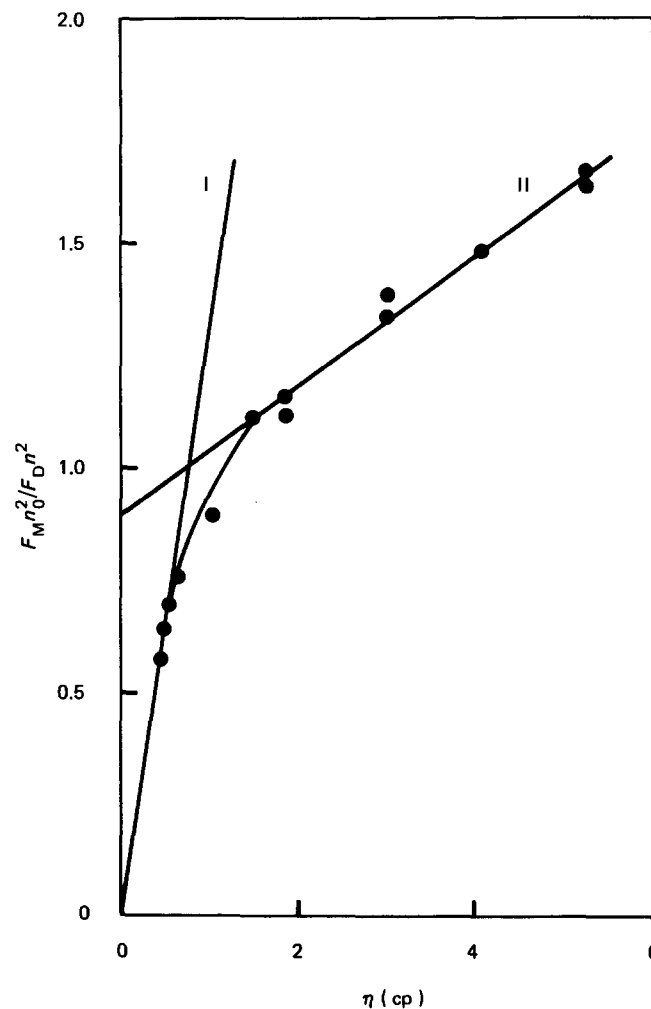


Figure 5 Plot of $(F_M n_0^2)/(F_D n^2)$ as a function of solvent viscosity η . Symbols are defined in the text

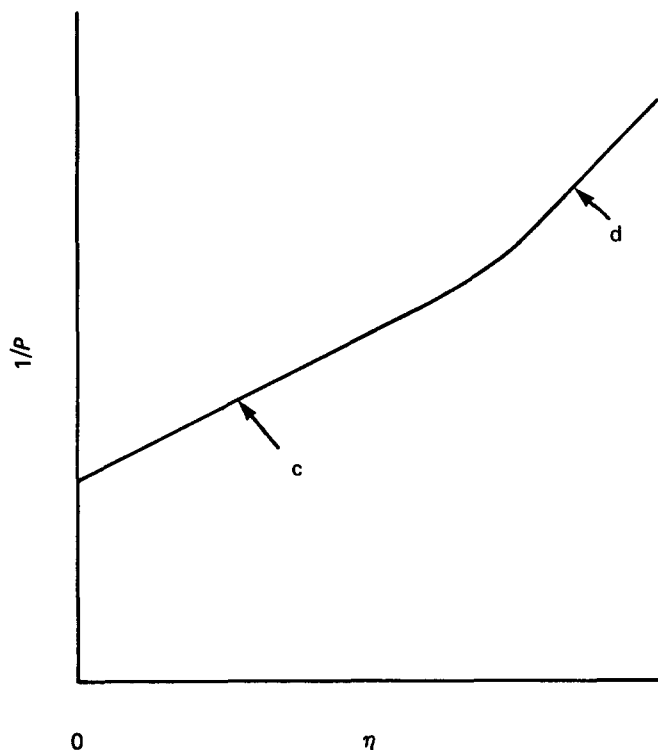


Figure 6 Inverse transition probability P^{-1} as a function of the solvent viscosity

the top of the potential barrier, respectively, and U_0 , the height of the potential barrier. In the case of high friction, $z/m \gg 2\omega_C$, the motion over the barrier is diffusional and P is given by^{21,22}:

$$P^{-1} = (2\pi z/\omega_A \omega_C m) \exp(U_0/kT) \quad (13)$$

On the other hand, for low friction, $2\omega_A \ll z/m \ll 2\omega_C$, P is given by^{21,22}

$$P^{-1} = (2\pi/\omega_A) [1 + z/(2\omega_C m)] \exp(U_0/kT) \quad (14)$$

Applying Kramers' theory, we shall consider k_a proportional to p . Furthermore, since z is proportional to the solvent viscosity, $k_a \eta$ and $(F_D n^2 \eta)/(F_M n_0^2)$, which is proportional to $k_a \eta$, must be independent of η in the diffusion limit of Kramers' theory. We see in Table 2 that $(F_D n^2 \eta)/(F_M n_0^2)$ is nearly independent of η only for the first four solutions with lower solvent viscosities ($\eta \leq 0.634$ cP). Hence, for the segmental motions of the π MMA-MMA copolymer, the diffusion limit of Kramers' theory is approximately obeyed only at lower solvent viscosities.

Figure 6 is a plot of P^{-1} as a function of the solvent viscosity η , when all other parameters are kept constant. Since z is proportional to η , the diffusional limit is obtained at large η values where P^{-1} curve approaches a straight line (labelled d in Figure 6) going through the origin. At small η values where P^{-1} is non-diffusional, the slope of P^{-1} curve (straight line c in Figure 6) is only half that of the other straight line, as is expected from equations (13) and (14). Thus, Kramers' theory predicts that a plot of the inverse rate constant k_a^{-1} , which is proportional to P^{-1} , as a function of the solvent viscosity shows an initial upward curvature.

Goldenberg and coworkers⁴ have measured the

fluorescence spectra for compounds of the type $\text{ArCH}_2\text{XCH}_2\text{Ar}$ in solvents of various viscosities, where the chromophore Ar is phenyl, 1-naphthyl, or 4-biphenyl and X is $-\text{CH}_2-$, $-\text{O}-$, $-\text{NH}_2^+$, $-\text{N}(\text{CH}_3)_2^+$ or $-\text{N}(\text{COCH}_3)-$. From their measurements, they obtained the viscosity dependence of the rates of conformational transitions. They have found that, for these compounds, the plot of the inverse rate constant against the solvent viscosity shows the initial upward curvature predicted by Kramers' theory and has a limiting slope which increases with the increasing bulk of the chromophore.

Figure 5 gives a plot of $(F_M n_0^2)/(F_D n^2)$, which is proportional to k_a^{-1} , as a function of η . The experimental curve of Figure 5 is concave downwards, in contrast to the results obtained by Goldenberg and coworkers⁴, and also in contrast to the prediction of Kramers' theory. However, our experimental result is very similar to the results from Biddle and Nordstrom's²³ fluorescence depolarization study of a diphenylanthracene-labelled polystyrene and the results from time-dependent fluorescence polarization study of an anthracene-labelled polystyrene²⁴. Thus, we do not find the straightforward application of Kramers' theory appropriate for the whole range of η .

We shall consider now the model of Cerf²⁵ to interpret the experimental results shown in Figure 5. According to this model, the highly diversified local conformational changes that bring two pyrenyl groups together are approximately represented by two classes of relaxation which coexist in the whole range of η and which both obey the diffusional limit, equation (13), and the non-diffusional limit, equation (14), of Kramers' theory. Class I conformational changes involve larger numbers of repeating units, with larger frictional coefficients, than Class II. On the other hand, Class II conformational changes demand surmounting of larger potential barriers (of the type discussed by Kuhn¹) than Class I.

Figure 7 gives the plots of the inverse rate constants for Class I and Class II conformational changes against the solvent viscosity. As in Figure 6, the inverse rate constant for each class of conformational changes is given by two straight lines, the diffusional limit (labelled Id or Id) at higher solvent viscosities and the non-diffusional limit (labelled Ic or Ic) at lower viscosities.

Using the model of Cerf, we now interpret the experimental plot of the intensity ratio $(F_M n_0^2)/(F_D n^2)$ vs. η in Figure 5. The contributions of Class I and Class II conformational changes to the intensity ratio, which is proportional to $1/k_a$, are given in Figure 5 by straight lines I and II, respectively. (These lines correspond to Id and Ic in Figure 7). Line I, which is the tangent at the origin, obeys the diffusional limit of Kramers' theory. Line II, which fits the data at higher values of η , has a non-zero intercept and obeys the non-diffusional limit of Kramers' theory. In addition, Line I has a larger slope than Line II, since Class I conformational changes involve polymer segments with larger frictional coefficients than Class II.

The dependence of the intensity ratio or $1/k_a$ on η then follow directly from the fact that the change in conformations is controlled by the fast process. At lower viscosities ($\eta < 0.6$ cp), Class I conformation changes are faster than Class II and more effective in bringing together two pyrenyl groups because they need to overcome smaller potential barriers. Hence, the intensity ratio of $1/k_a$ is well approximated by Line I. However, since Class I

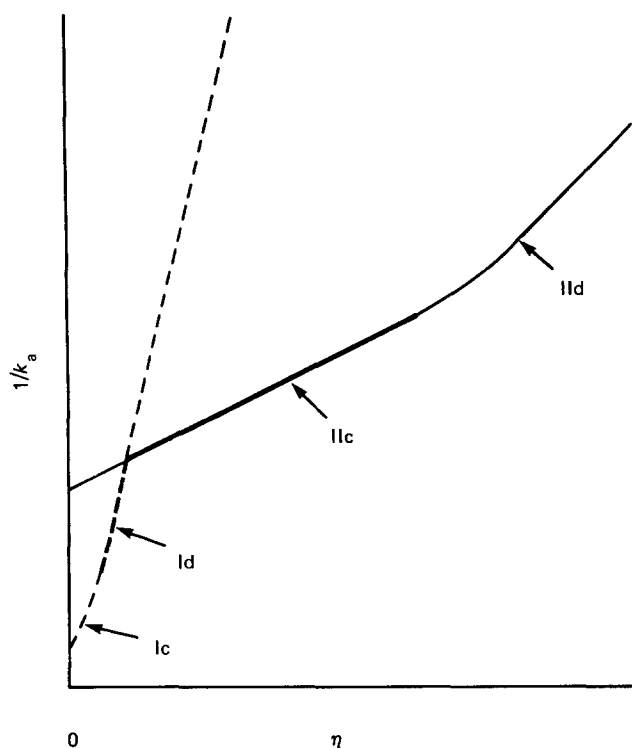


Figure 7 Inverse rate constants for Class I and Class II conformation changes against the solvent viscosity

conformation changes involve relatively large friction coefficients, they become slower than Class II at higher viscosities and less effective in bringing together pyrenyl groups. Consequently, the intensity ratio or $1/k_a$ is approximated by Line II at higher viscosities. The non-diffusional limit labelled Ic in Figure 7 is not observable because the solvent viscosity is never low enough. We expect to observe the diffusional limit labelled IId in Figure 7 if measurements are made at much higher viscosities.

The absolute value, η_i , of the x-intercept of Line II is a measure of internal viscosity and (η_i/η) gives the value of the dimensionless internal viscosity parameter defined by Cerf²⁶. From Line II, we obtained an η_i value of 6 cP for the π MMA-MMA copolymer containing 5.7 mol% π MMA (5.7%- π MMA/MMA). Similar measurements give an η_i value of 4 cP for a π MMA-MMA copolymer containing 3.2 mol% π MMA (3.2%- π MMA/MMA), and an η_i value of 3 cP for a copolymer of 1-pyrenylmethyl acrylate (π MA) and methyl acrylate (MA) containing 3.0 mol% π MA (3.0%- π MA/MA).

Comparison of η_i values of 3.2%- π MMA/MMA and 3.0%- π MA/MA, which are labelled with pyrenyl groups to nearly the same extent, led us to conclude that α -methyl groups have only a small effect on η_i or segmental mobility. Furthermore, we conclude from the higher η_i value for 5.7%- π MMA/MMA than for 3.2%- π MMA/MMA that segmental mobility is reduced as the extent of labelling with pyrenyl groups is increased.

Figure 8 gives a comparison of the intensity ratio $(F_M n_0^2)/(F_D n^2)$ as a function of the solvent viscosity for 5.7%- π MMA/MMA and for 1,3-bis-(1-pyrene)propane²⁷. We note that over the same viscosity range, the intensity ratio for 1,3-bis-(1-pyrene)propane is well represented by a straight line with a non-zero intercept (labelled C-3), while the one for 5.7%-

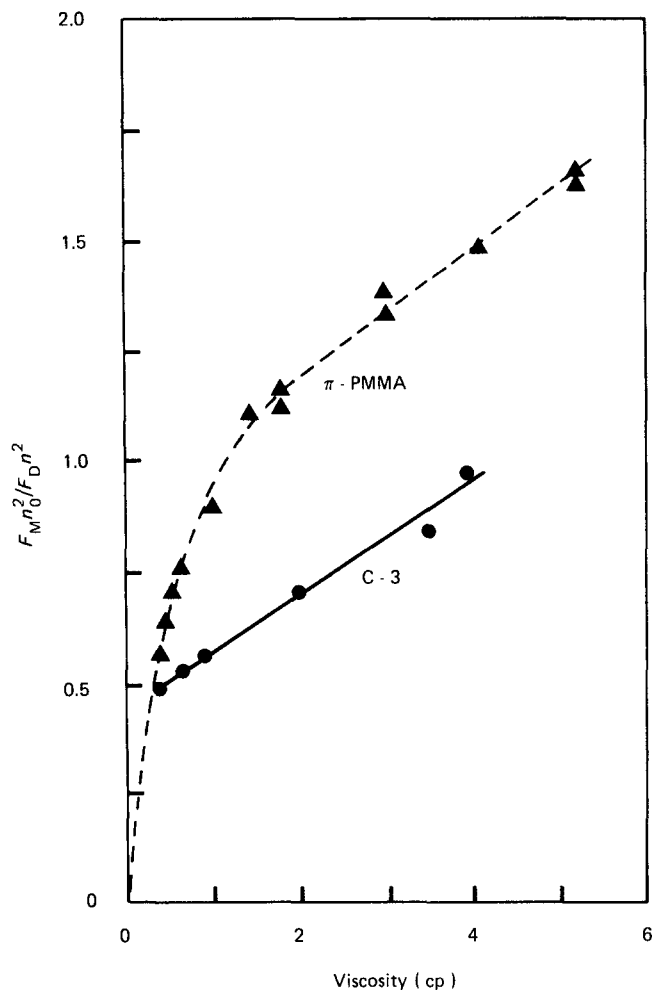


Figure 8 Plots of $(F_M n_0^2)/(F_D n^2)$ against the solvent viscosity for a pyrene-labelled poly(methyl methacrylate) polymer and 1,3-bis-(1-pyrene)propane. Symbols are defined in the text

π MMA/MMA (labelled π -PMMA) may be approximately represented by two lines obeying the diffusional and the non-diffusional limits of Kramer's theory, as we have discussed earlier. The intensity ratio for 1,3-bis-(1-pyrene)propane may be expressed by a line representing a single class of conformational changes because the chemical structure of 1,3-bis-(1-pyrene)propane has so few methylene units that conformational changes for bringing two pyrenyl groups together all require surmounting of potential barriers. These conformational changes therefore obey the non-diffusional limit of Kramer's theory in this viscosity range.

CONCLUSION

We have used the excimer fluorescence technique to study the effect of solvent viscosity on the rate constant of conformational changes that bring two pyrenyl groups together to form a pyrene excimer. We have shown that, for pyrene-labelled poly(methyl methacrylate) and poly(methyl acrylate), two classes of conformational changes, which obey the diffusional and non-diffusional limits of Kramers' theory, are needed to represent the inverse rate constant. We have also obtained for these polymers the values of the solvent-independent internal viscosity which exists when the conformational changes obey the non-diffusional limit of Kramers' theory.

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