

Excimer fluorescence as a probe of mobility in bulk poly(dimethyl-siloxanes)

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Intramolecular excimer formation of 10,10'-diphenyl-bis-9-anthrylmethyloxyde (diphant) in bulk poly(dimethylsiloxanes) has been investigated from -40°C to 160°C . The excimer/monomer fluorescence ratio, as well as the activation energy for excimer formation appear to be independent of host matrix molecular weight. The results are consistent with high local mobility of the macromolecular chains.

Keywords Fluorescence; intramolecular excimer; polymer mobility; diphant; poly(dimethylsiloxanes); microscopic viscosity

INTRODUCTION

Fluorescence probe methods are increasingly used to obtain structural information on polymer systems. Intramolecular excimer fluorescence has been particularly used in the study of microscopic¹ properties of a medium. The formation of the intramolecular excimer results from the association of two aromatic groups, one of which has been electronically excited². The most convenient experimental measure of excimer fluorescence under photostationary-state conditions is the ratio of excimer to monomer fluorescence intensity I_D/I_M . This ratio, which corresponds to the efficiency of the excimer formation mechanism, reflects the conformational mobility of the probe.

This is a second paper concerning the dynamic properties of a small fluorescence probe dispersed in a polymer host matrix by means of excimer fluorescence. In the previous paper³, we examined intramolecular excimer formation in 10, 10'-diphenyl-bis-9-anthrylmethyloxyde (Diphant) molecularly dispersed in two elastomers, polyisoprene and polybutadiene. It was shown that the probe mobility is sensitive to the nature of the polymer and its behaviour may reflect a secondary transition of the two elastomers. In the present work, we report investigations concerning intramolecular excimer formation in Diphant dispersed in a series of poly(dimethylsiloxanes) (PDMS) covering a molecular weight range (\bar{M}_w) from 458 to 4×10^5 .

EXPERIMENTAL

Diphant was prepared according to the experimental procedure described previously⁴.

The four polymers used, the characteristics of which are summarized in *Table 1*, were synthesized at Rhone-Poulenc Industries. These bulk samples are fluids of widely differing macroscopic viscosity. The glass transition temperatures were determined on a Dupont Differential Thermal Analyser (heating rate $20^{\circ}\text{C min}^{-1}$).

A solution of diphant in cyclohexane (Merck spectrofluorometric grade) with an optical density of 0.2 at 397 nm is added to the polymer in the proportion 1/3. The mixture is stirred and dried by extensive pumping under vacuum at 60°C for 6 h to remove the solvent completely. In order to obtain samples free of bubbles, the most viscous polymers (A and B) were heated for several hours in an oven at 40°C . The final probe concentration in the samples was approximately $3 \cdot 10^{-9}$ mole per gram of polymer and the final optical density was less than 0.1 at 397 nm. At this concentration, only intramolecular interaction between the chromophores can occur.

Absorption spectra were made on a Cary Model 15 spectrometer. Fluorescence spectra were recorded on a Fica Model 55 MK II spectrofluorometer equipped with a 450 xenon lamp and a R 212 photomultiplier tube. Emission spectra were automatically corrected for

Table 1 Average molecular weight, viscosity at room temperature, and glass-transition temperature of polydimethylsiloxanes

Neat sample	\bar{M}_w	η (cp)	T_g ($^{\circ}\text{C}$)
A	400 000	$> 5 \cdot 10^8$	-119.0
B	150 000	$6 \cdot 10^4$	-119.5
C	5000	50	-124.5
D	458	1-2	-135.0

instrumental response; the excitation wavelength was 365 nm. Some samples were degassed by a repetitive freeze-pump-thaw cycle and sealed under vacuum. For purpose of comparison with the previously reported results, the intensities of the monomer emission I_M , and of the excimer emission I_D , were measured at 430 and 550 nm, respectively. At these wavelengths, there is no overlap of the two emission bands and no scattering correction had to be applied.

Fluorescence decay measurements were carried out on a single photon decay fluorimeter described previously⁵. The excitation wavelength was selected to be 357 nm and the emission was observed through a Schott OG 550 filter.

RESULTS

Room temperature

The emission spectrum at room temperature of diphtant in an aerated PDMS (C) shows a strong structureless band with a maximum around 550 nm ascribed to the excimer fluorescence (Figure 1).

The I_D/I_M ratios obtained in the different polymers, and in cyclohexane for comparison, are listed in the 2nd column of Table 2. The most striking feature of these data is the independence of I_D/I_M on molecular weight, and thus on viscosity, of the host polymer. One possible explanation would be to assume that conjugated effects of oxygen quenching and viscosity could balance each other. In order to make this point clear, further experiments were carried out concerning the influence on excimer formation of oxygen dissolved in the samples studied here.

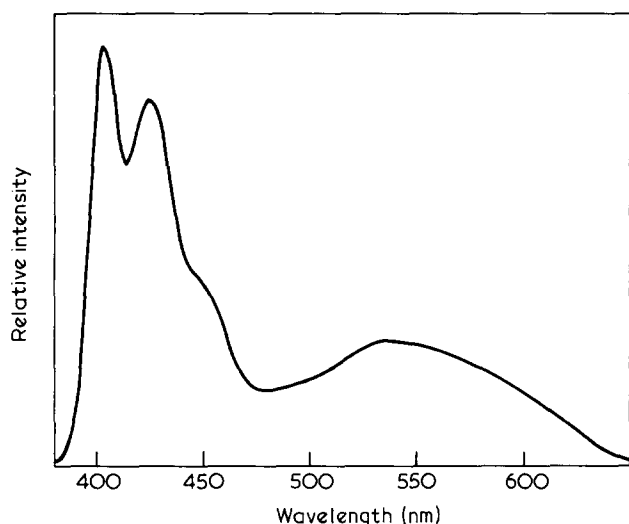
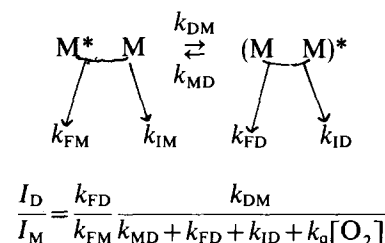


Figure 1 Corrected fluorescence spectrum at 20°C of diphtant in an aerated PDMS (C)

The less viscous samples (C and D) were degassed, and I_D/I_M measured (Table 2, 4th column). The ratio R_1 of I_D/I_M in degassed samples to that in oxygenated ones is given in the 6th column. The high value of R_1 reveals the importance of oxygen quenching on excimer fluorescence. Such experiments could not be performed in the other PDMS (A and B) on account of their high viscosity. Nevertheless it is necessary to know if oxygen quenching is the same in all the polymers.

Another way to analyse oxygen quenching effect is to measure the excimer lifetime τ_D , more affected than the excited monomer lifetime. As is seen in Figure 2, and calculated following a method described previously⁶, the decay of excimer fluorescence observed at 550 nm is strictly monoexponential over the whole curve implied, at room temperature. The excimer lifetime is directly related to this single exponential decay. According to the general kinetic scheme:



where k_{FD} and k_{FM} are the fluorescence decay rate constants for the excimer and monomer. k_{ID} and k_{IM} represent the rate constants of non radiative decay from the excimer and monomer. k_{DM} and k_{MD} are the rate

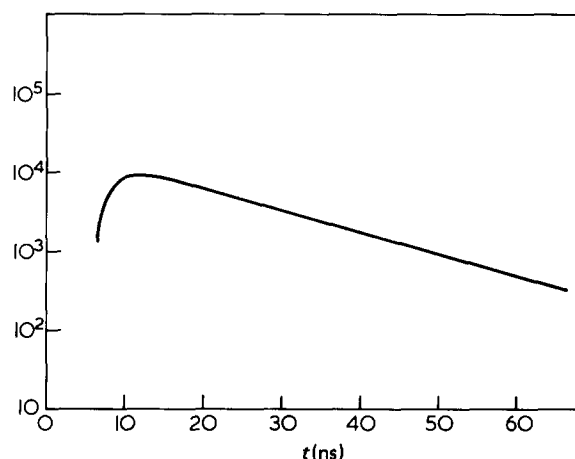


Figure 2 Experimental fluorescence decay curve of diphtant in an aerated PDMS (C) at room temperature, analysed at 550 nm

Table 2 I_D/I_M ratios and excimer lifetimes τ_D

Sample	Undegassed samples		Degassed samples		(2)	
	I_D/I_M (20°C)	$\tau_D^{(1)}$ (ns)	I_D/I_M (20°C)	$\tau_D^{(1)}$ (ns)	R_1	R_2
A	0.30	16.7	—	—	—	—
B	0.30	17.1	—	—	—	—
C	0.33	15.9	0.51	26.0	1.5	1.6
D	0.38	13.3	0.67	27.1	1.8	2.0
cyclohexane	0.47	15.1	0.81	26.2	1.7	1.7

¹ At room temperature

² See text

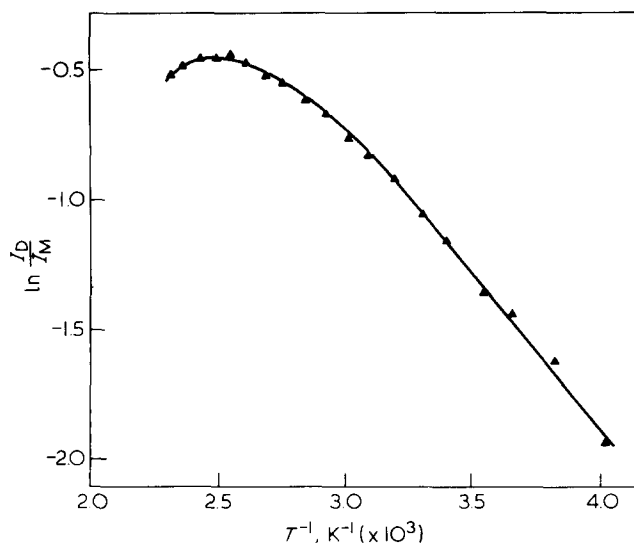


Figure 3 Temperature dependence of $\ln I_D/I_M$ for diphtant in C

constants for excimer association and dissociation. The dissociation of the excimer k_{MD} being negligible with regard to $k_{FD} + k_{ID}$ at room temperature, we can write:

$$R_1 = (I_D/I_M)/(I_D/I_M)_{O_2} = \tau_D/\tau_D(O_2),$$

where

$$\tau_D = \frac{1}{k_{FD} + k_{ID}},$$

and

$$\tau_D(O_2) = \frac{1}{k_{FD} + k_{ID} + k_q[O_2]}$$

where $k_q[O_2]$ is the rate constant of oxygen quenching of the excimer. The experimental values of τ_D reported in the 3rd column of Table 2 for all samples at room temperature show no significant variation in the three most viscous PDMS matrices, as in the case of I_D/I_M . We can then conclude that oxygen quenching of diphtant fluorescence is equally effective in these samples despite their widely differing viscosity. The excimer lifetimes in degassed samples and the ratio R_2 of τ_D in degassed samples to that in undegassed ones are listed in Table 2 (columns 5 and 7). In each sample, R_1 is very similar to R_2 , which is consistent with the general kinetic scheme developed above.

From these results, it is clear that combined effects of oxygen quenching and viscosity cannot explain the quasi-constancy of I_D/I_M over the wide range of PDMS involved in this work.

In order to know whether diphtant presents the same behaviour in other media as in PDMS, experiments were carried out in mixtures of decreasing viscosity of tripropionine and ethylacetate, which are solvents of similar chemical nature. The ratio I_D/I_M of diphtant fluorescence intensities in degassed samples exhibits a significant decrease in passing from ethylacetate ($I_D/I_M = 0.40$) to tripropionine ($I_D/I_M = 0.08$). Contrary to the case of PDMS, the viscosity of the surrounding medium influences to some extent the rate of conformational change of the probe.

Temperature effect

This study was performed in undegassed samples on account of the high viscosity of some polymers.

The initial purpose of this work was to analyse the mobility of the probe reflected by the I_D/I_M ratio as low as the glass-rubber relaxation of the host matrix, this ratio being somehow a rough measure of the free volume offered by the polymer and accessible to the probe. Unfortunately, crystallization of the polymers occurs at about -40°C , limiting the temperature range to -40°C , $+160^\circ\text{C}$.

In the low temperature range (-40°C , 0°C), the presence of an isolampic point in the fluorescence spectra of diphtant in aerated C PDMS, and the increase of excimer emission with temperature indicate that quenching processes and dimer dissociation are not competing with excimer fluorescence. The apparent activation energy E_{DM} for excimer formation can be evaluated from the slope of the linear portion of logarithmic plot (Figure 3) of I_D/I_M against the reciprocal of temperature. It is noteworthy that the linear portion can be drawn well beyond the isolampic point temperature range. This effect is probably due to a temperature dependence of non radiative decay. Nevertheless, all E_{DM} values were calculated within the temperature range exhibiting the isolampic point (-40°C , 0°C). As temperature rises beyond 0°C , both emission bands decrease, owing to dissociation of the excimer and deactivation of the excited monomer. A linear behaviour of $\ln I_D/I_M$ against $1/T$ is not reached in the high temperature range, up to 160°C , making the determination of the binding energy of the intramolecular excimer impossible.

Oxygen quenching of the probe fluorescence is identical in the three most viscous PDMS. This allows the comparison of the apparent activation energies for intramolecular excimer formation, respectively equal to 2.7, 2.7, 2.8, and 2.2 kcal mol $^{-1}$, for A, B, C, and D. Similar values of E_{DM} show that the energy barrier for rotational transition in diphtant is unaffected by the molecular weight, and thus the viscosity, of the host polymer matrix. Moreover, the potential barriers are surprisingly low in view of the high viscosity of these media.

DISCUSSION

In a solvent medium, like tripropionine/ethylacetate, consisting of small molecular units, 'macroscopic' viscosity (η_{macro}) does not profoundly differ from 'microscopic' viscosity (η_{micro}), likely to influence the local mobility of the molecules. High values of η_{macro} give high values of η_{micro} .

In contrast, in a condensed macromolecular medium, the concept of 'viscosity' can be quite different on the macroscopic and microscopic scales. A large macroscopic viscosity η_{macro} due to chain length and chain entanglements does not exclude a small microscopic viscosity η_{micro} . Indeed PDMS is a typical case where this occurs. Whatever the hindrances to motion reflected by η_{macro} , the macromolecular chains of PDMS are locally very flexible, so that on a microscopic scale, the motions of very small parts of the chains (a few segments) remain very easy. If we assume this great flexibility to be independent of the length of the chains for $\bar{M}_w \geq 5000$, we can infer that PDMS matrices of increasing molecular weight exhibit a very low and constant η_{micro} , although η_{macro} increases from a virtually unentangled polymer ($\bar{M}_w = 5000$) to a highly entangled one 7 ($\bar{M}_w = 400\,000$).

Processes involved in intramolecular excimer

formation only concern local mobility of the fluorescence probe, probably affected by the shell of neighbouring molecules. From the lack of dependence of E_{DM} and I_D/I_M with molecular weight of PDMS, and from the results obtained in tripropionine/ethylacetate mixtures, it seems clear that the local environment of the probe is the important parameter in intramolecular excimer formation⁸. The low values of E_{DM} in the PDMS matrices reflect the considerable ease of molecular motion and conformational change of the probe.

It is interesting to compare our results with data obtained from proton n.m.r. study of molecular motion in polydimethylsiloxanes. Burnett and co-workers⁹ found that the high-temperature minimum of the proton spin-lattice relaxation time T_1 , which they attributed to a stretching and flexing motion at a high frequency of the PDMS chain, occurred at the same temperature in two samples of very different viscosity. Moreover, the activation energy for the motion concerned had the relatively low value of 2.3 kcal mol⁻¹, and was independent of sample molecular weight. Cohen-Addad and co-workers¹⁰ have recently observed the existence of two components in the proton spin-spin relaxation rate T_2 in molten PDMS. The long spin-spin relaxation time appears to be nearly independent of the chain molecular weight. The values of T_1 and T_2 given in the latter¹⁰ enable the calculation of a correlation time characteristic of high frequency segmental motions of the chain according to Woessner model¹¹. The calculated correlation time is of the same order of magnitude as characteristic times involved in intramolecular excimer formation. So it seems that the long component of the spin-spin relaxation rate reflects well the motions of PDMS chains implied in this study. Therefore, the quasi non-dependence of the long

spin-spin relaxation rate upon molecular weight is consistent with our results. Ultrasonic relaxation data⁷ in a high frequency range are also in good agreement with the constancy of the rate of segmental motion over a wide range of sample molecular weight.

CONCLUSION

The results displayed show that diphant probe is sensitive only to the microscopic viscosity of the host medium. It reflects the considerable local mobility of the segments of poly(dimethylsiloxane) chains, even in samples of large bulk viscosity. Further studies are in progress with other probes.

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