Studies of cyclic and linear poly(dimethylsiloxanes): 26. An investigation of the mobility of cyclic poly(dimethylsiloxane) in the melt through the excimer emission of small probes

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Intramolecular excimer formation of 10,10′-diphenyl-bis-9-anthrylmethyl oxide as well as of meso-2,4-di(*N*-carbazolyl)pentane in a cyclic poly(dimethylsiloxane) has been investigated. It is shown that the rate of conformational change of the probes contains an intramolecular component in addition to that of the local chain dynamics.

(Keywords: fluorescence; intramolecular excimer; polymer mobility; 10,10′-diphenyl-bis-9-anthrylmethyl oxide; meso-di(*N*-carbazolyl)pentane; cyclic poly(dimethylsiloxane))

INTRODUCTION

Cyclic poly(dimethylsiloxanes) (PDMS) with up to 1000 skeletal bonds have been prepared and their solution, melt and surface properties have been investigated previously[1,2]. In addition to various studies related to the physical properties and theoretical aspects, here we present a study of the polymer mobility through the excimer emission of a probe.

Bichromophoric molecules (where the two aromatic chromophores are separated by a three-atom linkage) give rise to intramolecular excimer formation. This intramolecular excimer formation involves rotational motion about the bonds of the linkage to achieve a conformation in which the two chromophores overlap in a sandwich-like arrangement. Since the excimer arises by a well described conformational transition, the analysis of the excimer formation is particularly convenient for investigating the microscopic properties of the environment.

In this paper we report an analysis of the emission behaviour of intramolecular excimer-forming probes dissolved at a low concentration in a cyclic PDMS sharp fraction. In previous studies[3-5] we have presented the results obtained with a linear PDMS. Unfortunately, its crystallization at about −40°C considerably reduced the temperature range of the experiments. In a recent investigation of PDMS at low temperature, however, it was reported that cyclic PDMS fractions with number-average number of skeletal bonds n_n in the range $24 \leqslant n_n \leqslant 79$ and linear PDMS fractions with $10 \leqslant n_n \leqslant 40$ did not crystallize and, hence, only showed a glass transition[6]. In order to extend the data reported on linear PDMS[3-5] a cyclic PDMS fraction that did not crystallize was chosen as the matrix for the excimer-forming probes.

EXPERIMENTAL

The intramolecular excimer-forming probes 10,10′-diphenyl-bis-9-anthrylmethyl oxide (diphant) and meso-2,4-di(*N*-carbazolyl)pentane (meso-DNCzPe) were chosen on account of their high excimer sampling rate and their good excimer stability, as reported previously[7-10]. The cyclic PDMS used in this study was obtained from a PDMS ring–chain equilibration reaction carried out in toluene at 383 K and was fractionated and characterized by methods described elsewhere[11,12]. The fraction had a number-average molar mass of 1630, a heterogeneity index of 1.02 and a number-average number of skeletal bonds of 44. The optical density of the probe was less than 0.1 at the excitation wavelength in order to avoid reabsorption effects. The emissive properties of these probes were studied using steady-state fluorescence and the time-correlated single-photon counting technique to obtain fluorescence decays[13]. The study was performed in undegassed samples.

RESULTS

As a typical example, the emission spectrum of meso-DNCzPe in cyclic PDMS is given in *Figure 1*. It exhibits, in addition to the normal molecular fluorescence of the monomer, a structureless band at lower energies, ascribed to the emission of the intramolecular excimer.

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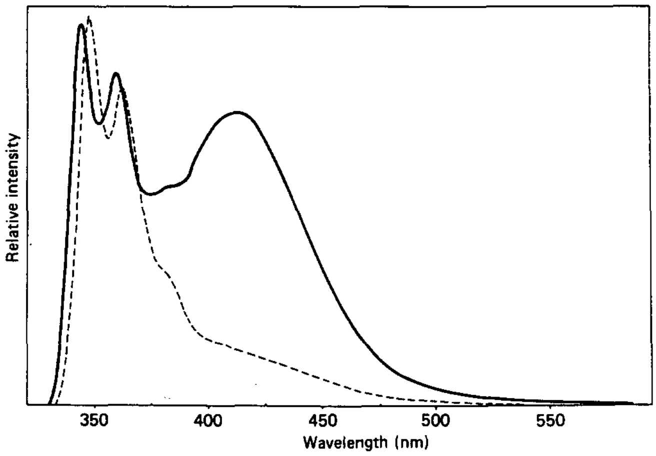

Figure 1 Corrected fluorescence spectra at 25°C of meso-DNCzPe in cyclic PDMS (full curve) and in polybutadiene (broken curve)

Comparison with the emission spectrum of meso-DNCzPe dissolved in polybutadiene[5] reveals the high efficiency of the excimer sampling process in the PDMS matrix. Besides the increase of the excimer emission, a hypsochromic shift in the locally excited state emission is observed in the cyclic PDMS. This shift, probably due to a matrix effect, is also observed with the diphant probe.

The determination of the rate constant for intramolecular excimer formation K_{DM} from the fluorescence decays allows us to evaluate the mobility of the probe in the host medium. Thus K_{DM} is given by the expression:

$$K_{DM} = (\tau_M)^{-1} - (\tau_0)^{-1}$$

where $\tau_M = 1/(K_{FM} + K_{IM} + K_{DM})$ is the excited monomer lifetime and $\tau_0 = 1/(K_{FM} + K_{IM})$ is the monomer decay (radiative plus non-radiative) in the absence of excimer formation. The latter quantity is commonly determined by measuring the fluorescence decay time of a model compound containing only one chromophore, the *N*-isopropylcarbazole for meso-DNCzPe and the 9-(methoxymethyl)-10-phenylanthracene for diphant. Nevertheless, the model lifetime is generally very slightly larger than that of the monomer excited state in the temperature range where the excimer formation is frozen out. Assuming that the monomer decay time of the probe, in the absence of excimer formation, follows the same temperature dependence as that of the model compound, we used the corrected values of the model lifetimes to calculate K_{DM}.

The monomer emission of meso-DNCzPe in cyclic PDMS decays monoexponentially at temperatures below 238 K. At temperatures above 238 K, it deviates from monoexponentiality on account of the excimer dissociation. In this case the decay can be analysed as a sum of two exponential terms and K_{DM} is determined by analysis like that of Birks[14] using the same procedure as previously described[15].

Examples of decay curves of meso-DNCzPe in cyclic PDMS monitored at 358 nm in different temperature regions are given in *Figures 2a* and *2b*. For diphant, back-dissociation occurs at about 268 K.

Figures 3a and *3b* represent respectively the temperature dependence of the monomer lifetime of meso-DNCzPe and diphant as well as that of their respective model compound. The onset of mobility of the probes, detected at the beginning of the decrease of the monomer lifetime, occurs at about −80°C for meso-DNCzPe and −60°C for diphant. The important decrease of the monomer lifetime at higher temperatures is partly related to the photophysical properties of the model compound.

Figure 4 gives a logarithmic plot of the rate constant for intramolecular excimer formation for each probe as a function of the reciprocal temperature.

DISCUSSION

The detection of excimer emission occurs at temperatures well above the normal glass transition temperature (152.1 K) of the cyclic polymer matrix[6]. This shift illustrates the strong influence of the frequency domain of

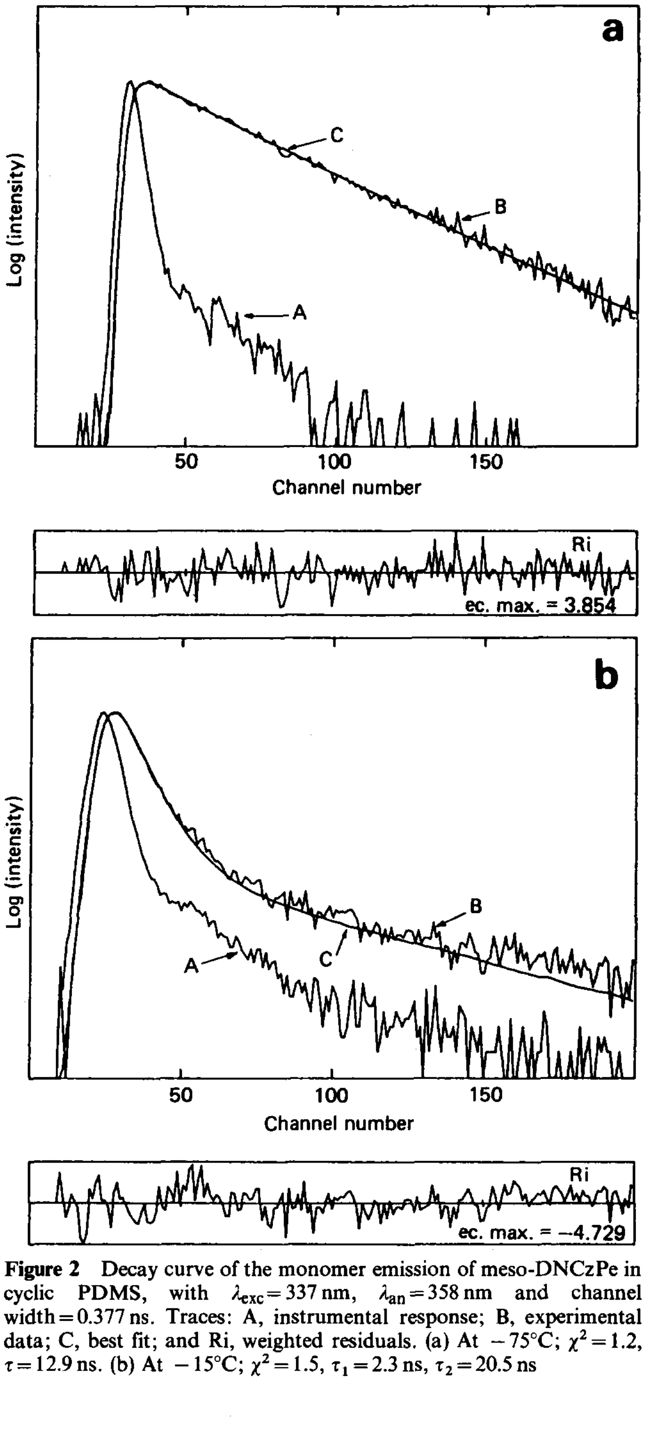

Figure 2 Decay curve of the monomer emission of meso-DNCzPe in cyclic PDMS, with $\lambda_{exc} = 337$ nm, $\lambda_{an} = 358$ nm and channel width = 0.377 ns. Traces: A, instrumental response; B, experimental data; C, best fit; and Ri, weighted residuals. (a) At −75°C; $\chi^2 = 1.2$, $\tau = 12.9$ ns. (b) At −15°C; $\chi^2 = 1.5$, $\tau_1 = 2.3$ ns, $\tau_2 = 20.5$ ns

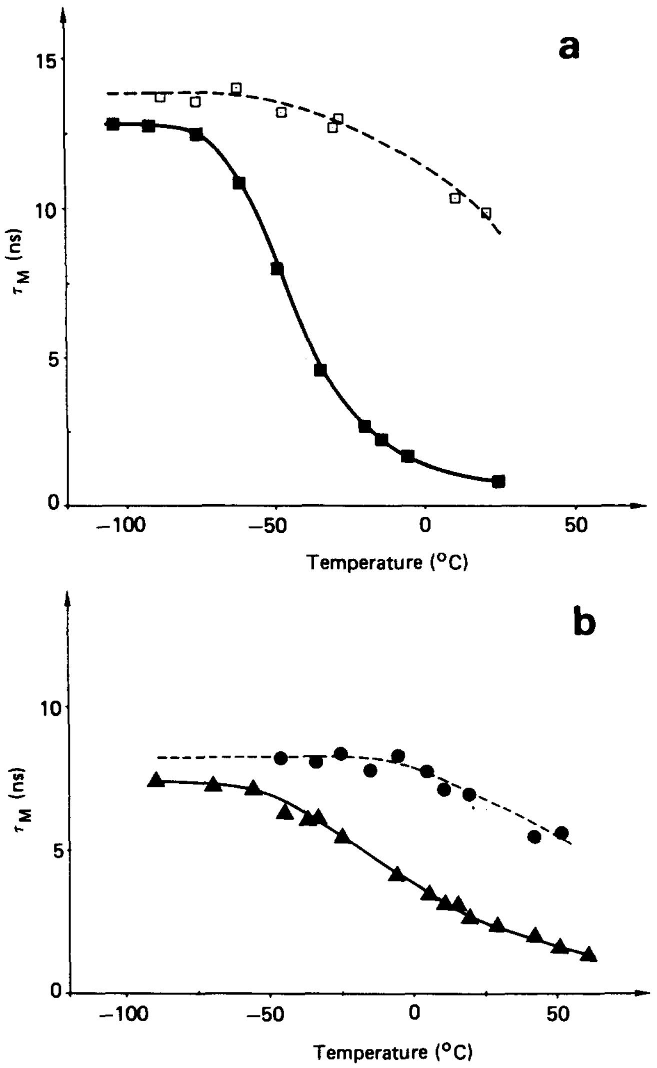

Figure 3 Temperature evolution of the monomer lifetime of each probe and its model compound in cyclic PDMS: (a) meso-DNCzPe (■) and its model compound (□); (b) diphant (▲) and its model compound (●)

the analysing technique on the temperature at which particular forms of molecular motions are observed.

For each probe, in the temperature range where a comparison can be made, there is no significant difference between the emission properties in the cyclic PDMS and in the linear PDMS previously investigated[4,5].

The data presented in *Figure 4* show that at the same temperature the rate of conformational change of meso-DNCzPe is higher than that of diphant. Such behaviour was already reported and was ascribed to a smaller volume swept out during the conformational change associated with the excimer formation in the carbazole probe[5] in addition to differences in the pre-exponential terms for excimer formation[8,10].

The temperature dependence of ln K_{DM} was compared to the familiar WLF equation:

$$\log a_T = -\frac{C_1^g(T-T_g)}{C_2^g+(T-T_g)} \qquad (1)$$

with $\log a_T = \log \tau_c(T) + \text{constant} = \log 1/K_{DM}(T) + \text{constant}$ where $\tau_c(T)$ is the correlation time at temperature T of the motion involved in intramolecular excimer formation defined as the reciprocal of the rate constant K_{DM} of this process; T_g is the glass transition temperature, C_1 and C_2 are two constants, the values of which are assumed identical with those given by Ferry[16]: $C_1^g = 6.1$, $C_2^g = 69.0$, $T_g = 150$ K. This equation usually describes the temperature dependence of the macroscopic viscosity and more generally of the polymer T_g relaxation processes. As is seen in *Figure 4*, the slope of ln K_{DM} is higher than that predicted by the WLF equation.

A more interesting way of looking at the temperature dependence of the correlation time of the rotational motion of the probe is obtained by considering for log a_T the Vogel type equation[17]:

$$\log a_T = A + E_\infty/2.3R(T-T_\infty) \qquad (2)$$

where $T_\infty = T_g - C_2$ has been shown[18] to be a specific parameter for temperature dependence of local flow and $E_\infty = 2.3RC_1^gC_2^g$. This representation has the advantage of giving a linear relation between log a_T and $1/(T-T_\infty)$. We have taken for T_∞ the value of 81 K provided by Ferry[16] for linear poly(dimethylsiloxane). Once more, the slope of log τ_c against $1/(T-T_\infty)$ (*Figure 5*) is higher than that obtained from equation (2), which means that the rate of conformational change of each probe is not only related to the local chain dynamics.

This disagreement prompts us to compare for meso-DNCzPe the data obtained in the cyclic PDMS to those obtained in a solvent medium of low viscosity. So the emission behaviour of meso-DNCzPe has been analysed in a mixture of *cis*- and *trans*-decalin for which the temperature dependence of viscosity is described by the familiar relationship:

$$\eta = A\exp(E_{visc}/RT)$$

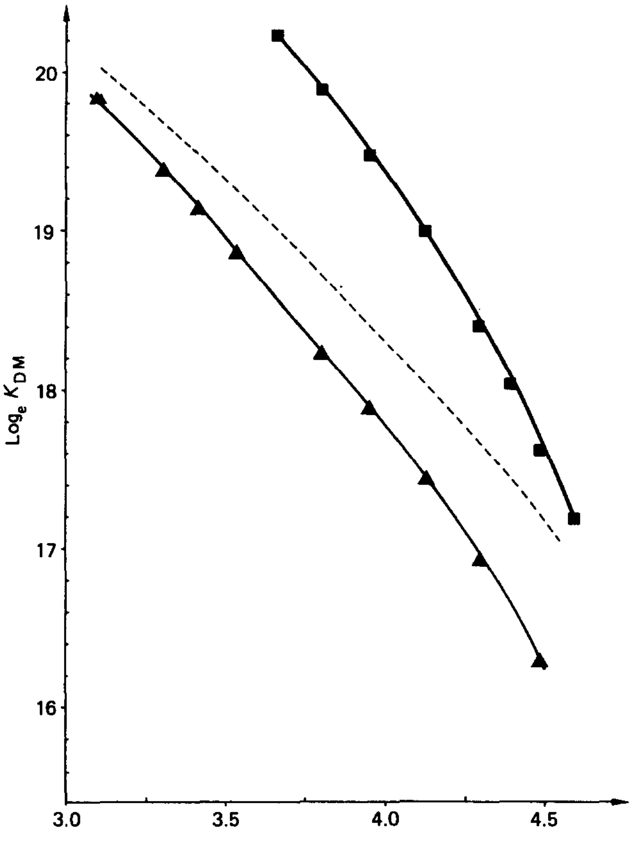

Figure 4 Logarithmic plot of the rate constant for intramolecular excimer formation K_{DM} vs. $1/T$ for the two probes dissolved in cyclic PDMS: meso-DNCzPe (■) and diphant (▲). The broken curve represents $-\ln a_T + 10$ calculated from equation (1)

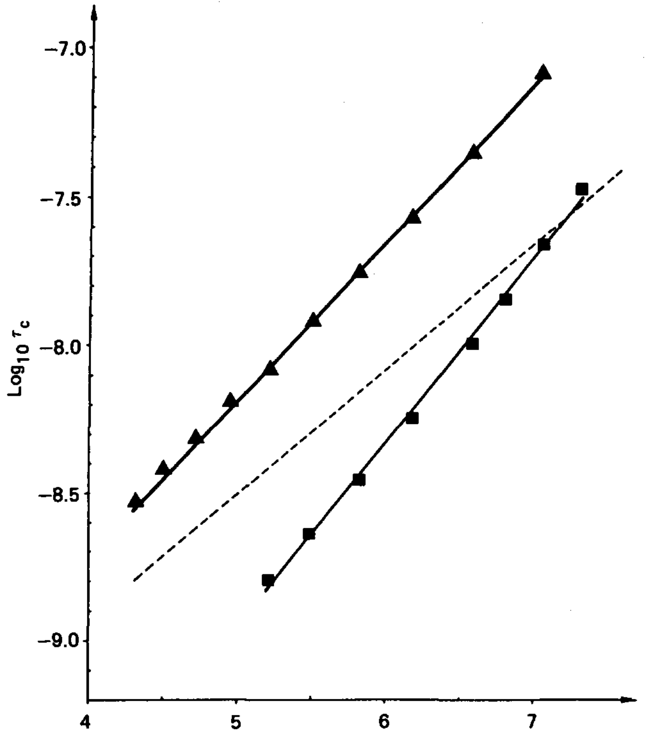

Figure 5 Logarithmic plot of the correlation time τ_c *versus* $1/(T-T_\infty)$ for the two probes dissolved in cyclic PDMS: meso-DNCzPe (■) and diphant (▲). The broken line represents $\log a_T - 4.5$ calculated from equation (2)

A value of 3.9 kcal mol^{-1} for E_{visc} was obtained from plots of $\ln \eta$ against $1/T$ with an A value of 3.38×10^{-5} (*Figure 6*). Using the same procedure, Dodgson *et al.*[19] reported for the cyclic PDMS an activation energy of about 4.0 kcal mol^{-1} and an A factor of 2.83×10^{-4}. As the two media exhibit a similar E_{visc}, at a given temperature, the ratio of about 10 of their macroscopic viscosities is ascribed to the difference between the two pre-exponential terms. The data displayed in *Figure 7* show that the rate constant of excimer formation is higher by a factor of about 2 in cyclic PDMS than in decalin despite the fact that the macroscopic viscosity of the PDMS is 10 times higher than that of decalin.

These results clearly show that for the intramolecular excimer formation process of a probe, polymeric media behave in a completely different way than a solvent medium consisting of small molecules. Indeed, for the latter, the macroscopic viscosity directly reflects the local dynamics of the surrounding probe and affects the rate of excimer formation. In polymeric systems, the process involved in intramolecular excimer formation is related to the dynamics of the local environment of the probe and not to the macroscopic viscosity, which is more sensitive to long-range correlations arising from the nature of the medium. The considerable ease of molecular motions and conformational changes of the probe in the cyclic PDMS reveals the high flexibility of these polymeric rings.

In decalin, an apparent activation energy of 5.6 kcal mol^{-1} has been estimated from logarithmic plots of K_{DM} against the reciprocal temperature. As the excimer is sampled by conformational change, this apparent activation energy contains an intramolecular component in addition to that of the solvent viscosity dependence. The two sets of data represented in *Figure 7* are nearly parallel. This indicates that in cyclic PDMS (as well as in decalin) the rate of conformational change contains an intramolecular contribution.

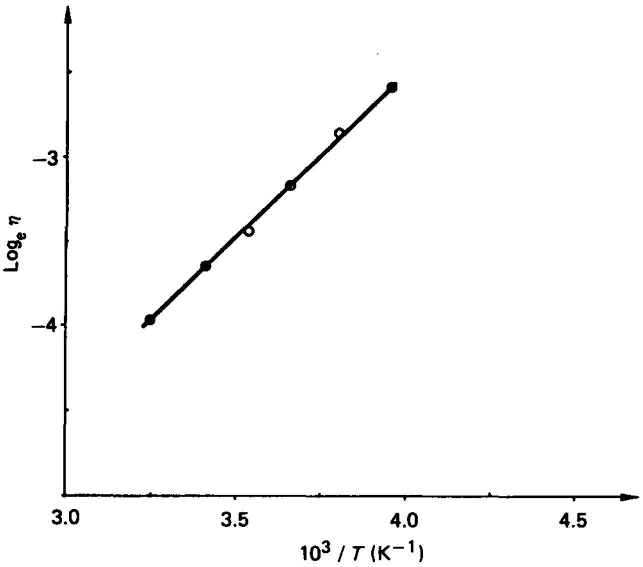

Figure 6 Logarithmic plot of the bulk viscosity of decalin against the reciprocal temperature

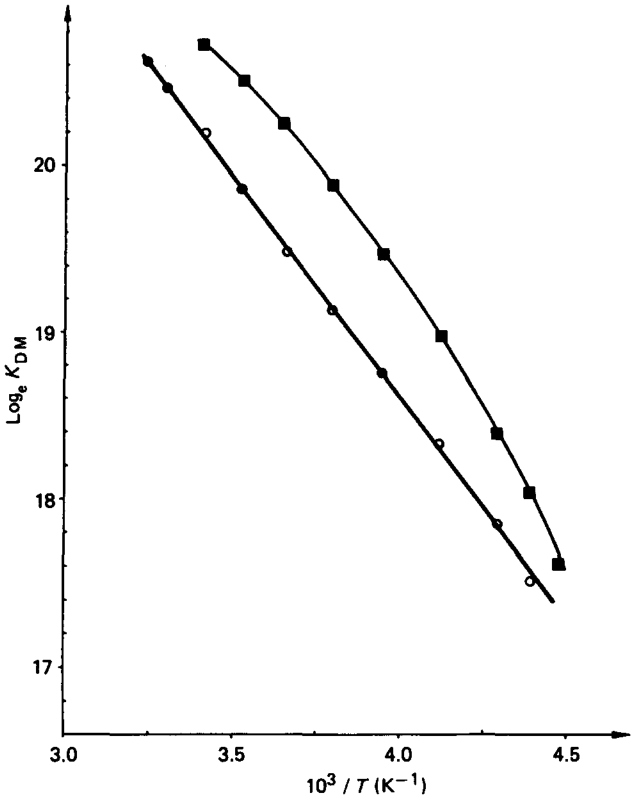

Figure 7 Temperature dependence of the rate constant of intramolecular excimer formation K_{DM} of meso-DNCzPe in cyclic PDMS (■) and in decalin (○)

CONCLUSIONS

In this paper, it has been shown that the rate of conformational change of the intramolecular excimer-forming probes dissolved in cyclic PDMS is not only ruled by the local dynamics of the polymer molecules. This behaviour is ascribed to the fact that the activation energy of viscous flow and the intrinsic potential barrier between the ground and excimer states of the probe are probably of similar magnitude.

REFERENCES

1 Semlyen, J. A. (Ed.), 'Cyclic Polymers', Elsevier Applied Science, London, 1986

2 Semlyen, J. A. and coworkers, Studies of cyclic and linear poly(dimethylsiloxanes), parts 1–22 *Polymer* 1977–86

3 Pajot-Augy, E., Bokobza, L., Monnerie, L., Castellan, A., Bouas-Laurent, H. and Millet, C. *Polymer* 1983, **24**, 117

4 Pajot-Augy, E., Bokobza, L., Monnerie, L., Castellan, A. and Bouas-Laurent, H. *Macromolecules* 1984, **17**, 1490

5 Pham-Van-Cang, C., Bokobza, L., Monnerie, L., Vandendriessche, J. and De Schryver, F. C. *Polym. Commun.* 1986, **27**, 89

6 Clarson, S. J., Dodgson, K. and Semlyen, J. A. *Polymer* 1985, **26**, 930

7 Castellan, A., Lacoste, J.-M. and Bouas-Laurent, H. *J. Chem. Soc., Perkin Trans. II* 1979, 411

8 De Schryver, F. C., Demeyer, K., Huybrechts, J., Bouas-Laurent, H. and Castellan, A. *J. Photochem.* 1982, **20**, 341

9 De Schryver, F. C., Vandendriessche, J., Toppet, S., Demeyer, K. and Boens, N. *Macromolecules* 1982, **15**, 406

10 Vandendriessche, J., Palmans, P., Toppet, S., Boens, N., De Schryver, F. C. and Masuhara, H. *J. Am. Chem. Soc.* 1984, **106**, 8057

11 Dodgson, K. and Semlyen, J. A. *Polymer* 1977, **18**, 1265

12 Dodgson, K., Sympson, D. and Semlyen, J. A. *Polymer* 1978, **19**, 1285

13 Valeur, B. and Monnerie, L. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 11

14 Birks, J. B., 'Photophysics of Aromatic Molecules', Wiley, New York, 1970

15 Bokobza, L. and Monnerie, L., 'Photophysical and Photochemical Tools in Polymer Science' (Ed. M. A. Winnik), Reidel, Dordrecht, 1986, pp. 449–66

16 Ferry, J. C., 'Viscoelastic Properties of Polymers', 2nd Edn., Wiley, New York, 1970

17 Vogel, H. *Physik.* 1921, **22**, 645

18 Brekner, M.-J., Cantow, H.-J. and Schneider, H. A. *Polym. Bull.* 1985, **14**, 9

19 Dodgson, K., Bannister, D. J. and Semlyen, J. A. *Polymer* 1980, **21**, 663