points $N_e \propto P \propto N^{1/2}$ which should be responsible for topological restrictions (i.e. possible self-intersections of the chain). This is in contrast to our estimates which give $N_e/N \simeq 0.24 - \theta(1/N)$ (*Table 1*). The reason for this discrepancy is presumably: Using the definition for the total number of direct contacts (see equation (I.4) in ref. 2), which is the sum of over all probabilities of binary contact between two monomers of positions (n) and (m) along the chemical sequence, gives $P \propto \sum_{m=1}^{N} \sum_{n=1}^{m} |n-m|^{-3/2} \sim N$ in contrast to their own phenomenological estimate $P \propto N^{1/2}$ (see equation (I.3) in ref. 2).

In summary, although the number of effective entanglement points in theta solvents, is far larger than expected, the characteristic correlation functions $g_r(t)$ and $g_{CG}(t)$ do not change qualitatively compared to the free draining limit. The diffusion constant of the centre of gravity is reduced by about 25%.

However, it is not clear how far topological interactions dominate the dynamics of dilute polymer solution in theta solvent compared to hydrodynamic interactions. In polymer melts where hydrodynamics are usually assumed to be negligible, our results indicate that at least for times where $g_{CG}(t) < 1$ (i.e. reptation dynamics is negligible) the dynamics should be of a Rouse type with topological interactions[6].

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A new and convenient fluorescence molecule for probing molecular motions in bulk polymers: 10, 10'-Diphenyl-bis-9-anthrylmethyloxide (Diphant)

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(*Received* 14 *June* 1981)

Fluorescence emission is a sensitive technique used to characterize the physical properties of molecular assemblies[1]. Non-conjugated bichromophores which can emit excimer and monomer (locally excited) fluorescence are used as probes: intramolecular excimer fluorescence formation requires conformational mobility of the linking chain, within the monomer lifetime, to allow the two chromophores to reach a binding distance[2]. Generally, the ratio of excimer to monomer fluorescence intensity (I_D/I_M) reflects the microscopic properties of the medium; inter alia bibenzylether[3] bisnaphthylmethylether[4] and bispyrenes[5] have recently been used to study the microviscosity of micelles or phospholipid membranes.

Excimer fluorescence of guest aromatic vinyl polymers dissolved at low concentration in a polymer host matrix have been investigated by Frank[6] in order to observe the relaxation process near the glass transition. The author shows that in a rigid medium, excimer sampling arises from an activated exciton migration to preformed excimer sites. As analysis of fluorescence spectra of polymers in a polymer matrix is complex, one way of simplifying the problem is to examine intramolecular excimer formation in a small molecule for which singlet exciton migration is not possible. The method of dispersing small molecules in a rigid medium has already been used to restrict the molecular motions and not as a means of investigating the effects of structure and morphology of the polymer on the rotational process of the probe.

The object of this work was to study the influence of the polymer matrix on the probe mobility by means of excimer fluorescence. Various reasons make Diphant a convenient probe and these are as follows:

A high quantum yield allows the use of Diphant in very small concentrations. Fluorescence quantum yields of Diphant in methylcyclohexane at 20°C are respectively $\Phi_M = 0.21$ and $\Phi_D = 0.34$ [7].

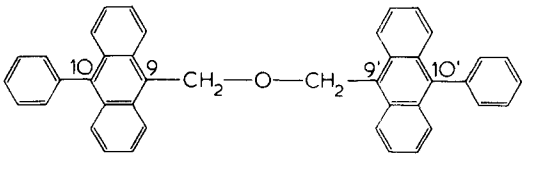
The excimer and monomer emission bands are well separated so that overlap between them is not important.

A good excimer stability allowing a study over a wide range of temperature.

A long wavelength of fluorescence excitation (365 nm) making possible the use of host polymers absorbing in the u.v.

In this communication, we report preliminary investigations concerning intramolecular excimer formation in Diphant dispersed in two elastomers, polyisoprene (PI) and polybutadiene (PB).

Experimental



Diphant (see formula) was prepared according to published procedure[7]; it is in the form of yellow crystals whose melting point is 203°–204°C. It is chemically stable

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and we did not notice any degradation during our experiments.

The commercially available polymers investigated are respectively a polyisoprene (Shell IR 307) with high *cis*-1,4 configuration (*cis* 92%, *trans* 5%, vinyl 3%) and a polybutadiene (Solprene 248) with *cis*-1,4 (37%), *trans* (51%) and vinyl (12%) microstructure. They were purified by extraction with acetone as solvent and mixed with small amounts of dicumyl peroxide (Dicup) as a cross-linking agent, then cured.

The films (about 0.3 mm thick) were swollen with solutions of the probe in benzene or methylcyclohexane and then dried in vacuo. The final probe concentration in bulk samples was approximately 2.10^{-7} mol per gram of polymer. It was verified that with this concentration we have solely intramolecular interactions. A sample containing 7.5×10^{-9} mol/g presents the same I_D/I_M ratio but was not selected for the measurements on account of the high level of light scattering. Fluorescence spectra were recorded on a Fica Model 55 MK II spectrofluorometer equipped with a 450W Xenon lamp and a R 212 photomultiplier tube. Emission spectra were automatically corrected for instrumental response. The spectra were observed by front-surface excitation (excitation wavelength 365 nm). The I_D/I_M ratio was calculated from intensities measured at 550 nm for the excimer band and at 430 nm for the monomer band. At the wavelength where the monomer intensity is taken, no scattering correction had to be applied and there is no overlap of the two emission bands.

Results and discussion

The temperature dependence of the excimer-monomer emission spectra of Diphant dispersed in PI is given in *Figure 1*. In view of the presence of an isolampsic point[8] which exists over the range of temperature studied, we can infer that quenching processes are not competing with fluorescence. However, as the excimer fluorescence increases with temperature, the region in which dissociation competes with dimer fluorescence has not been approached.

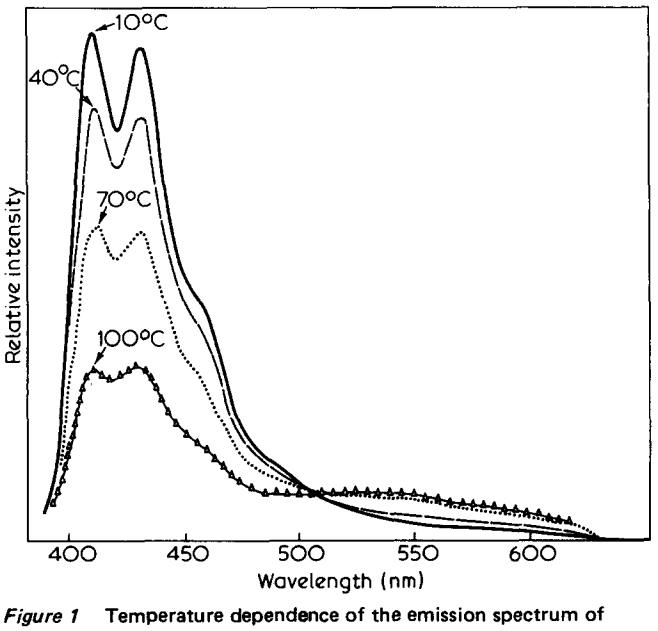

Figure 1 Temperature dependence of the emission spectrum of Diphant in polyisoprene

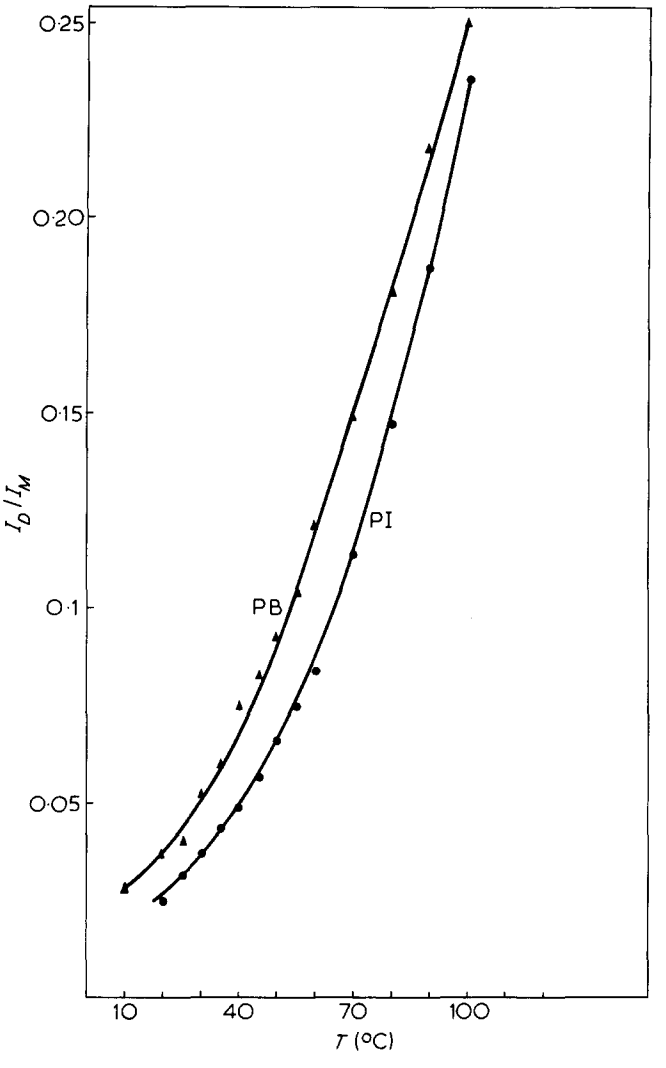

Figure 2 Temperature dependence of the ratio of excimer to monomer fluorescence intensity I_D/I_M. PI = polyisoprene, PB = polybutadiene

The I_D/I_M ratio for the two polymers is plotted against temperature in *Figure 2*. This ratio, which is an approximate measure of the rate of conformational transition is slightly higher in PB than in PI at the same temperature. As expected, the nature of the polymer influences the rate of conformational change of the chromophore. In order to know if the rotational process is associated directly with the glass-rubber relaxation pheomena of the polymer matrix itself, we have plotted in *Figure 3*, the I_D/I_M ratios *versus* $(T - T_g)$ for each polymer. The two curves do not coincide. A similar result has been observed in our laboratory using e.s.r. techniques with three nitroxide radical probes[9]. So the rotational mobility of Diphant does not reflect the glass–rubber relaxation of the polymer. This result is confirmed by the apparent activation energies for excimer formation (6.0 K cal mol^{-1} for PI and 5.2 K cal mol^{-1} for PB) estimated from log plots of I_D/I_M against the reciprocal of temperature. These values are similar in magnitude to barriers for rotational motion in solution, which is surprising on account of the rubbery state of the matrix. Nevertheless the results reveal a high local mobility of the polymeric chains in the temperature range studied. Although involving different physical phenomena, it is interesting to compare our results to those obtained from a fluorescence polarization study by Jarry and Monnerie[10] for 9,10-dimethylanthracene (DMA) dissolved in the same

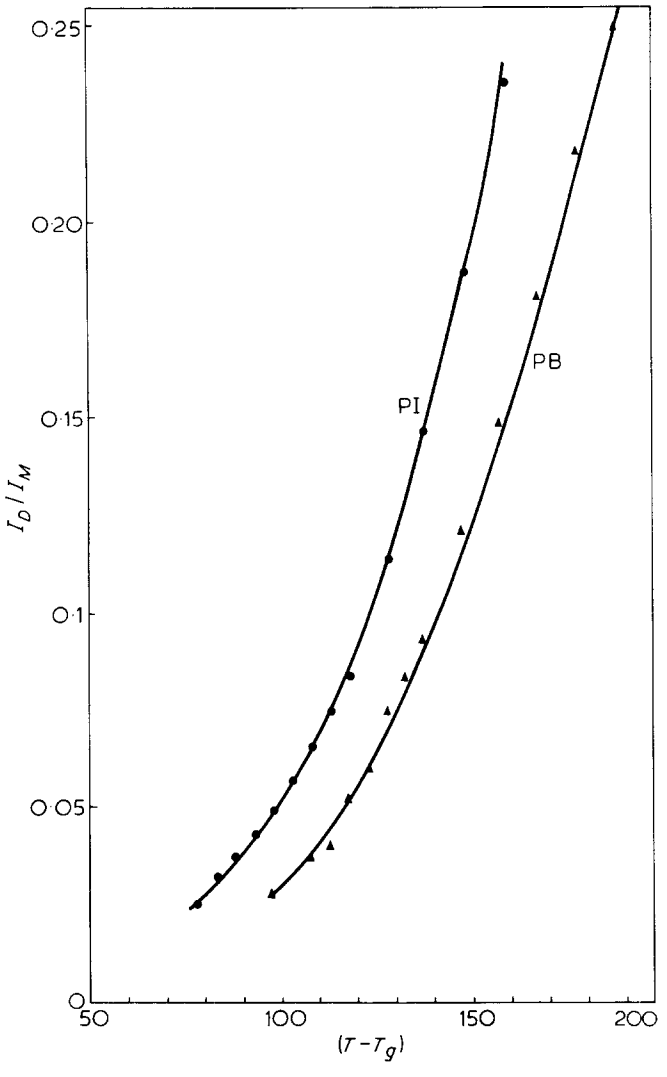

Figure 3 Excimer to monomer intensity ratio *versus* $(T - T_g)$

polyisoprene used in this work. An apparent activation energy of 6.5 K cal mol^{-1} was found for DMA, and its behaviour was related to a secondary transition of polyisoprene reported at 156K by Morgan *et al.*[11] for *trans* sequences of a polyisoprene sample. Taking this last data for the secondary transition of PI, our results would lead for PB to Tβ between 142–148K, a value not far from that (132K) given by Morgan *et al.*[11]. Therefore, it appears that in the bulk polymers studied, the mobility of Diphant reflected by means of excimer fluorescence, could be related to a secondary relaxation.

Another way to show that Diphant does not reflect the glass rubber relaxation of the host matrix is to examine the effect of swelling the polymer on the probe motion. Ethylbenzene is added to PI in order to lower the glass-transition. All the fluorescence spectra are taken at the same temperature which makes the results free of additional contribution in the rotational sampling rate due to a temperature effect, so that the glass-transition of the swollen polymer only varies.

The results are compared with the *WLF* equation:

$$\log a_T = \frac{-16(T-T_g)}{57+(T-T_g)}$$

[12], where T_g is the *ATD* glass-transition temperature of the swollen PI and $T=23°C$ the experimental

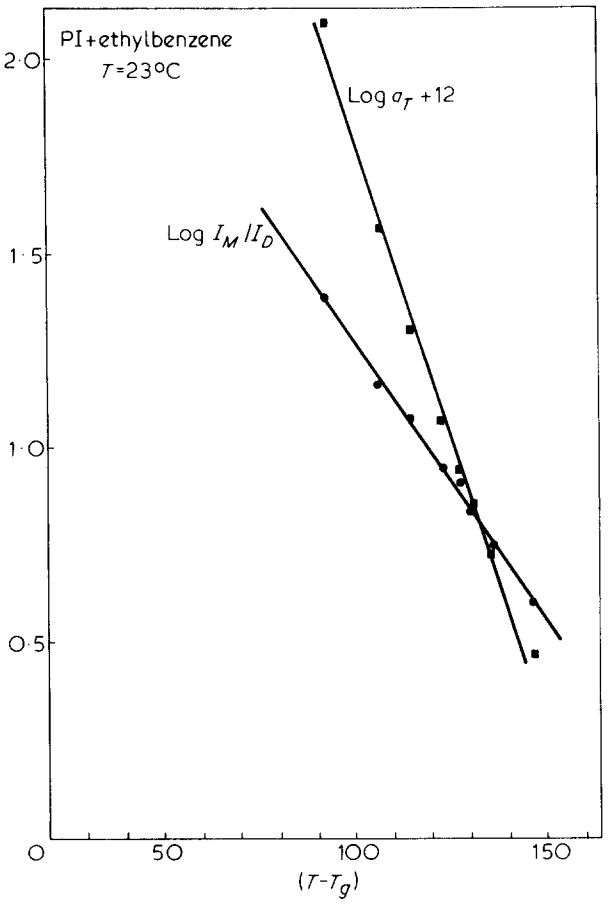

Figure 4 (●) Logarithmic plot of I_M/I_D *versus* $(T - T_g)$. (■) log a_T + 12

temperature. As can be seen in *Figure 4*, the probe does not obey the *WLF* equation.

Conclusions

From the above findings, it is quite evident that the probe mobility is sensitive to the nature of the polymer matrix but it does not reflect the glass–rubber relaxation. It appears possible to relate its behaviour to a secondary transition of the two elastomers. Studies are presently in progress with other polymers and probes of different size.

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