Investigation of local molecular motions in bulk polymers through the emission properties of an intramolecular excimer-forming probe

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Intramolecular excimer formation of meso-bis[1-(2-pyrenyl)ethyl] ether dissolved in different elastomers has been investigated. The intramolecular conformational change required for the excimer sampling process is shown to be controlled by the segmental motions of the polymer matrix involved in the glass transition phenomenon. The results show that, at a fixed frequency of the probe motion, the fractional free volume as well as the free volume per atomic group vary from one polymer to another.

(Keywords: fluorescence; intramolecular excimer; meso-bis[1-(2-pyrenyl)ethyl] ether; elastomeric matrices; polymer mobility; free volume)

INTRODUCTION

Spectroscopic techniques are increasingly used to investigate molecular motions in bulk polymers. Nevertheless, many questions still remain, especially about the understanding of the glass transition phenomenon on a molecular level.

In previous papers[1-8], we have emphasized the interest in using the excimer fluorescence technique for the analysis of local molecular dynamics of polymer chains. The excimer formation of extrinsic probes dispersed in a matrix can provide original information on the distribution and changes of free volume in polymer systems.

In the earlier papers[1-8], the dynamic behaviour of 10,10'-diphenyl-bis-9-anthrylmethyloxide (diphant) and that of meso-2,4-di(N-carbazolyl)pentane (meso-DNCzPe) was analysed. It was shown that each probe undergoes a conformational change via a free-volume-dependent molecular relaxation process. Indeed, the dependence of their correlation times on temperature obeys the characteristic Williams–Landel–Ferry (WLF) expression with coefficients that have been derived from the relaxation times deduced from viscoelastic measurements in the frequency range $1-10^3$ Hz. This expression is known to describe molecular processes associated with the glass transition phenomenon. Thus proving that the volume swept out by the interacting chromophores during the conformational change from the most stable conformation to the sandwich-like arrangement can be related to the segmental motions of the chains and to the free volume available.

In the present paper, we use meso-bis[1-(2-pyrenyl)ethyl] ether (meso-B2PEE) as the intramolecular excimer-forming probe. As in the previous studies, this probe is embedded in polymer matrices to sample the molecular dynamics. Our objective in choosing to study this particular probe is that the monomer lifetime of the excited pyrene is over 20 times longer than that of the carbazolyl or the phenylanthryl group, so that it is an appropriate probe for investigation of relaxation phenomena in the time range $10^{-9}-10^{-6}$ s.

EXPERIMENTAL

Samples

The intramolecular excimer-forming probe meso-bis[1-(2-pyrenyl)ethyl] ether (meso-B2PEE) (see formula) was chosen for its high excimer sampling rate ($k_{DM} = 3.8 \times 10^9$ s^{-1} at 298 K in isooctane)[9]. The steady-state fluorescence spectra in isooctane solution at room temperature show mainly excimer fluorescence, indicating the high mobility of the probe in fluid media. This probe presents a simple photophysical pattern on account of its single-chain conformation (TG) in the ground state and its unique excimer (TT) with total overlap of the pyrene groups.
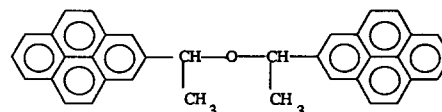
Commercially available polyisoprene (PI) (Shell IR 307, $cis = 92\%$, $M_w \simeq 1\,400\,000$) was provided by Manufacture Française des Pneumatiques Michelin (Clermont-Ferrand, France). Poly(propylene oxide)

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(PPO) ($M_w = 425$) was purchased from Janssen and ethylene–propylene copolymer (EP) ($M_w \simeq 410\,000$) presents an E/P ratio of 54/46. Polyisobutylene (PIB), supplied by Aldrich, has an average molecular weight of 1 300 000.

Films of raw polymers were obtained by solvent casting onto a face of 1 cm path cell from a cyclohexane solution containing the probe. On account of the importance of the oxygen quenching process owing to the long lifetime of the pyrene group, the films are allowed to dry slowly under vacuum, then degassed by pumping under extensive vacuum for at least 3 days. Finally the cell is purged with dry nitrogen, then sealed off.

The final probe concentration in the films does not exceed $3 \times 10^{-7}\,\mathrm{mol\,g^{-1}}$. In the case of poly(propylene oxide), which is a viscous fluid, the optical density of the probe was less than 0.2 at the excitation wavelength in order to avoid energy transfer and reabsorption effects.
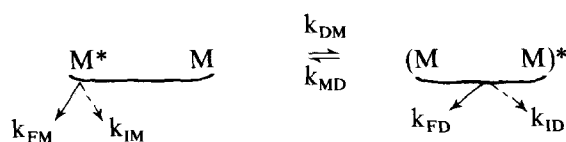
Apparatus

The fluorescence spectra were recorded on a Fica model 55 Mk II spectrofluorimeter equipped with a 450 W xenon lamp and an R212 photomultiplier tube. Emission spectra were automatically corrected for instrumental response. The excitation wavelength was 337 nm. Fluorescence decays were performed on a single photon-counting fluorimeter described previously[10]. Sample fluorescence was produced by the strong 337 nm emission line of the nitrogen discharge.

The glass transition temperatures T_g, reported in *Table 1*, were obtained using a Dupont d.s.c. apparatus, a heating rate of 5 K min^{-1} and cyclohexane calibration.

RESULTS

The excimer fluorescence technique

Analysis of the experimental data is performed according to the conventional kinetic scheme[11]:

$$
\begin{array}{ccc}
& & k_{DM} \\
M^* \quad M & \rightleftharpoons & (M \quad M)^* \\
& k_{MD} & \\
k_{FM} \quad k_{IM} & & k_{FD} \quad k_{ID}
\end{array}
$$

where k_{DM} and k_{MD} are the rate constants for intramolecular excimer formation and dissociation, respectively, k_{FM} and k_{FD} are the rate constants of fluorescence from the local excited state (monomer) and excimer, and k_{IM} and k_{ID} are the rate constants of non-radiative decay from the monomer and the excimer.

Values of k_{DM} can be evaluated from the fluorescence response function $I_M(T)$ of the locally excited state given by the expression:

$$I_M(t) = \frac{k_{FM}}{\beta_2 - \beta_1}[(X - \beta_1)\exp(-\beta_2 t) + (\beta_2 - X)\exp(-\beta_1 t)]$$

In this expression:

$$\beta_{1,2} = \frac{1}{2}\{(X + Y) \mp [(X - Y)^2 + 4k_{DM}k_{MD}]^{1/2}\}$$

$$X = 1/\tau_M = k_{FM} + k_{IM} + k_{DM}$$

$$Y = 1/\tau_D = k_{FD} + k_{ID} + k_{MD}$$

τ_M and τ_D represent the excited monomer and excimer lifetimes, respectively.

Besides the decay parameters β_1 and β_2 and their amplitude ratio $A = (\beta_2 - X)/(X - \beta_1)$, the monomer decay τ_M^0 in the absence of excimer formation is needed for the determination of k_{DM}. This monomer decay time τ_M^0, given by the expression:

$$\tau_M^0 = 1/(k_{FM} + k_{IM})$$

is commonly determined by measuring the fluorescence decay time of a model compound containing only one chromophore. Then k_{DM} is calculated as follows:

$$k_{DM} = 1/\tau_M - 1/\tau_M^0$$

The rotational motion involved in intramolecular excimer formation is characterized by a correlation time τ_c defined as the reciprocal of k_{DM}.

If an intramolecular interaction occurs between the two groups of the bichromophoric molecule, the model lifetime may be 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, the model lifetimes are normalized to those of the monomer obtained in the low-temperature range where the conformational change of the probe is hindered.

Temperature effects

As a typical example, the temperature dependence of the excimer–monomer emission spectra of *meso*-B2PEE dissolved in PI is given in *Figure 1*. Each spectrum exhibits, in addition to the locally excited-state emission, a wide band with a maximum around 480 nm ascribed to the intramolecular excimer. The existence of an isoemissive point shows that both the non-radiative decay constant, k_{ID}, and the rate constant of dissociation, k_{MD}, of the excimer are negligible with regard to its fluorescence. The efficiency of the excimer sampling mechanism as reflected by the ratio of excimer to monomer fluorescence intensities, I_D/I_M, is low in the matrix if compared in fluid solution where only excimer

Table 1

Polymer	T_g (K)	T_∞^a (K)	$C_1^{g\,a}$	$C_2^{g\,a}$ (deg)	$\alpha_f \times 10^{4a}$ (deg^{-1})	$C_1^g C_2^{g\,a}$ (deg)	Observed $C_1^g C_2^{g\,b}$ (deg)	τ_0 (s)
Poly(propylene oxide) (PPO)	195	174	16.2	24	11.3	389	428	1.10×10^{-11}
Polyisobutylene (PIB)	205	101	16.6	104.4	2.5	1733	1731	2.00×10^{-14}
Ethylene–propylene copolymer (EP)	209	175	13.1	40.7	8.1	533	532	5.62×10^{-12}
Polyisoprene (PI)	211	146	16.8	53.6	4.8	900	899	1.58×10^{-13}

^{a} From Ferry[13]
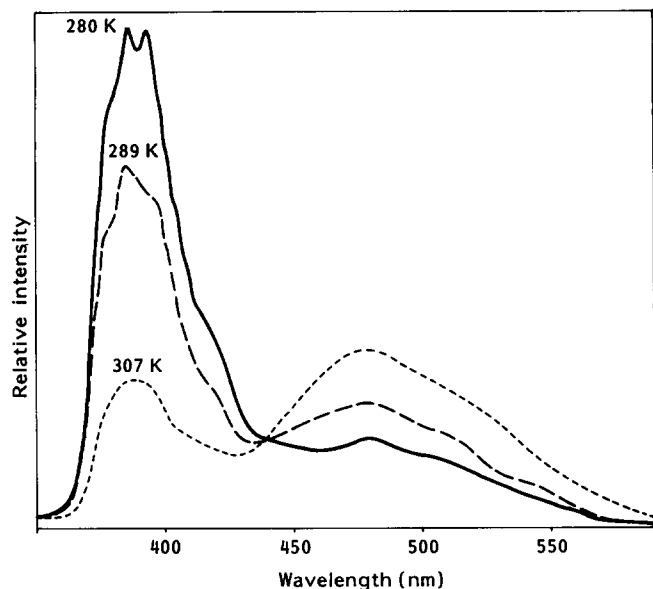^{b} Determined graphically from *Figure 3*

Figure 1 Temperature dependence of the emission spectrum of *meso*-B2PEE in polyisoprene (PI)
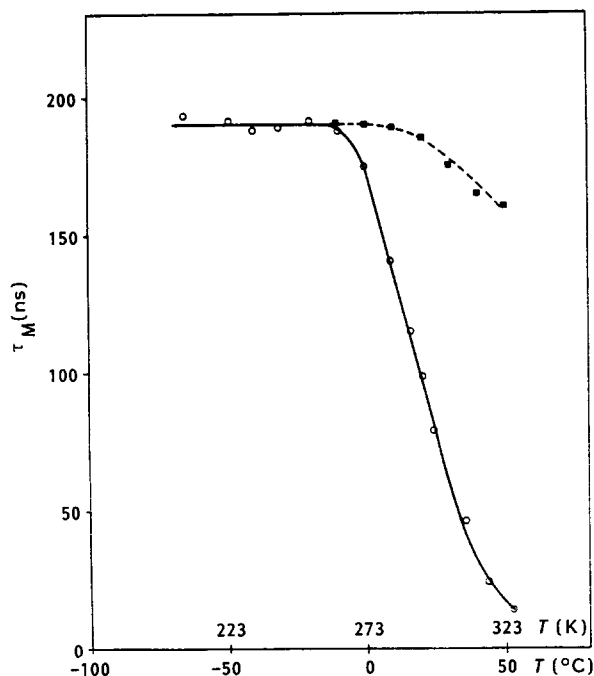

Figure 2 Temperature evolution of the normalized fluorescence decay time of the model compound (2PEE) (■) and of the monomer lifetime of *meso*-B2PEE (○) in polyisoprene (PI)

fluorescence is observed at room temperature[9]. From the steady-state fluorescence spectra, excimer formation is detectable in PI at 263 K.

The transient measurements are in agreement with the photostationary results. The temperature dependence of the monomer lifetime of *meso*-B2PEE as well as that of the normalized lifetime of (2-pyrenyl)ethyl ether (2PEE) taken as the monomeric model compound in PI is given in *Figure 2*. The nearly constant value of the monomer lifetime below 263 K indicates that the probe cannot undergo the conformational change required for the excimer formation process below that temperature. Above 263 K, the matrix chain motions allow the probe to adopt its excimer conformation; τ_M decreases rapidly and reaches a value of a few nanoseconds at 333 K on

account of the increasing value of the rate constant of excimer formation k_{DM}. It has to be pointed out that below 313 K, the monomer fluorescence decay of *meso*-B2PEE in PI can be fitted to a single-exponential decay law. At higher temperatures, the decays can be analysed as a double-exponential decay function; the deviation from the single exponential is ascribed to excimer dissociation.

Meso-B2PEE seems to present in the matrix molecular dynamics similar to that observed in solution[9]. In the ground state, only one conformation is present that can reach the excimer conformation through a rotation in the backbone chain.

DISCUSSION

The first purpose of this study is to identify if the probe rotational motion of *meso*-B2PEE responds to the primary relaxation of the matrix.

In a previous paper, the temperature dependence of the correlation time of *meso*-2,4-di(N-carbazolyl)pentane (*meso*-DNCzPe) has been compared to that predicted from the WLF time–temperature superposition equation[12], which can be written by using a Vogel expression:

$$\log \tau_c = \log \tau_c(T_g) - C_1^g + \frac{C_1^g C_2^g}{T - T_\infty} \tag{1}$$

where C_1^g and C_2^g are phenomenological parameters depending on the chemical structure of the matrix, and $T_\infty = T_g - C_2^g$ is the temperature at which the free volume in the system vanishes.

Figure 3 gives a logarithmic plot of the correlation time τ_c of the pyrenyl probe motion against $1/(T - T_\infty)$ in each matrix. The selected values of T_∞ reported in *Table 1* are those provided by Ferry[13].

In each matrix, a linear plot between $\log \tau_c$ and $1/(T - T_\infty)$ is obtained as predicted by equation (1). Moreover, the slopes of the curves listed in *Table 1* are in good agreement with the $C_1^g C_2^g$ product given by

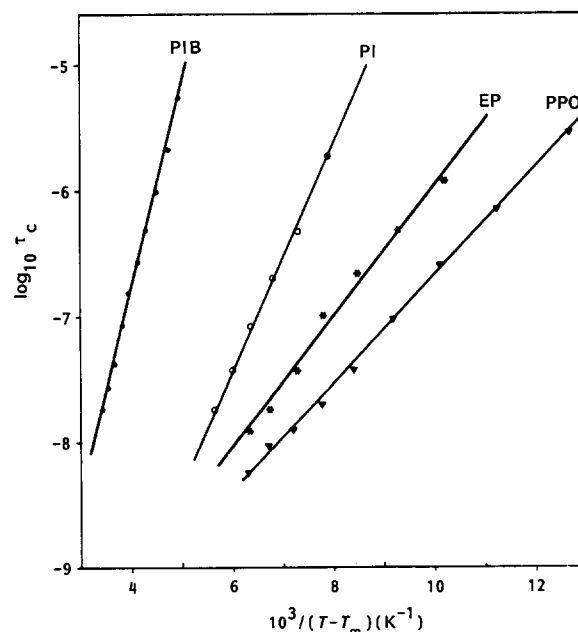
Figure 3 Logarithmic plot of the correlation time vs. $1/(T - T_\infty)$ for *meso*-B2PEE dissolved in the different matrices investigated

Ferry[13] from the low-frequency viscoelastic measurements. This proves, as in the case of *meso*-DNCzPe, that the probe dynamics is governed by the segmental motions of the polymer matrix involved in the glass transition phenomenon. This behaviour, which is encountered in spectroscopic probe methods, is not surprising. Effectively, these two probes are large enough to require complete cooperativity of the medium to perform their own motion.

An interesting aspect of the results is the influence of the chemical structure and the overall mobility of the host elastomer on the efficiency of excimer formation. At a constant $(T - T_\infty)$, large differences in log τ_c occur from one family to another, the mobility of *meso*-B2PEE decreasing respectively from PPO to EP, PI and PIB. The variation of the correlation time of the rotational motion of the probe can be related to the change of the fractional free volume present in the polymer system. Effectively, equation (1) can be rewritten as:

$$\log \tau_c(T) = \log \tau_c(T_g) - C_1^g + \frac{1}{2.303 f_T} = \log \tau_0 + \frac{1}{2.303 f_T}$$

(2)

since $C_1^g C_2^g = B/2.303\alpha_f$ (B is an empirical constant of unity and α_f is the thermal expansion coefficient of the free volume) and $f_T = \alpha_f(T - T_\infty)$.

Equation (2) predicts that, at a given fractional free volume, the correlation time will depend on the original coordinate:

$$\log \tau_0 = \log \tau_c(T_g) - C_1^g$$

This value, which is a characteristic of the matrix, can be considered as the prefactor of the Doolittle equation expressed in terms of correlation times:

$$\tau(T) = \tau_0 \exp(B/f_T)$$

where B is an empirical constant of the order of unity. The values of τ_0 calculated from *Figure 3* are reported in *Table 1*.

As τ_0 differs with the matrix, at a constant fractional free volume, the probe does not exhibit the same correlation time. So, let us now calculate the fractional free volume at a temperature at which the probe undergoes its rotational motion at a given frequency, 10^8 Hz for example. At this temperature (called T_{ref}), the dynamic behaviour of the probe is similar in each matrix, $\tau_c = 10$ ns. The values of T_{ref} deduced from *Figure 3* as well as those of f_{ref} calculated from the relation:

$$f_{ref} = \alpha_f(T_{ref} - T_\infty)$$

(3)

where α_f is the thermal expansion coefficient of the free volume, are listed in *Table 2*. From Van Krevelen's data[14] on molar volumes of rubbery amorphous polymers at 25°C, it is possible to determine the total volume at T_{ref} and the free volume $v_f(T_{ref})$ from f_{ref} since:

$$f = v_f/v$$

where v_f and v represent, respectively, the free volume and the corresponding total volume. We have calculated v_f per atomic group, which represents the free volume per mole of repeated units of the polymer divided by the number of atomic groups of the main chain.

The results reported in *Table 2* show that, at a temperature where the probe exhibits the same dynamic behaviour, the fractional free volume and the free volume

Table 2

Polymer matrix	T_{ref}^a (K)	f_{ref}^b	$v_f(T_{ref})$ per atomic group[c] (cm^3)
PIB	405	0.076	2.59
PI	333	0.090	1.69
EP	339	0.134	1.43
PPO	319	0.147	2.92

[a] Temperature at which log $\tau_c = -8$

[b] Calculated from the relation: $f_{ref} = \alpha_f(T_{ref} - T_\infty)$

[c] Calculated from f_{ref} and the total molar volume. It represents the free volume per mole of repeated units of the polymer divided by the number of atomic groups of the main chain

differ from one polymer to another. The segmental motions of the matrix involved in the glass transition phenomenon generate a fractional free volume more important in PPO than in EP, PI and PIB. This suggests that the sizes of the mobile units are probably different in each type of chain.

Similar conclusions have previously been deduced in the case of *meso*-DNCzPe. But though *meso*-DNCzPe and *meso*-B2PEE both respond to the glass transition of the matrix, we have to point out differences between the two sets of data.

In a given matrix, for each probe, if the slopes of equation (1) are similar within experimental error, the absolute value of the correlation time is imposed by the intercept log τ_0, which seems to be probe-dependent. For *meso*-B2PEE, the τ_0 values, calculated from *Figure 3* are reported in *Table 1*. They are higher than those obtained for *meso*-DNCzPe. At the present time, we are not able to explain such a difference. We have only to keep in mind that we approach polymer dynamics through a probe motion and a specific interaction – difficult to quantify – could possibly exist between the probe molecule and the host.

Another point of interest is the comparison between the temperatures at which excimer formation is detected within the same matrix for the two probes. The onset of mobility of *meso*-B2PEE, detected at the beginning of the decrease of the monomer lifetime, is observed at 243, 293, 243 and 263 K respectively in PPO, PIB, EP and PI. These values are lower than the corresponding ones (263, 343, 273 and 288 K) observed in the case of *meso*-DNCzPe. Two main factors control the observation of excimer fluorescence in a matrix. First, as the probe motion is linked to the chain segmental mobility, excimer formation can only occur when the free volume available in the neighbourhood of the chromophore is sufficient to allow the intramolecular conformational change to take place. Under the assumption that the probes do not themselves significantly perturb the distribution of free volume, the temperature at which excimer formation is observed is linked to the volume needed for probe molecular rearrangement. If only this factor has to be considered, the beginning of mobility of *meso*-B2PEE is expected to occur at a temperature higher than those obtained for *meso*-DNCzPe, since the volume swept out during the conformational change is higher for the pyrenyl probe (it has been estimated as 170 and 470 Å^3, respectively, for *meso*-DNCzPe and *meso*-B2PEE[15]). On the other hand, the time–temperature superposition principle predicts a dependence of the frequency of the experimental technique on the temperature at which the transition is observed.
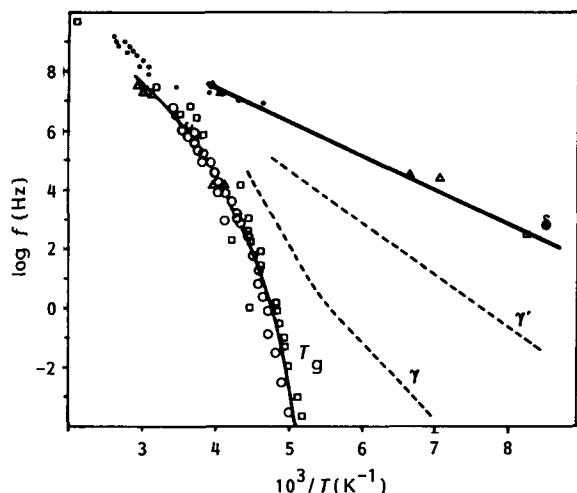
Figure 4 Relaxation map of PIB taken from ref. 16: dielectric data, ○; mechanical data, □; n.m.r. data, △; e.s.r. data, ●

In the excimer fluorescence technique, the probe is 'seeing' the glass transition of the host within the lifetime of the excited chromophore, which represents the observation time of the phenomenon. This experimental time being higher for the pyrene group, the probe will detect the polymer motions at a lower frequency than the other probes. Consequently, excimer formation is detected at lower temperatures. By looking at the temperatures of the beginning of mobility of the two probes in a given matrix, one may be surprised by the large difference occurring in PIB. The temperature dependence of the frequency of a particular motion differs from one matrix to another. Reporting the two temperatures in the relaxation map of PIB given by Törmälä[16], and reproduced in *Figure 4*, leads to a frequency ratio quite consistent with that expected from the monomer lifetimes of the two probes.

CONCLUSIONS

The use of *meso*-bis[1-(2-pyrenyl)ethyl]] ether as an intramolecular excimer-forming probe to investigate polymer dynamics provides an interesting test of the generality of the response observed in the case of *meso*-2,4-di(N-carbozolyl)pentane previously studied. Additionally, the pyrene molecule allows one to study longer timescales than the carbazole probe. From the behaviour of the pyrenyl probe, it was shown that the previous conclusions with regard to chain segmental mobility and to free volume are still valid.

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