Relation between excimer formation in small probes and free-volume theory in polymer melts

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Intramolecular excimer formation of meso-2,4-di(*N*-carbazolyl)pentane 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-2,4-di(*N*-carbazolyl)pentane; elastomeric matrices; polymer mobility; free volume)

INTRODUCTION

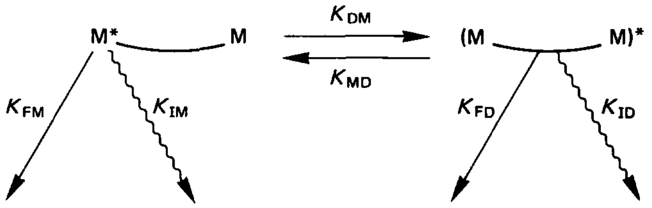
Relaxation behaviour of macromolecular chains in bulk polymers has been the subject of intensive investigation. Among the various techniques, the photoluminescence probe methods have been widely used in these studies. The validity of using the excimer fluorescence as a probe to study the mobility of macromolecular chains has been discussed in previous papers[1–5]. Intramolecular excimer formation in bichromophoric molecules requires conformational mobility of the linking chain to allow the two chromophores to overlap in a sandwich-like arrangement. For this reason, intramolecular excimer emission is particularly convenient to study the mobility of the surrounding environment. In earlier papers[1–5], the emission behaviour of 10,10′-diphenyl-bis-9-anthrylmethyloxide (diphant) and that of meso-2,4-di(*N*-carbazolyl)pentane (meso-DNCzPe) dissolved in various elastomers was investigated. It was shown that the variation of the correlation time of the rotational motion of the probe with $(T-T_g)$ was in qualitative agreement with the behaviour expected from the WLF equation, proving that each probe undergoes a conformational change via a free-volume-dependent molecular relaxation process related to the glass transition of the polymer matrix. Besides, it was emphasized that, at the same $(T-T_g)$, the rate of conformational transition is quite different from one matrix to another one.

In this paper, in addition to new results obtained on polypropylene oxide, polyisobutylene and ethylene–propylene copolymer, using meso-DNCzPe as a probe, we present a quantitative test of the WLF (Williams–Landel–Ferry) equation and compare the behaviours of the different polymers investigated.

EXPERIMENTAL

Technique

Analysis of the experimental data is performed according to the conventional kinetic scheme[6]:



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. The most important parameter to characterize the efficiency of the excimer sampling mechanism and thus the mobility of the probe in the host matrix is the rate constant for intramolecular excimer formation K_{DM} determined from fluorescence lifetime measurements. K_{DM} is given by the

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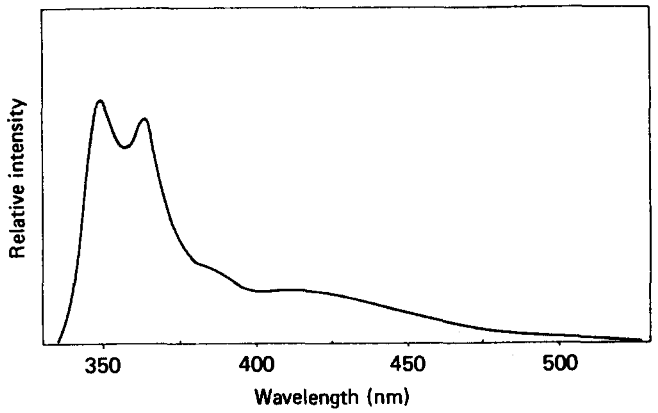


Figure 1 Corrected fluorescence spectrum at 312 K of meso-DNCzPe in poly(propylene oxide)

expression:

$$(\tau_M)^{-1}-(\tau_0)^{-1}$$

where $\tau_M = 1/(K_{FM}+K_{IM}+K_{DM})$ is the excited monomer lifetime and $\tau_0 = 1/(K_{FM}+K_{IM})$ the monomer decay time (radiative plus non-radiative) in the absence of excimer formation. The latter quantity is determined by measuring the fluorescence decay time of the model compound containing only one chromophore, the *N*-isopropylcarbazole (NIPCz). Nevertheless, the model lifetime is generally 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 emissive properties of meso-DNCzPe and of its model compound NIPCz were studied using steady-state fluorescence and the time-correlated single-photon counting technique to obtain fluorescence decays[7]. The deconvolution of the decays was performed on the CNRS CIRCE computer system.

Films of raw polymers were obtained by solvent casting onto a quartz plate from a cyclohexane solution containing the probe. The final probe concentration in the films does not exceed 2×10^{-7} mol g^{-1}. In the case of poly(propylene oxide), which is a viscous fluid, the optical density of the probe was less than 0.1 at the excitation wavelength in order to avoid reabsorption effects.

Samples

The commercially available polyisoprene (PI) (Shell IR 307, *cis* = 92%, $M_w \simeq 1\,400\,000$) and the polybutadiene (PB) (Shell BR 1220, *cis* = 96%, $M_w \simeq 470\,000$) were provided by Manufacture Française des Pneumatiques Michelin (Clermont-Ferrand, France). The poly(propylene oxide) (PPO) ($M_w = 425$) was purchased from Janssen and the ethylene–propylene copolymer (EP) ($M_w \simeq 410\,000$) from Uniroyal Chemical Company presents an E/P weight ratio of 54/46. The polyisobutylene (PIB), supplied by Aldrich, has an average molecular weight of 100 000.

The intramolecular excimer-forming probe, meso-2,4-di(*N*-carbazolyl)pentane (meso-DNCzPe), was chosen on account of its high excimer sampling rate and its good excimer stability[8,9].

RESULTS

As a typical example, the emission spectrum of meso-DNCzPe in PPO at 312 K is given in *Figure 1*. It exhibits, in addition to the normal fluorescence of the monomer, a structureless band at lower energies, ascribed to the emission of the intramolecular excimer.

The temperature dependence of the monomer lifetime of meso-DNCzPe as well as that of its model compound in each matrix is given in *Figures 2a–e*. At low temperatures, the monomer lifetime of meso-DNCzPe is nearly independent of temperature, which indicates that the conformational change of the probe is hindered. The onset of mobility, detected at the beginning of the decrease of the monomer lifetime, occurs at a temperature that is different in each matrix. In the case of PB (*Figure 2e*), the data in the low-temperature range have not been reported since anomalous effects were observed on account of the crystallization of this polymer.

DISCUSSION

In the analysis of the results, attention has been paid to the application of the free-volume theory to intramolecular excimer formation of small probes dispersed in host polymeric matrices.

The well known WLF equation, developed by Williams, Landel and Ferry[10]:

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

generally describes the temperature dependence of the ratio of the correlation time τ_c at temperature T to its value at the glass transition temperature T_g chosen as reference.

The correlation time τ_c of the probe motion, determined by the reciprocal of the rate constant of excimer formation K_{DM}, has been plotted in semi-log scale *versus* $(T-T_g)$ in *Figure 3*. The experimental data are in qualitatively good agreement with the related WLF equation represented in *Figure 3* by the various broken curves. Nevertheless, it has to be pointed out that, at the same $(T-T_g)$, the dynamic behaviour of the probe is quite different from one polymer to another.

Equation (1) can be rewritten by using the Vogel temperature, $T_\infty = T_g - C_2$:

$$\log \tau_c(T) = \log \tau_c(T_g) - C_1^g + C_1^g C_2^g \frac{1}{T-T_\infty} \qquad (2)$$

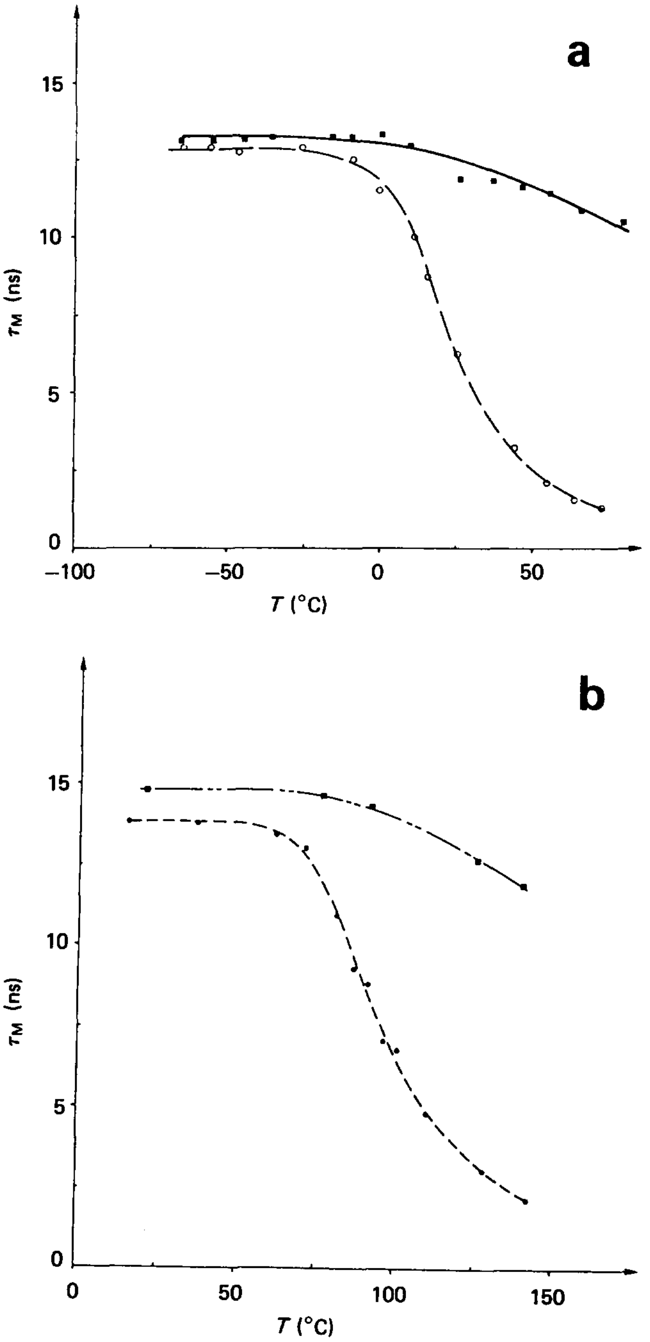
T_∞ is the temperature at which the free volume in the system is zero, leading to an infinite correlation time,

$$C_1^g = \frac{B}{2.303 f_g} \qquad C_2^g = \frac{f_g}{\alpha} \qquad \text{and} \qquad C_1^g C_2^g = \frac{B}{2.303\alpha}$$

f_g is the fractional free volume at T_g, α the thermal expansion coefficient of the free volume and $B \approx 1$.

Figure 4 gives a logarithmic plot of the correlation time τ_c of the probe motion against $1/(T-T_\infty)$ in each matrix. The selected values of T_∞, reported in *Table 1*, are those provided by Ferry[11].

In each matrix, a linear plot between $\log \tau_c$ and $1/(T-T_\infty)$ is obtained, which proves the validity of the



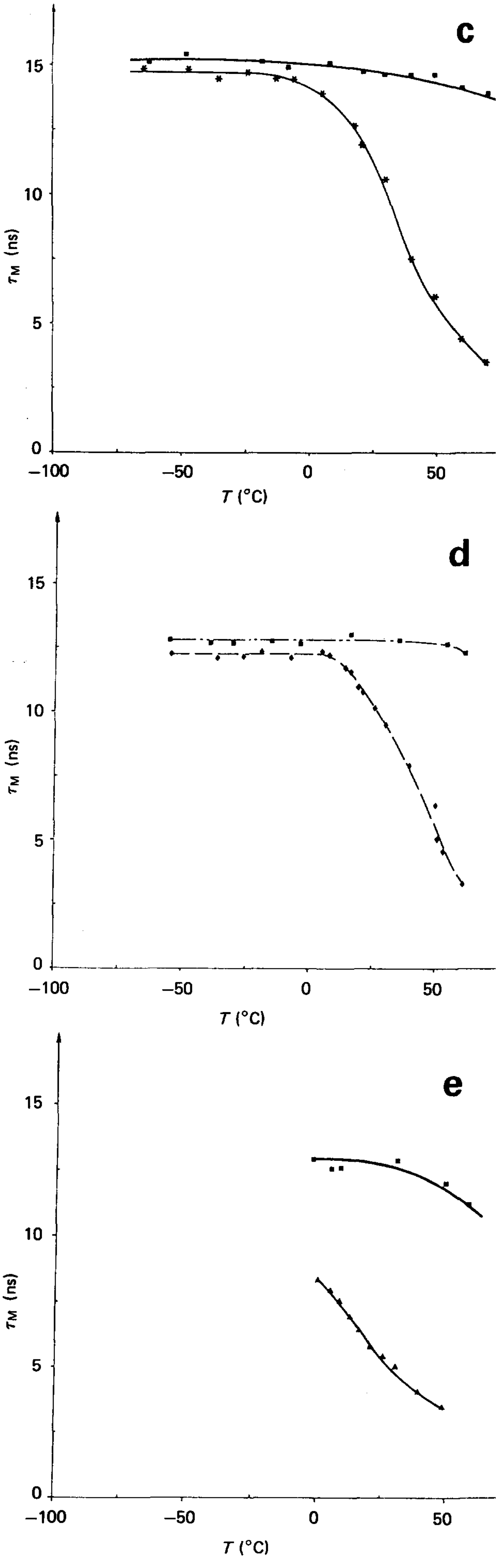


Figure 2 Temperature evolution of fluorescence decay time of the model compound (NIPCz) (■) and of the monomer lifetime of meso-DNCzPe in (a) poly(propylene oxide) (PPO) (○), (b) polyisobutylene (PIB) (●), (c) ethylene-propylene copolymer (EP) (*), (d) polyisoprene (PI) (◆) and (e) polybutadiene (PB) (▲)

free-volume theory and the form of the Vogel–WLF equation in describing intramolecular excimer sampling processes of small probes dissolved in polymer melts.

As is seen in *Table 1*, the observed products C_1C_2, which are the slopes of the curves represented in *Figure 4*, are in good agreement with those predicted by Ferry. This proves that, despite the high-frequency domain of the analysing technique, the results are similar to those obtained from mechanical measurements.

Figure 4 shows that at a constant $(T-T_\infty)$, the correlation times do not have the same value in each family of polymers. In fact, the rotational process involved in excimer formation can only proceed when the segmental motions of the polymer matrix are able to create the free volume, allowing the probe to achieve its conformational transition during the lifetime of the monomer excited state. It is clear that at the same $(T - T_g)$ or $(T - T_\infty)$, the free volume generated by the matrix is not similar in each family of polymers. So, one idea is to try to calculate the fractional free volume and the free volume at the temperature at which the probe undergoes its rotational motion at a fixed frequency, 10^8 Hz for example. In other words, it would mean that, at this temperature (called T_{ref}), the dynamic behaviour of the probe is similar in each matrix. T_{ref} has been deduced from *Figure 4* for each polymer. At T_{ref}, equation (2) becomes:

$$\log \tau_{c,ref} = \log \tau_c(T_g) - C_1^g + C_1 C_2 \frac{1}{T_{ref} - T_\infty} \tag{3}$$

The difference between equations (2) and (3) can be written as:

$$\log \tau_c(T) = \log \tau_{c,ref} + C_1 C_2 \left(\frac{1}{T - T_\infty} - \frac{1}{T_{ref} - T_\infty} \right) \tag{4}$$

The fractional free volume at temperature T is defined as:

$$f_T = v_f / v$$

where v is the total volume per gram and v_f the free volume. Quantity f_T is assumed to increase linearly with temperature according to the relation:

$$f_T = f_g + \alpha(T - T_g) \tag{5}$$

By using T_∞, equation (5) becomes:

$$f_T = \alpha(T - T_\infty) \tag{6}$$

According to equation (6), the fractional free volume at T_{ref} is given by:

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

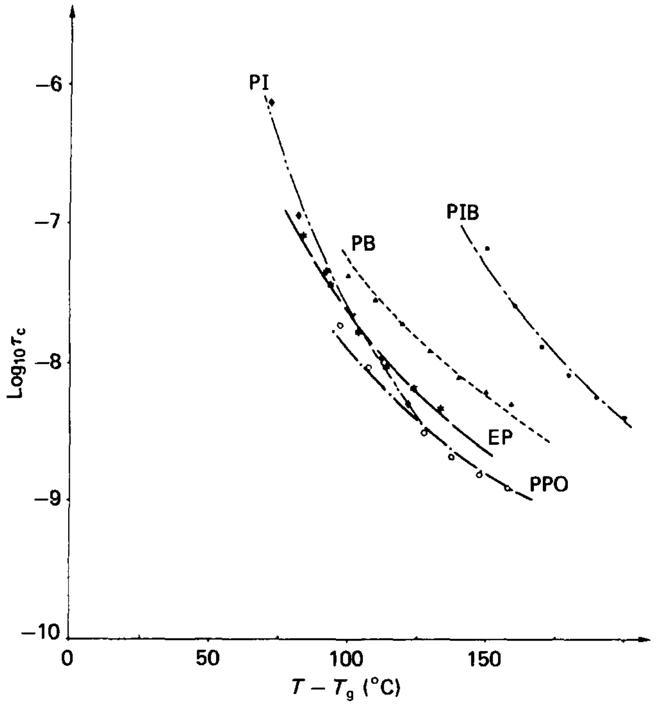


Figure 3 Logarithmic plot of the correlation time vs. $(T - T_g)$ for meso-DNCzPe dissolved in polybutadiene (▲), poly(propylene oxide) (○), polyisobutylene (●), ethylene–propylene copolymer (*) and polyisoprene (◆). The various curves represent the related WLF equations

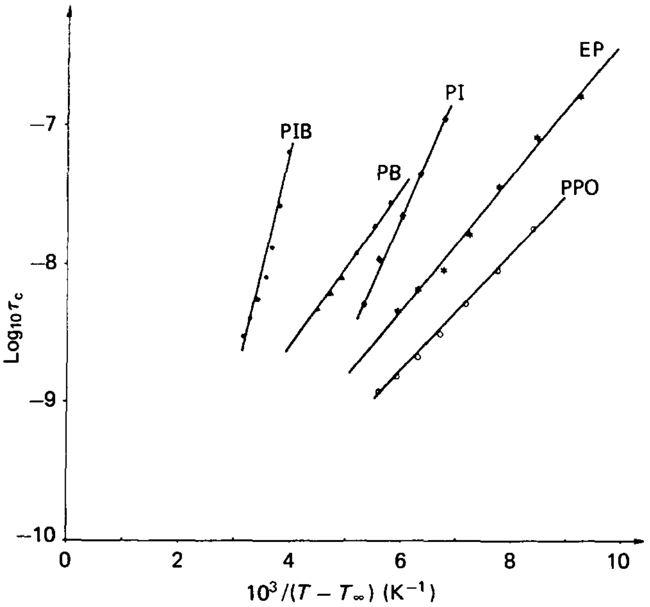


Figure 4 Logarithmic plot of the correlation time vs. $1/(T - T_\infty)$ for meso-DNCzPe dissolved in the different matrices investigated. The abbreviations and the signs are the same as those used in *Figure 3*

Table 1

Polymer matrix	T_g (K)	T_∞^{a} (K)	C_1^g^{a} (deg)	C_2^g^{a} (deg)	Predicted C_1C_2^{a} (deg)	Observed C_1C_2^{b} (deg)
Polybutadiene (PB)	164	101	11.3	60.0	678	604
Poly(propylene oxide) (PPO)	195	174	16.2	24	389	428
Polyisobutylene (PIB)	205	101	16.6	104.4	1733	1712
Ethylene–propylene copolymer (EP)	209	175	13.1	40.7	533	500
Polyisoprene (PI)	211	146	16.8	53.6	900	914

[a] From Ferry[11]
[b] Determined graphically from *Figure 4*

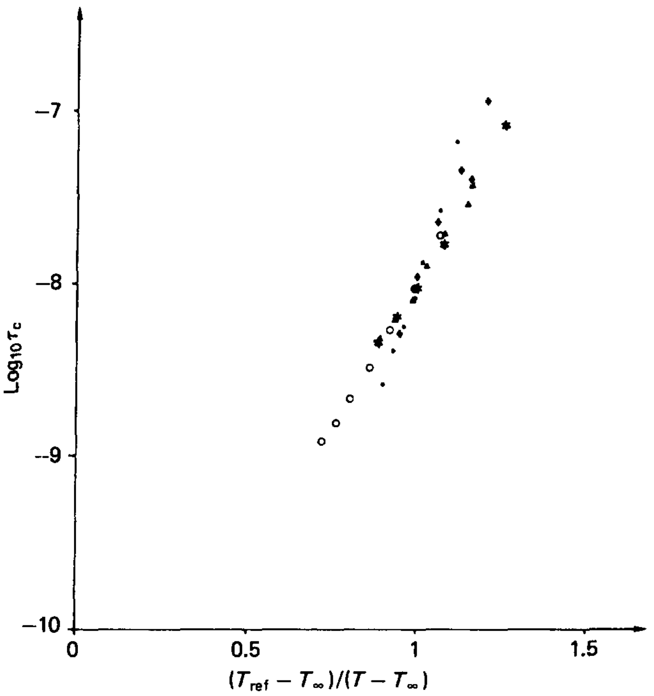


Figure 5 Logarithmic plot of the correlation time vs. $(T_{ref} - T_\infty)/(T - T_\infty)$ for meso-DNCzPe dissolved in the different matrices investigated. The signs are those used in *Figure 3*

As $C_1C_2 = B/2.303\alpha \approx 1/2.303\alpha$, equation (4) becomes:

$$\log \tau_c(T) = \log \tau_{c,ref} - \frac{1}{2.303f_{ref}} + \frac{1}{2.303f_{ref}}\left(\frac{T_{ref} - T_\infty}{T - T_\infty}\right) \quad (7)$$

Figure 5 gives a logarithmic plot of the correlation time τ_c of the probe motion against the parameter $(T_{ref} - T_\infty)/(T - T_\infty)$ representing the ratio of the fractional free volume at T_{ref} to the fractional free volume at T. The use of this reduced temperature leads to a more reduced curve contrary to what is obtained when plotting $\log \tau_c$ against $(T - T_g)$ or $(T - T_\infty)$. The values of f_{ref} calculated from the slopes of the curves represented in *Figure 5* are reported in *Table 2*. From Van Krevelen's data[12] on molar volumes of rubbery amorphous polymers at 25°C, it is possible to determine the volume at T_{ref} and the free volume $v_f(T_{ref})$ from f_{ref}. The results listed in *Table 2* show that at a reference temperature where the probe exhibits the same dynamic behaviour, the fractional free volume as well as the free volume differ from one polymer to another. Equation (3) can be rewritten as:

$$\log \tau_{c,ref} = \log \tau_c(T_g) - C_1^g + \frac{1}{2.303f_{ref}}$$

As we have found that f_{ref} differs with the matrix, this implies that the original coordinate $(\log \tau_c(T_g) - C_1^g)$ varies in each polymer matrix.

Another way of looking at the effect of the chemical structure of the matrix on the efficiency of the excimer process consists in determining the correlation time τ_c either at a fractional free volume (e.g. $f_T = 0.1$) or at a fixed free volume (e.g. $v_f = 2\,\text{cm}^3$ per atomic group). The corresponding values are summarized in *Table 3*.

Table 2

Polymer matrix	T_{ref}[a] (K)	f_{ref}[b]	$v_f(T_{ref})$ per atomic group[c] (cm^3)	$\log \tau_c(T_g)$
PB	298	0.141	2.14	0.24
PPO	302	0.130	2.53	4.86
PIB	382	0.068	2.31	2.51
EP	324	0.130	1.37	1.74
PI	323	0.084	1.57	3.64

[a] Temperature at which $\log \tau_c = -8$
[b] Determined graphically from *Figure 5*
[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

Table 3

	Fractional free volume $f = 0.1$		Free volume v_f per atomic group $v_f = 2\,\text{cm}^3$	
	$\log_{10} \tau_c$	T (K)	$\log_{10} \tau_c$	T (K)
PB	−6.72	257	−7.80	286.5
PPO	−7.00	263	−7.22	278
PIB	−9.75	501	−7.13	347
EP	−7.02	298	−8.95	382.5
PI	−8.82	354	−9.02	367

CONCLUSIONS

The results reported in this paper show that the probe motions of meso-DNCzPe are controlled in all the investigated matrices by the segmental motions involved in the glass–rubber phenomenon. Nevertheless, the fact that, in matrices of varying chemical structure, the intramolecular rotational motion of the probe with a given frequency (10^8 Hz) is achieved for different fractional free volumes of the considered matrices is evidence that other molecular factors such as fluctuations of free volumes and differences between sizes of mobile units in each type of chain have to be taken into account.

REFERENCES

1 Pajot-Augy, E., Bokobza, L., Monnerie, L., Castellan, A., Bouas-Laurent, H. and Millet, C. *Polymer* 1983, **24**, 117
2 Bokobza, L., Pajot-Augy, E., Monnerie, L., Castellan, A. and Bouas-Laurent, H. *Polym. Photochem.* 1984, **5**, 191
3 Pajot-Augy, E., Bokobza, L., Monnerie, L., Castellan, A. and Bouas-Laurent, H. *Macromolecules* 1984, **17**, 1490
4 Pham-Van-Cang, C., Bokobza, L., Monnerie, L., Vandendriessche, J. and De Schryver, F. C. *Polym. Commun.* 1986, **27**, 89
5 Bokobza, L. and Monnerie, L. in 'Photophysical and Photochemical Tools in Polymer Science' (Ed. M. A. Winnik), D. Reidel, Dordrecht, 1986
6 Birks, J. B. 'Photophysics of Aromatic Molecules', Wiley, New York, 1970
7 Valeur, B. and Monnerie, L. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 11
8 De Schryver, F. C., Vandendriessche, J., Toppet, S., Demeyer, K. and Boens, N. *Macromolecules* 1982, **15**, 406
9 Vandendriessche, J., Palmans, P., Toppet, S., Boens, N., De Schryver, F. C. and Masuhara, H. *J. Am. Chem. Soc.* 1984, **106**, 8057
10 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
11 Ferry, J. D. 'Viscoelastic Properties of Polymers', 2nd Edn., Wiley, New York, 1970
12 Van Krevelen, D. W. 'Properties of Polymers. Correlations with Chemical Structure', Elsevier, Amsterdam, 1972