

Studies of the mobility of probes in poly(propylene oxide): 2. Excimer fluorescence technique

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Intramolecular excimer formation of *meso*-2,4-di(*N*-carbazolyl)pentane dissolved in two poly(propylene oxides) of molecular weights 425 and 4000 as well as in 1,2-propanediol (monomer) 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 matrices involved in the glass transition phenomenon. The data obtained in 1,2-propanediol have been fitted by a Vogel-type WLF equation. The results show that intermolecular interactions in the monomer lead to a thermal expansion coefficient of the free volume smaller by a factor of about 2 than that of the polymer.

(Keywords: fluorescence; intramolecular excimer; *meso*-2,4-di(*N*-carbazolyl)pentane; polymer mobility; free volume; poly(propylene oxide); 1,2-propanediol)

INTRODUCTION

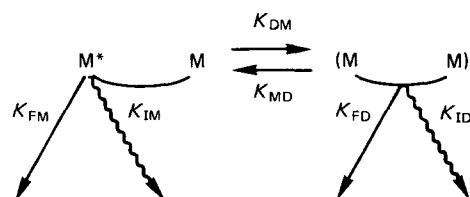
In a previous paper (part 1)¹ the mobility of poly(propylene oxide) has been investigated by the fluorescence anisotropy decay (FAD) of 1,6-diphenyl-1,3,5-hexatriene (DPH) probe. In this paper, we use another fluorescence technique based on the excimer formation of an intramolecular excimer-forming probe: the *meso*-2,4-di(*N*-carbazolyl)pentane (*meso*-DNCzPe). Indeed, photoluminescence involving excimers has proved to be a powerful tool to investigate relaxation processes of macromolecular chains in bulk polymers²⁻⁶. The formation of an intramolecular excimer results from the association of two aromatic groups separated by a three-atom linkage, one of which has been electronically excited. The excimer state arises from a well defined and localized conformational transformation in such a way that the volume swept out by the interacting chromophores can be related to the free volume induced by the segmental motions of the polymer matrix.

This paper reports an analysis of the emission behaviour of *meso*-DNCzPe dissolved in two poly(propylene oxides) of molecular weights 425 (PPO425) and 4000 (PPO4000) as well as in 1,2-propanediol (PD).

EXPERIMENTAL

Technique

Analysis of the experimental data is performed according to the conventional kinetic scheme⁷:



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 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

$$\tau_0 = 1/(K_{FM} + K_{IM})$$

the monomer decay (radiative plus non-radiative) in the

absence of excimer formation. The latter quantity is determined by measuring the fluorescence decay time of a model compound containing only one chromophore. In the case of *meso*-DNCzPe, the monomeric model compound is the *N*-isopropylcarbazole (NIPCz). The rotational motion involved in intramolecular excimer formation is characterized by a correlation time τ_c defined as the reciprocal of the rate constant of excimer formation K_{DM} .

Apparatus

The fluorescence spectra were recorded on a Fica model 55 MK II spectrofluorimeter equipped with a 450 xenon lamp and an R212 photomultiplier tube. Emission spectra were automatically corrected for instrumental response. The excitation wavelength was 320 nm. Fluorescence decays were performed on a single-photon-counting fluorimeter described previously⁸. Sample fluorescence was produced by the strong 337 nm emission

line of the nitrogen discharge. The monomer emission was analysed through an MTO A 2190 filter ($\lambda_{trans\ max} = 354\ \text{nm}$; maximum transmission = 22%; FWHM = 20 nm). The optical density of the probe was less than 0.1 at the excitation wavelength in order to avoid reabsorption effects.

Samples

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^{9,10}.

The poly(propylene oxides) as well as the 1,2-propanediol are the same as those used in part 1.

RESULTS

As a typical example, the temperature dependence of the excimer–monomer emission spectra of *meso*-DNCzPe dissolved in PPO425 is given in Figure 1. The existence of an isoemissive point shows that the non-radiative processes are not competing with fluorescence.

The temperature dependence of the monomer lifetime of *meso*-DNCzPe as well as that of the model compound in each matrix is given in Figures 2a–c. 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 about 273 K for the PPO and about 243 K for the PD.

Figure 3 gives a logarithmic plot of the correlation time of the intramolecular rotational motion against the reciprocal of temperature. A non-Arrhenian behaviour is shown, particularly for the two polymers. At a given temperature, the rate of conformational change is slightly higher in PPO425 than in PPO4000. This effect may be ascribed to the small difference between the glass transition temperatures T_g of the two polymers. So the correlation times τ_c of the probe motion have been plotted versus $(T - T_g)$ in Figure 4. At the same $(T - T_g)$, the conformational transition rate is quite similar in the two polymers but higher than in the monomer, 1,2-propanediol.

In the case of 1,2-propanediol (PD), the non-Arrhenian behaviour of the correlation time (Figure 3) as well as of

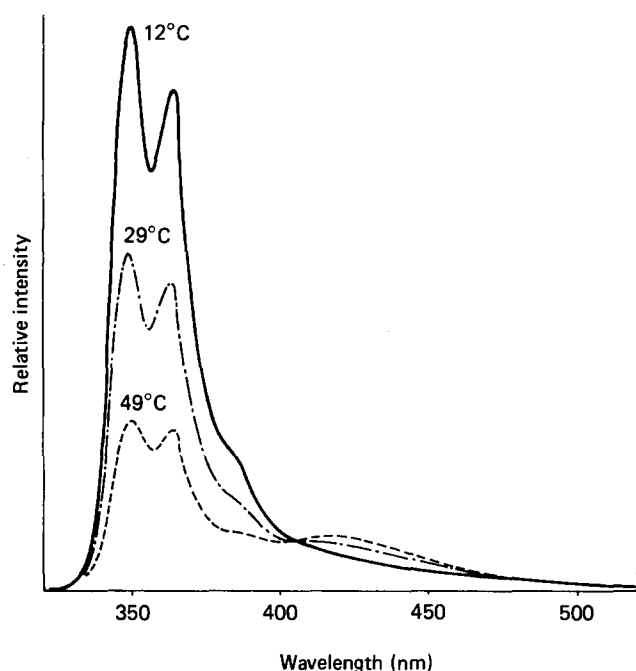


Figure 1 Temperature dependence of the emission spectrum of *meso*-DNCzPe in poly(propylene oxide) (PPO425)

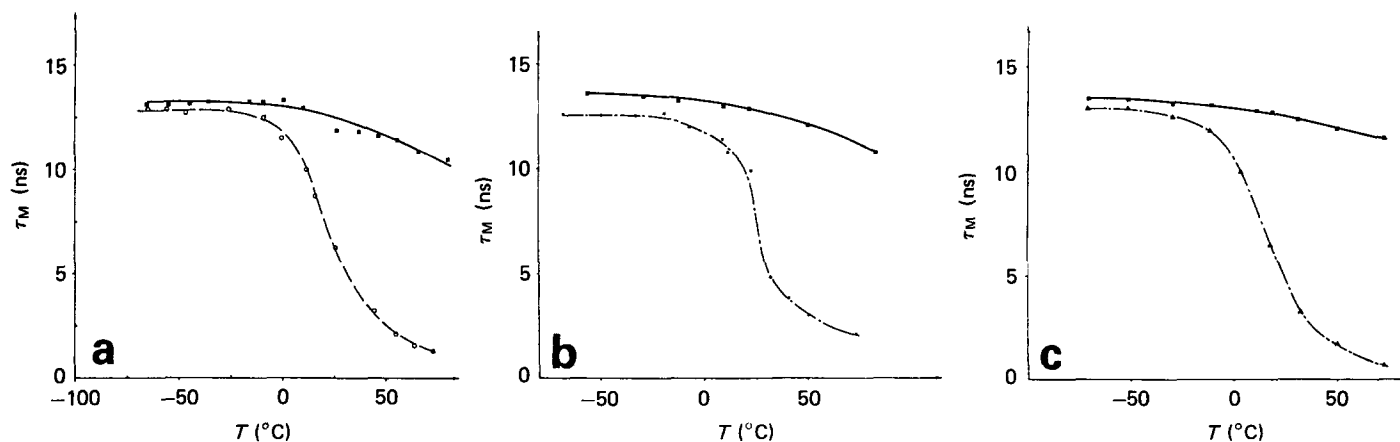


Figure 2 Temperature evolution of the fluorescence decay time of the model compound (NIPCz) (■) and of the monomer lifetime of *meso*-DNCzPe in (a) PPO425 (○), (b) PPO4000 (*), (c) PD (▲)

graphically by rewriting the WLF equation as a linear relationship:

$$-1/[\log(\tau_c/\tau_{c_0})] = -1/[\log(\eta/\eta_0)] = 1/C_1^0 + C_2^0/C_1^0(T - T_0) \quad (1)$$

The determination of the WLF constants has been made from precise viscosity measurements of PD between 253 and 313 K (Figure 6). With $T_0 = 254$ K, we get $C_1^0 = 6.0$ and $C_2^0 = 129.8$ K, $C_1 C_2 \approx 779$ K. At the glass transition temperature T_g , these values become: $C_1^g = 18$ and $C_2^g = 43.3$ K, and $T_\infty = T_0 - C_2^0 = T_g - C_2^g \approx 124$ K. This

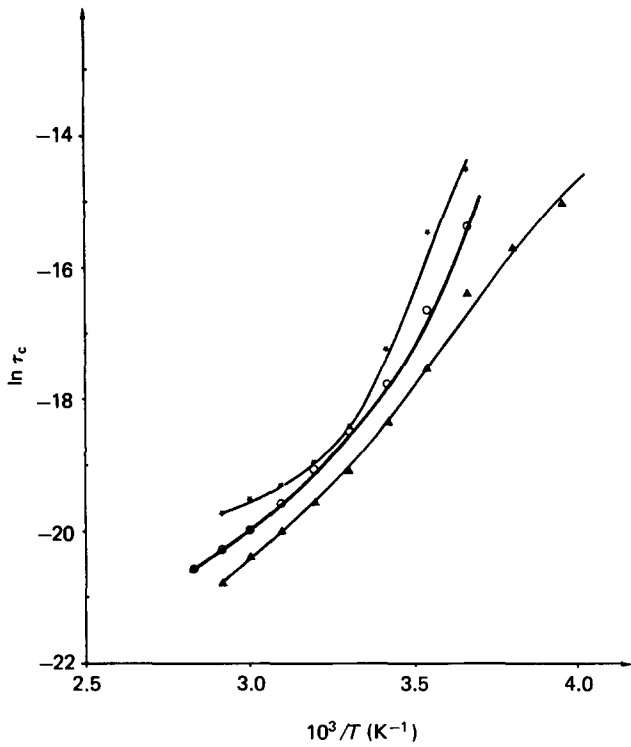


Figure 3 Temperature dependence of the correlation time for meso-DNCzPe dissolved in the different matrices investigated. The signs are the same as those used in Figure 2

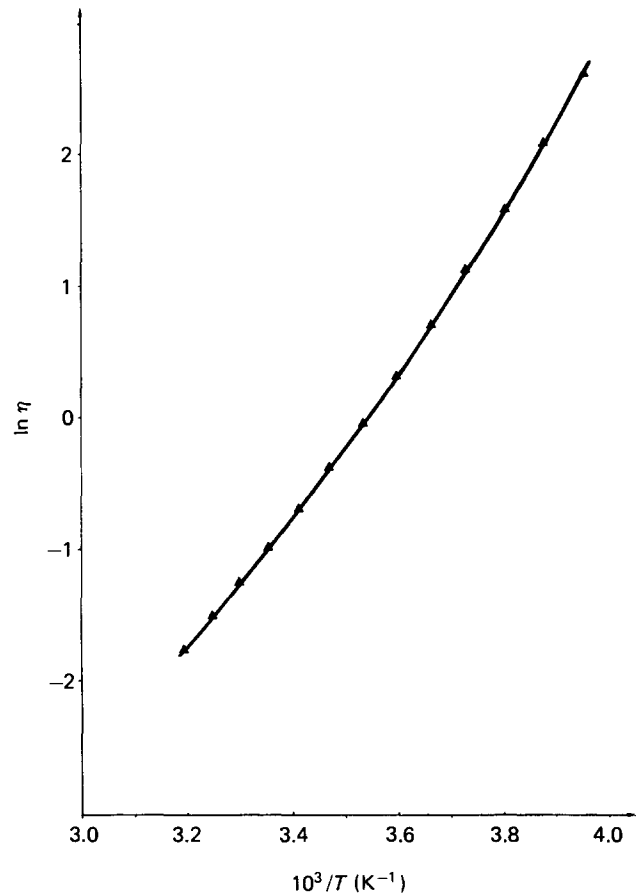


Figure 5 Logarithmic plot of the bulk viscosity of PD against the reciprocal of temperature

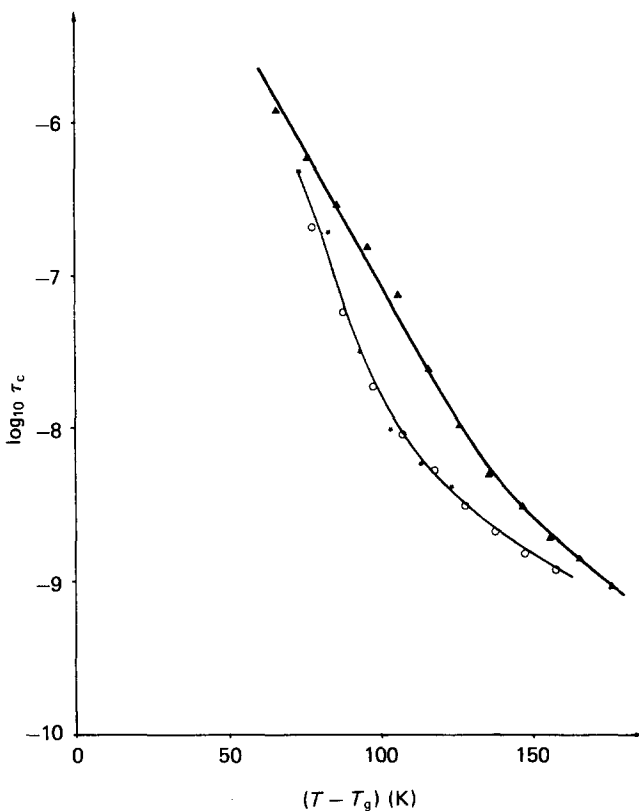


Figure 4 Logarithmic plot of the correlation time vs. $(T - T_g)$ for meso-DNCzPe dissolved in the different matrices investigated. The signs are the same as those used in Figure 2

the viscosity (Figure 5) is consistent with the observed glass transition temperature of 167.5 K for this compound. The data must be fitted by a Vogel-type expression. The constants C_1 and C_2 can be determined

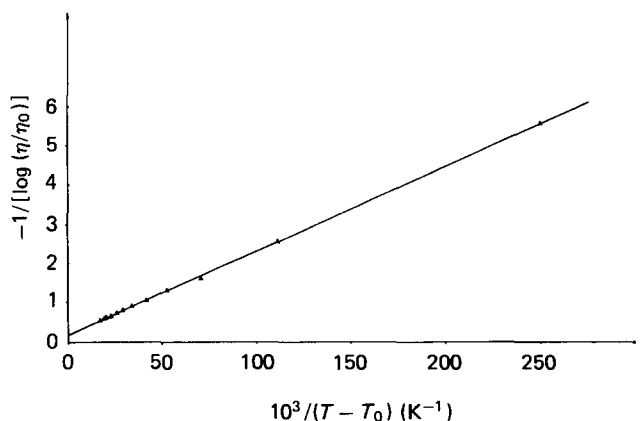


Figure 6 Determination of the C_1 and C_2 constants in the WLF equation by plotting $-1/[\log(\eta/\eta_0)]$ against $1/(T - T_0)$ according to equation (1)

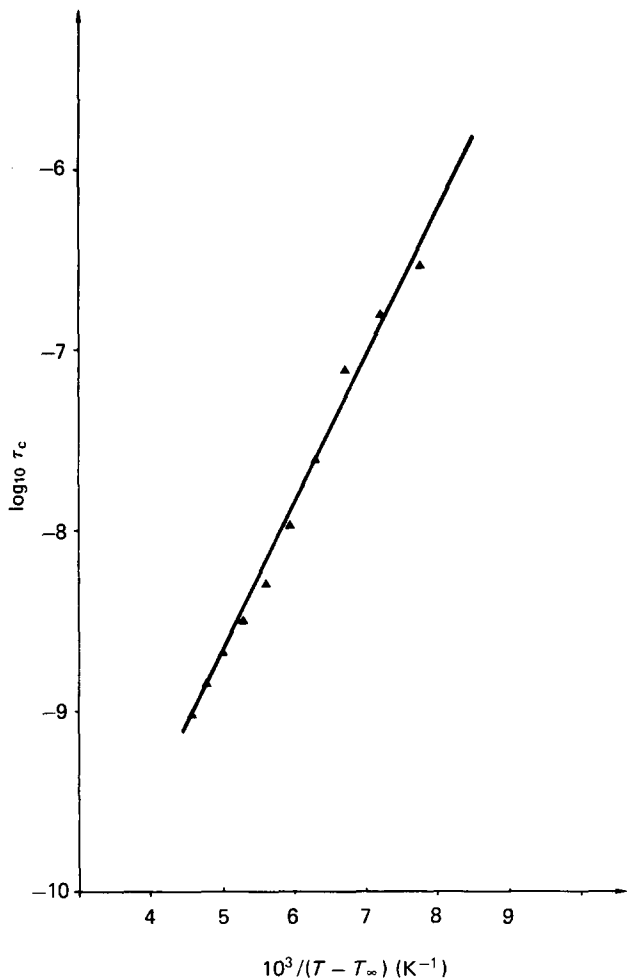


Figure 7 Logarithmic plot of the correlation time vs. $1/(T - T_\infty)$ for *meso*-DNCzPE in PD

value is close to that taken (120 K) by Davidson and Cole¹¹ to fit dielectric experimental data.

In Figure 7 are reported for *meso*-DNCzPe in PD, the plots of $\log \tau_c$ against $1/(T - T_\infty)$ with the value of T_∞ found from viscosity measurements. The slope of the curve equals 778, which is quite similar to the C_1C_2 product predicted from viscosity data.

Figure 8 gives the results obtained for PPO425 by using for T_∞ the value of 174 K given by Ferry¹².

DISCUSSION

As is shown in Figure 8, the fit of the correlation time τ_c of the rotational motion of the probe to the Vogel-type WLF equation:

$$\log \tau(T) = \log \tau_c(T_g) - C_1^g + C_1^g C_2^g / (T - T_\infty) \quad (2)$$

proves the adequacy of the free-volume theory to describe the excimer sampling process in PPO. The fact that the slope of the curve (428 K) is close to the C_1C_2 product predicted by Ferry (389 K) indicates that the probe motion is only ruled by the local dynamics of the macromolecular chains. In other words, the intramolecular conformational change of the *meso*-DNCzPe is modulated by the segmental motions of the polymer matrix which are involved in the glass-transition phenomenon.

Concerning the behaviours in the two polymers, the excimer fluorescence technique can detect a very slight effect of molecular weight. On the contrary, Wang *et al.*¹³, who studied by light scattering poly(propylene oxides) over the molecular weight range 425–4000, showed that the mean relaxation times for all polymers depend only on temperature and not on the shear viscosity associated with the difference in molecular weight.

In the case of PD, the close correspondence of the temperature dependence of the correlation time of the rotational probe motion (Figure 7) with that of the viscosity supports the conclusion that in this liquid the processes by which the excimer sampling mechanism and molecular flow in shear are realized must be intimately related.

Comparison of Figures 7 and 8 shows that at a constant $(T - T_\infty)$ the correlation time is higher in PD than in PPO425. The temperature dependence of the correlation time depends of course on the C_1C_2 product. In PD, which is a non-polymeric glass-forming liquid, the C_1C_2 product is higher by about a factor 2 than that obtained in the corresponding polymers. Miller¹⁴ has shown that the C_1C_2 product reflects energetic aspects and is related to the barrier of the rotation by the relation:

$$E_\infty = 2.3RC_1C_2$$

According to this model, the rotational barrier E_∞ about the chain backbone is equal to 1.97 kcal mol⁻¹ for PPO and to 3.58 kcal mol⁻¹ for PD. These values are obtained from the fit of the correlation times τ_c to equation (2). They are the same as those obtained from the viscosity data. The increase of E_∞ in PD can only be ascribed to intermolecular interactions by hydrogen bonding. C_1C_2 is also related to the thermal expansion coefficient α by the relation:

$$C_1C_2 = B/2.3\alpha$$

B is an empirical constant of order unity. Intermolecular

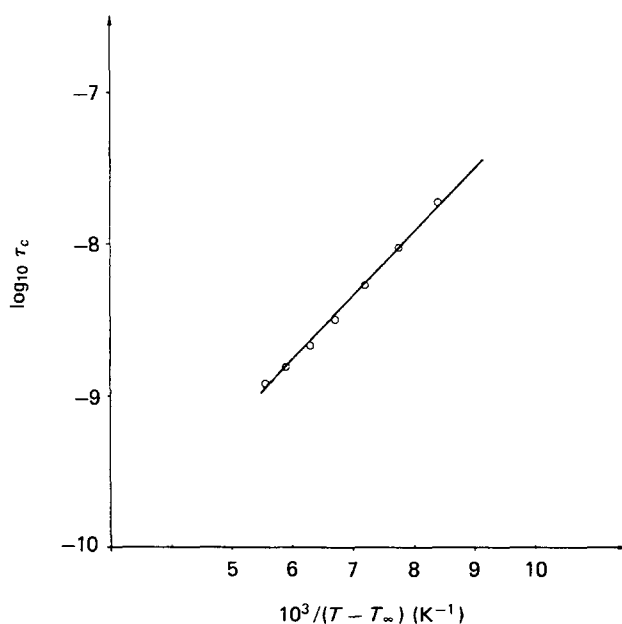


Figure 8 Logarithmic plot of the correlation time vs. $1/(T - T_\infty)$ for *meso*-DNCzPe in PPO425

Table 1

	PPO425				PD			
	log τ_c	T (K)	f_T^a	v_f^b per atomic group (cm ³)	log τ_c	T (K)	f_T^a	v_f^b per atomic group (cm ³)
Excimer	-8.77	341	0.189	3.84	-7.89	291	0.094	1.72
FAD	-9.31	341	0.189	3.84	-8.27	291	0.094	1.72

^a Calculated from $f_T = \alpha(T - T_\infty)$

^b Calculated from $v_f = f_T v$, where v is the total volume per gram

Table 2

	PPO425		PD	
	log τ_c	T (K)	log τ_c	T (K)
Excimer	-6.81	268.5	-8.50	315.5
FAD	-7.46	268.5	-8.86	315.5

interactions in PD lead to a smaller thermal expansion of the free volume than in the polymer.

Another point of interest is the comparison of the results obtained with the fluorescence anisotropy decay (FAD) and the excimer fluorescence technique. In the polymers, as well as in PD, at a same $(T - T_\infty)$, the correlation time of the DPH motion is always smaller than that of the excimer sampling process of *meso*-DNCzPe. At $1/(T - T_\infty) = 6 \times 10^{-3} \text{ K}^{-1}$ for example, the correlation times as well as the fractional free volumes f_T and the free volumes per atomic group v_f (which represents the free volume per mole of repeated units divided by the number of atomic groups) have been calculated. The results obtained are summarized in Table 1. It appears that the segmental motions of the matrix generate probe motions with a ratio of correlation times higher in the polymer than in the monomer. As the probe motions are modulated by the variation of the free volume, and these variations are different in the two matrices, it would be of interest to look at the dynamic behaviour of the probes at a fixed free volume (e.g. $v_f = 2 \text{ cm}^3$ per atomic group, for example). The results are reported in Table 2. They show that at a fixed free volume per atomic group, the efficiencies of the probe motions are higher in PD than in PPO. This may reflect a different degree of coupling or cooperative interaction between the

probe and the host matrix which leads to a ratio of 2.3 for the correlation times of the two probes in PD and 4.4 in PPO.

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