Comparison of the local chain dynamics in a series of bulk polymers at temperatures well above the glass transition temperature

Françoise Lauprêtre*, Liliane Bokobza and Lucien Monnerie
Laboratoire de Physico-Chimie Structurale et Macromoléculaire associé au CNRS, ESPCI,
10 rue Vauquelin, 75231 Paris Cédex 05, France
(Received 22 January 1992; revised 18 June 1992)

^{13}C n.m.r. spin-lattice relaxation times and excimer fluorescence data obtained on a series of bulk polymers at temperatures well above the glass transition temperature have been analysed in terms of local dynamics. Results thus obtained have shown that the intramolecular conformational changes of the excimer-forming probes are mostly governed by the segmental motions of the polymer chains involved in the glass transition phenomenon. Moreover, the frequency of these intramolecular motions is controlled by the monomeric friction coefficient of the surrounding matrix. Simultaneous analysis of ^{13}C n.m.r. spin-lattice relaxation times and excimer fluorescence data has led to an estimation of the displacement associated with the segmental motion of the chain. The jump amplitude is determined by the precise chemical nature of the polymer chain. In addition, ^{13}C n.m.r. data have shown that, in all the polymers investigated, libration of the C–H vector is superposed on the conformational reorientation. The libration amplitude depends on the chemical structure of the polymer and, for a given polymer, on the steric hindrance at the site of each carbon considered.

(Keywords: glass transition; fluorescence; spin-lattice relaxation)

INTRODUCTION

The local chain dynamics of bulk polymers at temperatures well above the glass transition temperature have been studied by a number of spectroscopic techniques including n.m.r.[1–33] and optical spectroscopy[34–41]. Some of these techniques, such as neutron scattering or n.m.r. spectroscopy, yield direct insight into polymer behaviour, whereas other methods allow the investigation of local dynamics through the motion of molecules dissolved in the polymer matrix, such as spin-probes or fluorescent probes. In the first case, the experiments are ruled by both polymer intramolecular conformational characteristics and intermolecular interactions. In the latter case, two factors may govern probe dynamics: intramolecular phenomena, as far as they permit conformational changes, and intermolecular interactions with the surrounding medium. In the particular case of intramolecular excimer-forming probes, the conformational changes are usually controlled by the dynamics of the polymer matrix[35,40]. This behaviour has been discussed from a theoretical point of view[42]. Therefore, for bulk polymers, n.m.r. spectroscopy and excimer fluorescence are complementary techniques that yield different information. Comparison of results from these two methods provides a detailed description of polymer intramolecular conformational characteristics and intermolecular interactions.

The purpose of this paper is to reach a deeper understanding of the different factors, both intra- and intermolecular, that govern the local chain dynamics in bulk polymers at temperatures well above the glass transition temperature. We compare experimental results obtained previously on a series of polymers by determination of ^{13}C n.m.r. spin-lattice relaxation times[25–28] and by the excimer fluorescence technique[41]. The excimer fluorescence technique is based on the emission behaviour of small intramolecular excimer-forming probes dissolved in polymer matrices. The excimer formation phenomenon has been thoroughly reviewed, especially for polymers, by Odani[43], Klöpffer[44], Semerak and Frank[45] and De Schryver *et al.*[46]. Formation of an intramolecular excimer results from association of two aromatic rings, one of which has been electronically excited. The excimer state arises from a well defined and localized conformational transition in such a way that the volume swept out by the interacting chromophores can be related to the free volume available in the polymer matrix. The excimer fluorescence technique is therefore a very useful tool providing information on the free volume in polymer systems. Where motions of the excimer probe are coupled with those of the polymer matrix, the technique can also be used to study the polymer local dynamics.

In contrast with the excimer fluorescence technique, ^{13}C n.m.r. allows a straightforward investigation of the polymer chain. Moreover, the selectivity of the n.m.r. technique allows independent studies of the relaxation of magnetically inequivalent carbons. The detailed analysis of ^{13}C n.m.r. spin-lattice relaxation times in a series of bulk polymers at temperatures well above the glass transition temperatures[25–28] has led to a general picture

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* To whom correspondence should be addressed

0032-3861/93/030468-08

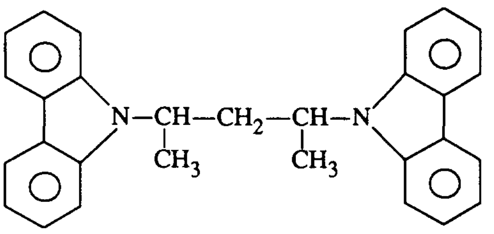
of local chain dynamics involving several types of motion. The segmental reorientation has been interpreted in terms of correlated conformational jumps which induce a damped orientation diffusion along the chain. It is satisfactorily described by well known autocorrelation functions derived from models of conformational jumps in polymer chains[47–49]. In addition to these conformational jumps, all polymers that have been investigated exhibit an additional fast process. This fast process has been observed in polymers of very simple vinyl chemical structure [such as poly(vinyl methyl ether) (PVME), poly(isobutylene) (PIB), crosslinked poly(ethylene oxide)s (PEOs) or poly(propylene oxide) (PPO)], as well as in polymers containing both single and double bonds [such as polybutadiene (PB) or polyisoprene (PI)]. The generality of this process and its high frequency have led us to assign it to a libration of limited but significant extent of the internuclear vector about its rest position. Such libration-type motions have also been observed by neutron scattering techniques[50].

EXPERIMENTAL AND DATA ANALYSIS

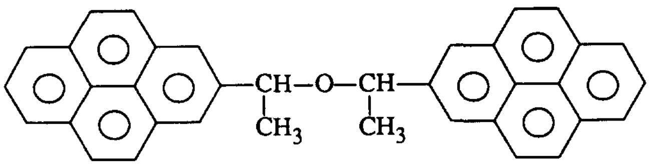
The molecular weight characteristics and glass transition temperatures of the polymers PVME, PIB, PPO, ethylene–propylene copolymer (EPR), PB and PI have been described elsewhere[25–28,35,40]. They are listed in *Table 1* together with the corresponding Williams, Landel and Ferry (WLF) constants[51].

Excimer fluorescence experiments

The intramolecular excimer-forming probes chosen for this work were the *meso*-2,4-di(*N*-carbazolyl)pentane (*meso*-DNCzPe):



and *meso*-bis[1-(2-pyrenyl) ethyl] ether (*meso*-B2PEE):



The fluorescence emission spectra of *meso*-DNCzPe and *meso*-B2PEE dissolved in the polymer matrices listed above were recorded as a function of temperature. Experimental details concerning the apparatus and measurement procedures of the emission spectra have been reported previously[35,40].

Analysis of the experimental data obtained from the excimer fluorescence technique was performed according to the conventional kinetic scheme[52]:

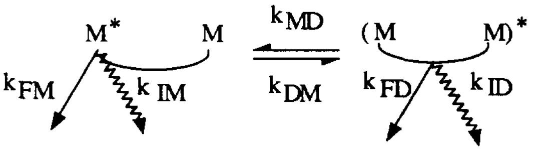


Table 1 Molecular weights, glass transition temperatures T_g obtained from d.s.c. measurements and T_∞, C_g^1, C_g^2, and α_f values for the polymers being studied

Polymer	M_w	T_g (K)	T_∞ (K)	C_g^1	C_g^2 (deg)	$\alpha_f \times 10^4$ (deg^{-1})
PPO	425[a]	200	174	16.2	24	11.3
	4000[b]	198	174	16.2	24	11.3
PIB	1.3×10^6	205	101	16.6	104.4	2.5
EPR	4.1×10^5	209	175	13.1	40.7	8.1
PI (%*cis*=92)	1.4×10^6	211	146	16.8	53.6	4.8
PB (%*cis*=96)	4.7×10^5 [a]	164	101	11.3	60	6.4
PB (%*cis*=98.8)	1.06×10^6 [b]	164	101	11.3	60	6.4
PVME	90 000	243	188[c]	11.5[c]	58.6[c]	6.4

[a] Used in excimer fluorescence experiments

[b] Used in n.m.r. experiments

[c] From Faivre[62]. Other T_∞, C_g^1, C_g^2 and α_f values have been taken from Ferry[51]

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

$$k_{DM} = (\tau_M)^{-1} - (\tau_0)^{-1} = (\tau_c)^{-1} \tag{1}$$

where

$$\tau_M = 1/(k_{FM} + k_{IM} + k_{DM}) \tag{2}$$

is the excited monomer lifetime and

$$\tau_0 = 1/(k_{FM} + k_{IM}) \tag{3}$$

is that of monomer 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. 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}.

Determinations of τ_c for the two excimer-forming probes adopted in this study and dispersed in PPO, PIB, EPR, PI and PB matrices at temperatures well above the glass transition temperature have been described[35,40].

^{13}C n.m.r. experiments

The determinations of ^{13}C n.m.r. spin-lattice relaxation times T_1 have been reported previously for PVME[25], PPO[26], PIB[28], PI and PB[27].

The orientation autocorrelation function[25] used to represent the n.m.r. data obtained on these polymers in bulk at temperatures well above the glass transition temperature or in solution has the following expression:

$$G(t) = (1-a)\exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1) + a\exp(-t/\tau_0) \tag{4}$$

where I_0 is the modified Bessel function of order 0, the correlation time τ_1 characterizes the conformational jumps, the correlation time τ_2 is associated with damping and τ_0 is the characteristic time of the libration described in terms of an anisotropic reorientation inside a cone of

Table 2 a_{CH}, Θ_{CH}, a_{CH_2}, Θ_{CH_2}, τ_1/τ_0, τ_2/τ_1 values deduced from ^{13}C n.m.r. relaxation data analysis

Polymer	a_{CH}	Θ_{CH}	a_{CH_2}	Θ_{CH_2}	τ_1/τ_0	τ_2/τ_1
PVME	0.40	33	0.40	33	$\geqslant 200$	2
PB	0.27	26	0.46	35	$\geqslant 150$	$\geqslant 500$
PI	0.17	20	0.40	33	$\geqslant 150$	40
PIB			0.21	23	$\geqslant 150$	$\geqslant 150$
PPO	0.24	25	0.49	37	$\geqslant 150$	80

half-angle Θ and an axis which is the rest position of the internuclear vector. The term a is related to the half-angle Θ of the libration cone through the relation:

$$(1-a)=[(\cos\Theta-\cos^3\Theta)/2(1-\cos\Theta)]^2 \quad (5)$$

Assuming that τ_0 is much shorter than τ_1 and τ_2 (a condition that has been checked in all the examples investigated[25–28]), the second term in the expression for $G(t)$ can be simplified. Under this condition the spin-lattice relaxation time T_1 obtained from a ^{13}C experiment by using the proton-noise decoupling technique is written as[25]:

$$\begin{aligned}(T_1)^{-1}=n\{&(1-a)\hbar^2\gamma_C^2\gamma_H^2\\ &\times[J_{HH}(\omega_H-\omega_C)+3J_{HH}(\omega_C)+6J_{HH}(\omega_H+\omega_C)]\\ &+a\hbar^2\gamma_C^2\gamma_H^2[J_0(\omega_H-\omega_C)+3J_0(\omega_C)\\ &+6J_0(\omega_H+\omega_C)]\}/10r_{CH}^6 \end{aligned}\quad (6)$$

where r_{CH} is the internuclear CH distance and:

$$J_{HH}(\omega)=Re[(\alpha+i\beta)^{-1/2}]$$

$$J_0(\omega)=\tau_0/(1+\omega^2\tau_0^2)$$

with

$$\alpha=\tau_2^{-2}+2\tau_1^{-1}\tau_2^{-1}-\omega^2$$

$$\beta=-2\omega(\tau_1^{-1}+\tau_2^{-1})$$

and n is the number of protons directly bonded to the carbon of interest.

Values of a, Θ, τ_1/τ_0 and τ_2/τ_1 have been calculated for PVME[25], PPO[26], PIB[28], PI and PB[27] by using expressions (4)–(6) as described in ref. 25. They are listed in *Table 2*.

RESULTS AND DISCUSSION

Nature of local chain motions

As shown previously[41], at temperatures well above the glass transition temperature, the correlation times of the intramolecular rotational motion of both the *meso*-DNCzPe and *meso*-B2PEE excimer-forming probes exhibit non-Arrhenius behaviour as a function of temperature in all the matrices investigated (PPO, PB, PI and EPR).

According to free-volume theory, the mobility of the polymer segments involved in the glass transition phenomenon should follow the well known WLF equation[53]:

$$\log\frac{\tau_c(T)}{\tau_c(T_g)}=\frac{-C_g^1(T-T_g)}{C_g^2+(T-T_g)} \quad (7)$$

which describes the temperature dependence of the ratio of correlation time derived from mechanical or dielectric relaxation at temperature T to its value at the glass transition temperature T_g taken as reference. The above equation can be rewritten by using the Vogel temperature[54], $T_\infty=T_g-C_g^2$:

$$\begin{aligned}\log\tau_c(T)-\log\tau_c(T_g)&=-C_g^1+C_g^1C_g^2/(T-T_\infty)\\ &=-C_g^1+C^1C^2/(T-T_\infty)\end{aligned} \quad (8)$$

T_∞ and the product $C_g^1C_g^2=C^1C^2$ are characteristic constants for a given polymer which do not depend on the reference temperature. T_∞, the temperature at which the free volume in the system is zero, corresponds to an infinite viscoelastic relaxation time.

Expression (8) can be written in terms of the fractional free volume f_T at temperature T:

$$\log\tau_c(T)=\log\tau_c(T_g)-C_g^1+\frac{1}{2.303f_T} \quad (9)$$

where

$$f_T=\alpha_f(T-T_\infty) \quad (10)$$

and α_f is the thermal expansion coefficient of the free volume.

Figure 1 shows the logarithmic plot of the correlation time, τ_c, of the *meso*-DNCzPe probe motion against $1/(T-T_\infty)$ in each matrix. The selected values of T_∞ are those reported by Ferry[51] and listed in *Table 1*. Similar results have been reported[41] for the correlation time of the *meso*-B2PEE probe motion. The fit of the correlation time for the rotational motion observed for both excimer-forming probes, to the Vogel-type WLF equation proves the adequacy of the free volume theory for describing the excimer sampling process in the polymer matrices investigated. Moreover, as shown in *Table 3*, the slopes of the curves are in good agreement with the C^1C^2 products predicted by Ferry[51] from low frequency viscoelastic measurements, which implies that the intramolecular conformational changes of the probe are mostly controlled by the segmental motions of the polymer chains involved in the glass transition phenomenon.

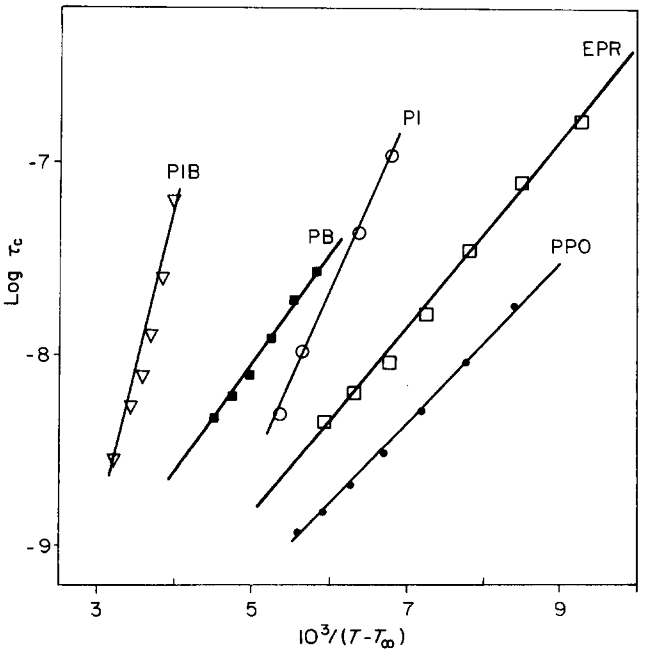


Figure 1 Variation of the correlation time, τ_c, of the *meso*-DNCzPe probe motion as a function of $10^3/(T-T_\infty)$ in the various polymer matrices

Table 3 Free-volume parameters at $T_{ref/meso\text{-}DNCzPe}$ for the excimer probe motion of meso-DNCzPe in polymer matrices

Polymer	C^1C^2 (from ref 51) (deg)	C^1C^2 (observed) (deg)	T_{ref} (K)	f_{ref}	$v_f(T_{ref})$ per atomic group (cm^3)
PIB	1733	1712	382	0.071	2.41
PI	900	914	323	0.084	1.57
EPR	533	500	324	0.129	1.36
PPO	389	428	302	0.130	2.53
PB	678	604	298	0.141	2.14

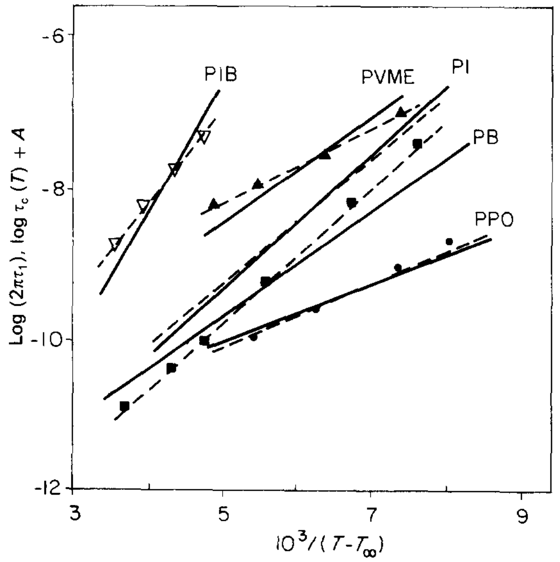


Figure 2 Dependences of log $\tau_c(T)+A$ as calculated from expression (8) (—) and $\log(2\pi\tau_1)$ (- - -) derived from ^{13}C T_1 n.m.r. experiments, as a function of $10^3/(T-T_\infty)$

The same type of approach can be used to understand the temperature behaviour of the correlation time τ_1 deduced from the ^{13}C n.m.r. determination of spin-lattice relaxation times. Within the motional description leading to expression (4), the correlation time τ_1 characterizes the conformational jumps of the polymer chain. Comparisons of the variations in $\log(2\pi\tau_1)$ and $\log\tau_c(T) + A$ calculated from expression (8) as a function of $(T-T_\infty)$ are shown in *Figure 2* for PB, PI, PIB, PVME and PPO. A is an arbitrary shift factor which depends on the polymer considered. The agreement between the two sets of data is very good for PPO and PI. It is not so good but still satisfying for the other systems under investigation. As concluded from the excimer fluorescence experiments, it implies that the segmental motions described by the correlation time τ_1 at temperatures well above the glass transition temperature are those responsible for the glass transition phenomenon. The differences in behaviour apparent for some polymers are likely to result from the fact that the n.m.r. measurements are carried out in a frequency domain where both glass transition and secondary relaxations merge[55].

Definition of a reference temperature

Data plotted in *Figure 1* show that at a constant $(T-T_\infty)$ difference, the mobility of the *meso*-DNCzPe probe decreases from PPO to EPR, PI, PB and PIB, respectively. Identical results have been reported[41] for the *meso*-B2PEE probe. The same type of behaviour is also observed from the n.m.r. data plotted in *Figure 2* where each polymer has its own dependence of $\log\tau_1$ as a function of $(T-T_\infty)$. These results indicate that the differences between the various polymers in segmental mobility, observed (by both techniques) at a given temperature, cannot be explained by the differences in the T_∞ temperatures. Similar results are observed when comparing the $\log\tau_c$ or $\log\tau_1$ variations as a function of $(T-T_g)$ for the different polymers: at a given $(T-T_g)$ difference, each polymer has its own dependence of $\log\tau_c$ or $\log\tau_1$ as a function of $(T-T_g)$. Although the intramolecular conformational changes of the probes, as well as the τ_1 processes, are controlled by the segmental motions of the polymer chains involved in the glass transition phenomenon, the polymer matrices do not share the same local dynamics at a given $(T-T_\infty)$ or $(T-T_g)$ difference. Therefore, neither T_∞ nor the glass transition temperature T_g can be considered as good descriptors for rescaling the segmental motions in bulk polymers at temperatures well above T_g.

It is of interest to define a reference state in which all the polymers are in equivalent states from the point of view of their local molecular mobility. To define such equivalent states, one has to look for a property in relation with the frequency window of each experiment. In the case of the excimer fluorescence technique, such a temperature can be the temperature at which the probe of interest undergoes its conformational change at a given frequency, 10^8 Hz for example, within the frequency window of the experiment. For the ^{13}C n.m.r. relaxation experiments, the temperature at which the spin-lattice relaxation time T_1 reaches its minimum may constitute an appropriate reference state. The T_1 minimum is directly related to the local mobility in the frequency range defined by $(\omega_H-\omega_C)$, (ω_C) and $(\omega_H+\omega_C)$ and can be easily determined experimentally. It is independent of the model used to describe the local dynamics. However, due to the flat character of the T_1 minimum, the uncertainty in determining the experimental values of $T_{ref/nmr}$ is quite large. Moreover the precise value of τ_1 at the T_1 minimum slightly depends on the τ_2/τ_1 ratio. An alternative definition of the n.m.r. reference temperature is the temperature $T_{ref/nmr10^{-9}}$ at which $\tau_1 = 10^{-9}$ s, in the centre of the ^{13}C T_1 frequency window. Unlike $T_{ref/nmr}$, $T_{ref/nmr10^{-9}}$ is model dependent. Reference temperatures ($T_{ref/nmr}$ at 25.15 MHz, $T_{ref/meso\text{-}DNCzPe}$ and $T_{ref/meso\text{-}B2PEE}$) thus determined from the different series of experiments have been obtained for each of the polymers investigated. The resultant values are listed in *Table 4* and show that, whatever the technique used, $(T_{ref}-T_g)$ varies strongly from one polymer to another. For example $T_{ref/nmr}-T_g$ is 36°C higher in PIB than in PI. This implies that equivalent mobilities (in terms of τ_1 processes) to those of PI are attained in PIB, only once a 36°C differential in temperature is established between the two polymers.

Table 4 $T_{ref/meso\text{-}DNCzPe}$, $T_{ref/meso\text{-}B2PEE}$ and $T_{ref/nmr}$ reference temperatures

Polymer	T_g (K)	$T_{ref/meso\text{-}DNCzPe}$ (K)	$T_{ref/meso\text{-}B2PEE}$ (K)	$T_{ref/nmr}$ (K)
PIB	205	382	405	333
PI	211	323	333	297
EPR	209	324	339	
PPO	198–200	302	319	270
PVME	243			344
PB	164	298		234

The next step of this approach is to relate the reference temperatures to data obtained from viscoelastic experiments. Fractional free volumes f_{ref} at $T_{ref/meso\text{-}DNCzPe}$ have been calculated from expression (10) for the different polymers. They are listed in *Table 3*. The dispersion of f_{ref} values is large. A dispersion of the same order of magnitude is observed at $T_{ref/meso\text{-}B2PEE}$. Clearly, attainment of a common rate of interconversion (within an excimer-forming probe) is not realized through establishment of a common fractional free volume between matrices. Similarly, the conformational jumps in polymers (as evaluated through τ_1, from n.m.r. experiments) do not (necessarily) occur at equivalent frequencies when the fractional free volumes of the matrices become equal.

The free volume $v_f(T_{ref})$ at the reference temperatures can be derived from f_{ref} and Van Krevelen's data on amorphous polymers[56]. They represent the free volume per mole of repeat unit of the poymer divided by the number of main-chain atoms per repeat unit. Once more, the values (*Table 3*) differ from one polymer to another, which implies that other molecular parameters have to be considered.

Another quantity of interest for the local dynamics is the monomeric friction coefficient ζ_0, which characterizes the resistance encountered by a monomer unit moving through its surroundings[57]. It has been shown to follow the WLF law. The variation of the monomeric friction coefficient ζ_0 as a function of temperature in PI, PIB and EPR is described by Ferry[51]. In the case of the *cis*-PB under study, there are no ζ_0 data. However, the friction coefficients of the chain unit and of a foreign molecule of similar size, ζ_0 and ζ_1, have been found[58] to be closely similar for several PB samples with different microstructures at temperatures well above T_g. In the following, we will use the approximation $\zeta_0 = \zeta_1$ for the *cis*-PB under study. ζ_0 values are plotted in *Figure 3* for PI, PIB, EPR and PB. For a given $(T - T_\infty)$ difference, their magnitude strongly depends on the polymer considered. However, $\log \zeta_0$ at $T_{ref/meso\text{-}DNCzPe}$ lies in the range from -7.0 to -7.25 for the four polymers, which implies that at these reference temperatures the polymers share a common value of ζ_0. As shown in *Figure 4*, the same behaviour is observed for the *meso*-B2PEE probe; at $T_{ref/meso\text{-}B2PEE}$, the friction coefficients of PB, PI and PIB are in the range from -7.4 to -7.5. For these reference temperatures too, the polymers share a common value of ζ_0. These results can be interpreted in the following way: at the reference temperatures, a given excimer-forming probe has the same motion in terms of both frequency (10^8 Hz) and amplitude, with the same volume always swept out, independent of the nature of the polymer matrix. Therefore at these reference temperatures, the intramolecular conformational changes of the probe are strictly identical. They are controlled by the monomeric friction coefficient of the bulk polymer.

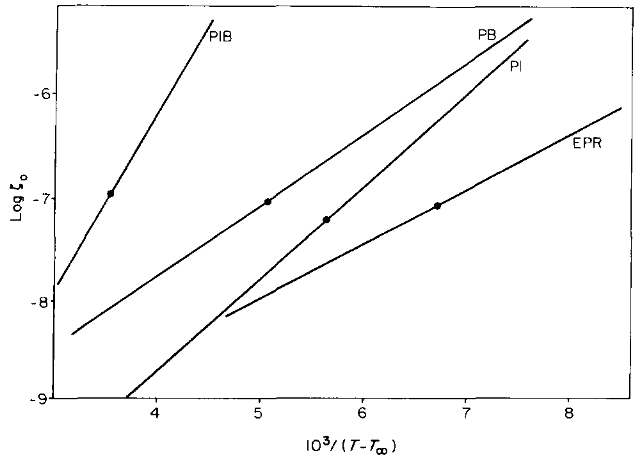


Figure 3 Plots of $\log \zeta_0$ as a function of $10^3/(T - T_\infty)$ and $\log \zeta_0$ values at the $T_{ref/meso\text{-}DNCzPe}$ (●) reference temperatures of the polymer matrices

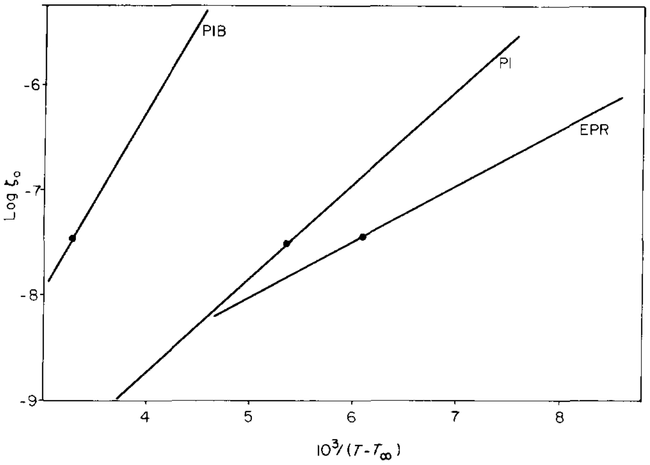


Figure 4 Plots of $\log \zeta_0$ as a function of $10^3/(T - T_\infty)$ and $\log \zeta_0$ values at the $T_{ref/meso\text{-}B2PEE}$ (●) reference temperatures of the polymer matrices

In terms of local dynamics for which one does not know precisely the number of monomer units involved in an elementary motion, one may wonder whether the friction coefficient per bond of the main chain, ζ_{0bond}, might be a still more appropriate descriptor than the monomeric friction coefficient. ζ_{0bond} is obtained from the ratio of ζ_0 to the number of backbone bonds inside the monomer unit. Calculations show that $\log \zeta_{0bond}$ lies in the range from -7.3 to -7.85 and -7.75 to -8.1 for the four polymers at $T_{ref/meso\text{-}DNCzPe}$ and $T_{ref/meso\text{-}B2PEE}$, respectively. The dispersion in ζ_{0bond} values at the reference temperatures is larger than that observed for the ζ_0 values under the same conditions. However, it must be noticed that the excimer-probe motion is controlled by its whole surroundings, meaning both polymer main chain and side groups, and this main-chain and side-group neighbourhood seems to be reflected in a better way by ζ_0 than by ζ_{0bond}.

Though ζ_0 is normally determined by mechanical measurements, it is evident from its definition that it is related in a simple manner to the polymer translatory diffusion, and in principle it can be determined from self-diffusion measurements in a polymer with sufficiently low molecular weight to avoid entanglements. The local motions observed through ^{13}C spin-lattice relaxation times are not significantly affected by entanglements. When the effects of entanglements can be neglected, ζ_0 can be written as[57]:

$$\zeta_0 = 2kT/\delta^2\varphi \qquad (11)$$

where φ is the probability of the monomer unit to jump in unit time and δ is the average length of each jump in a given direction. Within the limits of the motional model used to represent the n.m.r. experiments, φ is equal to $1/\tau_1$. However the jump amplitude, δ, should depend on the precise nature of the polymer considered. Therefore, in contrast with results observed for the excimer probe motion, the relation ζ_0 = constant should not hold true at the reference temperatures of the n.m.r. experiments. The values of $\log \zeta_0$ at $T_{ref/nmr}$ and $T_{ref/nmr\,10^{-9}}$ are shown in *Figure 5*. Whatever the definition of the n.m.r. reference temperatures, the dispersion in the $\log \zeta_0$ values is larger than that observed at $T_{ref/meso\text{-}DNCzPe}$ and $T_{ref/meso\text{-}B2PEE}$. This result underlines the influence of the precise chemical structure of the polymer chain on the mean size and motional amplitude of the reorienting units. In this respect, it is of interest to compare the values of the correlation time τ_1 obtained from the n.m.r. experiments on the different polymers (*Figure 2*) at $T_{ref/meso\text{-}DNCzPe}$. As demonstrated in *Figure 3*, the four polymers under study share a common value of ζ_0 at $T_{ref/meso\text{-}DNCzPe}$. At these reference temperatures, while the correlation time τ_c of the intramolecular probe motion derived from excimer fluorescence data is equal to 10^{-8} s, the correlation time τ_1 of the local chain motions observed by n.m.r. is 21, 28 and 37 times shorter than 10^{-8} s for PI, PIB and PPO, respectively. It is 240 times shorter in the case of PB. Use of relation (11), which implies that the $\delta^2/(\tau_1 T)$ ratio is a constant at $T_{ref/meso\text{-}DNCzPe}$, indicates that the PB chain is involved in jumps of small amplitude as compared to the other three polymers. While use of relation (11) yields an estimate of the amplitude δ of the τ_1 process in the range 2.7–3.6 Å for PIB, PI and PPO, roughly compatible with very small portions of the chain, the local dynamics of the PB chain consists of smaller amplitude and thus faster modes.

Evaluation of intramolecular energy barriers

More information on the detailed nature of the intramolecular processes of the polymer chain can be obtained from a careful examination of ^{13}C n.m.r. spin-lattice relaxation times.

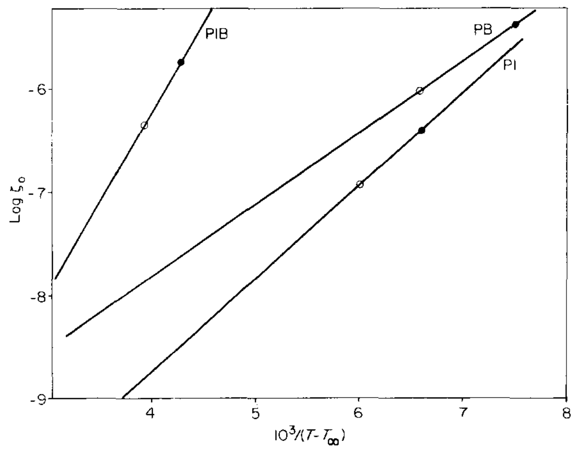


Figure 5 Plots of $\log \zeta_0$ as a function of $10^3/(T-T_\infty)$ and $\log \zeta_0$ values at the $T_{ref/nmr}$ (●) and $T_{ref/nmr\,10^{-9}}$ (○) reference temperatures of the polymer matrices

Table 5 Comparison of E^*/R obtained from ^{13}C n.m.r. relaxation analysis in solution and predicted $2.3\,C_g^1C_g^2$ values

Polymer	$E^*=E_{sol}-E_\eta$ (kJ mol^{-1})	E^*/R (deg)	$2.3\,C^1C^2$ (deg)
PVME	9.2	1.1	1.5
PI	13.4	1.6	2.1
PB	14.6	1.75	1.6
PIB	20.9	2.5	4.0

Interestingly, the limiting value at very high temperature of the quantity $2.3\,C^1C^2$ for the bulk polymers is expected to be the E^*/R factor involved in the Arrhenius equation for polymers in solution[59]. Values of $2.3\,C^1C^2$ for the polymers considered and reported by Ferry[51] are listed in *Table 5*. On the other hand, E^*/R factors can be determined from ^{13}C T_1 measurements in solution. Results reported previously[25–28] have shown that the dependence of $\log \tau_1$ on the reciprocal of absolute temperature T for the respective polymers in CDCl$_3$ solution are linear functions of $1/T$ in the temperature range under study. The slopes of the lines[25–28] lead to the apparent activation energies E_{sol}. These activation energies have been interpreted in terms of Kramers' theory for the diffusion of a particle over a potential barrier[60]. Kramers' theory has been applied to the case of conformational transitions in polymer chains by Helfand[61]. According to this theory, the correlation times associated with a motional mode involving the crossing of an energy barrier E^* in a hydrodynamic regime governed by viscous friction can be written as:

$$\tau = \eta C \exp(E^*/RT) \qquad (12)$$

where η is the solvent viscosity and C is a molecular constant.

The activation energy of the conformational jumps associated with the τ_1 correlation time can then be estimated from:

$$E^* = E_{sol} - E_\eta \qquad (13)$$

where E_η is the activation energy for the solvent viscosity. In the case of chloroform at 25°C, E_η is 5.85 kJ mol^{-1}. Values of E^*/R calculated from n.m.r. data in solution by using expressions (12) and (13) are given in *Table 5*.

Given the uncertainties in this type of data analysis, results reported in *Table 5* show a very good agreement between the two sets of data for most polymers. Only for PIB is $2.3\,C^1C^2$ somewhat higher than E^*/R. This observation tends to show that the detailed nature of the observed intramolecular processes picked up by ^{13}C T_1 measurements is identical in bulk at temperatures well above T_g and in solution.

Further support for this conclusion can be reached from the comparison of the ratios of the correlation times τ_1/τ_0 and τ_2/τ_1 and the angle of the libration cone Θ used to represent the T_1 relaxation data of polymers in bulk at temperatures well above the glass transition temperature and in solution. As an example, the τ_1/τ_0 and τ_2/τ_1 ratios and the Θ angle derived for PVME in bulk at temperatures well above the glass transition temperature[25] are given in *Table 2*. As shown by results reported in ref. 25, the relaxation data obtained from PVME in CDCl$_3$ solution are described by exactly the same values of the ratios of the correlation times τ_1/τ_0 and τ_2/τ_1 and the angle of the libration cone Θ listed in *Table 2* for the bulk local dynamics. Only the temperature dependence of the correlation times is different. Such a similarity in behaviour shows that the very nature of the motions involved in the magnetic relaxation at a given frequency is identical in bulk at temperatures well above T_g and in solution. For example, the libration which is revealed by the high value of the T_1 minimum has the same amplitude in PVME in solution and in bulk at temperatures well above the glass transition temperature. Similar results have been obtained for PI[27].

Complementary information on local motions

Although the τ_1/τ_0 ratio is not determined to a good accuracy when it reaches large values, it appears from results reported in *Table 2* that τ_0 is at least 150 or 200 times shorter than τ_1 for each polymer under investigation. This implies that the anisotropic mode, which is observed in addition to the segmental reorientation in the n.m.r. relaxation experiments, is a very fast process. The high frequency of this motion was one of the main reasons for its assignment to a libration of the internuclear vector about its rest position[25].

As shown by the values given in *Table 2*, the half-angle of the cone, Θ, is smaller for a methine carbon than for a methylene carbon except for PVME. Θ is large for PPO whereas it takes the smallest value for PIB. These results support the conclusion that Θ is related to the steric hindrance at the considered site; the larger the steric hindrance, the smaller is Θ. Besides, the fact that Θ takes on different values for neighbouring CH and CH_2 carbons inside the same polymer backbone is coherent with our interpretation of T_1 relaxation times in terms of an additional libration motion rather than with the existence of a distribution of τ_1 correlation times which should not depend on the exact CH or CH_2 site considered.

CONCLUSION

Results obtained on a series of bulk polymers at temperatures well above the glass transition temperature by the excimer fluorescence technique have clearly shown that the intramolecular conformational changes of the excimer-forming probes are mostly governed by the segmental motions of the polymer chains involved in the glass transition phenomenon. Moreover, the frequency of these intramolecular motions is controlled by the monomeric friction coefficient of the surrounding matrix. This monomeric friction coefficient appears to be a better descriptor for the dynamics of the excimer-forming probe than the friction coefficient per backbone bond.

Simultaneous interpretation of ^{13}C n.m.r. spin-lattice relaxation times and excimer fluorescence data has led to an estimation of the displacement associated with the segmental motion of the chain. The jump amplitude is determined by the precise chemical nature of the polymer chain.

Comparison with data obtained on polymer solutions has indicated that the intramolecular processes observed for a given polymer by ^{13}C T_1 n.m.r. measurements in bulk at temperatures well above the glass transition temperature and in solution are described by the same orientation autocorrelation function with the same amplitude of libration and the same value of the τ_1/τ_2 ratio, where τ_1 and τ_2 are the correlation times corresponding to the conformational jumps and the damping, respectively. The amplitude of the libration depends on the chemical structure of the polymer and, for a given polymer, on the carbon considered.

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