Investigation of polymer dynamics through the pressure effect on intramolecular excimer formation of a small probe

D. P. Jing, L. Bokobza*, P. Sergot and L. Monnerie
Laboratoire de Physico-Chimie Structurale et Macromoléculaire, ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France

and P. Collart and F. C. De Schryver
Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3030 Heverlee, Belgium

(*Received 1 July 1988; accepted 20 September 1988*)

The pressure effect on intramolecular excimer formation of meso-bis[1-(2-pyrenyl)ethyl]ether dissolved in polyisoprene and in polyisobutylene has been investigated. The rate of conformational change of the probe is free-volume dependent. The results show that, at a given fractional free volume, obtained by changing either temperature or pressure, the probe has the same mobility.

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

INTRODUCTION

Luminescence spectroscopy is a powerful tool for studying a large variety of phenomena occurring in natural and synthetic polymers. Its sensitivity results from the multiple aspects of the interaction of electronically excited states with the surrounding environment. In particular, the application of fluorescence probe methods for the investigation of mobility of polymeric media has become widespread. In previous papers[1-10], we have shown that the analysis of the emission behaviour of small intramolecular excimer-forming probes dissolved in elastomeric matrices can afford a way to determine the distribution and changes in free volume in polymer systems. If the probe motion is only modulated by the mobility of the media, the temperature dependence of its correlation time has been shown to follow that of the molecular relaxation of the matrix described by the WLF formula, thus proving that the volume swept out by the interacting chromophores is related to the free volume induced by the segmental motions of the polymer involved in the glass-transition phenomenon. Similarly, the viscoelastic relaxation times of a polymer depend on applied hydrostatic pressures. This behaviour can be understood in terms of the dependence of segmental mobility on the fraction free volume since the free volume must decrease with increasing pressure just as it does with decreasing temperature.

The present work focuses on the pressure dependence of the rate of intramolecular excimer formation of meso-bis[1-(2-pyrenyl)ethyl]ether (meso-B2PEE) dissolved in two polymers, polyisoprene and polyisobutylene, which have similar glass transition temperatures.

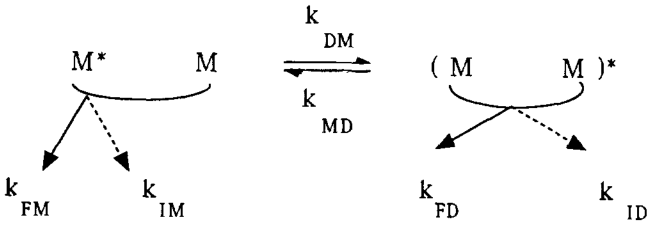
Pressure studies on intramolecular excimer formation in solution previously reported[11-13] were devoted to a comprehension of the viscosity dependence of the probe mobility. Hydrostatic pressure was used to achieve a continuous variation in viscosity without changing the chemical character of the solvent shell. High pressure studies of 1,3-di(1-pyrenyl)propane focused on the determination of micellar microviscosities have also been reported[14,15].

In this study, we have investigated the mobility of the host matrix through the pressure dependence of the rate constant of intramolecular excimer formation deduced from analysis of the transient decay kinetics of the probe.

EXPERIMENTAL

Technique

The experimental data are analysed according to the conventional kinetic scheme[16]



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

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*To whom correspondence should be addressed

0032-3861/89/030443-04$03.00

rate constant k_{DM} is calculated as follows:

$$k_{DM} = 1/\tau_M - 1/\tau_0$$

where

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

is the excited monomer lifetime and

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

is the monomer decay time in the absence of excimer formation. The rotational motion involved in intramolecular excimer formation is characterized by a correlation time τ_c defined as the reciprocal of k_{DM}. The monomer decay time τ_0 can be defined as the fluorescence lifetime of the aromatic moiety under the assumption that the probe does not undergo intramolecular excimer formation. It is commonly determined by measuring the fluorescence decay time of a model compound containing only one chromophore. On account of an interaction occurring 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.

When the excimer dissociation rate is very slow with respect to deactivation, i.e.

$$k_{MD} \ll k_{FD} + k_{ID}$$

which is the case at low temperatures or high pressures, the monomer decay is monoexponential with the decay parameter $\beta = 1/\tau_M$. When the excimer dissociation becomes efficient, the monomer decays as a sum of two exponentials and τ_M is determined from the amplitude ratio of these two exponentials according to Birk's analysis.

Apparatus

Fluorescence decays were performed on a single photon-counting fluorimeter described previously[17]. Sample fluorescence was produced by the strong 337 nm emission line of the nitrogen discharge.

The pressure cell (*Figure 1*) was constructed of Aubert et Duval X17U4 steel and was of cubic design with four window ports. It uses water as the pressure transmitting fluid. Two cylindrical single crystal sapphire windows (13 mm diameter, 9 mm length) were used at right angles for the fluorescence measurements from 0.1 to 4 kbar. The hydraulic system consisted of a Top Industries hand pump with a maximum operating pressure of 4 kbar. The pressure was calibrated with a pressure gauge JPB = G515. The temperature of the pressure cell can be monitored from 280 to 370 K by a Haak FK thermostat. The pressure can be kept constant for up to 24 h except for the critical period of the setting (10 min).

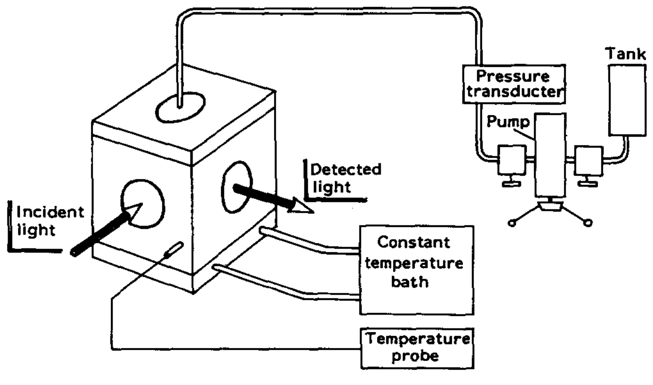
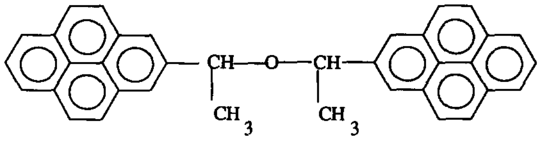


Figure 1 The high pressure equipment

Samples



The intramolecular excimer-forming probe: meso-bis[1-(2-pyrenyl)ethyl]ether (meso-B2PEE) (see formula above) was chosen for its high excimer sampling rate ($k_{DM} \approx 3.8 \times 10^9\,s^{-1}$ at 298 K in isooctane[18]).

The commercially available polyisoprene (PI) (Shell IR 307, *cis* = 92%, $M_w \approx 1\,400\,000$) was provided by Manufacture Française des Pneumatiques Michelin (Clermont-Ferrand, France). The 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 quartz plate from a cyclohexane solution containing the probe. The final probe concentration in the films does not exceed $3 \times 10^{-7}\,mol\,g^{-1}$. In the pressure apparatus, the film is immersed in water. The experiments were run isothermally (306 K in PI and 361 K in PIB) with increasing pressure (1–3 kbar). The temperatures were chosen in order to obtain similar variation of the monomer lifetime in the two matrices.

RESULTS

The effect of pressure on the monomer lifetime of meso-B2PEE and on the lifetime of (2-pyrenyl)ethyl ether (2PEE), taken as the monomeric model compound, is illustrated in *Figure 2*. The monomer lifetime of meso-B2PEE increases from atmospheric pressure to about 1000 bar, then slowly approaches a limiting value, which is that of the normalized model lifetime. As expected, the decrease of the free volume with increasing pressure leads to a decrease of the mobility of the probe. It is interesting to note that M* intensity decay remains monoexponential in the two high pressure studies. Such behaviour can be explained by the fact that pressure acts to compress the complex and thus stabilizes the excimer. So the probe is in a diffusion-controlled region, as it is in the low temperature range.

DISCUSSION

In a previous paper[10], it was shown that the temperature dependence of meso-B2PEE follows the WLF equation, which proves that the intramolecular conformational change of the probe is controlled by the segmental motions of the polymer matrix involved in the glass-transition phenomenon.

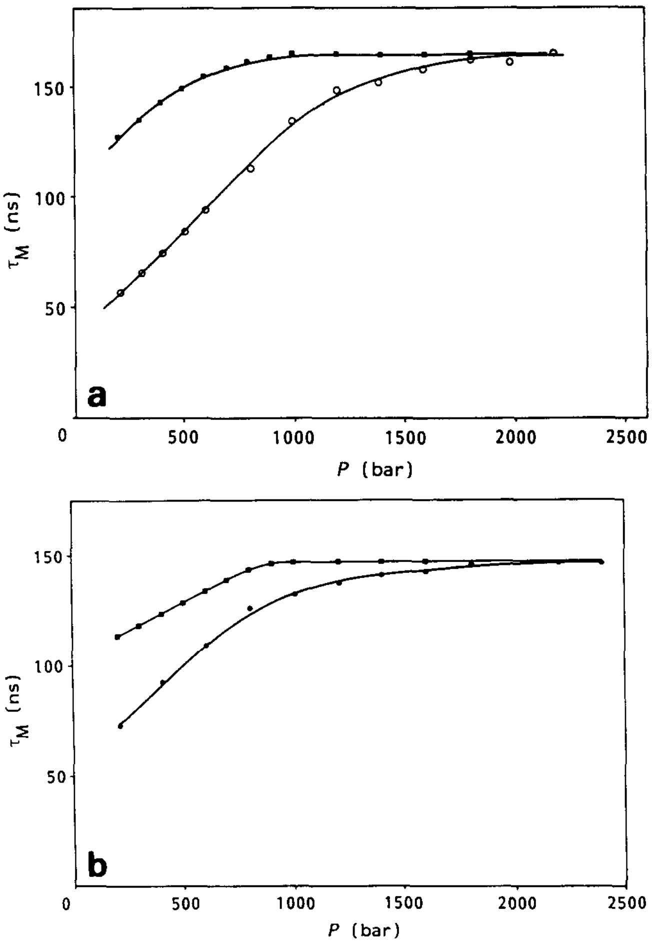


Figure 2 Pressure dependence of the normalized fluorescence decay time of the model compound (2PEE) (■) and of the monomer lifetime of meso-B2PEE in: (a) PI (○) at 306 K; (b) PIB (●) at 361 K

The theory of fluctuations of free volume is able to account for the effect of pressure. Effectively, the general formula

$$\log a_{1,2} = \log\frac{\tau_{c2}}{\tau_{c1}} = \frac{B}{2.303}\left(\frac{1}{f_2} - \frac{1}{f_1}\right) \tag{1}$$

which gives the ratio $a_{1,2}$ of the correlation times τ_{c2} and τ_{c1} associated with the fractional free volumes f_2 and f_1, respectively, can also be applied to the pressure studies.

If states 1 and 2 refer to atmospheric pressure P_0 and a higher pressure P, respectively, we obtain (at a constant temperature)

$$\log a_P = \frac{B}{2.303}\left(\frac{1}{f_P} - \frac{1}{f_0}\right) \tag{2}$$

The compressibility of the free volume, defined as

$$\beta_f = -\left(\frac{1}{v}\right)\left(\frac{\partial v_f}{\partial P}\right)_T \approx -\left(\frac{\partial f}{\partial P}\right)_T \tag{3}$$

is presumably a decreasing function of P.

Within the limited pressure range where β_f can be considered constant, the change in f with P can be written

$$f_P = f_0 - \beta_f(P - P_0) \tag{4}$$

where f_0 is the fraction of free volume at atmospheric pressure P_0. Equations (2) and (4) can be combined to obtain

$$\log a_P = \frac{(B/2.303 f_0)(P - P_0)}{f_0/\beta_f - (P - P_0)} = \frac{D_1^0(P - P_0)}{D_2^0 - (P - P_0)} \tag{5}$$

where $D_1^0 \approx 1/2.303 f_0$ (if B is set equal to unity) and $D_2^0 = f_0/\beta_f$. The D_1^0 coefficient only concerns the fractional free volume at atmospheric pressure and at the temperature at which the experiments are carried out. It is equal to the C_1^0 coefficient of the WLF equation related to temperature.

Comparison of the pressure evolution of the probe motion with that of the a_P factor requires knowledge of the D_1^0 and D_2^0 coefficients and more precisely of the fractional free volume f_0 and of the compressibility coefficient β_f of the free volume.

The constants D_1^0 and D_2^0 can be determined graphically from the experimental data by rewriting equation (5) as a linear relationship:

$$1/\log\frac{\tau_c}{\tau_{c_0}} = -\frac{1}{D_1^0} + \frac{D_2^0}{D_1^0}\frac{1}{(P - P_0)} \tag{6}$$

Therefore, a plot of $1/\log(\tau_c/\tau_{c_0})$ (where τ_{c_0} is the correlation time at atmospheric pressure) as a function of $1/(P - P_0)$ should be linear, and should give access to the D_1^0 and D_2^0 coefficients.

D_1^0 and D_2^0 determined from the curves represented in *Figures 3* and *4* are, respectively, equal to 5.74 and 6508.71 bar for PI, and 6.65 and 8619.0 bar for PIB.

f_0 and β_f deduced from the preceding values are reported in *Table 1*. The fractional free volume at atmospheric pressure can be calculated from the relation

$$f_T = \alpha_f(T - T_\infty) \tag{7}$$

where α_f is the thermal expansion coefficient of the free volume. T_∞, often called the 'Vogel' temperature, is the temperature at which the free volume in the system is zero and T is the temperature of the pressure experiments.

It is satisfactory to see that f_0 found from pressure dependence is consistent with that found from temperature dependence.

On the other hand, if states 1 and 2 in equation (1) involve both temperature and pressure differences, within

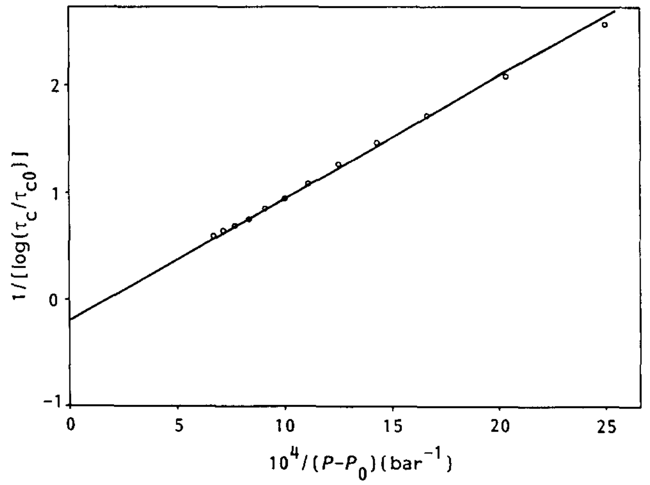


Figure 3 Determination of the constants D_1^0 and D_2^0 of equation (5) for PI

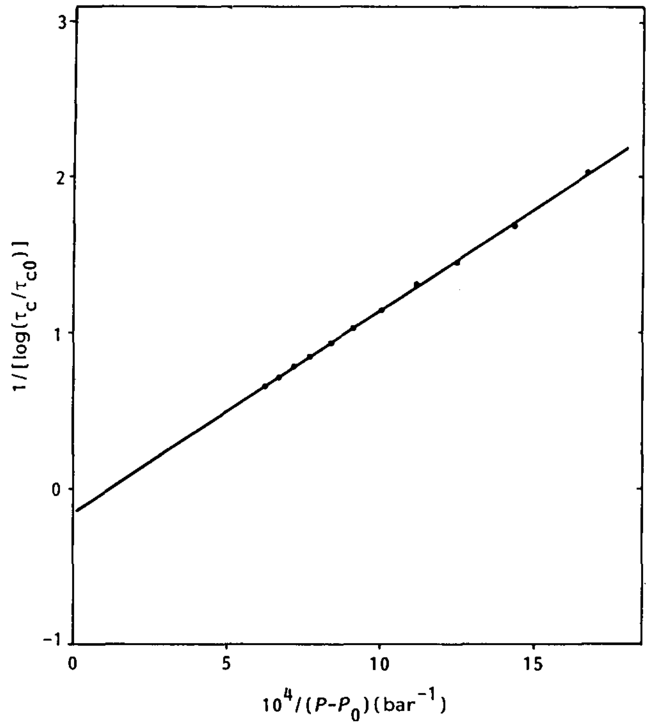


Figure 4 Determination of the constants D_1^0 and D_2^0 of equation (5) for PIB

the range where β_f is constant, if state 1 is specified by T_0 and P_0, we obtain

$$f_2 = f_1 + \alpha_f(T - T_0) - \beta_f(P - P_0) \qquad (8)$$

If the free volume is maintained constant by appropriately increasing both T and P, $a_{1,2}$ should remain unity with no change in the relaxation times. Differentiation of equation (8) gives for this condition:

$$\left(\frac{\partial T}{\partial P}\right)_\tau = \frac{\beta_f}{\alpha_f}$$

For a number of polymers, values of $(\partial T/\partial P)_\tau$ have been determined from bulk viscoelastic measurements or dielectric or nuclear magnetic resonance measurements. So, the compressibility coefficients of the free volume β_f deduced from the slopes of the curves represented in *Figures 3* and *4* can be compared to those estimated from the temperature–pressure shift ratios $(\partial T/\partial P)_\tau$ reported by Ferry[19]. As seen in *Table 1*, if there is very good agreement for PI, then for PIB the value found from pressure studies is higher than that deduced from Ferry's data. This increase in β_f can be ascribed to the fact that the pressure study has been carried out for PIB at a high temperature (361 K).

Finally, we have compared the results obtained by changing temperature and pressure. At a given pressure (500 or 1000 bar), we have calculated the correlation time of the rotational motion of meso-B2PEE from equation (5) and the corresponding fractional free volume f according to equation (4). Putting the values of f into the following equation, which gives the temperature dependence of the correlation time of the probe motion[10],

$$\log \tau_c = \log \tau_c(T_g) - C_1^g + \frac{1}{2.303 f_T} \qquad (9)$$

we can get the correlation time from temperature dependence. The results reported in *Table 2* show that $\log \tau_c$ is the same within experimental error.

Table 1

	f_0 [a]	$\beta_f \times 10^{-5}$ [a] (bar^{-1})	f_0 [b]	$\beta_f \times 10^{-5}$ [c] (bar^{-1})
Polyisoprene	0.076	1.16	0.077	1.15
Polyisobutylene	0.065	0.76	0.065	0.62

[a] Determined graphically from *Figures 3* and *4*
[b] Calculated from the relation: $f = \alpha_f(T - T_\infty)$, where $T = 306$ K for PI and $T = 361$ K for PIB
[c] Calculated from the values of $(\partial T/\partial P)_\tau$ reported by Ferry[19]

Table 2

	$P = 500$ bar			$P = 1000$ bar		
	f [a]	$\log \tau_c$ [b]	$\log \tau_c$ [c]	f [a]	$\log \tau_c$ [b]	$\log \tau_c$ [c]
Polyisoprene	0.070	−6.72	−6.60	0.064	−6.15	−6.02
Polyisobutylene	0.061	−6.33	−6.58	0.057	−5.87	−6.08

[a] Calculated from equation (4)
[b] Calculated from the equations of the curves represented in *Figures 3* and *4*
[c] Calculated from equation (9)

CONCLUSION

The results reported in this paper show that meso-B2PEE undergoes the conformational transition required for intramolecular excimer formation via a free-volume dependent relaxation process. No appreciable variation in the correlation time of the probe is observed at a given fractional free volume obtained by a temperature or by a pressure change.

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