

The effect of hydrostatic pressure on local polymer dynamics in polyisoprene

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The effect of hydrostatic pressure on the local molecular motion in bulk polyisoprene ($M_w = 1.4 \times 10^6$) has been studied by measuring the pressure dependence of the fluorescence lifetime of the intramolecular excimer-forming probe molecule, *meso*-2,4-di(*N*-carbazolyl)pentane, dissolved in the polymer. The experiments were performed at 323 K and covered a pressure range of 1 to 3000 bar. The results are compared with previous mechanical spectroscopy and excimer-based measurements of polymer dynamics. The range of frequency of polymer motion probed in these experiments was insufficient to discriminate between several empirical models of the pressure dependence of polymer dynamics.

(Keywords: hydrostatic pressure effects; polyisoprene; dynamics; molecular motion)

INTRODUCTION

Local- or molecular-scale motions in bulk polymers near the glass-rubber transition temperature have a strong influence on many polymer properties. These local-scale polymer chain motions may be studied by measuring the dynamics of intramolecular excimer-forming probes dispersed in polymer matrices¹⁻⁹. Intramolecular excimers are usually formed in bichromophoric molecules whenever the two aromatic chromophores are separated by a three-atom linkage¹⁰. When one of the chromophores is electronically excited and the molecule undergoes a rotation about the three-atom linkage that brings the two aromatic groups into a sandwich-like conformation where the π electronic orbitals overlap, the electrons in the excited and unexcited chromophores may interact to produce a stable excimer conformation. When the mobility of the environment surrounding the fluorescent molecule controls the rate of this intramolecular rotational motion, then the fluorescence lifetime of the excited chromophore (that is, the time for the chromophore to relax from the excited state back to the ground state) will be sensitive to the mobility of the medium. Because the motion of the chromophore to reach the excimer conformation is well defined, the volume swept out during the motion may be calculated. Therefore this technique provides a unique method for probing the state of free volume in the fluorescent molecule's environment. The probe molecule can also be changed; thus the volume required to reach the excimer conformation is changed. This extra degree of freedom permits quantitative access to the availability of free volume for molecular-scale motion of a fixed size on a timescale of the fluorescent lifetime of the probe molecule.

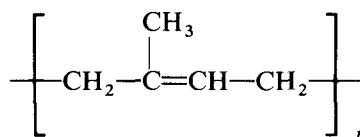
The temperature dependence of polymer dynamics has been studied by many different techniques and is generally well understood. On the contrary, the effect of

hydrostatic pressure on chain dynamics is still poorly understood. Therefore, the pressure dependence of the fluorescence lifetime of the intramolecular excimer-forming molecule, *meso*-2,4-di(*N*-carbazolyl)pentane, dissolved in polyisoprene has been measured at 323 K by single-photon-counting fluorescence decay spectroscopy. The results are compared with the excimer dynamics of a different probe molecule dispersed in polyisoprene⁹, with experimental data obtained by mechanical spectroscopy¹¹ and with the predictions of several models of polymer dynamics.

EXPERIMENTAL

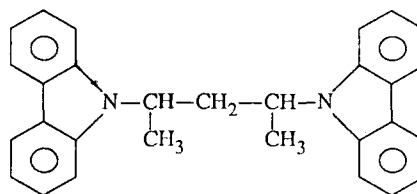
Polymer sample

The polyisoprene sample used in this study is a commercially available product (Shell IR 307, *cis* = 92%, *trans* = 5%, *vinyl* = 3%, $M_w \approx 1.4 \times 10^6$). It was kindly supplied by the Manufacture Française des Pneumatiques Michelin (Clermont-Ferrand, France). The glass transition temperature of this polymer is 211 K⁷. The monomer unit is shown below:



Excimer probe molecules

The *meso*-2,4-di(*N*-carbazolyl)pentane (*meso*-DNCZ) was kindly supplied by Professor F. C. De Schryver of the Department of Chemistry, University of Leuven, Heverlee, Belgium. The chemical structure is:

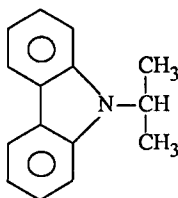


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This particular excimer-forming probe molecule was chosen because it has a high excimer sampling rate and good excimer stability^{12,13}. Additionally, it has a single ground-state conformation (*TG*), and it can form only one excimer conformation, which corresponds to a total spatial overlap of the electronic orbitals of the carbazole groups¹³. Based on these properties, the volume swept out by this molecule in order to reach the excimer conformation has been calculated¹⁴ to be approximately 170 \AA^3 .

To make quantitative mobility measurements by the intramolecular excimer technique, the fluorescent lifetime of a model compound must also be measured. This molecule must be electronically and structurally similar to the excimer-forming probe molecule, but it must not be able to form an intramolecular excimer. The model molecule for *meso*-DNCZ is *N*-isopropylcarbazole (NCZ), whose chemical structure is shown below:



This compound was purchased from ICN Pharmaceuticals Inc., of Plainview, NY, USA.

The fundamental fluorescence properties of these compounds in solution have been reported in the literature¹².

Sample preparation

The fluorescence lifetime measurements were made on film samples of polyisoprene that had been impregnated with either the model molecule or the excimer-forming probe molecule. To prepare these films, a weighed amount of polyisoprene was dissolved in cyclohexane. At the same time, a cyclohexane solution of the model or excimer-forming molecule was prepared. The concentration of this solution was determined from ultra-violet absorption spectroscopy and the known molar absorption coefficient of NCZ¹⁵. Since *meso*-DNCZ has two chromophores, its molar absorption coefficient was assumed to be twice that of NCZ. Then a weighed quantity of the fluorescent molecule solution was added to the polymer solution. The absorption and emission spectra of the carbazole moiety overlap strongly, giving rise to intermolecular reabsorption effects at sufficiently high concentrations. Therefore, the concentration of fluorescent molecules was kept below 4×10^{-7} mol/gram polymer, which has been shown not to give rise to reabsorption¹⁴. The polymer solution was stirred for several hours to ensure that the fluorescent molecules were homogeneously dispersed. Afterwards, a polymer film was cast onto a glass plate. This film was then dried at 40°C in a vacuum oven for at least 24 h to remove the cyclohexane.

Apparatus

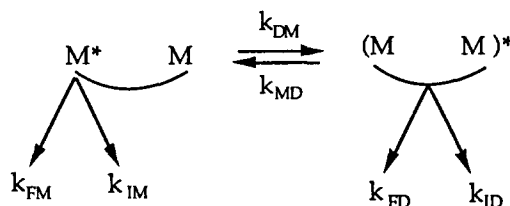
The fluorescence lifetime measurements were performed on a single-photon-counting fluorimeter whose principal characteristics have been described previously¹⁶. This instrument uses a nitrogen-filled flashlamp as the excitation light source. The excitation wavelength chosen for

this study was the 337 nm line of the nitrogen discharge, and the emission intensity was measured by a photomultiplier tube after passing through an MTO A 2190 filter ($\lambda_{\text{trans,max}} = 354 \text{ nm}$, maximum transmission = 22%, f.w.h.m. = 20 nm). The wavelength of maximum transmission corresponds to emission from the excited carbazole moiety¹². In order to avoid partial polarization effects from the monochromator, the excitation light was polarized at an angle of 55° with respect to the vertical direction. This angle of polarization corresponds to the so-called 'magic angle' where $\cos^2 \theta = 1/3$, θ being the angle between the polarization direction and the vertical direction. In this manner, the fluorescence emission intensity is proportional to the total luminescence intensity.

The high-pressure measurements were performed with a specially designed cell, which has been described elsewhere⁹.

DATA ANALYSIS

The analysis of the time dependence of the emission intensity from a molecule that forms an intramolecular excimer can be represented pictorially as follows¹⁰:



Here *M* is the unexcited chromophore, *M** represents the chromophore that has been excited by a photon and (*M M*)* is the excimer conformation. *M** is called the excited monomer state, and (*M M*)* is called the excimer state. In the probe molecule *meso*-DNCZ, *M* corresponds to the carbazole moiety. In the above, k_{IM} and k_{ID} are the rate constants for non-radiative decay from the excited monomer and excimer states, respectively. The radiative (or fluorescent) decay from the excited monomer and excimer states is characterized by the rate constants k_{FM} and k_{FD} , respectively. Finally, k_{DM} and k_{MD} are the rate constants characterizing the conversion of the excited monomer to the excimer conformation and vice versa, respectively. Based on this, from the solution of the rate equations governing the process shown above, the lifetime of the excited monomer may be written as follows¹⁰:

$$\frac{1}{\tau_{\text{M}}} = k_{\text{DM}} + \frac{1}{\tau_0} \quad (1)$$

where $\tau_0 = 1/(k_{\text{IM}} + k_{\text{FM}})$ is the excited monomer decay time in the absence of excimer formation; τ_0 is typically determined by measuring the lifetime of a model compound that cannot form an intramolecular excimer but is electronically and structurally similar to the probe molecule. The lifetime of this molecule is called τ_{mod} to distinguish it from τ_0 . It is generally observed that the maximum value of the excited chromophore lifetime (that is, the lifetime when the molecule cannot execute the motion needed to reach the excimer conformation) is not quite as large as that of the model compound⁴. Thus a small correction term, α , is added to the above equation

to account for this difference. Then the expression for the monomer lifetime becomes:

$$\frac{1}{\tau_M} = k_{DM} + \frac{1}{\tau_{mod} - \alpha} \quad (2)$$

It is through the rate constant for intramolecular excimer formation, k_{DM} , that the mobility of the environment influences the fluorescence lifetime of the excimer-forming probe molecule. A correlation time characterizing the rotational motion of the probe molecule to form the excimer conformation, τ_c , can be defined as the inverse of k_{DM} , so that:

$$\frac{1}{\tau_M} = \frac{1}{\tau_c} + \frac{1}{\tau_{mod} - \alpha} \quad (3)$$

When the mobility of the probe molecule's environment changes, the monomer lifetime will also change if the time needed to perform the rotation to reach the excimer conformation (characterized by τ_c) is controlled by the probe's surroundings. The environment's mobility can be significantly changed by changing the hydrostatic pressure of the sample. When the environment of the probe molecule is a polymer, the pressure dependence of the correlation time and, consequently, of the polymer mobility is customarily written in terms of the shift factor, a_p , as follows¹¹:

$$a_p = \tau_c(P)/\tau_c(P_0) \quad (4)$$

where P_0 is a reference pressure, generally taken as 1 bar. Thus the pressure dependence of the excimer monomer lifetime can be written as:

$$\tau_M = \left(\frac{1}{a_p \tau_c(P_0)} + \frac{1}{\tau_{mod} - \alpha} \right)^{-1} \quad (5)$$

MODELS FOR THE PRESSURE DEPENDENCE OF THE SHIFT FACTOR

There have been a number of models proposed for a_p . In polymers at conditions between the glass transition temperature T_g and $T_g + 100$ K, these models are typically based on free-volume concepts¹¹. The fractional free volume at a given temperature and pressure is defined as follows:

$$f_p = (V - V_{occ})/V = V_f/V \quad (6)$$

where V is the total volume of the sample, V_f is the free volume and V_{occ} is the so-called 'occupied volume', which cannot be used for molecular motion. In this model, the pressure dependence of the shift factor is related to the fractional free volume in the system by the Doolittle equation¹⁷:

$$\ln a_p = B \left(\frac{1}{f_p} - \frac{1}{f_0} \right) \quad (7)$$

where B is a constant generally taken to be equal to 1, and f_p and f_0 are the fractional free volumes at pressures P and P_0 , respectively. The various models for the pressure dependence of the shift factor differ in their description of how the free volume changes with pressure.

Model of constant free-volume compressibility

Ferry has suggested that the free volume decreases linearly with increasing pressure as shown below¹¹:

$$f_p = f_0 - \beta_f(P - P_0) \quad (8)$$

which leads to the following expression for the shift factor:

$$\ln a_p = \frac{(1/f_0)(P - P_0)}{(f_0/\beta_f) - (P - P_0)} \quad (9)$$

Here, β_f is the isothermal compressibility of the free volume. This expression can be cast in the following form:

$$\left[\ln \left(\frac{\tau_c(P)}{\tau_c(P_0)} \right) \right]^{-1} = -f_0 + \frac{f_0^2}{\beta_f(P - P_0)} \quad (9a)$$

In analogy with similar expressions for the temperature dependence of the shift factor, one may define P_∞ , the pressure where the fractional free volume is equal to zero, as follows:

$$P_\infty \equiv P_0 + \frac{f_0}{\beta_f} \approx \frac{f_0}{\beta_f} \quad (10)$$

Using this notation, the shift factor is given by

$$\ln a_p = \frac{1}{\beta_f(P_\infty - P)} - \frac{1}{f_0} \quad (11)$$

Models of variable free-volume compressibility

In analogy with the total isothermal compressibility, it has been suggested that the compressibility of the free volume must decrease significantly if the pressure is sufficiently large¹⁸. Several models have been proposed to describe the pressure dependence of the free-volume compressibility.

Exponential model. In many studies of mobility in polymer systems, it has been observed that the logarithm of the shift factor is a linear function of the applied hydrostatic pressure¹⁹⁻²³:

$$\ln a_p = \theta(P - P_0) \quad (12)$$

Using this model for the shift factor and equation (6), O'Reilly derived the following expression for the change in the free volume implied by equation (12)²¹:

$$f_p = \frac{f_0 \pi}{\pi + P - P_0} \quad (13)$$

where $\pi = 1/f_0\theta$ is an empirical material-dependent parameter that is taken to be independent of pressure. The compressibility of the free volume can be defined as follows¹¹:

$$\beta_f(P) = - \left(\frac{\partial f}{\partial P} \right)_T = \frac{f_p}{\pi + P - P_0} \quad (14)$$

Because of the form of equation (12), the coefficient θ has also been interpreted as an apparent activation volume as follows²³:

$$\theta = \Delta V^*/RT \quad (15)$$

where R is the gas constant and T is the temperature.

Tait model. In polymer melts, the empirical model of Tait has been used very successfully to represent pressure-induced changes in the volume and compressibility of polymers²⁴. By analogy, it has been proposed that the free-volume compressibility also follows this model¹⁸. The shift factor for this model is given by:

$$a_p = \left(1 + \frac{P - P_0}{B_f} \right)^{\theta_c} \quad (16)$$

where B_f depends on the polymer but not on pressure, and θ_c is given by:

$$\theta_c = C/f_g^2 \quad (17)$$

The fractional free volume at the glass transition temperature, f_g , is approximately 0.025 in a wide variety of polymers¹¹, and C is taken to be a universal constant with a value of 0.0894. When the ratio $(P - P_0)/B_f$ is small, the Tait model reduces to the exponential model as follows:

$$\ln a_p = \theta_c \ln \left(1 + \frac{P - P_0}{B_f} \right) \approx \frac{\theta_c}{B_f} (P - P_0) \quad (18)$$

RESULTS AND DISCUSSION

Fluorescence decays of polyisoprene films impregnated with either NCZ or *meso*-DNCZ were measured as a function of hydrostatic pressure. When the excimer dissociation rate is slow with respect to the rate of deactivation of the excimer state (i.e. when $k_{MD} \ll k_{FD} + k_{ID}$), Birk's analysis¹⁰ shows that, for a delta-function excitation pulse, the fluorescent decay spectrum of the excited monomer is a single exponential with a time constant of τ_M . When the rate of excimer dissociation is important compared to that of deactivation, then the monomer spectrum is a sum of two exponentials, and τ_M is determined from the time constants and amplitude ratios of the two exponentials according to Birks' analysis. Using this analysis, the pressure dependence of τ_M was determined from the experimental decays. The results are shown in Figure 1. Based on the standard deviation of repeat measurements at atmospheric pressure, the uncertainty in the measured lifetimes is approximately ± 0.3 ns. Figure 1 shows that the model-compound lifetime is approximately 13 ns and essentially independent of pressure. However, the monomer lifetime increases significantly with increasing pressure, reaching a plateau value of approximately 11.5 ns. This change in the monomer lifetime is caused by the effect of hydrostatic pressure on the correlation time, τ_c . As the pressure increases, the time needed to perform the rotational motion to reach the intramolecular excimer conformation increases (i.e. τ_c increases), and thus the monomer lifetime increases. Above approximately 1500 bar, the intramolecular excimer formation is completely blocked, and

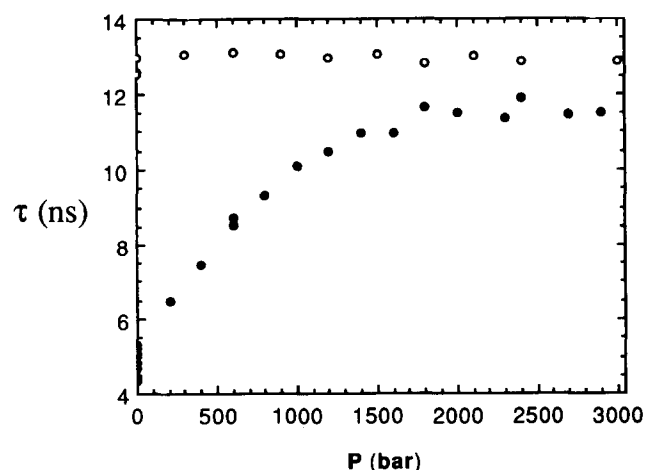


Figure 1 Pressure dependence of fluorescent lifetimes of model (○) and monomer (●) compounds dispersed in polyisoprene at 323 K.

the monomer lifetime does not change further. Thus above 1500 bar, the free-volume fluctuations in the polyisoprene are no longer sufficient to permit the probe molecule to execute the rotation required to reach the excimer conformation on the timescale of the excited chromophore lifetime.

The pressure dependence of the fluorescence lifetime of another excimer-forming probe (*meso*-bis[1-(2-pyrenyl)ethyl] ether) dispersed in polyisoprene has been measured previously by Jing *et al.*⁹. In this study, the data were interpreted using the model of constant free-volume compressibility (equation (9)). However, in contrast with the results of our work, Jing *et al.* were able to determine unambiguously the values of both f_0 and β_f from their experimental data by using an original graphical method described in their paper. They analysed their data using equation (9a) by plotting $\{\ln[\tau_c(P)/\tau_c(P_0)]\}^{-1}$ versus $(P - P_0)^{-1}$ and determining f_0 and β_f from the slope and intercept of the best line through the data points. We were unable to analyse our data using the same procedure; their analysis works well if the excited monomer lifetime changes strongly with pressure. The range of excited monomer lifetime (and, therefore, correlation time) covered in the experiments of Jing *et al.* was larger than in this study, and we believe that the narrow range of correlation times covered in our experiments caused their method of analysis to fail. Therefore, in this work the experimentally measured monomer lifetimes, τ_M , were fitted with a non-linear least-squares regression routine based on the Marquardt method²⁵ to equation (5) using the various models of the shift factor. In the regressions, best-fit values for the model parameters, the correction factor α and the correlation time at atmospheric pressure, $\tau_c(P_0)$, were determined.

In order to perform the regression using the model of constant free-volume compressibility, the value of one of the parameters controlling the evolution of the free volume with pressure (either f_0 or β_f in equation (9) or, equivalently, P_∞ in equation (11)) had to be fixed. We chose to fix the free volume at ambient pressure, f_0 , because it could be accurately determined from the Vogel equation ($f_0 = \alpha_f(T - T_\infty)$) using literature values of the parameters T_∞ , the temperature where the free volume is equal to zero, and α_f , the expansivity of the fractional free volume¹¹. Based on these literature values, f_0 at 323 K was fixed at 0.085. If the value of f_0 was not fixed, the regression algorithm could not determine a unique set of parameters based on the experimental data. Similarly, the value of the parameter θ_c in the Tait model (equation (16)) was fixed according to equation (17). Only the exponential model (equation (12)), which has only one adjustable parameter, required no *a priori* knowledge of parameters. The inability to determine precisely all of the parameters of the shift-factor models has been observed in studies of polymer dynamics using various experimental methods such as n.m.r., dynamic light scattering and fluorescence anisotropy decay^{23,26}. The range of correlation times sampled by these methods is too narrow to fix all of the parameter values precisely.

The parameters determined by the regression are collected in Table 1. It is encouraging to note that α and $\tau_c(P_0)$, which are not shift-factor-dependent parameters, are insensitive to the choice of the shift-factor model, within the uncertainty of the parameters. In the work of Jing *et al.*⁹, β_f was determined to be 1.16×10^{-5} bar⁻¹ at 306 K. From Table 1, the value of β_f determined from

Table 1

Parameters	Models		
	β_f constant	Exponential	Tait
β_f (bar ⁻¹)	$(1.43 \pm 0.07) \times 10^{-5}$	—	—
θ (bar ⁻¹)	—	$(2.25 \pm 0.13) \times 10^{-3}$	—
B_f (bar)	—	—	$(6.31 \pm 0.37) \times 10^4$
α (ns)	1.48 ± 0.12	1.35 ± 0.13	1.34 ± 0.13
$\tau_c(P_0)$ (ns)	8.62 ± 0.32	8.42 ± 0.32	8.41 ± 0.32

our results using the model of constant free-volume compressibility is $(1.43 \pm 0.07) \times 10^{-5}$ bar⁻¹ at 323 K. The similarity of the two results, both obtained by the excimer fluorescence technique, is striking evidence of the ability of this technique to sample polymer dynamics. The two results are expected to be somewhat different due to the difference in temperature of the two studies. The free-volume compressibility should be greater at 323 K than at 306 K. However, the temperature dependence of the total volume compressibility has been measured for polyisoprene²⁷, and the rate of change of the total compressibility with temperature can only account for approximately one-half of the observed change in the compressibility of free volume with temperature. The rest of the difference can be ascribed to the different methods of data treatment used to interpret the results from the two studies. Thus, the experimental data of the combined studies strongly suggest that the dynamics governing the probe molecule mobility are independent of the probe. Additionally, based on values of α_f and $(\partial T/\partial P)_f$ determined by bulk viscoelastic measurements of polyisoprene¹¹, β_f is estimated to be 1.15×10^{-5} bar⁻¹. Therefore, the excimer results also agree with mechanical measurements, which indicates that the probe mobility is controlled by local chain motions in the polymer, which are connected with the macroscopically observed glass transition phenomenon.

Using equation (15) and the parameter θ from Table 1, the activation volume (based on the exponential shift-factor model) is calculated to be 60 ± 4 cm³ mol⁻¹. This value is approximately the same as the molar volume of a repeat unit of polyisoprene (68 cm³ mol⁻¹). Using $f_0 = 0.085$ and θ , the parameter π is calculated to be $(5.2 \pm 0.3) \times 10^3$ bar, which is of the same order of magnitude as internal pressures determined for hydrocarbon polymers at room temperature²⁸.

Based on the model of constant free-volume compressibility, the pressure at which the free volume is equal to zero, P_∞ , is calculated to be 5200 ± 300 bar. It is highly unlikely that the compressibility of the free volume would remain constant to such high pressures, but this parameter is useful because equation (11) is a very convenient form for design calculations. It has the property, like the equivalent equation¹¹ involving T_∞ , of being independent of the reference pressure, P_0 .

Figure 2 shows the predictions of the exponential and constant free-volume compressibility shift-factor models and the experimental data. The predictions of the Tait model are not shown because (as can be seen from Table 1) the value of B_f is large enough that the approximation discussed in equation (18) is valid over the range of pressures studied. Thus the Tait model is mathematically equivalent to the exponential model. From this figure, it is clear that all of the proposed models can adequately

describe the experimental data. This good agreement has two sources. First, all of the models predict similar values of the pressure dependence of the shift factor in the pressure range of this study. In addition, equation (3) shows that the experimentally measured excited monomer lifetime is not sensitive to the mobility of the matrix, τ_c , when the correlation time is much larger than the corrected fluorescence lifetime of the model compound, $\tau_{\text{mod}} - \alpha$. In other words, when the probe molecule's environment is no longer sufficiently mobile to permit the motion necessary to reach the excimer conformation, the technique is no longer sensitive to further changes in the medium's mobility. From Figure 1, the pressure range over which the monomer lifetime of *meso*-DNCZ is sensitive to the polyisoprene dynamics is from 1 bar to ~1500 bar at 323 K. To test fully the various shift-factor models, further measurements must be made with other techniques that are sensitive to a wider range of correlation times.

Using a typical value of α of 1.4 ns, the pressure dependence of the correlation time can be calculated directly from the experimental results as follows:

$$\tau_c(P) = \left(\frac{1}{\tau_M(P)} - \frac{1}{\tau_{\text{mod}}(P) - \alpha} \right)^{-1} \quad (19)$$

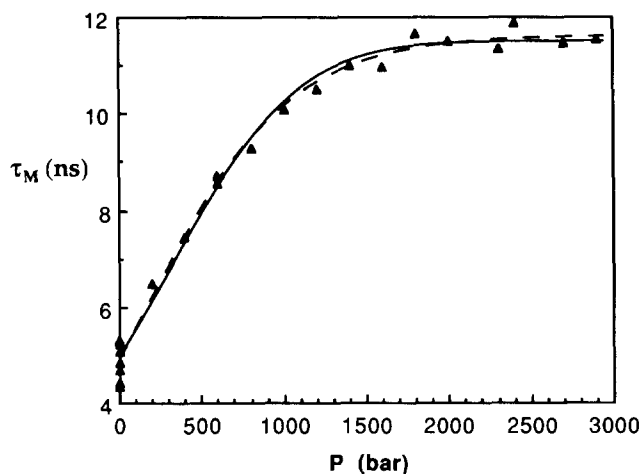


Figure 2 Comparison of theoretical models with experimentally measured monomer fluorescent lifetimes: (—) model of constant free-volume compressibility; (---) exponential model

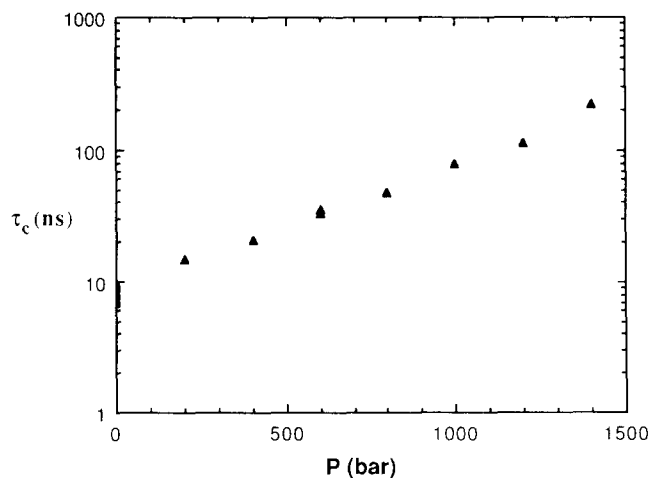


Figure 3 Pressure dependence of correlation time

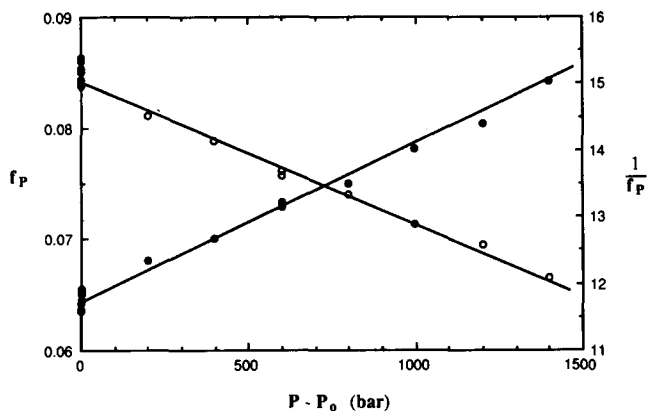


Figure 4 Dependence of fractional free volume (○) and its reciprocal (●) on pressure

These results are shown in Figure 3. This figure shows that approximately one-and-a-half decades of correlation time were covered in this experiment. From equation (7), the experimental correlation times in Figure 3 and the value of f_0 calculated from the Vogel equation (0.085), the free volume at a given pressure P , f_P , may be calculated. Figure 4 shows f_P and its reciprocal versus $P - P_0$, where P_0 is 1 bar. The model of constant free-volume compressibility predicts that f_P should decrease linearly with increasing pressure, and the exponential model (equation (13)) predicts that $1/f_P$ should increase linearly with pressure. Within the experimental uncertainty, both f_P and $1/f_P$ are linear functions of the hydrostatic pressure. This further test of the models clearly demonstrates that the differences in the pressure dependence of the free volume implied by the various models cannot be distinguished by this technique over the pressure range where the excited monomer lifetime is sensitive to the polyisoprene dynamics.

As a caveat concerning the use of the model of constant free-volume compressibility, it should be noted that it is widely believed that the compressibility of free volume in a polymer changes with both temperature and pressure. However, the coefficient of thermal expansion of the free volume, α_f , is typically regarded as a constant. If the free volume is to be a state function, then α_f must be a function of pressure and temperature if β_f changes with temperature and pressure. This paradox could be resolved by using more advanced equation-of-state theories for polymers, which predict the pressure and temperature dependence of the free volume and allow the compressibility and expansivity of the free volume to vary with temperature and pressure in a thermodynamically consistent way. This approach would also be a further step towards the ultimate goal of predicting dynamic properties based on equilibrium properties.

CONCLUSIONS

The technique of intramolecular excimer-forming probes has been shown to be a powerful tool for probing the pressure dependence of the dynamics of bulk polymers near the glass transition point. The results obtained in this work are in good agreement with previous excimer-based data and mechanical data. Owing to the limited

experimental window of the technique, it was impossible to differentiate between several empirical models of polymer dynamics.

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