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Effect of Hydrostatic Pressure on Local Polymer Dynamics in Poly(propylene oxide)

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ABSTRACT: The effect of hydrostatic pressure on the local molecular motion in bulk polymers has been studied by measuring the pressure dependence of the fluorescence lifetime of the intramolecular excimer-forming probe molecule *meso*-2,4-di-*N*-carbazolylpentane dissolved in poly(propylene oxide) of molecular weights 425, 2000, and 4000. The experiments were performed at 313 K and covered a pressure range of 1–3000 bar. The experimental data are compared with the predictions of several free volume based models of polymer dynamics and with previous dipole relaxation measurements of poly(propylene oxide) dynamics.

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 matrices.[1-9] Intramolecular excimers are usually formed in bichromophoric molecules whenever the two aromatic chromophores are separated by a three-atom linkage.[10] When one of the chromophores is electronically excited and the molecule undergoes a rotation about the three-atom linkage, which brings the two aromatic groups into a sandwichlike 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 media mobility. 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 time scale 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. However, the effect of hydrostatic pressure on chain dynamics is still poorly understood. The effect of temperature and hydrostatic pressure on the dipole relaxation in poly(propylene oxide) has been measured by Williams.[11] This work showed that the time–temperature superposition principle was obeyed by this polymer at all experimental conditions, that the temperature dependence of the frequency of maximum dielectric loss, $f_{\max}$, was consistent with the predictions of the WLF equation,[12] but that the pressure dependence of $f_{\max}$ was not consistent with predictions of the extension of the WLF equation to high pressure. In another study, the effect of temperature on the dynamics of excimer-forming probe molecules dispersed in poly(propylene oxide) has been measured.[8] This study indicated that the excimer dynamics probed the local scale polymer dynamics and that the results were consistent with the WLF equa-

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tion. In order to better understand the role of hydrostatic pressure in local polymer dynamics, the pressure dependence of the fluorescence lifetime of the intramolecular excimer-forming molecule *meso*-2,4-di-*N*-carbazolylpentane dissolved in poly(propylene oxides) of various molecular weights has been measured at 313 K by single photon counting fluorescence decay spectroscopy. The results are compared with the experimental dipole relaxation data and with the predictions of several models of polymer dynamics.

Experimental Section

Polymer Samples. Three poly(propylene oxide) (PPO) samples with molecular weights of 425, 2000, and 4000 were used in this study. The PPO425 and PPO4000 were purchased from the Aldrich Chemical Co. (Milwaukee, WI), and the PPO2000 was purchased from Aldrich-Chemie (Steinheim, West Germany). The glass transition temperatures of the PPO425, PPO2000, and PPO4000 are 198, 200, and 201 K, respectively.[13] These samples were used without further purification.

Fluorescent Probe Molecules. The excimer-forming probe molecule used was *meso*-2,4-di-*N*-carbazolylpentane (*meso*-DNCZ). This particular excimer-forming probe molecule was chosen because it has a high excimer sampling rate and good excimer stability.[14,15] 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 carbazole groups.[15] On the basis of these properties, the volume swept out by this molecule in order to reach the excimer conformation has been calculated to be approximately 170 Å^3.[16]

To make quantitative mobility measurements by the intramolecular excimer technique, the fluorescent lifetime of a model compound is also 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). This compound was purchased from ICN Pharmaceuticals, Inc. (Plainview, NY). The fundamental fluorescence properties of these compounds in solution have been reported in the literature.[14]

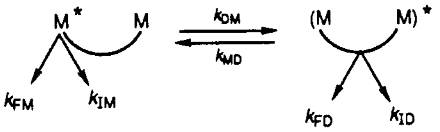
Sample Preparation. The polymers were in the liquid state at ambient conditions. Therefore, the samples were prepared for fluorescence lifetime measurements by dissolving either the model molecule or the excimer-forming probe molecule in the polymer. The samples were stirred with a magnetic stirbar to assure that the fluorescent molecules were homogeneously dispersed in the polymer. The absorption and emission spectra of the carbazole moiety overlap strongly, giving rise to intermolecular reabsorption effects at sufficiently high concentrations. Therefore, the optical density of the fluorescent molecules in the polymer was kept below 0.18 in a quartz cell with a 1-cm path length. This value of the optical density has been shown not to give rise to significant reabsorption.[16]

Apparatus. The fluorescence lifetime measurements were performed on a single photon counting fluorimeter whose principal characteristics have been described previously.[17] 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 nm, maximum transmission = 22%, fwhm = 20 nm). The wavelength of maximum transmission corresponds to emission from the excited carbazole moiety.[14] In addition to the normal fluorescence from the excited carbazole ring, the emission spectrum of the probe also exhibits a structureless band at lower energies. This band corresponds to emission from the intramolecular excimer conformation. In this study, only the fluorescence response function of the excited monomer state was analyzed. 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 $\cos^2 \gamma = 1/3$, γ 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. In any event, the measured lifetimes were found to be insensitive to the direction of polarization of the excitation light.

The high-pressure measurements were performed with a specially designed cell, which has been described elsewhere.[9] Because the samples were liquids, a special quartz tube (length = 25 mm, inside diameter = 12 mm, outside diameter = 15 mm) was designed to contain the samples. This quartz tube fits inside the high-pressure cell. The tube has aluminum pistons at both ends to contain the samples and transmit the pressure. Viton O-rings are used to form a seal between the pistons and the quartz tube. In use, the tube is charged with the sample, and the pistons are seated in the tube, taking care to eliminate any air bubbles in the sample. The tube is then loaded into the high-pressure cell. By means of a hand-cranked pressure generator connected to the cell, water surrounding the tube is compressed to reach the desired pressure. The pistons in the tube move in response to this pressure, thus transmitting the pressure to the polymer inside the tube, and at mechanical equilibrium, there is no difference in pressure between the interior and exterior of the quartz tube. This design permits the use of a small, thin-walled quartz tube for sample containment, while maintaining the ability to perform optical spectroscopy measurements at pressures up to 4 kbar. With such a design, one must guard against the possibility of water leaking into the sample cell at high pressure. Therefore, the fluorescence lifetime was measured repeatedly at atmospheric pressure before and after pressure cycles and at high pressures on both increasing and decreasing pressure cycles. None of the lifetimes at any pressure showed any measurable, systematic changes with the number of pressure cycles.

Data Analysis

The analysis of the time dependence of the emission intensity from a molecule that forms an intramolecular excimer can be represented by the following diagram:[10]



Here M is the unexcited chromophore, M* represents the chromophore that has been excited by a photon, and (M M)* denotes 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. k_{IM} and k_{ID} are the rate constants for nonradiative decay from the excited monomer and excimer states, respectively. The radiative (or fluorescence) 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. For a δ-function excitation pulse, the differential equations derived from the above kinetic scheme have been solved to obtain the expression for the time dependence of the total luminescence intensity from the excited monomer state[10]

$$I_M(t) \propto (X - \beta_1)e^{-\beta_2 t} + (\beta_2 - X)e^{-\beta_1 t} \qquad (1)$$

where

$$\beta_{1,2} = \frac{1}{2}\{(X + Y) \mp [(X - Y)^2 + 4k_{DM}k_{MD}]^{1/2}\} \qquad (2)$$

$$\frac{1}{X} = \frac{1}{k_{DM} + k_{IM} + k_{FM}} = \tau_M \qquad (3)$$

$$\frac{1}{Y} = \frac{1}{k_{MD} + k_{ID} + k_{FD}} = \tau_D \qquad (4)$$

τ_M and τ_D are the lifetimes of the excited monomer and excimer states, respectively. An important limiting case of these equations is that for which the excimer dissociation rate is slow with respect to the rate of deactivation of the excimer state (i.e., when $k_{MD} \ll k_{FD} + k_{ID}$). In this limit, the fluorescence decay spectrum of the excited monomer (eq 1) 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 as shown in eq 1, and τ_M is determined from the time constants and amplitudes of the two exponentials.

The lifetime of the excited monomer may be rewritten as

$$\frac{1}{\tau_M} = k_{DM} + \frac{1}{\tau_0} \tag{5}$$

where $\tau_0 = 1/(k_{IM} + k_{FM})$ 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 that 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 compound.[4] 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

$$\frac{1}{\tau_M} = k_{DM} + \frac{1}{\tau_{MOD} - \alpha} \tag{6}$$

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

$$\frac{1}{\tau_M} = \frac{1}{\tau_c} + \frac{1}{\tau_{MOD} - \alpha} \tag{7}$$

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 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[12]

$$a_p = \frac{\tau_c(P)}{\tau_c(P_o)} \tag{8}$$

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

$$\tau_M = \left[\frac{1}{a_p \tau_c(P_o)} + \frac{1}{\tau_{MOD} - \alpha}\right]^{-1} \tag{9}$$

Models for the Pressure Dependence of the Shift Factor. A number of models have been 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 concepts.[12] The fractional free volume at a given temperature and pressure is defined as

$$f_P = \frac{V - V_{\text{occupied}}}{V} = \frac{V_f}{V} \tag{10}$$

where V is the total volume of the sample, V_f is the free volume, and V_{occupied} 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 equation[18]

$$\ln a_p = B\left(\frac{1}{f_P} - \frac{1}{f_o}\right) \tag{11}$$

where B is a constant generally taken to be equal to 1, and f_P and f_o are the fractional free volumes at pressures P and P_o, 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[12]

$$f_P = f_o - \beta_f(P - P_o) \tag{12}$$

which leads to the following expression for the shift factor:

$$\ln a_p = \frac{\frac{1}{f_o}(P - P_o)}{\frac{f_o}{\beta_f} - (P - P_o)} \tag{13}$$

Here, β_f is the isothermal compressibility of the free volume. 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:

$$P_\infty \equiv P_o + \frac{f_o}{\beta_f} \approx \frac{f_o}{\beta_f} \tag{14}$$

When this notation is used, the shift factor is given by

$$\ln a_p = \frac{1}{\beta_f(P_\infty - P)} - \frac{1}{f_o} \tag{15}$$

This representation is useful because it is a very convenient form for design calculations. It has the property, like the equivalent equation in temperature,[12] of being independent of the reference pressure and temperature.

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 large.[19] Several models have been proposed to describe the pressure dependence of the free volume compressibility.

1. **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 pressure:[11,20–23]

$$\ln a_p = \theta(P - P_o) \tag{16}$$

Using this model for the shift factor and eq 11, O'Reilly derived the expression for the change in the free volume implied by eq 16[22]

$$f_P = \frac{f_o \pi}{\pi + P - P_o} \tag{17}$$

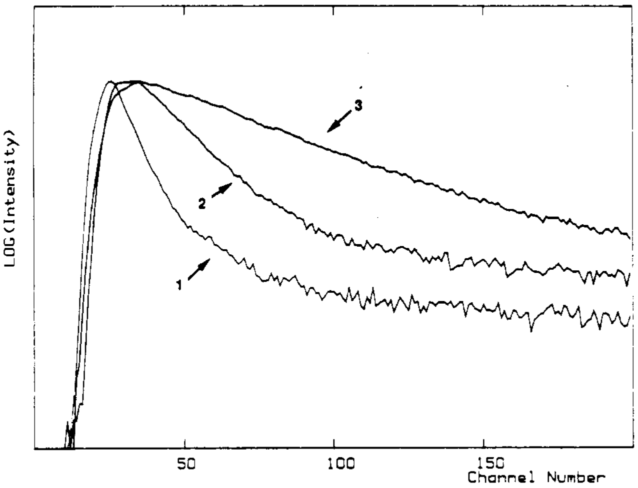


Figure 1. Experimentally measured fluorescent decay curves: (1) instrument response function; (2) *meso*-DNCZ dispersed in PPO425 at 313 K (1 bar); (3) *meso*-DNCZ dispersed in PPO425 at 313 K (1515 bar). The channel width is 0.32 ns.

where $\pi = 1/f_0\theta$ is an empirical material-dependent parameter, which is taken to be independent of pressure. The compressibility of the free volume can be defined as follows:[12]

$$\beta_f(P) = -\left(\frac{\partial f}{\partial P}\right)_T = \frac{f_P}{\pi + P - P_0} \tag{18}$$

Due to the form of eq 16, the coefficient θ has also been interpreted as an apparent activation volume[23]

$$\theta = \Delta V^*/RT \tag{19}$$

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

2. 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 polymers.[24] By analogy, it has been proposed that the free volume compressibility also follows this model.[19] The shift factor for this model is given by

$$a_p = \left(1 + \frac{P - P_0}{B_f}\right)^{\theta_c} \tag{20}$$

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

$$\theta_c = C/f_g^2 \tag{21}$$

The fractional free volume at the glass transition temperature, f_g, is approximately 0.025 in a wide variety of polymers,[12] 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:

$$\ln a_p = \theta_c \ln\left(1 + \frac{P - P_0}{B_f}\right) \approx \frac{\theta_c}{B_f}(P - P_0) \tag{22}$$

Results and Discussion

Fluorescence decays of poly(propylene oxide) containing either NCZ or *meso*-DNCZ were measured as a function of hydrostatic pressure. Typical decays of *meso*-DNCZ in PPO425 at two different pressures and the fluorimeter response function are shown in Figure 1. To analyze these data, the fluorimeter response function was convoluted with eq 1 as explained in the literature.[10] This new function was then compared to the experimentally measured decay spectra, and the amplitudes and time constants of eq 1 that gave the best fit were determined by a nonlinear regression algorithm based on the Marquardt method.[16] When this procedure and eqs 2–4 were used, τ_M was evaluated from the experimental decays. For the data shown in Figure 1, the decay at 1 bar was fit to two exponentials, which had time constants of 3.4 and 21.9 ns and amplitudes of 0.1718 and 1.259×10^{-3}, respectively. From these data, the monomer lifetime was calculated to be 3.45 ns and the excimer lifetime was 21 ns. On the basis of repeated measurements at atmospheric pressure, the uncertainty in the monomer lifetime was estimated to be ±0.24 ns. The uncertainty of the excimer lifetime is significantly larger because the relative amplitude of the second exponential is small. At 1515 bar, the polymer matrix is less mobile, and the excimer dissociation is slow with respect to the rate of excimer deactivation. Thus the decay is adequately fit by a single exponential with a time constant (the monomer lifetime) of 9.8 ns. In a similar fashion, the model compound lifetime was determined by using a single-exponential model for the time dependence of the total luminescent intensity.

The pressure dependences of the model compound lifetime and the excited monomer lifetime in the three polymers are shown in Figure 2. This figure shows that the model compound lifetime is between 11 and 12 ns in all of the polymers and is almost insensitive to pressure. On the contrary, the monomer lifetimes change significantly with pressure due to the effect of hydrostatic pressure on the correlation time, τ_c. As the pressure increases, the time to perform the rotational motion necessary to form the intramolecular excimer conformation increases (i.e., τ_c increases), and thus the monomer lifetime increases. In terms of the model discussed in eqs 1–4, this increase in monomer lifetime corresponds to a decrease in k_{DM}. In the range of 1800–2000 bar, the monomer lifetime becomes independent of pressure, indicating that the conformational change of the probe molecule is hindered ($k_{DM} = 0$). Thus above these pressures, the free-volume fluctuations in the polymer are no longer sufficient to permit the probe molecule to execute the rotation required to reach the excimer conformation on the time scale of the excited chromophore lifetime. Consequently, the monomer lifetime is no longer sensitive to changes in the polymer dynamics at higher pressures.

To analyze the fluorescence lifetime data, the measured monomer lifetimes, τ_M, were fit with a nonlinear least-squares regression routine based on the Marquardt method[25] to eq 9 using the experimentally determined values of the model molecule lifetime and the shift factor models described earlier. The value of the parameter α (the difference between the model and monomer lifetimes at high pressure) used in the regressions was determined from the experimental data as follows. First, since the model lifetime was practically independent of pressure, an average was taken over all of the experimental model lifetimes at pressures above 1000 bar in order to determine the average high-pressure value of the model compound lifetime. Then an average value of the high-pressure limit of the monomer lifetime was calculated using the high-pressure monomer lifetime data points which were nearly independent of pressure. The difference between these two numbers was taken to be α. The value of this parameter was 1.0 ns in PPO425, 0.4 ns in PPO2000, and 0.6 ns in PPO4000. Then in the regressions, best fit values for the model parameters and the correlation time at atmospheric pressure, $\tau_c(P_0)$, were determined.

In order to perform the regression using the model of

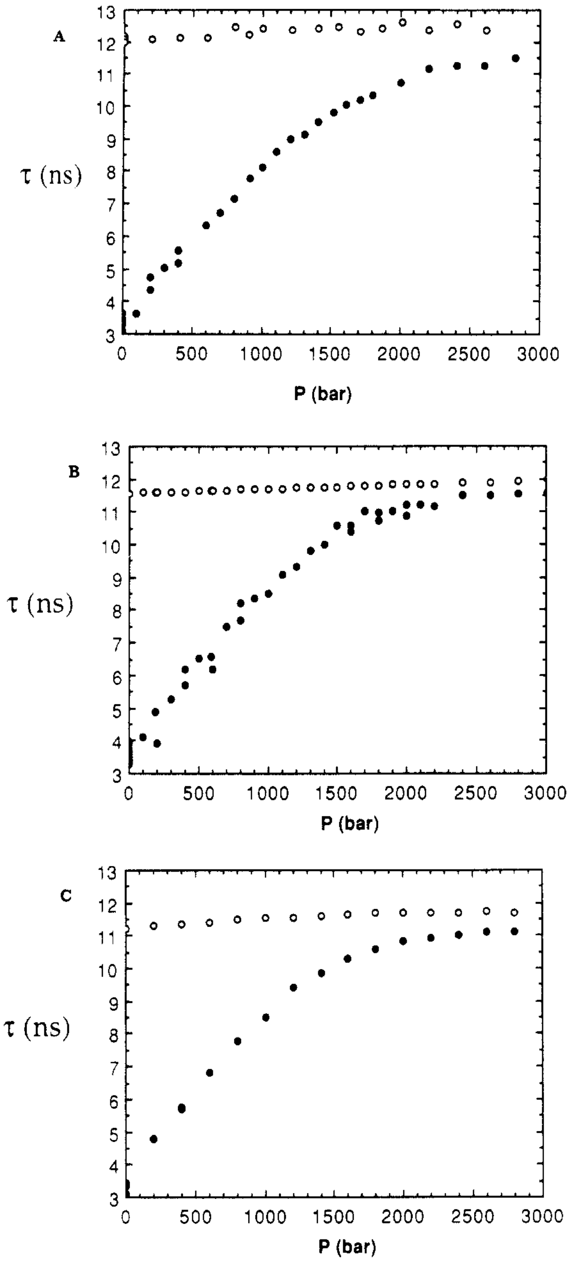


Figure 2. Pressure dependence of fluorescent lifetimes of model (○) and monomer (●) compounds dispersed in (A) PPO425, (B) PPO2000, and (C) PPO4000. The measurements were made at 313 K.

constant free-volume compressibility (eq 13), the value of one of the parameters controlling the evolution of the free volume with pressure (either f_o or β_f in eq 13 or, equivalently, P_∞ in eq 15) had to be fixed. We chose to fix the free volume at ambient pressure, f_o, because it could be accurately determined from the Vogel equation ($f_o = \alpha_f(T - T_\infty)$) 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 volume.[12] On the basis of these literature values, f_o at 313 K was fixed at 0.158. If the value of f_o 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 (eq 20) was fixed according to eq 21. Only the exponential model (eq 16), which has only one adjustable parameter, required no a priori knowledge of the parameters. The inability to precisely determine all of the parameters of the shift factor models has been observed in studies of polymer dynamics using experimental methods such as NMR, dynamic light scattering, and fluorescence anisotropy decay.[23,26] The range of correlation times sampled by these methods is too narrow to precisely fix all of the parameter values.

The parameters determined by the regression are collected in Table I. It is encouraging to note that $\tau_c(P_o)$, which is not a shift factor dependent parameter, is not very sensitive to the choice of the shift factor model. Figure 3 shows the experimentally determined monomer lifetime in PPO425 as a function of pressure and the predictions of the exponential and constant free-volume compressibility models. The experimental data are represented better by the exponential model. The results of Table I demonstrate that the parameter B_f in the Tait model is sufficiently large for the approximation in eq 22 to be valid for all three polymers. Thus the Tait model is mathematically equivalent to the exponential model over the pressure range of this study. The equivalence of the Tait and exponential models was also observed in polyisoprene.[27]

The exponential and constant compressibility models may also be compared based directly on their predictions of the pressure dependence of the free volume. The model of constant free-volume compressibility predicts that f_P should decrease linearly with increasing pressure, and the exponential model (eq 17) predicts that $1/f_P$ should increase linearly with pressure. To calculate the fractional free volume from the experimental data, we first calculate the correlation time at each pressure as follows:

$$\tau_c(P) = \left[\frac{1}{\tau_M(P)} - \frac{1}{\tau_{MOD}(P) - \alpha}\right]^{-1} \qquad (23)$$

The values of α determined earlier were used in this calculation. Then using the value of f_o (0.158) calculated from the Vogel equation, the free volume was calculated from the correlation times as follows:

$$f_P = \left[\frac{1}{f_o} + \ln\left(\frac{\tau_c(P)}{\tau_c(P_o)}\right)\right]^{-1} \qquad (24)$$

Figure 4 shows the fractional free volume and its inverse as a function of pressure. This figure clearly shows that f_P is not a linear function of pressure, whereas f_P^{-1} is a linear function of pressure. Thus for PPO425 at 313 K, the pressure dependence of the fractional free volume indicates that the compressibility of free volume is not independent of pressure.

The pressure dependence of the fractional free volume in PPO2000 and PPO4000 was calculated in the same manner. The resulting graphs are also shown in Figure 4. The figures illustrate that, in these polymers as well, the fractional free volume is not a linear function of pressure. In contrast, within the precision of the experimental results, f_P^{-1} is a linear function of pressure.

The correlation times for all of the polymers are shown in Figure 5. Over the entire pressure range studied, the correlation time in PPO425 is generally lower than in the higher molecular weight polymers. That is, the lowest molecular weight polymer is more mobile than the higher molecular weight polymers. This figure also shows that there is very little difference between the correlation times in the PPO2000 and PPO4000. This result is consistent with the observation by Johari that the glass transition temperature is almost independent of the molecular weight at molecular weights in excess of several thousand.[13] In each of the polymers, the logarithm of the correlation time is a linear function of the applied pressure. This result is consistent with the exponential

Table I

	models					
	β_f constant		exponential		Tait	
polymers	$\beta_f \times 10^5$, bar^{-1}	$\tau_c(P_o)$, ns	$\theta \times 10^3$, bar^{-1}	$\tau_c(P_o)$, ns	$B_f \times 10^{-4}$, bar	$\tau_c(P_o)$, ns
PPO425	3.23 ± 0.07	5.15 ± 0.15	1.81 ± 0.05	4.78 ± 0.15	7.84 ± 0.21	4.77 ± 0.15
PPO2000	3.59 ± 0.08	5.68 ± 0.17	2.02 ± 0.05	5.22 ± 0.16	7.02 ± 0.19	5.20 ± 0.16
PPO4000	3.83 ± 0.14	5.58 ± 0.24	2.15 ± 0.09	5.10 ± 0.24	6.58 ± 0.29	5.09 ± 0.24

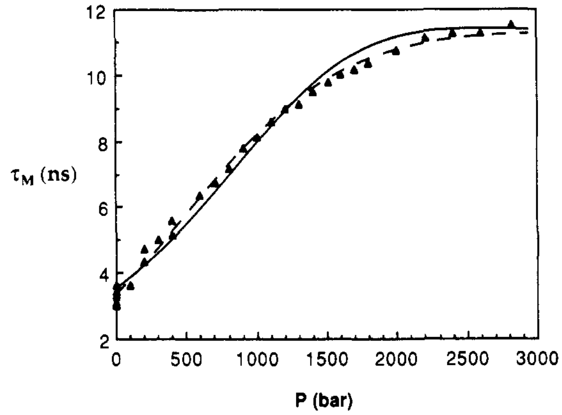


Figure 3. Comparison of theoretical models to experimentally measured monomer fluorescent lifetimes in PPO425: (—) model of constant free-volume compressibility; (- -) exponential model. The model parameters are from Table I.

shift factor model and the observation by Williams that the logarithm of the frequency of maximum dielectric loss was a linear function of pressure.

The slopes of the lines of log f_{max} versus pressure determined from the dielectric measurements are equivalent to the parameter θ in the exponential shift factor model. Williams observed that these slopes were a linear function of the inverse absolute temperature over the temperature range of his study (233-263 K).[11] In Figure 6, the slopes from the dielectric measurements are plotted against $1/T$. In the same figure, the values of the parameter θ determined for the polymers in this study are also plotted. The lowest temperature point (at 233 K) from the dielectric study is not included in this figure because it has a larger uncertainty than the others due to the difficulty of making the dielectric measurement at such low temperatures.[28] Figure 6 shows that, as the molecular weights of the PPO samples increase, the values of θ approach the value extrapolated from Williams' dielectric study, which was performed on a sample of very high molecular weight. Within the uncertainty of the extrapolation and the uncertainty in θ, the PPO4000 point lies practically on the line extrapolated from the dielectric measurements.

From the regression results in Table I, the coefficient of free-volume compressibility from the model of constant free-volume compressibility increases by about 17% as the molecular weight goes from 425 to 4000. The parameter θ from the exponential shift factor model increases by approximately the same amount over the same range of molecular weight. Both of these results indicate that the shift factor becomes progressively more sensitive to pressure as the molecular weight rises. That is, the free volume is more compressible in the higher molecular weight polymers. A similar result is observed in the temperature dependence of the viscosity of poly(propylene oxides). The thermal expansion coefficient of the free volume, which is a measure of the sensitivity of the viscosity to temperature, increases by 28% as the molecular weight increases from 400 to 4000.[29] This effect is even more pronounced in 1,2-propanediol, the monomer of poly(propylene oxide). Its thermal expansion coefficient of free volume is approximately half that of the PPO425.[8] There are two possible explanations for this molecular weight effect. The phenomenon could be due to hydrogen bonding by the terminal OH groups of the polymer chains. At lower molecular weights, there are more chain ends per unit volume of polymer, and thus more hydrogen bonds are formed than at higher molecular weights. The presence of these hydrogen bonds inhibits the thermal expansion or pressure-induced compression of the polymer matrix at low molecular weights. This effect would decrease in importance with increasing molecular weight. The observed dependence of the pressure sensibility on molecular weight could also be caused by the influence of chain connectivity on the polymer dynamics. In low molecular weight polymers, a large contribution to the segmental mobility comes from the chain ends, which are less constrained by chain connectivity requirements and, there-

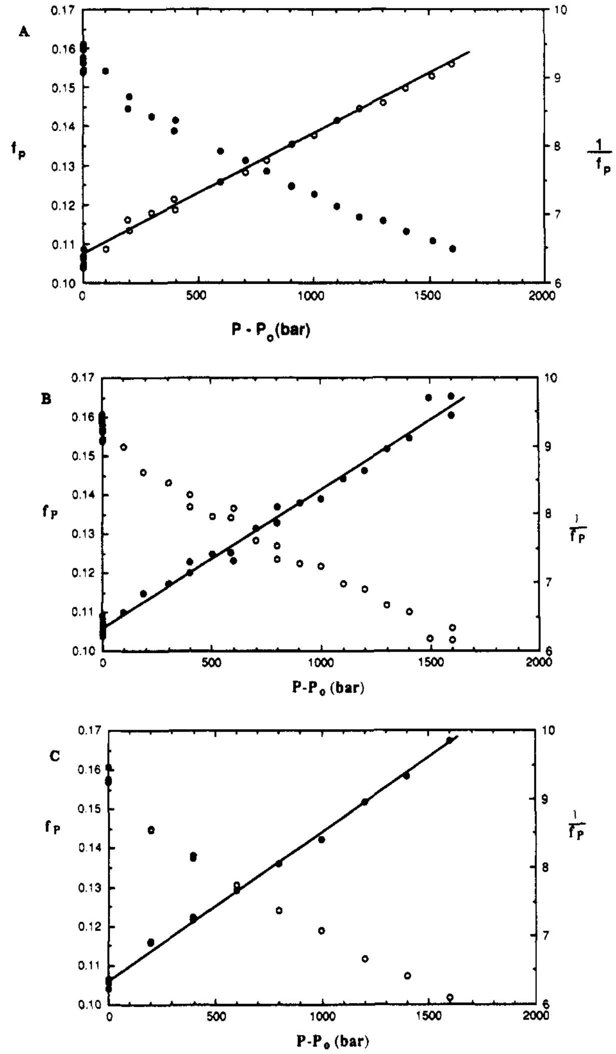


Figure 4. Dependence of fractional free volume (O) and its reciprocal (●) on pressure in (A) PPO425, (B) PPO2000, and (C) PPO4000. The solid line is the best fit to the exponential model using the parameters from Table I and a fractional free volume at atmospheric pressure of 0.158.

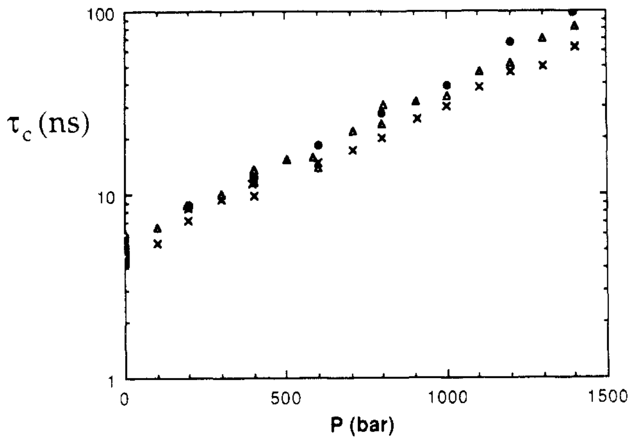


Figure 5. Pressure dependence of correlation time in PPO425 (×), PPO2000 (△), and PPO4000 (●).

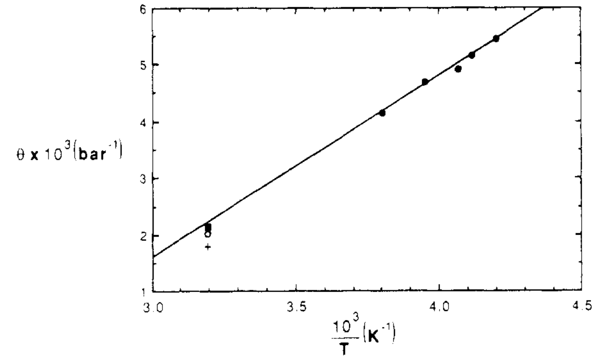


Figure 6. Comparison of excimer results (PPO425 (+), PPO2000 (○), and PPO4000 (■)) with dielectric relaxation data (●).

fore, more mobile than segments in the middle of the chain. This contribution decreases as the molecular weight increases. Because of chain connectivity, motion of a chain end may involve only one or two polymer backbone bonds, whereas motion of an atom in the middle of the chain requires the motion of many more backbone bonds. Consequently, a smaller volume is swept out by chain-end motions than by segmental motions in the middle of the chain. Thus it is likely that the effect of hydrostatic pressure on the dynamics of the chain ends will be weaker than its effect on the dynamics of interior segments of the chain. Therefore, the pressure sensitivity would increase with increasing molecular weight. Since the higher flexibility of chain ends relative to that of inner segments is also involved in the glass transition phenomena, the dependence of the pressure sensitivity of the dynamics on the molecular weight should parallel that of the change in the glass transition temperature with molecular weight. In poly(propylene oxides) the glass transition temperature increases at low molecular weights and then becomes insensitive to molecular weight at molecular weights greater than a few thousand.[13]

When eq 15 and the θ parameters from Table I are used, the activation volume (based on the exponential shift factor model) increases from 47 ± 1 cm^3/mol in PPO425 to 56 ± 2 cm^3/mol in PPO4000. This value is near the molar volume of a repeat unit of poly(propylene oxide) (58 cm^3/mol). Using f_0 = 0.158 and θ, the parameter π is calculated to be (3.5 ± 0.2) × 10^3 bar in PPO425, (3.1 ± 0.1) × 10^3 bar in PPO2000, and (2.9 ± 0.1) × 10^3 bar in PPO4000. These values are similar to the internal pressure of poly(propylene oxide), which has been measured to be 3800 bar at 293 K.[30]

Conclusions

The technique of intramolecular excimer-forming probes has been shown to be sensitive to the pressure dependence of the dynamics of bulk polymers near the glass transition point. The results demonstrated that the compressibility of free volume cannot be considered constant in poly(propylene oxide). The results obtained in this work are in good agreement with previous dielectric relaxation data. The exponential shift factor model satisfactorily describes the data over the pressure range studied. The sensitivity of the polymer dynamics to hydrostatic pressure increases with increasing molecular weight. This result is believed to be caused by either hydrogen bonding by the terminal OH groups of the chains or by the effect of chain connectivity. However, the present measurements cannot discriminate between the two possible explanations.

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Stress-Induced Infrared Frequency Shifts in Polyethylene

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ABSTRACT: The molecular dynamics technique is used to study the spectral response of a polyethylene chain in a crystal environment under a mechanical deformation. The MUSIC method, which was previously shown to accurately compute dispersion curves from the time-dependent structure factor, is used. A complete characterization of frequency shifts is presented for various lamellar thickness, temperatures, stress (or pressure), and mass defects.

I. Introduction

The study of the mechanical deformation of highly oriented polymeric materials is motivated by the possible use of these materials in structural reinforcement or other applications requiring maximum strength and minimum weight. Previous work has ranged from measuring the stress required to tear a film or break a fiber to more sophisticated methods designed to probe the molecular details of the deformation. One example of the latter category is the stress-IR or Raman experiments carried out in the 1970s and 1980s[1-3] in which the IR (or Raman) spectrum was monitored as the material was pulled along the polymer chain orientation axis. The materials varied, but we restrict our current study to ultraoriented polyethylene (PE) films. In the case of –C–C– backbone stretches, the frequencies shifted to lower values as the stress increased. These carbon skeleton modes exhibited the largest shifts and will exclusively occupy our attention in the present work. The shifts ($\Delta\nu$, in reciprocal centimeters) could be related to the stress (σ, in gigapascal) for small stresses via

$$\Delta\nu = \alpha\sigma \tag{1}$$

where α has units of reciprocal centimeters per gigapascal and is usually negative (indicating a shift of peaks to smaller frequencies under stress). Although some conclusions regarding the microenvironment of the stressed films were drawn indirectly from these experiments, more direct conclusions about the atomic response to the externally applied stress were drawn from theoretical investigations.[3,4] The earlier studies, using static methods[3-5] and incomplete models of the films,[3,4,6] showed that the polymer atoms had to be coupled anharmonically to induce the negative shifts observed experimentally. The magnitudes of the shifts were found to be approximately correct, and several other details concerning the relative contributions of bend and torsion to the relaxation of the induced stresses were presented.

More recently, the time-dependent theoretical technique of molecular dynamics (MD) has been used to follow the atomic motion during the stress event.[7,8] Among other results, workers noted that the frequency shift has a wavevector dependence[7] and that the nonbonded forces become more important when the polymer chain is under tension.[8] Both studies used multichain models with more than one type of interaction. Noid and Pfeffer[7] have calculated the IR spectrum of the PE (stressed and unstressed) via the extremely fast MUSIC[9] method and found $\Delta\nu$ directly; therefore, we concentrate upon their work. The present work extends the previous work by investigating the dependence of $\Delta\nu$ upon the wavevector, k, as certain model parameters are changed and for different temperatures, stresses, and chain lengths.

In section II, we discuss the theoretical methods. The results follow in section III, and a discussion of the work is given in section IV, the final section.

II. Theoretical Methods

Molecular Dynamics. Since this technique is well-known and recently reviewed,[10] only a minimum of detail is presented. Basically, one needs to solve Hamilton's equations or any other formulation of the classical equations of motion starting with some initial positions and momenta of all of the atoms in the polymer involved and propagate the solution at a series of (usually) equally spaced time steps. The solution method we used was ODE.[11] Our initial positions were those occupied by PE chains in an orthorhombic crystal structure[12] or some set of positions related to that structure. Our initial momenta were always chosen to give zero total momentum and depended upon the temperature we wished to obtain. For example, picking *all* initial momenta equal to zero gave a temperature of about 1 K or less. The temperature used here is based upon the calculated average kinetic energy through $^3/_2\,kT$. The potential energy is required in the

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