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Polystyrene Cyclization under High Hydrostatic Pressure

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ABSTRACT: Hydrostatic pressure effects on the cyclization of polystyrene chains ($M_n = 2600$, $M_w/M_n = 1.07$; $M_n = 4500$, $M_w/M_n = 1.08$), both ends labeled with 1-pyrenyl groups, were studied by measuring fluorescence spectra and pyrene monomer and excimer decay curves. The experiments were performed at room temperature in toluene (good solvent), cyclopentane (Θ solvent), and methylcyclohexane (poor solvent), covering a pressure range of 1−3500 bar. The cyclization rate constant decreases monotonically with pressure, as a result of the increase of solvent viscosity. However, changes in the quality of solvent for the polymer induced by pressure also influence chain cyclization. Activation volumes for chain cyclization compare well with solvent viscosity activation volumes when solvent quality to the polymer is pressure independent. The rate of excimer dissociation and ring-opening increases with pressure, especially in Θ and poor solvents. This effect is ascribed to the lowering of the excimer binding energy, induced by changes on the excimer conformation.

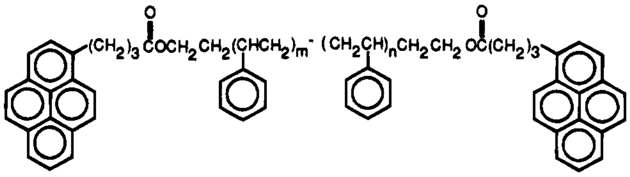
1. Introduction

Molecular fluorescent probes have proved to be very powerful in the study of conformational changes and dynamics of polymers.[1] Both are influenced by temperature, solvent, and hydrostatic pressure, for polymers either in bulk or in solution. The effects of temperature and solvent are better understood than the effect of hydrostatic pressure. Nevertheless, studies with hydrostatic pressure have the advantage of allowing large variations in viscosity without changing the character of the solvent.

Hydrostatic pressure effects on local dynamics of polymers in bulk[2−4] were studied using small fluorescent bichromophoric probes, able to form intramolecular excimers upon electronic excitation of one of the chromophores. The intramolecular conformational change required for excimer formation is shown to be controlled by polymer segmental motions involved in the glass transition phenomenon.[2−5]

In the case of isolated polymer chains the effect of hydrostatic pressure on conformational changes associated with the formation of excimers between adjacent chromophores was studied using polymers with fluorescent groups attached to the chain backbone.[6,7] The excimer formation rate constant reflects the local motions required to attain the adequate sandwich geometry between both groups. Hydrostatic pressure increases solvent viscosity, resulting in a decrease of the excimer formation rate constant. In poly(2-vinylnaphthalene) this effect is well described by assuming a free volume limited model in the high-friction limit.[6] For the intramolecular excimer formation in polystyrene solutions it was shown that hydrostatic pressure also influences the quality of solvent to the polymer.[7] These results agree with the decrease in both the second virial coefficient, A_2, and the radius of gyration, R_G, with a pressure increase for polystyrene in cyclohexane (poor solvent)[8] and *trans*-decalin (Θ solvent).[8−10] However, for polystyrene in toluene (good solvent), pressure has only a minor influence on A_2, R_G,[8−12] and the hydrodynamic radius.[13]

This paper presents the results of the cyclization of polystyrene chain **I**, both ends labeled with a pyrene derivative.



I

The excimer formation between chain ends of polymer **I** leads to cyclization of the chain and gives relevant information on the influence of both temperature and pressure on chain dynamics, since it is a diffusion-controlled process. Preliminary results indicate that the major effect of pressure is the increase of solvent viscosity.[14,15] Nevertheless, the variation of the quality of solvent to the polymer should also be considered, especially in Θ and poor solvents.

2. Experimental Section

The synthesis of polymer chains ($M_n = 4500$, $M_w/M_n = 1.08$; $M_n = 2600$, $M_w/M_n = 1.07$) and their characterization have been reported elsewhere.[16] Spectroscopic grade toluene and methylcyclohexane (Merck, Uvasol) were used as received. Cyclopentane (Fluka, >99%) was purified by fractional distillation at normal pressure. The viscosities of solvents at several pressures were taken from the literature.[17−19] Solutions of polymers ($C \approx 2 \times 10^{-6}$ M) were degassed by nitrogen bubbling.

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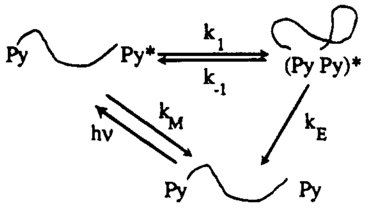
Scheme 1



Fluorescence spectra at normal pressure were obtained in a Spex Fluorolog 112 spectrofluorometer.

High-pressure measurements were made at room temperature (25 °C) in a Nova Swiss high-pressure cell fitted with two sapphire windows at right angles. Fluorescence spectra were measured on a home-built spectrofluorometer using as the excitation source a xenon lamp. Excitation and emission wavelengths were selected by H20 Jobin-Yvon monochromators.

Decay curves were obtained by the single photon timing technique and were analyzed using an iterative reconvolution method based on the algorithm of Marquardt.[20] The excitation source was a cavity dumped DCM dye laser synchronously pumped by a mode-locked argon ion laser. The emission of the dye was frequency doubled to obtain excitation light at $\lambda = 322$ nm. Monomer and excimer emissions were selected by appropriate interference filters with a bandwidth of ~20 nm and detected by a Philips XP2020 photomultiplier.

3. Data and Data Analysis

The cyclization of polymer chains, both ends labeled with 1-pyrenyl groups, has been described by the classical Birks' scheme (Scheme 1), where k_1 is the cyclization rate constant, k_{-1} describes the excimer dissociation and ring opening process, and k_M and k_E are the reciprocal lifetimes of the excited monomer and excimer, respectively.

Scheme 1 predicts that, after a δ pulse of excitation light, the monomer decays as a sum of two exponentials and the excimer as a difference of two exponentials,[21]

$$I_M(t) = a_1 \exp(-\lambda_1 t) + a_2 \exp(-\lambda_2 t) \qquad (1)$$

$$I_E(t) = a_3 \exp(-\lambda_1 t) + a_4 \exp(-\lambda_2 t) \qquad (2)$$

where

$$2\lambda_{1,2} = (A_x + A_y) \mp \sqrt{(A_x - A_y)^2 + 4k_1k_{-1}} \qquad (3)$$

$$A_x = k_M + k_1 \qquad A_y = k_E + k_{-1} \qquad (4)$$

and

$$a_2/a_1 = \frac{(A_x - \lambda_1)}{(\lambda_2 - A_x)} \qquad a_4/a_3 = -1 \qquad (5)$$

From the values of the decay constants (λ_1, λ_2) and the ratio a_2/a_1, all the relevant kinetic rate parameters (k_1, k_{-1}, and k_E) can be calculated, once the monomer lifetime, $\tau_M = 1/k_M$, is known. The τ_M values were obtained from the monoexponential decay of dilute solutions ($C \approx 2 \times 10^{-6}$ M) of one-end 1-pyrenyl labeled chains ($M_n = 5900$; $M_w/M_n = 1.33$) in several solvents at each pressure.

The experimental excimer decay curves are biexponentials, according to eq 2. However, the ratio of preexponential factors (a_4/a_3) deviates significantly from −1, the deviation being larger with pressure increase (see Figure 1).

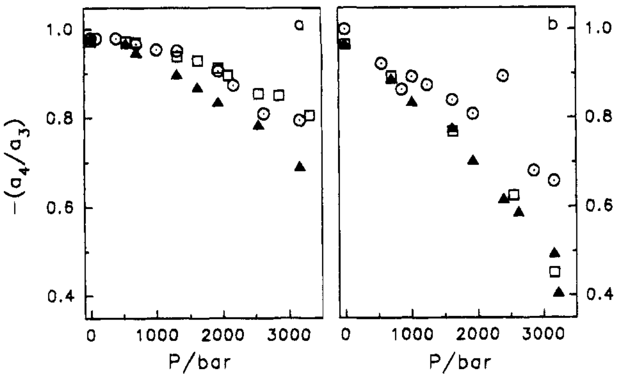


Figure 1. Ratio of the excimer decay curve preexponential factors for PyPSPy, at several pressures, in toluene (⊙), cyclopentane (□), and methylcyclohexane (▲): (a) $M_n = 2600$; (b) $M_n = 4500$.

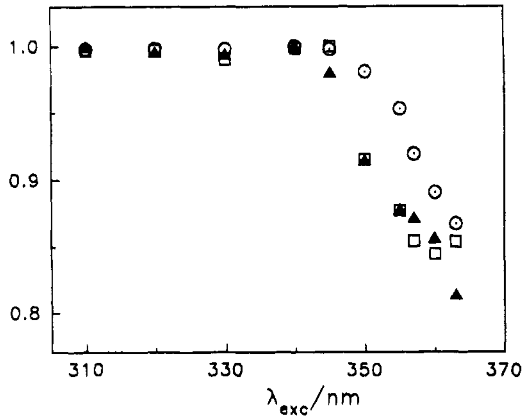
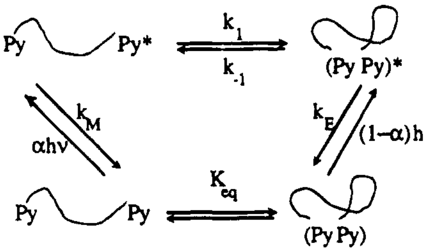


Figure 2. Dependence of the monomer to excimer fluorescence intensity ratio (I_M/I_E) on the excitation wavelength for PyPS2600Py (at $P = 1$ bar), in toluene (⊙), cyclopentane (□), and methylcyclohexane (▲).

Scheme 2



The deviation of $-(a_4/a_3)$ from unity is more pronounced for the longer chain and the poorest solvent (methylcyclohexane). This behavior supports the presence of preassociated pyrene dimers in solution, which absorb part of the excitation light. This is confirmed by the dependence of the monomer to excimer fluorescence intensity ratio (I_M/I_E) on the excitation wavelength (Figure 2). The I_M/I_E values are constant for wavelengths lower than 345 nm but decrease significantly for longer excitation wavelengths ($S_1 \leftarrow S_0$ pyrene absorption band) due to dimer absorption. Indeed, it is in the longer wavelength region that the dimer to monomer relative absorption should be higher since the pyrene $S_1 \leftarrow S_0$ absorption band is forbidden, with very low absorption coefficients ($\epsilon < 600$ L mol^{-1} cm^{-1} in cyclohexane).

In this case, Scheme 1 must be modified in order to account for the formation of pyrene ground-state dimers

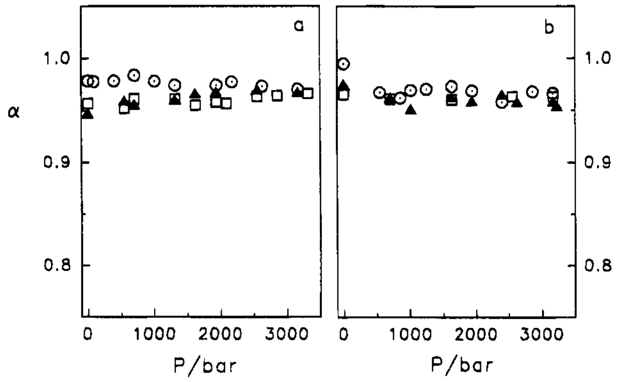


Figure 3. Fraction of light (α) absorbed by nonassociated chromophores for PyPSPy at several pressures, in toluene (⊙), cyclopentane (□), and methylcyclohexane (▲): (a) $M_n = 2600$; (b) $M_n = 4500$.

with equilibrium constant K_{eq} (Scheme 2), α being the fraction of light absorbed by nonassociated chromophores.

According to Scheme 2, eqs 1–4 remain valid,[22] but the ratios of pre-exponential factors are modified, in order to consider the fraction of light, α, absorbed by nonassociated chromophores in the ground state

$$\frac{a_2}{a_1} = \frac{\alpha(A_x - \lambda_1) - (1-\alpha)k_{-1}}{\alpha(\lambda_2 - A_x) + (1-\alpha)k_{-1}} \qquad (6)$$

$$\frac{a_4}{a_3} = \frac{(1-\alpha)(A_y - \lambda_1) - \alpha k_1}{(1-\alpha)(\lambda_2 - A_y) + \alpha k_1} \qquad (7)$$

The monomer decay curves were fitted with a sum of two exponentials, constraining the decay constants to the values recovered from the excimer decay curve fitting. For the chain with $M_n = 2600$, a weak long-lived third component ($\lambda_3 \cong \lambda_M$) was detected in the monomer decay, corresponding to the presence of some polymer containing only one end labeled with a 1-pyrenyl group. Using the set of equations (3), (6), and (7), all the rate constants and the fraction of light absorbed by nonassociated chromophores can be obtained. The values of the rate constants are within the experimental error equal to the ones obtained assuming no ground-state dimer formation. Notwithstanding the large deviation of (a_4/a_3) from −1, the values determined for α are not very far from 1 and do not change notably with pressure (Figure 3), which suggests a low and pressure independent pyrene dimer binding energy. This result emphasizes how sensitive the fluorescence decay kinetics experiments are to small amounts of pyrene association in the system.

4. Results and Discussion

Figure 4 shows the variation of the cyclization rate constant, k_1, with pressure in all solvents. The large decrease of k_1 with pressure results from the variation of solvent viscosity. Indeed, the cyclization process for long chains is diffusion controlled, with the rate constant depending on the translational diffusion coefficient, D, and the gyration radius, R_G, of the chain[23]

$$k_1 \propto \frac{D}{R_G^{\,2}} \qquad (8)$$

The major effect of pressure on k_1 comes from the diminution of D, owing to the increase of solvent viscosity. Assuming that D is proportional to η^{-1} a linear variation of ln k_1 *versus* ln η is expected. Figure 5 shows linear plots in toluene (good solvent, $\theta \approx -41$ °C[24]) and in cyclopentane (Θ solvent, $\theta \approx 20.5$ °C[25]), for both polystyrene chains in all the range of pressures studied. In methylcyclohexane (poor solvent, $\theta = 68$ °C[26]), a linear fit can only be obtained from 1 to 2000 bar. This seems to indicate that at very high pressures in poor solvents the chain is collapsed, its cyclization being not fully diffusion controlled.

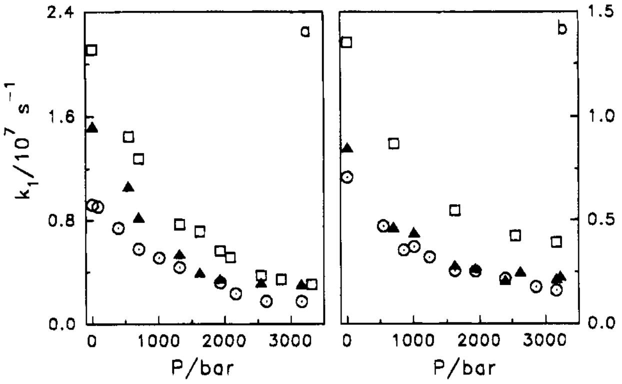


Figure 4. Pressure dependence of the cyclization rate constant, k_1, for PyPSPy, in toluene (⊙), cyclopentane (□), and methylcyclohexane (▲): (a) $M_n = 2600$; (b) $M_n = 4500$.

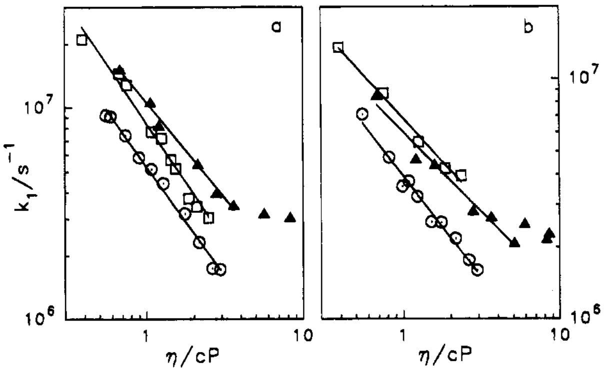


Figure 5. Plot for ln k_1 *versus* ln η for PyPSPy, at several pressures, in toluene (⊙), cyclopentane (□), and methylcyclohexane (▲): (a) $M_n = 2600$; (b) $M_n = 4500$.

The slope, a, of the straight lines in Figure 5 is smaller than unity for the longer chain ($M_n = 4500$) in all solvents, increasing in the order methylcyclohexane < cyclopentane < toluene (Table 1). For the smaller chain ($M_n = 2600$), the slope is near unity for toluene and cyclopentane and somewhat smaller in methylcyclohexane.

The diffusion coefficient of large molecules (like our polymer samples) in a continuum of small solvent molecules is proportional to the reciprocal of solvent viscosity, η, as predicted by the Stokes–Einstein equation. The bimolecular rate constant for excimer formation from pyrene itself at several pressures does not exhibit this behavior in low molecular weight solvents, as observed by Okamoto and Sasaki.[27] These authors found values of a lower than unity in several solvents (except toluene), which are explained by the invalidity of the Stokes–Einstein equation to predict diffusion coefficients of solute molecules moving among solvent molecules of similar size.[28] In our case, slopes lower than 1 are attributed to changes in solvent quality to the polymer with increasing pressure. Our results indicate that the variation in solvent quality is more pronounced for the longer chain and the poorest solvent.

Table 1. Activation Volumes ($P \leq 2000$ bar) and Related Parameters Associated with Polystyrene Cyclization

		PyPS2600Py		PyPS4500Py	
solvent	$\Delta V_\eta^\ddagger$ (cm^3/mol)	$\Delta V_{cy}^\ddagger$ (cm^3/mol)	a	$\Delta V_{cy}^\ddagger$ (cm^3/mol)	a
toluene	14.7 ± 0.6	13.9 ± 0.5	1.04 ± 0.03	13.4 ± 1	0.85 ± 0.04
cyclopentane	16.7 ± 2	16.7 ± 0.6	1.10 ± 0.06	13.8 ± 0.8	0.71 ± 0.04
methylcyclohexane	20.9 ± 0.8	19.6 ± 0.9	0.91 ± 0.04	14.9 ± 1	0.67 ± 0.05

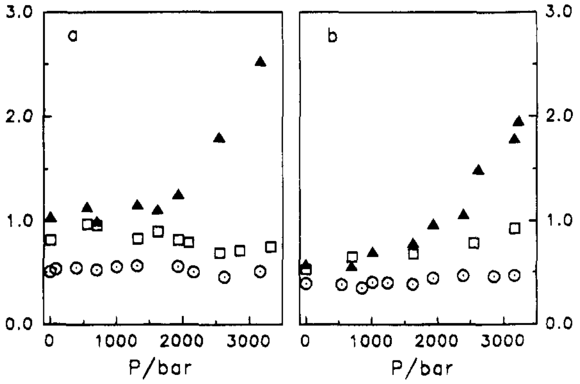


Figure 6. Plot of $k_1\eta$ for PyPSPy, at several pressures, in toluene (⊙), cyclopentane (□), and methylcyclohexane (▲): (a) $M_n = 2600$; (b) $M_n = 4500$.

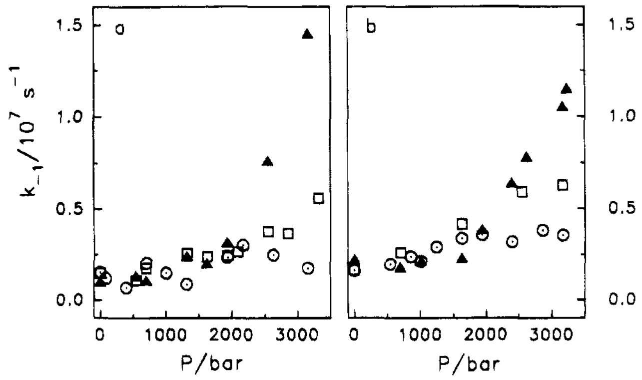


Figure 7. Pressure dependence of the excimer dissociation rate constant, k_{-1}, for PyPSPy, in toluene (⊙), cyclopentane (□), and methylcyclohexane (▲): (a) $M_n = 2600$; (b) $M_n = 4500$.

A polymer dissolved in a good solvent has, on one hand, an increase in the average chain dimensions and, on the other hand, a decreased probability of having the chain ends in proximity (the correlation hole effect). Both factors contribute to a decrease in the cyclization rate constant, the latter being more important for low molecular weight polymers.[29-31]

The effect of solvent quality changes on k_1 is more visible if the variation of viscosity with pressure is removed. This is done in Figure 6, where the cyclization rate constant values were multiplied by the solvent viscosity. The $k_1\eta$ values are approximately constant in toluene for both chains and in cyclopentane for the shorter chain. For the longer chain in the Θ solvent, a small increase in $k_1\eta$ with pressure is observed, but the most relevant feature is the significant increase in this value for both chains in methylcyclohexane, showing that this solvent becomes even poorer at high pressures. This type of pressure effect on the quality of a solvent for a polymer was observed previously for polystyrene in cyclohexane and decalin in light scattering experiments.[8-10]

For polystyrene in toluene and in cyclopentane, the cyclization rate constant is not very sensitive to changes which may occur in solvent quality due to pressure increases. This leads us to suggest that the effect of pressure on chain cyclization is more important when the polymer chain is partially collapsed (poor solvents), but not when it is expanded (good and Θ solvents). This type of behavior is in agreement with the experimental observation that for polymers in good solvents, the chain dimensions are often pressure independent.[8-13]

Activation volumes for the chain cyclization, $\Delta V_{cy}^\ddagger$, can be obtained by the equation

$$\left(\frac{\partial \ln k_1}{\partial P}\right)_T = -\frac{\Delta V_{cy}^\ddagger}{RT} \tag{9}$$

Table 1 displays the values of $\Delta V_{cy}^\ddagger$ obtained from the plots of ln k_1 *vs* pressure (linear up to ≈2000 bar), for both chains in all solvents. The activation volumes follow the order $\Delta V_{cy}^\ddagger$(toluene) < $\Delta V_{cy}^\ddagger$(cyclopentane) < $\Delta V_{cy}^\ddagger$(methylcyclohexane), which is in agreement with activation volumes for the solvent viscosity, $\Delta V_\eta^\ddagger$ (Table 1), calculated from eq 10.

$$\left(\frac{\partial \ln \eta}{\partial P}\right)_T = \frac{\Delta V_\eta^\ddagger}{RT} \tag{10}$$

The activation volumes for the cyclization of the smaller chain ($M_n = 2600$) are close to $\Delta V_\eta^\ddagger$ in all solvents, as is expected for a diffusion controlled process. For the longer chain ($M_n = 4500$), the values of $\Delta V_{cy}^\ddagger$ are smaller than $\Delta V_\eta^\ddagger$, especially in Θ and poor solvents, as a result of the diminution of solvent quality. Above 2500 bar, the activation volumes decrease significantly, approaching zero in some cases. This fact suggests that, at very high pressures, the polystyrene chain ends are already very close before excimer formation. However, the quantity of ground-state dimers is almost invariant with pressure (see Figure 3), indicating that the conformation attained at higher pressures is not suitable for enhancing the ground state dimer formation.

The excimer dissociation rate constant, k_{-1}, plotted in Figure 7, exhibits an interesting feature: it increases with pressure, this behavior being more pronounced when the quality of solvent is poor. In fact, due to solvent viscosity increase with pressure, the excimer dissociation rate should decrease, since the polymer chain ends must diffuse apart after disruption of the excimer.

This feature cannot be entirely explained by changes in solvent quality, thus we propose that pressure induces changes in the excimer conformation. This is supported from the variation with pressure of both bandwidth and spectral shifts of the intermolecular pyrene excimer in cyclohexane at room temperature, as reported by Johnson and Offen.[32] They found that the bandwidth increases monotonically with pressure, while the plot of the spectral shift versus pressure exhibits a maximum around 5000 atm. The spectrum is blue shifted at low pressures and red shifted in the high-pressure region.[32] If conformational changes do not occur with increasing pressure, then a red shift should be observed[33] due to the monotonic increase of solvent refractive index with pressure.[34] The blue shift can be attributed to conformational changes in the excimer

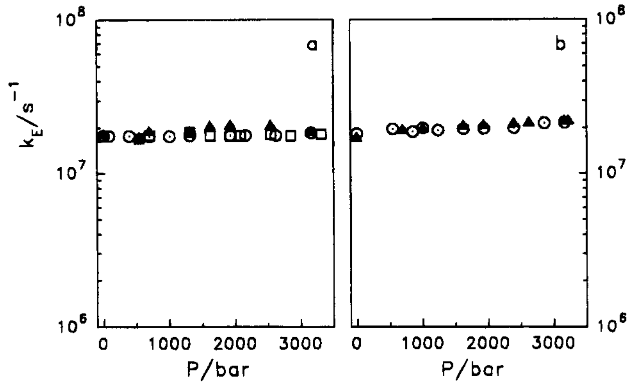


Figure 8. Pressure dependence of the reciprocal lifetime of the excimer, k_E, for PyPSPy, in toluene (⊙), cyclopentane (□), and methylcyclohexane (▲): (a) $M_n = 2600$; (b) $M_n = 4500$.

which result in a diminution of the excimer binding energy. This in turn explains the increase of k_{-1} with increasing pressure observed in our system.

The reciprocal lifetimes of the excimer, k_E, plotted in Figure 8, are practically independent of pressure. A similar observation was reported by Okamoto and Sasaki[28] for the pyrene intermolecular excimer. This is a nice result for us, since it supports our confidence in the validity of the kinetic analysis of our system as described above.

The radiative rate constant increases with pressure owing to the variation of the solvent refractive index. Indeed, the radiative rate constant is proportional to the square of the refractive index, and this increases slowly with pressure (an increase of ≈7% was observed in toluene when pressure varies from 1 to 5000 atm at room temperature[34]). On the other hand the nonradiative rate constant should decrease with pressure due to the increase of solvent viscosity, as observed for the intermolecular pyrene excimer in solvents of different viscosities.[35] Then, the variation in opposite directions with pressure of the radiative and nonradiative rate constants results in a rather small variation of the intrinsic excimer lifetime.

5. Conclusions

The influence of hydrostatic pressure on the cyclization of polystyrene chains with both ends labeled with 1-pyrenyl groups was studied in solvents (toluene, cyclopentane, and metylcyclohexane) of different qualities to the polymer by using both fluorescence spectra and monomer and excimer decay curve measurements. The major effect of pressure is the increase of solvent viscosity resulting in a large diminution of the cyclization rate constant. Nevertheless, it was shown that poor and Θ solvents become even poorer with a pressure increase in agreement with the same trends observed for both the second virial coefficient, A_2, and the radius of gyration, R_G. On the other hand k_{-1} increases with pressure which is associated with conformational changes in the excimer which result in the diminution of the excimer binding energy.

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