Influence of pressure on cyclization of a polystyrene chain. Time-resolved fluorescence measurements

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The cyclization of a polystyrene chain (Mₘ=4500, Mₘ/Mₘ=1.08), both ends labelled with 1-pyrenyl groups, was studied in toluene and methylcyclohexane from 1 to 3500 bar. The major effect of pressure on the cyclization rate constant comes from its effect upon the viscosity. Nevertheless, for a full understanding of the results, changes in the quality of the solvent for the polymer should occur in methylcyclohexane (a poor solvent), but not in toluene (a good solvent). The rate of the excimer dissociation process increases with pressure, this being attributed to a decrease of the excimer binding energy, owing to the diminution of the distance between pyrenes in an excimer sandwich conformation.

1. Introduction

Luminescence is a powerful tool for studying the dynamics and conformation of polymers [1]. One of the most interesting experiments is done with polymers labelled at both ends with 1-pyrenyl molecules [2].

Upon electronic excitation, an intramolecular excimer can be formed on the encounter of an excited pyrene at one chain end with the other pyrene of the chain which is in the ground state. The kinetics of this process are described by scheme 1, where kₑ and kₘ are the reciprocal of intrinsic lifetimes of the excited monomer and excimer, respectively, kₙ is the rate constant for excimer formation (cyclization of the chain) and k₋₁ is the excimer dissociation rate constant.

Scheme 1 predicts that upon electronic excitation by a δ pulse of light the monomer fluorescence decays as a sum of two exponentials and the excimer as a difference, both with the same decay constants [3]

Iₘ(t) = a₁ exp(−λ₁t) + a₂ exp(−λ₂t) ,
Iₑ(t) = a₃ exp(−λ₁t) − exp(−λ₂t) ,

where

2λ₁₂ = (Aₓ + Aᵧ) ± \(\sqrt{(Aₓ - Aᵧ)^2 + 4k₁k₋₁} \),
Aₓ = kₘ + k₁ , Aᵧ = kₑ + k₋₁ ,
and

\(a₂/a₁ = (Aₓ - \lambda₁) / (\lambda₂ - Aₓ) \).
The rate constants can be calculated from the values of \( \lambda_1, \lambda_2 \) and the ratio \( a_2/a_1 \), once the monomer lifetime, \( \tau_M = 1/k_0 \), is known [3].

The cyclization rate constant, \( k_1 \), and the excimer dissociation rate constant, \( k_{-1} \), are solvent dependent. This dependence has been correlated with viscosity changes and the quality of the solvent for the polymer [4,5]. The increase of hydrostatic pressure allows substantial changes in viscosity without modifying the nature of the solvent, which is important for the full understanding of the cyclization process.

In this Letter, the cyclization of a polystyrene chain I (\( M_n = 4500; M_w/M_n = 1.08 \)), both ends labelled with 1-pyrenyl groups, was studied in toluene (a good solvent) and methylcyclohexane (a poor solvent) from 1 up to 3500 bar.

The cyclization rate constant decreases with pressure in both solvents, this variation being explained by viscosity and solvent quality changes. The rate of the ring opening process increases with pressure for both solvents, the increase being more pronounced in methylcyclohexane. To explain this result it is suggested that the excimer binding energy changes with pressure owing to the decrease of the intermolecular distance between the pyrene moieties in the excimer.

2. Experimental

The synthesis of polymer I (\( M_n = 4500; M_w/M_n = 1.08 \)) and its characterization have been previously reported [6]. Spectroscopic grade toluene and methylcyclohexane (Merck, Uvasol) were used as received. The viscosities of the solvents at several pressures were taken from the literature [7,8]. Solutions of polymer I (\( C \approx 2 \times 10^{-6} \text{ M} \)) were degassed by nitrogen bubbling.

Measurements were made at room temperature (22°C) in a Nova Swiss high-pressure cell fitted with two sapphire windows at right angles. Fluorescence spectra were measured on a home-built spectrophotometer using a xenon lamp as the excitation source. 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 [9]. The excitation source is 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 \( \lambda = 322 \text{ nm} \). Monomer and excimer emissions were selected by appropriate interference filters with bandwidth of \( \approx 20 \text{ nm} \) and detected by a Philips XP2020 photomultiplier.

3. Data and data analysis

Decay curve analysis allows the determination of decay constants \( \lambda_1, \lambda_2 \) and the ratio \( a_2/a_1 \). The rate constants are then calculated using the monomer lifetime, \( \tau_M = 1/k_0 \), obtained from the decay of one-end 1-pyrenyl labelled chains in dilute solution. The cyclization rate constants of polymer I in toluene and methylcyclohexane versus pressure are shown in fig. 1. The variation of the cyclization rate constant with pressure results mainly from the increase of solvent pressure.

![Graph](image-url)
viscosity, as already shown by steady-state fluorescence measurements [10]. The cyclization process for long chains is diffusion controlled, with the rate constant proportional to the translational diffusion coefficient of the chain [11].

The effect of viscosity changes on the cyclization rate constant can be taken into account by multiplying \( k_i \) by viscosity, \( \eta \), at each pressure. Fig. 2 shows that \( k_i \eta \) is practically constant in toluene (the good solvent), while in methylcyclohexane (the poor solvent) a significant increase with pressure is observed.

The dependence of the cyclization rate on the quality of the solvent for the polymer is associated with excluded volume effects [45,121]. These effects perturb the chain conformation in two quite different ways: the first is by the increase of average chain dimensions; the second is by the decrease of the chain ends separation distribution function for small distances. Both effects decrease the cyclization rate constant, the second being predominant for low molecular weight polymers [4,5,121]. Our results show that in toluene (a very good solvent for polystyrene, with a Flory \( \Theta \)-temperature around \(-41^\circC \) [13]), small changes in the solvent quality owing to a pressure increase are not perceptible in \( k_i \). This agrees with the experimental observation that for good solvents for polystyrene the pressure does not influence the chain dimensions [14]. On the other hand in methylcyclohexane (\( \Theta = 68^\circC \) [15]) the variation of \( k_i \eta \) values with pressure indicates that this is a poorer solvent at high pressures. The same behaviour was also observed in cyclohexane and decalin using light scattering measurements [16]. Thus we speculate that pressure always influences chain conformation, this effect being visible when the polymer chain is coiled (as in a poor solvent) but not when it is expanded (as in a good solvent).

The reciprocal lifetime of the excimer, \( k_E \), and the excimer dissociation rate constant, \( k_{-1} \), are plotted in fig. 3. Both \( k_E \) and \( k_{-1} \) increase with pressure, the variation of \( k_{-1} \) being notably larger.

![Fig. 2. Pressure dependence of \( k_i \eta \) values in toluene (\( \bullet \)) and methylcyclohexane (\( \blacksquare \)).](image)

![Fig. 3. Pressure dependence of the excimer dissociation rate constant, \( k_{-1} \), and the reciprocal lifetime of the excimer, \( k_E \), in toluene (\( \bullet, \bigcirc \)) and methylcyclohexane (\( \blacksquare, \square \)). Filled and hollow symbols refer to \( k_{-1} \) and \( k_E \), respectively.](image)
The most interesting feature is the behaviour of \( k_{-1} \) since, instead of the observed increase with pressure, the opposite should occur owing to the increase of viscosity. Indeed, for excimer dissociation to take place, the polymer chain ends should diffuse apart, this process being hindered by viscosity. If the corrected values for viscosity changes \( (k_{-1}) \) were plotted versus pressure, a substantial increase with pressure is observed, which can not be completely explained by changes in solvent quality. We believe that pressure decreases the distance between pyrene moieties in the excimer sandwich conformation, lowering the excimer binding energy. Therefore, the excimer dissociation rate constant increases owing to the decrease of activation energy.

The ratio of the excimer \( (I_E) \) to monomer \( (I_M) \) fluorescence intensities [3], is often used to extract information on cyclization of polymer chains

\[
\frac{I_E}{I_M} \propto \frac{k_1}{k_E + k_{-1}}. \tag{6}
\]

This ratio becomes proportional to \( k_1 \) when \( k_E \) is pressure independent and \( k_{-1} \ll k_E \). Although \( k_E \) slowly increases with pressure, \( k_{-1} \) varies substantially, attaining at high pressures in methylcyclohexane values close to \( k_E \). Relation (6) should be applied cautiously when used to obtain conclusions about the variation of \( k_1 \) with pressure. Nevertheless, this relation can be useful to confirm the results obtained from time-resolved fluorescence measurements.

Fig. 4 shows the plot of the \( \frac{k_1}{(k_E + k_{-1})} \) and \( \frac{I_E}{I_M} \) values normalized at 1 bar. The agreement between the two sets in methylcyclohexane (A) and toluene (B) proves the adequacy of the method of decay curve analysis.

4. Summary and conclusions

The cyclization of a polystyrene chain \( (M_n=4500, M_w/M_n=1.08) \), both ends labelled with 1-pyrenyl groups, was studied in toluene and methylcyclohexane by fluorescence techniques. The major effect of hydrostatic pressure is to increase the viscosity, which slows down the cyclization rate constant. Nevertheless, a decrease of solvent quality with pressure was observed, this effect being particularly visible in methylcyclohexane (a poor solvent).

The excimer dissociation rate constant increases
with pressure for both solvents, this being attributed to the lowering of the activation energy. This behaviour results from the decrease of the excimer binding energy with pressure, owing to the diminution of the distance between pyrenes in the excimer sandwich conformation.

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References