Influence of pressure on cyclization of a polystyrene chain

A.T. Reis e Sousa, J.M.G. Martinho, F. Baros, J.C. André and M.A. Winnik

Centro de Química-Física Molecular da U.T.L., Complexo I, Instituto Superior Técnico, 1096 Lisboa Codex, Portugal

GRAPP, UA328 du CNRS, ENSIC/INPL, 1 rue Grandville, F-54001. France

Department of Chemistry and Erindale College, University of Toronto, Toronto, Ontario, MSS IA1 Canada

The effect of hydrostatic pressure on the cyclization of a polystyrene chain \((M_n = 4500)\) both ends labelled with a pyrene derivative molecule is studied in toluene (good solvent) and methylcyclohexane (poor solvent) in the range of 1–3500 bar. The cyclization rate constant decreases with pressure, mainly owing to the increase of medium viscosity. When the effect of viscosity is considered the cyclization rate coefficient still decreases with pressure in both solvents which indicates that pressure influences the polymer-solvent interaction energies.

1. Introduction

The enhancement of hydrostatic pressure has three effects on the rate of chemical reactions [1]. The isothermal compressibility will increase the concentration of reactants and thereby contribute to an increased rate of bimolecular reactions. It is also responsible for the variation of the volume of activation \(\Delta V^\ddagger\), given by the difference between the volume of the transition state complex and the volume of the reactants, and finally it increases the viscosity which will lead to a decrease in the rate of diffusion-influenced reactions.

For intramolecular reactions, concentration effects are unimportant, but for intramolecular reactions involving polymers, another factor comes into play. This factor is the effect of pressure on the quality of the solvent for the polymer [2]. The solvent-polymer interaction is normally expressed in terms of the Flory \(\chi\)-parameter which is equal to zero for isothermal mixing of solvent and polymer and takes the value 0.5 for \(\Theta\)-solvents. Good solvents for polymers have values of \(\chi \approx 0.45\) and poor solvents have \(\chi > 0.5\). A \(\Theta\)-solvent is one in which the unfavourable heat of mixing between polymer and solvent exactly compensates for steric interactions ("excluded volume") between segments remote along the backbone, and the mean dimensions of the polymer are exactly those predicted by random walk theory.

In this paper fluorescence measurements at room temperature of solutions of a polystyrene chain \((M_n = 4500)\) labelled at both ends with 1-pyrenyl group (scheme a) in toluene and methycyclohexane for pressures up to 3500 bar are presented.

To whom correspondence should be addressed.

Toluene is at room temperature a good solvent for polystyrene \((\chi = 0.4)\) and methycyclohexane a very poor solvent (the \(\Theta\) temperature is \(\sim 70^\circ C\)) [3]. The ratio of the excimer to monomer fluorescence intensities decreases with pressure for both solvents, owing to the decrease of the excimer formation (cyclization) rate constant. The major reason for this variation is the increase of solvent viscosity with pressure. Nevertheless, the ratio of intensities still decreases with increasing pressure after correction for the variation of viscosity. This indicates that the quality of the solvent for the polymer is pressure dependent, which influences the cyclization rate constant. Indeed, the cycliz-
ation rate in the vicinity of \( \chi = 0.5 \) is very sensitive to solvent quality because of the pair correlation effect on the contribution of excluded volume to the cyclization probability [4].

2. Experimental

The synthesis of polymers and their characterization have been reported previously [5]. The polystyrene chain of structure (a) and molecular weight \( M_n = 4500 \) (\( M_w/M_n = 1.07 \)) was characterized by gel permeation chromatography (GPC) using ethyl acetate as a solvent. The GPC analysis with UV-vis detection shows that low molecular weight compounds absorbing light at the excitation wavelength are less than 0.001 mol\%. The toluene and methylcyclohexane solvents (Merck, Uvasol) were used as received. Diluted solutions of the polymer (ca. \( 2.0 \times 10^{-6} \) M) in both solvents were degassed before the fluorescence measurements. High-pressure fluorescence measurements were performed at room temperature (\( \sim 25^\circ \text{C} \)) in a Nova-Swiss high-pressure apparatus. A stainless steel optical cell fitted with two sapphire ultraviolet quality windows was used. The excitation wavelength (\( \lambda = 340 \) nm) and the emission wavelengths (\( \lambda = 376 \) nm for the monomer emission and \( \lambda = 486 \) nm for the excimer emission) were selected by H20 Jobin-Yvon monochromators.

3. Data and data analysis

The cyclization process leading to intramolecular excimer formation is described by scheme b. Upon excitation, cyclization leads to intramolecular excimer formation.

\[
\begin{align*}
P Y + P Y^{*} \xrightarrow{k_1} & \quad \text{(PYPY)*} \\
\text{k}_{-1} & \quad \text{(PY)*} \\
\text{hv} & \quad \text{hv}
\end{align*}
\]

The rate constant \( k_1 \) describes the diffusion controlled cyclization step and \( k_{-1} \) the excimer dissociation and ring opening to reform the locally excited pyrenyl group, \( k_M \) and \( k_E \) being the reciprocal lifetimes of the locally excited pyrene monomer and excimer, respectively. The ratio of the excimer (\( I_E \)) to monomer (\( I_M \)) fluorescence intensities is given by [6]

\[
\frac{I_E}{I_M} = \frac{k_{FE}}{k_{FM}} \times \frac{k_1}{k_E + k_{-1}},
\]

where \( k_{FM}, k_{FE} \) are the radiative rate constants for the monomer and excimer emissions, respectively. At room temperature, for pyrene, \( k_{-1} \) is lower than \( k_E \), the ratio \( k_{-1}/k_E \) decreasing rapidly with increasing pressure [7]. As the effect of pressure on the ratio of radiative rate constants and \( k_E \) is nearly negligible (ca. 5%) [7,8], the \( I_E/I_M \) values are proportional to the cyclization rate constant \( k_1 \).

Figure 1 shows the variation of the ratio of excimer to monomer fluorescence intensities (\( I_E/I_M \)) for diluted solutions of polystyrene chain a in toluene and methylcyclohexane.

The ratio of intensities decreases with rising pressure; this is largely explained by the increment

\[
\frac{I_E}{I_M} = \frac{k_{FE}}{k_{FM}} \times \frac{k_1}{k_E + k_{-1}},
\]

Fig. 1. Plot of the ratio of the excimer to monomer fluorescence intensities of diluted solutions of chain a versus pressure. (+) toluene; (□) methylcyclohexane.
of the solvent viscosity. The cyclization rate constant is proportional to the reciprocal of viscosity [4c], since cyclization is a diffusion-influenced process. The viscosity of methylcyclohexane varies by more than a factor of 10 [9] and that of toluene by a factor of 6 [10] from 1 to 3500 bar, which explains the smaller variation of $I_E/I_M$ ratio observed in toluene. The cyclization rate constant, $k_{cy}$, is the product of a diffusion controlled rate constant $k_d (M^{-1} s^{-1})$ times the local concentration of one end in the vicinity of the other,

$$k_{cy} = k_d C_{local}. \tag{2}$$

In the absence of excluded volume, one can show that this is equivalent to stating that $k_{cy}$ is proportional to the ratio of the translational diffusion coefficient ($D$) to the mean-squared radius of gyration ($R_g^2$),

$$k_{cy} \propto \frac{D}{R_g^2} \tag{3}$$

where $D$ is sensitive to viscosity effects and $R_g^2$ is proportional to the cyclization probability. In the presence of excluded volume, an additional term $f(\chi)$ has to be considered [4]. For short chains, when the excluded volume is positive, $f(\chi)$ causes a decrease in $k_1$ because of the effect of the correlation hole on the cyclization probability, which causes a sharp decrease in $C_{local}$. The major effect of pressure is the decrease of $D$ owing to the increase of viscosity, $\eta$. In fig. 2 $I_E/I_M \times \eta$ versus pressure is plotted.

These values still decrease with pressure. This effect is more pronounced in toluene, where a maximum variation of $\sim 50\%$ was observed, compared to the corresponding variation of $\sim 25\%$ in methylcyclohexane. This is the opposite of what was observed in intermolecular pyrene excimer formation, where $k_1 \times \eta$ [7] and $I_E/I_M \times \eta$ [11] slightly increase with pressure. This is due to the increase of $D \times \eta$, as confirmed in methylcyclohexane, since the self-diffusion coefficient ($D_s$) times viscosity ($\eta$) increases with pressure [9]. Assuming similar trends for the translational diffusion of a polymer chain, the decrease of the corrected ratio of excimer to monomer fluorescence intensities with pressure reflects the presence of pressure effects on polymer-solvent interaction energies. In this hypothesis, the quality of both solvents for polystyrene should improve with pressure, and this effect is more pronounced for toluene. Unfortunately, essentially nothing is known about pressure effects on the quality of solvents, as the $\chi$ parameter is concerned.

### 4. Summary and conclusions

The cyclization of polystyrene in toluene and methylcyclohexane is largely influenced by hydrostatic pressure. The major effect of pressure is the increase of the medium viscosity which slows down the diffusion-influenced cyclization rate. When the effect of viscosity is considered the cyclization rate constant still decreases with pressure, which was interpreted as an indication that pressure improves the quality of both solvents to polystyrene. This conclusion was obtained assuming that the translational diffusion coefficient of the polymer chain times solvent viscosity is constant or increases with
pressure as in the case of the diffusion of small molecules. This will be tested in the future.

Acknowledgement

This work was supported by JNICT (Junta Nacional de Investigação Científica e Tecnológica) project PMCT/C/CEN/333/90, and INIC (Instituto Nacional de Investigação Científica).

References