Effect of Temperature and Solvent on the Cyclization of a Polystyrene Chain

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ABSTRACT: Cyclization rate measurements were carried out on a polystyrene chain (M_n = 4500; M_w/M_n = 1.08, both ends labeled with 1-pyrenyl groups) in toluene, cyclopentane, cyclohexane, and methylcyclohexane, between 22 and 95 °C. The solvent–polymer interaction energy changes with temperature, influencing both excluded volume effects, chain flexibility, and hydrodynamic properties of the chain. Excluded volume effects suppress the chain end pair distribution function for short distances, retarding the cyclization rate constant and accelerating the ring opening process. However, excluded volume effects alone are not able to explain all aspects of the cyclization process. It is necessary to invoke the variation of chain flexibility and hydrodynamic properties of the polymer chain with temperature.

1. Introduction

Temperature influences the quality of a solvent for a polymer. Phase separation can occur at low temperatures when the enthalpy of mixing is unfavorable, and it can occur at high temperatures, in the vicinity of the gas-liquid critical temperature of the solvent, where a free-volume mismatch between the solvent and the polymer occurs. Phase diagrams of polymer solutions are classified in two types according to the shape of the cloud point curve in the temperature concentration diagram.[1,2] One is characterized by the existence of a maximum, the upper critical solution temperature (UCST), which tends to move toward higher temperature and lower concentration with polymer samples of increasing molecular weight. The other has a concave shape with a minimum, the lower critical solution temperature (LCST), which shifts to lower temperatures and lower concentrations as the polymer molecular weight increases. In a polymer–solvent system exhibiting both a LCST and a UCST, there are two corresponding Flory Θ temperatures at which the polymers exhibit ideal mean dimensions. At high temperature, corresponding to the LCST of an infinitely long polymer, is the upper Θ temperature, Θ_L; and at low temperature is the Θ temperature, Θ_U, corresponding to the UCST of the infinite chain.

Between the Θ temperatures, the quality of solvent changes significantly. Light scattering[3-5] and intrinsic viscosity measurements[5,6] show an ideal behavior of the chain at both Θ temperatures. The plot of the expansion coefficient for the coil dimensions versus temperature increases first from Θ_U and thereafter passes through a maximum, before decreasing to the ideal value at Θ_L.

Polymer cyclization is very sensitive to solvent quality for the polymer. This was observed in both cyclization and ring opening rate constants and cyclization equilibrium constants. Nevertheless, very few cyclization studies at different temperatures have been reported.[7] In this paper, we describe results obtained with a polystyrene chain (M_n = 4500; M_w/M_n = 1.08) dissolved in toluene, cyclohexane, methylcyclohexane, and cyclopentane, at temperatures between 22 and 95 °C. This polymer has structure I with 1-pyrenyl groups attached to both chain ends.

I
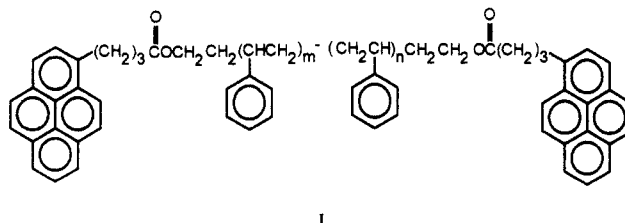
Upon UV excitation, chain cyclization can be detected, owing to intramolecular excimer formation. This process is summarized in Scheme I, where k_1 describes the diffusion-controlled cyclization step; k_{-1} describes the excimer dissociation and ring opening process to reform the initially excited chain; and k_M and k_E are the reciprocal lifetimes of the excited pyrene monomer and excimer, respectively.

Toluene is, in the range of temperatures studied, a very good solvent ($\Theta_U \cong -41$ °C;[8] $\Theta_L = 277$ °C[9]). Cyclopentane is a Θ solvent at room temperature ($\Theta_U = 20.5$ °C),[10] becoming a better solvent with temperature increase until $\cong 80$ °C, its quality decreasing thereafter to attain the upper Θ temperature, $\Theta_L = 154.5$ °C.[5,6] Cyclohexane and methylcyclohexane are poor solvents near room temperature ($\Theta_U = 34.5$ and 68 °C for cyclohexane and methylcyclohexane, respectively).[11] The quality of both solvents for polystyrene increases with increasing temperature over the full range covered in these experiments, since the Θ_L temperatures for both solvents are very high (Θ_L is 213 °C for cyclohexane and 211 °C for methylcyclohexane).[9]

We observe that k_1 is smaller and k_{-1} larger for toluene than for the remaining solvents at each temperature. This agrees with other cyclization studies in poor and good solvents[12] and in solvent mixtures.[13] This behavior was attributed[12,13] to excluded volume effects that strongly diminish the probability of end-to-end separations for chain ends in close proximity. Nevertheless, the cyclization rate constants corrected for the trivial dependence on the viscosity and temperature are practically constant with temperature in cyclopentane, cyclohexane, and methylcyclohexane, but not in toluene where a significant increase is observed for temperatures higher than 50 °C. We believe that this surprising behavior in toluene results from variations with temperature of "specific" solvent–polymer

Scheme I
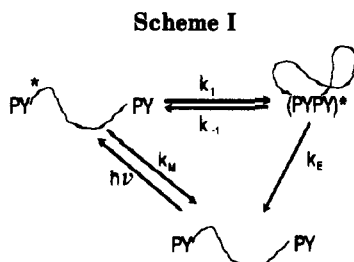
interactions that influence chain flexibility and the hydrodynamic properties of polystyrene. The near constancy of values in the other solvents probably indicates the offsetting effects of temperature on excluded volume and on hydrodynamic properties and/or chain flexibility.

2. Theory

The distribution function of polymer chain end-to-end separation, $W(r)$, is well described in Θ solvents for sufficient long chains by a Gaussian curve. In this case it is well-known that

$$W_0(0) \sim \langle r^2 \rangle_0^{-3/2} \tag{1}$$

If only a single scaling length was important in this problem, then the cyclization probability should decrease with chain expansion as

$$W(0) = W_0(0)[\langle r^2 \rangle_0 / \langle r^2 \rangle]^{3/2} = W_0(0)\alpha^{-3/2} \tag{2}$$

where the subscript refers to unperturbed dimensions and α is the expansion factor for end-to-end distance.[14,15] This is not the case for real chains, where a severe depression in $W(r)$ for small distances exists, owing to pair-correlation contributions to the excluded volume effect.[16] The effect of the correlation hole in $W(r)$ for small r is a pronounced decrease of the cyclization equilibrium constant, since the probability of chain conformations with small end-to-end distances is significantly diminished. The cyclization probability also decreases with chain stiffness[17] that is inherent in short chains. These features were for low molecular weight polymers recently confirmed by Monte Carlo simulations based on the rotational isomeric state (RIS) model.[18]

Polymer cyclization is an intramolecular diffusion-influenced process. Its rate can be characterized by a first-order coefficient, k_{cy}, available after solving the diffusion equation for the polymer chain with adequate models of polymer dynamics. Willemski and Fixman (WF)[19] examined polymer cyclization in terms of both the harmonic spring model and the more realistic Rouse–Zimm model. This pioneering work attracted the attention of other theoreticians, namely Doi[20] and Perico and Cuniberti.[21,22] These authors obtained the cyclization rate constant for Gaussian chains using the partial-draining Rouse–Zimm model. They showed that, in the limit of long chains and Θ solvents,

$$k_{cy} = 0.33 D_{ND} / R_G^2 \tag{3}$$

for nondraining chains, and

$$k_{cy} = 2.26 D_{FD} / R_G^2 \tag{4}$$

for the free-draining case, D being the translational diffusion coefficient and R_G^2 the mean-squared radius of gyration. High molecular weight polymers present a nondraining hydrodynamic behavior. However, low molecular weight polymers cannot be considered as nondraining and are better described by a partial-draining hydrodynamic behavior.[23] This is described in the Rouse–

Zimm model by a reduced bead friction coefficient that measures the strength of the hydrodynamic coupling. In the nondraining limit, the solvent is trapped inside the coil and the polymer experiences a lower friction than in the free-draining limit (Rouse model). Numerical results presented by Perico and Cuniberti[21] show that the cyclization rate constant depends on the strength of hydrodynamic interactions. For long chains the rate constant is larger for partial-draining than for free-draining chains, while for short chains the opposite occurs. However, for short chains the difference in k_{cy} with the hydrodynamic behavior is very small. Chain stiffness introduced in the WF theory *via* different statistical lengths is very important:[21,22] the cyclization rate constant increases with greater chain flexibility. Some of the approximations introduced in the formulation of WF theory were addressed by Monte Carlo simulation mentioned above. In addition, the simulation was used to compare the consequences of including or not including excluded volume effects.[24] When excluded volume effects were neglected, the simulated results agree qualitatively with the WF theory predictions. The differences observed were attributed to non-Gaussian equilibrium statistics, to the sink closure approximation, and to the method of calculating the hydrodynamic interactions.

3. Experimental Section

The synthesis of I and its characterization have been previously reported.[25] Toluene and cyclohexane from Merck, of spectroscopic-grade quality, were used as received. Methylcyclohexane from BDH Chemicals (>95% pure) and cyclopentane from Fluka (>99%) were purified by fractional distillation at normal pressure. The viscosities of solvents at several temperatures were taken from the literature.[26] Solutions of polymer I ($C \approx 2 \times 10^{-6}$ M) were degassed using the freeze–pump–thaw technique and sealed under a vacuum of better than 2×10^{-5} bar. Fluorescence spectra were measured on a Spex Fluorolog 112 spectrofluorometer. Decay curves were obtained by the single photon timing technique and were analyzed using an iterative reconvolution method based on the algorithm of Marquardt.[27] The excitation light ($\lambda = 337$ nm), from a coaxial flash lamp (Edinburgh Instruments, Model 199F) running in nitrogen, was selected by a Jobin-Yvon (Model H-20) monochromator. The monomer fluorescence ($\lambda = 376$ nm) and the excimer fluorescence ($\lambda = 520$ nm) were selected by a Jobin-Yvon (Model H-20) monochromator and detected by a Philips XP2020Q photomultiplier. In order to eliminate the color shift of the photomultiplier, the δ pulse convolution technique was utilized.[28] Reference decay curves of diluted solutions of 1,4-bis(5-phenyl-1,3-oxazol-2-yl)benzene (POPOP) in cyclohexane ($\tau = 1.1$ ns) and 2,5-bis(5-*tert*-butyl-2-benzoxazolyl)thiophene (BBOT) in 95% ethanol ($\tau = 1.47$ ns) were used in the analysis of the monomer and excimer decay curves, respectively.

4. Data and Data Analysis

The fluorescence spectra of diluted solutions of I normalized in the first peak of the monomer emission at 22 °C are presented in Figure 1. The excimer intensities vary with solvent, being smaller in toluene and larger in methylcyclohexane. The ratio of excimer to monomer fluorescence intensities is, according to Scheme I, given by[29]

$$\frac{I_E}{I_M} = \frac{k_{FE}}{k_{FM}} \frac{k_1}{(k_E + k_{-1})} \tag{5}$$

where k_{FM} and k_{FE} are the monomer and excimer radiative rate constants, respectively. The fluorescence intensities ratio essentially reflects the variation of the cyclization rate constant, k_1, with solvent, since at room temperature
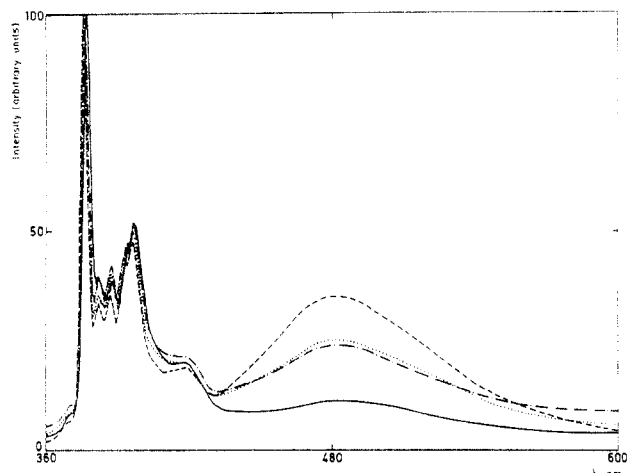
Figure 1. Corrected fluorescence spectra of diluted solutions ($c \approx 2 \times 10^{-6}$ M) of polystyrene chain I in different solvents. (—) Toluene; (- · -) cyclopentane; (···) cyclohexane; (- - -) methylcyclohexane.

$k_E \gg k_{-1}$, the radiative rate constants ratio is solvent independent, and k_E exhibits only small differences between solvents. This indicates that k_1 is smallest for the best solvent (toluene) and largest for the poorest solvent (methylcyclohexane).

A better understanding of the kinetics, with the evaluation of all the rate constants, can be obtained from an analysis of the monomer and excimer decay curves. Scheme I 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:[29]

$$I_M(t) = a_1 \exp(-\lambda_1 t) + a_2 \exp(-\lambda_2 t) \qquad (6)$$

$$I_E(t) = a_3[\exp(-\lambda_1 t) - \exp(-\lambda_2 t)] \qquad (7)$$

where

$$2\lambda_{1,2} = (A_x + A_y) \mp \{(A_x - A_y)^2 + 4k_1 k_{-1}\}^{1/2} \qquad (8)$$

$$A_x = k_M + k_1; \qquad A_y = k_E + k_{-1} \qquad (9)$$

and

$$a_2/a_1 = (A_x - \lambda_1)/(\lambda_2 - A_x) \qquad (10)$$

From the values of the decay parameters (λ_1, λ_2) and the ratio a_2/a_1, all the relevant kinetic rate parameters can be calculated, once the monomer lifetime, $\tau_M = 1/k_M$, is determined. These τ_M values were obtained from the monoexponential decay curves of dilute solutions ($c \approx 2 \times 10^{-6}$ M) of a polystyrene chain containing a pyrene at only one end ($M_n = 5900$; $M_w/M_n = 1.33$) in the several solvents at each temperature.

The excimer decay curves of solutions of chain I are biexponentials with a ratio of the pre-exponential factors close to –1. The monomer decay curves can only be fitted with a sum of three exponentials, the long decay constant being close to k_M. This indicates the presence of one-end-labeled polystyrene chains with a 1-pyrenyl group in the solution. The other two decay constants are close to the values obtained from the fitting of the excimer decay. In order to obtain the most reliable values of the rate constants, the monomer decay curves were fitted with a sum of three exponentials, constraining two decay constants to the values recovered from the excimer decay curve fitting. The k_{-1} values are obtained with poor precision at low temperatures ($T < 35$ °C), since they are calculated from eq 9 ($k_{-1} = A_y - k_E$) and k_E is, for low temperatures, 1 order of magnitude larger than k_{-1}.
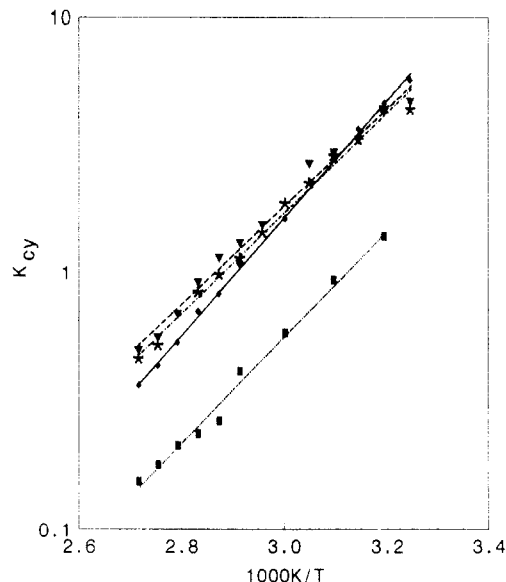
Figure 2. van't Hoff plot of the cyclization equilibrium constant in several solvents. (■) Toluene; (♦) cyclopentane; (▼) cyclohexane; (*) methylcyclohexane.

Table I. Experimental Values of the Enthalpy (ΔH°) and Entropy (ΔS°) of Polystyrene Chain I in Several Solvents from the van't Hoff Plot of K_{cy} (Columns 2 and 3) and Excimer Binding Energy from the Arrhenius Plot of $k_{-1}\eta/T$ (Column 4)

| solvent	$-\Delta H^\circ$/kcal mol^{-1}	ΔS°/cal mol^{-1} K^{-1}	ΔH/kcal mol^{-1}
toluene	9.5	–29.5	12.2
cyclopentane	10.5	–30.5	11.4
cyclohexane	8.7	–24.5	9.1
methylcyclohexane	8.9	–25.7	9.0

5. Results and Discussion

Figure 2 shows the Arrhenius plot of the cyclization equilibrium constant, $K_{cy} = k_1/k_{-1}$, for toluene, cyclopentane, cyclohexane, and methylcyclohexane. The K_{cy} values for toluene are much lower than for the other solvents. Toluene is a good solvent for polystyrene, and from eq 2 a decrease is expected in K_{cy}, owing to the increase of the expansion coefficient, α. However, it is well-known that the variation in chain dimensions is very small ($\approx 10\%$) for low molecular weight chains like the one examined here ($M_n = 4500$).[23] The large effect observed in toluene is more likely due to the correlation hole in the chain-end distribution function, $W(r)$, for small distances. For the same reason, K_{cy} values in cyclopentane are generally lower (except for low temperatures where the precision in k_{-1} is poor) than in cyclohexane and methylcyclohexane. The differences increase with temperature since the quality of solvent for polystyrene changes faster for cyclopentane than for the other solvents, attaining a maximum at ≈ 80 °C. The cyclization equilibrium constant is given by

$$K_{cy} = \exp(\Delta S^\circ/R) \exp(-\Delta H^\circ/RT) \qquad (11)$$

where ΔH° and ΔS° are the enthalpy and entropy of cyclization in the standard state, respectively. The values obtained from the fitting of the experimental equilibrium cyclization constants to eq 11 are presented in Table I. The entropy ΔS° is negative owing to the decrease in entropy when cyclization occurs.

The $-\Delta H^\circ$ values in column 2 of Table I are close to reported values for the binding energy of the intermolecular pyrene excimer (9–10 kcal mol^{-1}).[29,30] However, changes with temperature in both chain expansion and the correlation hole in $W(r)$ lead to variations of ΔS°,
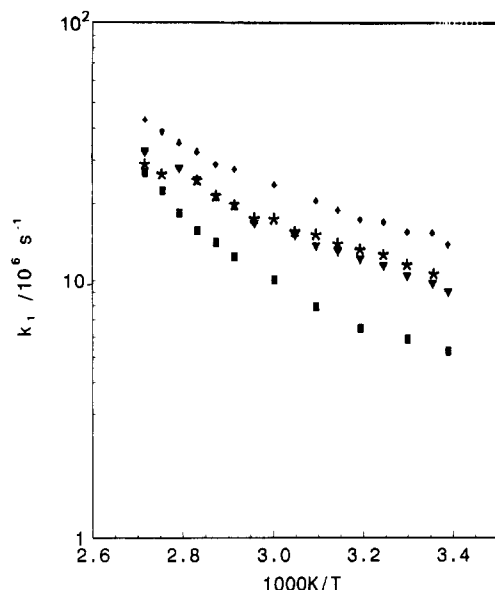
Figure 3. Cyclization rate constant versus $1/T$ in several solvents. (■) Toluene; (♦) cyclopentane; (▼) cyclohexane; (*) methylcyclohexane.
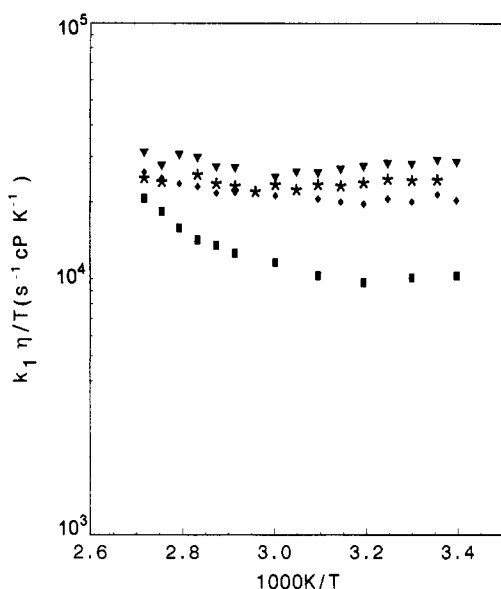
Figure 4. Cyclization rate constant multiplied by η/T versus $1/T$ in several solvents. (■) Toluene; (♦) cyclopentane; (▼) cyclohexane; (*) methylcyclohexane.

indicating multiple contributions to the cyclization enthalpy and entropy.

Figure 3 shows the plot of the logarithm of the cyclization rate constant versus the reciprocal of temperature. The plots are nonlinear, the values of k_1 being solvent dependent. The cyclization rate constants can be compared in different solvents at several temperatures if variations in the diffusion coefficients can be accommodated, and excluded volume effects, chain stiffness, and hydrodynamic properties of the polymer do not change significantly with solvent and temperature. Since the diffusion coefficient is proportional to T/η, its influence on k_1 is simply removed by multiplying the cyclization rate constants by η/T.

The $k_1\eta/T$ values presented in Figure 4 for cyclopentane, cyclohexane, and methylcyclohexane are similar in magnitude and essentially constant over the entire range of temperatures examined here. The results for toluene are quite different. At temperatures below 50 °C, $k_1\eta/T$ values for the polymer in toluene are significantly smaller than in other solvents, and the η/T term corrects effectively for the changes in rate due to viscosity changes. This

difference is consistent with excluded volume effects suppressing cyclization in toluene. At higher temperatures, there is a striking increase in $k_1\eta/T$ which is difficult to explain in terms of excluded volume effects. Toluene remains a good solvent for polystyrene at all of the temperatures examined. No such change is seen in Figure 2, which describes the effect of temperature on the cyclization equilibrium. As a consequence, we conclude that some aspect of the polymer–solvent interaction is changing which operates on the dynamics of the chain.

The change in the draining of the polymer coil has a minor effect in the cyclization rate for low molecular weight polymers as the one examined here.[21,22] Since we observe a large increase on the $k_1\eta/T$ values above 50 °C, we speculate that "specific" polymer–solvent interactions may be affected. Indeed, the $\pi-\pi$ interaction energy between the pendant phenyl groups along the chain is very large (ca. 5 kcal mol^{-1}) for local conformations with phenyl groups in proximity, limiting access of the solvent.[31]

Temperature and strong solvation forces may operate to disrupt these interactions. This can lead to solvent-dependent conformational statistics and possibly solvation effects on the microscopic friction coefficient and chain flexibility.

The excimer dissociation process is a ring opening reaction that involves disruption of the excimer binding force before the two chain ends can diffuse apart. Such a process can be described by the equation:

$$k_{-1} = (3D_e/R_e^2) \exp(-\Delta H/RT) \qquad (12)$$

where R_e is the encounter distance; D_e, the mutual diffusion coefficient of the chain ends; and ΔH, the excimer binding energy. This equation is derived assuming that the dissociation process is diffusive and that the encounter terminates at an arbitrary separation of $1.7R_e$. Equation 12 is particularly appropriate for excimer dissociation between free chromophores, where D_e refers to the mutual diffusion coefficient for the excited- and ground-state partners. When the chromophores are attached to the ends of a polymer chain, the process described by k_{-1} is necessarily more complex, reflecting all aspects of the polymer–solvent interaction that operate on the conformation and dynamics of the chain.

Arrhenius plots of $k_{-1}\eta/T$ values and the best fit lines to eq 12 are presented in Figure 5. One sees that k_{-1} values are larger in toluene than in cycloalkane solvents except at low temperatures, where the precision in k_{-1} values is poor. The ΔH values obtained in this way are presented in column 4 of Table I. In principle, these values should be sensitive only to the excimer binding enthalpy and to temperature-induced changes in excluded volume, since the η/T term should correct for temperature effects on chain dynamics. In practice, since this ΔH value is determined from k_{-1}, any effect of temperature on polymer dynamics that is not accommodated by the η/T correction will make a contribution to ΔH. When we compare the ΔH values in column 4 with the $\Delta H°$ values in column 2 in Table I, we note a much larger difference in toluene than in the other solvents. We interpret this to mean that the peculiar temperature effects that we found on the cyclization rates in toluene, which we attributed to specific solvation effects, also appear in the ring opening rates. When we consider cyclization equilibria ($K_{cy} = k_1/k_{-1}$), these unusual effects cancel.

6. Conclusions

Experimental results on polystyrene cyclization show that this process is very sensitive to the conformation and
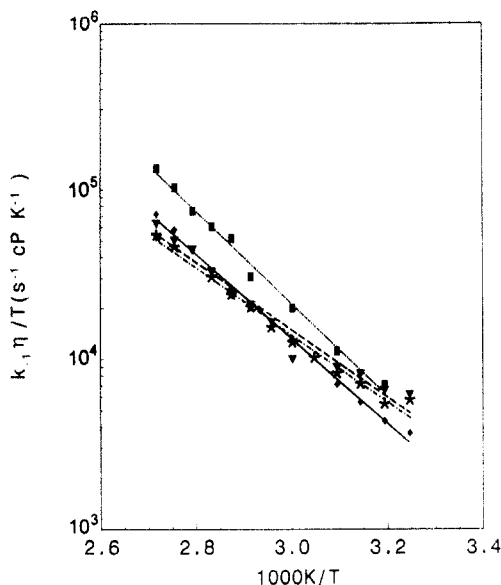
Figure 5. Arrhenius plot of $k_{-1}\eta/T$ in several solvents. (■) Toluene; (♦) cyclopentane; (▼) cyclohexane; (*) methylcyclohexane.

dynamics of polymer chains in solution. Temperature influences solvent–polymer interactions in several ways. The cyclization equilibrium constant K_{cy} is significantly smaller in toluene than in three cycloalkane solvents. This is a reflection of excluded volume effects, which for this oligomeric chain (M_n = 4500) operate almost exclusively at the level of the correlation hole in the distribution of the end-to-end distances. Over the range of temperatures examined, there is also an indication of increasingly important excluded volume effects in cyclopentane as the temperature is raised. Our most peculiar finding is of an enhancement in the cyclization and ring opening kinetics of polystyrene in toluene, beyond that which can be explained by a decrease in solvent viscosity, at temperatures between 50 and 90 °C, where no changes in the solvent quality for the polymer are anticipated. Here we speculate that temperature-dependent specific solvent–polymer interactions are involved.

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