Coil−Globule Transition of Pyrene-Labeled Polystyrene in Cyclohexane: Determination of Polymer Chain Radii by Fluorescence

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The coil−globule transition of a polystyrene chain (M_w = 113 000, M_w/M_n = 1.03) randomly labeled with a pyrene derivative was studied in cyclohexane under dilute conditions by fluorescence. The coil−globule transition temperature was found to be around 25 °C from the presence of a break point in the pyrene excimer-to-monomer fluorescence intensity ratio plot with temperature. Analysis of the pyrene monomer fluorescence intensity decays with the fluorescence blob model modified to consider the presence of ground-state pyrene pairs allowed for the determination of the chain radii at several temperatures between 12 and 50 °C and confirmed the occurrence of a coil−globule transition. Fluorescence was found to be a reliable technique for studying the coil−globule transitions in dilute solutions of low-molecular-weight polymers where stable globules exist without the interference of polymer aggregates in a large temperature interval.

1. Introduction

The conformation of a polymer chain in solution varies from an extended random coil in good solvents to a compact globule in poor solvents. In 1960, Stockmayer was the first to predict the collapse of a polymer chain from a coil to a compact globule as the quality of the solvent is changed.[1] Over the past 40 years, significant interest in both experimental and theoretical aspects of this transition has been expressed, not only because of its importance in biology (used as a simplified model for enzymatic activity, protein folding, or DNA packing)[2−4] but also because of its fundamental role in the understanding of polymer segment−segment and segment−solvent interactions.[5] The initial experimental results were obtained with polystyrene solutions in cyclohexane below the upper critical solution temperature (UCST).[6−8] Poly(*N*-isopropylacrylamide) (PNIPAM) in water has also been extensively studied, above its lower critical solution temperature (LCST).[9−11] Coil−globule transition studies are difficult to perform because aggregation occurs simultaneously with the formation of globules at the polymer concentrations required by the limits of detection of the most common experimental techniques (light scattering, intrinsic viscosimetry, etc.). To avoid aggregation, dilute solutions of high-molecular-weight polymer chains are frequently used. However, the phase diagrams of high-molecular-weight polymer solutions show very asymmetric coexistence curves and very small or even inexistent temperature gaps between the coil−globule transition temperatures and the binodal lines. For this reason, many experiments have been carried out with polymer solutions located in the metastable region of the phase diagram, where polymer globules coexist with aggregates.[12−14]

The use of a very dilute solution (0.002 wt %) of a low-molecular-weight poly(ε-caprolactone) chain (M_n ≈ 20 000, $M_w/$ M_n = 1.1) in THF allowed us to follow the coil−globule transition and to detect isolated globules in a temperature interval as large as ∼40 °C.[15] Stable globules were also observed in an even larger temperature interval (∼50 °C) with a shorter poly(ethylene oxide) chain (M_n ≈ 4000, M_w/M_n = 1.1) in toluene (0.0004 wt %).[16] These results were obtained with polymers labeled at both ends with pyrene and were feasible because of the high sensitivity of fluorescence. Recently, using randomly pyrene-labeled poly(dimethyl acrylamide) (PDMA) in methanol, the chain radii were calculated along the coil−globule transition[17] using the fluorescence blob model (FBM) developed by Duhamel and co-workers.[18]

In the present work, the coil−globule transition of a polystyrene chain (M_w ≈ 113 000, M_w/M_n = 1.03), randomly labeled with a pyrene derivative, is studied in dilute cyclohexane solutions (0.0001, 0.001, and 0.01 wt %). The coil−globule transition occurs at 25 °C and was identified from a break in the plot of the pyrene excimer-to-monomer fluorescence intensity ratio with temperature. The pyrene fluorescence decay curves were fitted with the blob model, and the chain radii were calculated from the fitting parameters. A plot of the radius data in terms of a master curve of the scaled contraction factor versus the scaled reduced temperature is compared with the available results from the literature.

The most concentrated polymer solution (0.01 wt %) led to the formation of high-density polymer aggregates below the coil−globule transition temperature. There were also problems associated with the very dilute solution (0.0001 wt %) since the fluorescence signal was overwhelmed by intense light scattering. Consequently our discussion focuses mostly on the results obtained with the 0.001 wt % solution.

Fluorescence provides an alternative method for calculating polymer chain dimensions in solution and studying the coil−globule transition of small chains in dilute conditions where aggregation does not occur and conventional techniques (light scattering, intrinsic viscosity) are not sensitive enough.
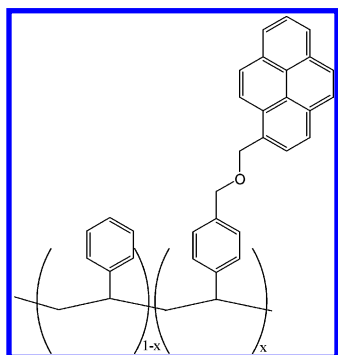
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CHART 1

Figure 1. (A) Fluorescence spectra of PS11Py (0.0001 wt %) and PS02Py (0.006 wt %) in cyclohexane at 65 °C by excitation at λ_{ex} = 330 nm: (—) PS11Py, (- - -) PS02Py, (•••) excimer plus dimer emission obtained by subtraction of the monomer emission (PS02Py spectrum) from the PS11Py spectrum. (B) Fluorescence spectra of the PS11Py (0.0001 wt % solution) at several temperatures by excitation at λ_{ex} = 330 nm. The intensities of all spectra are normalized to 1 at λ = 376 nm.

2. Experimental Section

Instrumentation. Fluorescence spectra were recorded on a SPEX Fluorolog F112A fluorometer at several temperatures using a cryostat from Oxford Instruments (DN 1704) that allows temperature control to within ±0.5 °C. The fluorescence spectra were recorded between 370 and 600 nm (2.25 nm bandwidth) using 330 nm (4.5 nm bandwidth) as excitation wavelength.

Time-resolved picosecond fluorescence decays were obtained by the single photon timing (SPT) technique using excitation laser light at 328 nm. The system consists of a mode-locked Coherent Inova 440-10 argon ion laser that synchronously pumped a cavity-dumped Coherent 701-2 DCM dye laser, delivering 5−6 ps pulses at a repetition rate of 460 kHz. The fluorescence was selected by a Jobin-Yvon HR320 monochromator with a grating of 100 lines/mm (6 nm bandwidth). Before entering the emission monochromator, the light beam passes through a cutoff filter to eliminate the excitation scattered light, as well as a polarizer oriented at the magic angle (54.7°) with respect to the vertically polarized laser light, to avoid polarization effects. The fluorescence was detected by a Hamamatsu 2809U-01 microchannel plate photomultiplier. All decays were fitted using a nonlinear least-squares method based on the Marquardt−Levenberg algorithm.[19]

The absorption spectra were recorded with a UV−vis−NIR scanning spectrophotometer (Shimadzu, UV-3101 PC).

Polymer Characterization. The synthesis of the polystyrene chains and their random chloromethylation and pyrene labeling with a pyrene derivative was described before.[18] The molecular structure of the final polymer is shown in Chart 1.

The two polymer chains (PS11Py and PS02Py) were characterized by GPC (M_w = 113 000, M_w/M_n = 1.03) and the pyrene content established by UV−vis absorption in THF using 1-pyrenemethanol ($\epsilon_{344\ nm}$ = 42 700 cm^{-1} M^{-1}) as a model compound. The polystyrene chains differ in the degree of labeling, the average number of pyrenes per chain being 11 and 0.2 for PS11Py and PS02Py, respectively. [18]

Sample Preparation. Three solutions of PS11Py were prepared in cyclohexane with pyrene concentrations of 10^{-7}, 10^{-6}, and 10^{-5} M (corresponding to polymer contents of 0.0001, 0.001, and 0.01 wt %, respectively). A solution of PS02Py in cyclohexane at 10^{-7} M in pyrene (corresponding to 0.006 wt % in polymer) was also prepared. Cyclohexane (spectroscopic grade from Aldrich) was dried with CaH$_2$ before being freshly distilled under argon. Fluorescence measurements of the polymer solutions were performed in quartz cells that were sealed after being degassed with argon (saturated with the solvent) for 20 min. Samples were maintained in an oven for one night at 42 °C before measurements to reach equilibrium.
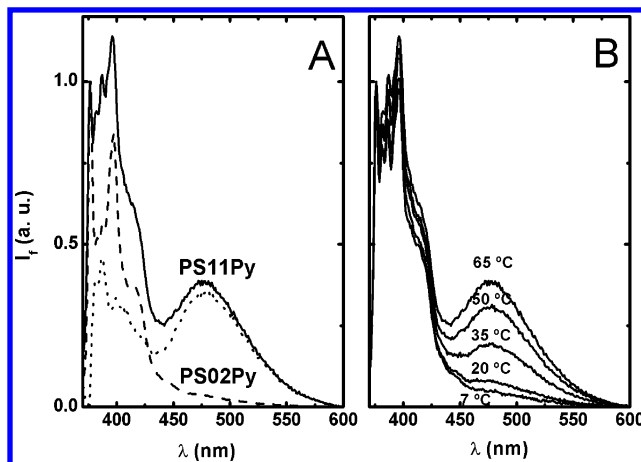
3. Results and Discussion

Fluorescence Spectra. Figure 1A shows the fluorescence spectra upon excitation at 330 nm of two polystyrene chains (PS11Py, 0.0001 wt %; PS02Py, 0.006 wt %) in cyclohexane at 65 °C.

The fluorescence spectrum of the PS02Py polymer solution is mainly composed of several structured bands in the blue region, characteristic of pyrene monomer emission. [20] The excimer emission is practically absent because most of the chains have, on average, fewer than two pyrenes and the polymer coils are far away (low polymer concentration), not allowing for diffusive encounters to occur between pyrenes attached to different chains. As the PS11PY chain has a higher degree of labeling, the distances between pyrene groups are shorter, favoring intrachain excimer formation. The spectrum obtained after subtraction of the monomer emission (see Figure 1A, dotted line) has a broad band centered at ∼480 nm attributed to the excimer and a structured band attributed to the emission of pyrene dimers. This emission, with vibronic peaks around 380, 400, and 420 nm, has been observed before in doped silica glasses,[21] sol−gel systems,[22,23] and Langmuir−Boldgett films.[24]

Figure 1B shows that, in addition to the monomer, the excimer and dimer emission bands persist for the whole temperature range studied (between 7 and 65 °C) and that the relative amount of excimer to monomer increases with temperature. All spectra at a given temperature remained invariant with time over several weeks.

Figure 2 shows the excitation spectra of the PS11Py solution at 65 °C, recorded at the emission wavelengths of the pyrene monomer (λ_{em} = 376 nm) and excimer (λ_{em} = 500 nm). As excimers (referred to as E*) cannot be formed by direct excitation (their ground state is dissociative), the spectrum recorded at 500 nm reflects the spectra of all absorbing species that produce excimers. The spectra recorded at the excimer (λ_{em} = 500 nm) and monomer (λ_{em} = 376 nm) wavelengths do not overlap, revealing the presence of ground-state species in addition to the pyrene monomer that, once excited, produce excimers. The existence of ground-state species can be established from the broadness of the 0−0 UV−vis absorption peak, quantified by the ratio between the absorbance at 344 nm and
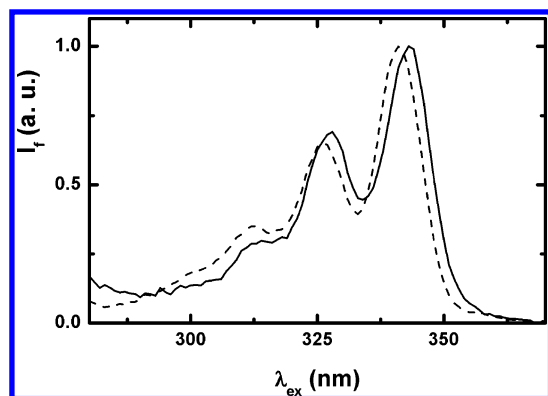
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Figure 2. Excitation spectra of the PS11Py 0.0001 wt % solution in cyclohexane at 65 °C recorded at λ_{em} = 376 nm (- - -) and λ_{em} = 500 nm (—). The intensities of both spectra were normalized to 1 at the wavelength of maximum intensity.
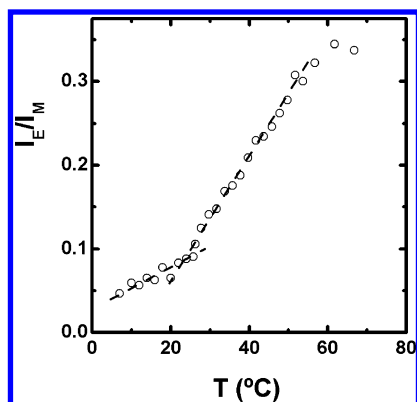

Figure 3. Temperature dependence of the excimer-to-monomer fluorescence intensity ratio I_E(500 nm)/I_M(376 nm) by excitation at λ_{exc} = 330 nm. The lines are given to guide the eyes.

the nearest valley.[25] A ratio of 3.0 indicates the absence of pyrene aggregates, whereas a lower value points to their existence. The experimental values are around 2.9 and almost independent of temperature, showing that the amount of ground-state species aside from the pyrene monomer is small and does not change significantly with temperature. Therefore, the fluorescence from the dimer in the 380−420 nm spectral region (cf. Figure 1A,B) and from the excimer, should result mainly from excited-state processes occurring upon excitation of ground-state pyrene monomers.

Figure 3 shows the variation of the excimer-to-monomer fluorescence intensity ratio, I_E/I_M, as a function of temperature, by excitation at λ_{exc} = 330 nm.

It is well-known that, at low temperatures, the dissociation rate of the pyrene excimer is negligible when compared to its intrinsic decay and the I_E/I_M ratio increases with temperature. In contrast, at high temperatures, when pyrene excimer dissociation predominates over the intrinsic deactivation, I_E/I_M decreases with temperature. The transition temperature between the two regions for pyrene is usually around 50 °C.[26] Figure 3 shows that I_E/I_M increases with temperature below ∼60 °C, as predicted for the low-temperature regime. The break in the I_E/I_M plot at 25 °C suggests a change in the conformation of the polystyrene chains that influences the rate of the kinetic processes. A similar transition was detected for PDMA in methanol at 45 °C,[17] despite its less clear assignment, because both the conformation transition and the pyrene kinetic transition occur more or less at the same temperature. The break at 25 °C is attributed to the coil−globule transition temperature of polystyrene in cyclohexane. This value is reasonable as coil−
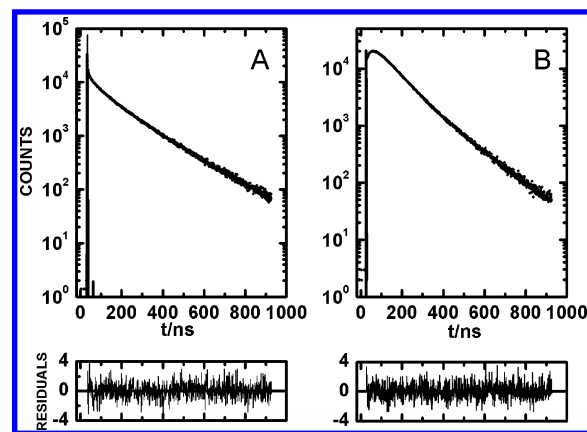

Figure 4. Fluorescence decay curves of the PS11Py 0.001 wt % solution in cyclohexane at 40 °C, by excitation at λ_{ex} = 328 nm: (A) pyrene monomer decay (λ_{em} = 376 nm) and (B) pyrene excimer decay (λ_{em} = 500 nm) were fitted by eqs 1 and 2, respectively, using a global analysis.

globule transition temperatures of 32 °C (M_w = 27 000 000) and 28.5 °C (M_w = 8 000 000) have been reported for other polystyrene chains in cyclohexane[7,27] and it is known that the coil−globule transition temperature increases with molecular weight.[28,29]

Time-Resolved Fluorescence Decays. Figure 4 shows the pyrene monomer and excimer fluorescence decay curves of a 0.001 wt % PS11Py polymer solution in cyclohexane at 40 °C upon excitation at λ_{ex} = 328 nm.

The decays are complex and cannot be fitted by a sum (monomer) or a difference (excimer) of two exponentials. This complexity is observed for any type of polymer randomly labeled with pyrene and has two main causes. The first is the strong dependency of the excimer formation rate constant on the chain length between two pyrenes.[30,31] The random attachment of pyrene moieties along the polymer backbone induces a distribution of chain lengths between two pyrene labels, leading to a distribution of rate constants of excimer formation.[32] Consequently, the monomer and excimer decays are expected to be represented by an infinite sum of exponentials, instead of the biexponential behavior predicted by the Birks' scheme in the case of a single rate constant of excimer formation. To account for the distribution of rate constants for excimer formation, Duhamel and co-workers developed the blob model.[18] Within the framework of this model, a blob is defined as the volume probed by an excited pyrene during its lifetime. In the formulation of the model, the parameters $\langle n \rangle$, k_{diff}, and k_e[blob], which refer to the average number of pyrene groups per blob, the rate constant of excimer formation inside a blob containing one excited pyrene and one ground-state pyrene only, and the rate at which pyrene groups exchange between blobs, respectively, were defined. The validity and applicability of the blob model have been demonstrated for various polymers randomly labeled with pyrene during the past several years.[17,18,33,34]

The second cause for the complicated behavior of the fluorescence decays of these polymers resides in the randomness of the labeling procedure. Previous studies have shown that four pyrene species should be considered when dealing with such polymeric systems, namely, Py^*_{diff}, Py^*_{free}, E0*, and D*, which represent electronically excited pyrenes that form excimers via diffusion, that are too isolated to form excimers and fluoresce with the lifetime τ_M, that are close to a neighboring pyrene and form an excimer instantaneously upon direct excitation (pre-formed excimers), and that are close to a neighboring pyrene but do not have the proper geometry to form an excimer and

form a loose long-lived dimer (preformed dimer) upon absorption of a photon, respectively.[34-38] The species E0* and D* emit with intrinsic lifetimes of τ_E and τ_D, respectively.

This comprehensive approach is unable to handle the monomer decays of PS11Py in cyclohexane, because of the presence at early times of a short-lived component. The excited pyrene monomer undergoes a rapid quenching (cf. Figure 4A) with a quenching rate constant of about 3×10^8 s^{-1}. Because no short, $1/(3 \times 10^{-8}$ s$^{-1})$, ~3 ns-rise-time component is found in the excimer decays, the rapid quenching of the pyrene monomer does not produce an emissive excimer. Probably, this process originates from pyrene pairs that do not adopt the proper geometry to form an excimer and form an emissive dimer once a pyrene is electronically excited whose structured emission overlaps the pyrene monomer emission (cf. Figure 1). Nevertheless, the possibility that this process creates a nonemissive excimer (dark species), as was suggested before, cannot be discarded.[39] To handle this process, a third monomer species, Py$_Q^*$, was introduced that represents those pyrene monomers that are quenched on a fast time scale with a quenching rate constant of k_Q.

The monomer and excimer decays were fitted globally with eqs 1 and 2, respectively

$$[Py^*]_t = [Py_Q^*]_{t=0} \exp[-(k_Q + 1/\tau_M)t] +$$
$$[Py_{diff}^*]_{t=0} \exp\left\{-\left(A_2 + \frac{1}{\tau_M}\right)t - A_3[1 - \exp(-A_4 t)]\right\} +$$
$$[Py_{free}^*]_{t=0} \exp(-t/\tau_M) \quad (1)$$

$$[E^*] = -[Py_{diff}^*]_{t=0} e^{-A_3} \sum_{i=0}^{\infty} \frac{A_3^i}{i!} \frac{A_2 + iA_4}{\frac{1}{\tau_M} - \frac{1}{\tau_{E0}} + A_2 + iA_4}$$
$$\exp\left[-\left(\frac{1}{\tau_M} + A_2 + iA_4\right)t\right] + \left([E0^*]_{t=0} + \right.$$
$$\left. [Py_{diff}^*]_{t=0} e^{-A_3} \sum_{i=0}^{\infty} \frac{A_3^i}{i!} \frac{A_2 + iA_4}{\frac{1}{\tau_M} - \frac{1}{\tau_{E0}} + A_2 + iA_4}\right) e^{-t/\tau_{E0}} +$$
$$[D^*]_{t=0} e^{-t/\tau_D} \quad (2)$$

The parameters A_2, A_3, and A_4 are given by

$$A_2 = \langle n \rangle \frac{k_{diff} k_e[\text{blob}]}{k_{diff} + k_e[\text{blob}]} \quad (3a)$$

$$A_3 = \langle n \rangle \frac{k_{diff}^2}{(k_{diff} + k_e[\text{blob}])^2} \quad (3b)$$

$$A_4 = k_{diff} + k_e[\text{blob}] \quad (3c)$$

Because a substantial fraction of the pyrene monomers form pairs or aggregates, the distribution of pyrenes inside the polymer coil is not random. As a result, the parameter $\langle n \rangle$ must be replaced by $\langle n_{Pydiff} \rangle$ in eqs 3a and 3b, where $\langle n_{Pydiff} \rangle$ represents the average number of quencher species that undergo dynamic excimer formation with the rate constant k_{diff}. Assuming that the amount of ground-state dimers is negligible (according to

the UV−vis absorption spectra), $\langle n_{Pydiff} \rangle$ is given by

$$\langle n_{Pydiff} \rangle = f_{diff} \langle n \rangle \quad (4)$$

where f_{diff} is the fraction of pyrenes that form excimers via diffusion.

The monomer decays of the PS11Py solution in cyclohexane (0.001 wt %) were well fitted by eq 1 over the entire temperature range, after convolution with the instrumental response function (χ^2 smaller than 1.3). Although the overall features of the monomer decays were not altered with temperature (all monomer decays exhibited a strong quenching at the early times followed by a smooth multiexponential decay at the longer times), a short decay component did appear in the excimer decays for temperatures below 30 °C, i.e., for temperatures below the coil−globule transition temperature. Such a short decay component has already been observed in excimer decays for other polymeric systems where pyrene aggregates are formed.[15] This observation supports the assignment of the 25 °C breakpoint of Figure 3 to the coil−globule transition of PS11Py in cyclohexane, because the more compact conformation of the polymer globule is expected to increase the local pyrene concentration, which, in turn, favors the formation of pyrene aggregates. Although the presence of pyrene aggregates certainly complicates the analysis of the excimer decays, it should not affect the monomer decays, if one assumes that the aggregates do not dissociate during their short decay time. However, the presence of the short decay component in the excimer decays prevented the use of eq 2 to fits the excimer decay acquired at temperature below 30 °C. Nevertheless, the fluorescence decays of the monomer and excimer were very well fitted from 30 to 50 °C using the global analysis with eqs 1 and 2, respectively. The parameters $\langle n \rangle$, k_{diff}, and $k_e[\text{blob}]$ were kept common to eqs 1 and 2 while the global analysis was performed. The lifetime of the isolated pyrenes (τ_M) was fixed to the value obtained from the decay of a dilute solution of PS02Py in cyclohexane at the same temperature. The quality of the fits was good ($\chi^2 < 1.3$) and was judged by visual inspections of the distributions of the residuals and the autocorrelation of the residuals. The fractions

$$f_M Q = \frac{[Py_Q^*]_{t=0}}{([Py_Q^*]_{t=0} + [Py_{diff}^*]_{t=0} + [Py_{free}^*]_{t=0})} \quad (5a)$$

$$f_{Mdiff} = \frac{[Py_{diff}^*]_{t=0}}{([Py_Q^*]_{t=0} + [Py_{diff}^*]_{t=0} + [Py_{free}^*]_{t=0})} \quad (5b)$$

$$f_{Mfree} = \frac{[Py_{free}^*]_{t=0}}{([Py_Q^*]_{t=0} + [Py_{diff}^*]_{t=0} + [Py_{free}^*]_{t=0})} \quad (5c)$$

were obtained from the fit of the monomer decay, whereas the fractions

$$f_{Ediff} = \frac{[Py_{diff}^*]_{t=0}}{([Py_{diff}^*]_{t=0} + [E0^*]_{t=0} + [D^*]_{t=0})} \quad (6a)$$

$$f_{EE} = \frac{[E^*]_{t=0}}{([Py_{diff}^*]_{t=0} + [E0^*]_{t=0} + [D^*]_{t=0})} \quad (6b)$$

$$f_{ED} = \frac{[D^*]_{t=0}}{([Py^*_{diff}]_{t=0} + [E0^*]_{t=0} + [D^*]_{t=0})} \quad (6c)$$

were obtained from the fit of the excimer decays.

The parameters obtained from the fits are listed in Table 1. Above 30 °C, where the global analysis was carried out, excellent fits were obtained. The results indicate that there is virtually no difference whether the fits are performed on the monomer decay alone or by the global analysis of the monomer and excimer decays. This can be visualized more easily in Figure 5.

The fractions f_{MQ}, f_{Mdiff}, f_{Mfree}, f_{Ediff}, f_{EE}, and f_{ED} obtained by the global analysis can be combined to determine the fractions of ground-state pyrenes f_Q, f_{diff}, f_{free}, f_E, and f_D present under the forms of Py^*_Q, Py^*_{diff}, Py^*_{free}, $E0^*$, and D^*, respectively, upon electronic excitation. Within experimental error, the fractions f_Q, f_{diff}, f_{free}, f_E, and f_D are constant and equal 0.42 ± 0.02, 0.45 ± 0.02, 0.04 ± 0.01, 0.09 ± 0.01, and 0.01 ± 0.01, respectively. The strongest contributions to the decays appear to be that of the pyrenes being quenched with a rate constant k_Q equal to (3.1 ± 0.3) × 10⁸ s⁻¹ and that of pyrene monomers forming excimers via diffusion. One can also note that f_{diff} (0.45 ± 0.02) obtained from the global analysis of the pyrene monomer and excimer between 30 and 50 °C is very close to f_{Mdiff} (0.50 ± 0.02) obtained from the analysis of the monomer decays with eq 1 over the same temperature range. This is because the fractions f_E and f_D of the preformed excimer and dimer species represent a small fraction of all other pyrene species ($f_E = 0.09 ± 0.01$ and $f_D = 0.01 ± 0.01$). Consequently, f_{Mdiff} will be used as a substitute for f_{diff} for temperatures at which the global analysis cannot be used.

The good fits obtained from the global analysis of the pyrene monomer and excimer decays with eqs 1 and 2 confirm that the rapid quenching of pyrene does not give emissive excimers because the fast decay component with reciprocal lifetime $1/\tau_M + k_Q$ used in eq 1 for the monomer decay analysis has no equivalent in eq 2 for the excimer. The fractions f_{MQ}, f_{Mdiff}, and f_{Mfree} shown in Table 1, where the subscript M indicates that these fractions were derived from the analysis of the monomer decays, remained constant over the entire temperature range and equal 0.46 ± 0.02, 0.47 ± 0.04, and 0.07 ± 0.03.

The recovered fraction of the loose long-lived dimers ($f_D = 0.01 ± 0.01$) is too small to support their presence in the current system. This long decay can be simply caused by the fitting procedure or by a very small contamination of the excimer decays by the monomer emission. The lifetime of the excimer,
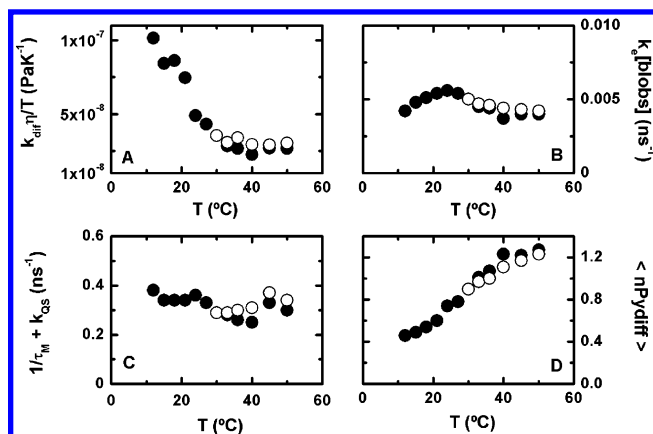

Figure 5. Parameters recovered from the fit of the pyrene monomer and excimer decays (eqs 1 and 2) with the FBM analysis as a function of temperature for the PS11Py 0.001 wt % solution in cyclohexane: (A) rate constant for excimer formation (k_{diff}) corrected for the influence of temperature and viscosity, (B) product of the rate constant for pyrenes exchange between blobs by the concentration of blobs (k_e[blob]), (C) sum of the reciprocal pyrene intrinsic lifetime with the quasi-static quenching rate constant of pyrene in pairs ($1/\tau_M + k_{QS}$), (D) average number of pyrenes per blob that can form excimers by diffusion ($\langle n_{Pydiff} \rangle$). The filled symbols refer to values obtained from the analysis of the pyrene monomer decay (eq 1), and the open symbols are for the global analysis of the pyrene monomer and excimer decays (eqs 1 and 2).

τ_E, was found to increase smoothly from 54 to 68 ns with decreasing temperature. The values and range of these excimer lifetimes are reasonable for pyrene[20] and have been found for other pyrene-labeled polymers.[31,34−37]

Figure 5 shows the variation of the kinetic parameters k_{diff}, $\langle n_{Pydiff} \rangle$, k_e[blob], and $1/\tau_M + k_{QS}$ with temperature, calculated with eqs 3 using the parameters of the fit. Both rate constants for pyrene exchange between blobs, k_e[blob], and the sum $1/\tau_M + k_{QS}$ are practically invariant with temperature (cf. Figure 5B,C). The mean number of quencher species per blob, $\langle n_{Pydiff} \rangle$, decreases with decreasing temperature (see Figure 5D), with a diffuse break at the coil−globule transition temperature that reflects a decrease of the number of blobs. The diffusion rate constant corrected for changes in temperature and solvent viscosity ($k_{diff}\eta/T$) is partially constant from 50 to 30 °C, increasing rapidly until 12 °C. The increase observed below 30 °C reflects, according to eq 8, a reduction of the blob size.[33]

Lee and Duhamel[40] suggested that the diffusion rate constant, k_{diff}, for two pyrenes attached to the backbone of a short polymer

TABLE 1: Parameters retrieved from the FBM Analysis of the Fluorescence Decays of the PS11Py 0.001 wt % Solution in Cyclohexane[a]

T (°C)	$1/\tau_M + k_Q$ (10⁹ s⁻¹)	f_{MQ}	k_{diff} (10⁷ s⁻¹)	$\langle n_{Pydiff} \rangle$	k_e[blob] (10⁶ s⁻¹)	f_{Mdiff}	τ_M (ns)	f_{Mfree}	f_{Ediff}	f_{EE}	τ_{E0} (ns)	f_{ED}	τ_D (ns)	χ^2
50	0.34 (0.30)	0.47 (0.45)	1.6 (1.4)	1.23 (1.27)	4.2 (4.0)	0.49 (0.50)	249	0.04 (0.04)	0.83	0.15	54	0.02	158	1.17 (1.15)
45	0.37 (0.33)	0.50 (0.48)	1.4 (1.3)	1.17 (1.22)	4.3 (4.0)	0.46 (0.47)	252	0.04 (0.04)	0.83	0.16	58	0.01	182	1.20 (1.25)
40	0.31 (0.25)	0.45 (0.44)	1.3 (1.0)	1.11 (1.23)	4.4 (3.7)	0.50 (0.52)	256	0.05 (0.05)	0.83	0.16	60	0.01	195	1.14 (1.15)
36	0.30 (0.26)	0.43 (0.43)	1.4 (1.1)	1.00 (1.07)	4.6 (4.4)	0.52 (0.52)	259	0.05 (0.05)	0.83	0.17	65	0.00	286	1.18 (1.19)
33	0.29 (0.28)	0.45 (0.45)	1.2 (1.1)	0.97 (1.01)	4.7 (4.5)	0.50 (0.50)	261	0.05 (0.05)	0.83	0.15	64	0.01	185	1.13 (1.13)
30	0.29 (0.29)	0.45 (0.45)	1.3 (1.3)	0.90 (0.90)	5.0 (5.0)	0.49 (0.49)	263	0.06 (0.06)	0.82	0.17	68	0.01	291	1.06 (1.06)
27	(0.33)	(0.49)	(1.5)	(0.78)	(5.4)	(0.46)	266	(0.06)						(1.23)
24	(0.36)	(0.49)	(1.6)	(0.74)	(5.6)	(0.44)	268	(0.06)						(1.07)
21	(0.34)	(0.45)	(2.3)	(0.60)	(5.4)	(0.47)	271	(0.09)						(1.08)
18	(0.34)	(0.44)	(2.5)	(0.54)	(5.1)	(0.45)	274	(0.10)						(1.05)
15	(0.34)	(0.45)	(2.3)	(0.49)	(4.8)	(0.42)	276	(0.13)						(1.09)
12	(0.38)	(0.48)	(2.6)	(0.46)	(4.2)	(0.39)	279	(0.13)						(1.08)

[a] Results in parentheses indicate that they were obtained by using eq 1 to fit the monomer decay only. Results not in parentheses were obtained by fitting the monomer and excimer decays globally with eqs 1 and 2

chain can be estimated as

$$k_{\text{diff}} = \frac{2}{3} k_B T \frac{1}{\eta} \frac{1}{V_{\text{coil}}} \frac{R_c}{\sigma} \tag{7}$$

where k_B is the Boltzman constant, T is the temperature, η is the viscosity, V_{coil} is the volume of the polymer coil, R_c is the encounter radius between the two pyrenes, and σ is the reaction radius. The expression for k_{diff} would be more complex if chain dynamics was considered.[41] Assuming that the diffusion inside the blob can be described by the same equation with $R_c = \sigma$, and $V_{\text{coil}} = V_{\text{blob}}$, an expression for the volume of the blob can be obtained as

$$V_{\text{blob}} = \frac{2}{3} \frac{k_B T}{\eta k_{\text{diff}}} \tag{8}$$

The volume of the polymer coil is given by $\bar{V}_{\text{coil}} = V_{\text{blob}} \times \bar{N}$, where $\bar{N}$ represents the average number of blobs per chain. This parameter is given by the ratio of the number of pyrenes per chain ($\bar{n}$) to the average number of pyrenes in a blob ($\langle n \rangle$). The chain radius can then be determined by[17]

$$\bar{R}_{\text{fluor}} = \left(\frac{\bar{n}}{2\pi} \right)^{1/3} \times \left(\frac{k_B T}{k_{\text{diff}} \eta \langle n \rangle} \right)^{1/3} \tag{9}$$

using the values found in Table 1 and $\langle n \rangle$ calculated by eq 4. The average number of pyrenes per chain, $\bar{n} = 11$, was determined by UV−vis absorption measurements. The viscosities of cyclohexane (mPa s) at different temperatures were calculated from an extrapolation performed with the viscosity values provided in the CRC handbook [$\eta = \exp(1439/T - 4.94)$].[42] The value of the fluorescence radius at the θ temperature (34.5 °C),[43] $\bar{R}^{\theta}_{\text{fluor}} = 7.5$ nm, compares well with both the gyration radius, $R^{\theta}_g = 10.0 \pm 0.1$ nm ($R_g = 297 \times 10^{-4} M_w^{1/2}$)[44,45] and the hydrodynamic radius, $R^{\theta}_h = 6.64 \pm 0.07$ nm, calculated by $R^{\theta}_h = 3/8\pi^{1/2} R^{\theta}_g$.[46]

The reasonable agreement between radii is surprising owing to both the empirical derivation of eq 7 and the complication of having a nonrandom distribution of pyrenes inside the polymer coil. The contraction factors $\alpha_{\text{fluor}} = \bar{R}_{\text{fluor}}/\bar{R}^{\theta}_{\text{fluor}}$ are expected to be more accurate because they can benefit from a cancellation of errors during the division of radii. Figure 6A represents the variation of α_{fluor} with temperature for the PS11PY 0.001 wt % solution.

The trend shown in Figure 6A for the PS11Py 0.001 wt % solution indicates that the globules contract no more than 20% with respect to the radius of the polymer coil under θ conditions. This contraction is much smaller than most of the published values for polystyrene chains of similar molecular weight in the same solvent.[7,8,47] Some authors have, however, reported contraction factors similar to ours,[12−14] with even longer chains. They suggested that the higher degrees of contraction were caused by the presence of small aggregates of higher densities, as theoretically predicted by Raos and Allegra.[48] The results shown in Figure 6B are in agreement with these predictions because a contraction of ~40% was observed for the most concentrated solution, PS11Py 0.01 wt %, where aggregates were formed (detected by the time variation of the fluorescence spectra at the lowest temperatures).

Above the θ temperature, α seems to be constant or to decrease slightly. The unexpected decrease is caused by the uncertainty in the radius evaluations for temperatures above 45
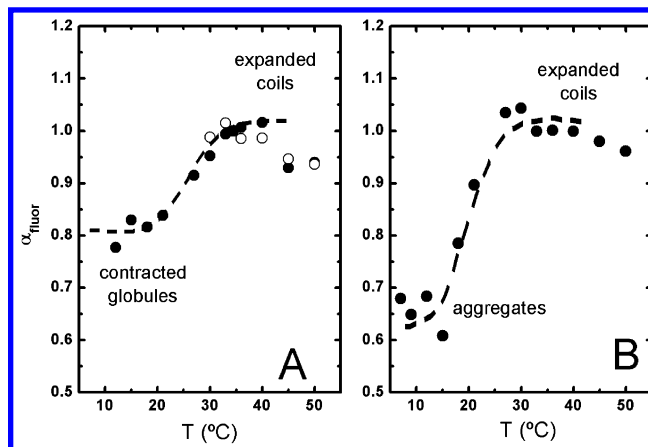

Figure 6. Plot of the contraction factors determined by fluorescence versus temperature: (A) PS11Py, 0.001 wt % solution; (B) PS11Py, 0.01 wt % solution, where aggregation occurs simultaneously with globule formation. The contraction factors were obtained from the analysis of the pyrene monomer (filled symbols) and the global analysis of the monomer and excimer decays (open symbols). The lines are provided to guide the eyes.
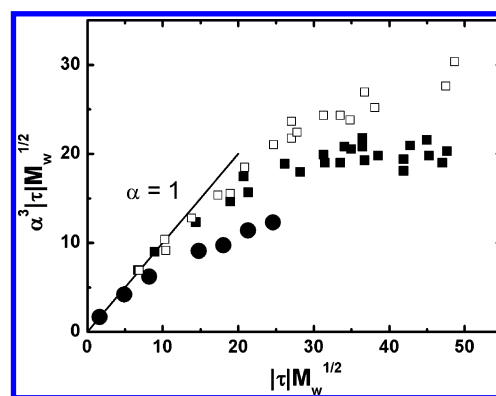

Figure 7. Variation of the scaled expansion factor determined from fluorescence data, $\alpha^3 |\tau| M_w^{1/2}$, with the scaled reduced temperature, $|\tau| M_w^{1/2}$, for the PS11Py 0.001 wt % solution in cyclohexane (●). Plots of gyration (■) and hydrodynamic (□) radii for other polystyrene−cyclohexane solutions.[12]

°C, caused by the beginning of excimer dissociation, not considered in the decay curve analysis.

Figure 7 shows the universal plot of the scaled expansion factor ($\alpha^3 |\tau| M_w^{1/2}$) as a function of the scaled reduced temperature ($|\tau| M_w^{1/2}$), where $\tau = T/\theta - 1$. The data obtained from the fluorescence contraction factors (for the PS11Py 0.001 wt % solution) fall on a straight line with unitary slope for $|\tau| M_w^{1/2} < 10$ in the vicinity of the θ temperature. The figure shows also other values collected by B. Chu and co-workers[12] for polystyrene−cyclohexane systems in the absence of aggregation. The $\alpha^3 |\tau| M_w^{1/2}$ values point toward distinct plateau values for each average radius as found before for the hydrodynamic and gyration contraction factors.[12]

4. Conclusions

The blob model, modified to consider the presence of pyrene pairs, was successfully applied to fit the pyrene monomer and excimer decays of a polystyrene chain ($M_w = 113\,000$) randomly labeled with pyrene in cyclohexane. The radii of the polystyrene coil at temperatures below and above the θ temperature were calculated from the fitted parameters of the pyrene monomer decays. The contraction coefficients follow the master curve of $\alpha^3 |\tau| M_w^{1/2}$ vs $|\tau| M_w^{1/2}$ in the absence of aggregation, which seems to tend to a plateau with a lower value

than those found for plots of the hydrodynamic and gyration radii. At higher polymer concentrations, the aggregation of polymer chains results in apparently higher contraction factors. Fluorescence was found to be a reliable technique for calculating the radii of polymer chains in solution, which opens the opportunity for studying the coil−globule transition of low-molecular-weight polymer chains in dilute polymer solutions, where conventional techniques are not applicable.

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