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Anomalous Fluorescence of Linear Poly(methylphenylsiloxane) in Dilute Solution at Temperatures below −50 °C

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ABSTRACT: Fluorescence spectroscopy and ^{1}H NMR were used to study linear poly(methylphenylsiloxane) (PMPS) in dilute solution (2×10^{-4} to 4×10^{-3} M) at temperatures below −50 °C. Several PMPS samples covering a range of number-average molecular weights ($(1.9-93) \times 10^3$) and of low polydispersity were employed. The temperature dependence of steady-state fluorescence results show two different trends, depending on chain length: (i) for the high molecular weight samples, the Stevens−Ban plot of excimer−monomer intensities levels off when reaching temperatures below −50 °C and yields an apparent rate constant for excimer formation (k_a) which is independent of temperature; (ii) for the low molecular weight samples, the expected bell-shaped plot is observed, and k_a increases with temperature in the whole range here studied (153−293 K), including also the temperatures below −50 °C. Likewise, light scattering at the incident radiation wavelength increases abruptly upon decreasing temperature below −50 °C for the high molecular weight samples. An anomalous behavior of high molecular weight samples is also observed in ^{1}H NMR spectra; the signals disappear in the baseline at temperatures below −50 °C, indicating a drastic loss of mobility in the millisecond time range. A conformational change coupled with interchain aggregation is argued to explain these results.

Introduction

Silicones as materials have applications closely related to the molecular properties of the siloxane chain. Its backbone is so flexible that the silicones can show elastomeric properties down to unusually low temperatures (−40 °C is the melting temperature of PDMS, for example).[1] Among the techniques that can be used to study conformational flexibility in polymeric chains, fluorescence spectroscopy is nowadays considered as very useful, especially if the polymer gives excimer emission.

Excimer formation occurs between two chromophores, one of which is in its excited state. When this chromophore becomes excited, it can either return to the ground state, with a rate constant equal to the reciprocal lifetime of the monochromophoric molecule, or form an excimer, which in turn can also decay to the ground-state dimer or dissociate back to the excited monomer. When the polymer concentration is sufficiently low, excimers are formed intramolecularly between pairs of chromophores belonging to the same chain. In this case, the approach of the two chromophores to give the sandwich-like conformation typical of the excimer state is accomplished by some kind of motion within the chain.

Temperature affects the overall process because conformational stability, transitions between conformations, and the lifetimes of excited states are all sensitive to the temperature of the system. The temperature depence of steady-state fluorescence can yield a lot of interesting kinetic parameters in systems that form excimers.

Two limiting regimes can be observed: the low-temperature limit (LTL), in which excimer formation is under kinetic control, and the high-temperature limit (HTL), in which excimer formation−dissociation define an equilibrium. In the low-temperature limit (LTL), it is possible to obtain the rate constant of the motion needed to form the excimers and the corresponding activation energy. In the high-temperature limit (HTL), it is possible to obtain the excimer binding enthalpy (determined by the relative orientation of pairs of close chromophores). Both LTL and HTL limits, as well as the intermediate crossover between them, have been obtained with the flexible chains of poly(methylphenylsiloxane).[2,3]

The temperature dependence is customarily analyzed representing the emission intensities in the form of Stevens−Ban plots. In these plots, the ratio of excimer (I_E) to monomer (I_M) intensities, I_E/I_M, and the ratio of monomeric model compound (I_0) to monomer intensities, I_0/I_M, are plotted as $\ln(I_E/I_M)$ vs $1/T$ and $\ln [(I_0/I_M) - 1]\tau_0^{-1}$ vs $1/T$ (with τ_0 equal to the fluorescence lifetime of the monomeric model compound). A monomeric model compound is a monochromophoric molecule that enjoys photophysical properties identical to the monomer of the chain but cannot form excimers.

In the Stevens−Ban representation, when both the LTL and the HTL are reached, the plots give bell-shaped curves with an ascending branch for the HTL, a descending branch for the LTL, and a maximum inbetween.[2−5]

The present work reports on the anomalous Stevens−Ban plots observed for high molecular weight linear samples of poly(methylphenylsiloxane) (PMPS): at temperatures below −50 °C, instead of following the usual

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Table 1. Number-Average Molecular Weight (M_n) and Polydispersity Index ($r = M_w/M_n$) of PMPS Samples

sample	M_n	r	sample	M_n	r
PMPS25	1 890	1.06	PMPS284	19 510	1.12
PMPS82	5 730	1.05	PMPS443	27 100	1.09
PMPS176	12 860	1.15	PMPS1285	93 000	2.00

continuous decrease typical of the LTL side, they level off, suggesting that excimer formation is, in that range of temperatures, a non-thermally activated process. Also, by ^{1}H NMR spectroscopy an anomalous loss of chain mobility is detected for temperatures below −50 °C, in the case of high molecular weights. The possible origin of both types of anomalous results is discussed.

Experimental Section

Polymer samples of low polydispersity were synthesized and characterized by Clarson and Semlyen.[6] Samples are named PMPS*N*, *N* being the number-average number of skeletal bonds. The average degrees of polymerization and polydispersities, determined by means of size exclusion chromatography (SEC) and high-performance liquid chromatography (HPLC),[6] are shown in Table 1. Solutions were prepared in methylcyclohexane (MCH) from BDH (laboratory grade reagent). Polymer concentrations (M) are given in moles of monomeric units per liter (same as moles of chromophore units per liter).

Ultraviolet absorption spectra were recorded on an Olis-15 spectrophotometer with low stray light. Matched silica cells with path lengths of 10 mm were used. Steady-state fluorescence measurements were performed in Spex Fluorolog F212I (slit width 1 mm; geometry at right angle, no polarizers). Temperature control was achieved using a system based on cooled N_2 and electric heating, which is automatically controlled by the reading of a PT100 thermometer.

Solutions of absorbance less than 0.5 (at a reference excitation wavelength of 260 nm) were degassed by the freeze−pump−thaw technique (six cycles at 10^{-4} Torr) and then sealed for temperature-dependent measurements. Solutions of the monomeric model compound were prepared with exactly the same absorbance (at the excitation wavelength). Methyldimethoxyphenylsilane (MS) has been used as the proper monomeric model compound for this polymer.[7]

I_M is the monomer peak intensity, I_E is the excimer band intensity, and I_0 is the emission intensity of the monomeric model compound, MS. I_M and I_0 are measured at 280 nm, and I_E is measured at 320 nm on the spectra of PMPS after subtracting the spectra of MS obtained under the same conditions and normalized at 280 nm. Emission spectra are presented in figures as obtained. Only for numerical work, and when its contribution was significant, has the baseline been subtracted.

Polymer concentrations were in the range 2×10^{-4}−4×10^{-3} M, quite below the critical values for coil overlap (which, for these molecular weights, are in the range 10^{1}−10^{-1} M), and that makes unlikely intermolecular chain contacts in the homogeneous solutions. On the other hand, the low optical density of the samples prevents self-absorption or the inner filter effect.

Light scattering was measured on the fluorescence spectra at an incident radiation of $\lambda = 350$ nm, a wavelength at which the samples do not absorb.

^{1}H NMR spectra of PMPS25 (1.28×10^{-3} M), PMPS284 (1.28×10^{-3} M), and PMPS1285 (4.11×10^{-3}, 1.28×10^{-3}, and 2.1×10^{-4} M) in deuterated methylcyclohexane (99.5% deuteration, Cambridge Isotope Laboratories Inc.) were obtained in a Bruker AMX-300 spectrometer. The solvent peaks were used to calibrate the chemical shifts.

Results

Fluorescence Spectra. Spectra of PMPS*N* show monomer emission centered at about 280 nm and excimer emission at 320 nm. Figure 1 shows fluorescence spectra of PMPS284 in MCH dilute solutions, at 20 °C, with several absorbances at the excitation wavelength, corresponding to different polymer concentrations in the range 7.7×10^{-4}−3.12×10^{-3} M. The excimer-to-monomer intensities ratio I_E/I_M does not change when polymer concentration increases by a factor of 4, and therefore this ratio can be ascribed, mostly, to intramolecular excimer formation, and it must be concluded that, at room temperature, in the range of polymer concentrations employed in this work, there is no coil overlap or polymer aggregation.

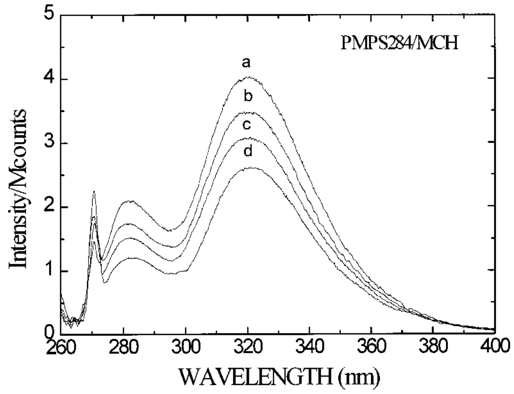

Figure 1. Fluorescence spectra of PMPS284 in dilute MCH solutions at several concentrations ($\lambda_{ex} = 250$ nm) at 20 °C: (a) $c = 3.12 \times 10^{-3}$ M, $I_E/I_M = 2.03$; (b) $c = 1.53 \times 10^{-3}$ M, $I_E/I_M = 2.04$; (c) $c = 1.02 \times 10^{-3}$ M, $I_E/I_M = 2.07$; (d) $c = 7.7 \times 10^{-4}$ M, $I_E/I_M = 2.05$.

Plots of the steady-state fluorescence ratios vs the reciprocal temperature are shown in Figure 2 for PMPS samples covering a wide range of molecular weights. The shape of the curves is as follows. In the case of the low molecular weight samples (Figure 2a,b), the curves are typically bell-shaped and identical to that found with the dimer (the dichromophoric compound diphenyltetramethyldisiloxane, Si(Me$_2$Ph)−O−Si(Me$_2$Ph)).[2] In the case of the high molecular weight samples (Figure 2c−f), the curves are also of the same type, except that a "plateau" is observed at low temperatures.

The interpretation of excimer formation follows the usual Birks scheme.[8] According to this scheme, the quantities plotted in the Stevens−Ban plots are related to the rate constants for excimer formation (k_a) and excimer dissociation (k_d):[8]

$$\left(\frac{I_0}{I_M} - 1\right)\tau_0^{-1} = \frac{k_a}{1 + k_d\tau_E} \tag{1}$$

$$\frac{I_E}{I_M} = \left(\frac{k_{FE}}{k_{FM}}\right)\frac{\tau_E k_a}{1 + k_d\tau_E} \tag{2}$$

where k_{FE} and k_{FM} are the radiative rate constants for excimer and monomer decays, respectively, and τ_E is the excimer lifetime. The most useful expression is the one for I_0/I_M (the ratio of the monochromophoric model compound emission intensity, I_0, divided by the monomer peak intensity, I_M). In the low-temperature limit (LTL), $k_d\tau_E \ll 1$ and $(I_0/I_M - 1)\tau_0^{-1}$ is equal to k_a, while in the high-temperature limit (HTL), $k_d\tau_E \gg 1$ and $(I_0/I_M - 1)\tau_0^{-1}$ is proportional to k_a/k_d, the excimer equilibrium constant.

Therefore, the plateau observed in the Stevens−Ban plots (for the high molecular weights at very low temperatures) can be interpreted as meaning that (in

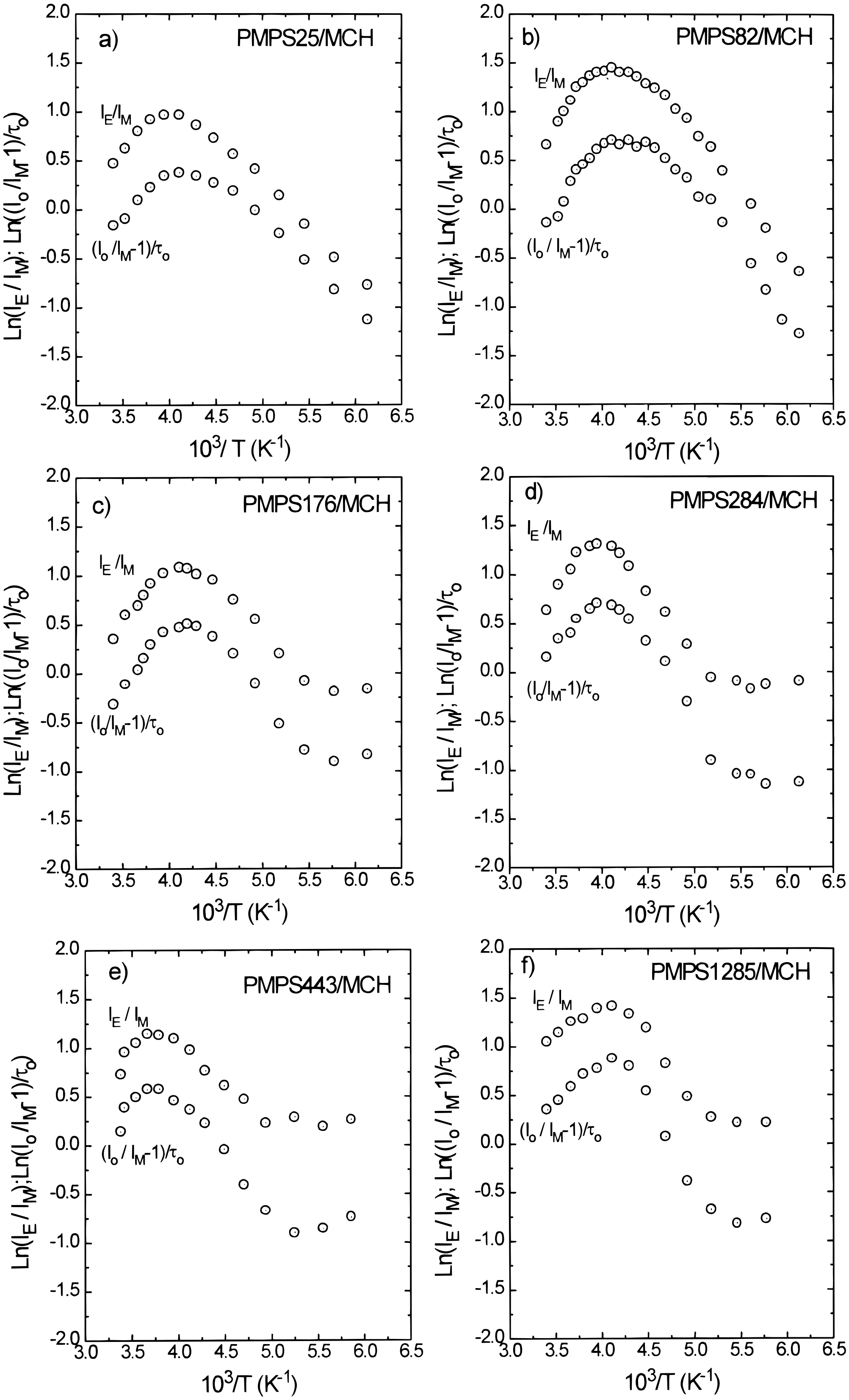

Figure 2. Temperature dependence of the two fluorescence ratios, (I_E/I_M) and $[(I_0/I_M) - 1]/\tau_0$, for PMPS*N* dilute MCH solution; $\lambda_{ex} = 250$ nm.

this temperature region) excimer formation becomes temperature independent; that is, it becomes a static process. This implies that k_a and $k_a\tau_E$ are independent of temperature, since in the low-temperature limit (LTL), $k_d\tau_E \ll 1$. Besides, τ_E is usually assumed to be temperature independent, and consequently plots of the two fluorescence ratios, ln (I_E/I_M) and ln $[(I_0/I_M) - 1])\tau_0^{-1}$, vs $1/T$ should be parallel, as is usually observed.[2,3]

We had already found a deviation from the bell shape in the Stevens–Ban plot at low temperatures, with

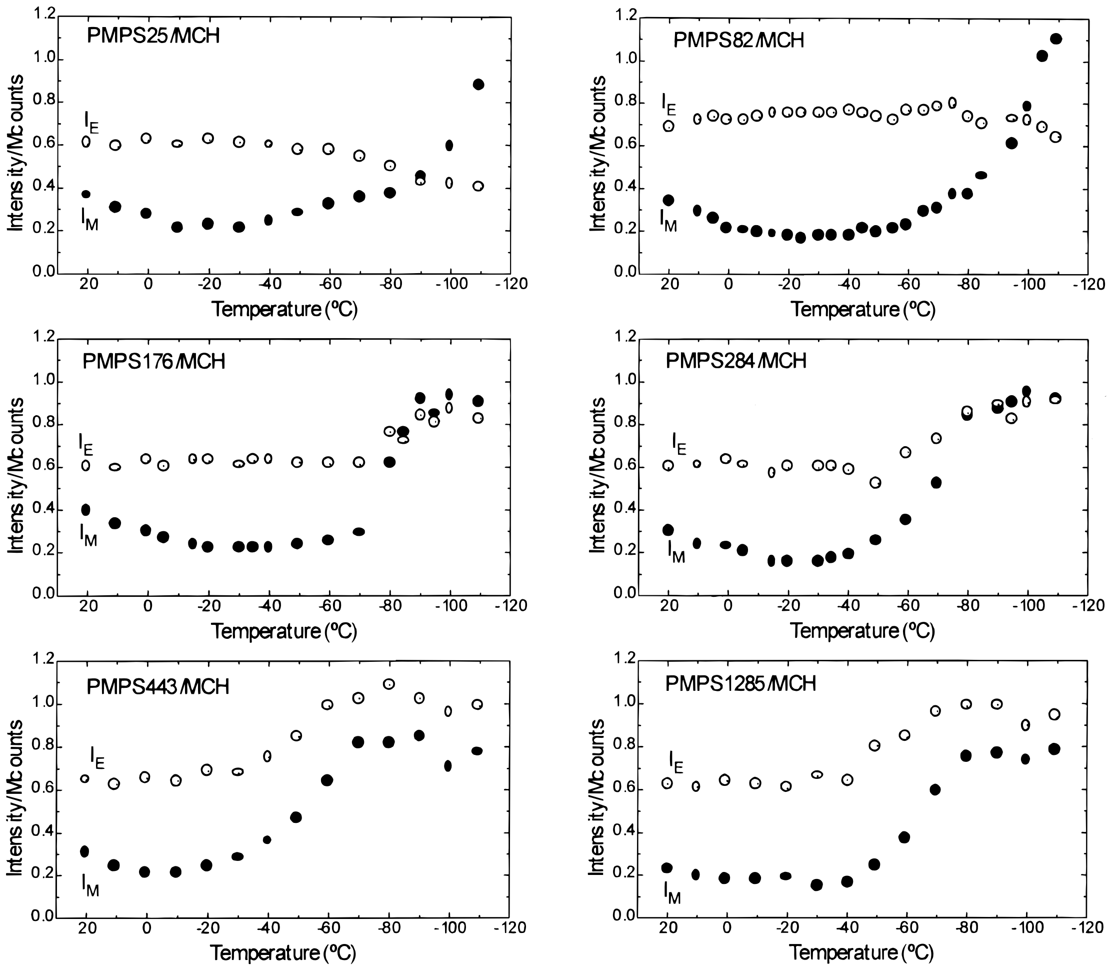

Figure 3. Temperature dependence of the excimer, I_E, and monomer, I_M, emission intensities for several PMPSN samples of different chain length in MCH solution.

another high molecular weight sample ($M_w = 1.15 \times 10^5$) studied before.[2] The proposal then was that, at very low temperatures, excimer formation through ground-state preformed dimers substitutes to excimer formation through chain motions. In fact, preformed dimers are present in these polysiloxanes at all temperatures,[2] due to the dominance of attractive interactions between phenyl rings over their steric repulsion, because of the long bonds and open bond angles in the siloxane backbone.[9] If α represents the fraction of monomers that are in ground-state preformed dimers, then the Birks model is modified to yield[2]

$$\left(\frac{I_0}{I_M} - 1\right)\tau_0^{-1} = \frac{k_a + \alpha\tau_0^{-1}}{1 - \alpha + k_d\tau_E} \tag{3}$$

$$\frac{I_E}{I_M} = \left(\frac{k_{FE}}{k_{FM}}\right)\frac{\tau_E(k_a + \alpha\tau_0^{-1})}{1 - \alpha + k_d\tau_E} \tag{4}$$

The influence of α on the rate constant, k_a, obtained from the LTL was found to be small, because of the high k_a values of these polysiloxane chains.[2] Only for very low temperatures (such that k_a decreases sufficiently) can ground-state preformed dimers have a leading influence.[2] In the limit $\alpha\tau_0^{-1} \gg k_a$, the fluorescence ratio of eq 3 is equal to $\alpha\tau_0^{-1}/(1 - \alpha)$. If we attribute the plateau entirely to $\alpha\tau_0^{-1}/(1 - \alpha)$, this would correspond to about 85% preformed dimers. As we shall see, the plateau is a more complex phenomenon.

Let us explore the separate intensities of monomer and excimer, I_M and I_E, as well as the excimer peak wavelength, λ_E, as a function of temperature, in the range from 20 °C down to −120 °C. Figure 3 shows the excimer intensity, I_E. For the lowest molecular weight sample (PMPS25) it varies as expected:[2,8] it very slightly increases from room temperature down to about −20 °C, and below that, it decreases upon decreasing temperature. (The rate for excimer formation diminishes and should tend to zero near the freezing point of MCH.) For PMPS82, a qualitatively similar trend is observed, but only below −80 °C does I_E decrease.

The high molecular weight samples show a totally different temperature dependence of I_E at low T. Starting at room temperature and down to about −50 °C, the excimer emission intensity of those samples (PMPS1285, PMPS443, PMPS284, and PMPS176) has a very slight increase, with values close to those of low molecular weight samples. But, for temperatures lower than −50 °C for PMPS1285, −40 °C for PMPS443, −50 °C for PMPS284, and −70 °C for PMPS176, the excimer intensity suffers a steplike increase to a higher value. This result could be ascribed to the existence of an additional mechanism of excimer formation, exclusive for the high molecular weight samples, which starts operating below a certain temperature. But let us consider the monomer emission now.

In Figure 3 we can see also I_M. It shows a minimum corresponding to about the crossover temperature between the LTL and HTL. The low molecular weight

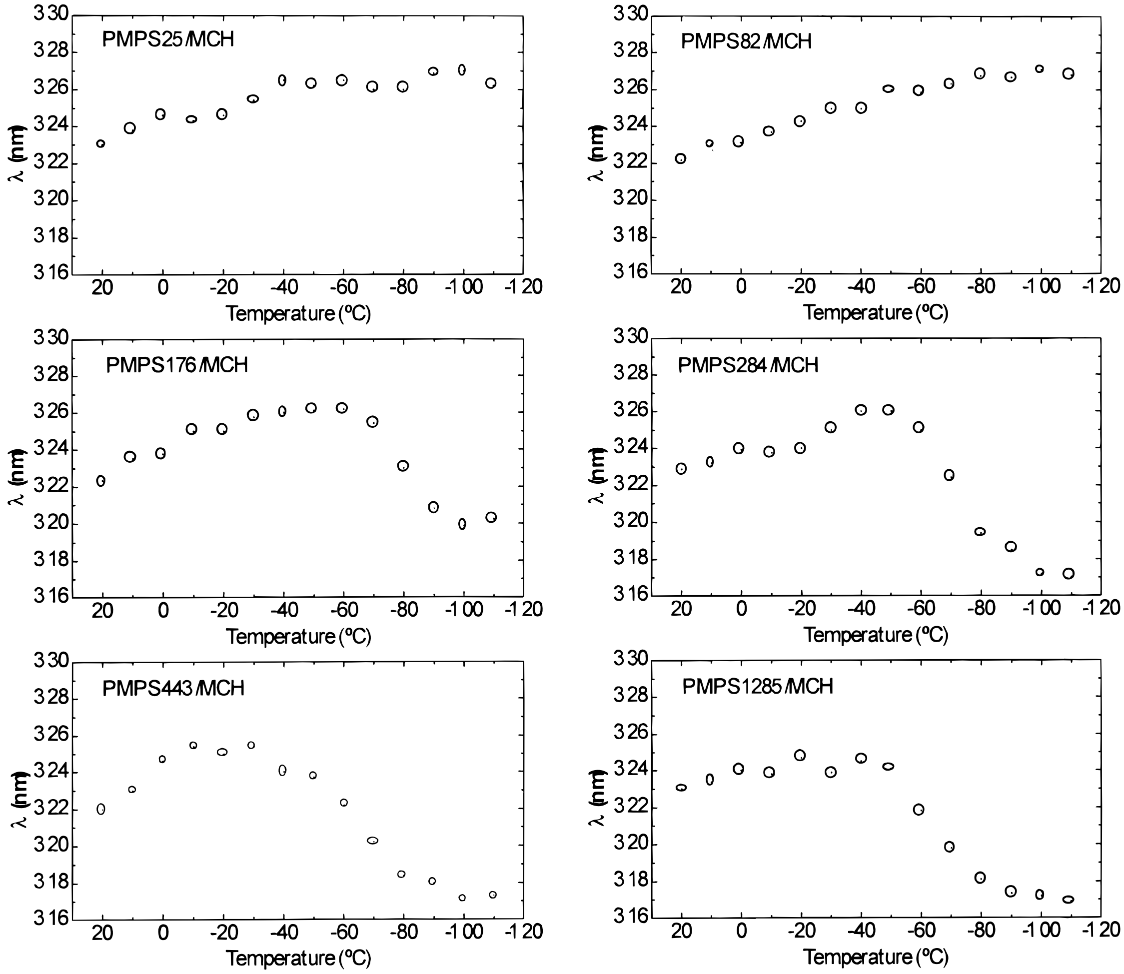

Figure 4. Temperature dependence of the wavelength of the maximum excimer emission, λ_E, for several PMPSN samples of different chain length in MCH solution.

samples (PMPS25 and PMPS82) behave as expected:[2,8] I_M increases with respect to the minimum both on decreasing T and on increasing T (on decreasing T, because k_a decreases; on increasing T, because k_d increases). The high molecular weight samples again show an anomalous behavior. At temperatures lower than −50 °C for PMPS1285, −50 °C for PMPS443, −50 °C for PMPS284, and −70 °C for PMPS176, I_M suffers a steplike increase to a higher value, similar to what happens with I_E. This result discards the possibility of an additional mechanism of excimer formation which starts operating below a certain temperature, because it would produce quenching of monomer emission with respect to the low molecular weight samples, the opposite to the observed result.

It seems better that the rate constants for nonradiative decay of monomer and excimer emission both decrease in the lowest temperature region because of a change in chain mobility, which is evident only in long chains, and reaches some kind of saturation or final temperature-independent state at −90 °C. This change in chain mobility could very well be accompanied by a modification in the nature of the excimers being formed.

Figure 4 shows the temperature dependence of the excimer stability, measured by the wavelength of the maximum excimer emission intensity, λ_E. It is also different for high and low molecular weight samples. The largest stability of an excimer corresponds to conformations with perfect parallelism and maximum overlap of the aromatic groups, which yields the largest red shift of excimer emission with respect to monomer emission.[10] PMPS excimers do not have the largest stability,[11,12] which can be attributed to the nonzero angle formed by the phenyl planes in the excimer-forming conformation. Since excimer formation is an exothermic process, on decreasing temperature more stable excimers (largest λ_E) are formed, and this expected behavior is what in fact is observed for the low molecular weight samples PMPS25 and PMPS82 (Figure 4). But, for the high molecular weight samples the behavior is different. The stability of the excimers in the high molecular weight samples PMPS176, PMPS284, PMPS443, and PMPS1285 suffers a steplike decrease on cooling at temperatures below −70, −50, −40, and −50 °C, respectively. It must therefore be concluded that a new excimer-forming site is adopted for long chains at the lowest temperatures.

Summarizing what we have from the temperature variation of I_M, I_E, and λ_E, in the high molecular weight samples, it is a kind of transition between two states. At the low-temperature state, there are more preformed dimers and more efficient monomer and excimer emissions, but the excimers are of a lower stability.

The differences between these two temperature regimes goes much further than just the emission spectra. An anomalous change with temperature has also been observed for light scattered by the high molecular weight samples. Figure 5 shows the temperature dependence of the light scattering intensity normalized to unit concentration (I_{LS}), measured on the fluorescence

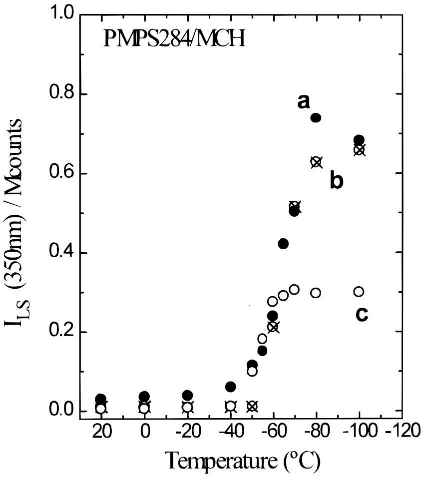

Figure 5. Light scattering intensity, I_{LS}, at 350 nm, as a function of temperature, for three solutions of PMPS284 in MCH, having different concentrations: (a) $c = 5.1 \times 10^{-4}$ M; (b) $c = 1.53 \times 10^{-3}$ M; (c) $c = 4.09 \times 10^{-3}$ M. I_{LS} values normalized to unit concentration.

spectra at 350 nm, for PMPS284 solutions of different concentrations. (Other high molecular weight samples have a similar temperature dependence.) In Figure 5 we can see clearly a transition between two different states, existing at temperatures below −60 °C and above −40 °C. The temperature (−40 °C) where this transition starts is the same where I_M, I_E, and λ_E also start their anomalous behavior in this sample. Normalized values of I_{LS} depend on the size of the scattering particles (through the weight-average molecular weight), on their shape (through the shape factor), and on solvent characteristics such as the second virial coefficient and the refractive index increment.[13] Changes of I_{LS} by a factor as large as 10−100, as corresponds to those shown in Figure 5, cannot be ascribed to changes of solvent characteristics or by a simple change in polymer chain conformation alone; they demonstrate that the scattering particles are very large, probably formed by macromolecular aggregates with aggregation numbers around 10−100.

The concentration dependence of I_{LS} would ascertain the existence and nature of the aggregation. A certain concentration dependence is detected, since in Figure 5 the ratio of I_{LS} below −60 °C and above −40 °C is lower for the more dilute solution (but in general we cannot see a unique correlation of I_{LS} with concentration). However, the results for the excimer-to-monomer ratio indicate that the concentration has no influence on the plateau at low temperatures (Figure 6). Despite this, we have to admit that the high molecular weight PMPS samples, below a certain temperature, which depends on chain length, experience an aggregation process, even at concentrations as low as 10^{-3} M. The consequence of such a process is the loss of mobility (decreasing nonradiative decays of monomer and excimer and therefore increasing I_M and I_E) and the creation of a new excimer-forming site with smaller excimer stability.

^{1}H NMR Spectra. The analysis of ^{1}H NMR spectra[14−17] of PMPS high molecular weight samples, used in this work, show that they are practically 50% heterotactic, with the remaining 50% triads almost equally distributed between isotactic and syndiotactic triads, so that they conform to Bernouillian statistics.

In Figure 7 we can see the spectrum of a high molecular weight sample, PMPS1285. The signal of the methyl groups appears close to 0 ppm and the signal of the phenyl groups close to 7 ppm. At the higher temperatures these signals are clearly visible. The intensity of these signals suffer a sharp decrease when the temperature decreases. The spectra taken at several temperatures are compared in Figure 7 to see this effect (it is reversible). At −50 °C the signals of the polymer have practically disappeared in the spectrum baseline. This indicates that a loss of mobility is taking place below −50 °C. This loss of mobility can be due to a chain transition, but it could also be due to aggregation, since it has been shown[18,19] that, in simple liquid-sample NMR techniques, the bands of aggregated units are so broad that they cannot be detected in high-resolution spectra. However, in our case, no influence of concentration is seen. Spectra of PMPS1285 obtained at concentrations differing by a factor of 20 yield the same sharp decrease of signals and in the same temperature interval.

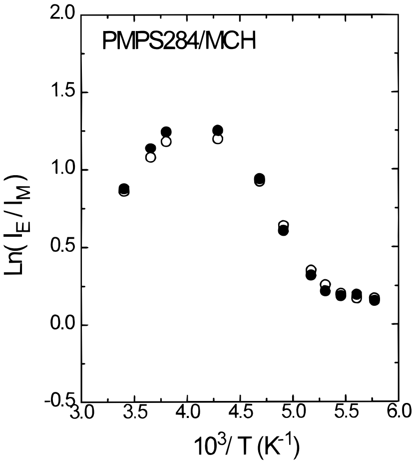

Figure 6. Stevens−Ban plots of I_E/I_M for PMPS284, in dilute MCH solutions, with two different concentrations: (●) $c = 7.7 \times 10^{-4}$ M; (○) $c = 1.53 \times 10^{-3}$ M; $\lambda_{ex} = 250$ nm.

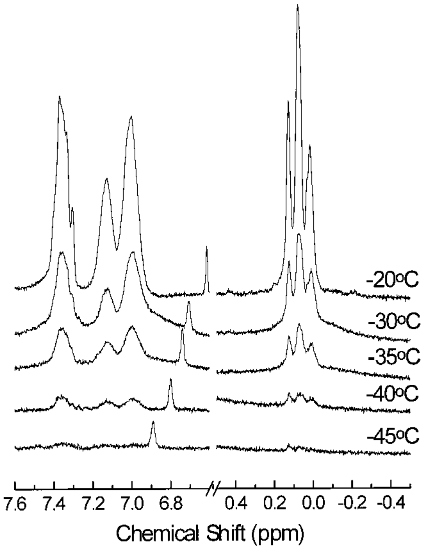

Figure 7. ^{1}H NMR spectra of PMPS1285, in deuterated MCH solution, at different temperatures.

This loss of mobility is not detected in the low molecular weight sample PMPS25. Thus, the spectrum of PMPS25 remains normal below −50 °C. This difference between high and low molecular weight samples is shown in Figure 8. The integrated intensity of the

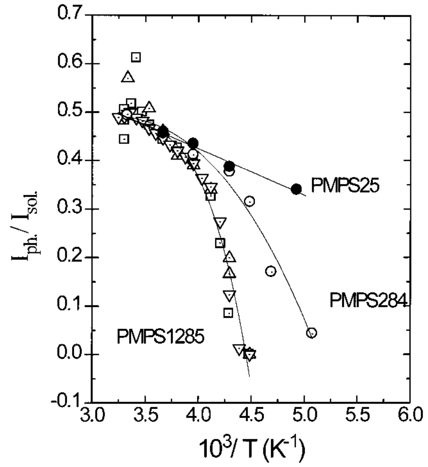

Figure 8. Temperature dependence of the integrals ratio phenyl/solvent of ^{1}H NMR spectra, in deuterated MCH, for samples PMPS25 ($c = 1.28 \times 10^{-3}$ M), PMPS284 ($c = 1.28 \times 10^{-3}$ M), and PMPS1285 at three concentrations: (△) $c = 2.1 \times 10^{-4}$ M; (▽) $c = 1.28 \times 10^{-3}$ M; (□) $c = 4.11 \times 10^{-3}$ M.

phenyl signal is compared with the integrated total intensity of the solvent (deuterated MCH), which is taken as reference. The ratio (area of phenyl)/(area of solvent) is plotted vs reciprocal temperature for three samples: PMPS25, PMPS284, and PMPS1285. For the high molecular weight samples, PMPS284 and PMPS1285, this ratio decreases sharply to zero (at −80 and −50 °C, respectively) as a consequence of the disappearance of the polymer signals in this interval. But the ratio for the low molecular weight sample, PMPS25, shows only a slight decrease in this same temperature interval. Thus, the loss of mobility at low temperatures occurs only for the high molecular weights.

The temperatures at which this loss of mobility is detected by ^{1}H NMR cover the same range where the fluorescence shows a plateau in excimer emission and also where light scattering is enhanced. All these results, obtained with different techniques, should reflect a common phenomenon.

Discussion

Several hypothesis can be proposed at this point:

(i) Since in the LTL $(I_0/I_M - 1)\tau_0^{-1}$ is equal to k_a, the plateau in Figure 2 means that k_a remains constant in that range of temperatures, and its value (determined from steady-state measurements) is larger than the extrapolated k_a values assuming kinetic control under the Birks scheme. It could be argued that the rate constant for energy migration, with zero activation energy, would overpass the rate constant for excimer formation through chain motions at temperatures below −50 °C.

Nevertheless, photophysical effects cannot explain the increase of light scattering and the disappearance of signals of ^{1}H NMR spectra in the same range of temperatures and chain length where the plateau of the fluorescence ratio occurs. It must be a polymer effect better than a photophysical effect.

(ii) The hypothesis of a conformational transition would be supported by the temperature dependence of the excimer emission intensity and wavelength, assuming that the conformation stable at the lower temperatures is able to show larger excimer emission intensity but having less stable excimers than those formed at higher temperatures. But it is hard to accept that only high molecular weight samples may suffer such a conformational transition, and besides, this hypothesis alone does not explain the enormous enhancement of light scattering by large chains at low temperatures.

(iii) Polymer aggregation is an intermolecular phenomenon unexpected for such dilute solutions (about 0.01% w/v), except in the case that solvent thermodynamic quality would decrease significantly, as occurs by diminishing temperature and increasing polymer molecular weight. At 20 °C, MCH is a good solvent of PMPS, but the Mark−Houwink exponent for intrinsic viscosity at this temperature is not very high: $a = 0.58$,[20] which could likely decrease to values below $a = 0.5$ on descending the temperature around − 50 °C and then rendering MCH as a bad solvent which induces polymer−polymer contacts.

Polymer aggregation would explain the increase of light scattering (directly proportional to the apparent molecular weight of the scattering particles) and the loss of intensity of ^{1}H NMR spectra (due to the loss of chain mobility), as much as the temperature dependence of the excimer emission intensity (intermolecular excimers are an additional contribution and the loss of mobility also decreases nonradiative decays) and of the maximum excimer emission wavelength (smaller than for intramolecular excimers as corresponds to less stable intermolecular excimer contribution).

Intermolecular association can be questioned taking into account that the intensity of ^{1}H NMR spectra at temperatures below −50 °C and the fluorescence ratio do not show appreciable dependence on polymer concentration in the range of concentrations here studied. We can justify this by saying that the aggregates probably are formed at all concentrations and that these techniques detect just the accompanying loss of mobility, while in light scattering we can see some changes with concentration because light scattering is sensitive to the variation in size of the aggregates being formed.

The light scattering results could also suggest phase separation or a gelification process induced by temperature decrease for the high molecular weight PMPS solutions. However, these possibilities are discarded because (a) our concentrations are much lower than those at which gelification usually occurs and (b) phase separation would give some disappearance of fluorescence due to settling of the more dense (polymer-rich) phase.

Deviations from the linear decrease of $\ln(I_E/I_M)$ vs $1/T$ at low temperatures (having some resemblance with our plateaus) have been reported for isotactic polystyrene in decalin.[21] In dilute solution a coil-to-helix transition is proposed to occur. However, atactic polystyrene in decalin does not give an anomalous $\ln(I_E/I_M)$ vs $1/T$ variation but yields aggregation (becomes insoluble).[21]

A conformational transition may also occur in our system, coupled with an intermolecular association or being the signal that triggers such association. Segment mobility is drastically restricted, and excimer stability diminishes; these are clues to a change in conformer distribution, but also light scattering detects large particles, so interpolymer association is taking place. A minimum chain length is necessary to observe these phenomena, under the present conditions, possibly because (a) polymer solubility is lower for the longer chain lengths and (b) some kind of cooperativity may be acting in the system.

At the lower temperatures, the distribution of conformational states should be skewed toward the most stable ones, which in PMPS are those close to the sandwich conformation, due to the attractive interactions between phenyl rings.[9] At room temperature, these conformations are only slightly favored, and the coupling between rings occurs predominantly in pairs (dimers). But at temperatures of −100 °C, the coupling should extend over longer sequences (multimers), yielding ordered strands with little mobility. These multimer strands may propagate more in the longer chains, which is reasonable in view that at the plateau temperatures new excimers are formed and nonradiative decays decrease because of the mobility loss. It is also reasonable that due to these multimer strands, the excimers formed are less stable at the plateau temperatures, because in each pair of consecutive units the rings cannot couple as perfectly as in a single dimer, due to the restraint imposed by the other neighbors in the strand. The hypothesis of multimer strands is reasonable also to justify the onset of interchain aggregation. Thus, it is possible that not all the rings that couple in a multimer strand belong to the same chain; some may come from a different chain, and interlocking between the two chains occurs, thus creating a knot between them.

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