

Intramolecular Pyrene Excimer in Probing the Sol-Gel Process

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The sol-gel-xerogel process in a system consisting of tetraethyl orthosilicate (TEOS)/water/ethanol with acid catalysis was monitored, using as probes polystyrene chains labeled either at one or both ends with a 1-pyrene derivative, in very low concentrations ($<10^{-6}$ M). The probe labeled at one end enabled us to conclude that at these concentrations pyrene emits only in the monomeric form. For the chain labeled at both ends, besides the monomeric emission, a new band centered at 470 nm was observed, which was attributed to intramolecular excimer emission. The excimer forms either by a dynamic process, in which an excited pyrene at one end of the chain encounters a ground state monomer at the other end, or by a static process, in which a ground state dimer resulting from the cyclization of the chain is excited and rearranges to the excimer. The ratios of excimer to monomer fluorescence intensities at two excitation wavelengths (345 and 360 nm) are different even at the beginning of the hydrolysis reactions, showing that some pyrene dimers are preformed in the initial solution. From the evolution of this ratio at 345 nm with time (which mainly monitors the dynamic excimer formation process), it has been possible to detect an increase in the local medium viscosity with the progress of reaction. The same ratio at 360 nm (which mainly monitors the excimer formation via the dimer) increases over time, initially slowly and afterwards very steeply, and finally attains a plateau, allowing the determination of the gel point and probably of the critical point of drying of the gel. A type I nitrogen adsorption isotherm was determined for the xerogel. Being characteristic of a microporous solid, it indicates that the average radius of the pores is around 10 Å, which is lower than the radius of gyration of the polymer chain, supporting that in the xerogel the polymers are constrained in one pore, enhancing the intramolecular pyrene aggregation.

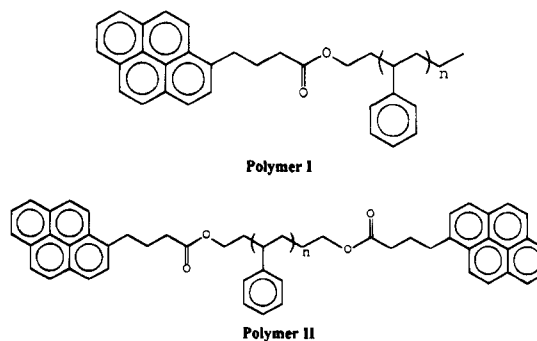
Introduction

The sol-gel process has gained importance, in the past 10 years, as a method for preparing inorganic gels and glasses: an appropriate precursor, like TEOS, tetraethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$), undergoes hydrolysis/polycondensation reactions at low temperature in a suitable solvent.^{1,2} The starting recipe, temperature, and pressure are determinant of the evolution of the microstructure as gel forms. This technique has also proved to be a clean, low-temperature process for doping inorganic gels and glasses with organic molecules, thus developing composite materials with specific optical and mechanical properties.¹⁻³ On the other hand, when the guest molecules are adequately selected and incorporated in the sol-gel starting solution, they can act as probes to monitor the gelation process, providing information on the local viscosity, polarity, structural and chemical changes, and, eventually, on the porosity of the final xerogel.⁴

Pyrene has been used successfully to probe the polarity of the medium during gelation,^{3,5} since the vibronic structure of the fluorescence spectrum is dependent on the environment.⁶ In high concentrations, pyrene forms ground state dimers, observed by UV-vis absorption⁷ and

fluorescence excitation spectra⁸ from the initial stages of the hydrolysis of TEOS. The fluorescence spectrum of pyrene at high concentrations shows, besides the monomeric emission, a new broad band centered at 470 nm, characteristic of the excimer, which is formed either by a collisional process of an excited with a ground state monomer or by deactivation of the excited dimer.⁹ The excimer band almost disappears after drying (xerogel stage), and the absorption and excitation spectra resemble the pyrene spectra in diluted solution, showing that monomer molecules were isolated in individual pores.^{3,7}

This work uses the steady-state fluorescence of 1-pyrenyl attached at one end (polymer I) and both ends (polymer II) of a polystyrene chain to follow the sol-gel-xerogel process of TEOS, with acid catalysis.



The concentration of polystyrene chains is kept very low ($<10^{-6}$ M) to avoid intermolecular processes and interference in the course of the sol-gel reaction. The fluorescence studies of the one-end-labeled polystyrene

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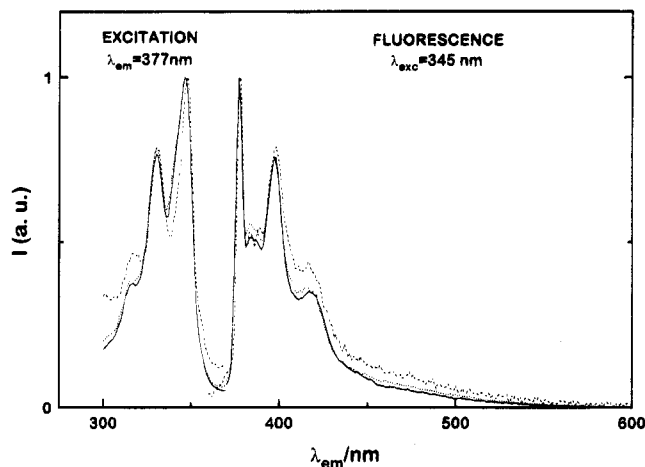


Figure 1. Fluorescence ($\lambda_{\text{exc}} = 345$ nm) and excitation ($\lambda_{\text{em}} = 377$ nm) spectra of the polymer chain PS5900-Py in the TEOS/water/ethanol solution at the beginning of hydrolysis (solid line), just after gelation and in the xerogel stage, 180 days after preparation (dashed line).

chain allow us to show that pyrene does not aggregate at the concentration used. The fluorescence and excitation spectra of both-ends-labeled chain show the intramolecular aggregation of pyrene. The ratio of the excimer to monomer fluorescence intensities obtained with excitation light at 360 nm increases slightly from the beginning and drastically at some stage of the ageing and drying process, before a plateau is attained. This allows the determination of the gel point as the intersection of two lines with different slopes.

Experimental Section

Sample Preparation. Pyrene-labeled polymers I ($M_n = 5900$; $M_w/M_n = 1.33$) and II ($M_n = 1700$; $M_w/M_n = 1.07$) were synthesized and labeled as described in ref 10. They will be referred to as PS5900-Py and Py-PS1700-Py, respectively. These samples were kindly supplied by Dr. M. A. Winnik of the University of Toronto. TEOS was purchased from Alfa Products (99%) and ethanol was spectroscopic grade, from Merck. Deionized water was used to assist hydrolysis, and HCl p.a. from Merck was used as catalyst.

Solutions of PS5900-Py and Py-PS1700-Py in ethanol were prepared in advance, with concentrations respectively 1.02×10^{-6} M (solution I) and 3.5×10^{-6} M (solution II). The starting solutions contained 20 mL of TEOS, 6 mL of water, and 6 mL of solution I or II. pH was initially set at 1.2 (using a previously prepared 1 N HCl solution). The molar ratios $\text{H}_2\text{O}:\text{TEOS}:\text{C}_2\text{H}_5\text{OH}$ obtained in the final solutions were approximately 4:1:1 and the concentrations of PS5900-Py and Py-PS1700-Py were respectively 1.9×10^{-7} and 6.6×10^{-7} M. These solutions were maintained at 70 ± 2 °C for 40 min to accelerate hydrolysis.

Gelation Process. The starting solutions were placed in partially covered silica cells and kept at room temperature (≈ 20 °C). The gelation process was followed by fluorescence emission and excitation spectra, recorded at regular intervals during several weeks, until complete drying of the gel. The measurements were performed at constant temperature, in a Spex Fluorolog 112 spectrofluorometer. The BET isotherms were obtained in a ASAP 2000 from Micromeritics.

Results and Discussion

The fluorescence spectra ($\lambda_{\text{exc}} = 345$ nm) of the TEOS solution doped with polystyrene chain I (PS5900-Py) at the beginning of hydrolysis, just after gelation and at the xerogel stage are shown in Figure 1.

The ratio of the fluorescence intensities at 397 nm (fifth peak) and at 377 nm (first peak) is almost invariant along the hydrolysis and polymerization, in contrast to the

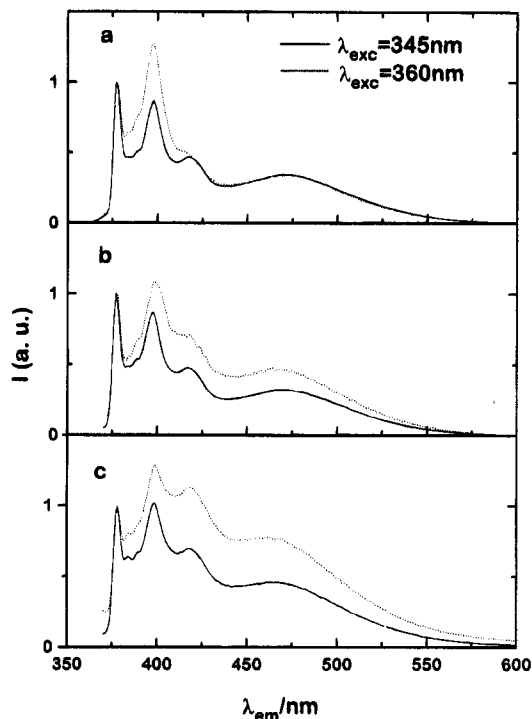


Figure 2. Fluorescence spectra of the polymer chain Py-1700PS-Py in the TEOS/water/ethanol solution for $\lambda_{\text{exc}} = 345$ nm (solid line) and $\lambda_{\text{exc}} = 360$ nm (dotted line): (a) for the starting solution; (b) just after gelation 7.5 days after preparation; (c) at the xerogel stage, 180 days after preparation. All spectra were normalized to 1 at 377 nm.

decrease in this ratio observed when free pyrene is the probe.^{11–13} On the other hand, the fluorescence spectrum appears more resolved in the xerogel stage, with the characteristic vibronic structure of pyrene.¹² These two observations indicate that, in the sol, pyrene “sees” the polystyrene chain that is coiled around it.¹⁴ In the course of reaction, the labeled polymer starts being adsorbed in the silica porous structure and the typically well-resolved spectrum of pyrene emerges. On the other hand, the excitation spectra ($\lambda_{\text{em}} = 377$ nm) recorded for the starting solution and after gelation (Figure 1) are similar, revealing that pyrene is always in the monomeric form. This was expected, since at the low concentration used (always lower than 10^{-6} M) bimolecular processes are very improbable.¹⁵

In a new series of measurements, the polymerization and drying of the same system doped with polymer chain II (Py-PS1700-Py) was monitored. Figure 2 shows the fluorescence spectra recorded at the beginning of the hydrolysis (a), just after gelation (b), and at the xerogel stage (c).

The fluorescence spectra for $\lambda_{\text{exc}} = 345$ nm show the characteristic emission of the monomer, whose shape is modified only during aging and drying. When $\lambda_{\text{exc}} = 360$ nm, the emission spectrum in the region 370–450 nm is different from the monomeric pyrene emission, modifies during the gelation and substantially with drying. This is caused by pyrene aggregation that occurs already in the beginning of the sol–gel process, since the mixture of water and ethanol is a poor solvent for both the polymer

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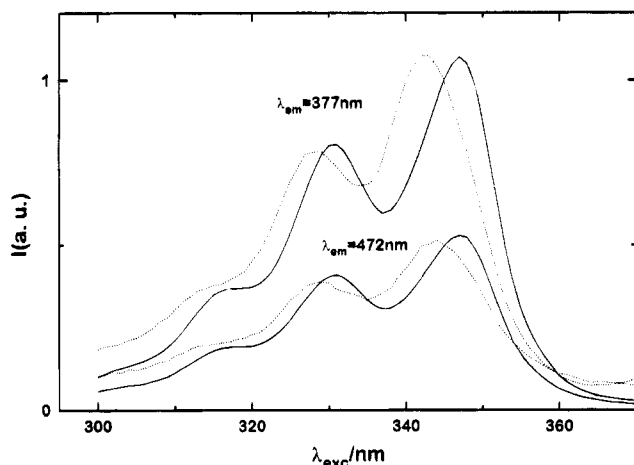
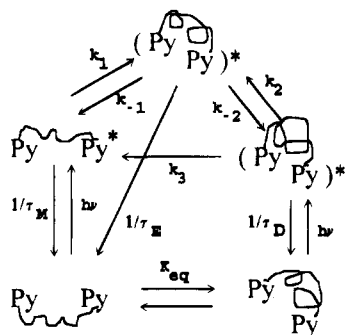


Figure 3. Excitation spectra for $\lambda_{em} = 377\text{ nm}$ and at $\lambda_{em} = 472\text{ nm}$, normalized at 345 nm , of the polymer chain Py-1700PS-Py in the TEOS/water/ethanol solution at the beginning of hydrolysis (solid lines) and during drying (dotted lines).

Scheme 1



and pyrene. At 345 nm ($S_2 \leftarrow S_0$ absorption band) due to a high absorption coefficient of pyrene, the emission is mainly from the pyrene monomer. In contrast, at 360 nm ($S_1 \leftarrow S_0$ absorption band) the pyrene absorption coefficient is minimum and therefore the excitation light can be absorbed by a pyrene dimer, whose structured emission superposes that of the monomer.⁹ All spectra show also a structureless broad band centered at 470 nm , characteristic of the excimer emission. For free pyrene at high concentrations, the excimer emission decreases upon drying of the gel, being suppressed in the xerogel, which was explained by the trapping of isolated pyrene molecules in different pores as they shrink.^{3,7} In our studies, the intensity of the excimer emission relative to the monomer emission increases after drying, which provides an indication that the polymer chain is collapsed and trapped in one pore in the xerogel stage.

The excitation spectra at the beginning of hydrolysis and during drying (Figure 3) are shifted both for emission at $\lambda_{em} = 377\text{ nm}$, and $\lambda_{em} = 472\text{ nm}$, confirming that the pyrene dimer is present and absorbs in the same region as the monomer.

The different emissions can be explained following the kinetic Scheme 1,¹⁶ where the excimer is formed by a dynamic process involving the encounter of an excited pyrene at one end of the chain with the one at the other end (cyclization of the polystyrene chain) or indirectly from excited pyrene dimers.¹⁷

The ground state loose pyrene dimer with equilibrium constant K_{eq} is formed by polystyrene chain cyclization.

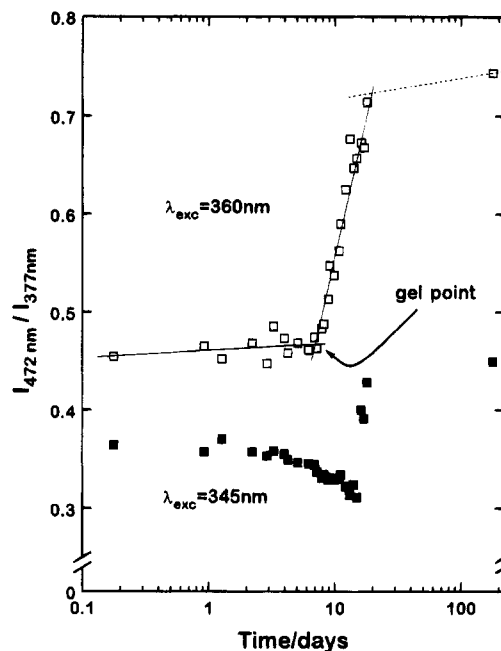


Figure 4. Ratios of excimer to monomer fluorescence intensities (I_{472}/I_{377}) at excitation wavelengths 345 nm (■) and 360 nm (□) as a function of time.

Both the monomer and the dimer can be promoted to the excited state by UV excitation. The percentage of each species in the excited state is wavelength dependent *via* the optical densities. The monomer decays with intrinsic lifetime τ_M or encounters a pyrene molecule at the other end of the chain and forms an excimer with rate constant, k_1 (characteristic of the diffusion-controlled cyclization process). [Two different pyrene excimers were observed in sol–gel⁹ and LB films:¹⁸ one appears immediately after excitation and decays some hundreds of picoseconds afterwards; the other, with a sandwich conformation, has a longer lifetime (tens of nanoseconds) and is mainly the emission detected in this study.] The excited dimer can reversibly originate the excimer, with rate constant k_2 .¹⁶ Both the excimer and the excited dimer decay with intrinsic lifetimes τ_E and τ_D , respectively, or dissociate with rate constants k_{-1} and k_3 , originating the excited monomeric species. On the course of the reaction, the rate constant values change either due to the variation of the medium viscosity or due to the adsorption of the species on the surface of the pores.

The fluorescence spectra recorded at 345 and 360 nm were obtained at different stages of the aging and drying process for about 180 days after sol preparation. The ratios of the excimer to monomer fluorescence intensities (I_{472}/I_{377}) are plotted in Figure 4 for both excitation wavelengths versus time. Taking into account the high absorption coefficient of pyrene at 345 nm , this ratio essentially monitors the dynamic excimer formation process. As time develops, the excimer to monomer ratio slightly decreases, due to the increase of the local viscosity with time, the gel point not being clearly defined. In contrast, the same ratio at $\lambda_{exc} = 360\text{ nm}$, which monitors mainly the static (via dimer) excimer formation process, increases slowly for 7.5 days and afterwards shows a dramatic increase up to a plateau approximately 8 days later. The gel point can be defined as the intersection point of the two lines with different slopes. The difference of the two ratios at the starting point confirms the presence of preformed intramolecular pyrene dimers in the sol. The slight

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increase observed in the curve for $\lambda_{\text{exc}} = 360$ nm at the beginning can be interpreted as the result of the increasing percentage of ground state pyrene dimers due to the silica structure developing with the formation of large pores. The large increase of the same ratio is explained by the shrinking of the pores motivated by simultaneous aging and drying processes, which substantially enhances pyrene dimer formation. Therefore, the intersection of the two lines with different slopes defines the gel point, which occurs in this system 7.5 days after sol preparation. Visual observation of the sample with time provided an independent method of detecting the gel point, although with a great uncertainty. Indeed, a transition from a viscous solution to a gel was observed about 7 days after sample preparation. A plateau is achieved when no more dimers are formed. This can correspond to the critical point where the gel slightly expands as drying continues, because the compressive forces exerted on the network are released as the residual solvent evaporates.¹ If this is the case, then the critical point in this system occurs at about 15 days after preparation of the sol. Note that the ratio of intensities at 345 nm excitation starts increasing near the critical point until attaining a plateau lower than the one observed at 360 nm.

A type I nitrogen adsorption isotherm was obtained for the xerogel, which is characteristic of a microporous solid (average pore radius lower than 10 Å).¹⁹ We should distinguish between the pores which are readily accessible to the adsorbed gas and those cavities in the bulk matrix which may not be accessible to the nitrogen. It was observed, for oxygen quenching of pyrene, that most of the probe molecules are located in the pores accessible to

the oxygen.²⁰ If this is the case, and as the average pore radius from BET isotherms is lower than the radius of gyration of the chain in a Θ solvent (11.8 Å),²¹ this supports our assumption that the reduction of the pore dimension with drying induces intramolecular pyrene aggregation. Nevertheless, the observation of pyrene monomeric emission in the xerogel suggest that the structure of some pores is probably cylindrical, with a very small diameter, not allowing polymer cyclization to form pyrene dimers.

Summary

A pyrene derivative group attached to one or both ends of a polystyrene chain was proved to be useful to follow the sol–gel acid-catalyzed polymerization of TEOS. The probe has the great advantage of being used in a very low concentration, not perturbing the sol–gel reactions. The ratio of the excimer to monomer emission versus time, for excitation at 360 nm, where pyrene absorption coefficient is very low and pyrene dimers are predominantly excited, has different regions allowing the determination of the gel point and probably of the critical point of drying. These results were correlated with the variation of the pore dimensions in the course of the sol–gel–xerogel process and are compatible with the average pore dimension obtained from a nitrogen adsorption isotherm.

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