

Use of Pyrene Excimer Fluorescence to Probe Polymer Chain Diffusion between Latex Particles during Film Formation

R. Casier, J. Duhamel, M. Gauthier

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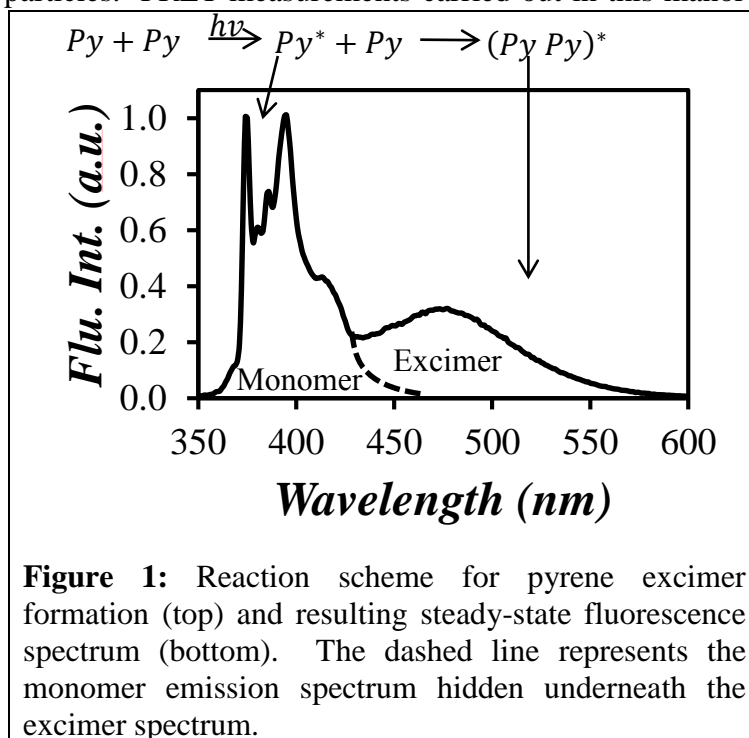
Introduction

The diffusion of polymer chains across particle boundaries in latex films has been an area of active studies for over 30 years.¹⁻⁴ The formation of latex films prepared from aqueous dispersions occurs typically in three stages: water evaporation, particle deformation, and particle coalescence.^{1,3} In the first stage, water evaporates and leaves behind a matrix of packed latex particles with numerous voids. In order to have particle deformation and coalescence, the film must be heated above a minimum temperature, the minimum film formation temperature (MFT), which is usually close to the glass transition temperature (T_g) of the polymer constituting the latex.¹ As the film is heated above its MFT, the particles will begin to deform and fill in the voids left from the first stage. With continued annealing, polymer chains contained within latex particles begin to diffuse across the particle boundaries into surrounding particles. This interparticle polymer diffusion (IPD) results in the formation of entanglements between polymer chains from adjacent particles. Since the mechanical properties of a film are directly related to the level of IPD, or the number of interparticle entanglements, it is vital to be able to measure the extent of IPD.⁴

Over the years there have been several techniques developed to measure the extent of IPD between particles. Currently, two of the most widely used methods are small angle neutron scattering (SANS) and fluorescence resonance energy transfer (FRET).^{1,3,5} In order to use FRET to measure IPD, two fluorescently-labelled latex particles with very carefully chosen dyes must be prepared. The extent of IPD can be calculated by measuring the amount of energy transfer between a mixture of the two labelled particles. FRET measurements carried out in this manner

require the use of a time-resolved spectrofluorometer. SANS uses a film prepared out of a mixture of deuterated and native latex particles. As the film anneals, the diffusion of the deuterated polymer can be monitored. Although this method requires the preparation of only a single labelled latex, the latex is very expensive due to the high cost of deuterated monomer and access to a neutron source is needed. Both of these methods provide a powerful tool to probe IPD, however we believe that the same information can be measured in a simpler manner using a single fluorophore, pyrene (Py).

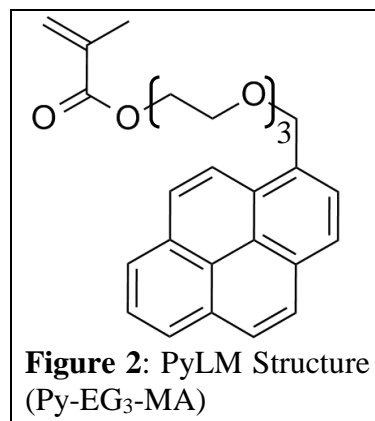
An excited pyrene has the ability to form excimer if it comes



into direct contact with another ground-state pyrene as depicted in Figure 1. The amount of excimer formed can be measured using a steady-state fluorometer, and quantified as the fluorescence intensity of the excimer over that of the monomer, the I_E/I_M ratio. The amount of excimer formed, and thus the I_E/I_M ratio, is directly proportional to the local pyrene concentration (C_{Py}). By preparing a latex fluorescently-labelled with pyrene and incorporating it into a matrix of native latex, C_{Py} will initially be high inside the labelled particles, resulting in a high I_E/I_M ratio. As the film is annealed above the MFT, the pyrene-containing polymer chains will diffuse into the surrounding native particles causing a decrease in C_{Py} and I_E/I_M . Since the changes in I_E/I_M reflect the extent of IPD, the I_E/I_M ratio is being monitored over the annealing time to quantitatively describe the diffusion of polymer chains across the particle boundaries.

Experimental

A pyrene-labelled monomer (PyLM), 1-pyrenylmethoxy-2-ethoxy-2-ethoxy methacrylate (Py-EG₃-MA), with the structure drawn in Figure 2 was synthesized. First, triethylene glycol was protected on a single end with a trimethylsilane group by reacting triethylene glycol with chlorotrimethylsilane and trimethylamine. Vacuum distillation was used to isolate the mono-protected derivative. Next the mono-protected triethylene glycol was deprotonated with sodium hydride in DMF, and 1-pyrenemethylbromide was added to the solution. The final product was obtained after removing the trimethylsilane group by washing with 1 M HCl_(aq) and purifying by column chromatography on silica with a mixture of ethyl acetate and hexanes (2:1).



The pyrene-labelled latex was prepared by using a free radical semi-batch emulsion process. The reactor was heated to 80 °C and then was charged with ammonium persulfate and dioctyl sodium sulfosuccinate (AOT) as a surfactant. A pre-emulsified monomer feed containing PyLM, n-butyl methacrylate, AOT, and water was fed into the reactor over a three hour period. After the feed had completed, the emulsion was cooled to room temperature and was then filtered to remove any coagulum that had formed over the reaction period. The latex particles were analysed by dynamic light scattering (DLS) to determine the particle size and particle size distribution. The polymer molecular weight and dispersity (\bar{D}) were determined by gel permeation chromatography (GPC) in conjunction with differential refractive index (DRI), light scattering, viscosity, and UV-Vis absorbance detectors. The level of PyLM incorporated into the latex was determined by comparing the UV absorbance at 344 nm of the latex to a pyrene standard.

Films composed of pyrene-labelled latex in a non-fluorescent poly(butyl methacrylate) (PBMA) latex matrix were prepared by mixing the appropriate amount of each latex and then depositing the mixture onto a quartz plate. The film was then left to dry under a gentle flow of nitrogen for three hours. Steady-state fluorometry was used in front face geometry to quantify both monomer and excimer emission of pyrene. The film was excited at 344 nm and the emission scanned from 350 to 600 nm. The I_E/I_M ratio was calculated as the area under the excimer from 500 to 530 nm over the area under first monomer peak (372 to 378 nm). These integration boundaries were chosen such that the integrated fluorescence intensity represented solely either monomer or excimer emission and did not result from an overlap of the two. The films were annealed under nitrogen in a glass tube partially submerged in an oil bath maintained

at a constant temperature. After the film had annealed for a given period of time, the film was removed from the tube and quickly cooled to room temperature on an aluminum plate. The rapid cooling process to below the MFT (T_g PBMA ~ 27 °C)¹ prevented any further annealing from occurring, allowing for its analysis by fluorescence. The film was then reintroduced into the tube for further annealing, and the process repeated.

Results and Discussion

An emulsion was carried using 5 mol% of the PyLM shown in Figure 2. The produced latex particles had a diameter of 115 nm with a particle size distribution of 1.04. The polymer chains constituting the latex were characterized by GPC, the corresponding DRI and UV-Vis absorption traces shown in Figure 3. The M_n was calculated to be 650 kg/mol with a \bar{D} of 1.5. The overlapping unimodal peaks of the DRI and UV-Vis traces illustrate that the PyLM is incorporated into the polymer backbone. The small peak around an elution volume of 34 mL in the UV trace is from low molecular weight pyrene-containing species. In order to obtain accurate measurements

of IPD during annealing, it is vital that all the pyrene present in the sample be covalently attached onto the polymer. Since the diffusion of all the pyrene species were measured, any unbound pyrene would diffuse much more quickly thus distorting the diffusion values calculated for the polymer chains. To remove the low molecular species, the emulsion is dialysed against a mixture of 20 vol% ethanol in water and 2.5 mM AOT using a 50 kg/mol MWCO dialysis tube. The ethanol and surfactant were used to enhance the solubility of the hydrophobic PyLM to help accelerate the rate of removal of the unbound pyrene. The amount of pyrene removed was monitored by measuring the intensity of monomer fluorescence in the dialysate using steady-state fluorescence. To insure that all the unbound pyrene was removed, the dialysis was continued until the fluorescence intensity of the dialysate reached zero. Once all the unbound pyrene was removed, the pyrene content was found to equal 1.9 mol%, lower than the 5 mol% aimed for. The low pyrene incorporation may be due to the high hydrophobicity of the PyLM limiting transport of the monomer from the monomer droplets to the latex particles during the emulsion.

A native PBMA latex was prepared with a particle size of 95 nm and a size distribution of 1.04. GPC analysis yielded a M_n of 510 kg/mol with a \bar{D} of 2. A film was prepared from a mixture of 5 wt% pyrene-labelled latex in 95 wt% native latex. As the film was heated above the MFT, the particles began to coalesce. The level of coalescence was described by the volume fraction of mixing (f_m) between the particles. Experimentally, f_m at annealing time t is calculated with Equation 1, where $I_E/I_M(t)$, $I_E/I_M(0)$ and $I_E/I_M(\infty)$ are the I_E/I_M ratios at annealing time t ,

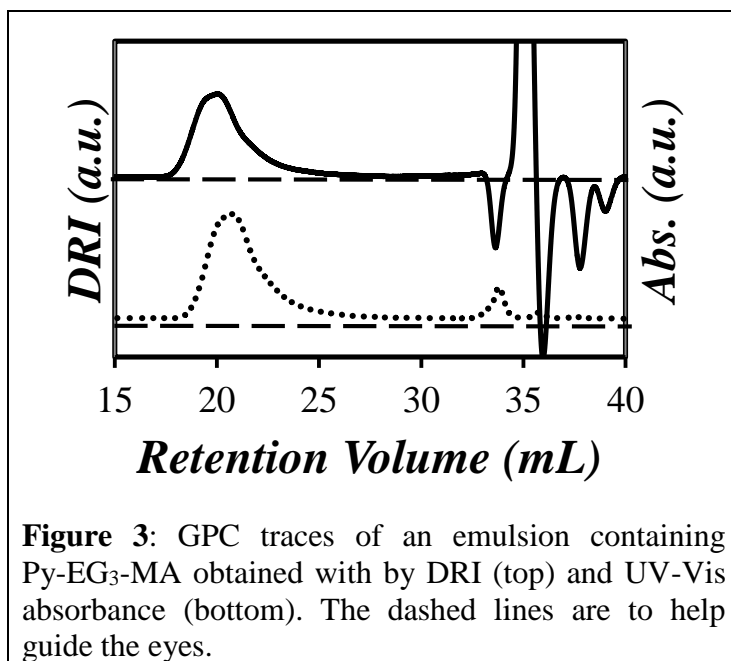


Figure 3: GPC traces of an emulsion containing Py-EG₃-MA obtained with by DRI (top) and UV-Vis absorbance (bottom). The dashed lines are to help guide the eyes.

before any annealing occurs, and after the film has fully annealed, respectively. $I_E/I_M(\infty)$ was found by preparing a homogeneous film from a solution of labelled and native latex dissolved in THF.

$$f_m(t) = \frac{I_E/I_M(t) - I_E/I_M(0)}{I_E/I_M(\infty) - I_E/I_M(0)} \quad (1)$$

Figure 4 displays the change in the steady-state fluorescence spectrum of a film annealed at 81 °C for various times. At time zero, the film exhibited the maximum amount of excimer with an I_E/I_M ratio of 0.30. As the film annealed, the amount of excimer decreased resulting in an I_E/I_M ratio of 0.06 after the film had fully annealed. The volume fraction of mixing was calculated using Equation 1 for two annealing temperatures of 81 and 114 °C. The results are plotted in Figure 5. As expected, the particles in the film annealed at 114 °C coalesced more quickly than at 81 °C as demonstrated by the higher f_m at each annealing time.

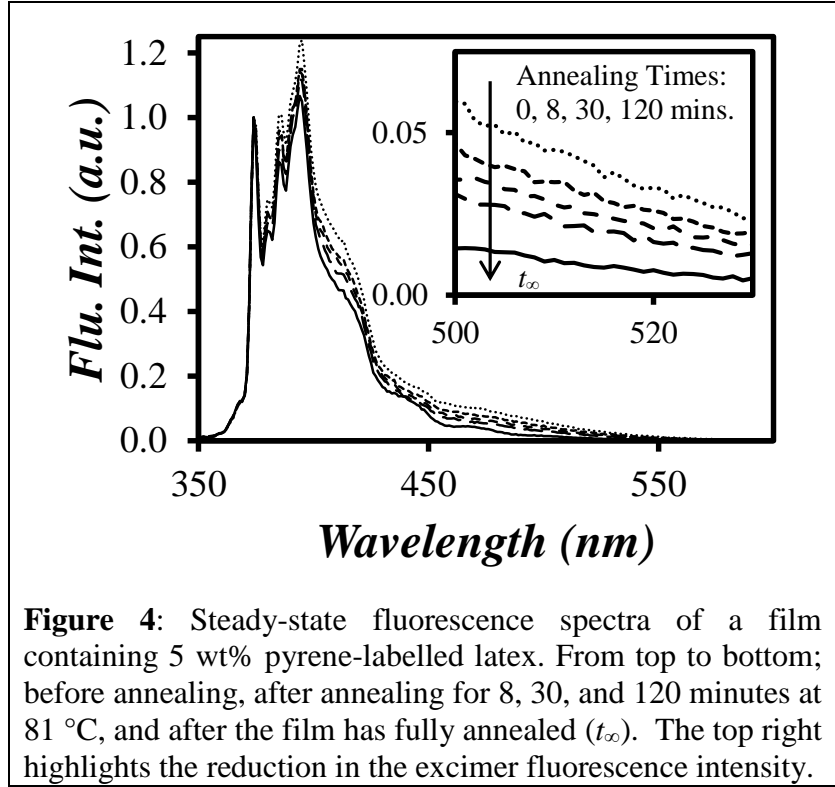


Figure 4: Steady-state fluorescence spectra of a film containing 5 wt% pyrene-labelled latex. From top to bottom; before annealing, after annealing for 8, 30, and 120 minutes at 81 °C, and after the film has fully annealed (t_∞). The top right highlights the reduction in the excimer fluorescence intensity.

In addition to measuring the volume fraction of mixing, the diffusion coefficient of the pyrene-labelled polymers (D) could be determined. In order to obtain this information, the experimental data were fitted to a model. In previous FRET studies, the model of choice used to describe the diffusion was a spherical diffusion model.^{1,2,3} The model is derived from applying Fick's law molecules diffusing out of a spherical particle with radius R .⁶ The concentration of pyrene $C_{Py}(r,t)$ at a distance r from the particle centre at time t is given by Equation 2, where C_0 is the initial concentration within the particle and D is the diffusion coefficient.

$$C_{Py}(r,t) = \frac{C_0}{2} \left[\operatorname{erf} \left(\frac{R+r}{2(Dt)^{1/2}} \right) + \operatorname{erf} \left(\frac{R-r}{2(Dt)^{1/2}} \right) \right] - \frac{C_0}{r} \left(\frac{Dt}{\pi} \right)^{1/2} \left[\exp \left(\frac{(R-r)^2}{4Dt} \right) - \exp \left(\frac{(R+r)^2}{4Dt} \right) \right] \quad (2)$$

The level of mixing between particles is the amount of pyrene that has diffused across the interface at time t (M_t) over the total amount of pyrene within the particle (M_∞) before any annealing occurs. M_t can be equated to M_∞ minus the amount of pyrene that remains within the particle at time t as shown in Equation 3, with M_∞ equal to $4/3\pi R^3 C_0$.

$$M_t = M_\infty - \int_0^R C_{Py}(r,t) \cdot 4\pi r^2 dr \quad (3)$$

The diffusion coefficient was calculated by setting M_t/M_∞ equal to the experimental f_m , whose expression was given in Equation (1), and solving for D by numerical integration of Equation 2. The diffusion coefficients calculated from the f_m values in Figure 5 are displayed in Figure 6. In conjunction with the results from f_m , D is higher in the film annealed at the higher temperature. The decrease in diffusion coefficient as annealing occurred is an important trend that has been observed in previous studies.^{1,5} The decrease is attributed to the dispersity of the polymer chains. At shorter annealing times the prominent diffusion observed is due to smaller polymer chains. As the film anneals for longer periods of time the diffusion of larger, and diffusively slower, polymer chains is probed. Additionally, in cases where the particles are small, or molecular weight is high, there can be an additional driving force for chain diffusion at early times caused by conformational distortion of the polymer chains near the surface of the particle.⁵

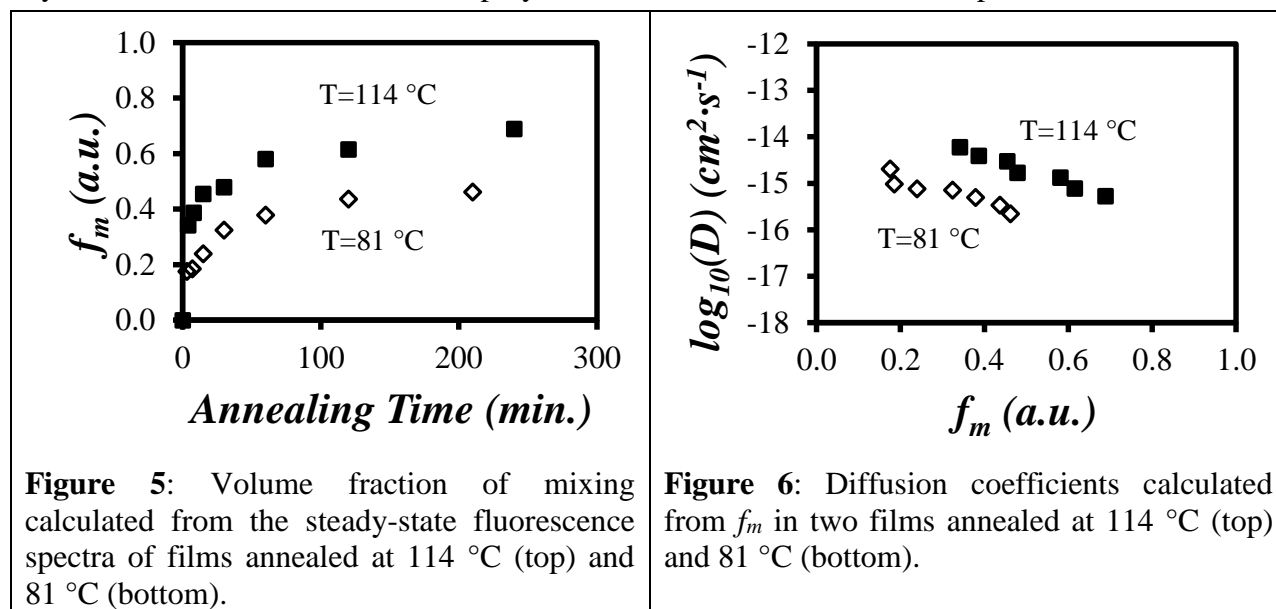


Figure 5: Volume fraction of mixing calculated from the steady-state fluorescence spectra of films annealed at 114 °C (top) and 81 °C (bottom).

Figure 6: Diffusion coefficients calculated from f_m in two films annealed at 114 °C (top) and 81 °C (bottom).

References

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