Using Visible Light to Probe Interparticle Diffusion in Latex Films

Remi Casier, Jean Duhamel, Mario Gauthier
Department of Chemistry
Institute for Polymer Research (IPR)
University of Waterloo

Introduction

Films formed by aqueous latex dispersions have many applications, particularly in the paint industry. The conditions in which a uniform film is formed from latex particles strongly affect the rate at which the polymer chains in the particles interdiffuse. A film in which the latex particles are not allowed to fully coalesce can lead to poor mechanical strength and a performance below expected standards.[1,2] The formation of latex films is generally divided into three main stages, as depicted in Figure 1.[1,3,4]

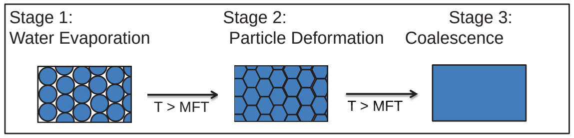


Figure 1: The formation of a homogeneous film from an aqueous latex dispersion.

In stage 1, the water is evaporated leaving behind a matrix of packed latex particles. Stage 2 involves the deformation of the latex particles as they fill in the voids in the matrix left from Stage 1. In Stage 3, interparticle polymer diffusion (IPD) generates the homogeneous film. In order for the latex particles to deform and coalesce, a certain minimum temperature is required, namely the minimum film formation temperature (MFT), which is generally close to or slightly above the glass transition temperature (T_g) of the polymer that constitutes the latex.

Fluorescence can be used to probe the diffusion of polymers in the latex as the films are being formed.[1,2,5] In previous studies, two different fluorescently labeled latex polymers were required to probe the degree of IPD and the MFT of the latex film. Our proposal is to prepare a polymer randomly labeled with pyrene (Py) by emulsion polymerisation and use it to characterize the IPD and MFT of a latex film by probing pyrene excimer formation which avoids the use of a second fluorescently labeled latex.

Pyrene Fluorescence

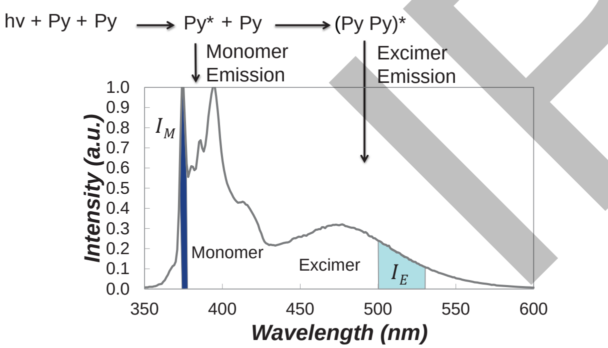


Figure 2: Reaction scheme for pyrene excimer formation (top) and resulting steady-state fluorescence spectrum (bottom).

Interparticle Polymer Diffusion

When pyrene is excited by a photon of light, it emits a blue colour. If an excited pyrene encounters a ground-state pyrene, it forms an excited dimer (excimer) which emits a turquoise colour, as described in Figure 2. The amount of excimer formed can be quantified with a steady-state (SS) fluorometer, by obtaining the ratio of the fluorescence intensity of the pyrene excimer (I_E) over that of the pyrene monomer (I_M), namely the I_E/I_M ratio.

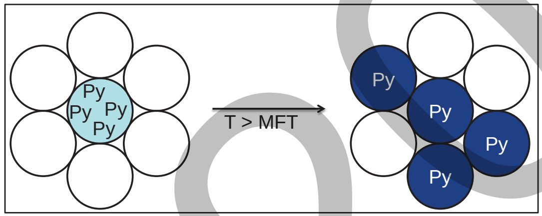


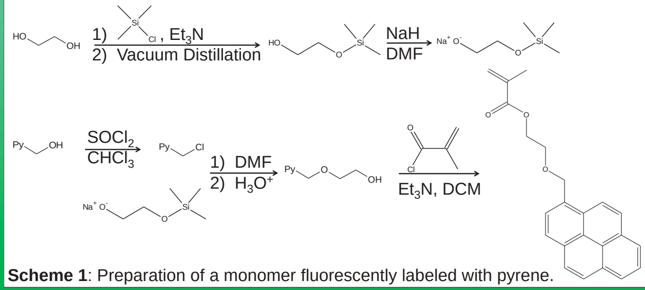
Figure 3: Interparticle diffusion of a pyrene labeled latex particle with neighbouring latex particles before (left) and after (right) annealing.

By preparing a polymer randomly labeled with pyrene by emulsion polymerization and incorporating it into a matrix of non-fluorescent latex particles, the I_E/I_M ratio can be used to determine the MFT and monitor the degree of IPD. The I_E/I_M ratio at annealing time t depends on the local concentration of pyrene (C_{Py}) in the film. When the fluorescently labeled latex particles are first mixed into a matrix of native latex the $I_E/I_M(t=0)$ ratio is expected to be high, and the film should fluoresce with a turquoise colour. As the film is heated above its MFT and the pyrene-labeled polymer diffuses throughout the matrix, C_{Py} should decrease and the $I_E/I_M(t>0)$ ratio decreases.

In order to quantitatively describe IPD, the fraction of mixing at annealing time t ($f_m(t)$) can be calculated using the experimental $I_E/I_M(t)$ ratios via Equation 1, where $(I_E/I_M)_{t\infty}$ is the I_E/I_M ratio after a long annealing time. Further by applying Fick's law to molecules diffusing out of a spherical particle, the polymer diffusion coefficient D can also be found.[2,5]

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

Pyrene Labeled Monomer



Scheme 1: Preparation of a monomer fluorescently labeled with pyrene.

Proof of Concept

To demonstrate that pyrene-labeled latex films can generate sufficient excimer fluorescence to monitor film formation, a *n*-butyl methacrylate copolymer randomly labeled with 4.7 mol% of pyrene from Scheme 1 (Py[4.7]-PBMA) was synthesized by free radical polymerization. The film prepared from this copolymer had a high I_E/I_M ratio. The film was then diluted down to 1 wt% using a non-fluorescent PBMA polymer to represent a time when the film has fully annealed. This resulted in a significant decrease in I_E/I_M as is demonstrated in Figure 4.

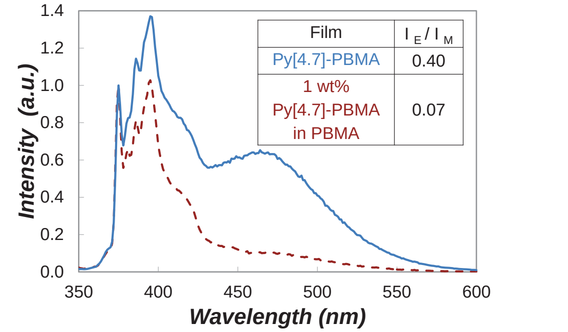


Figure 4: Steady-state fluorescence spectrum of films prepared with Py[4.7]-PBMA (—) and 1 wt% Py[4.7]-PBMA in PBMA (- - -).

Emulsion Polymerization

A surfactant-free approach was used with a low solids content (1.5 % solids) using ammonium persulfate as the initiator. Polymerizations with *n*-butyl methacrylate at 90 °C for 2 hours produced well defined latex with a particle size of 150 nm.

Thus far, incorporation of the pyrene labeled monomer (Scheme 1) has met several challenges. The current obstacles faced are the low incorporation of pyrene, low molecular weight of the resulting polymers, and removal of pyrene that is not covalently attached to the polymer chains.

References

1. Gauthier, C.; Guyot, A.; Perez, J.; Sindt, O. Film Formation and Mechanical Behavior of Polymer Laticies. *Film Formation in Waterborne Coatings,* Chapter 10, **1996,** 163-178. Washington, DC: American Chemical Society.
2. Winnik, M.A. Latex Film Formation. *Current Opin. Colloid Interface Sci.* **1997**, *2*, 192-199.
3. Eckersley, S.T.; Rudin, A. Film Formation of Acrylic Copolymer Laticies: A Model of Stage II Film Formation. *Film Formation in Waterborne Coatings,* Chapter 1, **1996,** 2-21. Washington, DC: American Chemical Society.
4. Wang, Y.; Winnik, M. A. Polymer Diffusion across Interfaces in Latex Films. *J. Phys. Chem.* **1993**, *97*, 2507-2
5. Zhao, C.; Wang, Y.; Hruska, Z.; Winnik, M.A. Molecular Aspects of Latex Film Formation: An Energy-Transfer Study. *Macromolecules* **1990**, *23*, 4082-4087

Acknowledgements

- Xiaozhou Chen