Introduction

Latex film formation has been of commercial importance for many years, particularly in the paint industry. Since the 1960s latex paints have largely replaced oil-based paints, which have been known to contain hazardous amounts of lead. The film formation process begins with latex particles in an aqueous dispersion. As the water evaporates, the particles come into close contact and start deforming before they coalesce and the polymer chains interdiffuse. The interparticle polymer diffusion (IPD) undergone by the polymer chains leads to the formation of a homogenous film with good mechanical properties.

Several methods have been investigated in the past to probe IPD, but all have significant drawbacks. A new method recently proposed to probe IPD involves the introduction of pyrene labels into the latex particles.

Pyrene is a fluorescent molecule, widely used because of its good quantum yield and high molar extinction coefficient, which makes it possible to acquire noise-free fluorescence spectra at low pyrene concentrations. Pyrene is typically excited in the UV region, and fluoresces with a lifetime $\tau_M$. If an excited pyrene molecule encounters a ground-state pyrene, an excimer is formed which emits with a lifetime $\tau_E$. The reaction scheme for pyrene excimer formation is depicted in Figure 1 along with the corresponding fluorescence spectrum.

To enable IPD probing during latex film formation, some latex particles will be labelled with pyrene. Pyrene-containing monomers are very hydrophobic and difficult to incorporate into polymeric chains by emulsion polymerization, since they must diffuse across the water phase. To reduce this inherent hydrophobicity of pyrene, an oligo(ethylene glycol) spacer can be incorporated into the monomer.

Experimental Procedures

The synthesis of the pyrene-labelled monomer (PyLM) requires first to ethoxylate 1-pyrenemethanol. This can be achieved by either a coupling reaction (Scheme 1) or anionic polymerization (Scheme 2). The first approach is useful mainly for smaller spacers, up to penta(ethylene glycol). Anionic polymerization is more suitable for longer oligo(ethylene glycol) spacers. In Scheme 1, silver oxide serves as a monoprotecting agent. After the ethoxylolation of 1-pyrenemethanol, it is reacted with methacrylic anhydride in the presence of 4-dimethylamino pyridine (DMAP) to promote the acylation reaction and obtain the desired PyLM (Scheme 3).
Once the PyLM has been obtained, the latex particles may be synthesized. Methacrylate monomers are typically used in latex paints. The copolymerization of butyl methacrylate and the synthesized PyLM was performed via an emulsion polymerization, a heterogeneous free radical polymerization technique. This requires diffusion of the monomer across the water phase and into the particles where the polymerization takes place.

The labelled latex was then mixed with non-labelled latex in a 5:95 weight ratio. The latex mixture was deposited onto a quartz plate, dried overnight, and the resulting film was annealed in a tube immersed in an oil bath. Changes in excimer formation were monitored as a function of the annealing time via steady state fluorescence spectroscopy.

**Results**

For optimal results, the PyLM must be hydrophilic enough to diffuse readily across the water phase during the emulsion polymerization and ensure good incorporation into the latex, but hydrophobic enough not be water-soluble. The monomer must also be sufficiently small so as to not modify properties of the latex such as the glass transition temperature ($T_g$). PyLMs prepared with longer oligo(ethylene glycol) spacers have also been shown to be susceptible to crosslinking in the emulsion polymerization process, which must be avoided.

A PyLM with a tetra(ethylene glycol) linker was first synthesized according to Scheme 1. The reaction was monitored by characterizing the reaction product by proton Nuclear Magnetic Resonance ($^1$H NMR) spectroscopy. The ethylene glycol peaks at 3.5-4.0 ppm confirmed the successful ethoxylation of 1-(bromomethyl)pyrene, while the peaks at 5.5 and 6.2 ppm indicated methacrylation. The $^1$H NMR spectrum and gel permeation chromatography (GPC) analysis results suggested that the desired PyLM had been synthesized; however the monomer was found to have two lifetime components via time-resolved fluorescence, corresponding to the presence of two pyrene species. The existence of a second lifetime might be due to silver oxide complexing and quenching some of PyLMs, but emulsion polymerization was still performed using that monomer.

PyLMs with seven and eight units were also synthesized according to Scheme 2. Only one major lifetime was observed for both PyLMs, which had polydispersivity indices of ca. 1.5 in GPC analysis. This approach is distinct from the method described in Scheme 1, since anionic polymerization really yields a mixture of monomers with different space lengths *averaging* seven ethylene glycol units. Emulsion polymerization was attempted using these monomers, but the resulting polymer was crosslinked. Typical analysis results for the PyLMs are shown in Figure 2.
Figure 2: Characterization of a PyLM using PyEG\textsubscript{7}MA as an example. a) Time-resolved fluorescence decay showing monoexponential behaviour, indicative of one lifetime, b) \textsuperscript{1}H NMR spectrum with assigned signals, c) GPC traces acquired with UV and DRI detectors, d) steady-state fluorescence spectrum.

Once the PyLMs were synthesized, their emulsion copolymerization with butyl methacrylate could be performed to obtain the desired polymer. Currently, the latex prepared with PyEG\textsubscript{4}MA is the only useable product synthesized. The latex prepared with PyEG\textsubscript{7}MA and PyEG\textsubscript{8}MA were crosslinked and not suitable for film formation.

Figure 3: Spectra for PyEG\textsubscript{4}MA-labelled film after various annealing times. a) Full spectrum, b) close-up of excimer formation.
Steady state fluorescence was applied to monitor pyrene excimer fluorescence during film annealing. Initially, the local pyrene concentration \([Py]_{\text{loc}}\) in the fluorescently labeled latex particles was large, which resulted in the formation of numerous pyrene-pyrene dimers that led to strong excimer fluorescence. As the film was annealed, the latex boundaries disappeared and the pyrene-labelled chains diffused out of the fluorescently labelled particles to enter the non-fluorescent particles. This process reduced \([Py]_{\text{loc}}\), the formation of pyrene-pyrene dimers, and thus the excimer fluorescence intensity. The use of PyLMs prepared with longer oligo(ethylene oxide) spacers should result in higher incorporation of the PyLM into the fluorescently labeled latex, which should boost excimer fluorescence and thus enable more efficient detection of the fluorescence signal during film formation.

**Further work**

The chemical composition of the PyLM remains to be optimized to maximize the pyrene excimer fluorescence in the latex, while minimizing possible changes in \(T_g\) due to the incorporation of the PyLM. PyLMs with 5 and 6 ethylene glycol units will be synthesized and characterized. A chain transfer agent may be used in the emulsion copolymerization procedure to prevent crosslinking as was observed during the emulsion polymerization of the PyEG\(_7\)MA and PyEG\(_8\)MA monomers.