

# Photo-Enforced Stratification

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## Introduction

Traditional polymerization techniques result in a homogenous final polymer. However, it is advantageous to have different properties at the surface compared to the bulk of the polymer film, as achieved by differences in chemical composition. Current methods for achieving such a composition gradient include wet on wet coating,<sup>1</sup> incorporation of low surface energy monomers,<sup>2-4</sup> and solvent evaporation.<sup>5</sup> Most of these methods involves multiple step processes, are expensive, and/or time consuming. Photo-enforced stratification could potentially yield films with a controllable surface chemical composition that differs from the bulk average composition in a straightforward, single step process. This level of control over the surface chemical composition would allow for significant advances in photo-cured systems.

Photopolymerization is an efficient method of polymerization with many intrinsic advantages over other polymerization methods including low to no volatile organic compound emissions and low energy consumption for polymerization.<sup>6,7</sup> Additionally, photopolymerization affords spatial and temporal control.<sup>8,9</sup> Taking advantage of the spatial and temporal control of photopolymerization yields the control over the polymerization reaction that is necessary for photo-enforced stratification to occur.

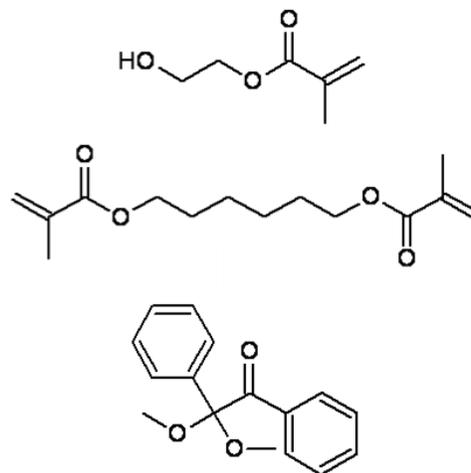
Photo-enforced stratification exploits differences in monomer reactivity of monomers in a co-photopolymerization to allow for the possible creation of stratified films in a single reaction. To allow such a process, the photopolymerization takes place in the presence of a light gradient with the most intense light at the surface of the thin film. This light gradient is established by the addition of a chromophore that absorbs the same wavelength of light that is used to initiate the polymerization. When the polymerization occurs in the presence of the light gradient, the monomer with a higher reactivity will preferentially polymerize inducing a reduced localized concentration. As a result of the lower localized concentration, more monomer will diffuse from the bulk to the surface which induces a counter diffusion of the other monomer to the bulk. The diffusion and counter diffusion, with a sufficient light gradient and difference in monomer reactivity, would therefore result in a polymer film that has a different surface chemical composition from the bulk average. For example, diene monomers react much faster than comparable mono-enes.<sup>10</sup> As dienes polymerize, after the first double bond reacts with a radical, the second unreacted double bond of the diene monomer is in close proximity to the active site of the growing chain end resulting in faster reaction kinetics compared to mono-ene monomers. The inherent difference in the reactivity of a mono-functional versus a di-functional monomer could be used as a driving force for photo-enforced stratification which could result in higher functionality monomers being enriched at the surface of the polymeric thin film.

## Experimental

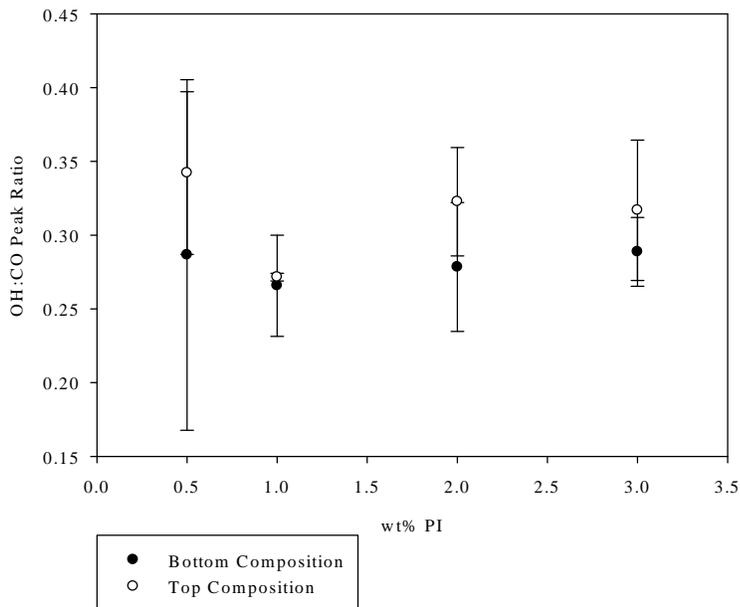
The monomers used for these studies were 2-hydroxyethyl methacrylate (HEMA), and 1,6-hexanediol dimethacrylate (HDDMA) (see Figure 1 for chemical structures). All formulations were composed of a one to one weight ratio of mono-functional monomer to the di-functional monomer. The photoinitiator used was  $\alpha$ ,  $\alpha$ -dimethoxy- $\alpha$ -phenylacetophenone (DMPA). Films were polymerized under nitrogen and between two glass slides with additional glass slides used as spacers. This results of approximately one millimeter thick films. The top and bottom of the films were analyzed with attenuated total reflectance (ATR) infrared Fourier transform spectroscopy. Quantitative information regarding the composition of the surfaces of the film was determined by examining the height ratio of the hydroxyl peak which is only present in the mono-functional monomers, to the carbonyl peak, which is present in both monomers.

## Results and Discussion

Copolymerization mixtures utilizing both a di-ene and mono-ene monomer that form cross-linked networks were investigated. The light gradient is created by the photoinitiator and the strength of the light gradient is controlled with the concentration of the photoinitiator. The films lend themselves to analysis by ATR infrared Fourier transform spectroscopy because the only molecule in the formulation that contains the hydroxyl functional group is the mono-ene monomer. ATR yields a vibrational spectrum of the very near surface region, and therefore is an ideal analytical tool to determine if photo-enforced stratification has occurred. By tracking the location and relative abundance of the hydroxyl peak, the location and relative concentration of the mono-functional monomer can be determined.



**Figure 1.** Chemical structure of 2-hydroxyethyl methacrylate (HEMA), 1,6-hexanediol dimethacrylate (HDDMA), and  $\alpha$ ,  $\alpha$ -dimethoxy- $\alpha$ -phenylacetophenone (DMPA) from top to bottom respectively.



**Figure 2.** Calculated peak ratio of various one to one HEMA to HDDMA systems when polymerized using 7 mW/cm<sup>2</sup> light. The top and bottom compositions are approximately equal showing that photo-enforced stratification does not occur.

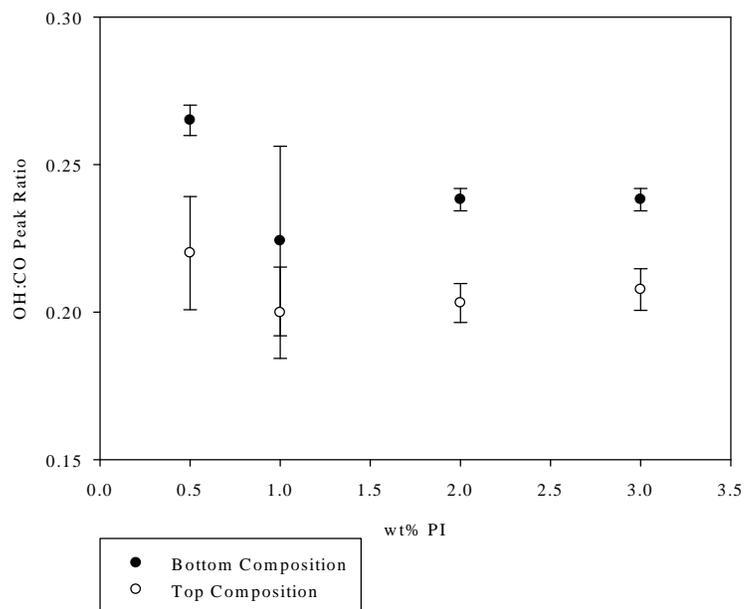
A mixture containing a one to one ratio, by weight, of HEMA and HDDMA was produced with various amounts of photoinitiator, DMPA. HDDMA will react faster than HEMA and as such should be found enriched at the surface of the film if photo-enforced stratification takes place. From the ATR-IR spectra the peak height of the hydroxyl peak and carbonyl peak was determined and a ratio of the hydroxyl to carbonyl peak heights was calculated. The peak height ratio was used as a means for quantifying the relative amount of HEMA to HDDMA at the top and bottom surfaces of the film. When the films were polymerized with a light intensity of 7 mW/cm<sup>2</sup> at 365 nm, there is a small difference between the top and bottom hydroxyl to carbonyl ratio. Due to the large error bars, however, the top and bottom composition are statistically the same (Figure 2), implying that little, if any, photo-enforced stratification is achieved.<sup>11</sup>

In order to test if this system will undergo photo-enforced stratification by polymerizing the system more slowly, the rate of polymerization was decreased by decreasing the light intensity to 1.4 mW/cm<sup>2</sup> which should decrease the rate to approximately half the rate of polymerization when using 7 mW/cm<sup>2</sup> (Figure 3). This decrease in the rate of polymerization allows for a longer time for diffusion and thus perhaps for photo-enforced stratification. Again, the hydroxyl to carbonyl peak ratio was calculated to determine the relative amounts of HEMA to HDDMA at the top and bottom of the film. Interestingly for all formulations, the top ratio is lower than the bottom ratio with a maximum difference of about thirty percent. The difference is direct evidence that the chemical compositions at the top and bottom of the film is substantially different and that a chemical composition gradient has been achieved. Slowing the polymerization down allows sufficient time for monomer diffusion to occur resulting in stratified films. This behavior illustrates that it is possible to observe photo-enforced stratification in cross-linked systems with sufficiently slow rates of polymerization. Additionally, the inherent differences in the reaction rates of mono-methacrylate and di-methacrylate monomers are sufficient to allow for enrichment of the di-functional monomer at the surface.

Substantial photo-enforced stratification is observed at almost all photoinitiator concentrations, (Figure 7). Since the hydroxyl is attached to the HEMA and the top ratio is lower than the bottom ratio, this photo-enforced stratification process results in an enrichment of the cross-linking HDDMA at the surface. The enrichment of HDDMA appears to be approximately thirty percent at higher initiator concentrations.

## Conclusions

Photo-enforced stratification is a processing technique that allows for the production of polymer films with controllable surface chemistries in a single reaction step by taking advantage of the spatiotemporal control of photopolymerization. Differences in monomer reactivity are a prerequisite for stratification to occur and the stratification can be predicted with the preferentially reacting monomer enriching the surface of the film. The difference in reactivity for a dimethacrylate versus a mono-methacrylate is sufficient to allow such enrichment. At appropriate polymerization conditions, thirty percent enrichment of the dimethacrylate is achieved at the surface.



**Figure 3.** Calculated peak ratios of various one to one HEMA to HDDMA systems polymerized using 365 nm light at 1.4 mW/cm<sup>2</sup>. The top and bottom compositions differ at virtually all photoinitiator compositions, showing that photo-enforced stratification has occurred with enrichment of HDDMA at the surface.

At appropriate polymerization conditions, thirty percent enrichment of the dimethacrylate is achieved at the surface.

## References

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