



Characterizing Cleavage of Photolabile Polymers

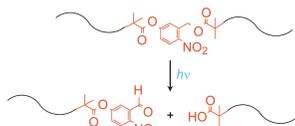
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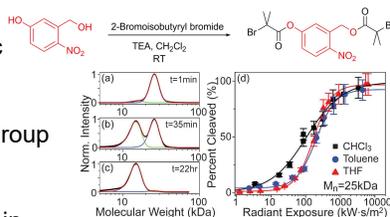
Abstract

Smart polymeric materials respond to well-defined stimuli, such as light or mechanical energy. Given the selectivity of the response, these materials have found applications in therapeutics and in defense. In the present work, we synthesize a series of smart polymers that respond to UV light by integrating a UV cleavable group into the center of the polymer chain. When the material is exposed to UV light, it breaks in half. Because the response rate is governed by the interaction of the polymer with the environment, one strategy for tuning this behavior is to change the polymer composition. The series of polymers synthesized in the present work begins to study this dependence.



Background

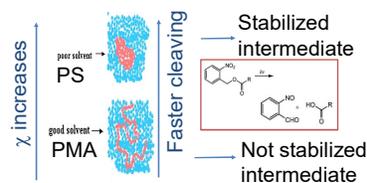
In previous work, the Armani lab synthesized a bifunctional asymmetric initiator for an atom transfer radical polymerization (ATRP) reaction. The initiator contained the photocleaving group (ortho nitrobenzyl, ONB). Using this initiator, photo-responsive PMA was synthesized and its cleaving behavior in three different solvents and in film was characterized. A clear dependence on solvent was observed.



(a)-(c) GPC of the reaction at three different time points. (d) % cleaved vs. UV exposure of the photo-responsive PMA in three different solvents.

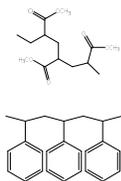
Synthesis of UV Polymers

One of the theories behind why different polymers might affect the rate at which the system cleaves is that different polymer chains might stabilize the ONB cleaving intermediates.



To extend this previously work and verify the theory that the rate is dependent on the interaction between the solvent and the polymer, I synthesized PMA and PS. Additionally, the synthesis of pHEMA is underway. To characterize the polymers I created I used both Gel Permeation Chromatography (GPC) and Nuclear Magnetic Resonance (NMR). The NMR and GPC both informs the percent conversion of the polymerization reaction as well as molecular weight and the GPC informs the PDI of the polymers. A narrow PDI is one below 1.5.

Name	MW	PDI	Ratio ¹
Poly(Styrene)	5k	1.09	300:1:1.5:1.5 (10%)
Poly(Methyl Acrylate)	8k	1.03	800:1:2:2 (10%)
Poly(HEMA) ²	--	---	---



¹The ratio is defined as: [Monomer]:[ONB]:[PMDETA]:[CuBr] and then the volume % of solvent.

²Currently working on creating poly(HEMA)

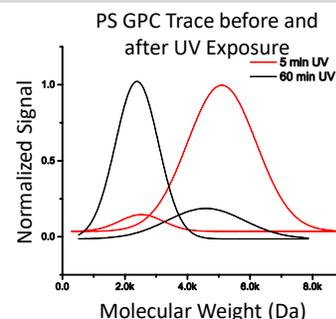
³C.E.H. Bawn, M.A. Wajid. "Vapour pressure of polystyrene solutions in acetone, chloroform and propyl acetate." Trans. Faraday Society, 1956 (52), p. 1658-1664 (<http://pubs.rsc.org/en/content/articlelanding/1956/ft/f9565201658#divAbstract>)

⁴Journal Chem Engr Data, 1994 (39) (<http://pubs.acs.org/doi/pdf/10.1021/je00016a024>)

⁵Determination of Solvent-Polymer and Polymer-Polymer Flory-Huggins Interaction Parameters for Poly(3-hexylthiophene) via Solvent Vapor Swelling. Macromolecules, 2013. (<http://pubs.acs.org/doi/pdf/10.1021/ma400597j>)

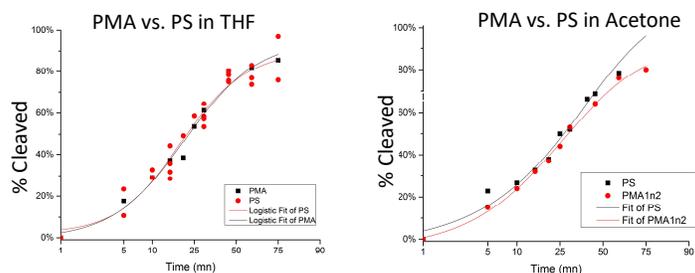
Photocleavage Characterization

To test if the polymers would bifurcate after exposing them to UV light I would take a Gel Permeation Chromatography (GPC) spectrum before and after exposure. If the GPC spectrum showed a shift from a certain MW to 1/2 that molecular weight then the ONB functional group could be confirmed as being in middle of the polymer.



To study the photocleaving rate dependence in the different solvents, I first did UV exposure experiments on PMA and PS in THF since both polymers have similar Flory-Huggins parameters in THF ($\chi = 0.425^3$, $\chi = 0.414^4$, for PMA and PS). I created two 20-mL vials. One with 0.05-mM polymer in THF, and the other in HPLC-grade THF. I placed 1-mL of the polymer in a glass cuvette and exposed the cuvette for times ranging between 0-min and 90-min at 500 lumens. I put each exposed aliquot of polymer into a GPC vial and measured its GPC trace.

These same experiments were also performed in Acetone where the Flory-Huggins parameters for each solvent differed ($\chi=0.482^4$, $\chi= 0.6^5$ for PMA and PS, respectively, at same conditions).



PMA and PS cleave at similar rates under a THF solution where they have similar polymer-solvent interaction parameters. They cleave at different rates under an Acetone solution where they have different polymer-solvent interaction parameters. This reinforces the hypothesis that the interaction between the polymer and solvent plays a role in the cleaving kinetics and cleaving mechanism of the polymer with the ONB photo-responsive group.

Future Work

I am currently attempting to synthesize poly(HEMA) as this polymer has very different solvent-polymer interaction and it is FDA approved, bio-degradable and water-soluble, which could be useful in many biological applications.

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