Title: Light Initiated Radical Polymerization of Ethylene glycol dimethylacrylate (EGDMA) and 2-hydroxyethyl acrylate (HEA)

Introduction:

The following experiment is investigating photo-polymerizations and polymeric cross-linking. We will be investigating the effects of the presence of oxygen, the wavelength of applied light, and the presence and concentrations of different monomers on polymerization reactions. We will use macroscopic observations to monitor a variety of polymerizations.

Procedure:	Notes:
Prepare six samples in glass vials. ~~Each~~ To each vial, add 1.0mL of 0.0156M DMPA in N,N-dimethyl formamide (photoinitiator soln.) and 1.0g EGDMA. ~~Close the vials~~ Seal the vials - 3 with plastic caps and 3 with septa — and insert a ~~need~~ needle into each of the 3 septa. Collect a balloon syringe and have it filled with N_2 by the TA. Pierce the septum of ~~the~~ a DeOx vial with the needle on the syringe, make sure the needle is under the liquid level and degas the vial. Repeat for each DeOx vial.	* Capped vials will be referred to as "Ox" and septum, "DeOx"
Collect 3 photoreactors of 3 different ~~type of light~~ wavelengths of light. Place a DeOx vial and an Ox vial in each photoreactor. Activate the photoreactors and allow the samples to react for 45mins, checking progress every ~15min.	

Notes:

Record observations in a data table after ~~the 45 min. ends~~ each 15min interval. After the 45 min., use a spatula to test the hardness of the polymers created.

Calculate a low, medium, and high mole ratio of HEA to EGDMA.

low: 1:1 - 10:1
med: 10:1 - 25:1
high: ≥ 25:1

Collect a mold from the TA and add 2.00mL DMPA in DMF along with a calculated ratio of monomers. Do this for each of the 5 calculated ratios. Record physical properties for each ratio of monomers. Place the copolymer in a 100mL beaker of water in the lab drawer. Weigh the polymer after a week in the H_2O.

*Weigh polymer

Pre-Lab Questions:

① The Violet photoreactor ~~emits~~ emits higher energy photons. Violet light ~~is composed of photons with a higher frequency and shorter~~ occurs at a higher frequency and shorter wavelength than red light. Light with a shorter wavelength ~~(λ)~~ (λ) and higher frequency (ν) is higher in energy.

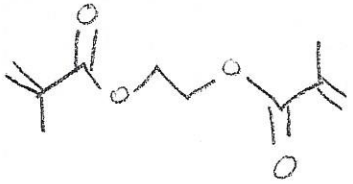
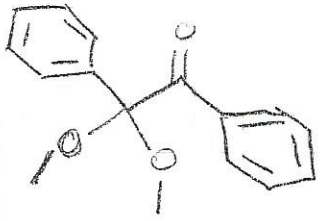
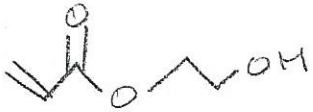
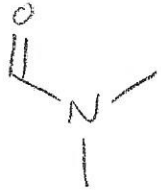
② A peroxide is a bond between adjacent oxygens. The most simple peroxide is H_2O_2. O–O bonds are relatively weak and nonpolar, so they are easy to cleave and cleave homolytically.

③



Structure (A) is the least stable, as there can be no resonance stabilization and the radical is primary. Structure (B) is the most stable as it is the only structure that ~~can~~ is resonance stabilized.

Pre-Lab Data

Compound	Molecular Mass (g/mol)
 EGDMA	198.22
 DMPA	256.30
 HEA	116.116 g
 DMF	73.10

Amount Photoinitiator: 1.0 mL
Amount EGDMA: 1 mL

	Red		Violet		~~UV~~ UV	
	Ox.	DeOx	Ox	DeOx	Ox	DeOx
Initial	- Transparent - light viscosity (more than H_2O) - No polymerization	- Transparent - Low Viscosity (more than H_2O) - No polymerization	True for all at time: 0 min. → (written incorrectly, switch boxes)			
15 min	- no change - no obvious polymerization	- no change - no obvious polymerization	- Opaque - polymer starting to form - liquid on surface	- Starting to polymerize, - becoming opaque - thin layer solid (bottom)	- polymerized - solid/gel-like	- polymerized - solid/gel-like
30 min	- no change - no polymerization	- no change - no polymerization	- ~~Opaque~~ Half solid (opaque); half clear liquid - Half polymerized	- Opaque - completely solid - (fully) polymerized.	- completely polymerized - wrinkled solid - Opaque	- completely polymerized - Smooth, even solid - Opaque
45 min.	- no change - no polymerization	- no change - no polymerization	- Completely polymerized	- ~ 3/4 polymerized - layer of liquid on top	- completely polymerized - Opaque - Same as at 30 min	- completely polymerized - Opaque - Same as 30 min.

$$\text{EDGMA mass (g)} = 2\left(\frac{\text{EDGMA molar mass}}{\text{EDGMA molar mass} + (\text{ratio numerator} \times \text{HEA molar mass})}\right)$$

Low Ratio (5:1) $\text{EDGMA mass (g)} = 2\left(\frac{198.22\ g/mol}{198.22\ g/mol + (5 \times 116.116\ g/mol)}\right) = 0.509\ g$

$\text{HEA Mass (g)} = 2 - 0.509\ g = 1.491\ g$ HEA

Q1 When applying a dental filling, the filling would need to be liquid in order to be maleable enough to completely fill a cavity. After application, a solid filling is necessary. Temperature resistance, hardness, ~~not toxic~~, impact resistance, and resistance to swelling/shrinking would be ~~true~~ necessary for a dental filling. Chewing is a ~~constant~~ act performed daily that involves a variety of temperatures and pressures. Teeth are put under harsh conditions, which requires a certain level of resiliance.

Calculations (Cont.):

Middle Ratio (20:1) $EDGMA\ mass(g) = 2\left(\frac{198.22\ g/mol}{198.22\ \frac{g}{mol} + (20 \times 116.116\ \frac{g}{mol})}\right)$

$= 0.157g$ EDGMA

$HEA\ mass(g) = 2 - 0.157g = 1.843g$ HEA

High Ratio (40:1) $EDGMA\ mass(g) = 2\left(\frac{198.22\ g/mol}{198.22\ \frac{g}{mol} + (40 \times 116.116\ \frac{g}{mol})}\right)$

$= 0.082g$

$HEA\ mass(g) = 2 - 0.082g = 1.918g$

Q2 I expect that a ~~polymer~~ high cross-linking polymer will be more viscous and more opaque than a similar polymer with fewer cross-linkages. If the polymers form a solid material, the high-cross-linking polymer will be harder and less-maleable. The increased number of cross-linkages would allow polymer less movement and provide support, much like bracing, for a material.

Part 2 Conditions:

UV light = caused fastest polymerization

DeOxygenated - produced fastest-forming and most uniform polymer in Part 1.

HEA: EDGMA

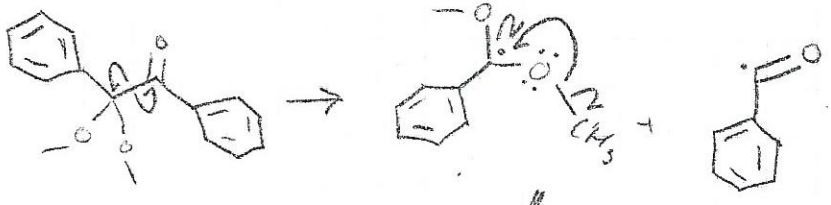
low: 5:1

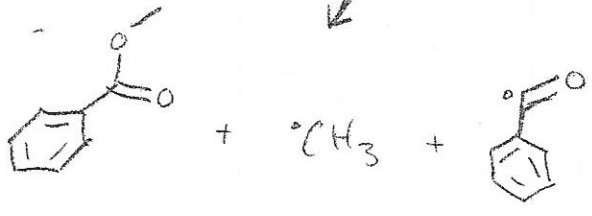
Med: 20:1

High: 40:1

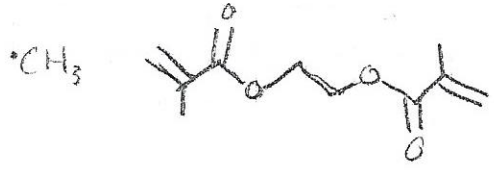
Q3

~~Extinction~~ Initiation:

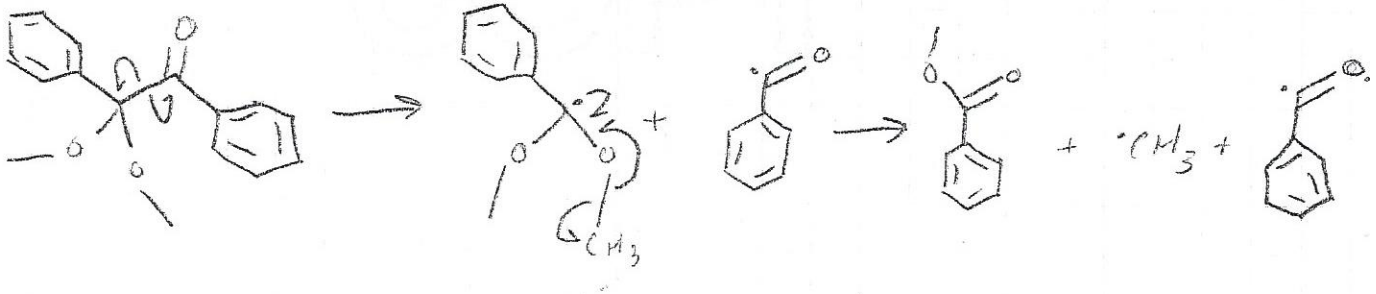




Propagation:



Initiation:



Q4 The high cross-linking polymer is closer to the polymer made in Part 1. EGDMA has two π-bonds ~~that~~ from which a polymer chain can propagate. This allows each individual EGDMA monomer to foster cross ~~linking~~ linkages. This explains the solid product of the polymerization in Part 1.

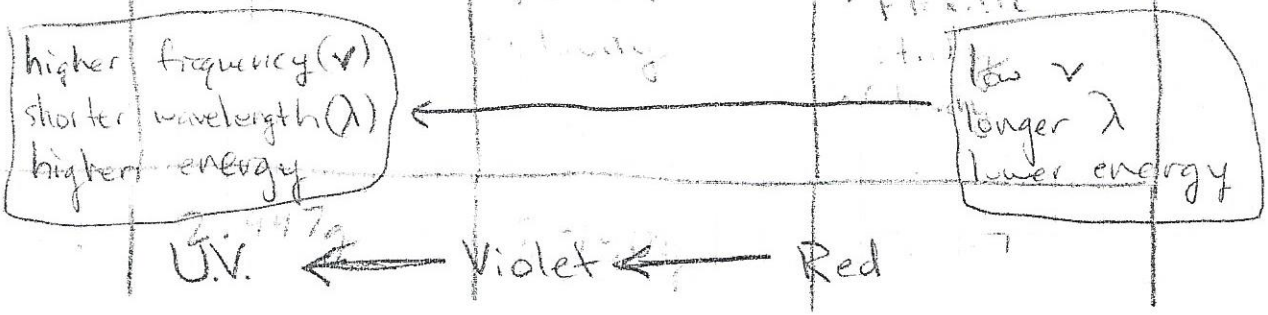
Part 2: Observations

	Ratios		
~~Observations~~	5:1 (Low)	20:1 (Med)	40:1 (High)
Observations	• Hard • Rigid	• Moderately Soft • Flexible • Cloudy	• Softest • Flexible • Sticky • Cloudy
Mass (before H_2O)	2.997g	3.780g	3.027
Mass (After)	3.487g	6.139g	3.618
H_2O absorbed	0.490g	2.359g	0.591g
% Mass increase	~~16.3%~~ 16.3%	62.41%	19.52%

The Report

Q5 The diradical character of O_2 provides sites for the radical initiator or propagating polymer chain to terminate. The radical on ~~the~~ a propagating polymer chain would react with one of the radicals on molecular oxygen. This would remove a radical species from the reaction, thereby inhibiting propagation and terminating the chain. So, when O_2 is present in a radical polymerization, less polymerization will occur, as seen in the only-partially-reacted sample reacted with O_2 present in violet light, while the ~~sample~~ same sample under the same conditions, but deoxygenated instead, polymerized quickly and entirely.

Q6



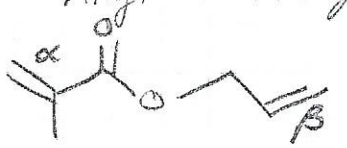
The wavelength of light increases in the order: UV, Violet, Red. The frequency of light increases in the following order: Red, Violet, U.V. A lower wavelength necessitates a higher frequency, so light with a higher frequency and shorter wavelength, like U.V., will have more energy. Red light ~~too~~ is of lower energy. Violet visible light is between U.V. and Red light. The higher energy UV light initiated the reaction quickly whereas the lower energy Red light cleaved no DMPA and generated no radicals to start the reaction.

Q7 DMPA absorbs little to no light at wavelengths ~~where~~ around 600-700nm, which is the light produced ~~at~~ by the Red photoreactor. Light with wavelengths shorter than 400nm ~~for~~ (such as U.V. light) are absorbed by DMPA extensively, as seen in the U.V.-Vis Spectrum of DMPA. The increased absorbance of the U.V. light ~~does~~ in DMPA allows the U.V. light to transmit energy to DMPA, allowing a ~~DMPA~~ DMPA bond to homolytically cleave and form radicals. Red light doesn't transmit sufficient energy to DMPA required to cleave a bond homolytically. Therefore, U.V. can initiate polymerization quickly and Red light cannot form radicals to initiate the polymerization.

Q8 During propagation, a polymerization of ethylene glycol diacrylate (EGDA) would proceed at a faster rate than a polymerization of EGDMA. This is because the radicalized propagating form of EGDA contains a secondary radical, which is more reactive and less stable than the tertiary radical ~~formed~~ present in the propagating EGDMA. Because the radical for EGDA is more reactive, EGDA will propagate at a faster rate in the propagation phase than EGDMA.

Q9

Allyl methacrylate



The left C=C ~~bond~~ bond would react first (labeled α above). The reaction of the left C=C would generate a tertiary ~~carbocation~~ radical, which could also be stabilized by resonance with the local C=O bond. The tertiary structure and resonance possibilities make the radical formed by reaction of the left C=C exceedingly more stable than any radical that can be formed by reaction of the right C=C bond. Since this radical intermediate is so much more stable than the alternatives, it is the most likely to form.

Q10

It takes more energy to dissociate a C=O bond than it does to dissociate a C=C bond. This means that a greater energy input is needed to break the C=O π-bond required for polymerization than for a C=C π-bond to be broken. This barrier of energy for the dissociation of C=O is too high for a realistic polymerization to occur with benzaldehyde. The C=C in styrene ~~has negligible~~ has a dissociation energy roughly 25% lower than O=C in benzaldehyde, which is a more realistic boundary to overcome in π-bond dissociation and radical formation. Additionally, the energy ~~released~~ released by the formation of two C-C bonds is greater than the energy required to break a C=C bond, meaning ΔG can remain negative. For a C=O bond (and C-O formation), this is not true.

Q11 Change in enthalpy (ΔH) for the polymerization reaction must be negative. The reaction performed in the experiment increases order in the system, which means that the change in entropy (ΔS) for the reaction is negative. If we look at the equation for change in Gibbs free energy, ~~$\Delta G = \Delta H$~~ $\Delta G = \Delta H - T\Delta S$, we see that a negative ΔS would make $(-T\Delta S)$ an overall positive value. Since we need the free energy of the system to decrease, we want a negative ΔG. The only way for ΔG to be negative when entropy is decreasing (ΔS is negative) is for enthalpy to decrease (ΔH is negative). So, the driving force behind the polymerization reaction is enthalpy and the system's desire to decrease its enthalpy. to be specific.

Q12 The polymer with the lowest HEA:EGDMA ratio would be the most fitting for a dental filling. The 5:1 (HEA:EGDMA) polymer ~~is~~ is the hardest polymer we made and it absorbed the least amount of water. EGDMA is difunctional and HEA is monofunctional, so EGDMA facilitates cross linking and HEA does not. ~~We won the~~ The larger relative amount of EGDMA in the 5:1 (HEA:EGDMA) lead to a more cross-linked polymer, which is more rigid and less absorbant because of the increased ~~rig~~ rigidity of the polymer's structure. The other polymers made were more flexible and tended to break up when handling. They also absorbed significantly more water. These are not properties desired in a dental implant and these properties are a result of the lack of cross-linkages.

Q13 Our ~~methacrylate~~ 20:1 (HEA:EGDMA) polymer absorbed significantly more water than our 5:1 and 40:1 polymers. Our 5:1 and 40:1 polymers absorbed minimal water, with 5:1 gaining the least mass. The most rigid polymer was the 5:1 polymer and the ~~most~~ least rigid polymer was the 40:1 polymer with the 20:1 polymer being in the middle. After a week in deionized water, the 5:1 polymer's mass increased by 16.3%, the 20:1 polymer's mass increased by 62.4%, and the 40:1 polymer's mass increased by 19.5%. If I were designing diapers, I would look for the most absorbant material I could find. Of the polymers made in part 2, the ~~&~~ 20:1 (HEA:EGDMA) polymer was the most absorbant, which would make it the best material for diapers. Additionally, the 20:1 polymer was not rigid, so it would more readily work in a wearable item, such as a diaper.

~~Q10 (redo)~~

~~2(C=O) 799 =~~

~~2(C=O) + (C=O) = energy of~~