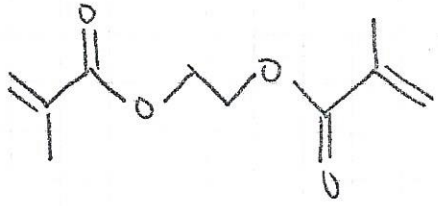
Introduction

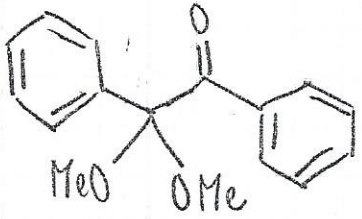
The purpose of this lab is to synthesize polymers via a photopolymerization reaction. We will also look at the effects of the wavelenght of light on photopolymerization.

Preliminary Data

compound	molecular weight	m.p	b.p.	density
DMPA	256.30 g/mol	67-70°C	109°C	—
N,N-dimethyl-formamide	73.09 g/mol	-61°C	153°C	0.944 g/cm^3
EGDMA	198.22 g/mol	-40°C	260°C	1.055 g/cm^3
nitrogen	14.001 g/mol	-210°C	-195.8°C	0.808 g/cm^3 liquid
HEA	116.116 g/mol	-60.2°C	210°C	1.1 g/cm^3



EGDMA



DMPA



HEA

Pre-lab questions

1. The violet will emit higher energy photons this is because a higher frequency will emit higher energy photons and violet is a higher frequency than red.
2. A peroxide is ROOR. It may be a good initiator because it is a high energy bond that could easily be broken into two •OR radicals.
3. • this is the most stable because of conjugation.

   • this is the least stable because it is on a primary carbon with no conjugation

Procedure

Part 1:

You will need 6 glass vials, 3 septa, 3 vial caps, 3 short needles, 3 long needles, and 3 balloon syringes.

Add 1.0mL of the photoinitiator solution and 1.0g of EGDMA into each glass vial. Cap 3 of the samples and cover the other three with septa. Carefully insert a short needle into the middle of each septum.

Insert the long needle through the septum until the tip of the needle is submerged in the liquid. Gently squeeze the balloon to purge the solution with nitrogen.

Place two samples into each of the three photoreactors. Allow to react for 45 minutes. Record your observations every 15 minutes.

Part 2:

Prepare 3 samples: (1) low mole-to-mole ratio of HEA to EGDMA (less than 10:1) (2) medium ratio (between 10:1 and 25:1), (3) a high ratio (more than 25:1).

For each sample, obtain a mold and add 2.0mL of the DMPA in DMF solution, followed by the 3 different amounts. Allow to react for 45 minutes in the optimal photoreactor. Record your observations.

Record the mass of your polymer. Fill a 100mL beacker half full with distilled water and place your sample in the beaker.

		15minutes	30minutes	45minutes
red	oxy	clear; appears liquid still; no change; not polymerizing	no noticable change	no polymerization present
	deoxy	clear; appears liquid still; no change; not polymerizing	no noticable change	no polymerization present
violet	oxy	half solid and half liquid; somewhat maintained form when flipped over	cloudy at the bottom; more solid but still a lot of liquid on top.	no difference; some polymerization; very hard
	deoxy	this was mostly solid and a little liquid on top; mostly maintained form	very cloudy and solid on the bottom but some clear liquid on top.	no difference; some polymerization; very hard.
ultraviolet	oxy	flipped it upside down and it didn't move; very cloudy; solid	same amount of cloudiness and just as solid; no noticable change	very hard but dented when hit with the spatula
	deoxy	flipped it upside down and it didn't move; very cloudy; solid	no real change; the top layer seemed to have some bubbles; rough	cracked but very hard

low ratio: (5:1) EGDMA mass $= 2\left(\frac{198.22}{198.22+(5\times116.116)}\right) = 0.509\text{g} = 0.48\text{mL}$

HEA mass $= 2 - 0.509 = 1.491\text{g} = 1.36\text{mL}$

medium ratio: (15:1) EGDMA mass $= 2\left(\frac{198.22}{198.22+(15\times116.116)}\right) = 0.204\text{g} = 0.19\text{mL}$

HEA mass $= 2 - 0.204 = 1.796\text{g} = 1.63\text{mL}$

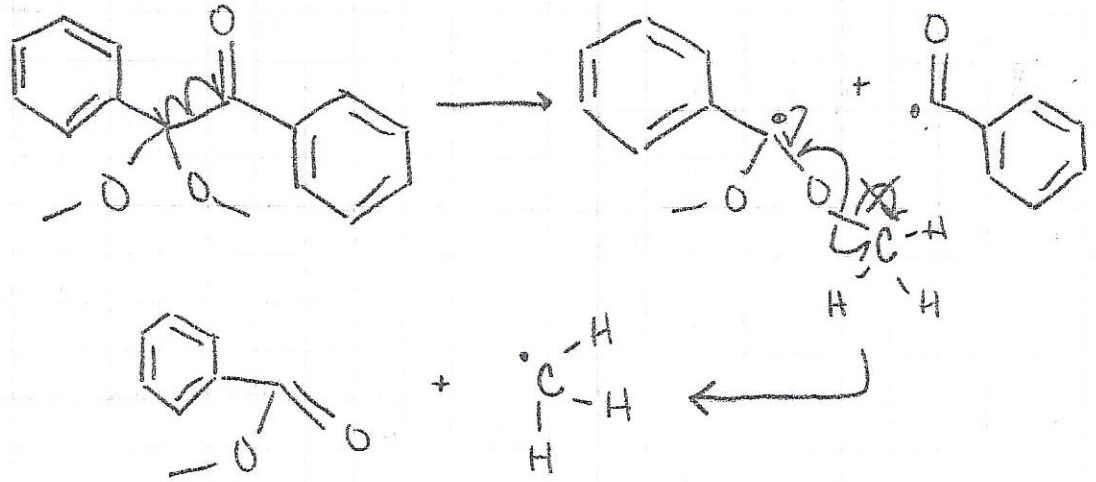
high ratio: (30:1) EGDMA mass $= 2\left(\frac{198.22}{198.22+(30\times116.116)}\right) = 0.108\text{g} = 0.10\text{mL}$

HEA mass $= 2 - 0.108 = 1.892\text{g} = 1.72\text{mL}$

Q1. You would want the material to be liquid and pliable. After applied, it should become solid and cemented to the tooth so it won't move.

Q2. High cross linking for the polymer will lead to a solid state of matter, unflexibility and hardness. This is because they are more tightly packed and less free to move around. Low cross linking for the polymer will lead to a liquid state of matter, flexibility and softness. This is because they are spread out and free to move.

Q3.



Q4. We think our polymer has a high amount of cross-linking because it is very hard and not flexible.

Observations for Part 2:

After 22 minutes, all three had polymerized. All pretty hard, a little flexible.

mass 5:1 = 4.107g		after sitting	4.366g
mass 15:1 = 3.955g		in distilled	6.013g
mass 30:1 = 3.894g		water:	6.502g

Q5. Polymerization might be inhibited by the presence of oxygen because the diradical of oxygen may react with the other radicals, causing it not to polymerize.

Q6. Ultra violet has the shortest wavelenght and red has the longest wavelength. Waves with a short wave length have the most energy, therefore ultraviolet has the most energy and red has the least amount of energy. The shorter the wave length and the greater the energy the better the reaction proceeds towards polymerization.

Q7. The absorbance is much higher for a wavelength like ultraviolet compared to the absorbance for a wavelength like red. Therefore, the reactivity is much higher for ultraviolet, which makes sense from our results.

Q8. Ethylene glycol diacrylate will be a faster reaction because it will be less stable. This is because there are no methyl groups so the carbons are less substituted.

Q9. The double bond on the left will be incorporated into the polymer first because it leaves a 3° radical and there will also be resonance so it will be the most stable molecule.

Q10. The radical energy will provide enough energy to break the carbon-carbon double bond but not enough energy to break the carbon-oxygen double bond.

Q11. The ΔH will be the driving force for this reaction because the entropy change is very negative. The change in enthalpy must be less than $T\Delta S$ because $\Delta G = \Delta H - T\Delta S$. and ΔG has to be negative for a spontaneous reaction.

Q12. Out of all of the polymers generated, the deoxy in ultraviolet light aligned best with our desired properties. The other ones didn't allign because they didn't form quick enough, weren't hard enough or they crumbled under touch. The greater the cross linkage the harder the material.

Q13. 5:1 absorbed 0.259 g of water, 15:1 absorbed 2.058g of water and 30:1 absorbed 2.668g of water. 5:1 absorbed 6.3% of its original weight in water. 15:1 absorbed 52% of its weight in water and 30:1 absorbed 69% of its original weight in water.

The 5:1 was the hardest but it still broke when touched and the others were pretty pliable and broke easily.
The 30:1 ratio polymer absorbed the most liquid compared to its weight, therefore, this polymer would be the best to use in a diaper because it absorbs a lot. We believe having an even higher HEA to EGDMA ratio (around 50:1) would have an even higher absorbance, therefore being better for diapers.

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