Pre-lab Questions:

1. The violet photoreactor emits higher energy photons because it has a smaller wavelength. The red photoreactor has a wavelength between 620-750 nm and the violet photoreactor has a wavelength between 380-450 nm. The smaller the wavelength, the higher the frequency which means higher energy.

2. A peroxide is a compound with an oxygen-oxygen bond, RO-OR. A peroxide would be a good initiator for radical reactions because the O-O bond is very unstable so it will undergo homolytic bond cleavage, leaving two radicals that are able to react.

3. 

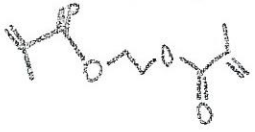
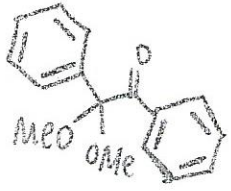
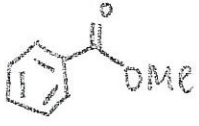
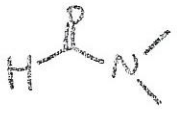
least stable ⟶ most stable
1 3 2

Structure 1 is least stable because the radical is on a primary carbon which cannot stabilize it. Structure 2 is most stable because it has a double bond which allows for resonance. Resonance structures stabilize radicals very well.

Introduction:

The purpose of this lab is to learn how to synthesize cross-linked polymers using monomers. These polymers will be made in oxygenated and deoxygenated conditions and it will be determined which is favorable. The effect of the wavelength of light on photopolymerization will be determined using three photoreactors (red, violet, and ultraviolet). The macroscopic properties of the various polymers, such as water absorbance, will also be determined.

Preliminary data:

Compound	Structure	mp (°C)	bop (°C)	density (g/mL)	MW (g/mol)
ethylene glycol dimethacrylate (EGDMA)		-40	98-100	1.05	198.22
2,2-dimethoxy-phenylacetophenone (DMPA)		67	169		256.3
Methyl Benzoate		-15	199	1.08	136.15
N,N-dimethylformamide (DMF)		-61	153	0.948	73.09
2-hydroxyethyl acrylate (HEA)		-60.2	210	1.1	116.116
water		0	100	1	18.02

Procedure:

Obtain six glass vials, three septa, three vial caps, three short needles, ~~three~~ three long needles, and three balloon syringes. For each sample, add 1.0 mL of the photoinitiator solution and 1.0 gram of EGDMA. Cap three and cover the other three with septa. Insert a short needle into the septum. Take a balloon syringe and a long needle to the nitrogen tank. Insert the needle until the tip is submerged in liquid. Gently squeeze

the balloon to purge the solution. Remove the short needle and then the balloon syringe. Place two samples, one oxygenated and one deoxygenated, into each of the three photoreactors. Allow them to react for 45 minutes. Monitor the reactions every 15 minutes and record observations. If you get a polymer, touch it with a spatula tip to gauge the hardness. Calculate monomer amounts.

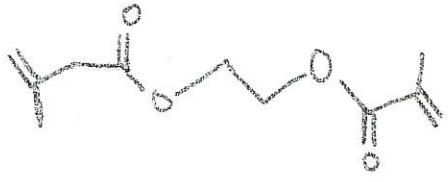
Part 2:

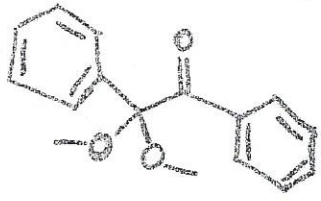
Summarize observations. Prepare three samples: (1) a low mole-to-mole ratio of HEA to EGDMA, (2) a medium ratio, and (3) a high ratio. Obtain a plastic mold. Add 2 mL DMPA & PMF solution to the mold. Then add the correct amount of monomer. Place this in the optimal photoreactor. Record all observations after the 45 minutes has passed. Record mass of polymer. Fill a 100 mL beaker halfway with distilled water and put the sample in the beaker. Store the beaker in the lab drawer. Record mass of polymer next lab period. Calculate the water absorbance ratio by dividing the final mass of the polymer by its initial mass.

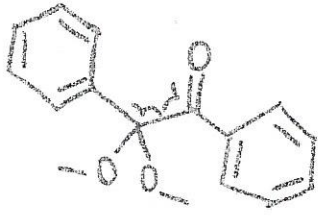
(Q1) When the material is being applied, you want it to be liquid, but once it has been applied, you want it to be a solid. You would want the solid to be hard and insoluble. Initially you want it to be a liquid so it flows easily and can conform to the tooth but after applied you want it to be hard so it doesn't break and insoluble with everyday acids so it does not dissolve.

(Q2) As the amount of cross-linking increases, the hardness increases and the flexibility of the polymer decreases. The polymer with high cross-linking is tightly packed and this structure would be harder and less flexible than one with less cross-linking.

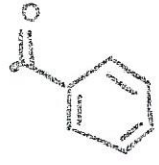
(Q3)

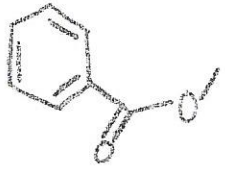














(Q4) The high amount of cross-linking polymer is the polymer we made in part 1 (better resembles it) because it was hard when we touched it with the spatula tip. The EGDMA is divinyl which allows for high cross linking which is why the polymer was hard.

Part 1 Observations:

Photoreactor	Time (min)	oxygenated/deoxygenated	observations
violet	15	oxygenated	liquid
violet	15	deoxygenated	mostly solid with a little liquid
~~violet~~ red	15	oxygenated	liquid
red	15	deoxygenated	liquid
UV	15	oxygenated	opaque solid, rough
UV	15	deoxygenated	opaque solid
violet	30	deoxygenated	same as 15 min.
violet	30	oxygenated	small layer of polymer with liquid on top
red	30	oxygenated	liquid
red	30	deoxygenated	liquid
UV	30	oxygenated	same as 15 min.
UV	30	deoxygenated	same as 15 min.
violet	45	deoxygenated	same as 30 min.
violet	45	oxygenated	slightly thicker polymer layer
red	45	oxygenated	same as 30 min.
red	45	deoxygenated	same as 30 min.
UV	45	oxygenated	less rough
UV	45	deoxygenated	same as 30 min.

Photoreactor	oxygenated/deoxygenated	strength
UV	oxygenated	mildly strong
UV	deoxygenated	strongest
violet	deoxygenated	strong but more jelly-like than UV

Decision: UV photoreactor is the best in deoxygenated conditions and second best in oxygenated conditions so UV light

Calculations:

Low: 5:1 HEA to EGDMA

$$\text{EGDMA Mass (g)} = 2\left(\frac{198.22}{198.22+(5\times116.116)}\right) = 0.51\text{ g } (0.509\text{ g})$$

$$0.51\text{ g} \times \frac{1\text{ mL}}{1.05\text{ g}} = \boxed{0.48\text{ mL}}$$

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

$$1.491\text{ g} \times \frac{1\text{ mL}}{1.1\text{ g}} = \boxed{1.36\text{ mL}}$$

Medium: 20:1

$$\text{EGDMA Mass (g)} = 2\left(\frac{198.22}{198.22+(20\times116.116)}\right) = 0.157\text{ g}$$

$$0.157\text{ g} \times \frac{1\text{ mL}}{1.05\text{ g}} = \boxed{0.15\text{ mL}}$$

$$\text{HEA Mass (g)} = 2 - \text{EGDMA Mass} = 2 - 0.157 = 1.843\text{ g}$$

$$1.843\text{ g} \times \frac{1\text{ mL}}{1.1\text{ g}} = \boxed{1.68\text{ mL}}$$

High: 50:1

$$\text{EGDMA Mass (g)} = 2\left(\frac{198.22}{198.22+(50\times116.116)}\right) = 0.066\text{ g}$$

$$0.066\text{ g} \times \frac{1\text{ mL}}{1.05\text{ g}} = \boxed{0.063\text{ mL}}$$

$$\text{HEA Mass (g)} = 2 - \text{EGDMA Mass} = 2 - 0.066 = 1.934\text{ g}$$

$$1.934\text{ g} \times \frac{1\text{ mL}}{1.1\text{ g}} = \boxed{1.76\text{ mL}}$$

(Q5) In part one we found that the presence of oxygen inhibited the polymerization. Radicals are very reactive so the diradical character of oxygen reacted with the other radicals and terminated polymerization rather than propagated it. An increased amount of radicals in the starting material will inhibit polymerization.

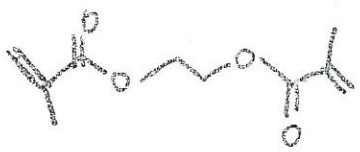
(Q6) The red light has the longest wavelength and UV has the shortest wavelength. As wavelength increases, energy decreases. This is why ultraviolet light has the greatest energy. The light with the most energy, shortest wavelength, created the best polymer. This occurs because initiation of the radicals starts with the addition of light so the light with the highest energy will make the reaction go the best.

(Q7) The figure shows the highest absorbance peak around 320-360 nm which is the wavelength of UV light. The figure shows the absorbance peak to be zero around 620-750 nm which is red light's wavelength.

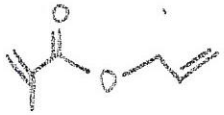
(Q8) If we used ethylene glycol diacrylate instead of EGDMA the speed of the reaction would be slower during the propagation phase because it can not stabilize through resonance. Without resonance, you would have to break the double bond in order to propagate the polymer and that takes a lot of energy.



ethylene glycol diacrylate



EGDMA

Q9 

The double bond on the left will be incorporated into the polymer first due to resonance. Another reason is that this double bond is more substituted so it is more stable than the C=C on the right.

Q10 Styrene will readily polymerize whereas benzaldehyde will not because C-C double bonds have less energy than C-O double bonds. A C-C double bond has 602 KJ/mol whereas benzaldehyde has 799 KJ/mol. Since it has less bond energy, C-C double bonds are easier to break than C-O double bonds.

Q11 The entropy is negative because as a polymer forms it becomes a solid which is more ordered. Enthalpy is the driving force because a negative entropy is not favorable so in order to make the reaction occur, you would need a ~~positive~~ negative enthalpy. Enthalpy has to be ~~positive~~ negative because ΔG must be negative for spontaneous reactions to occur and we know that entropy (ΔS) is negative. Enthalpy has to be strongly negative.
$\Delta G = \Delta H - T\Delta S$

Q12 The polymer that best aligned with the desired properties was the polymer made in UV deoxygenated conditions from part one because it was the hardest, least flexible, and most solid-like. The polymers made in violet photoreactors from part one were not as hard and were more flexible which is not favorable. The polymers made in part two were not high cross linking polymers so they do not have the desired properties we were looking for. These polymers were not as durable and were brittle compared to the polymers made in part 1.

Mass (initial):
Low: 3.654 g
Medium: 3.690 g
High: 3.738 g

Mass (final):
Low: 3.872 g
Medium: 5.745 g
High: 8.262 g

Initial observations:
The low (5:1) was the hardest polymer and the high (50:1) was the ~~the~~ most flexible and softest.

Water absorbance ratio:
$\frac{\text{final mass}}{\text{initial mass}}$

Low: $\frac{3.872 g}{3.654 g} = \boxed{1.06}$

Medium: $\frac{5.745 g}{3.690 g} = \boxed{1.56}$

High: $\frac{8.262 g}{3.738 g} = \boxed{2.21}$

(Q13) Initially we observed that the 5:1 polymer was the hardest and least flexible out of the three polymers. After being submerged in water for a week, we observed that the low conditions (5:1) absorbed the least amount of water and the water absorbance ratio increased as the ratio increased, so the high conditions (50:1) had the highest water absorbance ratio. The 50:1 polymer was also still the most flexible and softest out of the three polymers. The monomeric composition should be 50:1 (a high amount of HEA compared to EGDMA) because HEA is a monofunctional monomer that does not allow for high cross-linking so the polymer would be

soft and flexible. A soft and flexible composition is ideal for diapers because you want them to absorb a lot of fluid but still be flexible.