Part 1 Procedure

First we will collect 6 glass vials, 3 septa, 3 vial caps, 3 short needles, 3 long needles, & 3 balloon syringes. For each of the 6 samples add 1.0 mL of the photoinitiator solution (DMPA in N,N-dimethylformamide) & 1.0 g of ethylene glycol dimethacrylate (EGDMA) into a glass vial. Then cap 3 of the samples & cover the other 3 w/ septa. Insert a short needle into the middle of each septum to allow deoxygenation. For the septum-covered sample, we will take a balloon syringe & a long needle to the nitrogen tank & let the TA inflate the balloon & fasten the needle. Then uncap the needle, & carefully insert it through the septum until the tip of the needle is in the liquid. Squeeze the balloon, then remove the short needle & balloon syringe. Remove long needle from balloon syringe & discard. Then place both a oxygenated & deoxygenated sample into each of the 3 photoreactors & allow them to react for 45 mins, removing & recording observations every 15 mins. If any of the samples polymerized, open & touch w/ spatula tip to record hardness.

Part 2 Procedure

To begin, we will prepare 3 samples. One will be a low mole-to-mole ratio of HEA to EGDMA, another a medium ratio, & the third a high ratio. For each sample, we will obtain a plastic mold from the TA. Then, add 2.0 mL of DMPA in DMF solution to the mold, followed by the determined amounts of monomers. We will place the mold in the photoreactor that is optimal, waiting for 45 mins. Then, remove & poke w/ spatula recording observations. Then record the mass of the polymer, fill a 100 mL beaker ½ full w/ H_2O & place sample in the beaker. Store in our drawer & record the mass again next week.

Pre-Lab

1) The violet photoreactor emits higher energy photons than the red photoreactor. This is because photons with the higher energy have a higher frequency & since $c = \lambda \cdot \nu$ ($\lambda = c/\nu$, $\nu = c/\lambda$), the higher energy, higher frequency photons have a shorter wavelength. Violet light wavelength is much shorter than red light, indicating that the photoreactor emits higher energy photons.

2) A peroxide is a compound containing 2 oxygen atoms bonded together w/ a structure such as R-O-O-R. A peroxide would be a good initiator for radical rxns bc the O-O bond is weak & has a small bond dissociation energy. It can be readily cleaved to give 2 oxygen-centered radicals.

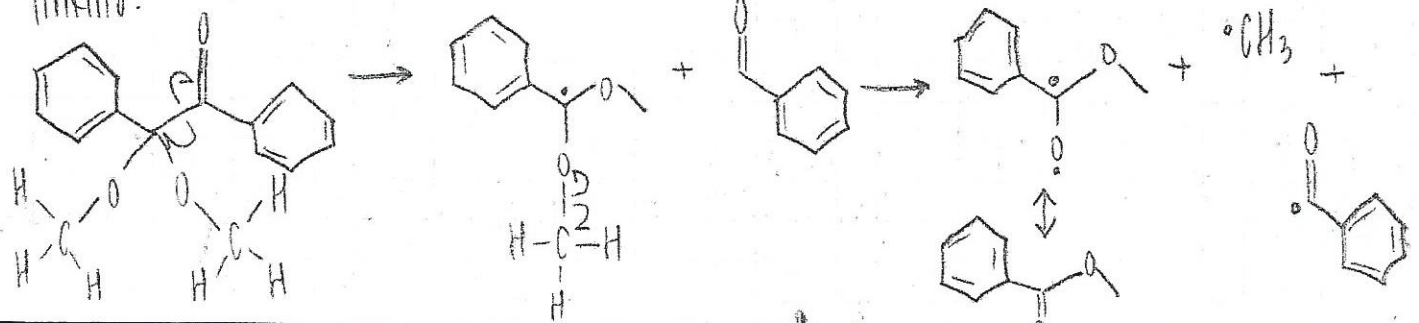
3) The species that is least thermodynamically stable is  This is because it is a primary radical, which is the least stable between primary, secondary, & tertiary radicals. This species is not able to be stabilized by resonance, making it less stable than the 2nd species.

The species that is most thermodynamically stable is  This is because it can be resonance stabilized & although it is a primary radical, this ability greatly attributes to thermodynamic stability, even more than a secondary radical. (third species)

Part I

1) When the material is being applied, we would want it to be in the liquid state so that it can readily mold & form the filling needed. After it has been applied we would want the material to solidify so that it covers the purpose of the filling & does not move around. Another property we would want it to have would be non-toxic & insoluble in water.

2) As the amount of cross-linking increases, the polymer solidification also increases. This is because the monomers are much more closer together & have less freedom of motion. Another factor that would change bc of cross-linking is the size. The polymers would shrink w/ increasing cross-linking.

3) 

5 min

vial	appearance	polymerization
red oxygenated	clear liquid	NO - no solid layer
red deoxygenated	clear liquid	NO - NO solid layer
violet oxygenated	clear-gray solid on bottom layer, clear liquid in top	YES, there is a solid layer on the bottom ~50%
violet deoxygenated	grayish-white solid layer on bottom, small amt of clear liquid on top	YES, there is a solid layer on bottom ~90%
UV oxygenated	clear solid layer	YES, bc the vial contains 100% solid
UV deoxygenated	clear solid layer	YES, bc the vial contains 100% solid

30 min

vial	appearance	polymerization
red oxygenated	clear liquid	NO - no solid layer
red deoxygenated	clear liquid	NO - NO solid layer
violet oxygenated	clear-off-white solid on bottom w/ clear liquid on top	YES, bc there is still solid. ~60%
violet deoxygenated	white solid w/ a drop of liquid on top	YES, still solid layer. ~98%
UV oxygenated	clear solid	YES - solid 100%
UV deoxygenated	clear solid	YES - solid 100%

45 min

vial	appearance	polymerization	hardness
red oxygenated	clear liquid	no- no solid layer	—
red deoxygenated	clear liquid	no- no solid layer	—
violet oxygenated	clear, off-white solid layer w/ clear liquid on top	yes- solid layer on bottom ~5%	soft/soft- can be compressed/scratched
violet deoxygenated	white solid w/ a drop of liquid on top	yes, solid layer on bottom ~98%	hard, but less than the UV samples
UV oxygenated	clear solid layer	yes- vial contains 100% solid	very hard
UV deoxygenated	clear solid layer	yes- vial contains 100% solid	very hard- brittle

4) The cross-linked polymer better resembles the polymers made in lab 1 because they were all very hard & could not be compressed. This supports the claim that molecular structure is resulting from cross-linking of the monomers.

5:1 HEA to EGDMA

EDGMA mass: $2\left(\frac{198.22}{(198.22 + (5 \times 116.12))}\right) = 0.50902$ g

HEA mass: 2 - 0.50902 = 1.49098 g

20:1 HEA to EGDMA

EDGMA mass: $2\left(\frac{198.22}{198.22 + (20 \times 116.12)}\right) = 0.15728$ g

HEA mass: 2 - 0.15728 = 1.84272 g

30:1 HEA to EGDMA

EDGMA mass: $2\left(\frac{198.22}{198.22 + (30 \times 116.12)}\right)$

= 0.10768 g

HEA mass: 2 - 0.10768 = 1.89232 g

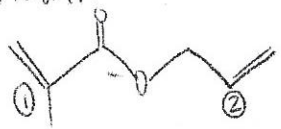
Vial	appearance	polymerization	mass (g)	hardness
5:1	clear, hard, pliable solid layer : flat slippery on top	yes - solid pliable structure, 100%.	3.925	fairly hard, pliable, flat
20:1	rounded, textured, rubbery clear solid	yes, bent solid structure 100%.	2.929	soft, pliable
30:1	rounded, textured, rubbery, clear solid (smaller)	yes, bent solid structure, 100%.	2.953	soft, pliable

5) polymerization may be inhibited by the presence of oxygen in the diradical form because this gives oxygen the ability to terminate polymerization. It can do this by using the radical to form a bond w/ another radical in the reaction ~~fr~~ rather than inducing another radical. This would limit or prevent polymerization & is supported by our experimental results since our oxygenated violet sample polymerized less than the deoxygenated violet sample. (~75% & 98%)

6) The wavelength of light gets shorter across the 3 photoreactions in the order red > violet > ultraviolet. The energy of light increases in the order red < violet < ultraviolet. Based on our observations, the effect of this is that the photoreceptors w/ the shorter wavelength, higher energy light have a greater ability to break the bonds homolytically, inducing radicals & polymerization of our samples. The red light did not have enough energy to do so, which is why these samples did not polymerize.

7) Based on the spectrum, the difference in reactivity between the red & UV photoreactors is expected. The UV photoreactor was extremely reactive, whereas the red was very inactive. This is because the absorbance spectrum for DMPA only absorbs light of shorter wavelength, such as UV. For light of higher wavelength, such as red DMPA is inactive, bc it is unable to absorb any light at such a wavelength.

8) I would expect the speed of the rxn to be slower than it would be w/ EDGMA. This is bc the radical formed when using ethylene glycol diacrylate would be secondary, compared to the tertiary radical formed w/ EDGMA. Since tertiary radicals are more stable, the formation of a secondary radical would require a higher activation energy, thus reacting slower.

9) 

C=C bond #1 would be incorporated into the polymer first. One reason for this is bc the radical formed would be tertiary here, vs secondary on C=C #2. Another reason is that the radical on C=C #1 is able to be resonance stabilized w/ the C=O bond.

10) This difference in reactivity is due to the fact that the C=C bond is lower in energy than the C=O bond. This more readily allows the formation of a radical, inducing polymerization. The C=O bond is stronger than the C=C bond & thus does not readily wish to form radicals via bond breaking.

11) The sign of the entropy change for a polymerization reaction is negative bc the system becomes more ordered. (from liquid to solid state) Enthalpy is also negative because the system is releasing heat as it forms sigma bonds from pi bonds so enthalpy is the driving force.

vial	mass (week 2) (g)	water absorbance ratio
5:1	3.863	3.863 / 3.925 = 0.9842
20:1	5.651	5.651 / 2.929 = 1.929
30:1	5.713	5.713 / 2.953 = 1.935

12) The polymer that best aligned w/ our desired properties were the 2 polymers made from the UV light in part 1. This is because the polymers solidified the fastest and were also the hardest, strongest polymers formed in the lab. The other polymers in the red light did not solidify at all so would not work for a filling. The polymers in the violet light took a little longer to form & did not 100% polymerize in the end. They were also softer than the UV polymers. The polymers made in part 2 would not be good for fillings because they are very soft & pliable & absorb a great deal of water.

13) For the polymers ~~formed~~ in part 2, the vials in order of decreasing flexibility are ~~30:1 < 20:~~ 30:1 > 20:1 > 5:1. The polymers from the vials in increasing water absorbativity are 5:1 < 20:1 < 30:1. Based on these results, I would suspect that the monomers composition be in a high ratio of HEA to EGDMA, such as our ratio of 30:1. This would be a good composition for a diaper because the polymerization occuring forms a fairly pliable, soft polymer, creating a flexible, comfortable fit. Another reason is that this ratio is able to retain the most amount of water.