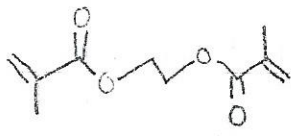
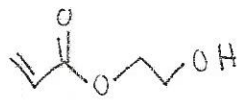
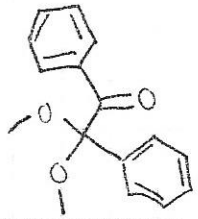
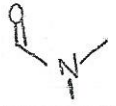
Title: Polymerization of EGDMA and HEA

Introduction: Polymerization is the process of forming macromolecules from forming bonds between monomers. these polymers can form connections between different chains, called cross-links. Polymers can be formed using radicals going through 3 steps: ~~initiation~~ initiation, propagation, and termination. Another way to synthesize polymers is the use of monomers with more than one vinyl groups. The purpose of this lab is to synthesize cross-linked polymers, observe photopolymerization, preform radical reactions with oxygen, and to look at the properties of polymers with different structures.

Prelim data:

| Compound | Structure | Density | Molar Mass (g/mol) | Mp °C | Bp °C |
|---|---|---|---|---|---|
| EGDMA ($C_{10}H_{14}O_4$) |  | 1.05 g/cm$^3$ | 198.22 | −40 | 98-100 |
| HEA ($C_5H_8O_3$) |  | ~~1.01 g/cm$^3$~~ 1.1 g/cm$^3$ | 116.116 | −60.2 | 210 |
| $H_2O$ |  | 1.009 g/cm$^3$ | 18.016 | 0 | 100 |
| DMPA ($C_{16}H_{16}O_3$) |  | 1.1 g/cm$^3$ | 256.30 | 67-70 | 169 |
| DMF ($C_3H_7NO$) |  | 0.944 g/cm$^3$ | 73.09 | −61 | 153 |

Procedure:

**Part 1:** 1.0mL of 0.0156M DMPA in DMF and 1.0g EGDMA were added to 6 glass vials. 3 of the vials were capped and the other 3 were covered with septa. A short needle was inserted in each septum. A deoxygenation setup was made for the 3 vials. ~~this~~ Vials were purged with nitrogen, and the needles and syringe were removed. The vials were placed in photoreactors; one oxygenated and one deoxygenated in red, violet, and ultraviolet photoreactors. Samples were allowed to react for 45 minutes, monitoring each every 15 minutes. Observations were recorded. After 45 minutes, the hardness of the formed polymer was recorded.

**Part 2:** 3 samples; less than 10:1, between 10:1 and 25:1, and more than 25:1, of HEA to EGDMA were made. Total ~~m~~mass ~~of~~ equalled 2g. This was done using the equations:

$$\text{EGDMA (g)} = 2 \frac{\text{EGDMA molar mass}}{\text{EGDMA molar mass} + (\text{ratio num.} \times \text{HEA molar mass})}$$

$$\text{HEA (g)} = 2 - \text{EGDMA mass}$$

A plastic mold was obtained for each sample and 2.0mL of DMPA in DMF was added to it. Determined amounts of the monomers were added. Mold was placed in photoreactor that was best in part 1 for 45 minutes. Physical properties and observations were recorded.

Prelab Questions:

① The violet photoreactor emits higher energy photons than the red photoreactor. This is true based on the equations $E=hf$ and $c=\lambda f$ where $c$ is the speed of light (constant) and $h$ is ~~Bohr's~~ Planck's constant. We know violet light has shorter wavelengths than red light so from $c=\lambda f$, we know violet light has a higher frequency than red light. Because $f$ of violet light is greater than that of red light and $E=hf$, we can conclude violet light emits higher energy photons than red light.

② A peroxide is a compound with the structure R-O-O-R. Peroxides are good radical reaction initiators because the O-O bond is easily broken into oxygen-centered radicals with just heat. These radicals are so unstable that they quickly move to propagation to form more stable carbon-centered radicals. Also the lone pairs on the oxygen atoms in a peroxide repel eachother making that bond much easier to break.

③

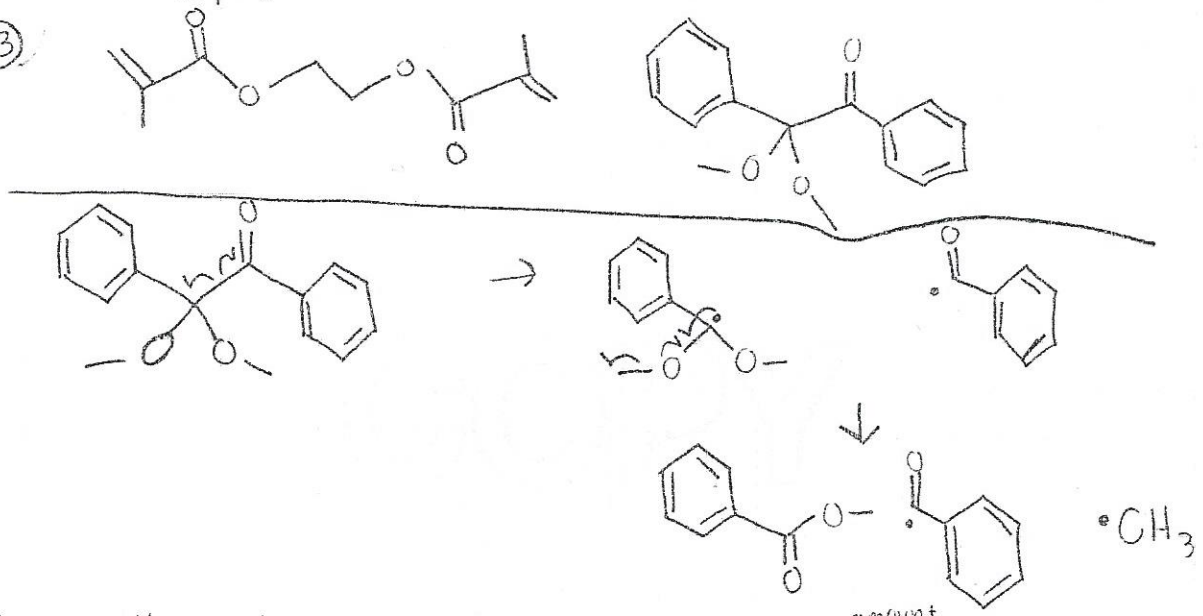



The most stable radical is B and the least stable is A. Radical stability is based on bond dissociation energy (BDE). The bond bond in B draws in electrons so the sigma bond with a carbon radical is weaker, having a lower BDE. The lower the BDE, the more stable the radical. ~~Because~~ so B is the most stable. C is more stable than A because the radical favors the more substituted carbon. B is also most stable because of resonance stability.

(Q1) When the dental filling material is being applied, you want it to be liquid, but after it has been applied you want it to be solid. You would want the solid to be hard, insoluble, and white colored. Initially you want a liquid so it flows easily, and can conform to the desired shape but after you want it to be a solid that is hard and insoluble so that it is long lasting, doesn't get destroyed with every day acids like juice/soda, and resembles a tooth.

(Q2) As the amount of cross linking increases, the hardness of the polymer increases and the flexibility decreases. This is true because higher amounts of cross-linking causes the polymer to be tightly packed so the hardness increases and the flexibility decrease. Low amount of cross-linking means loosely-packed polymers thus more flexibility, and more liquid-like.

(Q3)



(Q4) The better polymer in Part 1 is a high amount cross-linking polymer because the best polymer was hardest and least flexible, meaning it was more solid-like, which means the molecules are tightly packed.

Part 1 observations

| Time (min) | photoreactor | observations | vial |
|---|---|---|---|
| 15 | red | still liquid | oxy |
| 15 | red | still liquid | deoxy |
| 15 | violet | still liquid | oxy |
| 15 | violet | mostly solid, little liquid, opaque | deoxy |
| 15 | UV | all solid, opaque, raggity/rough | oxy |
| 15 | UV | all solid opaque | deoxy |
| 30 | red | still completely liquid | oxy |
| 30 | red | still completely liquid | deoxy |
| 30 ~~30~~ | violet | mostly liquid, layer of opaque solid starting to form | oxy |
| 30 | violet | mostly solid, opaque | deoxy |
| 30 | UV | all solid, opaque, rough | oxy |
| 30 | UV | all solid, opaque | deoxy |
| 45 | red | complete liquid | oxy |
| 45 | red | complete liquid | deoxy |
| 45 | violet | liquid, slightly more solid layer | oxy |
| 45 | violet | mostly opaque solid, harder, jellylike | deoxy |
| 45 | UV | opaque solid, less rough softer | oxy |
| 45 | UV | opaque solid, hardest | deoxy |

Part 2 calculations:

LOW: 5:1 HEA to EGDMA

$$\text{EGDMA mass (g)} = 2\left(\frac{198.22}{198.22 + (5 \times 116.116)}\right) = 0.509\text{g}$$

$$\text{vol. EGDMA} = \frac{m}{d} = \frac{0.509\text{g}}{1.059\text{g/mL}} = \boxed{0.48\text{mL EGDMA}}$$

~~HEA mass(g) = 2 - 0.48 = 1.52g~~

$$2 - 0.509 = 1.491\text{g}$$

$$\text{vol. HEA} = \frac{m}{d} = \frac{1.491}{1.1} = \boxed{1.36\text{mL HEA}}$$

medium: 20:1

$$\text{EGDMA mass (g)} = 2\left(\frac{198.22}{198.22 + (20 \times 116.116)}\right) = 0.157\text{g}$$

$$\text{vol EGDMA} = \frac{0.157}{1.05} = \boxed{0.15\text{mL EGDMA}}$$

$$\text{HEA mass (g)} = 2 - 0.157 = 1.85\text{g}$$

$$\text{vol HEA} = \frac{1.85}{1.1} = \boxed{1.68\text{mL HEA}}$$

high: 50:1

$$\text{EGDMA mass (g)} = 2\left(\frac{198.22}{198.22 + (50 \times 116.116)}\right) = 0.066\text{g}$$

$$\text{vol EGDMA} = \frac{0.066}{1.05} = \boxed{0.063\text{mL EGDMA}}$$

$$\text{HEA mass (g)} = 2 - 0.066 = 1.93\text{g}$$

$$\text{vol HEA} = \frac{1.93}{1.1} = \boxed{1.76\text{mL HEA}}$$

*Based on Part 1 observations, deoxygenated in UV light was the best followed by oxygenated in UV light.

**UV light**

Part 2

a) UV with deoxygenated photoreactor conditions were the best

b) This is true because UV formed a polymer the fastest and the deoxygenated vial gave a harder, smoother polymer.

5:1 initial mass: 3.654g
20:1 initial mass: 3.690g
50:1 initial mass: 3.738g

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

12/6/17 Part 2

5:1 final mass: 3.872g
20:1 final mass: 5.745g
50:1 final mass: 8.262g

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

5:1 ratio: $\frac{3.872g}{3.654g} = \boxed{1.06}$

20:1 ratio: $\frac{5.745g}{3.690g} = \boxed{1.56}$

50:1 ratio: $\frac{8.262g}{3.738g} = \boxed{2.21}$

The Report:

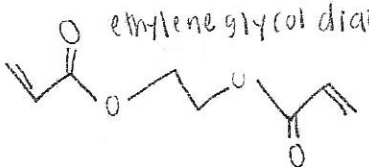
(Q5) In Part one, we found that the presence of oxygen inhibited the polymerization. This is true because of the diradical charcter of oxygen. ~~This characteristic makes the radical very unstable so it will react in the propagation step creating a different polymer than the desired one.~~ Radicals are very unstable and reactive so having more radicals as a result of having oxygen promotes chances that two radicals will combine causing termination instead of propogation, decreasing the chance of cross-linked polymers.

(Q6) The wavelength increases from UV to violet to red having the longest. Because $c = \lambda f$ where c is constant, wavelength increases as frequency decreases so UV has the highest energy and red has the lowest energy. The photoreactor with the shortest wavelength and highest energy created the best polymer because more energy means the photons are better able to start the initiation stage promoting polymerization.

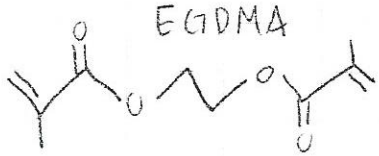
(Q7) The figure shows the highest absorbance peak around 320-360 nm which is the range of the wavelength of UV light. The figure shows the absorbance to be 0 at 620-750 nm which is the wavelength of red light. This supports that UV is better at polymerization.

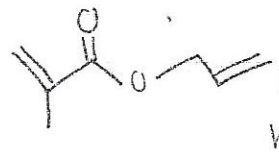
(Q8) If we used ethylene glycol diacrylate instead of EGDMA, the reaction would be slower for propagation because it cannot have resonance stabilization like EGDMA can. Without resonance, you would have to break that double bond in order to propagate the polymer which requires more energy.

ethylene glycol diacrylate



EGDMA



(Q9)  The farthest left C-C double bond would be incorporated into the polymer first. This would happen due to resonance and the fact that the C is more substituted. Resonance is the major contributor to this but a more substituted carbon means the bond dissociation energy is lower so the bond breaks easier which promotes propagation.

(Q10) In the presence of a radical initiator, styrene readily polymerizes and benzaldehyde does not because of the differences in the bond energies. The end of a styrene has a C=C with a BDE of 602 kJ/mol and the end of a benzaldehyde has a C=O with a BDE of 799 kJ/mol. The lower BDE means it is polymerized easier because that bond is more easily broken. The same can be seen for the results C-C and C-O with BDE of 646 kJ/mol and 358 kJ/mol, respectively. The C-C bonds are more reactive than C-O.

(Q11) The sign of entropy is negative because as a polymer forms, it gets more solid-like therefore it gets more ordered. Enthalpy is the driving force based on the equation $\Delta G = \Delta H - T\Delta S$. We know $\Delta S$ is negative and $\Delta G$ is also negative because after formation of radicals the reaction occurs spontaneously, which was observed in lab. Because of this $\Delta H$ has to be strongly negative making it the driving force.

(Q12) Out of all the polymers formed in Parts 1+2, ~~the low concentration of 5:1 HEA to EGDMA~~ the deoxygenated with UV would best align with the desired physical properties for dental fillings. This polymer was observed to be the hardest, least flexible, most solid-like polymer compared to the others. As identified you want dental fillings to be hard, insoluble, durable, and not easily eroded with common acids, which most closely is represented by the ~~5:1 polymer in Part 2~~ deoxygenated conditions under UV light in part 1. From part 1, this condition gave the hardest solid polymer, while the other conditions gave softer liquid-like polymers indicating there was less crosslinking. In part 2, we used EGDMA with a monofunctional monomer, meaning it cannot form cross-linking which while it led to hard polymers, gave brittle and non-durable polymers. Dental fillings should have polymers with high cross-linking in order to give hard and durable polymer.

(Q13) Initially, we observed that the 5:1 polymer was the hardest and the least flexible while the 50:1 was the softest and most flexible. After a week of absorption, we observed that the 5:1 polymer was less hard than initially but still hard giving the lowest water absorption ratio. The 50:1 gave the largest water absorption ratio and was very flexible and gel-like. Because of this, the 50:1 HEA to EGDMA would be most ideal for ~~the~~ diapers giving a high ratio of monofunctional monomers to difunctional monomers in the composition. HEA is a monofunctional monomer so it cannot form cross-links, promoting flexiblity and inhibiting hard, non absorbant polymers that result from high cross-linking. Diapers should be absorbant and flexible, so you want higher concentration of HEA.