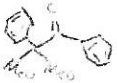
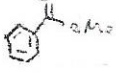
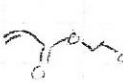
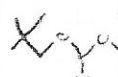
An Investigation into the effect of Light Wavelength on polymerization Reactions.

Purpose: The purpose of this experiment is to explore the effect of light on certain compounds. This lab will specifically be dealing with 5 compounds used in dental filling. When light of a certain wavelength hits the dental filling, it triggers a chemical reaction that produces a state change.

Name	Structure	M.W (g/mol)	B.P (°C)	M.P (°C)	Density	Solubility	Flam.	Toxicity
EGDMA		198.218	260	-40	1.005	—	—	skin/eye irritant
DMPA		240.37	—	—	—	—	—	skin irritant
Methyl Benzoate		152.149	220.5	131	—	2.5 g/100 mL	—	skin/eye irritant
HEA		116.116	210	-70	1.1	1×10⁶ g/L	—	skin/eye irritant
N,N-dimethylformamide		231.30	—	—	—	—	∞ !	skin/eye irritant

Procedure:

Each group will need six samples. Add 1.0 mL of photoinitiator solution and 1.0 g of ethylene glycol in a glass vial. Let these samples deoxygenate. Insert a balloon syringe into each vial. Squeeze the balloon to purge with nitrogen. Place two samples into each of the photoreactors. Monitor the progress of each reaction every 15 minutes. Describe appearance of mixture

After 45 min. check for polymerization.
As a group you should prepare 3 samples. Use the formulas to determine EGDMA mass.

$$\text{EGDMA mass} = 2\left(\frac{\text{EGDMA molar mass}}{\text{EGDMA molar mass} + (\text{ratio number} \cdot \text{HEA molar mass})}\right)$$

$$\text{HEA mass} = 2 - \text{EGDMA mass}$$

Obtain plastic molds. Add 2 mL DMPA to the molds. Place molds in photoreactor. Allow reaction for 45 min Record observations. Record mass. Fill a 100 mL beaker with distilled water and your sample. Store the beaker in your drawer. Record mass again during next lab period. Calculate water absorbance ratio.

Pre-lab questions

(1) The red photoreactor emits higher energy photons. This is discernible based on the brightness of each photoreactor. High energy photons will appear brighter.

(2) A peroxide is a compound with the structure R-O-O-R. Peroxides are good radical initiators because it is not difficult to force homolytic bond cleavage, resulting in two O· radicals.

(3) ~~The most stable radical species is~~ This is because ~~the~~ radical is ~~located on a secondary carbon. The adjacent carbons can help stabilize the radical via hyperconjugation.~~



The least stable radical species is This is because the radical is on a primary carbon and no R groups can help with hyperconjugation stabilization.



The most stable radical species is .
This is because this form can be resonance stabilized. This outweighs the fact that the radical is on a primary carbon.

Part 2 calculations:
Medium Ratio: 15:1
EGDMA molar mass = 198.22
HEA molar mass = 116.12

$$\text{EGDMA Mass} = 2\left(\frac{\text{EGDMA molar mass}}{\text{EGDMA molar mass} + (\text{ratio numerator} \cdot \text{HEA molar mass})}\right)$$

$$\text{EGDMA Mass} = 2\left(\frac{198.22}{198.22 + (15 \cdot 116.12)}\right)$$

$$\text{EGDMA Mass (g)} = 2\left(\frac{198.22}{1940.02}\right) \qquad \frac{0.204}{1.055}$$

EGDMA Mass (g) = 0.204 g.
EGDMA vol. = 0.193 mL.
HEA Mass (g) = 2 - 0.204

HEA Mass (g) = 1.796 HEA vol. = 1.778 mL.

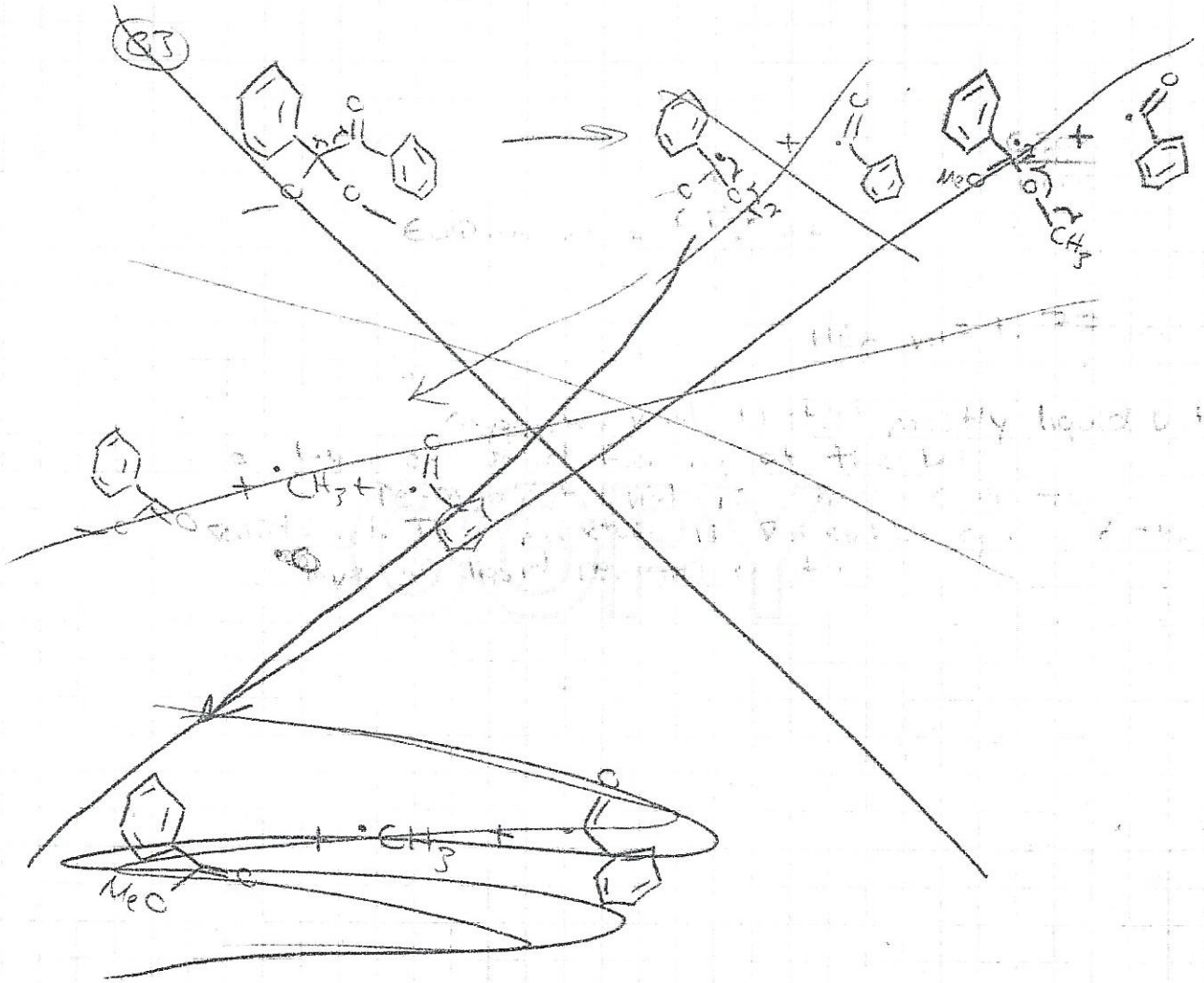
Part 1 observations: Violet Light
15-min mark: oxygenated vial is still mostly liquid with a layer of solid forming at the base.
De-oxygenated vial is almost completely solidified. The mixture is somewhat opaque. A thin layer of liquid remains on top.
30 min mark: oxygenated vial has formed a slightly thicker layer of solid. A thin layer of liquid still exists on top. The color is more opaque.
The deoxygenated vial is completely solidified and somewhat translucent.
45-min mark: The oxygenated vial has an almost completely solidified mixture. There is still a tiny layer of liquid left on top.
The de-oxygenated vial is completely solidified. The oxygenated vial is mildly hard. It is a little squishy. The de-oxygenated vial is completely hard. Very tough.

Q1. For practical use, we would like for it to begin as a liquid so it's shape can be morphed. After application we would want it to become solid so it retains shape and hardness.

Q2 It will be used as a teeth so it will have to endure wear and tear.

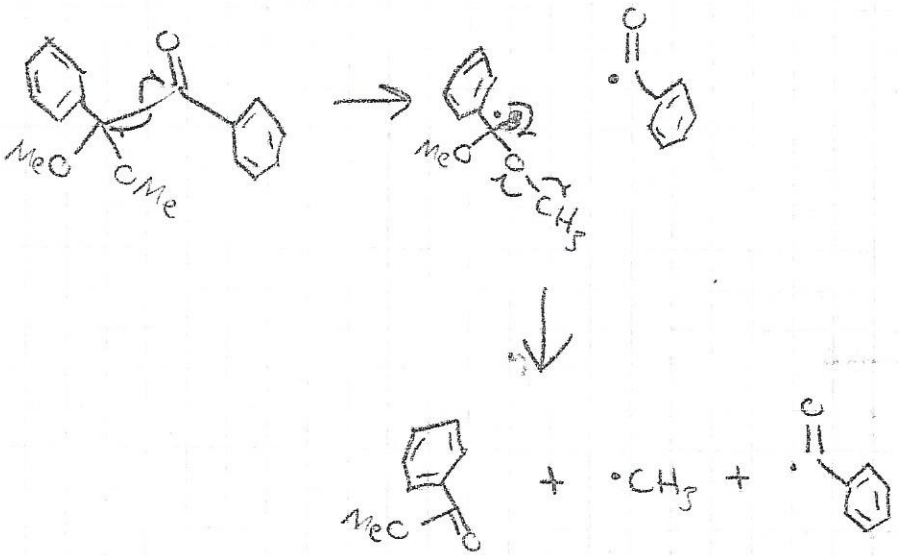
Q2 Based on the depictions, ~~it~~ I would predict that as cross-linking increases, freedom of movement decreases. As cross-linking increases the mixture should more mimic the properties of a solid. Density appears to increase

Q3



Q4. I believe the polymer we made more closely resembles the picture with more cross-linking. This is because the mixture turned from liquid to completely solid in de-oxygenated conditions. This is consistent with traits we would expect from a highly cross-linked polymer.

Q5.

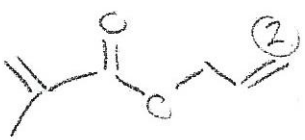


Q5. Diradical character could inhibit polymerization because the increase in available radicals could interfere with the mechanism. The more radicals present in a mixture, the higher the chance two of those radicals could interact and terminate the radicals.

Q6. Red → Violet → Ultraviolet
As you move along this scale, wavelength decreases. This means the energy of the light is increasing. Based on our experiment, higher energy light tended to polymerize our mixture faster than low-energy light.

(Q7.) DMPA only absorbs light between the wavelengths of ~320-390 nm. Red has a much larger wavelength so it most likely isn't being absorbed by the DMPA. If the light isn't being absorbed then radicals won't be formed, and polymerization can't occur.

(Q8.) Ethylene glycol diacrylate is missing two methyl groups compared to EGDMA. This vastly limits resonance options for ethylene glycol diacrylate. Because of this lack of resonance contributors it is less likely to form radical polymers with the chosen radical initiator. This would slow the reaction.

(Q9.) (1)  (2)

Double bond #1 would react ~~[illegible]~~ and be incorporated into the polymer first.
Reason #1: The first double bond involves a tertiary carbon, which is more stable than a secondary due to hyperconjugation.
Reason #2: The tertiary carbon allows for resonance stabilization which ~~greatly~~ is greatly favored

(Q10.) If a radical approaches styrene, it must only overcome 602 kJ/mol of energy to break the pi bond and start an addition reaction. If a radical approaches benzaldehyde, it must overcome 799 kJ/mol of energy to break the pi bond. ~~Also~~ Also, in the case of benzaldehyde you would be left with a peroxide. Peroxides are excellent radical initiators, so the formation of one would not be as stable as a C-O bond.

(Q11) In polymerization reactions, entropy will always be decreasing due to the simplification of multiple molecules into a single molecule.

$\Delta G = \Delta H - T\Delta S$

IF we know that ΔS is negative and we can be sure the reaction is spontaneous (ΔG is negative) then we know ΔH is also very negative. So the reaction is exothermic and spontaneous. Enthalpy is the driving force in this reaction because it is thermodynamically favored to eliminate one C-C pi bond and form two C-C sigma bonds.

(Q12) Out of all our tested polymers, the Part 1 mixture treated in UV light was the stiffest, and most solid. This must have been the polymer that cross-linked the most. The other polymers were either liquid or still rubbery and flexible. This is not desirable for dental work. These must have formed more loosely packed cross-links.

(Q13.) ~~All polymer mixtures formed somewhat rubbery blocks. However, the lower the HEA : EGDMA ratio, the stiffer the block was.~~ Lower ratios also ~~had~~ better water absorbency. ~~Based~~ on that information, a ~~diaper~~ company would be best using a monomeric comporition of 5:1 or lower.

Mass: 3.851 g. - Before Water

5.2[illegible] g. - After Water

water absorbance ratio : 1.372

Q15. When comparing the 3 mixtures on a scale of toughness, the lower HEA:EGDMA ratio provided a sturdier polymer. The 30:1 ratio was very flexible and rubbery while the 5:1 was extremely tough.

On a water absorbency scale the trend is the opposite. The 30:1 ratio mixture absorbed much more water than the 15:1 and 5:1 mixtures. I would therefore recommend that the diaper company use a very high ratio of HEA:EGDMA so the absorbency is at its best.