

The Pennsylvania State University

The Graduate School

**DIRECTED ENERGY EFFECTS ON CHEMICAL TRANSFORMATIONS RELEVANT  
TO POLYMERIZATIONS**

A Thesis in

Chemistry

by

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## Abstract

Common polymerization reactions can take hours to days of reaction time in refluxing solvent to build sufficient molecular weight. To overcome these slow reaction kinetics and to produce materials with useful properties, some non-traditional methods have been implemented to decrease the required reaction times, while not sacrificing yield or chemical fidelity. One of these rapid synthesis methods is microwave-induced heating. Microwave reactors produce a magnetic and electric field which can cause superheating effects on microwave absorbing molecules and particles and thus accelerate polymerizations. These microwave reactions can have heating similar to traditional reactions in minutes rather than hours with the proper monomer and solvent selection. Microwaves have three fundamental modes of action, ionic, dipole, and magnetic, that can be exploited to make traditional reactions occur faster with little impact on yield. The main focus of this work identified what chemistries can be superheated, and what solvents and additives can be used to achieve high heating in short amounts of time.

To further expand on another fast polymerization method, laser photopolymerization (including photothermal effects) can also be used to obtain extreme heating for rapid chemical reactions. An interesting facet of this method is that when deployed under specific circumstances the photochemical reaction or heating will only occur at the laser's focal point which can lead to the development of 2D and 3D polymer structures that can be deposited with micrometer precision. Both methods have the potential to lead to novel, rapid polymerization techniques as well as functional polymers not possible by conventional methods, due to the origin of the directed energy of these techniques and rapid heating. This work mainly focuses on laying the foundation for laser induced polymerizations as well as monomer selection for polymerizations in microwave reactors

and the capability to develop polymers and composite materials in significantly less time than traditional methods

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## **List of Abbreviations**

**SEM** – Scanning Electron Microscopy

**GO** – Graphene Oxide

**IR** – Infrared Spectroscopy

**PEGDA** – Poly(ethyleneglycol diacrylate)

**μW** – Microwave

## **Acknowledgements**

Firstly, I would like to thank my advisor Dr. Mike Hickner for guiding me throughout my time at Penn State and the support he has given me. I would not have come near this far without him and the effort he has put into my personal development. I would also like to thank my committee for the support they have given to me throughout my research career. I would like to give a special thanks to Dr. Scott Showalter for encouraging me throughout the many obstacles I have faced. I would like to thank my family for the support and encouragement I have received. Lastly, I would like to dedicate this in memory of Stella Wiencek, Cynthia Santillan, and Chester Polejewski who passed away before they could see the person I have become today.

## **Chapter 1. Introduction and Literature Review**

This work focuses on utilizing directed energy to induce chemical transformations through rapid heating. Specifically, this work used microwave energy to directly heat molecules and induce a rapid change in the temperature of the molecules, and thus accelerate reactions. Increasing the temperature of specific monomers allows us to perform rapid polymerization reactions not attainable through traditional polymerization techniques. This work centers on developing the fundamental principles, identifying ideal monomers, and demonstrating polymerizations capable with rapid microwave or photo(thermal)polymerization polymerization techniques.

Rapid polymerization reactions and novel material formation are useful for many types of advanced fabrication technologies and novel synthesis of advanced functional materials. Conventional heating using ovens or thermal baths often requires hours of reaction time to build molecular weight in materials or to accomplish curing reactions, for instance in cross-linkable composites. Thus, new methods to rapidly polymerize novel polymers and functional composites are desired. This thesis details two such methods where energy can be directed towards reactions of interest. The two methods covered in this work are laser-induced photo/thermal polymerizations and microwave-induced polymerizations. The fundamentals of each technique are discussed below.

### *1.1 Laser Photopolymerization*

One method to induce rapid heating in a short period of time is laser induced photopolymerization – with embodied thermal effects from the high intensity light. By focusing a strong laser on a certain point, it is possible to develop localized heating gradients able to cause

thermal polymerizations. This focused laser can also induce a photopolymerization at a focused point. What makes this method unique is that the laser's focal point, with a size on the order of a few microns, is essentially the only place the reaction/polymerization takes place. This allows for the possibility of developing unique 2D and 3D patterns, as well as precision material synthesis on the microscale, which is not attainable by other traditional methods. Both above discussed methods have one thing in common, directing energy to do materials transformations. Using these two non-conventional methods, it is possible to decrease polymerization times while maintaining chemical synthesis fidelity. This work mainly focuses on microwave-based transformations, and a foundation for laser-induced polymerization work to be continued on in the future.

The work in this thesis regarding laser-induced polymerization focused on a simple photopolymerization to form poly(diurethane-co-ethyleneglycol) using a type II photoinitiator. An illustration describing photopolymerization is shown below, Figure 1.

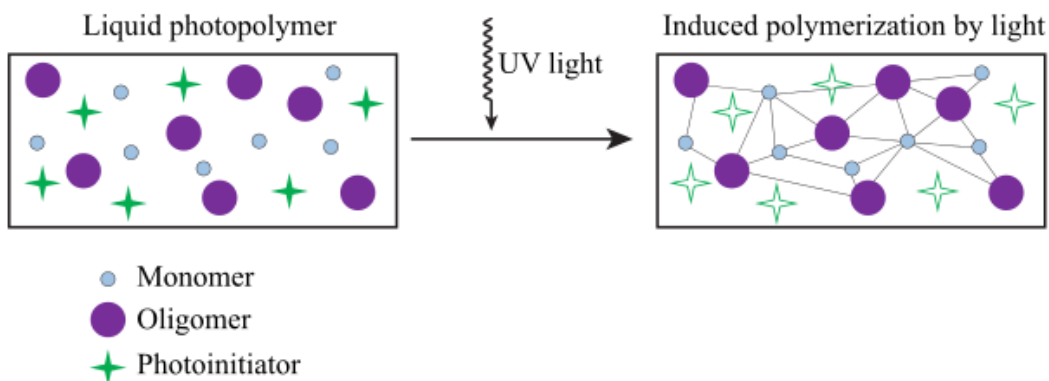


Figure 1. Basic photopolymerization scheme.

To utilize this system, a 785 nm near IR laser setup and a type II initiator (Commercial H-Nu IR 780 initiator) was implemented. A type II initiator requires a co-initiator that can have a hydrogen readily abstracted, typically an amine<sup>9-10</sup>. The typical radical mediated photopolymerization

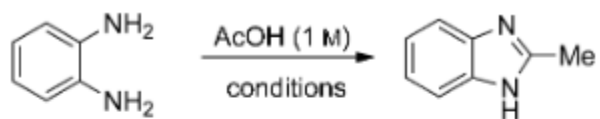
follows the basic steps of photoinitiation, propagation, and termination which is the basic premise of this work. This work focuses simply on the fact that a basic polymerization can be initiated and that a metal can be incorporated and included to polymerize a metal-polymer composite.

## 1.2 *Microwave Polymerizations*

Many typical polymerization reactions require hours to days of reaction time in conventional heated flasks. A non-traditional way of heating these reactions and accelerating the increase of molecular weight is using a microwave reactor. A microwave is unique because it couples both an electric and magnetic fields to allow for the possibility of super heating the reaction mixture. This allows for thermal-based reactions to occur in minutes rather than hours, as shown in work later discussed. Microwaves can be used for a wide variety of reactions because they influence the heating of molecules through dipole effects, electric field, magnetic field, or thermal effects, and act on a range of ionic and polar aromatic molecules<sup>1</sup>. In addition to these effects, susceptors can also be added to increase heating of solutions that are not typically microwave susceptible. Finally, unique situations can exist, such as performing reactions in high-heating solvents, or using susceptible monomers in solvents that do not heat in the microwave. Thus, there is interesting potential to target microwave heating to specific components of the reaction mixture.

Originally, there was a vast amount of debate and speculation regarding the effect of microwave irradiation to accelerate chemical transitions. This debate was mainly centered on the idea that all the observed effects from the microwave can be reduced to a thermal effect. However, in the organic chemistry community there are many nonthermal microwave effects discussed that are postulated to result from a direct, often stabilizing interaction of the electromagnetic field with either molecules, intermediates, intermediates, transition states or the solvent. This cannot be observed in a change in the reaction temperature and is rather hard to identify conclusively.<sup>2</sup> It has

been argued that the electric field affects the orientation of dipolar molecules or intermediates and hence changes the pre-exponential factor  $A$  or the activation energy in the Arrhenius equation for certain types of reactions. A similar effect has been proposed for polar reaction mechanisms, where the polarity increases going from the ground state to the transition state, resulting in an enhancement of reactivity by a decrease of the activation energy. Specific microwave effects are caused by the uniqueness of the microwave dielectric heating mechanisms. Some of these mechanisms include the superheating effect of solvents at atmospheric pressure, the selective heating of strongly microwave absorbing heterogeneous catalysts or reagents in a less lar reaction medium, formation of molecular radiators by direct coupling of microwave energy to specific reagents, and the elimination of wall effects caused by inverted temperature gradients.<sup>1,7</sup> Microwave chemistry relies on the ability of the reaction mixture to efficiently absorb microwave energy, taking advantage of microwave dielectric heating phenomena such as dipolar polarization and ionic conduction mechanisms. Under these conditions, rapid internal heating by the direct interaction electromagnetic radiation with the molecules can occur, accelerating reaction time.



	conditions ( $T/p$ )	$t$
CONV	25 °C / -	9 weeks
CONV	60 °C / -	3 d
CONV	100 °C / -	5 h
MW	130 °C / 2 bar	1 h
MW	160 °C / 4 bar	10 min
MW	200 °C / 9 bar	3 min
MW	270 °C / 29 bar	1 s

Figure 2. Thermal microwave effects in the synthesis of 2-methylbenzimidazole.<sup>4</sup>

Kappe, et al. is one of the many examples of microwave accelerated heating to increase reaction time.<sup>1-2,4,6</sup> Using conventional heating methods, reactions time ranged on hours to days, but when using the microwave, they were able to complete the reaction in minutes. This illustrates how powerful the thermal effects of the microwave can be, but it also makes it hard to distinguish whether it is purely the thermal effects of the microwave or if there are non-thermal effects such as superheating or molecular radiators are present. One major piece of evidence for non-thermal microwave effects is a higher yield in a microwave system that is not attainable in conventional heating methods. In their reaction of 2-methylbenzimidazole they observed a purely thermal microwave effect and do not believe a non-thermal effect is a common occurrence in microwave assisted reactions, Figure 2.<sup>4</sup> There have been groups to support such effects, although it is often debated throughout the community whether they exist or not. Siguemoto, et al. did an extensive study on the inactivation of pectin methylesterase, polyphenol oxidase, and peroxidase under conventional and microwave heating to evaluate the validity of non-thermal microwave effects. To analyze if the process observed was purely thermal or not they used kinetic modeling and a time temperature profile, which led to them determining that the process observed was purely thermal. Non-thermal microwave effects were observed by Li, et al.<sup>5</sup> Their work focused on processing of glass ceramics, where they compared heating profiles of various glass-ceramics heated conventionally and with microwave assistance. They tested the crystallization of four groups of samples at two different temperature programs, using identical heating times and target temperatures for each pair of samples. To understand the samples tested they employed XRD, Raman spectra, SEM images, physical characterization, and mechanical testing. All of these methods provided clear evidence that a non-thermal enhancement effect occurred during the microwave crystallization. Experimental evidence also indicated that the microwave radiation

reduced the crystallization activation energy from 375.7 kJ/mol to 214.9 kJ/mol, accelerated the grain growth during crystallization, enhanced the formation of the diopside crystal structure, and improved the physicochemical properties of the final materials. It is of great debate in the community whether non-thermal effects take place in the microwave or not, although in almost all cases the thermal phenomena derived from the effects described above is dominant.

According to Kappe, et al., thermal microwave effects can cause the superheating of solvents at atmospheric pressure alongside the selective heating of strongly microwave absorbing heterogeneous catalysts in a less-polar solvent. Kappe also discussed the theory of molecular radiators which describes the direct coupling of microwave energy to specific reagents in solution, which can lead to hot spots.<sup>1</sup> This allows for molecular selective heating, which means the energy can be target and used to only heat certain reagents. This method also eliminates wall effects that are observed in traditional heating methods. A diagram explaining this effect is shown below, Figure 3.



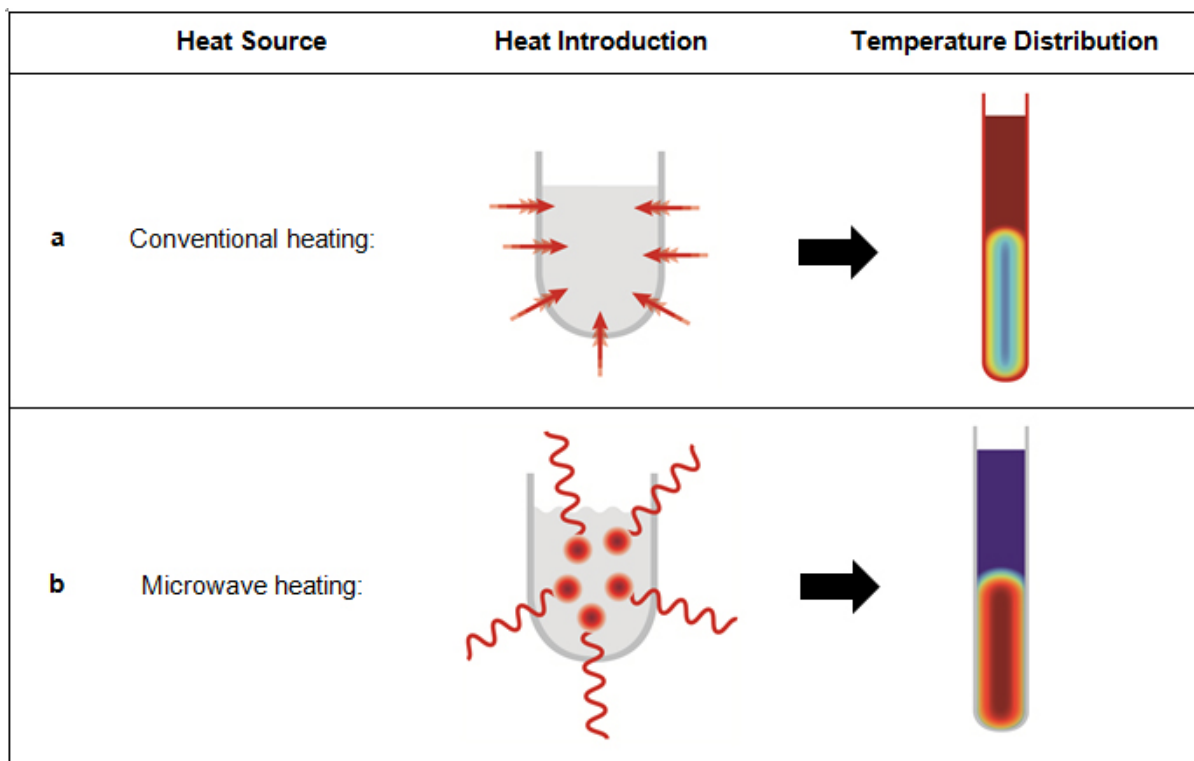
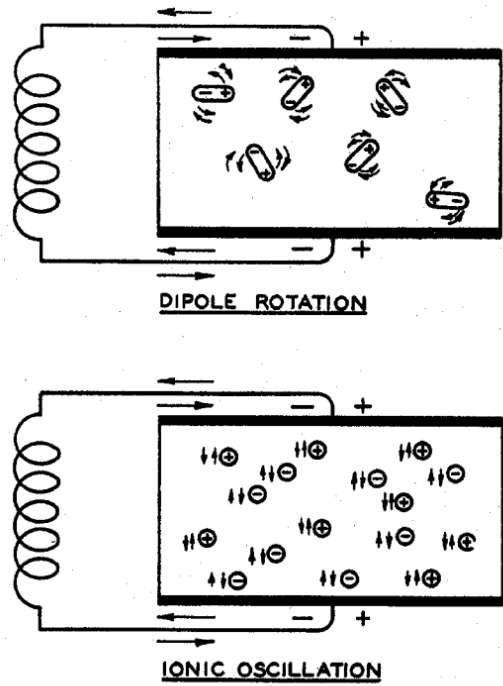


Figure 3. Conventional versus microwave heating.<sup>6</sup>

The diagram above illustrates wall effects, and how due to the frequency emitted by the microwave the molecules get directly heated rather than the vessel. This leads to a better heat distribution throughout the entire solution.<sup>2,6</sup>

Dakin, et al. discussed different effects present in the microwave including the dipole and ionic effect while emphasizing that this is all derived through thermally driven phenomena. The dipole effect discusses how the magnetic field component of the microwave causes polarity-based heating. The higher polarity of the molecule, the more rotations will occur, causing higher heating. A diagram of this and the ionic effect are shown below in Figure 4.



**Figure 1. Sources of Dielectric Heating**

Figure 4. Dipole and ionic effect.<sup>3</sup>

An ionic effect is also present due to oscillations caused by the electric field component of the microwave<sup>3,7</sup>. This oscillation is essentially vibrations that are building up energy and giving it off to the solution and surrounding molecules as heat, being another thermally driven phenomenon. Dipole rotation is what is responsible for heating of water in cooking applications and is the primary effect for microwave generated heat. The magnetic field induces rotation due to alteration of charges. This leads us to be able to use dipole moment as a prediction for how well a substance will heat under microwave irradiation.

Dudley, et al. further explored this concept by looking at microwave heating of select polar aromatics. Their results are shown below in Figure 5.

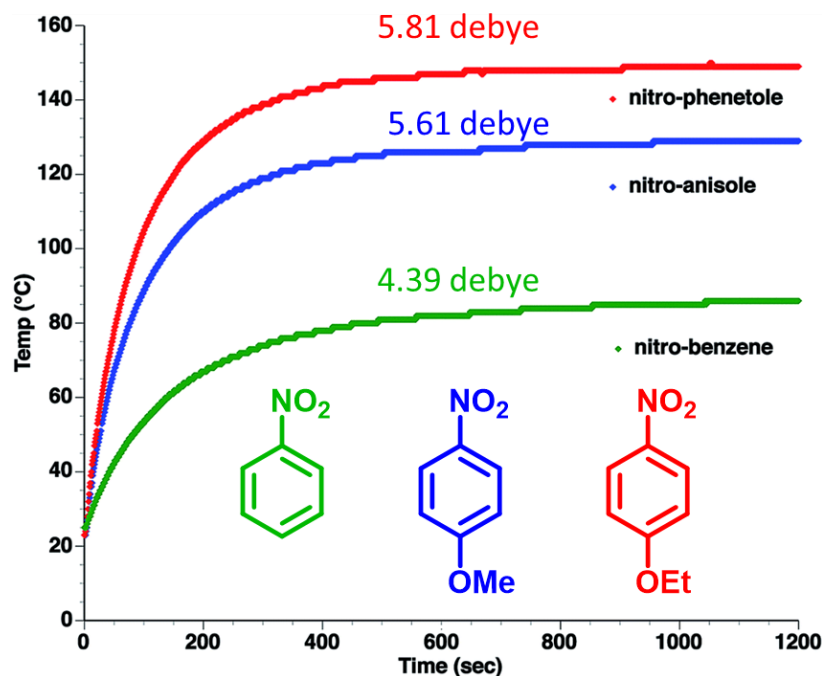


Figure 5. Heating of polar aromatics.<sup>5</sup>

This figure illustrates that the rate of heating roughly correlates to the dipole moment of the molecule tested. It also shows that not only does the molecule heat faster, but it is also capable of reaching a higher temperature. This is most likely due to the nature of the molecule and is likely to depend on the conjugation and resonance forms the molecules can take. Dudley further discussed polar aromatics and the conjugation they bring to the table. Below is an illustration of a “push-pull” aromatic, Figure 6.<sup>5,8</sup>

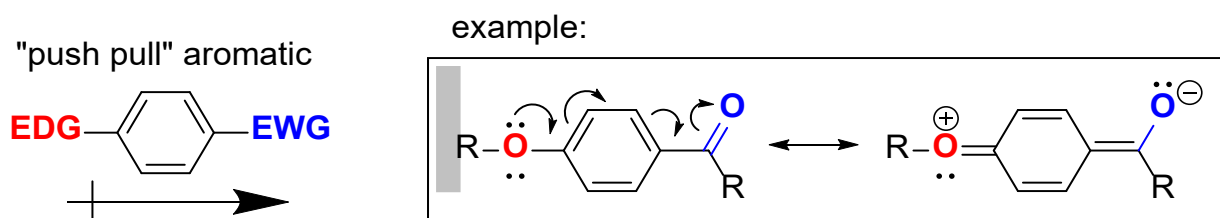


Figure 6. Conjugation of polar aromatics.<sup>8</sup>

This push-pull behavior can lead to further resonance states with greater charge separation that leads to molecules with greater heating than the dipole moments would suggest. It is possible to select polar monomers that exhibit this effect. The main focus of this work regarding microwave polymerization methods is to develop a foundation and set of rules that can be used to develop microwave polymerizations that happen in much less time with similar yield, as well as help develop novel polymer composites that are not obtainable using traditional methods.

In order to accomplish this goal, this work focused on developing a palette of polymerizations and fundamental set of rules for microwave heating of monomers. Different chemistries such as acrylamides, styrenes, and polar aromatics were tested for their heating profile, maximum temperature, and overall viability for being monomers used for polymerizations in the microwave. The ideal monomer would have fast heating with a high maximum temperature in order to complete the polymerization in as little time as possible.

Microwave polymerizations offer the opportunity to accelerate traditional polymerization methods and lower reaction times from several hours or days to minutes and can give similar yields. This work aimed to prove this concept and demonstrate a sample polymerization with comparable yield to that of traditional techniques in a shorter timeframe.

## **Chapter 2: Materials and Experimental Methods**

### *Microwave Polymerization*

A CEM Discover Microwave Synthesis System with a 2.5 GHz frequency and pressure attachment was used for all experiments. A range of 50-300 W microwave power was used. 10 mL pressure vials were used for the reactions. Reactions were run for 7 minutes unless otherwise noted. All chemicals were purchased through Sigma-Aldrich and used as received.

### *Typical polymerization procedure*

For typical microwave reactions, each component would be added and solubilized several hours before being introduced to microwave irradiation. Each sample was run for 7 minutes unless otherwise stated, with temperature being reported through a built-in probe in the CEM Discover.

### *Laser Induced Photopolymerization procedure*

All experiments employed a titanium:sapphire laser operating at 760 nm in pulsed mode. The laser output was adjusted by using optics in conjunction with an oil-immersion objective. For more information about the laser deposition setup refer to Kindle, C., et al. ACS Appl. Nano Mater. 2019, 2, 5, 2581-2586. DOI: 10.1021/acsnm.9b00360.

### *Scanning Electron Microscopy and Energy Dispersive Spectroscopy*

A Zeiss Sigma FESEM microscope was used to image the surface of various polymers cured during laser photopolymerization. The parameters for each scan are included on each image. An additional attachment on the SEM allowed for EDS scans of the samples as well.

*Raman Spectroscopy* A Horiba LabRam HR Evolution Vis-IR optimized & AIST-NT Scanning Probe was used to take Raman spectra of laser deposited materials using a 488nm source.

### Chapter 3: Laser Induced Polymerization

One part of this work was to develop a photocurable resin that when exposed to a laser, would be able to be polymerized with micrometer precision. For this work, a simple crosslinking polymerization was used, and the composition is shown below, Figure 7.

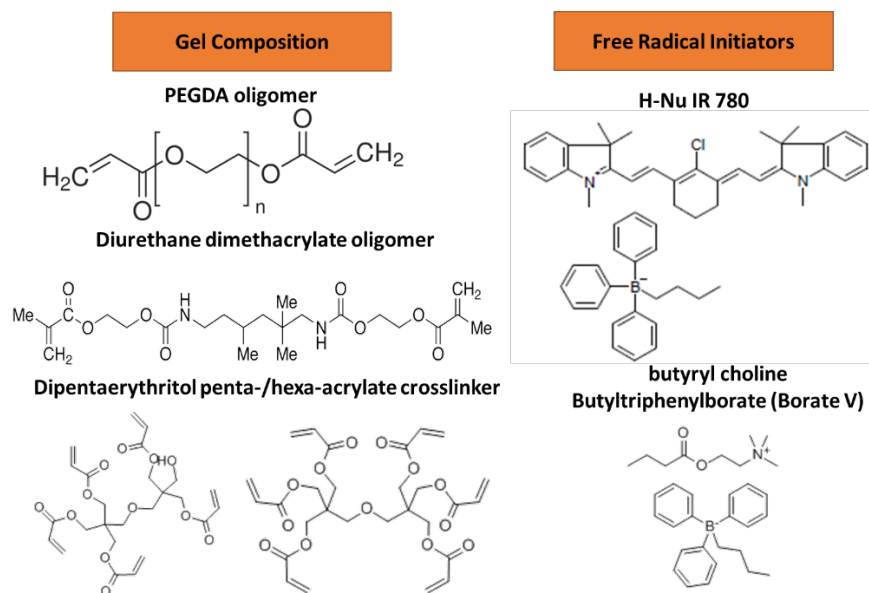


Figure 7. Photochemical Gel Composition.

The initiator used was selected to match the wavelength of the laser used. H-Nu IR 780 initiator was chosen due to its high absorption in the near-IR region. A multitude of polymerization recipes were initially tested, Table 1, such that an understanding of whether thermal polymerization or photopolymerization was occurring and what factors dictate the overall curing or polymerization of the resin.

Table 1. Different Compositions of Resins Tested.

Number	Weight Percent %							Comments	Experimental Notes
	PEGDA	DUDMA	Crosslinker	H-Nu-IR 780	Borate V	DMAA	VBC		
1	29.20	47.30	6.10	0.470	0.490	2.30	14.10	Type II Initiators	Cured, heterogeneous
1a	29.40	47.60	5.10	0.430	0.540	2.70	14.30	Type II Initiators	Cured, heterogeneous
2	33.70	56.40	6.10	0.510	0.540	2.70	0.00	No Quaternization	Cured, heterogeneous
3	34.68	58.68	5.76	0.460	0.430	0.00	0.00	No Solubilizing Agent	Cured, heterogeneous
4	34.77	57.99	6.40	0.440	0.400	0.00	0.00	0.44% Nu	Cured, heterogeneous
5	34.21	59.07	6.00	0.400	0.320	0.00	0.00	0.40% Nu	Cured, heterogeneous
6	34.67	58.28	6.60	0.210	0.240	0.00	0.00	0.21% Nu	Cured, heterogeneous
7	34.84	58.27	6.64	0.130	0.130	0.00	0.00	0.13% Nu	Cured, more homogeneous
8	35.10	58.93	5.84	0.067	0.060	0.00	0.00	0.06% Nu	Longer Cure, homogeneous
8a	35.00	58.76	6.02	0.057	0.159	0.00	0.00	0.06% Nu	Longer Cure, homogeneous
M1	31.49	53.02	5.63	0.079	0.090	0.00	0.00	9.7% Copper Nitrate	Cured when sputtercoated (Almost all Cu)
M2	31.83	52.93	5.46	0.062	0.073	0.00	0.00	9.64% Nickel (II) Nitrate	Solidified
M3	31.39	51.56	5.35	0.075	0.081	0.00	0.00	11.54% Zinc Nitrate	Solidified
M4	31.89	52.58	5.45	0.105	0.118	0.00	0.00	9.86% Iron (III) Nitrate	Solidified
8b	34.64	58.58	6.66	0.062	0.056	0.00	0.00	0.062% Initiators	Longer Cure, homogeneous
9	34.99	59.12	5.90	0.000	0.000	0.00	0.00	No Initiators	No cure, sputter to be tested
M5	37.12	56.10	6.39	0.057	0.067	0.00	0.00	0.26% Copper Nitrate	No cure, sputter to be tested
M6	34.94	58.60	5.77	0.080	0.080	0.00	0.00	0.52% Zinc Nitrate	Solidified
A1	27.21	45.69	4.97	0.00	0.00	0.00	0.00	0.01% AuNR, H2O dec wt%	No cure
A2	22.60	37.09	4.31	0.00	0.00	0.00	0.00	0.01% AuNR, H2O dec wt%	No cure

By testing the above resins, we were able to observe that polymerization was obtainable only with some form of initiator present, whether that be a metal or the photoinitiator. It was also possible to cure metal-polymer composites with or without initiators which will be shown later. In order to see the structure formed and composition of the polymer cured, Scanning electron microscopy (SEM), Infrared Spectroscopy (IR), and Raman spectroscopy were used.

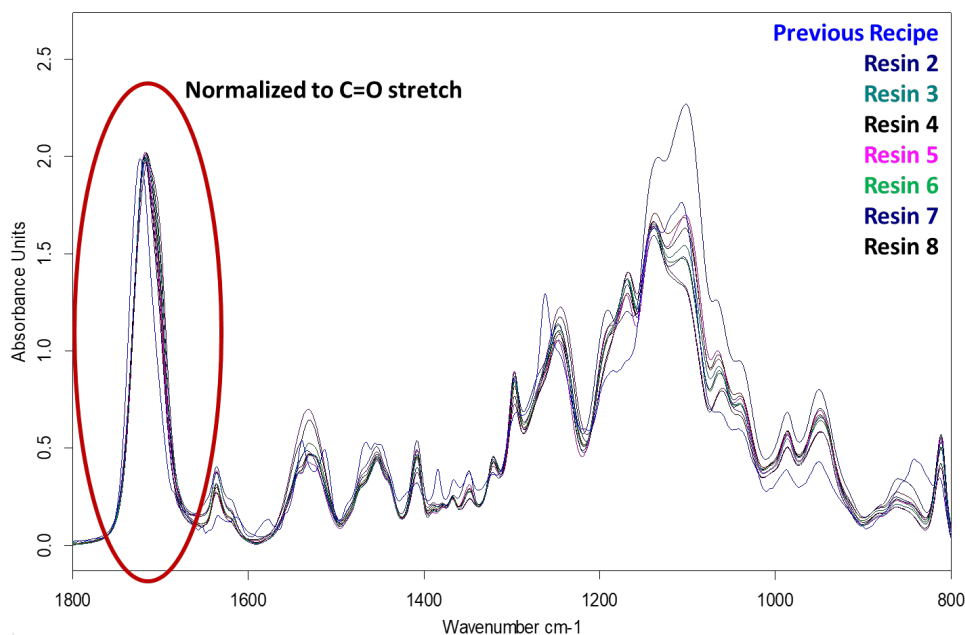


Figure 8. IR normalization.

As shown above, Figure 8, in order to measure the composition of the resin post cure, we normalized to the carbonyl stretch as it should be preserved throughout the reaction.

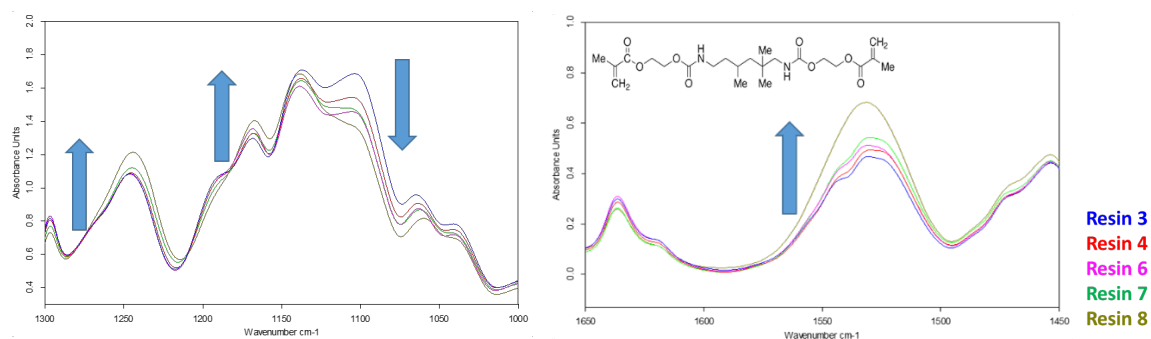


Figure 9. IR spectra post laser exposure.

From the IR spectra it was possible to identify four key changes taking places during the polymerizations at 1100, 1160, 1240, and 1515-1570 cm<sup>-1</sup>, Figure 9. These are due to changes in ester, formate, C-H bending, and secondary amine respectively. This indicates that throughout the reaction we were able to observe a decrease in the amount of initiator present and reaction progress through C-H bending which illustrates that crosslinking has occurred. To further understand the origins of the polymerization, the role of power on the cure time of the resin was varied.

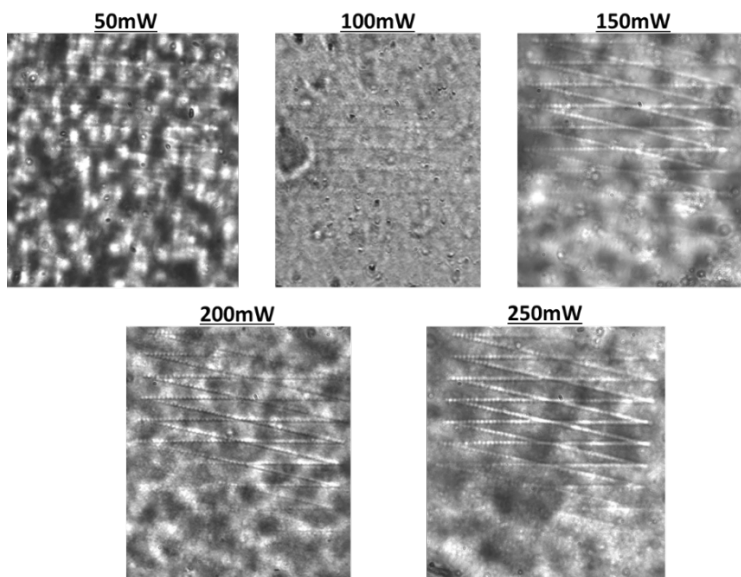




Figure 10. Effect of power on cure over a 10 0 $\mu$ m square.

In Figure 10 above, the role power has on the ability for the resin to cure is demonstrated at a constant scanning speed of 300 $\mu$ m/s and a translation speed of 20 $\mu$ m/s. The higher the power, the better the cure as indicated by the clarity of the pattern, but there was more bleeding present with higher power. This is apparent through the development of the scissor figure being prevalent at higher powers. Looking at the different resin formulations, it was possible to get an idea for cure time based off of the definition of the scissor structure. This definition represents a change in refractive index of the material, which implies that the polymerization or curing has taken place.

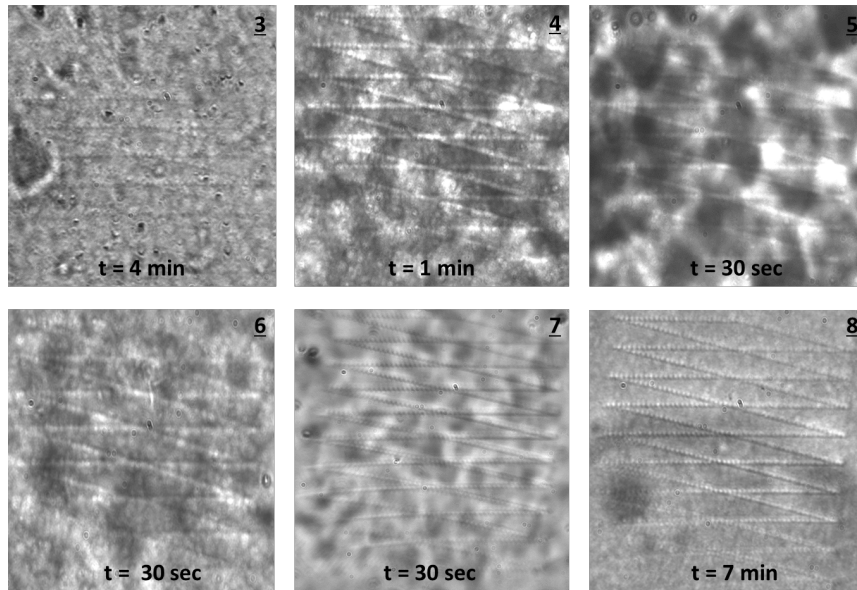


Figure 11. Effect of time on cure.

When investigating the amount of initiator present in each of these resins, there seemed to be an optimal concentration between 0.2-0.4 wt% where curing would occur between 30-60 s of exposure to the 785 nm laser (Figure 11 above). Above or below this threshold resulted in longer curing times. Since these structures cured had a much smaller surface area and could not be investigated with IR, Raman spectroscopy was used to examine the composition of the material.

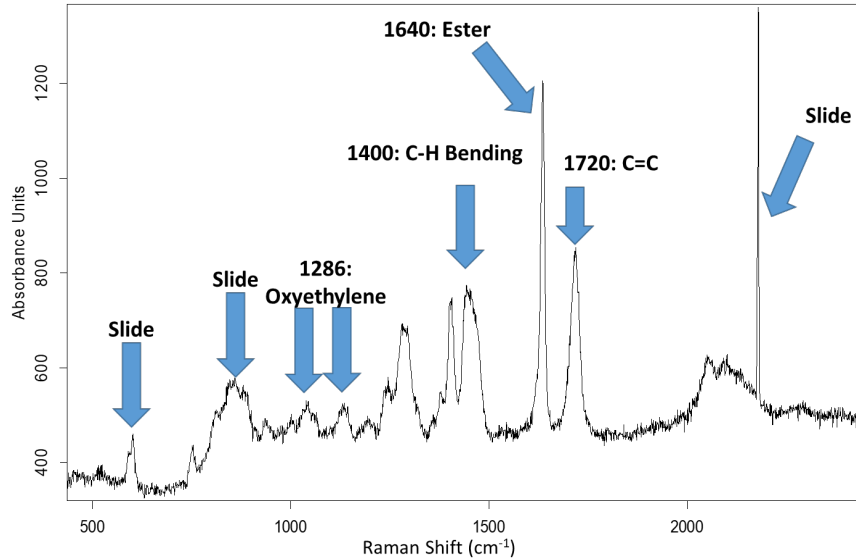


Figure 12. Raman spectra of deposited material.

The Raman spectrum of resin formulation 8, Figure 12, was acquired using a 488 nm source and is consistent with structures observed in the IR spectra although noise was too significant to identify changes throughout the polymerization using such a small sample size.

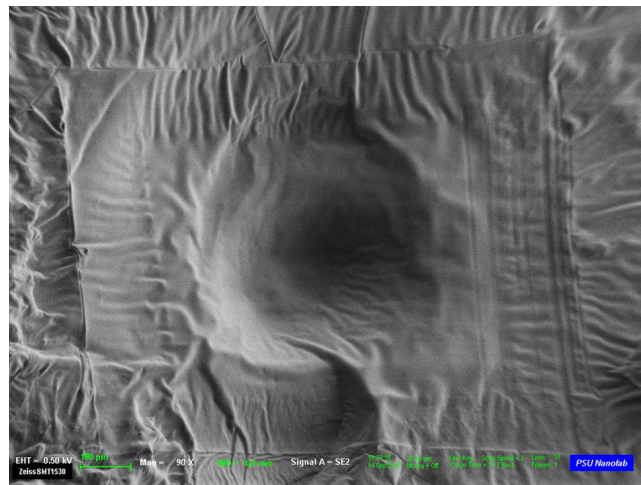


Figure 13. SEM image of deposited material.

One issue with the base resins is that bleeding can occur which is represented by the polymerization taking place outside the square in the base image of resin 7, Figure 13. Ideally, the polymerization

would stop at the end of the square, but due to the laser exposure and propagation the polymer forms more than the desired structure. It was possible to measure EDS images of the resin to get an idea of the percent composition of different elements present in the polymer or composited produced, Figure 14.

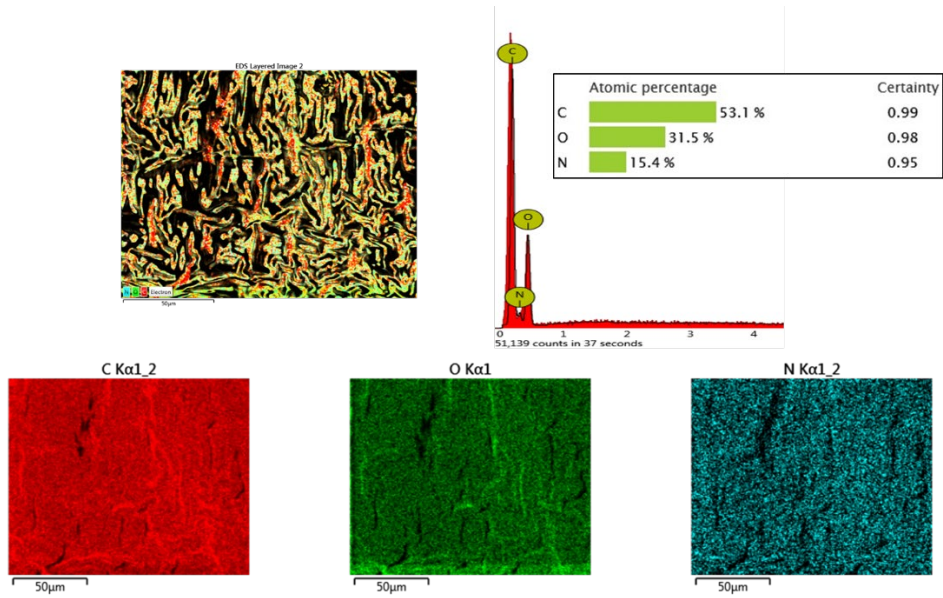


Figure 14. EDS analysis of Resin 7.

Examining the area that the laser traced, it was determined that the polymer produced had roughly the correct atomic percentages of carbon, oxygen, and nitrogen as modeling suggests for the starting materials. A similar analysis was used for a metal-polymer composite, Figure 15.

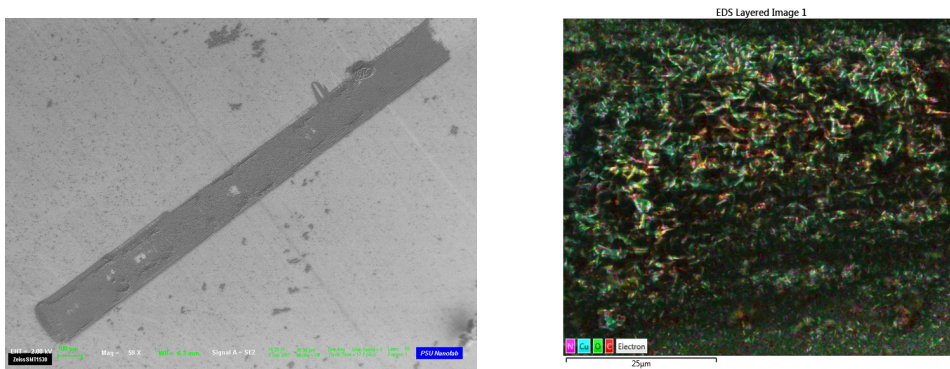


Figure 15. SEM and EDS image of polymer composite.

Above is a metal-polymer composite of  $\text{Cu}(\text{NO}_3)_2$ , which when exposed to the same analysis showed both the metal and the polymer present. EDS spectra shown below, Figure 16.

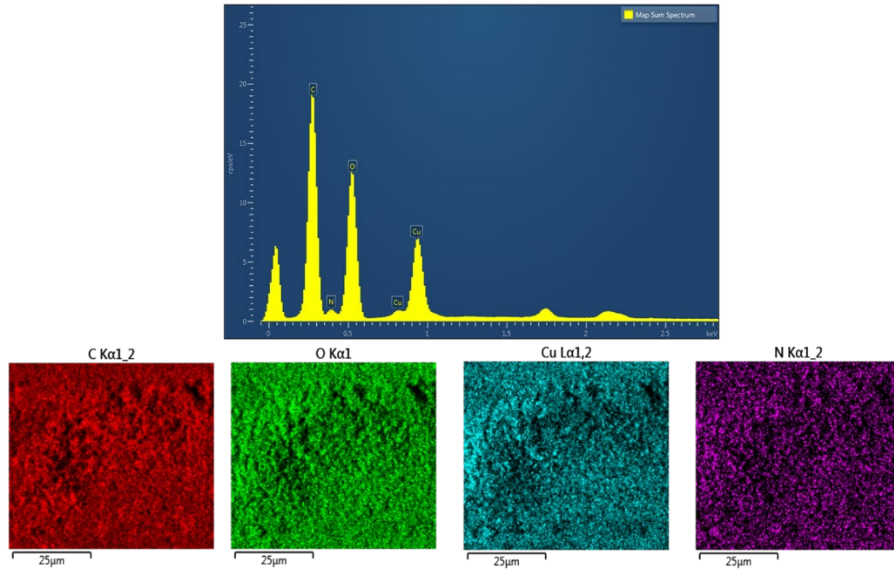


Figure 16. EDS analysis of polymer composite.

The EDS spectra shows that carbon, oxygen, copper, and nitrogen are all present in the material deposited proving that not only polymeric materials can be deposited using this technique, but rather more complex materials can also be deposited via this laser-deposition method. This work focused more on proof of concept and simple material deposition, to lay the foundation for a future student to study the extent of materials possible and further understand the reaction conditions necessary for fast and precise deposition.

## Chapter 4: Monomer Selection for Microwave Polymerizations

The work in this chapter was focused on determining what types of chemical structures effectively heat in the microwave, what molecular features dictate the extent of heating, and the ability to perform a thermal based polymerization with high yield in significantly less time than a traditional polymerization. One of the first sets of chemistry explored were polar aromatics, similar to the work done by Dudley, et al. They examined different aromatics and determined that rate of heating roughly correlated with dipole moment. This is interesting because it allows us to predict potential monomers that will heat well in the microwave and be ideal for polymerizations. In order to identify general trends with polar aromatic molecules and how well this idea could be applied to our work, 10 wt% solutions of polar aromatics in toluene were exposed to the microwave at 50W for 7 minutes. The data is shown below, Figure 17, along with the dipole moments of each molecule tested and a depiction of the general trend observed.

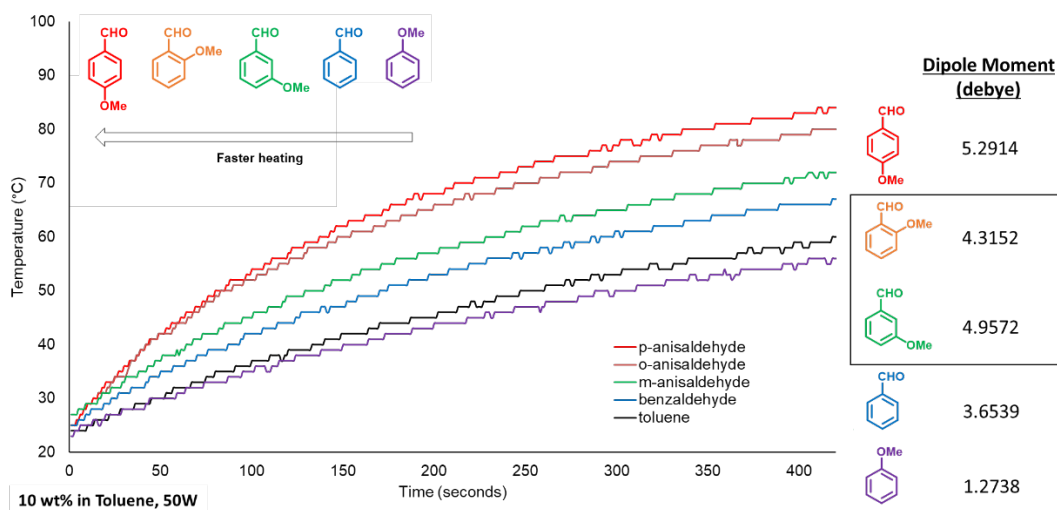


Figure 17. Heating curves of various polar aromatics.

Figure 17 above suggests that molecules with a greater “push-pull” behavior have faster heating profiles in the microwave. One interesting thing to note is that the dipole was not perfect in predicting which aromatics would be the most effective at heating quickly. Upon examination it became apparent that there is also a resonance effect present, where depending on the conjugation and resonance forms, there can be an enhanced dipole present which will lead to higher heating in certain structures. One example of this is shown below in Figure 18.

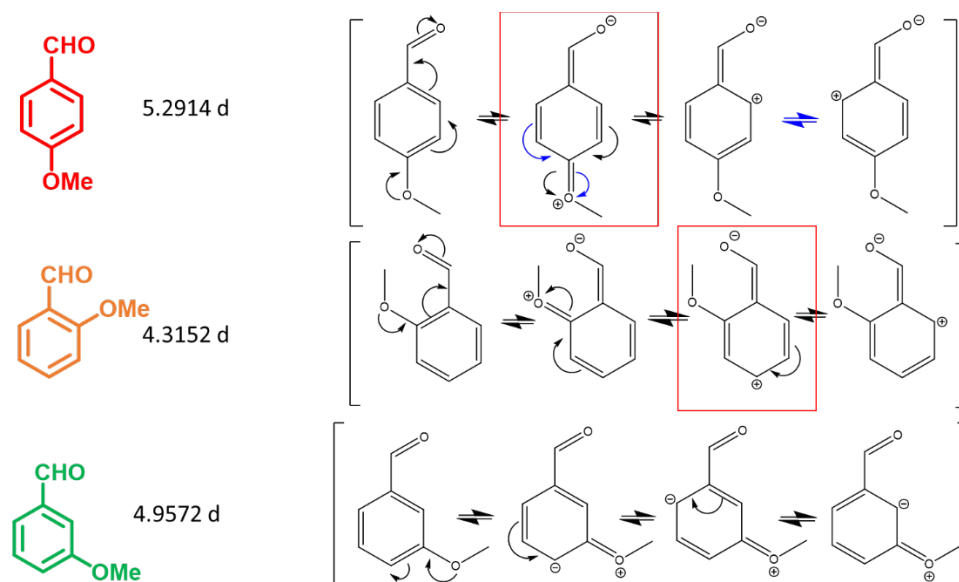


Figure 18. Enhanced dipole moment through conjugation.

Figure 18 illustrates that although the molecule with the methoxy group in the meta position has a higher dipole, it does not have as effective of charge separation as the ortho and para positions, leading to less effective heating. This is most likely due to the fact that dipole rotation and magnetic fields play a large role in microwave heating. From looking at these polar aromatics and a few other constraints it was possible to determine several general trends to also consider when selecting monomers for experiments.

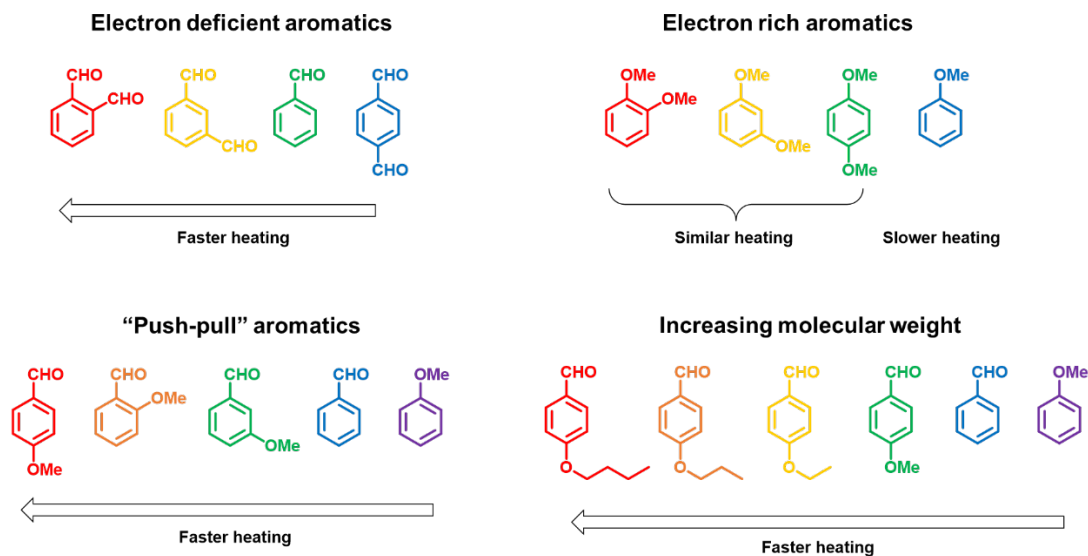


Figure 19. General trends observed in microwave heating.

Four general trends appeared in this study, Figure 19, while also considering the enhanced resonance effect. The further electron deficient an aromatic ring was, the faster the overall heating was. There did not really seem to be an impact based on how electron rich an aromatic ring was, and this is most likely due to a minimal change in polarity. The trend of “push-pull” aromatics was discussed earlier, and it was also observed that the molecular weight of the substituent or overall length of the carbon chain attached to the para position, allowed for faster heating. It is possible that the chain acts as a rotor or further impacts the charge separation, but more studies would be needed to determine the overall role of molecular weight. The next set of chemistry that we looked at was acylates with different chain lengths, polarities, and functional groups. A similar test of 10 wt% in toluene at 50W for 7 min is shown below, Figure 20.

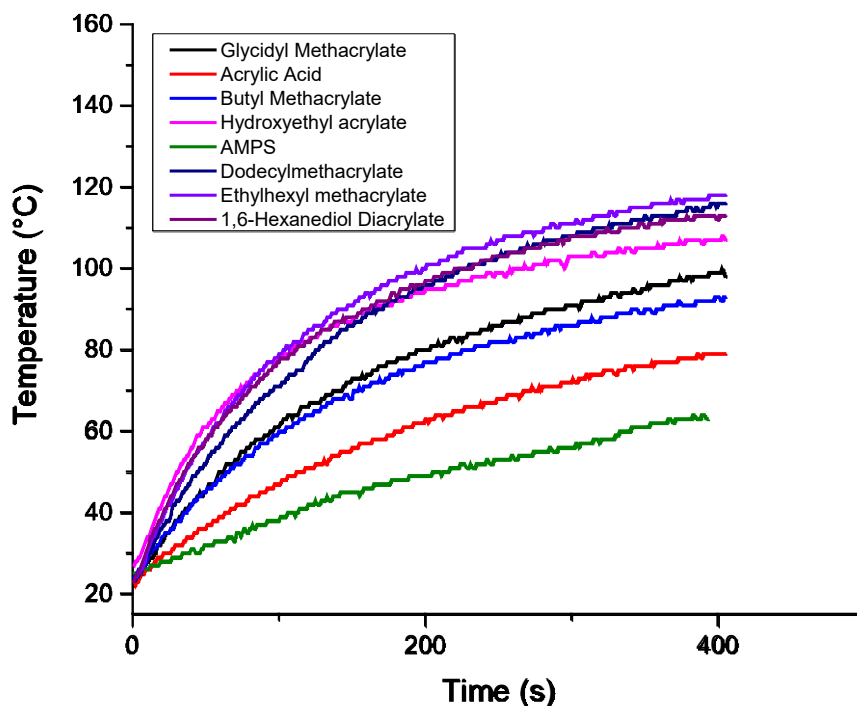


Figure 20. Microwave heating of various acrylates.

For acrylates, it was observed that again a larger chain length led to higher heating and a higher dipole (shown below) tended to mean higher heating. Below is the same data, plotted based off dipole moment, rather than time. Dipole moment is not nearly as good of an indicator for acrylates, this is most likely due to either viscosity or how freely the molecule can rotate, but it does still give an idea if it will be susceptible to microwave heating (shown below – Figure 21).



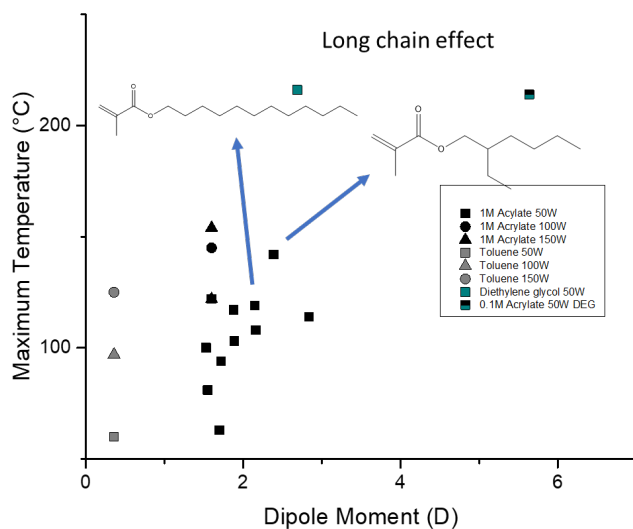


Figure 21. Maximum temperature vs dipole moment of acrylates.

Other chemistry investigated consisted of diols, diacids, and styrene. Diols and diacids tended to not heat or show an increase in heating based off dipole moments. Styrene, by itself, exhibited similar behavior and showed minimal heating. Several ionics were studied as well, these results are shown below in Figure 22.

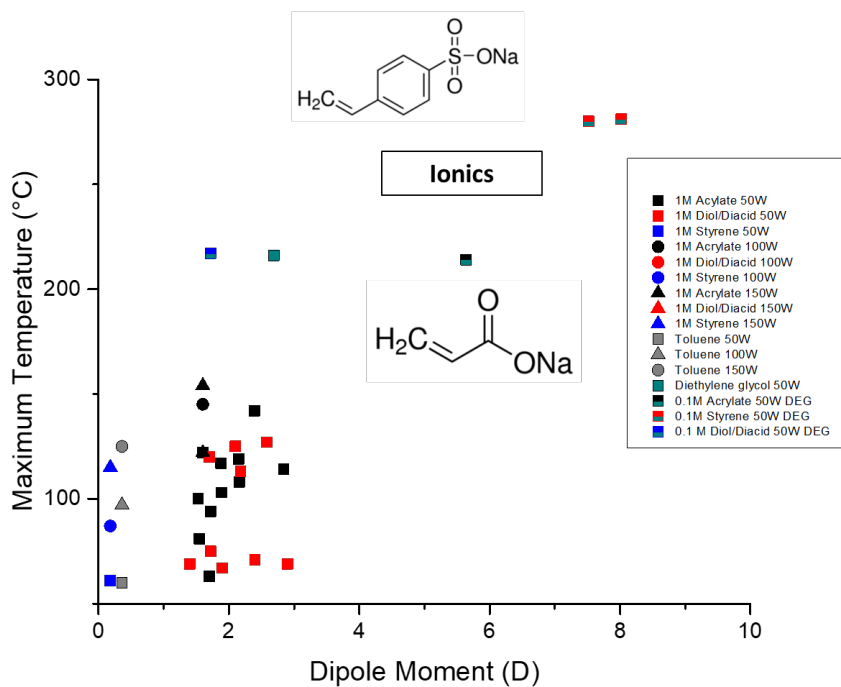


Figure 22. Summary of heating profiles.

The figure above shows a summary of all types of chemistry tested and illustrates a few outliers. One set of chemistry that had interesting properties were ionics. Acrylates and styrene behaved different under microwave irradiation, but with the addition of the ionic substituent sodium styrene sulfonate exhibited the most heating out of any molecule. This is interesting because ionics increased heating in both sets of chemistry tested, but it also was able to make a less microwave susceptible chemistry heat extremely well and extremely fast making ionics an ideal choice for polymerizations.

## Chapter 5: Thermal Polymerization via Microwave Heating

The objective of this portion of the thesis is to lay the foundation for future work on novel polymerizations as well as to support the concept that microwave heating can be used to perform accelerated polymerizations with highly susceptible monomers. Also explored were the role that the initiator plays in the polymerization rate and included is a demonstration of the possibility of synthesizing new ionic polymers/graphene oxide composites using rapid microwave synthesis. First, the solvents were studied to understand whether the heating was due to the solvents or the components for polymerization themselves. Below are common solvents at 50W and 150W for 7 min, Figure 23.

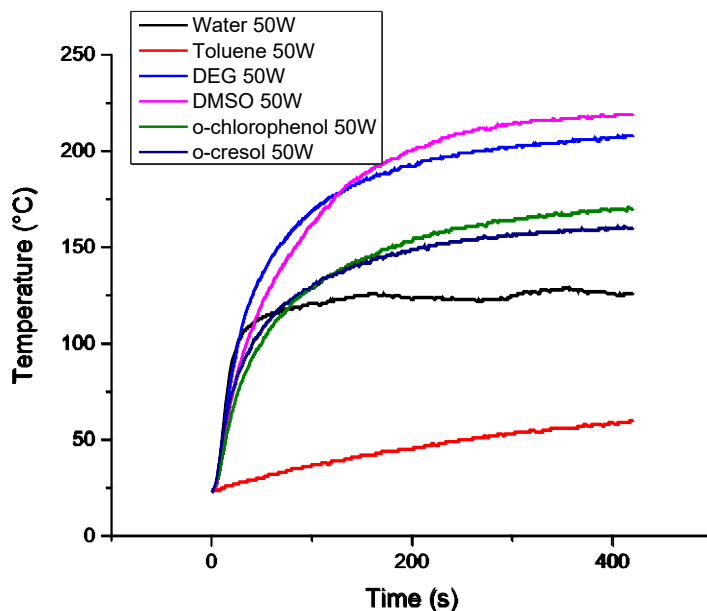


Figure 23. Solvent heating at 50 W.

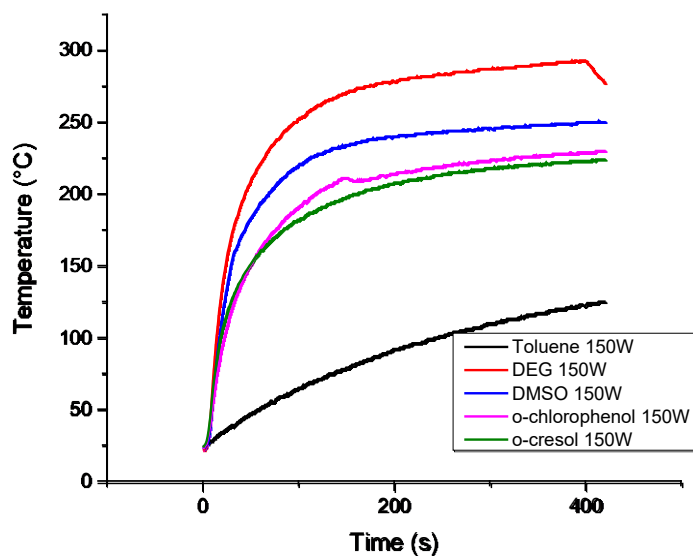


Figure 24. Solvent heating at 100 W.

Figure 24 again illustrates the more polar the solvent, the more heating that will take place. For these studies, the goal was to pick the least heating solvent that has a reasonable solubility with sodium styrene sulfonate, graphene oxide, and the RAFT agent. In this case, water was the chosen solvent due to its lower heating and high solubility of the polymerization materials. To further isolate what is being heated in the polymerization and what is necessary for the reaction to take place, baselines were taken to understand the heating (Figure 25).

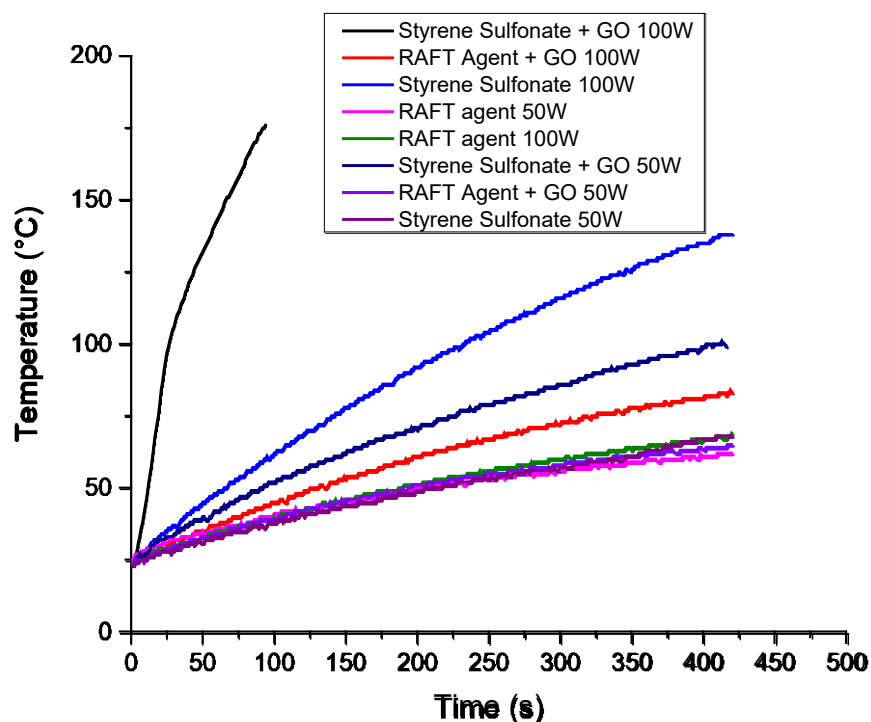


Figure 25. Baseline heating for polymerization.

Examining the data above, neat styrene sulfonate in water did not exhibit a significant amount of heating which is different then the results presented before when it was in a higher heating solvent. When graphene oxide was added to the solution, there was an increase in overall heating which became apparent at higher microwave powers. When exposed at 100W, the styrene sulfonate and graphene oxide mixture had a rapid heating effect and reached over 175°C in under two minutes. It is likely that these molecules have a synergistic effect and are highly susceptible to microwave irradiation whereas the RAFT agent is going to serve a different role in the reaction. Another instance where graphene oxide helps initiate heating is with acrylamides (Figure 26).

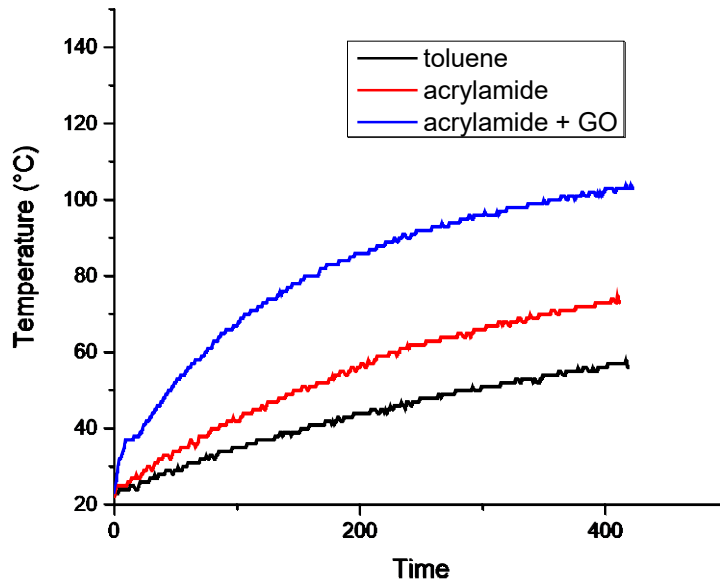


Figure 26. Effect of GO on MW heating.

In this instance GO also plays a large role when added to acrylamide. This is interesting because graphene oxide does not heat well when by itself in solution, but with the addition of another heating molecule it experiences effective heating. The nature of the graphene oxide heating may be due to its semiconductor properties and the excitation of electrons from the valence band to the conduction band or it may stem from its structure and dipole moment. A simple study was used to see if the polymerization would take place, shown below in Table 2.

Table 2. Polymerization composition mixtures.

Styrene Sulfonate (g)	Graphene Oxide (g)	RAFT Agent (g)	Solvent (mL)	Power (W)	Time
1.0	0	0	4	50, 100	30 min, 1 hr, 3 hrs
1.0	0.01	0	4	50, 100	30 min, 1 hr, 3 hrs
1.0	0.01	0.05	4	50, 100	30 min, 1 hr, 3 hrs
1.0	0	0.05	4	50, 100	30 min, 1 hr, 3 hrs

For the 30 min and 1-hour trials, there was no polymer obtained in any of the reactions tried. The only trial with polymer obtained was the 100W trials of solution containing all three components for 3 hours. The heating curve is shown below in Figure 27.

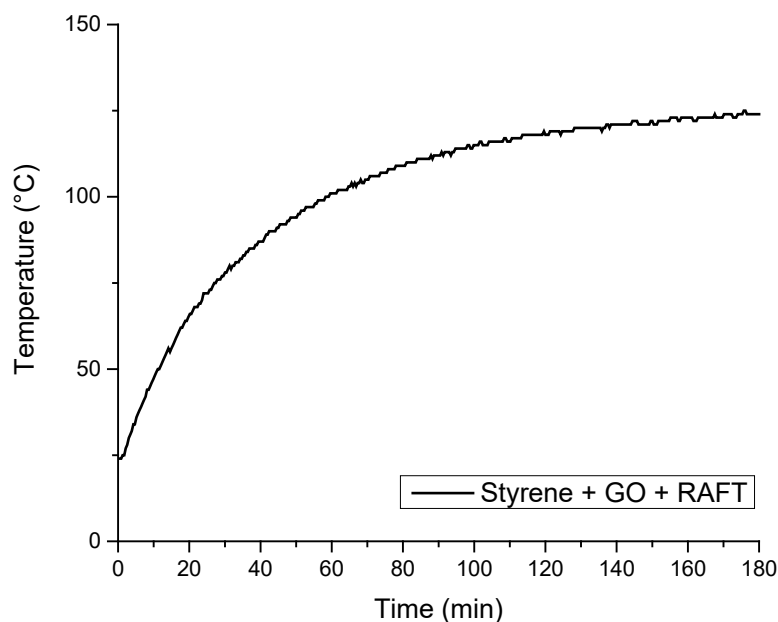


Figure 27. Heating curve of styrene + GO + RAFT agent at 100W for 3-hours.

The heating was much slower in this case, which may be due to the presence of the RAFT agent and the reaction taking place. From the 1.032g of styrene sulfonate added to the solution, 0.742g of polymer was produced, giving a yield of ~72% for the reaction. For this same reaction at 50W, further testing at longer time lengths should be done to evaluate if the graphene oxide creates an energy barrier that needs to be crossed for the reaction to initiate. The synthesis of this polymer indicates that this method can be used and tailored for different polymer/polymer composites under the right conditions. Further work should be done exploring the range of

polymerizations possible and studying whether polymerizations can be achieved in the microwave relying on solvent heat transfer rather than monomer and component heating.

When Saito, et al.<sup>17</sup> polymerized styrene sulfonate using traditional methods and RAFT agent, he was able to attain between 75-90% yield depending on the reaction time, which was over the course of 24 hrs. The microwave induced method allowed for a 72% yield over the course of a 3-hour polymerization, validating that it can be used as an effective polymerization method and can be used in industrial applications.



## **Chapter 6: Conclusions and Future work**

This work has shown that both laser-induced photopolymerization and microwave polymerizations have the capability of advancing not only polymerization methods but have the capability of making novel materials in non-traditional methods. The laser deposition technique discussed throughout this paper has shown that polymers and polymer composites can be produced while also having control over the architecture produced. This work will serve as foundation for a further student to explore more composites possible as well as what parameters will dictate the accuracy and precision of the structures desired.

For microwave synthesis, a foundation of rules for what chemistries heat in the microwave has been established as well proof that a polymerization can occur in significantly less time than traditional methods with high yield can occur. This work will open the door to testing more complex chemistries and polymerizations, as well as help develop novel polymer composites that will be unattainable using traditional methods.

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