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LDRD PROJECT TITLE: Probing photochemical kinetics and mechanisms using photoNMR

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ABSTRACT:

Nuclear magnetic resonance spectroscopy (NMR) is a form of spectroscopy that yields detailed mechanistic information about chemical structures, reactions, and processes. Photochemistry has widespread use across many industries and holds excellent utility for additive manufacturing (AM) processes. Here, we use photoNMR to investigate three photochemical processes spanning AM relevant timescales. We first investigate the photodecomposition of a photobase generator on the slow timescale, then the photoactivation of a ruthenium catalyst on the intermediate timescale, and finally the radical polymerization of an acrylate system on the fast timescale. In doing so, we gain fundamental insights to mission relevant photochemistries and develop a new spectroscopic capability at SNL.

INTRODUCTION AND EXECUTIVE SUMMARY OF RESULTS:

Photochemical reactions are key processes in a wide range of technologies, including additive manufacturing,[1-3] catalysis,[4-7] and coatings and adhesives.[8] In-depth understanding of the mechanisms and kinetics of photochemical processes enables the optimization and development of new photochemistries. Current methods for characterizing photochemical mechanisms include ultraviolet-visible (UV-Vis), infrared (IR), fluorescence, electron paramagnetic resonance (EPR) spectroscopies and ultrafast spectroscopic techniques for probing excited state lifetimes and photophysics.[9-12] While useful, most of these techniques do not provide as much atomic-level specificity and therefore do not provide as much structural and mechanistic information as nuclear magnetic resonance (NMR) spectroscopy.[9, 11, 13-17] UV-Vis and IR spectroscopies can identify functional groups within molecules and measure the concentrations of known molecular species.[10] While these techniques possess great utility, they are limited in structural resolution, and are often convoluted by overlapping signals. Similarly, fluorescence is used to characterize radiative energy transfer and excited state lifetimes but does not provide direct information about the molecular structures of reactive species. While EPR is similar to NMR, it is limited in that it targets unpaired electron spins rather than nuclear spins can thus only provide information on the local environment of the unpaired spin and not on the complete molecular structure.[16] EPR is also less widely available than NMR. NMR enables the complete characterization of the molecular structures of reactive species and allows the study of dynamic processes, such as diffusion, across timescales ranging from picoseconds to hours.[9] Using advanced NMR techniques, researchers can determine chemical reaction mechanisms and intermediates.[11, 16, 18-20] When photochemical processes are slow, samples can be irradiated ex situ and then studied via NMR. However, the ex situ irradiation method is not suitable for fast timescale processes or intermediates, which necessitates in situ irradiated NMR (photoNMR, Figure 1a).[15] PhotoNMR can provide detailed mechanistic information about photochemical reactions than cannot be obtained from other methods.[20] While in situ irradiation can provide improved detection of fast processes, irradiation can also form radicals that broaden NMR signals, making development and implementation of photoNMR capabilities nontrivial.[14, 16, 21] Our research goal for this 15-week exploratory project is to investigate the use of photoNMR for application to additive manufacturing relevant photochemical systems with varied timescales. In this work we used photoNMR to analyze the photodecomposition of a photobase generator, the photoactivation of a ruthenium catalyst, and photoinitiated radical polymerization of an acrylate monomer (Figure 1b).

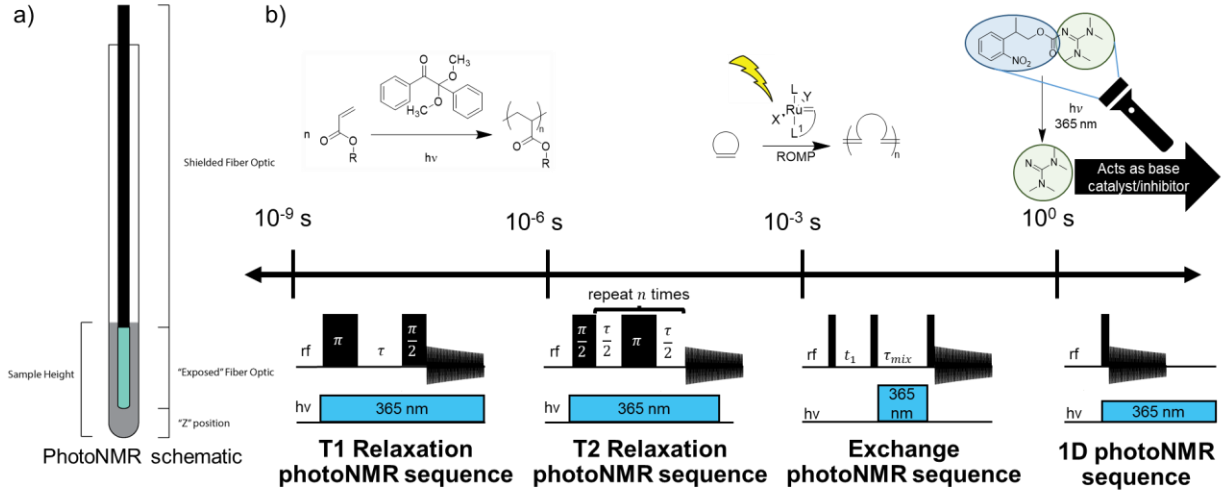

Figure 1: (a) schematic of photoNMR testing set up and (b) exemplar chemical process schematics and pulse sequence schematics corresponding to their timescales representing slow, medium, and fast chemistries. The slow chemistry is the release of a photocaged base upon irradiation, the medium rate system is photoactivation of a ruthenium catalyst to perform ROMP AM, and the fast system is a radical cure acrylate used as an adhesive and coating.

In this study we first measure the kinetics of a known photochemical system, photogeneration of a base from 2-(nitrophenyl)propoxycarbonyl-1,1,3,3-tetramethylguanidine (NPPOC-TMG, Figure 1b). NPPOC-TMG has been used as a photobase generator (PBG) for additive manufacturing photocontrol[3] and for base catalyzed reactions, such as thiol-Michael addition, ring opening polymerizations, ionic polymerizations, and peptide binding.[22] NPPOC-TMG photogeneration rates have been well defined by Zhang et al. using real time FTIR.[7] Walbert, et al. demonstrate an intramolecular H abstraction mechanism using nanosecond laser flash photolysis and HPLC.[23] Next, using information and techniques developed from studying NPPOC-TMG, we studied photoactivation of ruthenium catalysts for ring opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD). The Ru catalyst HeatMet is thermally latent has also been shown to be photoactive, especially in combination with photosensitizers, though some polymerization occurs without them.[1] While the kinetics of ROMP with Ru catalysts have been explored, the mechanism of photoactivation of HeatMet has not been determined. Finally, we attempted to study the radical lifetime of an acrylate system. While the bulk polymerization kinetics of acrylates can be measured with techniques such as UV-rheology and FTIR,[24] photoNMR enables measurement of radical lifetimes during polymerization.

EXPERIMENTAL:

2-(2-Nitrophenyl)propyl-N-(1,1,3,3-tetramethylguanidinyl)carbamate (NPPOC-TMG) synthesis: 2-(2-Nitrophenyl)propanol (3.50 g, 14.32 mmol, 1 eq) was loaded into a 150-mL round-bottom flask equipped with a magnetic stir bar. CH_2Cl_2 (55 mL) was added, followed by carbonyl diimidazole (4.85 g, 29.94 mmol, 1.55 eq) portion-wise. The reaction was capped with a septum equipped with a gas regulator, covered in aluminum foil to prevent light from entering, and stirred at room temperature for 4 hours. Tetramethylguanidine (9.94 mL, 79.20 mmol, 4.1 eq) was then added slowly and the reaction was stirred at room temperature for 18.5 hours. The reaction was quenched with water (30 mL) and extracted with CH_2Cl_2 (20 mL). The organic extracts were combined, washed with water (3 x 15 mL), brine (20 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in a rotary evaporator at 60 °C and the crude product was purified using column chromatography (SiO_2, 20% MeOH/CH_2Cl_2, liquid-loading on Teledyne Isco CombiFlash NextGen 300+), resulting in **NPPOC-TMG** as a dark red-orange oil that crystallized under high vacuum (<50 mTorr). Yield: 5.23 g, 84%.

NMR spectroscopy:

NMR spectra were collected at 14.1 Tesla on a Bruker Avance III 500 MHz spectrometer with $CDCl_3$ as a solvent in a 5 mm tube at room temperature unless otherwise noted. Temperature is controlled using a heating probe and liquid nitrogen cooled purge gas.

PhotoNMR:

PhotoNMR experiments were conducted with New Era PhotoNMR sampling devices (NE-379-5-BR) with a ThorLabs fiber optic patch cord (FG910LEC) connected to a ThorLabs LED (M365FP1) and LED driver (LEDD1B). The fiber was stripped with a razor to the length of the capillary neck in the photoNMRtube. A ThorLabs integrating sphere (S142C) was used to quantify the light intensity in the bare region of fiber and from the LED. Samples were placed in a spinner and the fiber was secured in place inside the tube using tape at the top of the capillary. The spinner was then inserted into a polypropylene tube to guide the fiber and secured with a Teflon set screw. The entire apparatus was then lowered into the spectrometer and locked to the solvent. Standard tuning, shimming, and gain adjustments were made using Bruker software.

Time resolved 1D experiments:

Single scan dark spectra were taken after inserting the prepped samples into the spectrometer to check the shim. Sequential one-dimensional scans were taken every ~20 s for ~32 minutes, and the light was turned on manually after a predetermined number of scans. Integrations were determined for relevant peaks for each scan using a custom Python code with nmrglue.

RESULTS AND DISCUSSION:

NPPOC-TMG photodecomposition: NPPOC-TMG kinetics have been studied previously by Zhang et al.[7] Using UV-vis and FTIR with in situ irradiation, Zhang et al. developed a kinetic model for photodecomposition of NPPOC-TMG that correlates the rate of decomposition to light intensity and NPPOC-TMG concentration(Equation 1). $[I]$ is the concentration of NPPOC-TMG, t is time, I_0 is light intensity, λ is the wavelength of light and $\varepsilon\varphi$ is a fit value for photolytic efficiency at that wavelength (N_{AV}, h, and c are Avogadro's number, Planck's constant, and the speed of light, respectively). The value 2.303 is the log conversion factor.

$$-\frac{d[I]}{dt} = \frac{2.303\varepsilon\varphi[I]I_0\lambda}{N_{AV}hc} \qquad (1)$$

To calibrate our photoNMR equipment, we used the known photobase generation kinetics of NPPOC-TMG. First, we take an unirradiated ^{1}H NMR spectrum (Figure 2a) then begin time resolved scans after 5 minutes we turn on the irradiation and continue collecting scans until disappearance of the signal corresponding to the starting material. Upon irradiation we note the gradual disappearance of the doublet peak representing the methyl group on NPPOC-TMG and the development of a new allylic singlet (Figure 2a). Using nmrglue in python,[25] we are able to track the integrations of the aforementioned peaks over time (Figure 2b), and see that they follow first-order reaction kinetics as reported by Zhang et al. We could fit the kinetics data to the proposed model by varying the light intensity to determine the actual light intensity at the sample. We found the light intensity applied to our sample to be ~0.7 mW/cm^2. We also measured the light intensity from the fiber optic with an integrating sphere and found the output to be ~6 mW/cm^2 and the source intensity to be ~200 mW/cm^2. The discrepancy between the intensity applied to the sample and the power of the lamp indicates that the fiber optic used in these tests severely limits the intensity reaching the sample and thus the ability to measure photochemical processes which will only progress very slowly, or possibly not at any measurable level, with such low light intensity.

However, with the NPPOC-TMG system the intensity was sufficient to promote the photodissociation and base generation. We also observe the development and disappearance of new peaks representing intermediates of the proposed photodecomposition. To probe the lifetimes of these intermediates, we conducted a test wherein we begin the time resolved scan experiment, turn the light on until intermediates develop, and then stop the light while continuing our scans. We find that the intermediate peaks continue to grow when the light is turned off although the reaction and product peaks are level during the dark period. After the dark period the intermediate peaks are consumed during the next light pulse. Future work will attempt to characterize these intermediates using 2D spectroscopy to identify these intermediates to confirm the hypothesized mechanism for NPPOC-TMG photobase generation (Figure 2d).

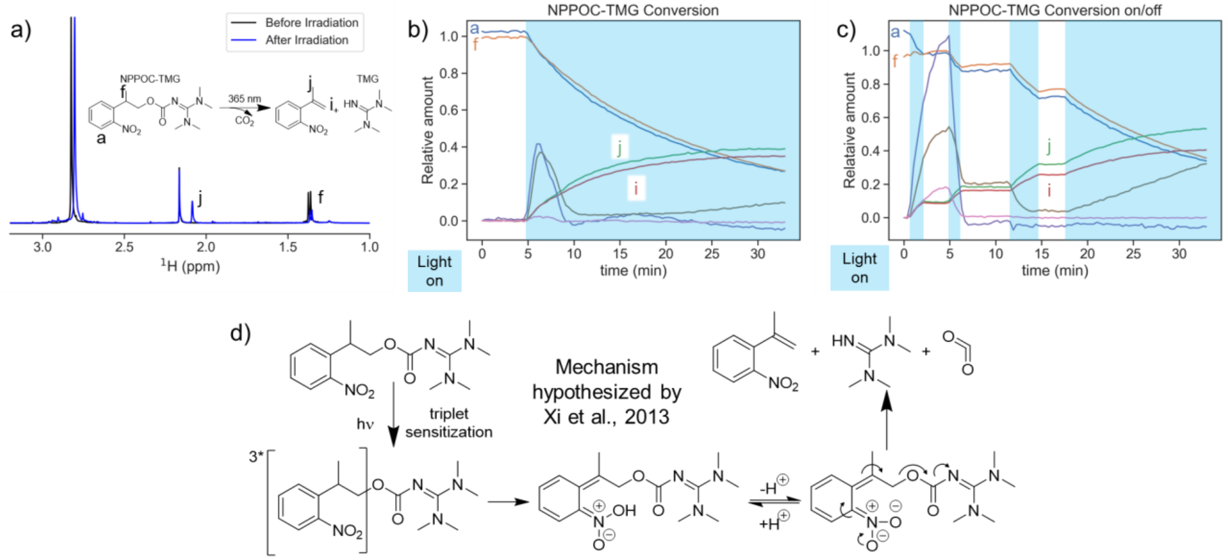

Figure 2: (a) ^{1}H NMR spectra of NPPOC-TMG before and after irradiation (black and blue, respectively) with peaks denoted that are tracked by (b) total peak integrations as a function of time by taking sequential scans under irradiation to quantify reaction kinetics. The blue region denotes time under irradiation. The same notation is used in (c) where the LED is turned on and off to identify the peaks of long-lived intermediates that appear and disappear over the course of the reaction. Reactant peaks are normalized to their maximum intensities and products are normalized to stoichiometric ratios relative to starting materials (intermediates assumed to be 1 proton for each peak) (d) a previously proposed mechanism for the photodecomposition of NPPOC-TMG.[4, 23]

HeatMet photoactivation: HeatMet is thermally latent and has also been shown to be photoactivated for ROMP. The photoiniatied ROMP of a 95:5 wt./wt. mixture of DCPD and ethylidene norbornene (ENB) has been used for the additive manufacturing of thermosets (Figure 3a).[2, 26] While the kinetics of this process have been characterized by Leguizamon et al.,[1] we seek to investigate the mechanism of activation. Several techniques can monitor the rate of ROMP, however photoNMR allows full characterization of the catalyst during activation. Understanding the photoactivation mechanism for HeatMet will help guide catalyst and monomer selection and design for improved additive manufacturing. We first attempted to characterize the ROMP kinetics of HeatMet with dicyclopentadiene (DCPD) both with and without light to see if the low intensity light can activate the catalyst. We added a small quantity (1-2 mg) of HeatMet and dissolved in $CDCl_3$ to 10 mg/mL. We then add a 95:5 mixture of DCPD:ENB volumetrically to yield a 5:1 molar ratio of monomer to catalyst and pipet the solution into an NMR tube. Minimizing the time before beginning tests, we take a dark spectrum of the sample (Figure 3b) and begin time-resolved scans either with or without light (Figure 3c). We then use nmrglue[25] to track the progress of the reaction and find that the rates of reaction between irradiated and unirradiated HeatMet with DCPD are very similar. This appears to be a function of low light intensity as previous work has shown that HeatMet can initiate photoROMP, even in the absence of photosensitizers.[1] To improve light intensity provided to the sample in future work a fiber optic with a lower wavelength range should be employed and higher power light sources could be investigated.

There are small shifts in the alkylidene and ester peaks of HeatMet that indicate some chemical change in the molecule with irradiation (Figure 3d). This is readily apparent in the downfield shift of the alkylidene peak when irradiated. To test what might be causing this shift, we ran ^{1}H NMR scans at varied temperatures and noted a linear relationship between the alkylidene peak shifting downfield as the temperature increases toward the HeatMet activation temperature of ~85°C (Figure 3e,f). Due to the parallels in alkylidene peak shift between increasing temperature and irradiating the sample, we hypothesize that the UV exposure at low irradiance may be equivalent to a slight temperature increase. To test this hypothesis, light intensity must be increased to determine if the observed peak shift with increased intensity matches that observed with increased temperature. To rule out a light induced change in temperature, we conducted an experiment to ensure that the UV light is not simply warming the sample using a methanol standard and measured no significant change in temperature with irradiation. Due to the low power of our light source, we cannot significantly increase the light intensity to test this hypothesis. Prior UV-rheology work was conducted with 120 mW/cm^2 light at 365 nm and demonstrated full polymerization of a pDCPD thermoset within ~5 min, and ~2 J/cm^2 required to gel instantaneously.[2] Light intensity is correlated with ROMP activity, and by extension photoactivation of HeatMet. Future efforts will be focused on increasing the power of our light source to enable higher light intensity testing, and tuning HeatMet concentrations to optimize optical density in the sample and ensure homogeneous light penetration throughout the sample.

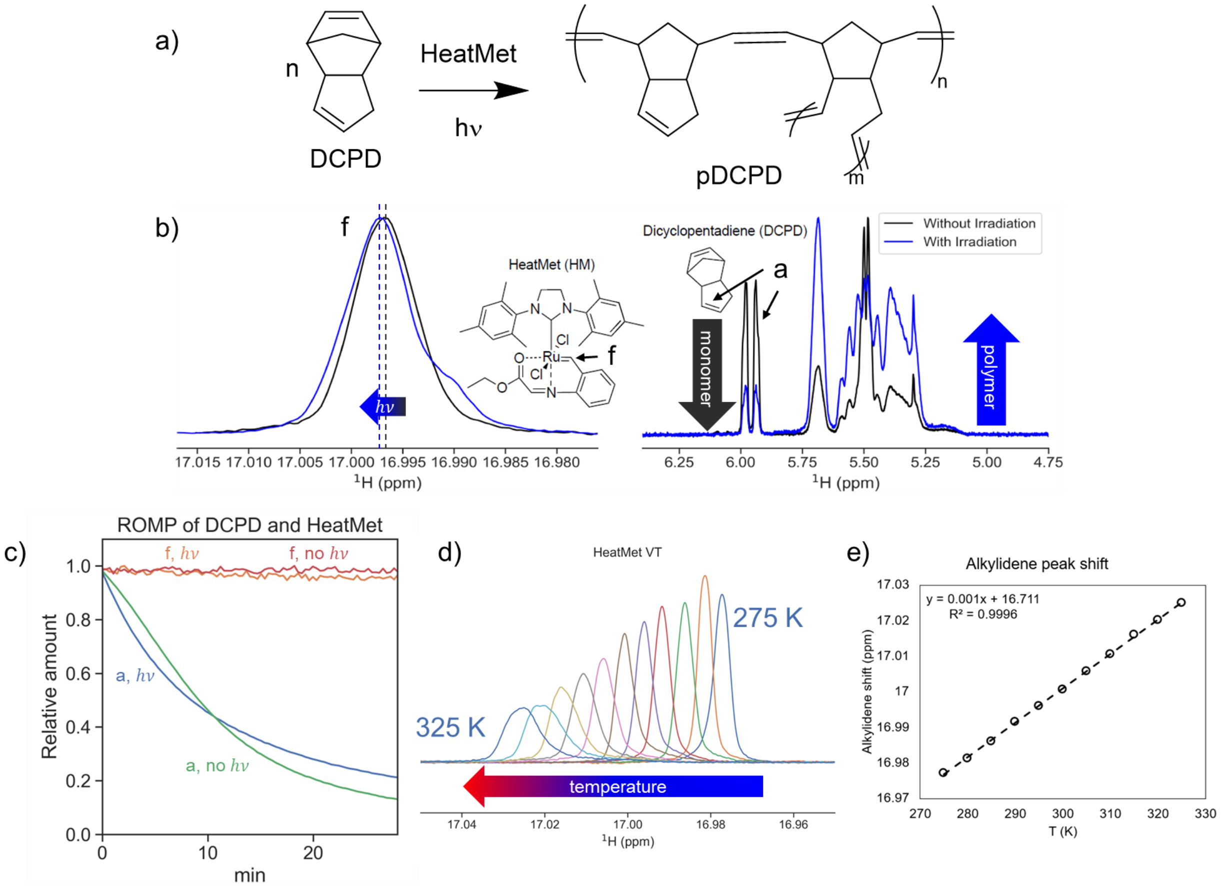

Figure 3: (a) reaction scheme for ROMP of DCPD. (b) ^{1}H NMR spectrum of 5:1 molar ratio DCPD:HeatMet at ~10 mM HeatMet, and (c) kinetics profile with and without irradiation (blue and green curves, respectively). (d) Shows the slight downfield shift in the alkylidene peak upon irradiation. (e) tracking alkylidene peak shift across temperatures, which is plotted in (f).

Acrylate radical relaxation: Acrylate cured photopolymers represent a low energy, economical alternative to thermally cured polymers. They can be used for a variety of applications, including coatings,[8] adhesives,[27] biomedical applications,[28] and additive manufacturing.[24] In this study we used ethoxylated BPA dimethacrylate (SR348), a commercial difunctional monomer which has been used for UV-assisted direct-ink-write additive manufacturing. Using the radical photoinitiator 2,2-dimethoxy-2-phenylacetophone (Irgacure 651) we attempted to characterize the radical lifetime of the initiator and monomer species using T1 relaxation experiments. However, we did not see significant peak broadening indicative of radical formation in the irradiated sample. We hypothesize that this was due to the low light intensity resulting in minimal radical formation below the threshold for detection by NMR techniques. Future work should emphasize increasing the light intensity within the NMR tubes to more closely match relevant irradiances used for the reactions of interest, which are 10-100 times greater than our current capabilities.[3]

ANTICIPATED OUTCOMES AND IMPACTS:

We have accomplished our key goal of developing photoNMR at Sandia and understanding the capabilities and limitations. In doing so, we developed better understandings of photochemistries pertinent to ongoing ROMP AM research at Sandia, including, but not limited to, ACT FY24 Project "Vat Polymerization of Functional Materials for Next-Generation Components", MSRF LDRD Project "Understanding and Developing Dual-Wavelength Olefin Metathesis Polymerizations for the Rapid, Continuous Additive Manufacturing of High-Performance Thermosets" (LDRD 23-0034), and DOE Energy Frontiers Research Center for Regenerative Energy-Efficient Manufacturing of Thermoset Polymeric Materials. Techniques developed in this study and the improved understanding of the challenges associated with this method will enable further characterization of photosystems relevant to AM and other processes. Knowledge gained in the pursuit of this capability development, while useful, will be more fully developed by continuing to improve the capabilities developed in this ExEx. After initial demonstration of capabilities LDRD 23-0034 will fund purchase of a fiber optic to enable higher light intensity studies of HeatMet activation.

The results of this project will be presented in a poster presentation at the 2023 Photopolymerization Fundamentals conference in Boulder, CO. If improvements to the instrumentation can increase the light intensities to levels relevant to the study of photochemical systems of interest a full proposal to the MSRF IAT focusing on the use of photoNMR to characterize photoprocesses for additive manufacturing, lithography, and photopolymerized coatings and adhesives will be pursued.

CONCLUSION:

Nuclear magnetic resonance spectroscopy (NMR) can provide detailed mechanistic information about chemical structures, reactions, and processes. By integrating in situ irradiation to NMR (photoNMR), we can study the kinetics, mechanisms, and intermediates of photochemical processes. Photochemical processes are widely used in modern chemistry and particularly useful for additive manufacturing (AM) processes. Here, we investigated three photochemical processes spanning different AM timescales. First, we investigated the photodissociation of the photobase generator NPPOC-TMG. By fitting the photodissociation kinetics to kinetic equations reported in the literature, we were able to calculate the intensity of light reaching our samples. In this study we were also able to identify potential intermediate species for further study.

We then investigated the photoactivation of a ruthenium catalyst, HeatMet, that is used in ring opening metathesis polymerization. Here, we found minimal differences in ROMP kinetics with irradiation, due to the low intensity of light in our current system. However, we did observe a slight downfield shift in the alkylidene peak analogous to a peak shift observed from increasing temperature. Due to this similarity, we hypothesize that the thermal and light induced ROMP activation of HeatMet may have a similar first step in the activation mechanism. Future photoNMR work on HeatMet, once instrumentation modifications are implemented to improve irradiance at the sample, will focus on building a kinetic model for the activation of HeatMet in the presence of DCPD. Expanding the photoNMR work from this ExEx would lead to an impactful publication as the photoactivation mechanism of HeatMet is currently unknown. To do this, we must define a wider temperature range for HeatMet behaviors (to include the activation temperature) and increase the intensity of light applied to identify correlations between the spectra of the two activation methods. Further, we must define kinetics at varied temperatures and light intensities as well as introduce photosensitizers.

Finally, we investigated a photoinitiated radical reaction with a methacrylate monomer. In this study we saw no differences in peak broadening in the irradiated sample, indicating that radical species were not generated at a sufficient concentration to be detectable by NMR. This is likely due to the low light intensity failing to generate sufficient radicals to initiate polymerization or broaden the NMR signals. Future efforts to characterize the systems tested in this work and to improve the utility of photoNMR at SNL should be focused on increasing light intensity and optimizing sample optical density to ensure uniform reaction conditions and minimize light gradient effects. Through our studies of mission-relevant photochemistries we successfully developed photoNMR capabilities at SNL and identified shortcomings and challenges in implementing this technique. By identifying the current shortcomings of this technique during development, we have identified a path forward for adoption and productive implementation by other current and future projects at SNL.

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ADDENDUM:

Probing photochemical kinetics and mechanisms using photoNMR, LDRD 23-1180

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Purpose, Approach, and Goal

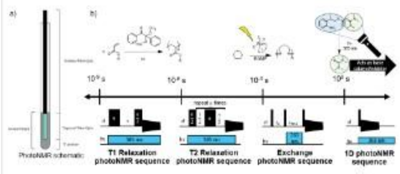
Motivation: Photochemical reactions are ubiquitous to modern chemistry and materials techniques. Several approaches are used to track the kinetics of these processes such as UV-vis, IR, and fluorescence. However, these techniques do not provide as much structural or mechanistic information as nuclear magnetic resonance spectroscopy (NMR). In-situ irradiated NMR (photoNMR) allows identification and tracking of chemical structures, intermolecular interactions and detailed chemical kinetics during photochemical reactions.

Hypothesis: PhotoNMR will provide **improved mechanistic insight** into photochemical reaction mechanisms on the relevant timescales **through elucidation of active species, intermediates and side products**

R&D approach: Using AM relevant photochemical systems with varied timescales, we seek to develop techniques to investigate kinetics and mechanisms of other photochemical systems while improving our understanding of the selected AM systems.

Key Goal: Development and adoption of photoNMR for Sandia mission needs.

Representative Figure



A photoNMR schematic alongside three photochemical systems indexed to pulse sequences that can be used to probe them along a timescale axis to represent slow, medium and fast chemistries. The slow chemistry is the release of a photocaged base upon irradiation (s-min), the medium rate system is photoactivation of a ruthenium catalyst to perform ROMP AM, and the fast system is a radical cure acrylate used as an adhesive and coating.

Key R&D Results and Significance

Summary

- Developed and demonstrated photoNMR capabilities at SNL
- Identified intermediate peaks during photodecomposition of a photobase generator
- Discovered long-lived intermediates that need further characterization
- Investigated the activation of a ruthenium catalyst (HeatMet)
- Began developing a kinetic model to understand activation
- Attempted to measure the radical lifetime of a commercially available acrylate resin used in AM
- Determined low light power severely limits utility of this technique

Go/no-go

We achieved our key goal of developing photoNMR as a spectroscopic technique at Sandia, and have implemented it toward photochemistriy that will be used in other work.

Lessons learned

- Find a higher power light source to increase the light intensity in my tests to increase the breadth of our testing capabilities.

Follow-on plans/activities

1. Conduct 2D NMR experiments to characterize long lived intermediates in PBG decomposition. The selected PBG is used in ring opening metathesis additive manufacturing with ruthenium catalysts, and understanding its mechanism will help us design and select PBGs
2. Develop a kinetics model for HeatMet exchange states to try to relate to ring opening metathesis polymerization (ROMP) kinetics. Understanding the kinetics and mechanisms of HeatMet activation will enable us to better utilize this and other catalysts for ROMP efforts.
3. We will share our work with others at Sandia so that this capability can be applied to other photochemical systems and we can advance SNL mission goals.

Impact of follow-on plans

We will continue to apply this technique to other questions and problems at SNL. The following projects expressed interest in this technique during our initial inquiries:

- ACT FY24 Project "Vat Polymerization of Functional Materials for Next-Generation Components"
- DOE EFRC REMAT
- AM LDRD#23-0034 (Leguizamon 1815)
- Aging & Lifetimes Dragonfly

Publications, awards, staff development & IP

- Career and skill development for involved postdocs and interns (Daniel Darby, Hannah Gruenwald, Michael Holzmann, Alex Commisso, David Fairchild)
- Poster presentation at Photopolymerization Fundamentals conference titled “Probing photochemical kinetics and mechanisms using photoNMR” in Boulder, CO on 09/21/2023

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Probing photochemical kinetics and mechanisms using photoNMR
LDRD Number #23-1180





PRESENTED BY

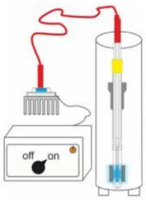
Daniel Darby (1853)
Hannah Gruenwald, Keith Fritzsching, Leah Appelhans (1853),
Michael Holzmann, Alex Commisso, Samuel Leguizamon (1815)

TOTAL COST $55K

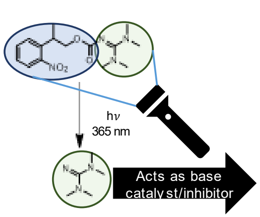
Research plan—overview

Hypothesis: PhotoNMR will provide **improved mechanistic insight** into photochemical reaction mechanisms on the relevant timescales **through elucidation of active species, intermediates and side products**

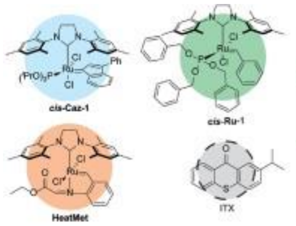
- photodecomposition (slow)
- additive manufacturing (intermediate)
- photoactive coatings and adhesives (fast)



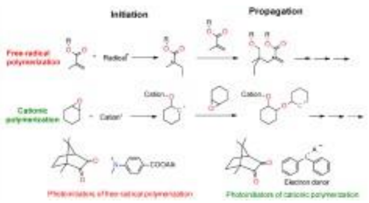
Objective 1: develop and calibrate Sandia photoNMR capabilities



Objective 2a: characterize photodecomposition of NPPOC-TMG and evaluate its potential for developing photocontrol of ROMP AM



Objective 2b: measure photoactivation of ruthenium catalyst used in photoROMP AM



Objective 2c: capture fast photochemistry of acrylates including radical mechanisms

Overall mission success

Developed capability, gained insight into 2a,b

2c underway with remaining time and budget

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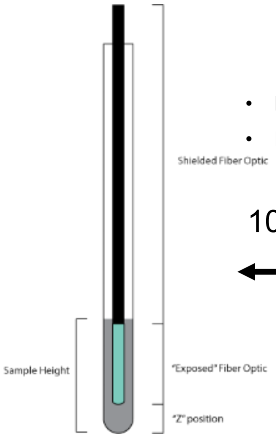
Nitschke , *et al., Prog Nucl Magn Reson Spectrosc* **2019** , 114, 86 -134.
Jacovella *et al., J. Phys. Chem Lett.* **2020** , *11* (15), 6045 –6050.
Leguizamon *et al., Macromolecules.* **2022** , *55*, 82738282
Topa *et al., Materials.* **2020,** *13* (18), 4093

Summary of initial proposal

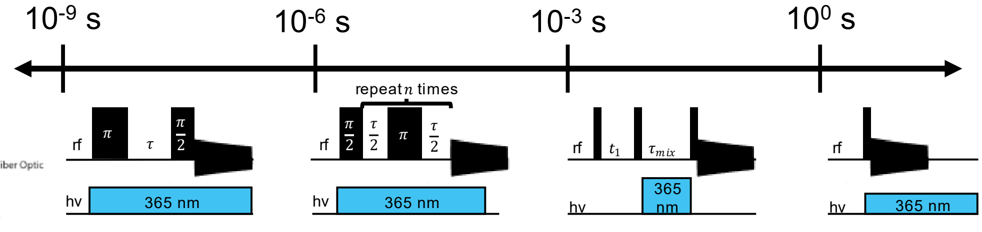
Initially proposed to develop photoNMR capabilities at Sandia for use at various additive manufacturing (AM) timescales

- **Slow**—photoisomerization of norbornadiene to quadricyclane*
  - Process too slow for in situ irradiation to be interesting and required photosensitizers
    - Switched to photodecomposition of NPPOC -TMG
- **Intermediate**—photoactivation of ruthenium catalysts
- **Fast**—radical cure of acrylate system

Key success metric: Adoption of photoNMR for Sandia mission needs



PhotoNMR schematic



T1 Relaxation photoNMR sequence

T2 Relaxation photoNMR sequence

Exchange photoNMR sequence

1D photoNMR sequence

Goez , M. Chapter 3 Photo -CIDNP Spectroscopy. Annual Reports on NMR Spectroscopy, 2009; pp 77 -147.

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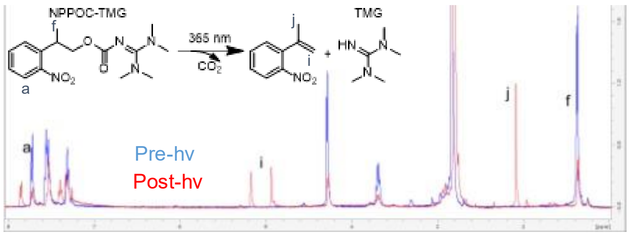
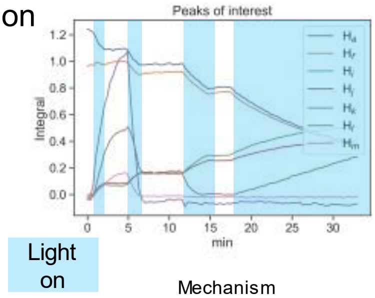
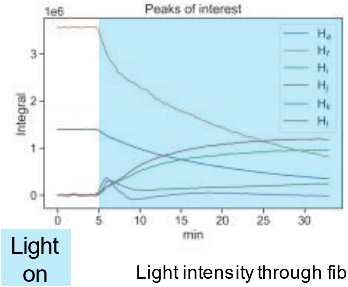
Stadler, E.; Tassoti , S.; Lentes , P.; Herges , R.; Glasnov , T.; Zangger, K.; Gescheidt , G. *Anal Chem* **2019** , *91* (17), 11367 -11373.

R&D Summary—NPPOC-TMG decomp/validation





Intermediate peaks exaggerated for clarity—not normalized



Kinetic model for NPPOC-TMG developed by Zhang et al., 2018.

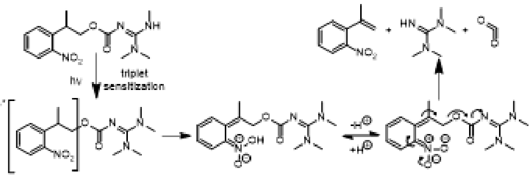
$$-\frac{d[I]}{dt}=\frac{2.303\varepsilon\varphi[I]I_0\lambda}{N_{AV}hc}$$

$[I]$ = concentration of PBG
t = time
$\varepsilon\varphi$ = photolytic efficiency
I_0 = light intensity
λ = wavelength of light

Light intensity through fiber optic ~0.7 mW/cm^2

Integrating sphere measurement: ~6 mW/cm^2

Mechanism hypothesized by Xi et al., 2013



Need to irradiate NPPOC -TMG to develop intermediates and conduct 2D NMR to identify

(1) Zhang, X.; Xi, W.; Gao, G.; Wang, X.; Stansbury, J. W.; Bowman, C. N. *ACS Macro Lett* **2018** , *7* (7), 852 -857.
(2) Xi, W., et al. *Macromlecules* **2013** , *47* (18), 6159 -6165.

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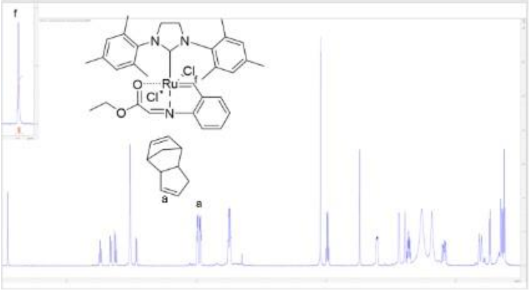
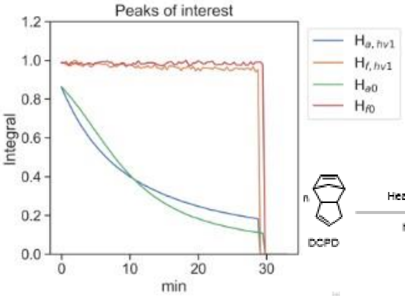
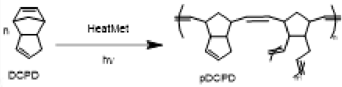
R&D Summary—Ruthenium catalyst activation

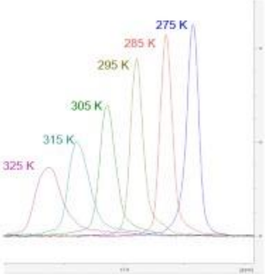


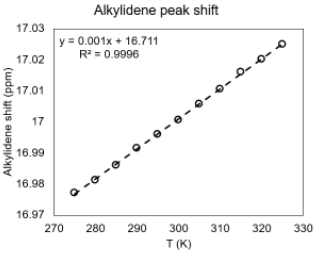


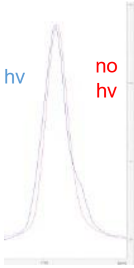
Due to low light intensity, likely need photosensitizer to accelerate ROMP with light



Alkylidene peak shifts with T, small shift with hv







Is the light induced peak shift due to the same chemical process as the temperature induced shift?

Exchange experiments so far inconclusive

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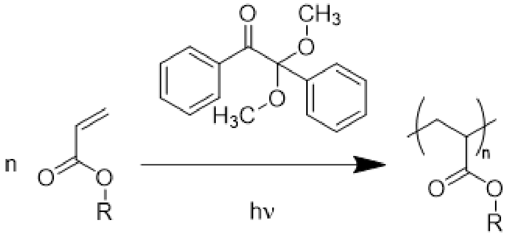
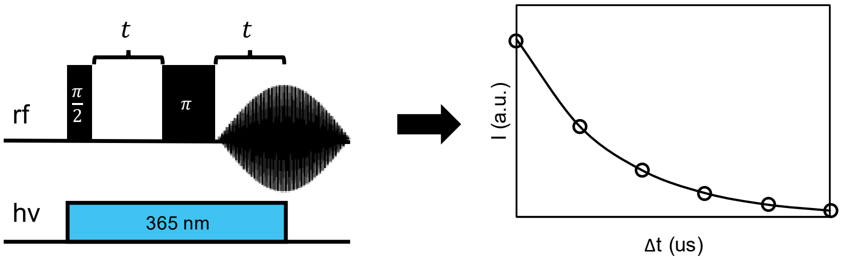
R&D Summary—on-going acrylate work

Acrylate work is underway and will be shown in the final SAND report



Generalized acrylate radical reaction



Decay of signals can reveal temporal profile of radical formation

Goez, M. Chapter 3 Photo-CIDNP Spectroscopy. Annual Reports on NMR Spectroscopy, 2009; pp 77-147.

Project Legacy

Key Technical Accomplishment

- Developed photoNMR capabilities at SNL

- Tangible results from this ExEx will boost outlook for several ongoing projects
  - ACT FY24 Project "Vat Polymerization of Functional Materials for Next-Generation Components"
  - DOE EFRC REMAT
  - AM LDRD#23-0034 (Leguizamon 1815)
  - Aging & Lifetimes Dragonfly
- Intend to leverage new capability for aforementioned projects
- Share work to SNL and external colleagues to evaluate future applications
  - PI will share work at conference NLT 9/22/23
  - PI will present at group meeting NLT 12/31/23

With more time could complete characterizations of selected systems

Thanks to our ExEx work we have data collection and processing abilities to apply to other projects

Thank you to my collaborators, the ExEx committee, and Nicole for this opportunity!

LDRD Project Metrics

Presentations and Publications

- Poster presentation at Photopolymerization Fundamentals in Boulder, CO
- Intend to publish on HeatMet activation work once complete

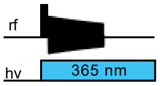
Tools and Capabilities

- Developed photoNMR capabilities generally
  - Time resolved 1D HNMR
  - EXSY
  - Radical relaxation with pulsed light

Staff Development

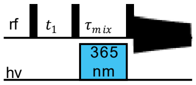
- Method development experience for three postdocs and one graduate intern
- Project management experience for postdoc PI
  - Including experience writing and defending grants at SNL

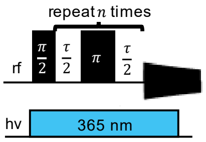
PHOTOPOLYMERIZATION
FUNDAMENTALS



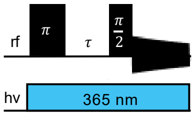
Sample 1D photoNMR sequence

Sample exchange photoNMR sequence





T2 Relaxation photoNMR sequence



T1 Relaxation photoNMR sequence