

MODIFICATION OF SOFT POLYMERS

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Degree

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ABSTRACT

The idea of polymer upcycling revolves around using the functional groups that are already present in a polymer, especially in the backbone, to produce high-value derivatives or encourage controlled degradation. This strategy uses polymers as substrates for functionalization or selective degradation processes. However, the intrinsic stability of C–H and C–X bonds limits advancement in this field. Building a library of polymer modification techniques and widening the scope of applicable chemical transformations are crucial to increasing the chemical space available for creating novel and varied polymeric materials. This research employed both photoredox catalysis and hydrogen bonding catalysis.

Polyolefins and polyvinyl chlorides (PVC), which have fully saturated carbon–carbon backbones, make up most commodity polymers. Nevertheless, the backbones of several widely used polymers, such as polyisoprene, polynorbornene and polybutadiene include alternative topologies with olefinic connections. Despite being produced in lesser quantities than polyolefins, these polymers nonetheless present environmental problems when manufactured on a big scale. Notably, olefin units due to unsaturation, provide a helpful reactive location for chemical modification and reactivity. In previous work, my lab colleagues used generated radical cation intermediates via electrochemistry to achieve electrochemical degradation and functionalization by taking advantage of the olefinic reactivity of polyalkenamers. Slow degradation rates, severe oxidative conditions from constant voltage application, and a restricted functionalization range were some of the disadvantages of this strategy. We used photocatalytic redox techniques to get beyond

these obstacles. When exposed to blue light, or even solar source, we were able to efficiently degrade polyalkenamers using triphenylpyrylium tetrafluoroborate(metal free) as the photocatalyst in both ambient and inert atmospheres and also functionalize polyalkenamers via nucleophile trapping.

Motivated by small-molecule organocatalysis' substitution selectivity and C-X bond activation, where urea or thiourea motifs offer exceptional site-specificity through noncovalent interactions, suggested the idea for macromolecular applications. With this method, H-bond donor motifs are used in the substitution reactions of PVC. PVC is a polymer rich in C-Cl bonds and occupies a significant proportion of plastic production due to its high tensile strength and durability. By examining a library of H-bond motifs, the planned interactions activate leaving groups, allowing replacement at otherwise unreactive locations without the need for harsh or metal catalysts. The activation was proposed to occur via the stabilization of the halide leaving group by weakening the carbon-halide bond. This mode of activation enhances nucleophilic substitutions. Under these metal-free circumstances, attempts to functionalize PVC using hydrogen bond donor (HBD) catalysis saw little potential. We proposed that this chemical route would serve a better functionalization tool as compared to the dehydrohalogenation functionalization of PVC with the emission of HCl. Little discernible substitution or alteration was found in spite of evaluating different HBDs, nucleophiles, and reaction configurations. The hydrogen bonding induced substitution reaction was probably hampered by the poor reactivity and restricted accessibility of the C-Cl bonds.

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CHAPTER ONE : INTRODUCTION

1.1 Polymer Production and Impact in recent times

Polymers are usually large macromolecular structures generated from monomer units discovered by Staudinger.¹ Plastics are composed of polymers and very essential in our daily lives. Compared to materials like glass and metals, plastics are frequently employed because of their low costs, adaptability and low cost of energy requirements during production. Additives can be used to tailor polymers for a variety of applications ranging from common packaging to healthcare products.² Despite the major advantages of plastics, there are also underlying disadvantages, especially threats posed towards human health and the environment due to plastic pollution and chemical migration.² Overuse and improper disposal are major contributors to environmental pollution. Hence there is an ever-increasing desire to create plastic treatment.² As chemists, we are usually interested in the chemical modification of polymers that make up plastics.

In the year 2024, over 400 million metric tons of plastics were produced or manufactured annually from crude oil with increasing demands annually.³ There are high demands and usage of lightweight and resilient plastics that offer enhanced functionality and convenience to consumers.⁴ There are over 7.5 billion metric tons of plastic materials with the expectation of 40 billion metric tons by 2050.⁴ Common examples of polymer units and their total plastics production percentages in manufactured plastics are: polyvinyl chloride PVC (12%), polypropylene PP (21%), and polyethylene PE (36%), with polystyrene (PS), polyethylene terephthalate (PET) and polyurethane (PUR)(<10% each)⁵ being the constituents of plastic bags, garbage cans, buttons, electronic cases, containers and many household models. These various plastics have generated high

amount of plastic waste that come with relatively inefficient plastic waste treatment options as shown in (**Figure 1.1**). These plastic applications and features arise from tacticity, branching, and crystallinity which are all examples of polymer microstructure, that plays a major role in determining the plastic or polymeric material's mechanical, thermal, and barrier properties. In addition, a polymer's solubility, processability, and environmental stability are further tailored by the repeating unit's chemical makeup, chain size, and topology dictate plastic applications. Controlling the polymer microstructure is the best method for future significant alterations. Directly tailoring polymer microstructure has many advantages because extant materials can be worked on.

1.2 Chemical Upcycling Methods

End of plastic-waste treatments include mechanical recycling (eg. shredding, granulating, remelting), incineration (eg. pyrolysis and gasification), biological degradation (eg. enzymatic and microbial degradation).^{6,7} This can also be seen in (**Figure 1.1**). But all the above-mentioned plastic-waste treatments come along with high costs and very high energy requirements.⁶ A very small fraction of plastics is upcycled due to less known methods, low funding and more wrong methods. Also, it has widely been reported that small changes in polymers potentially constitute significant impacts on polymer properties opening a new chapter of investigation and literature contribution.⁸ An example is cis-polybutadiene making up the interior of a golf ball and trans-polybutadiene making up the exterior part of the same golf ball, (**Figure 1.2**) hence impacting the physical properties. Polymers are usually chemically upcycled by altering components of either the backbone or sidechain. Polyolefins constitute a greater majority

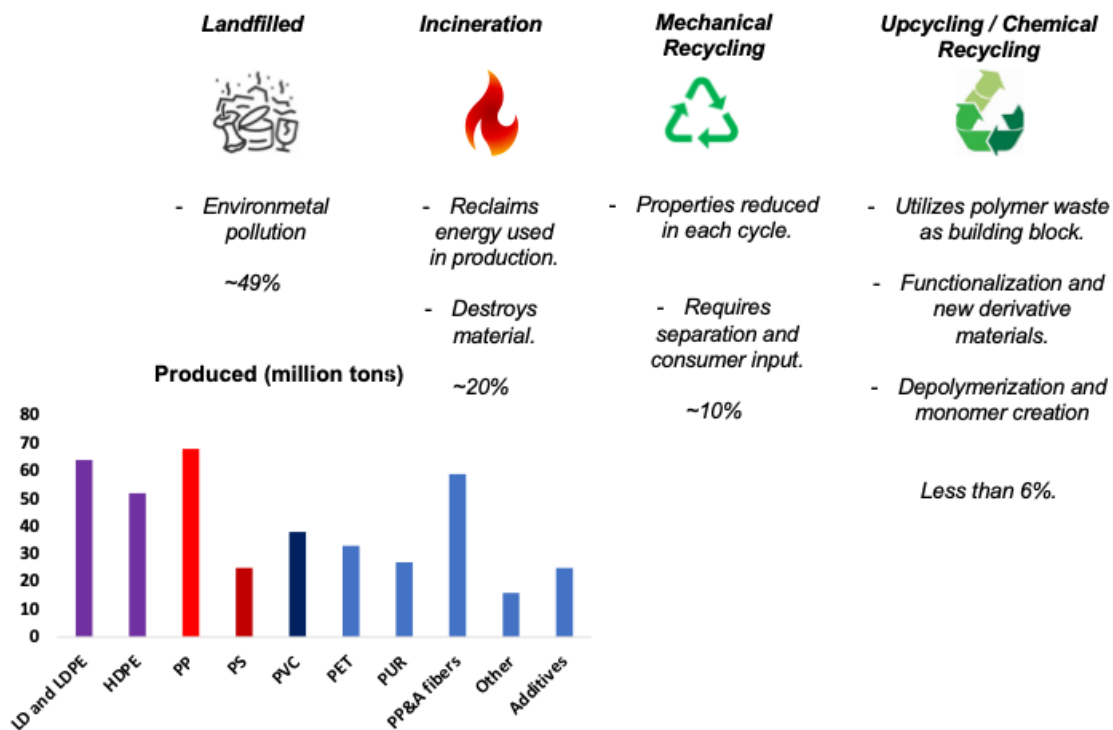


Figure 1.1. Plastic Production and the need for chemical upcycling.

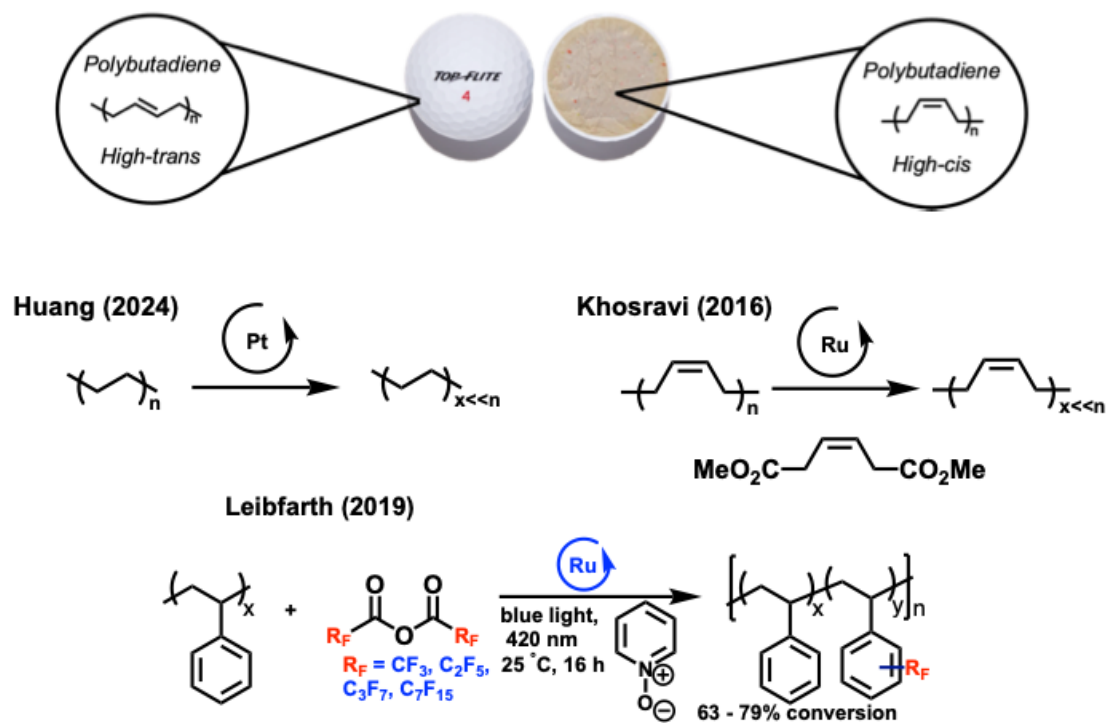


Figure 1.2. Significance of polymer modification and some chemical upcycling tools.

of the world's plastic production and some of the challenges of editing these group of polymers also arise because of C-H, C-X and C-C bond activities. This problem is because of their large bond dissociation energies and hence the need for relatively high energy intermediates to be activated for effective polymer modification. This problem has been addressed by Coates and Goldman proving catalytic hydrogenation with reactive alkenes can be embed with iridium pincer complexes.^{9,10} Leibfarth demonstrated C-H activation(Figure 1.2) methods for polyolefin functionalization.¹¹⁻¹³ Hartwig and Hillmyer demonstrated Rhodium catalyst and Hydrogen peroxide to functionalize polyisoprene via hydroxylation (incorporating a polar functional group).¹⁴ Huang and colleagues reported a cross-metathesis method via tandem dehydrogenation occurring for the conversion of long chain polyethylene to short chain polyethylene (**Figure 1.2**).¹⁵ Khorsravi and Pilard reported polyisoprene and polybutadiene degradation using Grubb's second-generation catalyst via cross metathesis shown in **Figure 1.2**.^{16,17} Recently, our lab group reported the chain scission of long chain polyalkenemers to yield short chain polyalkenemers via electrolysis.⁸ Clearly, there is a need for new strategies to access more chemical space in relation to chemical upcycling.

1.3 Photoredox Chemistries and Single-Electron Oxidation Strategies

Polymer modification via high energy species can provide the solution of overcoming thermodynamic and kinetic (high energy of activation) barriers.¹⁸ One way of employing these reaction manifolds is by exploring other alternate routes or attempts to enhance reactivity of relatively inert bonds by the generation of radical ions (high energy species).¹⁸ The possibility of macromolecular editing of polymers has been explored

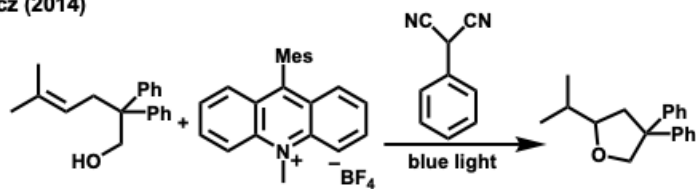
via electrochemistry. This employs the creation of high energy intermediates (radical cation) inside the polymer backbone specifically the olefin functionality. Both nucleophilic attack on the carbocation and beta-scission of the backbone were made possible by the radical cationic intermediate via strong oxidative conditions.⁸

Photoredox catalysis is a promising and more sustainable method of managing plastic waste.¹⁹ The field of photocatalysis entails the selective irradiation of photonic energy on a photocatalyst that can cause electronic changes in a substrate, secondary catalyst or reagent with this mechanism having provided novel additions to literature with alternatives to other pathways involving thermal control.²⁰ The accomplished reactivity reached through the intermediary of an open shell reactive species, which is otherwise impossible or less likely via conventional chemical catalysis method, can be a way of overcoming usual chemical barriers.²¹ Photoredox catalyst can work on various substrates under various conditions as both a single electron reductant or single electron oxidant fueling the redox activity of the reaction and this is one of the reasons photoredox catalysts can start and mediate a very wide range of ionic and free radical processes.²² Photoredox catalysis is proven to be another emerging strategy employed in the synthesis of small molecules and polymerization of monomers.

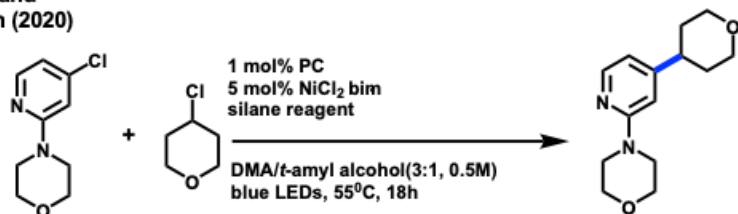
Additionally, photoredox catalysis has been used to functionalize small molecules and polymers. Macmillan and Nicewicz have employed iridium and ruthenium based photoredox catalyst in different C-H functionalizations (Figure 1.3). Yoon and colleagues revealed the synthesis of endoperoxides by photocatalytically cyclotrimerizing linked bis-styrenes using Ru(II) photocatalyst and molecular oxygen.^{23,24} Fors and Hawker

demonstrated that Ir photoredox catalyst could be used to mediate methyl methacrylate polymerization, affording a photoredox catalyzed Atom transfer radical polymerization (ATRP) method.²⁵ Bergbreiter and Liang demonstrated photocatalysis utilizing Ru(II) complex (photoredox catalyst) for photomediated polymerizations (radical polymerizations) of acrylates.²⁶ König and colleagues demonstrated a direct C-H arylation(metal-free) of heteroarenes employing photoredox catalysis.^{24,27} Aldehydes' enantioselective alkylation via a mixture of organocatalysis and photoredox catalysis was developed by MacMillan and co-workers.²⁸ Chemical upcycling was the focus of this research with Photo-mediated degradation and functionalization of soft polymers being the main scheme. Unfortunately, photoredox catalysis is not widely used for polymer modification because it can be difficult to regulate radical reactivity across different polymer backbones, which might result in undesirable degradation or crosslinking. Nicewicz functionalized unactivated alkenes using photocatalysis and the Langlois reagent for generating cyclic ethers (**Figure 1.3**).²⁹ This concept may enable functionalization and potential degradation of polymers when combined with the application of electrochemical redox techniques to polymers demonstrated by our earlier work. As part of mechanistic studies to validate the radical cation intermediate, a photoredox catalyst that undergoes a single electron transfer upon excitation after being irradiated was used in a photoredox reaction with the polynorbornene in the presence of DCM and Hydrogen atom transfer agent.⁸

Nicewicz (2014)



Nicewicz and
Macmillan (2020)



Theato (2021)

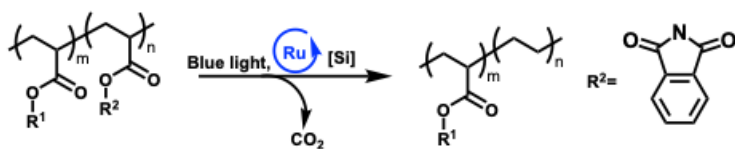
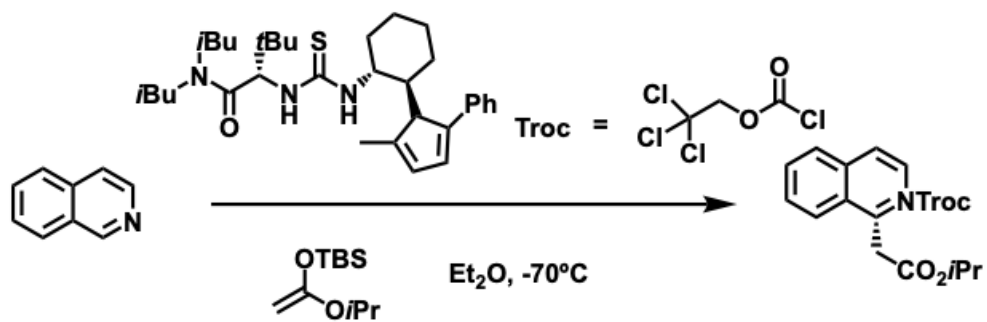


Figure 1.3. Examples of applications of photoredox reactions.

1.4 Hydrogen Bonding influenced Substitution Reactions

One essential method for modifying material properties is polymer functionalization via substitution reactions. However, when applied to dense or chemically inert polymer matrices, such transformations frequently encounter selectivity, efficiency, or site-accessibility constraints.³⁰ Untapped potential for overcoming these obstacles is provided by non-covalent interactions, particularly hydrogen bonding. Under mild circumstances, hydrogen bonding can speed up ordinarily slow substitution reactions by pre-organizing reactive partners, adjusting local polarity, or improving leaving-group activation.³¹ Recent developments in macromolecular chemistry indicate that post-polymer modification events could be regulated and accelerated by hydrogen-bond-assisted activation, which is observed in small-molecule catalysis. For instance, directed recognition and reaction site preorganization may be made possible by carefully positioned urea, amide, or hydroxyl groups on the substrate or the polymer backbone, providing a new degree of control over regioselectivity and reaction speeds.³² Without the need for harsh chemicals or metal catalysts, this offers new functionalization techniques that improve polymer modification's selectivity, mildness, and programmability. Jacobsen showed that racemic tertiary electrophiles are converted into quaternary stereocenters with strong enantiocontrol in the first successful enantioselective SN1-type reaction (**Figure 1.4**).³² He also demonstrated Isoquinolines undergoing acylative Mannich additions with elevated enantioselectivity when facilitated by chiral thiourea catalysts as shown in (**Figure 1.4**).³¹

Jacobsen (2006)



Jacobsen (2018)

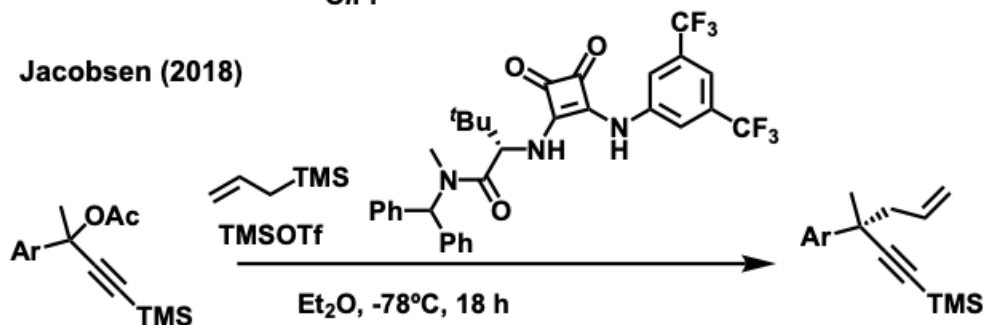


Figure 1.4. Examples of Hydrogen bonding reactions.

The chlorinated backbone of Polyvinyl Chloride (PVC), a common commodity polymer, provides a potentially reactive site for substitution chemistry. We investigated the use of urea, thiourea, and squaramide derivatives in hydrogen bond donor (HBD) catalysis to encourage nucleophilic substitution on PVC in mild, metal-free environments.^{33,34} Successful small-molecule transformations in which HBDs activate electrophiles through directed, noncovalent contacts served as the model for this strategy. Reinecke demonstrated that PVC could be modified or functionalized with aromatic thiols (good nucleophiles).³⁵ Pestov also showed the modification of PVC with thiourea.³³ Inspiration from both ideas suggested we employ strong nucleophiles (aliphatic thiols) and hydrogen bond donors to investigate possible substitution reactions with PVC.

1.5 Conclusions

Discovering novel strategies to modify polymers is essential for generating polymers with improved chemical reactivity. There is the need to broaden the chemical space of accessible editing techniques since polymer modification techniques are frequently used in chemical upcycling motifs. This study describes how we increased our knowledge and comprehension of generating novel polymer modification techniques by utilizing synthetic expertise. Here, we describe the functionalization and degradation of polyalkenamer scaffolds and investigated possible substitution reactions with PVC.

CHAPTER TWO : PHOTOMODIFICATION OF POLYMERS USING SINGLE- ELECTRON LOGIC

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2.1 Abstract

The chemical space available for molecular transformations has significantly increased by the ability to access the chemistry of reactive intermediates, preferably under mild conditions. Photoredox catalysis has demonstrated the capacity to generate reactive intermediates. There are relatively few reports of photoredox catalysis as a technique for polymer modification, despite the large body of literature precedents for this potential and well-proven technique to construct complex targets. We describe a mild photoredox method that allows the degradation and functionalization into useful feedstocks. In a range of substrates, easy chain scission was facilitated by visible light (including solar source) exposure combined with a pyrillium photoredox catalyst. High molar mass polymeric materials (>300 kDa) were broken down to low molar mass polymeric materials (>15 kDa) in 10 minutes devoid of metal-centered catalysis or approach. Furthermore in 96 hours, we could finally breakdown the polymer chain of high molar masses to a variety of beneficial targets (C₁₆–C₂₉ species). For further comprehension of this reactivity, kinetic experiments were conducted, and some mechanistic studies were explored.

2.2 Introduction

Photochemical reactions have significantly changed modern chemistry through the introduction of light-driven reactions that provide increased selectivity, energy efficiency and access to novel reaction pathways.³⁶ Advances in sustainable chemistry, materials science and catalysis have propelled its recent revolution, influencing both industry and research applications.³⁷ Some major reactions that have been made easier via photoredox catalysis are: Cross coupling reactions devoid of transition metals, C-H functionalization,³⁸ reductive dehalogenation, radical cyclizations and additions.

The first proof of anti-Markovnikov cation radical-mediated reactivity was presented in seminal work by Arnold³⁹ and Gassman.^{40,41} Furthermore, single electron photooxidants that function as efficient single electron oxidants to afford labile olefin radical cations, were shown by Gassman and Arnold separately.⁴¹ Due to limitations involved in transferring small molecule reactivity to polymer substrates, photoredox catalysis is still an underutilized platform for polymer modification.

Hung et al. used organic photoredox catalysis and Hydrogen Atom Transfer catalysts under blue LED light to describe a metal-free, radical hydrosilylation.⁴² They showed successful addition of silanes and crosslinked networks to alkene containing polymers perfect for biomedical applications and adhesives.⁴² The Makihara group created molecular probes for biological research by functionalizing fluorophores onto polyamines employing photoredox catalysis.⁴³ An acridine photoredox catalyst was utilized by Sumerlin's group to directly decarboxylate polyacrylic acid/polyacrylate aided by HAT donors and Cobalt co-catalysts for polymer modification.⁴⁴ These examples show that

photoredox catalysis can be used to modify polymers in a chemoselective, spatiotemporally controlled manner, but they also show that there is still a significant under-exploration of chemical space with regards to polymer modification with photoredox catalysis as a tool. Reports of employing photoredox catalysis to create polyvinyl ethers,⁴⁵ poly(4-methoxystyrene),⁴⁶ polynorbornene and other polymer substrates⁴⁷ via radical cation-based processes piqued our interest. According to microscopic reversibility, we reasoned that polymer modification (degradation) using this tool should be feasible. We hypothesized that producing high energy species on polyalkenamer substrates would promote β -scission which would lead to polymer chain cleavage and potential reactive intermediate vulnerable to being trapped by foreign species for functionalization especially since olefins are subject to single electron oxidations via organic photoredox catalysis^{48,49} as shown in (**Figure 2.1**).

2.3 Results and Discussions

2.3.1 Initial Reaction Condition Optimization

To explore this concept, polynorbornene (**2.1**, $E_{red} = +2.18$ V)⁸ was selected as our model substrate. A high number average molar mass (M_n) sample of **2.1** was prepared using a commercially available Z-selective Grubbs catalyst⁵⁰ ($M_n = 330$ kDa). Organic photoredox catalysts with excited state reduction potentials matching those of unactivated olefins,⁵¹ such as 2,4,6-triphenylpyrylium tetrafluoroborate (**2.2**, $E^*_{red} = +2.55$ V vs SCE⁵²) and 9-mesityl-10-methylacridinium tetrafluoroborate (**2.3**, $E^*_{red} = +2.18$ V vs SCE⁵²), were selected for our preliminary photoediting studies. We also selected diphenyldisulfide (PhS)₂ as an H-atom transfer (HAT) catalyst, as this has been shown to

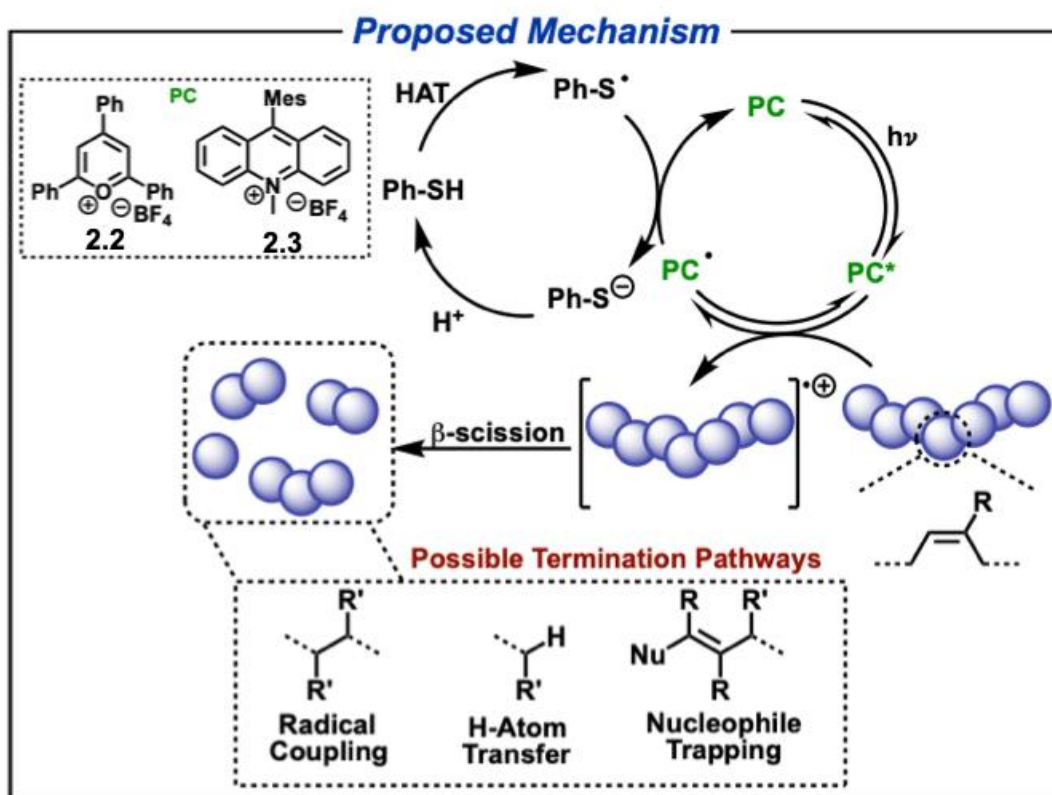
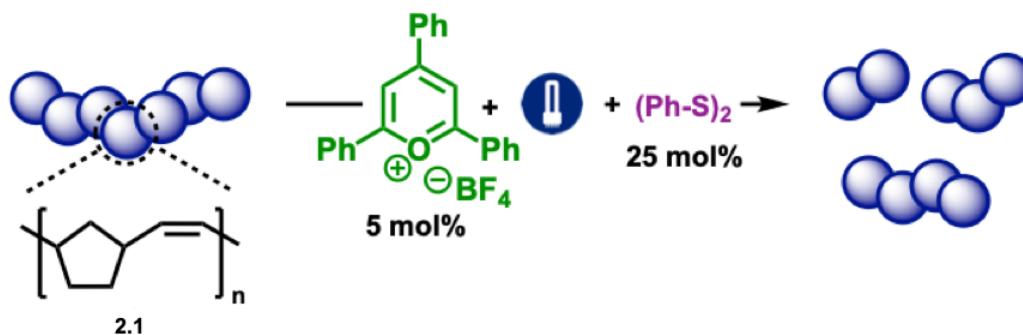


Figure 2.1. Proposed mechanism for Polyalkenamer single-electron photomodification.

turn over photoredox catalysts.^{53,54} Initially, (PhS)₂ (6.1 mg; 0.28 mmol; 10 mol%) and **2.2** (5.6 mg; 0.014 mmol; 5 mol%) were dissolved in DCM (0.5 mL) and added to a solution of **2.1** (26 mg; 0.28 mmol; 0.075 M in anhydrous DCM) under an N₂ atmosphere in a glovebox. The reaction mixture was then irradiated with a 12W blue LED lamp (λ_{EM} = 450-460 nm) for 1 h. Following irradiation, the mixture was diluted with DCM, filtered through a short plug of silica, and concentrated under a stream of N₂. Excess MeOH was added to precipitate any polymeric material, which was isolated with good mass recovery (76%) following centrifugation. Consistent with our initial hypothesis, analysis of this material by size- exclusion chromatography (SEC) revealed a 59% reduction in M_n relative to **2.1** (ΔM_n = - 192 kDa; **Figure 2.11**; **Table 2.2**).

We briefly explored other reaction conditions to ascertain their impact on polymer degradation. Surprisingly, chain scission was observed when **2.1** was irradiated in the absence of both **2.2** and (PhS)₂ (**Table 2.1** and **Scheme 2.1**). Analysis of the post-irradiated material by ¹H NMR spectroscopy revealed scrambling of the backbone olefin stereochemistry (**Figure 2.49**). Presumably, the diradical intermediate during olefin isomerization can also undergo a background -scission reaction. However, a sufficiently oxidizing catalyst is necessary to observe enhanced degradation. For example, irradiating **2.1** in the presence of a weakly oxidizing catalyst, Ru(bpy)₃Cl₂ (E_{red}^* = +0.77 V vs SCE⁵⁵), resulted in only background scission (**Table 2.1**). Conversely, **2.3** was also found to be a competent catalyst for degradation, albeit with poorer control (as determined by the increased dispersity of the degraded material; **Figure 2.9**). These data suggest that a slight overpotential is required to achieve larger reductions in M_n with good fidelity.



Scheme 2.1. Control experiments for polyalkenamer photomodification.

Table 2.1. Control experiments for polyalkenamer photomodification.

Entry	Deviation from Standard Conditions	Initial M_n (kDa) ^a	Final M_n (kDa)	Yield (%) ^b
1	None	328	103	96
2 ^c	-(PhS) ₂	328	--	90
3	- 2.2 ; -(PhS) ₂	328	138	88
4	+Ru(bpy) ₃ Cl ₂ ; - 2.2	328	137	82
5	+Ambient Atmosphere	328	12	66

^aCalculated using triple detection. ^bRecovered mass. ^cIsolated material was intractable.

Replacing (PhS)₂ with alkyl thiols (such as 1-adamantanethiol or 1-dodecanethiol) afforded intractable materials that could not be further characterized. Increasing the loading of (PhS)₂ to 25 mol% increased the observed extent of degradation ($\Delta M_n = -245$ kDa); however, higher loadings of (PhS)₂ (50 mol%) did not substantially improve beyond this ($\Delta M_n = -244$ kDa). Interestingly, the loading of **2.2** (1 mol% and 10 mol%) appeared to have minimal impact on the extent of polymer degradation. For example, addition of 1 mol% **2.2** resulted in degradation that was similar to what was observed with 10 mol% **2.2** ($\Delta M_n = -223$ kDa versus -230 kDa, respectively; **Table 2.2**). As such, we elected to use an intermediate loading of **2.2** (5 mol%) and (PhS)₂ (25 mol%) for all subsequent studies.

We were also curious if this reactivity would be operative under less rigorous conditions (i.e., ambient atmosphere and technical-grade solvent), as **2.2** has been shown to facilitate transformations in the presence of oxygen.⁵² To our delight, we could achieve nearly complete polymer degradation (~96%) under an ambient atmosphere ($\Delta M_n = -315$ kDa; **Figure 2.13**; **Table 2.1**). Additionally, we found that natural sunlight⁵⁶ could also be used in this ambient photomodification methodology. As a proof of concept, a solution of **2.1** (0.075 in DCM) was placed in sunlight under otherwise identical conditions to those described above for 2 h. We were delighted to observe that SEC characterization of the isolated polymeric residue revealed an 81% reduction in molecular weight ($\Delta M_n = -131$ kDa; **Figure 2.30**). Finally, other polyalkenmers were competent substrates for our photoredox degradation. For example, both *cis*-1,4-polyisoprene (**2.4**) and *cis*-1,4-polybutadiene (**2.5**) showed 98% and 93% degradation under our optimized conditions

(c.f. $\Delta M_n = -611$ kDa and -160 kDa, respectively; **Figures 2.27 and 2.28**). Importantly, **2.4** and **2.5** could also be degraded (92% and 86%) using ambient sunlight as described above ($\Delta M_n = -205$ kDa, and $\Delta M_n = -115$ kDa, respectively; **Figures 2.31 and 2.32**).

2.3.2 Impact of H₂O and O₂ on Degradation

Given the enhanced activity observed under ambient conditions, we surmised that either H₂O or O₂ must be playing some role. Initially, we suspected that increased H₂O could provide a secondary source of H-atoms, which would enable rapid turnover of the HAT catalyst and faster regeneration of the ground state photoredox catalyst. To test this, we prepared a solution of **2.1** (26 mg; 0.028 mmol) in technical-grade DCM (3 mL) in a Schlenk flask. Oxygen was removed via two degassing (freeze/pump/thaw) cycles, after which a DCM (0.7 mL) solution of **2.2** and (PhS)₂ (prepared as described above) was added to the vessel. The reaction was subjected to a final degassing cycle, placed under a balloon of argon, and irradiated for 1 h with blue light. The resulting polymeric material was isolated, and subsequent SEC analysis revealed a ~75% reduction in M_n relative to **2.1** had been achieved (**Figure 2.25**). Considering these results, O₂ seemed the more likely origin of the enhanced degradation. Pyrillium catalysts, among others, are known to sensitize ¹O₂, which can add to olefins to form reactive peroxide species (which, in turn, are known to promote polymer cracking).⁵³ To investigate this hypothesis, samples of **2.1** (25.1 mg; 0.27 mmol), **2.2** (5.5 mg; 0.014 mmol), and (PhS)₂ (15.2 mg; 0.07 mmol) were dried over P₂O₅ for 16 h. The dried reagents were dissolved in anhydrous DCM (0.075 M) in a glovebox and irradiated with blue light under a balloon of O₂. After irradiation for 1 h, SEC analysis revealed a 96% reduction in M_n relative to **2.1** ($\Delta M_n = -$

113 kDa), which mirrored the enhanced activity we originally observed under ambient conditions (**Figure 2.25**; **Table 2.1**). Conducting a similar experiment in the presence of a colorimetric peroxide indicator was consistent with the formation of organic peroxides under the reaction conditions (**Figure 2.4**). We note that no peroxide formation was observed when an analogous experiment was conducted with O₂ being rigorously excluded (**Figure 2.5**). Furthermore, irradiating **2.1** under an argon atmosphere in the presence of an exogenous peroxide (i.e., *t*-butyl hydroperoxide) resulted in a 94% reduction compared to an analogous experiment conducted without added peroxide (i.e., 72% reduction) (**Figure 2.26**). These results are consistent with previous observations of peroxide-mediated polymer degradation,^{57,58} and they suggest that photoredox catalysis can couple multiple single-electron editing coordinates to achieve nearly quantitative polymer consumption under mild conditions.

Not only does ambient atmosphere afford more degradation, but it also increased the rate at which polymer degradation occurred. Using standard air-free techniques, a DCM (3 mL) solution of **2.1** (25 mg; 0.27 mmol; 0.075 M) was added to a Schlenk flask under N₂, followed by a DCM (0.55 mL) solution of **2.2** (5.4 mg; 0.013 mmol) and (PhS)₂ (14.5 mg; 0.07 mmol). The vessel was irradiated with blue light under an N₂ atmosphere, and aliquots (0.1 mL) were removed every minute for a period of 10 min. The samples were diluted with THF, and the changes in polymer molar mass were determined using SEC (**Figure 2.19**), which indicated a ~60% reduction in molar mass. A plot of M_n vs irradiation time revealed a monotonic decrease in molecular weight (**Figure 2.2**), which would be consistent with random chain-scission along the backbone. We posited that a

model used to empirically elucidate the rate of stochastic degradation, such as the example (eq 1) developed by Malhotra and coworkers,⁵⁹ could be used fit our data.

$$\frac{1}{M_t} = \frac{1}{M_i} + K't \quad (1)$$

Here, $K' = k_{\text{obs}}/M_0$, k_{obs} is the polymer cleavage rate constant, M_0 is the molar mass of the repeat unit, M_i is the initial M_z of the polymer, and M_t is the M_z following irradiation for time t . A representative plot of $1/M_t - 1/M_i$ versus irradiation time (**Figure 2.2**) reveals the expected linear correlation ($k_{\text{obs}} = 1.96 \times 10^{-2} \pm 2.37 \times 10^{-4}$). We then repeated these kinetic studies under an ambient atmosphere. A DCM (3 mL) solution of **2.1** (27 mg; 0.28 mmol) was added to a vessel, followed by a DCM (0.7 mL) solution of **2.2** (5.6 mg; 0.014 mmol) and (PhS)₂ (15.4 mg; 0.07 mmol). The reaction solution was irradiated with a blue LED lamp, and aliquots (0.1 mL) were removed as described above for SEC analysis, which revealed an 88% reduction in molar mass. A representative plot of $1/M_t - 1/M_i$ versus irradiation time revealed the observed rate of degradation increased 6-fold relative to the inert conditions ($k_{\text{obs}} = 1.21 \times 10^{-1} \pm 6.66 \times 10^{-3}$; **Figure 2.2**). Furthermore, irradiating **2.1** under ambient conditions in the presence of a radical trap (i.e., (2,2,6,6-tetramethylpiperidin-1-yl)oxyl; TEMPO) resulted in a near complete shutdown of the degradation activity ($k_{\text{obs}} = 2.35 \times 10^{-3} \pm 5.65 \times 10^{-4}$; **Figure 2.2**), which further implicated the need for oxidatively generated radical species.

2.3.3 Prolonged Degradation of *cis*-Polyisoprene

We tried longer irradiation times (e.g., 96 h) to see if it results in products with significantly reduced molar mass that would be analogous to fuels and waxes (i.e., C₂₀ - C₆₀). To test this concept, a DCM (18 mL) solution of **2.4** (78.6 mg; 1.45 mmol) was

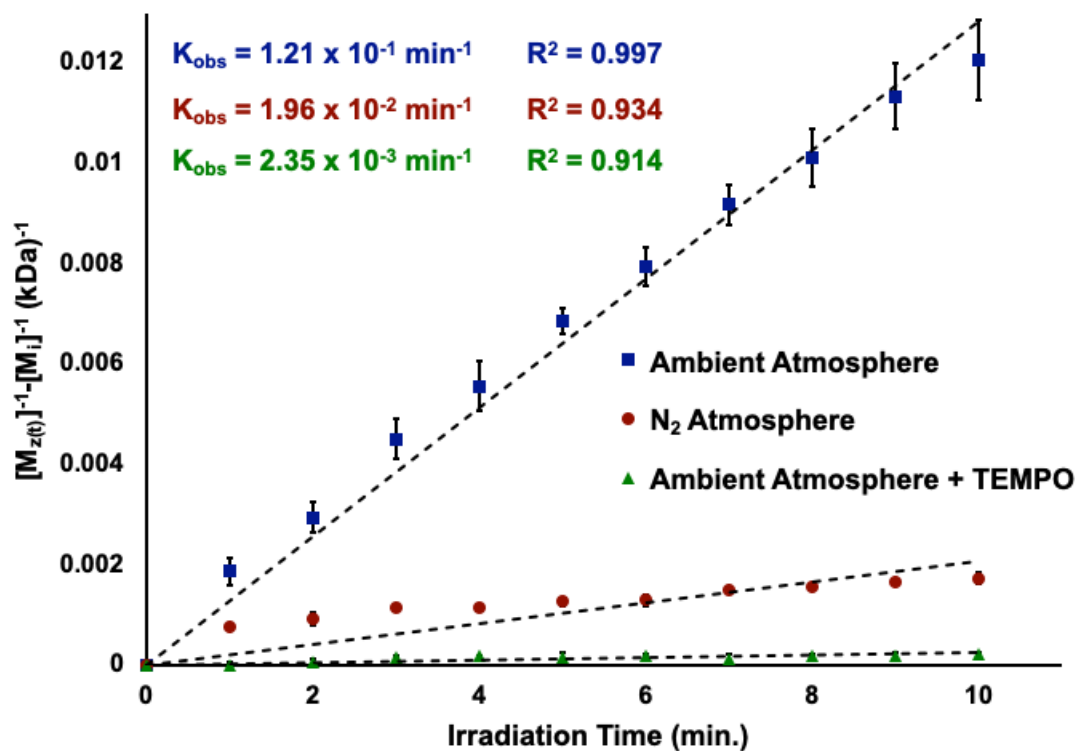


Figure 2.2. Representative kinetic plots for photomodification of 2.1 highlighting the differences in rates when conducted under ambient atmosphere (blue squares), under N_2 atmosphere (red circles), or under ambient atmosphere with an added radical trap (green triangles).

added to a scintillation vial followed by a DCM (1 mL) solution of **2.2** (29 mg; 0.070 mmol) and (PhS)₂ (79.5 mg; 0.36 mmol). The vessel was irradiated with a blue LED lamp under ambient conditions for 96 h. The crude mixture was passed through a short plug of silica and solvent was removed under a gentle stream of N₂. Subsequent SEC analysis of the isolated residue (**2.6**) revealed a 99% reduction in molar mass ($\Delta M_n = -445$ kDa) (**Figure 2.28**), however, this was accompanied by thiol-ene coupling supported by ¹H NMR spectroscopic analysis (note: >5% of thiol-ene coupling is only observed reactions that go for extended periods [> 6 h]). We conducted a simple desulfurization protocol with Raney Nickel to remove the coupled thioethers, in the presence of H₂. A THF (10 mL) solution of **2.6** (124 mg) was added to a THF (10 mL) suspension of Raney Nickel, placed under a balloon of H₂, and stirred for 20 hours. After which the mixture was filtered through short plugs of celite and basic alumina. The resulting suspension was filtered after 24 h and concentrated in vacuo, and the resulting oily residue (**2.7**; 17.7 mg) was analyzed by gas-chromatography mass spectrometry (GC-MS; **Figure 2.2**). To facilitate our analysis, our GC-MS method was first calibrated using commercial C₁₀–C₄₀ n-alkane standards (even carbon numbers) and paraffin wax (i.e., parafilm; **Figures 2.3**). **2.7** was found to contain products primarily in the C₁₆–C₂₉ range (with other species present up to C₃₆; **Figure 2.3**). We observed the formation of C₁₆ (1.2%), C₂₁ (1.14%), C₂₄ (3.7%), and C₂₉ (1.16%) n-alkane species, which are used as lubricants/waxes and fuels (**Figure 2.3**).

2.3.4 Hydroaddition Substrate Scope

Finally, we explored the possibility of trapping the proposed cationic intermediate with nucleophiles to access functionalized species. We began by targetting hydroetherifications.⁴⁸ We prepared a solution of **2.3** (5 mg; 0.013 mmol; 5 mol%) and (PhS)₂ (6 mg; 0.028 mmol; 10 mol%) in 50:50 DCE:DCM (0.5 mL). The catalyst solution was added to a separate vessel containing **2.1** (25 mg; 0.26 mmol; 0.075 M in 50:50 DCE:DCM), followed by MeOH (30 μ L; 0.78 mmol; 300 mol% relative to **2.1**). The reaction mixture was then irradiated under an N₂ atmosphere with blue light. After 48 h, the reaction mixture was filtered through a short plug of silica gel and concentrated to afford a viscous solution. Polymeric materials were precipitated by adding excess MeOH, isolated by filtration, and washed with excess pentane. The resultant solid, **2.7**, (50% yield) was subjected to ¹H NMR spectroscopic analysis, which revealed the presence of characteristic methoxy and methine protons (δ = 3.35 and 3.02 ppm, respectively; **Figure 2.39**) consistent with hydroetherification. Integration of the new methoxy protons relative to the residual olefin protons was consistent with ~50% hydroetherification (**Figure 2.39**). SEC analysis of the isolated material revealed an 86% reduction in molar mass, consistent with our prior observations (**Figure 2.15**). We found that alcohols with bulkier substituents (i.e., benzyl alcohol) could also be coupled to the polymer fragments using an analogous protocol (**Figure 2.41**). We tried to investigate other nucleophilic species such as thiols and carboxylic acids,⁶⁰ chemical space for other functionalities. These experiments were carried out using the same conditions described above (**2.3**, 5 mol%, (Ph-S)₂ 10 mol%, 50:50 DCM:DCE) with nucleophiles (300 mol%).

such as acetic acid and thiophenol. Extended reaction times (3-7 days) were required to achieve significant conversion (7-30%; **Figure 2.3**; Bottom). More specifically, hydroacetoxylation was achieved in low conversion (~7%), and respectable yield (97%) (see experimental; **Figure 2.45**). This protocol also facilitates the hydroaddition of simple thioethers (i.e., thiophenol) (**Figure 2.3**). ¹H NMR spectroscopic analysis of the isolated residue (76% yield) revealed new aromatic and methine signals consistent with thioetherification ($\delta = 6.9 - 7.3$ ppm, and 2.9 ppm, respectively) which indicated 21% conversion (**Figure 2.43**). These results illustrate that this strategy will facilitate hydroadditions of polyalkenamers to generate functionalized species.

2.4 Conclusions

We demonstrated that olefin photoredox manipulation may be suited to alter different polyalkenamer substrates. With this single-electron modification tool, the molar mass can be lowered by 96%. Because it makes even lower molecular weight species accessible, oxygen plays a crucial role in the degradation pathway. This polymer modification method can encourage the breakdown of different polyalkenamers by using a solar source. We have also demonstrated that common linear polyalkenamers can yield high-value small molecule products (C₁₆–C₂₉ n-alkyl species). Lastly a wide range of functionalized polyalkenamers can be obtained by combining degradation and nucleophilic trapping (hydrofunctionalizations).

2.5 Acknowledgements

For assistance with synthesis and degradation experiments, I thank Dominic Coughlin.

For assistance with GC-MS method development, I thank Max Mortenson.

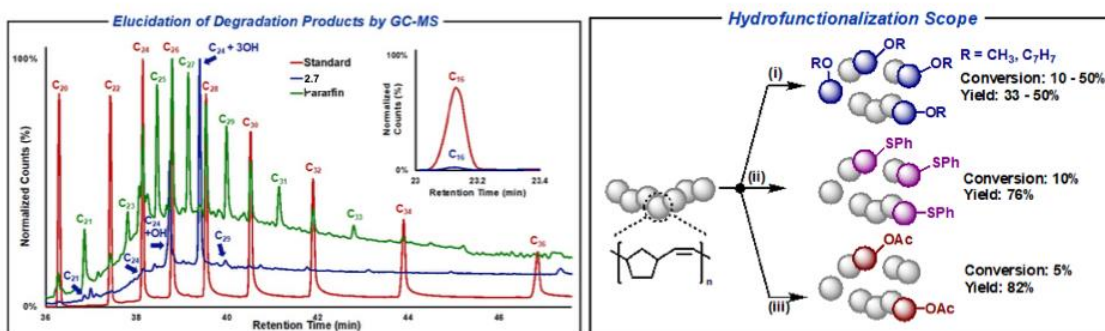


Figure 2.1. Cartoon depicting hydroaddition substrate scope of 2.1 (Polynorbornene) on the (right) and GC chromatogram on the (left) depicting C₁₀ – C₄₀ n-alkanes standards (red), commercial paraffin wax (green), and 2.7 (blue). Carbon counts are denoted and select product peaks are highlighted with arrows. Inset highlights the presence of a C₁₆ n-alkane degradation product when compared to the known standards.

2.6 Experimental

2.6.1 General Materials and Methods

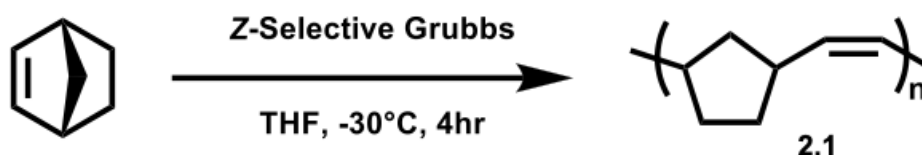
Unless otherwise noted, solvents were dried on an MBraun solvent purification system with 3Å molecular sieves and degassed via three freeze-pump-thaw cycles. *Cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene (purified by precipitation from methanol) were purchased from Sigma. All other reagents and materials were obtained from commercial sources and used without further purification unless otherwise noted. Oxygen and water sensitive manipulations were performed in a N₂ filled MBraun glovebox or using standard Schlenk techniques with oven- and flame- dried glassware. ¹H and ¹³C NMR spectral data were collected on a Bruker 500 MHz NMR, Varian 600 MHz NMR, Varian 500 MHz NMR, or Varian 300 MHz NMR spectrometer. Chemical shifts (δ) are reported in ppm using the residual solvent as reference. IR spectra were collected on a Bruker Alpha II FT-IR with Platinum ATR accessory or a Thermo Scientific Nicolet IS5 spectrometer with an ATR id7 attachment (germanium crystal). Centrifugation was

conducted using a OHAUS Frontier 5306 mini centrifuge spun at 6,000 rpm for 20-minute cycles. Size Exclusion Chromatography (SEC) data were collected on an Omnisec Resolve and Omnisec Reveal System using triple detection with detectors in series: UV, light scattering, viscometer, and refractive index and three Viscotek styrene divinylbenzene copolymer columns (in series T3000, T4000, and T5000) at a flow rate of 1 mL/min and thermostatted to 30°C using tetrahydrofuran (THF) as the eluent (SEC 1) or an Agilent 1260 infinity II SEC equipped with a Wyatt Dawn Helios 8 multiangle light scattering detector, ViscoStar III, and an Optilab T-rEX at a flow of 1 mL/min with THF as the eluent (SEC 2). Unless otherwise noted, Molecular weight data were acquired with SEC 1. Molecular weight and dispersity data calculated from triple detection or conventional calibration relative to polystyrene standards are reported. All photochemical transformations were performed using an ABI 12w Blue LED lamp ($\lambda_{\text{EX}} = 450 - 460$ nm), where the reaction vessels were placed 10 cm away from the light source and the temperature did not exceed 35 °C. Paraffin standard used is Parafilm “M” Laboratory Film from Bemis.

2.6.2 Representative Procedure for the Z-selective Ring Opening Polymerization of Polynorbornene (2.1)

A flame dried 250 mL Schlenk flask was charged with norbornene (3.0179 g; 31.9 mmol), THF (126 mL), and a Teflon stir bar. The monomer solution was degassed via three cycles of freeze-pump-thaw and cooled to -30 °C. A solution of Z-selective Grubbs catalyst (40 mg; 0.05 mmol in 1 mL THF) was prepared in an N₂ filled glovebox and then added to the monomer solution via syringe. The reaction temperature was maintained

between -40 °C and -20 °C for 4 h, as demonstrated in (**Scheme 2.2**) after which the polymerization was quenched with ethyl vinyl ether (2 mL; 25.05 mmol) in THF (1 mL). Polymeric material was precipitated from methanol, collected on a medium porosity fritted funnel, and dried in vacuo. The polymer was dissolved in minimal DCM, precipitated from MeOH a second time, collected via filtration, and dried in vacuo. The polymer was dissolved in THF and precipitated from methanol two additional times. The title material (**2.1**) was recovered as a white solid (1.4323 g, 47.5% yield) representative SEC data for this isolated polymer shown in **Figure 2.6** (red Trace, 328 kDa). Spectral data were consistent with literature reports, and representative ^1H and ^{13}C NMR spectra are shown in **Figure 2.33** and **Figure 2.34**, respectively. Olefin E:Z ratio of 1:24 was determined based on the relative integrations of the Z ($\delta = 5.20$) and E ($\delta = 5.35$) olefin resonances. SEC data for all polymer used in this study are shown in **Figure 2.6**.



Scheme 2.2. Z-selective Polymerization to afford **2.1**.

2.6.3 Representative Procedure for the Z-selective Ring Opening Polymerization of Low M_n Polynorbornene (2.1)

A flame dried 25 mL Schlenk flask was charged with norbornene (500 mg; 5.31 mmol), DCM (20 mL), and a Teflon stir bar. A solution of Grubbs 3rd generation catalyst (85 mg; 0.10 mmol in 1.5 mL DCM) was added via syringe. The reaction was stirred at 0 °C

for 30 min, after which the polymerization was quenched with excess ethyl vinyl ether (0.5 mL; 0.91 mmol) and concentrated to minimal volume. The solution was passed over a plug of basic alumina twice and concentrated to minimal volume for precipitation from MeOH before drying in vacuo. The title material was recovered as an off-white powder (423 mg, 85% yield). SEC data for all polymers utilized for SEPE degradation and hydroaddition studies is provided in **Figure 2.7**. Spectral data were consistent with literature reports.⁶¹

2.6.4 Procedure for Inert Atmosphere's Photomodification of Polyalkenamers (Method 1)

In a N₂ filled glovebox, a 2-dram vial was charged with **2.1** (25 mg; 0.266 mmol), a Teflon stir bar, and DCM (3.54 mL). The mixture was stirred until all polymer was dissolved. In a separate vessel, **2.2** (5.3 mg; 0.013 mmol), and (PhS)₂ (14.5 mg; 0.067 mmol) were added followed by DCM (0.5 mL). After which the combined catalyst solution was added to the mixture of **2.1**, sealed with a Teflon lined cap, removed from the glovebox, and irradiated with a 12W blue LED lamp ($\lambda_{EM} = 450 - 460$ nm) for 1 h with stirring. After which the crude reaction mixture was filtered over a plug of silica and concentrated to a volume of ~1mL under a gentle stream of N₂. Polymeric material was precipitated from addition to MeOH, followed by centrifugation. The resulting supernatant was decanted, and the isolated solids were dried for 16 in vacuo. Representative spectral data are shown in **Figures 2.35** and **2.36**.

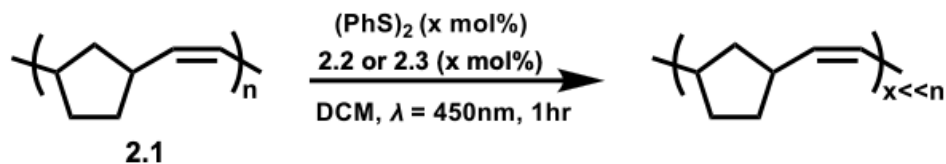
2.6.5 Procedure for Ambient Atmosphere's Photomodification of Polyalkenamers

(Method 2)

A 2-dram vial was charged with **2.1** (25 mg; 0.266 mmol), a Teflon stir bar, and technical-grade DCM (3.04 mL). The mixture was stirred until all polymer was dissolved. In a separate vessel, **2.2** (5.3 mg; 0.013 mmol), and (PhS)₂ (14.5 mg; 0.067 mmol) were added followed by DCM (0.5 mL). After which the combined catalyst solution was added to the mixture of **2.1** and irradiated with a 12 W blue LED lamp (λ_{EM} = 450 – 460 nm) for 1 h with stirring. After which the crude reaction mixture was filtered over a plug of silica and concentrated to a volume of ~1mL under a gentle stream of N₂. Polymeric material was precipitated from addition to MeOH, followed by centrifugation. The resulting supernatant was decanted, and the isolated solids were dried for 16 h in vacuo. Representative spectral data are shown in **Figures 2.37** and **2.38**.

2.6.6 Details for Photomodification Reaction Optimizations

Reaction optimizations were conducted under N₂ and followed the general procedure outlined above (Method 1). We varied conditions such as: HAT catalyst identity (note: alkyl thiols such as 1-adamantane thiol and 1-dodecanethiol afforded intractable materials which precluded characterization), Photoredox catalyst identity (2,4,6-Triphenylpyryllium tetrafluoroborate; **2.2**, & 9-Mesityl-10-methylacridinium tetrafluoroborate; **2.3**) and their loadings (1-10 mol%), HAT catalyst loadings (10-50 mol%), Reaction concentrations (0.075M & 0.15M), and reaction atmosphere (N₂ and Ambient) (see **Table 2.2**) as shown in (**Scheme 2.3**) and representative SEC data shown in **Figures 2.8 – 2.13**.



Scheme 2.3. Generalized Photomodification Scheme.

2.6.7 Details for Photomodification Control Experiments

Control experiments were conducted under N₂ following the general procedure outlined above (Method 1). Deviations and Molecular weight data are shown in **Table 2.1**. SEC data shown in **Figure 2.14**. Representative spectral data are shown in **Figures 2.47**.

2.6.8 Degradation of *cis*-1,4-polyisoprene (2.4) via Photomodification

A 20 mL scintillation vial was charged with **2.4** (50 mg, 0.734 mmol), DCM (8.88 mL), and a Teflon stir bar. A separate 1-dram vial was charged with (PhS)₂ (41 mg, 0.184 mmol), **2.2** (14.9 mg, 0.037 mmol), DCM (1 mL) and added to the solution of **2.4**. The reaction mixture was irradiated with 12W Blue LED for 1 hour with stirring. After which the crude solution was filtered through plug of silica, concentrated to a minimal volume, and precipitated from addition to MeOH. Polymeric material was isolated following centrifugation and decanting of the supernatant. The residue was washed with hexanes and dried for 16 in vacuo. SEC data of the isolated solids (40 mg; 80% mass recovery) shown in **Figure 2.27**. Representative spectral data shown in **Figures 2.48 and 2.49**. This material was also utilized for prolonged degradation experiments. (i.e., 96 h irradiation)

Table 2.2. Results from optimization experiments.

Entry	(PhS) ₂ (Xmol%)	Atmosphere	PC (Xmol%)	[M]	Initial <i>M_n</i> (kDa)	Final <i>M_n</i> (kDa)	Reduction (%)	Yield (%)
1	25 mol%	Nitrogen	2.2 (5mol%)	0.075M	328	103	68.6	95.7
2	25 mol%	Nitrogen	2.3 (5 mol%)	0.075M	328	124	62.2	27.9
3	25 mol%	Nitrogen	2.2 (1 mol%)	0.075M	328	106	67.7	82.1
4	25 mol%	Nitrogen	2.2 (10 mol%)	0.075M	328	100	69.5	98.1
5	10 mol%	Nitrogen	2.2 (5 mol %)	0.075M	328	136	58.5	75.5
6	50 mol%	Nitrogen	2.2 (5 mol %)	0.075M	328	100	69.5	90.2
7	25 mol%	Nitrogen	2.2 (5 mol %)	0.150M	328	128	61.0	82.9
8	25 mol%	Ambient	2.2 (5 mol %)	0.075M	328	12	96.3	65.8

Note: the degradation of **2.4** could also be prolonged (96 h) to afford materials with a 99% reduction in molar mass. This was conducted on a larger scale to aid in subsequent characterization. **2.4** (95.3 mg, 1.399 mmol), **2.2** (27.7 mg, 0.070 mmol), (PhS)₂ (76.4 mg, 0.350 mmol), and DCM (18.7 mL). Reaction setup and purification was outlined above (Method 2). SEC data of the isolated pale-yellow residue shown in **Figure 2.29**. Spectral data shown in **Figures 2.52 – 2.53**.

2.6.9 Degradation of cis-1,4-polybutadiene (2.5) via Photomodification

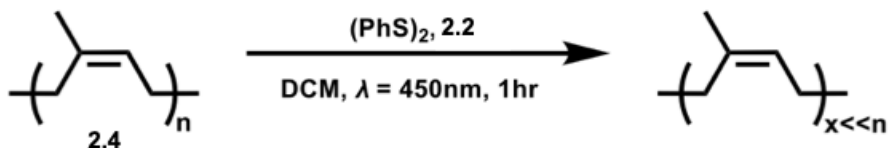
A 20 mL scintillation vial was charged with **2.5** (57.3 mg, 1.06 mmol), DCM (13 mL), and a Teflon stir bar. A separate 1-dram vial was charged with (PhS)₂ (57.8 mg, 0.233 mmol), **2.2** (21 mg, 0.053 mmol), DCM (1.1 mL) and added to the solution of **2.5**. The reaction mixture was irradiated with 12W Blue LED for 1 hour with stirring. After which the crude solution was filtered through plug of silica, concentrated to a minimal volume, and precipitated from addition to MeOH. Polymeric material was isolated following centrifugation and decanting of the supernatant. The residue was washed with hexanes and dried for 16 in vacuo. SEC data of the isolated solids (50 mg; 88% mass recovery) shown in **Figure 2.28**. Representative spectral data shown in **Figures 2.50 and 2.51**.

2.6.10 Degradation of 2.1,2.4 and 2.5 using Solar Source

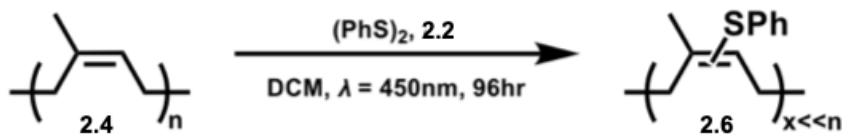
Reaction setup was consistent with our general procedure (Method 2). **2.1** (26.3 mg, 0.279 mmol), (PhS)₂ (15.1 mg, 0.069 mmol) **2.2** (6.1 mg, 0.015 mmol), and technical-grade DCM (3.72 mL). Reaction vessels were placed on a raised windowsill in direct sunlight for 2 h. A thermometer was placed next to vials and the temperature did not exceed 40 °C. Workup of **2.1**, after which a final degas cycle was performed and allowed to thaw under an argon balloon. The vessel was irradiated with 12W Blue LED for 1hr with stirring. The workup and isolation were performed as outlined above (Method 2) Experiment was conducted in triplicate as shown in (**Scheme 2.4**). Average SEC data shown in **Figure 2.30**.

Reaction setup was consistent with our general procedure (Method 2). **2.4** (20.4 mg, 0.299 mmol), (PhS)₂ (16.7 mg, 0.076 mmol) **4.2** (6 mg, 0.015 mmol), and technical-grade DCM (4 mL). Reaction vessels were placed on a raised windowsill in direct sunlight for 2 h. A thermometer was placed next to vials and the temperature did not exceed 40 °C. Workup and isolation is outlined above (Method 2). Experiment was conducted in triplicate as shown in (**Scheme 2.5**). SEC data of the isolated solids (20.2 mg; 99% mass recovery) shown in **Figure 2.31**.

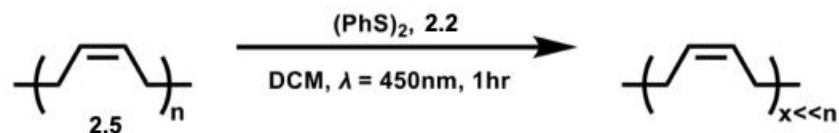
Reaction setup was consistent with our general procedure (Method 2). **2.5** (20.4 mg, 0.377 mmol), (PhS)₂ (21 mg, 0.096 mmol) **4.2** (7.5 mg, 0.019 mmol), and technical-grade DCM (5 mL). Reaction vessels were placed on a raised windowsill in direct sunlight for 2 h. A thermometer was placed next to vials and the temperature did not exceed 40 °C. Workup and isolation is outlined above (Method 2). Experiment was conducted in triplicate as shown in (**Scheme 2.6**). SEC data of the isolated solids (18.7 mg; 92% mass recovery) shown in **Figure 2.32**.



Scheme 2.4. Photomodification of **2.4**.



Scheme 2.5. Prolonged photomodification of **2.4**.



Scheme 2.6. Photomodification of 2.5.

2.6.11 Impact of Water

A 10 mL Schlenk flask was charged with a technical grade DCM (2.71 mL) solution of **2.1** (26.2 mg, 0.278 mmol) and a Teflon stir bar. The vessel was sealed with a rubber septum followed by 2 cycles of degassing (freeze/pump/thaw). In a separate vessel, **2.2** (6.1 mg, 0.017 mmol), (PhS)₂ (15.2 mg, 0.070 mmol) were added followed by technical grade DCM (1.0mL). The catalyst solution was taken up in a syringe and added to the frozen solution of **2.1**, after which a final degas cycle was performed and allowed to thaw under an argon balloon. The vessel was irradiated with 12W Blue LED for 1hr with stirring. The workup and isolation were performed as outlined above (Method 2). Experiment was conducted in triplicate. Average SEC data shown in **Figure 2.25**.

2.6.12 Impact of O₂

In a N₂ filled glovebox, a 10 mL Schlenk flask was charged with an anhydrous/degassed DCM (2.57 mL) solution of **2.1** (25.2 mg, 0.268 mmol) and a Teflon stir bar. The vessel was sealed with a rubber septum, removed from the glovebox and the atmosphere removed via 2 cycles of degassing (freeze/pump/thaw). In a separate vessel, **2.2** (5.5 mg, 0.015 mmol), (PhS)₂ (15.0 mg, 0.069 mmol) followed by anhydrous/degassed DCM (1.0mL). The catalyst solution was taken up in a gas-tight syringe and the needle inserted into septa-capped 1-dram vial to protect from air exposure. This solution was injected into frozen solution of **2.1** under positive N₂ flow followed by a final degassing cycle.

The solution was allowed to thaw under a balloon of ~98% oxygen, which was passed over 3 Å molecular sieves. The solution was irradiated with a 12W Blue LED for 1hr with stirring. The workup and isolation were performed as outlined above (Method 2). Experiment was conducted in triplicate. Average SEC data shown in **Figure 2.25**.

2.6.13 Impact of Exogenous Peroxides

A 10 mL Schlenk flask was charged with a technical-grade DCM (2.57 mL) solution of **2.1** (25.2 mg, 0.268 mmol) and a Teflon stir bar. The vessel was sealed with a rubber septum, and the atmosphere was removed via 2 degassing cycles (freeze/pump/thaw). In a separate vessel, **2.2** (5.5 mg, 0.015 mmol), (PhS)₂ (15.1 mg, 0.069 mmol) and *t*-Butyl hydroperoxide (51 µL, 0.535 mmol; ~5-6M in decane) were added, followed by technical-grade DCM (1.0mL). This catalyst/peroxide solution was taken up in a syringe and added to the frozen solution of **2.1** under positive N₂ pressure followed by a final degassing cycle. The solution was allowed to thaw under a balloon of argon. The solution was irradiated with a 12W Blue LED for 1hr with stirring. The workup and isolation were performed as outlined above (Method 2). Experiment was conducted in triplicate. SEC data shown in **Figure 2.26**.

2.6.14 Qualitative Investigation for the Presence of Peroxides

The experimental setup was outlined above (Method 2) and used the optimized conditions on a 0.27 mmol scale with respect to **2.1**. Prior to irradiation a CTL Scientific Supply Corp QUANTOFIX Peroxide Test Strip was dipped into the solution and allowed to dry (**Figure 2.4**, top). The solution was irradiated with 12W Blue LED for 10 minutes with stirring. A second peroxide test strip was dipped into the solution and allowed to dry

(**Figure 2.4**). The dry test strip turned a blue color, which indicated presence of organic peroxides. A control experiment (using Method 1) was conducted as described above, and a peroxide strip was dipped in the solution under positive N₂ pressure before irradiation (**Figure 2.5 top**), and a second test strip was dipped into the solution after 10 minutes of irradiation under positive N₂ pressure (**Figure 2.5**). No change in color indicated a negative result for presence of peroxides. Photographs of each experiment shown below.

2.6.15 Degradation Kinetics of 2.1 under N₂ atmosphere (Inert Conditions)

In a N₂ filled glovebox, a 10 mL Schlenk flask was charged with a DCM (3.18 mL) solution of **2.1** (26 mg, 0.276 mmol) and a Teflon stir bar. The vessel was sealed with a rubber septum and covered with aluminum foil. In a separate vessel, **2.2** (5.5 mg, 0.014 mmol) and (PhS)₂ (15.1 mg, 0.069 mmol) were dissolved in DCM (0.5 mL), taken up in a syringe and added to the solution of **2.1**. The vessel was removed from the glovebox, equipped to a Schlenk line and the solution placed under an atmosphere of N₂. After which an aliquot (0.1 mL) was removed and diluted to 1 mL with THF for SEC analysis (t₀). Aluminum foil was removed, and the bulk solution was irradiated with a 12w Blue LED. At 1-minute intervals, an aliquot (0.1 mL) was removed, the process for t₀ was repeated until 10 aliquots had been removed (t₁-t₁₀). Aliquot vials were covered from ambient light for the remainder of the experiment. Aliquot solutions were filtered through a 0.2µm syringe filter into autosampler vials for SEC characterization. Experiment was conducted in triplicate. The rate of chain cleavage was calculated according to equation 1



Figure 2.4. Photograph showing peroxide test strips after being dipped into the solution prior to irradiation (top) and after 10 minutes (bottom) during the photomodification of 2.1 under ambient atmosphere.



Figure 2.5. Photograph showing peroxide test strips after being dipped into the solution prior to irradiation (top) and after 10 minutes (bottom) during the photomodification of 2.1 under N₂.

to be $1.96 \times 10^{-2} \pm 2.37 \times 10^{-4} \text{ min}^{-1}$. A plot of $1/M_t - 1/M_i$ versus irradiation time is shown in **Figure 2.2**. M_n over time is shown in **Figures 2.20** and **Table 2.3**. SEC data shown in **Figure 2.19**.

2.6.16 Degradation Kinetics of 2.1 under Ambient atmosphere

A 2-dram vial was charged with a technical-grade DCM (3 mL) solution of **2.1** (26.6 mg, 0.283 mmol) and a Teflon stir bar. The vial was sealed with a septa-cap with a needle inserted for venting. In a separate vessel, **2.2** (5.6 mg, 0.014 mmol) and (PhS)₂ (15.1 mg, 0.071 mmol) were dissolved in DCM (0.77 mL) and injected into polymer solution. An aliquot (0.1 mL) was quickly removed and diluted to 1 mL with THF for SEC analysis (t_0). After which the bulk solution was irradiated with a 12W Blue LED. At 1-minute intervals, an aliquot (0.1 mL) was removed, the process for t_0 was repeated until 10 aliquots had been removed (t_1 - t_{10}). Aliquot vials were covered from ambient light for the remainder of the experiment. Aliquot solutions were filtered through a 0.2 μ m syringe filter into autosampler vials for SEC characterization. Experiment was conducted in triplicate. The rate of chain cleavage was calculated according to equation 1 to be $1.21 \times 10^{-1} \pm 6.66 \times 10^{-3} \text{ min}^{-1}$. A plot of $1/M_t - 1/M_i$ versus irradiation time is shown in **Figure 2.2**. SEC data shown in **Figure 2.21**. M_n over time is shown in **Figure 2.22** and **Table 2.4**. SEC data shown in **Figure 2.21**.

2.6.17 Degradation Kinetics of 2.1 under Ambient atmosphere with TEMPO

A 2-dram vial was charged with a DCM (3 mL) solution of **2.1** (26.2 mg, 0.278 mmol) and a Teflon stir bar. The vial was sealed with a septa-cap with a needle inserted for venting. In a separate vessel, **2.2** (5.6 mg, 0.014 mmol) and (PhS)₂ (15.1 mg, 0.069

Table 2.3. Kinetic study for photoediting degradation of 2.1 under N₂.

Entry	Irradiation Time (min)	M_n^a (kDa)	M_z^a (kDa)
1	0	292 ±9	960±59
2	1	188±2	549±14
3	2	171±5	509±25
4	3	156±7	459±7
5	4	152±4	457±6
6	5	144±7	432±12
7	6	139±6	428±15
8	7	134±3	393±6
9	8	130±3	383±4
10	9	123±2	368±6
11	10	116±2	362±12

^aAverage of three runs**Table 2.4.** Kinetic study for photoediting degradation of 2.1 under ambient atmosphere.

Entry	Irradiation Time (min)	M_n^a (kDa)	M_z^a (kDa)
1	0	271±	865±71
2	1	138±	330±24
3	2	109±	243±15
4	3	87±	176±10
5	4	69±	149±9
6	5	62±	125±3
7	6	52±	110±4
8	7	45±	97±3
9	8	42±	89±4
10	9	36±	80±4
11	10	33±	76±4

^aAverage of three runs

mmol) and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO, 131mg, 0.838mmol) were dissolved in DCM (0.71 mL) and injected into the polymer solution of **2.1**. An aliquot (0.1 mL) was removed and diluted to 1 mL with THF for SEC analysis (t_0) (**Table 2.5**). After which the bulk solution was irradiated with 12W Blue LED. At 1-minute intervals, aliquots (0.1) were removed, via the same technique as described above, and diluted to 1 mL with THF (samples t_1 - t_{10}). Aliquot vials were covered from ambient light for the remainder of the experiment. Solutions filtered through a 0.2 μ m syringe filter into SEC vials for characterization. Experiment was conducted in triplicate. The rate of chain cleavage was calculated according to equation 1 to be $2.35 \times 10^{-3} \pm 5.65 \times 10^{-4} \text{ min}^{-1}$. A plot of $1/M_t - 1/M_i$ versus irradiation time is shown in Figure 2.2. SEC data shown in **Figure 2.23**. M_n over time is shown in **Figures 2.24** and **Table 2.5**.

2.6.18 Raney Nickel Catalyzed Desulfurization of Degraded 2.4

Raney Nickel (12 mL of 50% w/w in H₂O) vacuum filtered through a fritted filter sealed with a septum. The Raney Nickel solids were washed with 1,4-dioxane (2 x 5 mL) and dry/degassed Tetrahydrofuran (THF, 2 x 10 mL) and subsequently dried for 16 h in vacuo. The dry Raney Nickel solids were suspended in dry/degassed THF and transferred via syringe into 20mL scintillation vial to prepare a ~6g Raney nickel suspension in 20mL THF. This solution was sparged with a H₂ balloon, and (3g, 10mL) of this solution was transferred to a 50 mL Schlenk flask under an H₂ atmosphere. After which a THF (10 mL) solution of **2.6** (124mg, 0.052mmol) was added to the Raney Nickel suspension under positive H₂ pressure followed by methanol (2 mL, 49.4 mmol) according to **Scheme 2.7**. The reaction mixture was stirred for 20 hours at room temperature. The

Table 2.5. Kinetic study for photoediting degradation of **2.1** under ambient atmosphere + TEMPO.

Entry	Irradiation Time (min)	M_n^a (kDa)	M_z^a (kDa)
1	0	240 $\pm$ 7	677 $\pm$ 41
2	1	234 $\pm$ 8	672 $\pm$ 41
3	2	226 $\pm$ 6	646 $\pm$ 41
4	3	225 $\pm$ 7	606 $\pm$ 11
5	4	223 $\pm$ 7	604 $\pm$ 16
6	5	220 $\pm$ 6	608 $\pm$ 31
7	6	218 $\pm$ 6	601 $\pm$ 21
8	7	217 $\pm$ 5	624 $\pm$ 34
9	8	216 $\pm$ 5	594 $\pm$ 21
10	9	215 $\pm$ 5	599 $\pm$ 18
11	10	214 $\pm$ 5	591 $\pm$ 28

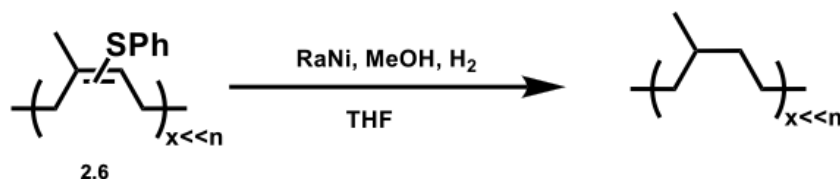
^aAverage of three runs

crude suspension was filtered through a plug of celite and basic alumina to remove Raney Nickel solids. The product was stored as THF solution and aliquots were removed as needed for subsequent characterization. Representative spectral data are shown in **Figures 2.52** and **2.53**. SEC data of the desulfurized material are shown in **Figure 2.29**.

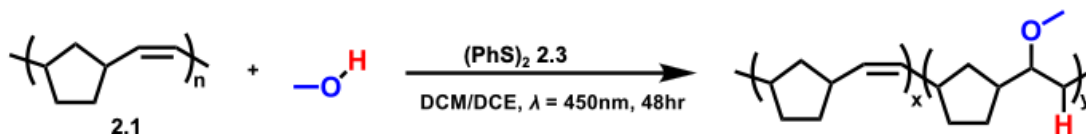
2.6.19 Hydroetherification with Methanol of 2.1

In a N₂ filled glovebox, a 10 mL Schlenk flask was charged with 50:50 DCM:DCE (3 mL) solution of **2.1** (24.6 mg; 0.261 mmol) and a Teflon stir bar. The vessel was sealed with a rubber septum, removed from the glovebox, and MeOH (30 μ L; 0.783 mmol) was added under a positive flow of N₂ followed by 2 cycles of degassing via freeze/pump/thaw. In a separate vessel, **2.3** (5.2 mg; 0.013 mmol) and (PhS)₂ (6 mg; 0.027 mmol) were dissolved in 50:50 DCM:DCE (0.5 mL), taken up in a gas-tight syringe and the needle inserted into a septa-capped 1-dram vial to protect from air exposure. This catalyst solution was added to the frozen solution of **2.1** under positive N₂

pressure, after which a final degas cycle was performed. The reaction mixture was warmed to ambient temperature (23 °C) and irradiated with a 12W blue LED lamp ($\lambda_{EM} = 450 - 460 \text{ nm}$) for 48 h under static N_2 with stirring. The crude reaction mixture was filtered through a silica plug and concentrated to a minimal volume ($\sim 1 \text{ mL}$). Polymeric material was precipitated from addition to pentane followed by centrifugation and decanting of the supernatant. The solids were dried for 16 h in vacuo (14.3 mg, 49.7% yield). Representative spectral data are shown in **Figures 2.39 – 2.40**. ^1H NMR of the residual olefin ($\delta = 5.2 - 5.4 \text{ ppm}$) against the new methoxy signal ($\delta = 3.35 \text{ ppm}$) suggest $\sim 50\%$ conversion to the hydroetherified product according to **Scheme 2.8**. Representative SEC data shown in **Figure 2.15**.



Scheme 2.7. Raney Nickel Catalyzed Desulfurization of 2.6.

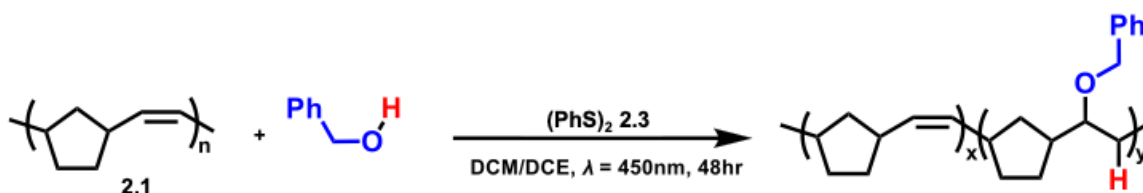


Scheme 2.8. MeOH hydroetherification of 2.1.

2.6.20 Hydroetherification with Benzyl Alcohol of 2.1

In a N_2 filled glovebox, a 10 mL Schlenk flask was charged with 35:65 DCM:DCE (3 mL) solution of low M_n **2.1** (24 mg, 0.255 mmol) and a Teflon stir bar. The vessel was

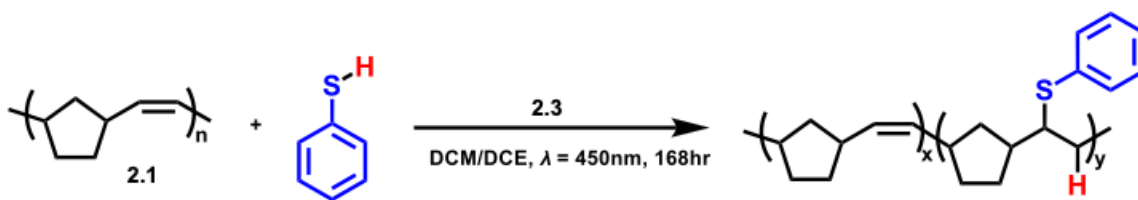
sealed with a rubber septum, removed from the glovebox, and benzyl alcohol (163 μL , 0.765 mmol) was added under a positive flow of N_2 followed by 2 cycles of degassing via freeze/pump/thaw. In a separate vessel, **2.3** (2.3 mg; 0.006 mmol) and $(\text{PhS})_2$ (6.6 mg; 0.030 mmol) were dissolved in 50:50 DCM:DCE (0.4 mL), taken up in a gas-tight syringe and the needle inserted into septa-capped 1-dram vial to protect from air exposure. This catalyst solution was added to the frozen solution of **2.1** under positive N_2 pressure, after which a final degas cycle was performed. The reaction mixture was warmed to ambient temperature (23 °C) according to **Scheme 2.9** and irradiated with a 12 W blue LED lamp ($\lambda_{\text{EM}} = 450 - 460 \text{ nm}$) for 48 h under static N_2 with stirring. The crude reaction mixture was filtered through a silica plug and concentrated to a minimal volume ($\sim 1 \text{ mL}$). Polymeric material was precipitated from addition to pentane followed by centrifugation and decanting of the supernatant. The solids were dried for 16 h in vacuo (10.2 mg, 33% yield). Representative spectral data are shown in **Figures 2.41 – 2.42**. ^1H NMR of the residual olefin ($\delta = 5.2 - 5.4 \text{ ppm}$) against the new benzyl methylene signal ($\delta = 4.53 \text{ ppm}$) suggest $\sim 20\%$ conversion to the hydroetherified product. Representative SEC data shown in **Figure 2.16**.



Scheme 2.9. Benzyl alcohol hydroetherification of low Mn **2.1**.

2.6.21 Hydroetherification with Thiophenol of 2.1

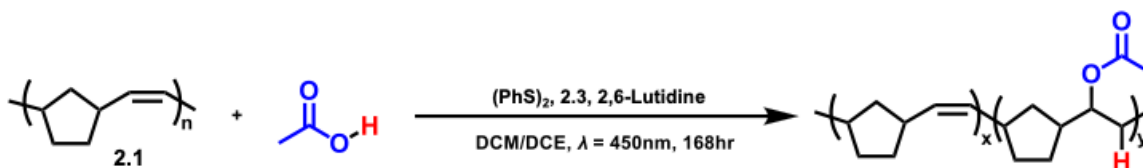
In a N₂ filled glovebox, a 10 mL Schlenk flask was charged with 50:50 DCM:DCE (3.1 mL) solution of **2.1** (25.5 mg, 0.271 mmol) and a Teflon stir bar. The vessel was sealed with a rubber septum, removed from the glovebox, and thiophenol (110 μ L, 1.08 mmol) was added under a positive flow of N₂ followed by 2 cycles of degassing via freeze/pump/thaw. In a separate vessel, **2.3** (5.5 mg, 0.014 mmol) was dissolved in 50:50 DCM:DCE (0.5 mL), taken up in a gas-tight syringe and the needle inserted into septa-capped 1-dram vial to protect from air exposure. This catalyst solution was added to the frozen solution of **2.1** under positive N₂ pressure, after which a final degas cycle was performed. The reaction mixture was warmed to ambient temperature (23 °C) according to **Scheme 2.10** and irradiated with a 12 W blue LED lamp (λ_{EM} = 450 – 460 nm) for 168 h under static N₂ with stirring. The crude reaction mixture was filtered through a silica plug and concentrated to dryness under N₂ pressure. The solids were washed with pentane (2 x 3 mL) and dried for 16 h in vacuo (24 mg, 75.5% yield). Representative spectral data are shown in **Figures 2.43 – 2.44**. ¹H NMR of the residual olefin (δ = 5.2 – 5.4 ppm) against the new methine signal (δ = 2.90 ppm) suggest ~21% conversion to the hydrothioetherified product. Representative SEC data shown in **Figure 2.17**.



Scheme 2.10. Hydrothioetherification of **2.1**.

2.6.22 Hydrocarboxylation with Acetic Acid of 2.1

In a N₂ filled glovebox, a 10 mL Schlenk flask was charged with a DCM (4.23 mL) solution of **2.1** (36.9 mg, 0.392 mmol) and a Teflon stir bar. The vessel was sealed with a rubber septum, and removed from the glovebox. Glacial acetic acid (230 μ L, 3.92 mmol) and 2,6-Lutidine (45 μ L, 0.392 mmol) were added under a positive flow of N₂ followed by 2 degassing cycles (freeze/pump/thaw) and kept frozen under N₂. In a separate vessel, **2.3** (7.8 mg, 0.020 mmol) and (PhS)₂ (8.56 mg, 0.039 mmol) were dissolved in DCM (1 mL). The mixed catalyst solution was added to the vessel with **2.1** via gas-tight syringe. Upon freezing, the atmosphere was evacuated and replaced with N₂. The reaction mixture was warmed to ambient temperature (23°C) according to **Scheme 2.11** and irradiated with a 12 W blue LED lamp (λ_{EM} = 450 – 460 nm) for 72 h under static N₂ with stirring. The crude reaction mixture was filtered through a silica plug and concentrated to a minimal volume (~1 mL) and precipitated from addition of the concentrated solution to pentane followed by centrifugation and decanting of the supernatant. The residue was dried for 16 h in vacuo (34.8 mg, 80.2% yield). Representative spectral data are shown in **Figures 2.45 and 2.46**. ¹H NMR of the residual olefin (δ = 5.2 – 5.4 ppm) against the new methine signal (δ = 4.87 ppm) suggest ~5% conversion to the hydroacetoxyated product. IR spectra shown in Figure 2.56. Representative SEC data shown in **Figure 2.18**. Representative IR data shown in **Figure 2.54**.



Scheme 2.11. Hydrocarboxylation of 2.1.

2.6.23 GC-MS Analysis of Extended Degradation Products

The GC-MS method used was as follows: The column flow rate was set to 1.2 mL/min. With an inlet temperature of 400 °C, the oven temperature was increased from 80 °C to 100 °C with a ramp rate of 30 °C/min. The oven temperature was held at 100 °C for 12 minutes and then increased from 100 °C to 160 °C with a ramp rate of 40 °C/min. The oven temperature was held at 160°C for 15 minutes and then increased from 160 °C to 300°C with a ramp rate of 40°C /min. The oven temperature was then held at 300 °C for 22 minutes. The standards used in this experiment were linear C₁₀-C₄₀ alkanes (even numbers of carbon atoms) as a solution in heptane, as well as parafilm dissolved in THF stabilized with butylated hydroxytoluene (BHT). Chromatogram and mass spectra are shown in **Figure 2.3**.

2.6.24 Mark-Houwink Analysis of Degradation Products

A plot of intrinsic viscosity vs retention volume was generated from the beginning polynorbornene sample and the resultant polymer after 10 minutes of standard degradation parameters under a nitrogen atmosphere. This plot is shown in **Figure 2.55**.

APPENDIX

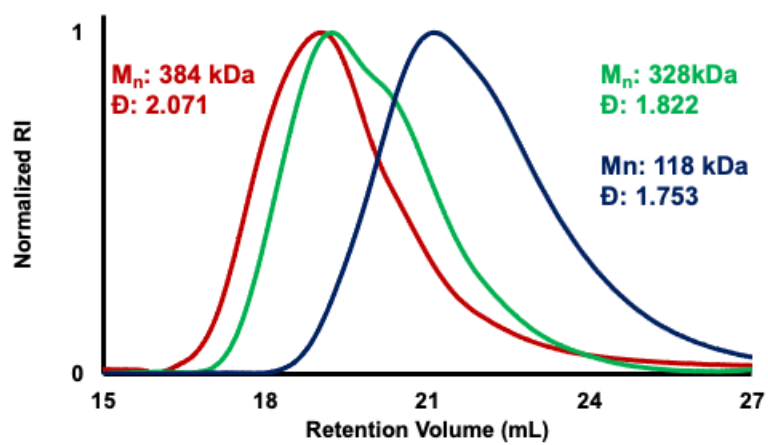


Figure 2.6. SEC data from triple detection for high M_n 2.1 samples used in this study.

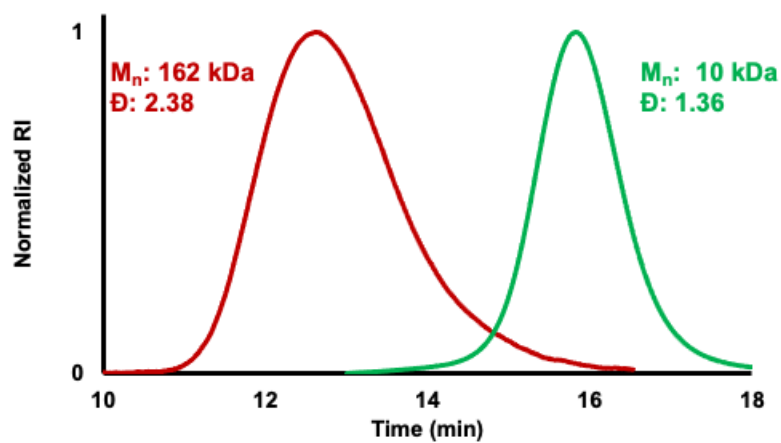


Figure 2.7. SEC data from conventional calibration (acquired on SEC 2) for high and low M_n 2.1 samples used in this study.

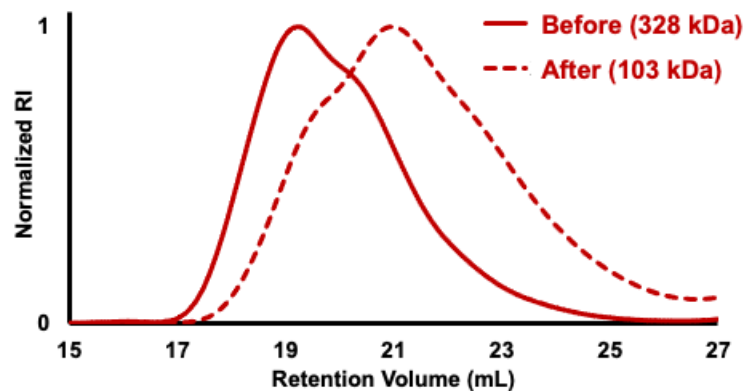


Figure 2.8. SEC data from triple detection for the degradation of 2.1 with 2.2 under N₂ (Table 2.2, entry 1). Solid trace represents starting polymer, and the dotted trace represents the isolated material following irradiation.

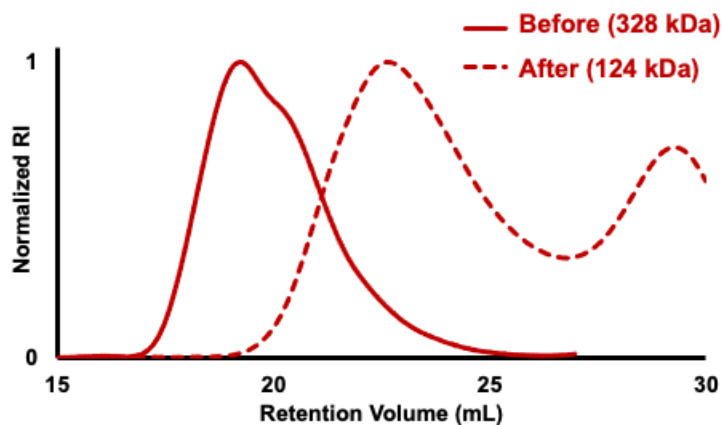


Figure 2.9. SEC data from triple detection for the degradation of 2.1 with 2.3 under N₂ (Table 2.2, entry 2). Solid trace represents starting polymer, and the dotted trace represents the isolated material following irradiation.

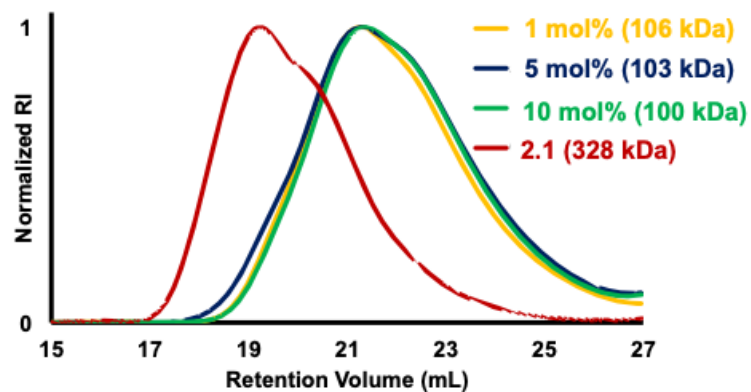


Figure 2.10. SEC data from triple detection for varied catalyst loadings of 2.2 (Table 2.2).

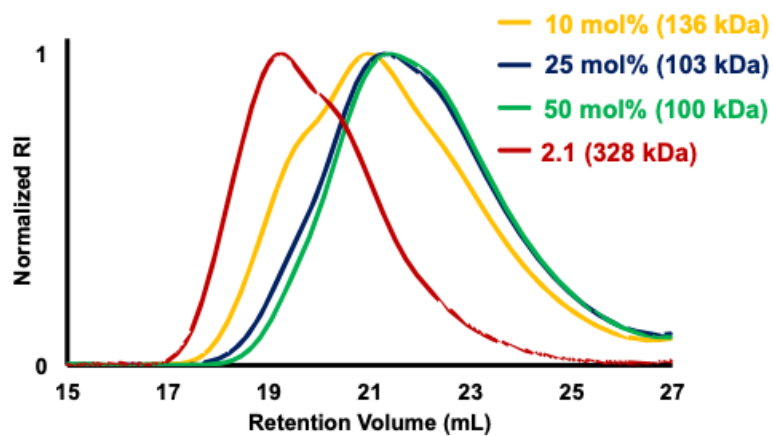


Figure 2.11. SEC data from triple detection for varied catalyst loadings of (PhS)₂ (Table 2.2).

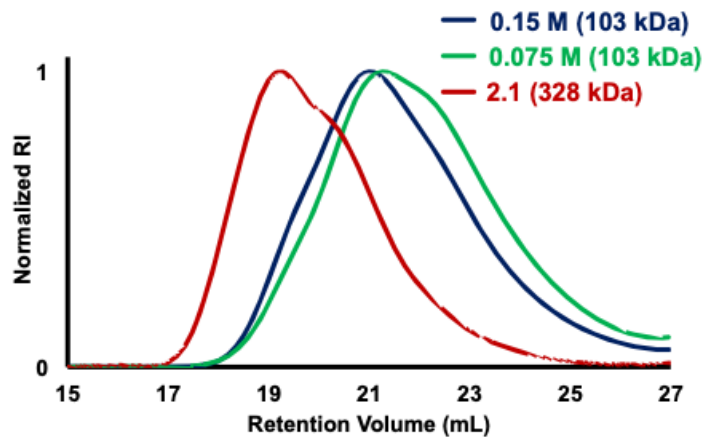


Figure 2.12. SEC data from triple detection for varied concentrations (**Table 2.2**).

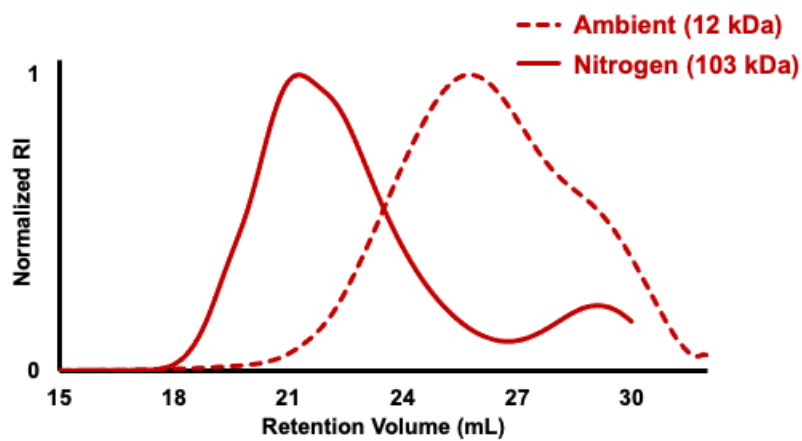


Figure 2.13. SEC data from triple detection for degradation of 2.1 under inert and ambient conditions (**Table 2.2**).

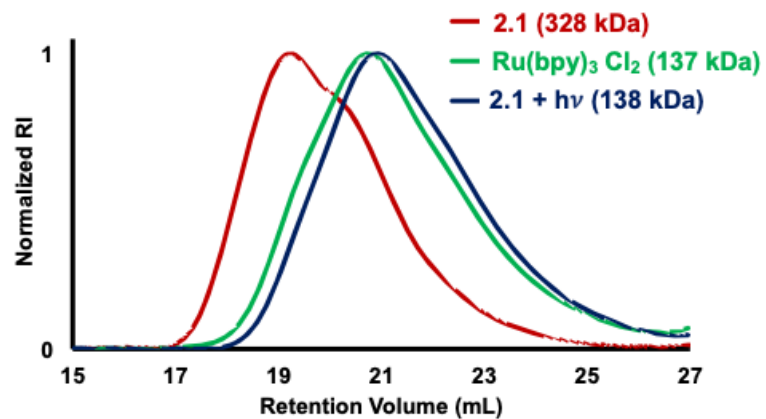


Figure 2.14. SEC data from triple detection for control experiments (Table 2.1).

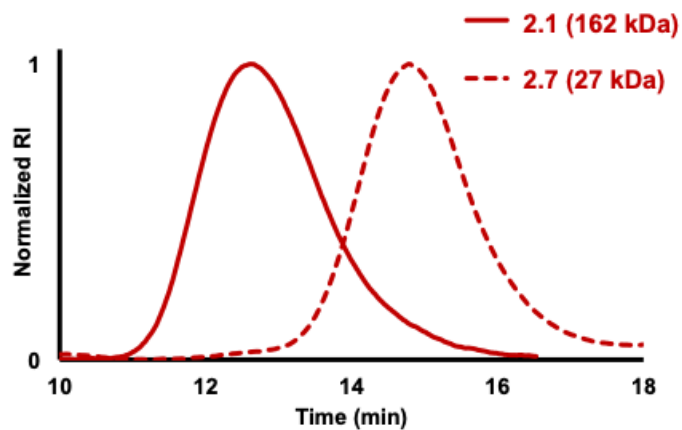


Figure 2.15. SEC data from conventional calibration (SEC 2) for the hydroetherification (MeOH) of 2.1.

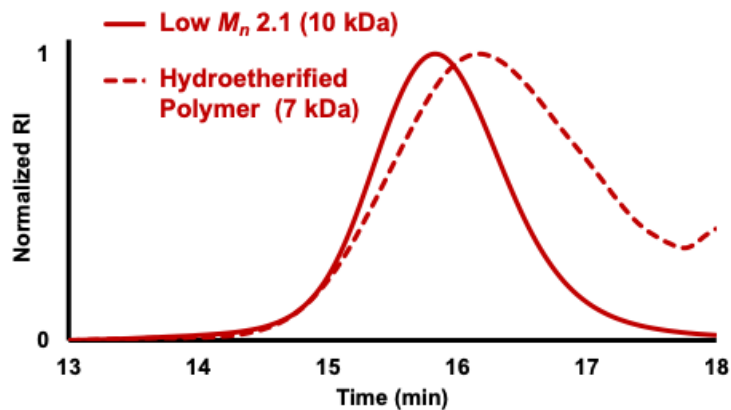


Figure 2.16. SEC data from conventional calibration (SEC 2) for the hydroetherification (BnOH) of low M_n 2.1.

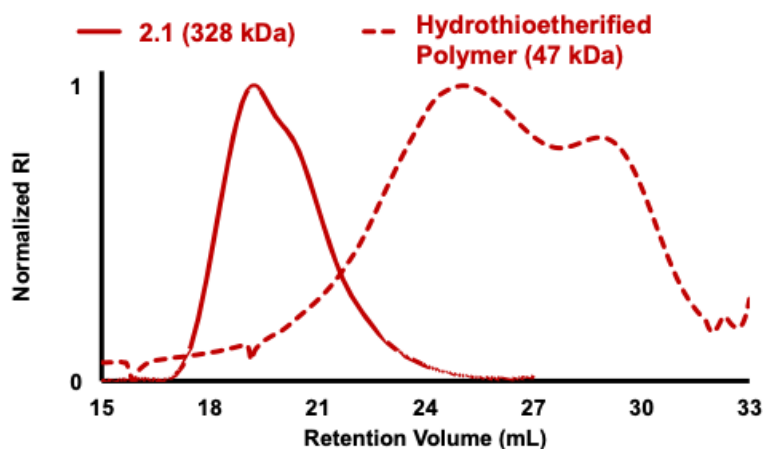


Figure 2.17. SEC data from conventional calibration for the hydrothioetherification (PhSH) of 2.1.

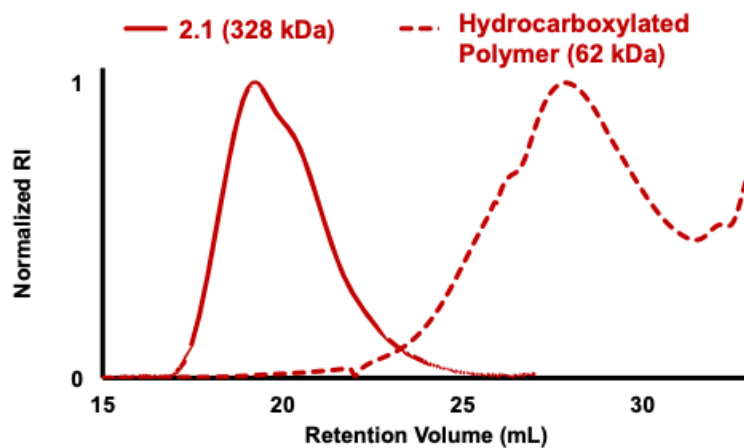


Figure 2.18. SEC data from triple detection for the hydrocarboxylation (AcOH) of 2.1.

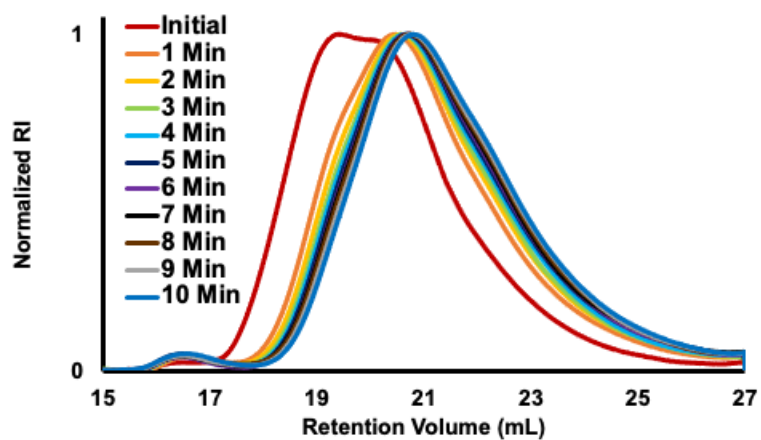


Figure 2.19. SEC data from triple detection for the degradation kinetics of 2.1 under N_2 .

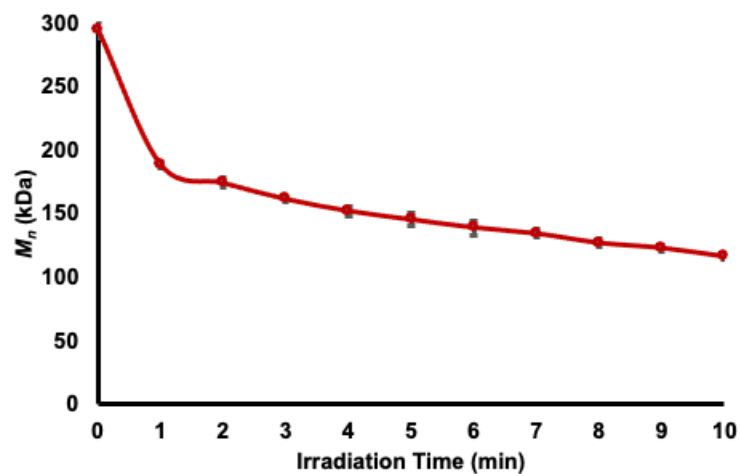


Figure 2.20. M_n (determined by triple detection SEC) as a function of irradiation time during photomodification of 2.1 under N_2 .

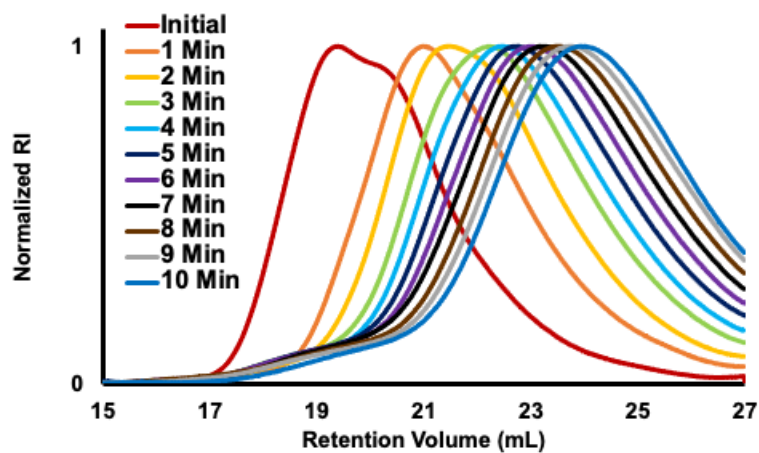


Figure 2.21. SEC data from triple detection for the degradation kinetics of 2.1 under ambient atmosphere.

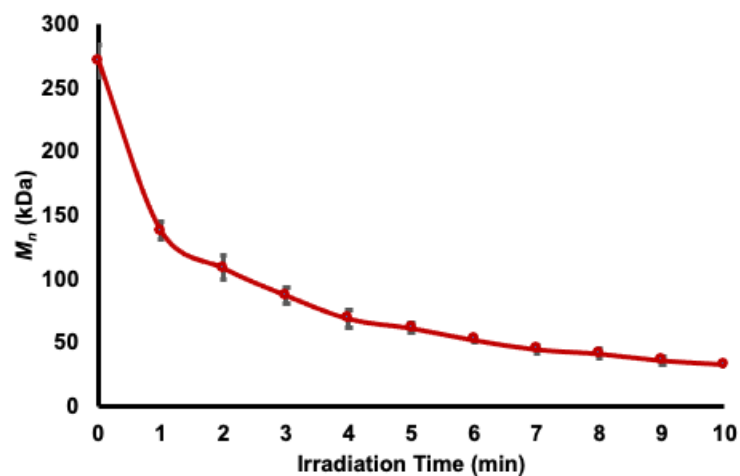


Figure 2.22. M_n (determined by triple detection SEC) as a function of irradiation time during photomodification of 2.1 under ambient atmosphere.

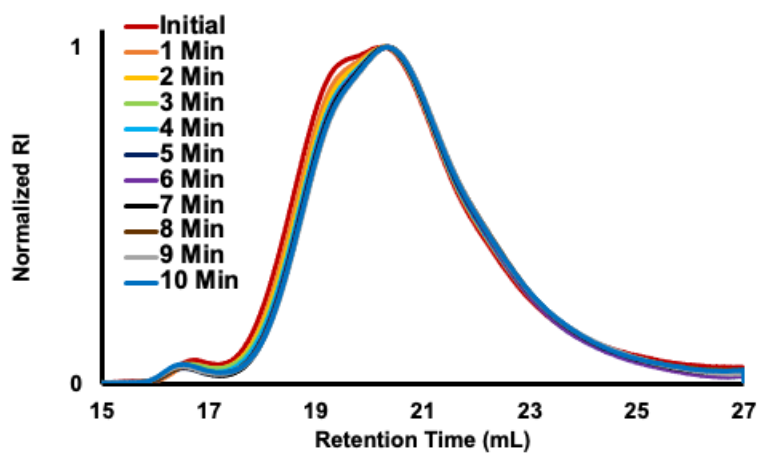


Figure 2.23. SEC data from triple detection for the degradation kinetics of 2.1 under ambient atmosphere with TEMPO additive.

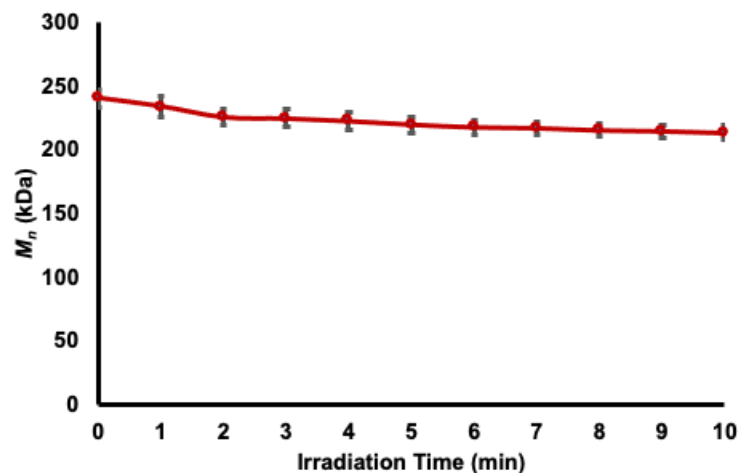


Figure 2.24. M_n (determined by triple detection SEC) as a function of irradiation time during photomodification of 2.1 under ambient atmosphere with TEMPO additive.

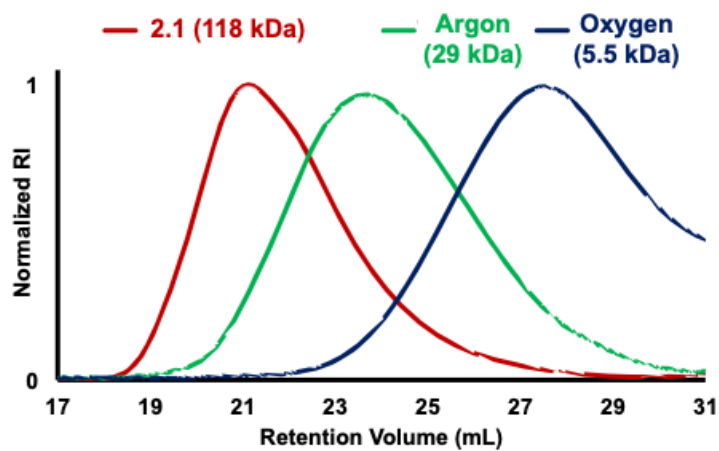


Figure 2.25. Overlaid SEC data from triple detection for the impact of H_2O and oxygen on the degradation of 2.1.

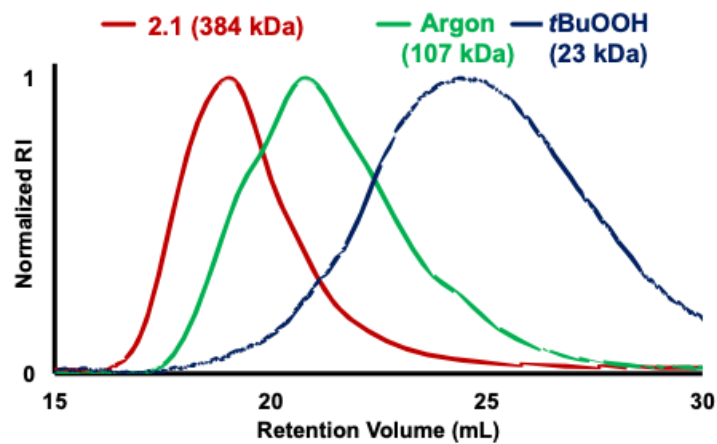


Figure 2.26. Overlaid SEC data from triple detection for the impact of exogenous *t*BuOOH on the degradation of 2.1.

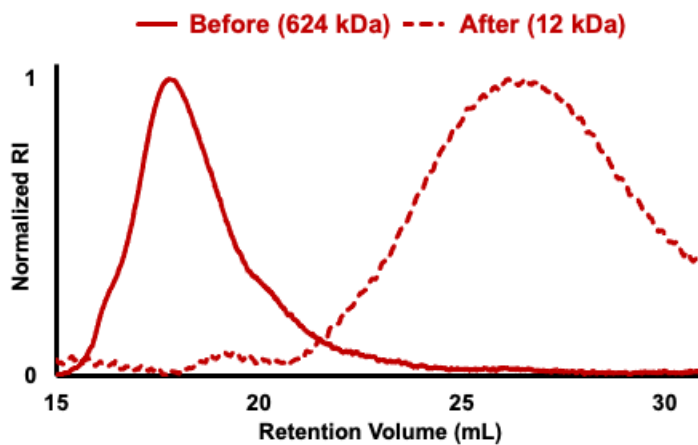


Figure 2.27. SEC data from conventional calibration for the photomodification of 2.4.

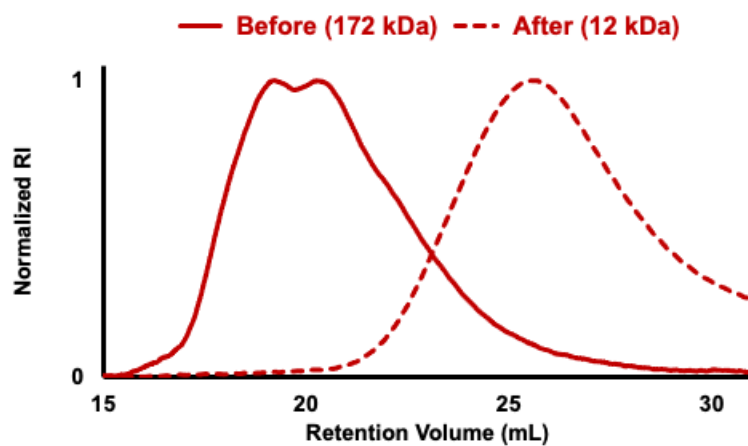


Figure 2.28. SEC data from conventional calibration for the photomodification of 2.5.

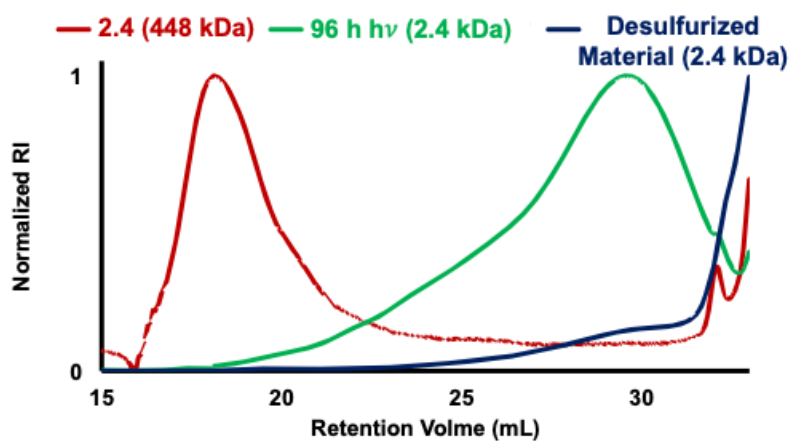


Figure 2.29. SEC data from triple detection for the prolonged (96 h) photomodification of 2.4 and the products after desulfurization.

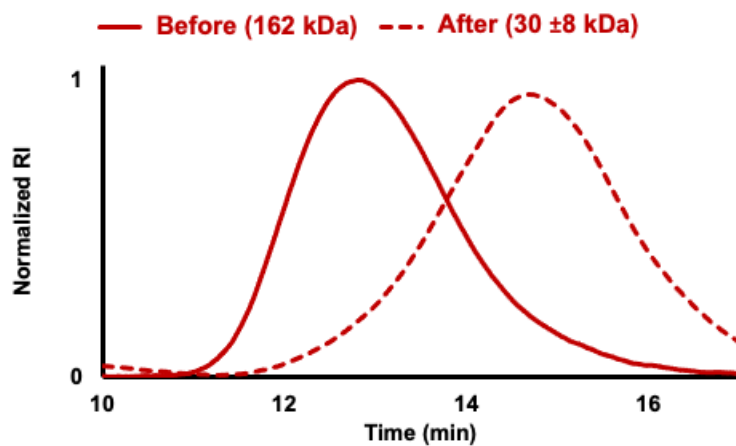


Figure 2.30. SEC data from conventional calibration (SEC 2) for the sunlight mediated photomodification of 2.1.

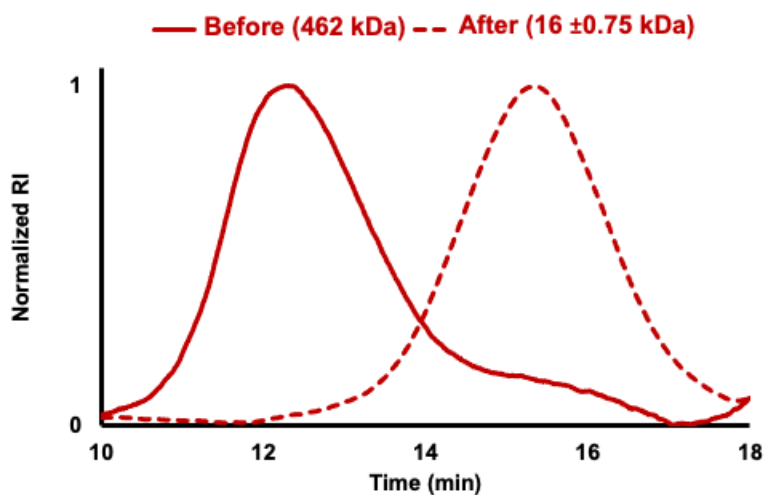


Figure 2.31. SEC data from conventional calibration (SEC 2) for the sunlight mediated photomodification of 2.4.

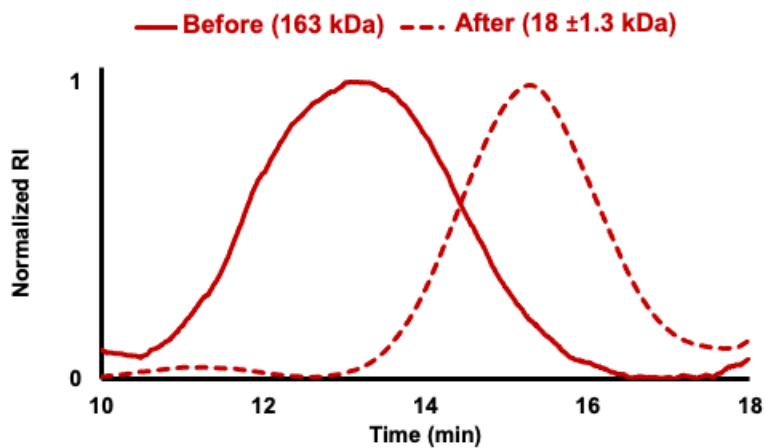


Figure 2.32. SEC data from conventional calibration (SEC 2) for the sunlight mediated photomodification of 2.5.

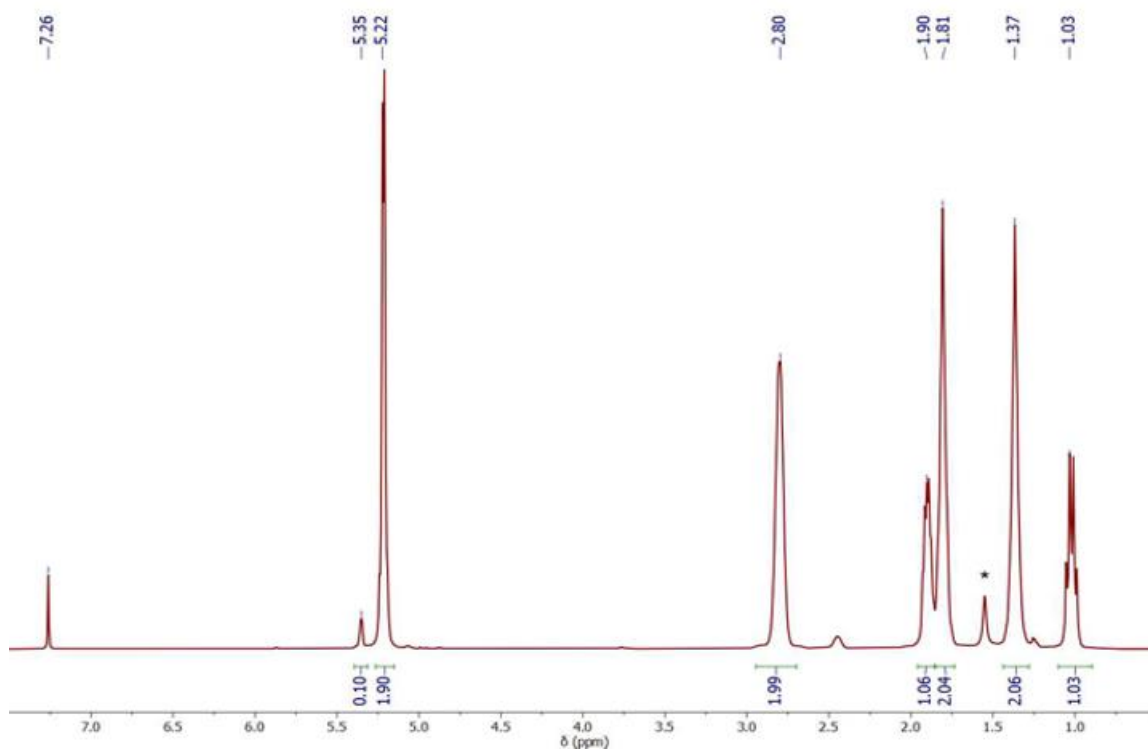


Figure 2.33. Representative ¹H NMR spectrum of 2.1 in CDCl₃. (* denotes water).

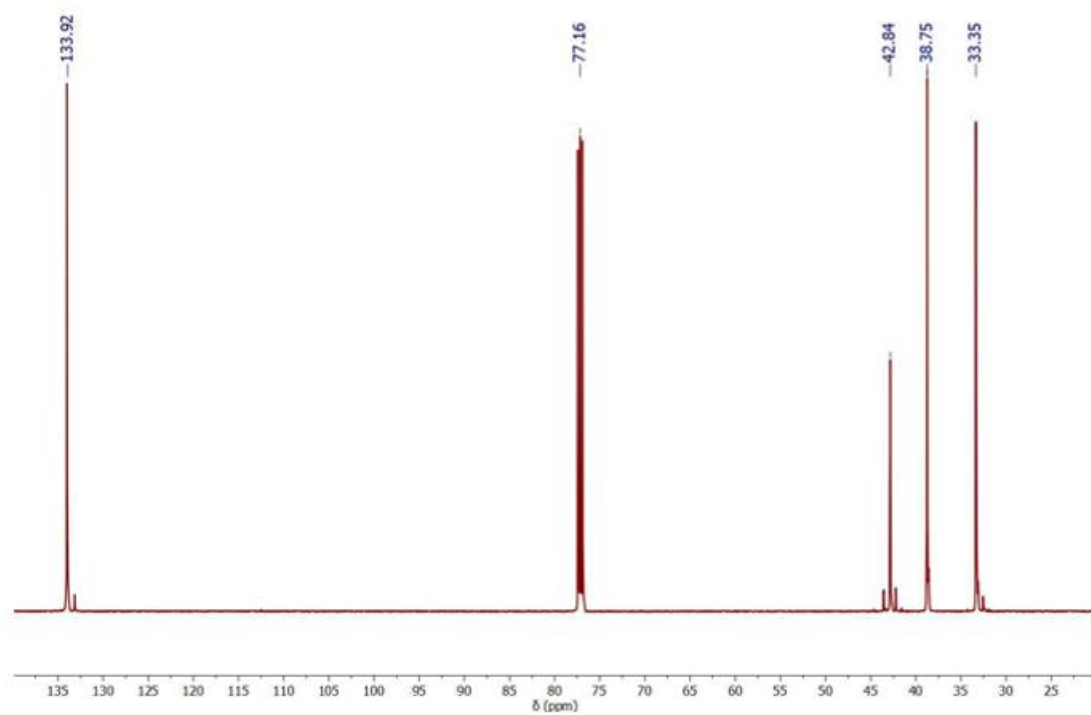


Figure 2.34. Representative ^{13}C NMR spectrum of 2.1 in CDCl_3 .

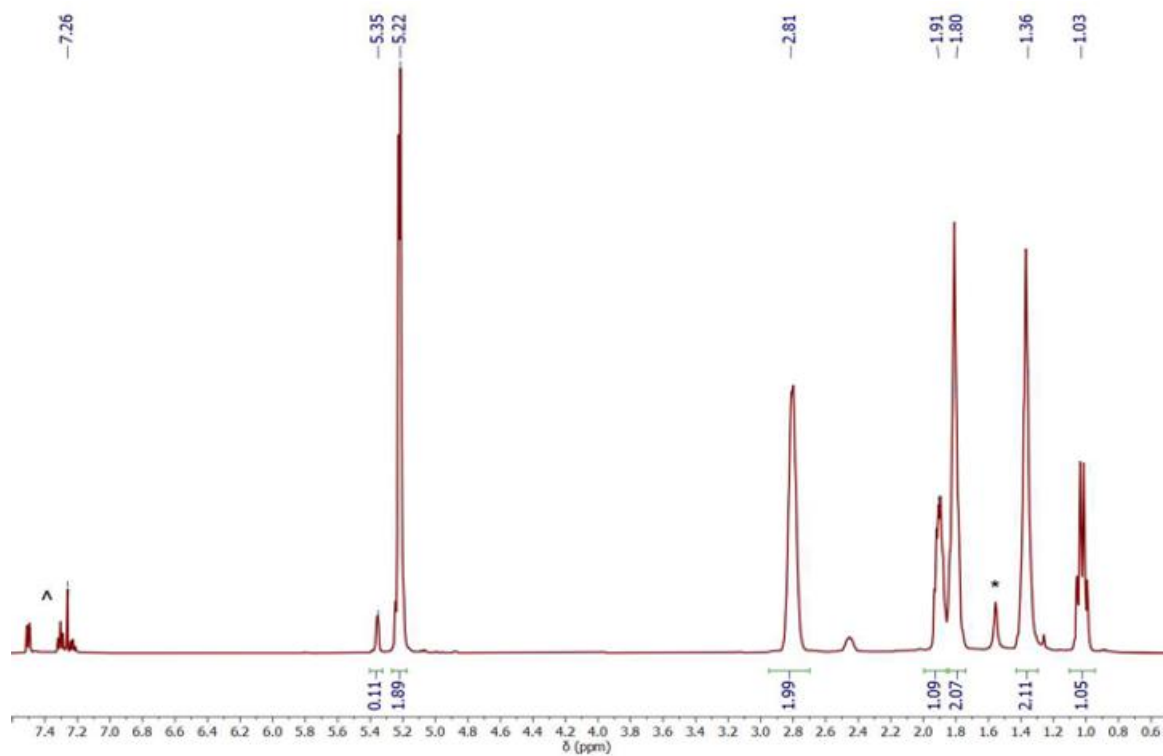


Figure 2.35. Representative ^1H NMR of the reduced molar mass product from the photoediting of 2.1 under N_2 (* denotes water $\delta=1.56$ ppm; $\wedge$ denotes diphenyl disulfide $\delta=7.3, 7.5$ ppm).

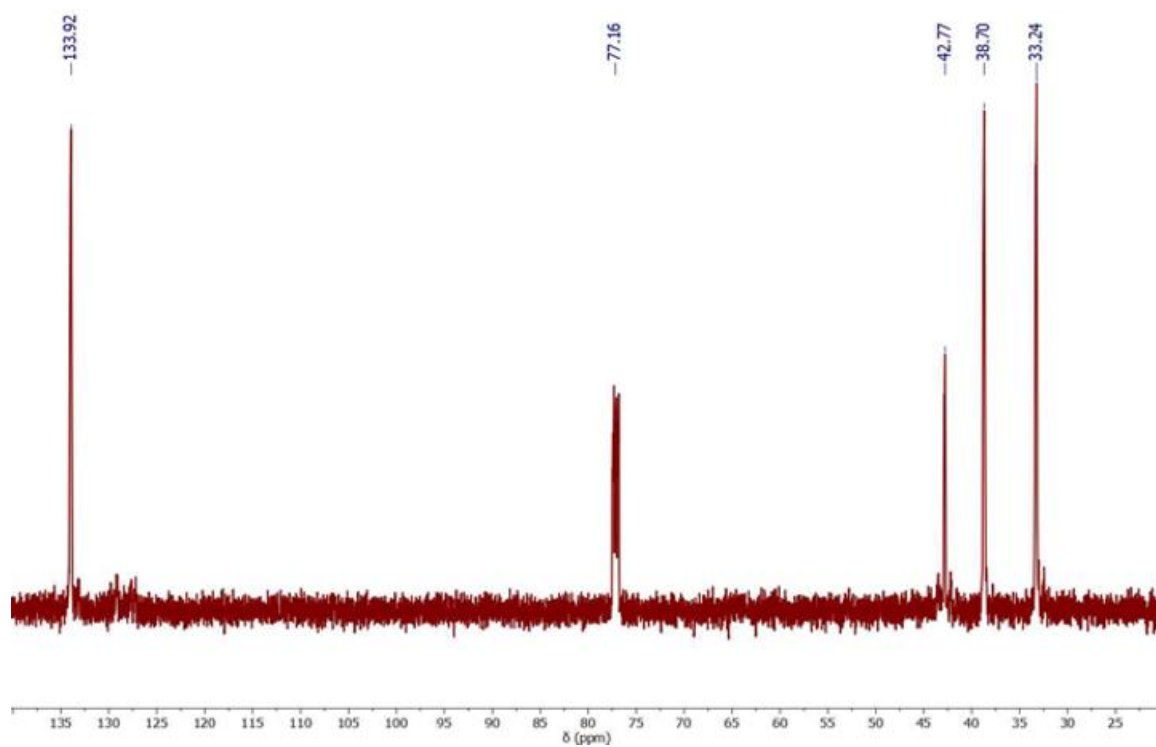


Figure 2.36. Representative ^{13}C NMR of the reduced molar mass product from the photoediting of 2.1 under N_2 .

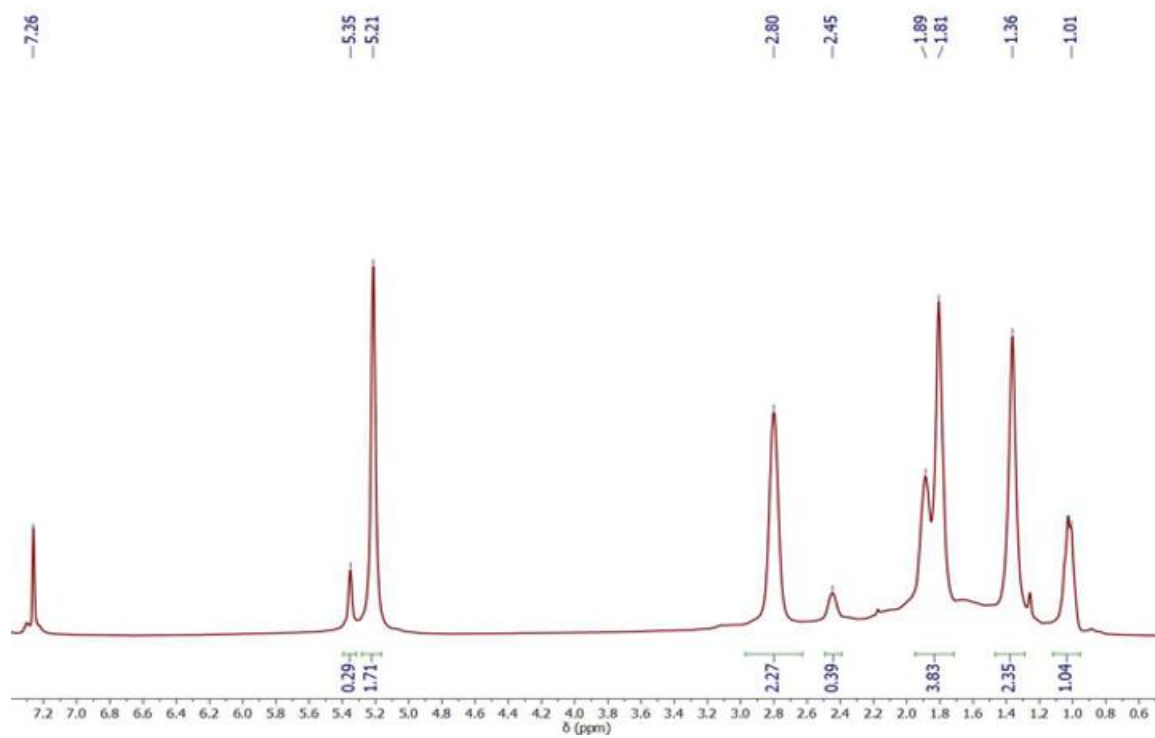


Figure 2.37. Representative ^1H NMR of the reduced molar mass product from the photoediting of 2.1 under ambient atmosphere.

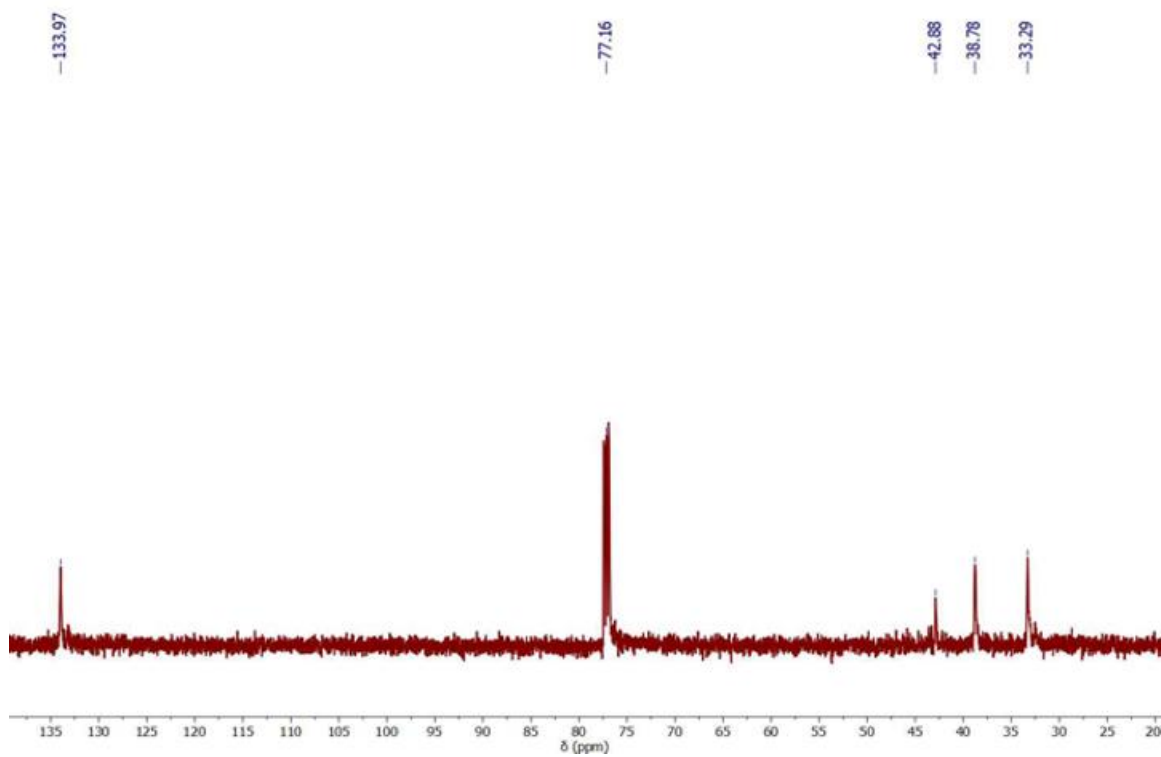


Figure 2.38. Representative ^{13}C NMR of the reduced molar mass product from the photoediting of 2.1 under ambient atmosphere.

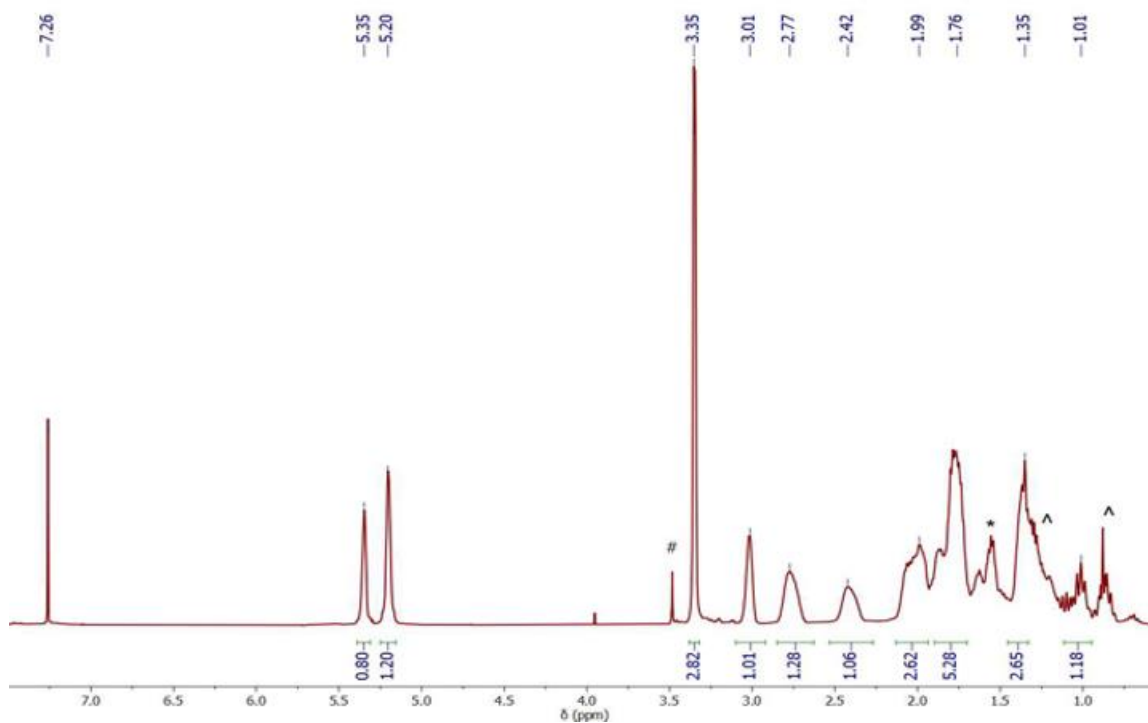


Figure 2.39. Representative ^1H NMR of methoxy product in CDCl_3 (* denotes water $\delta=1.56$; ^ denotes pentane $\delta=0.88$, and 1.29 ppm; # denotes methanol $\delta=3.49$ ppm).

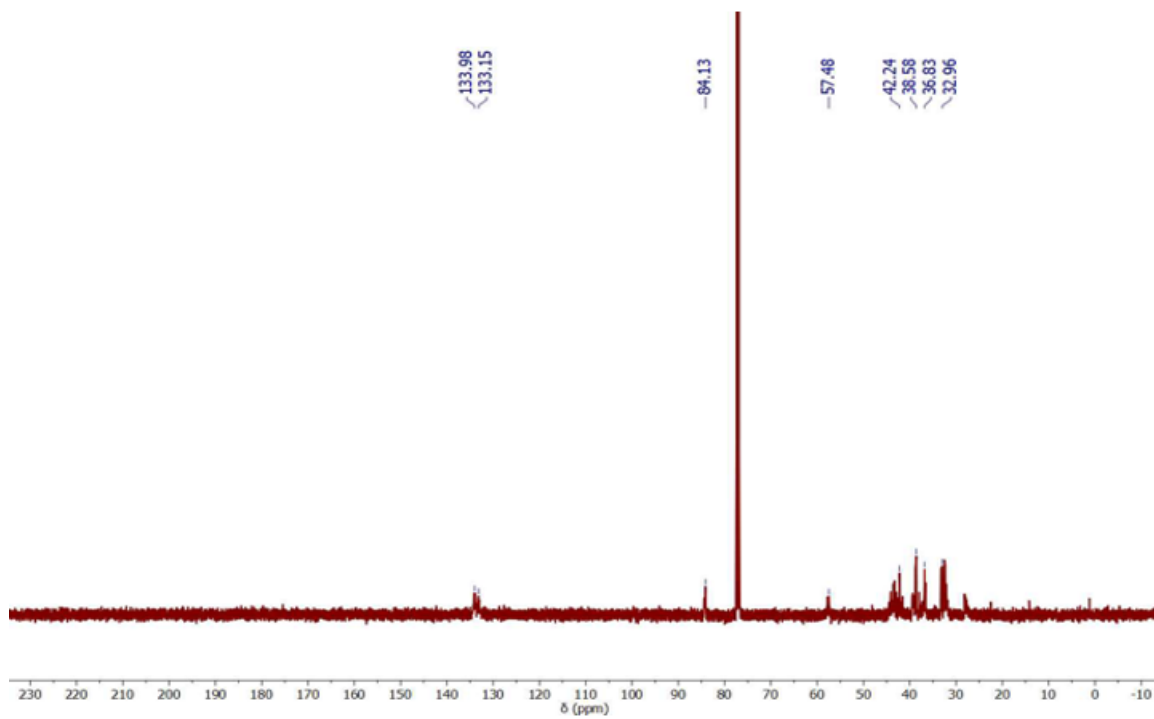


Figure 2.40. Representative ^{13}C NMR of methoxy product in CDCl_3 .

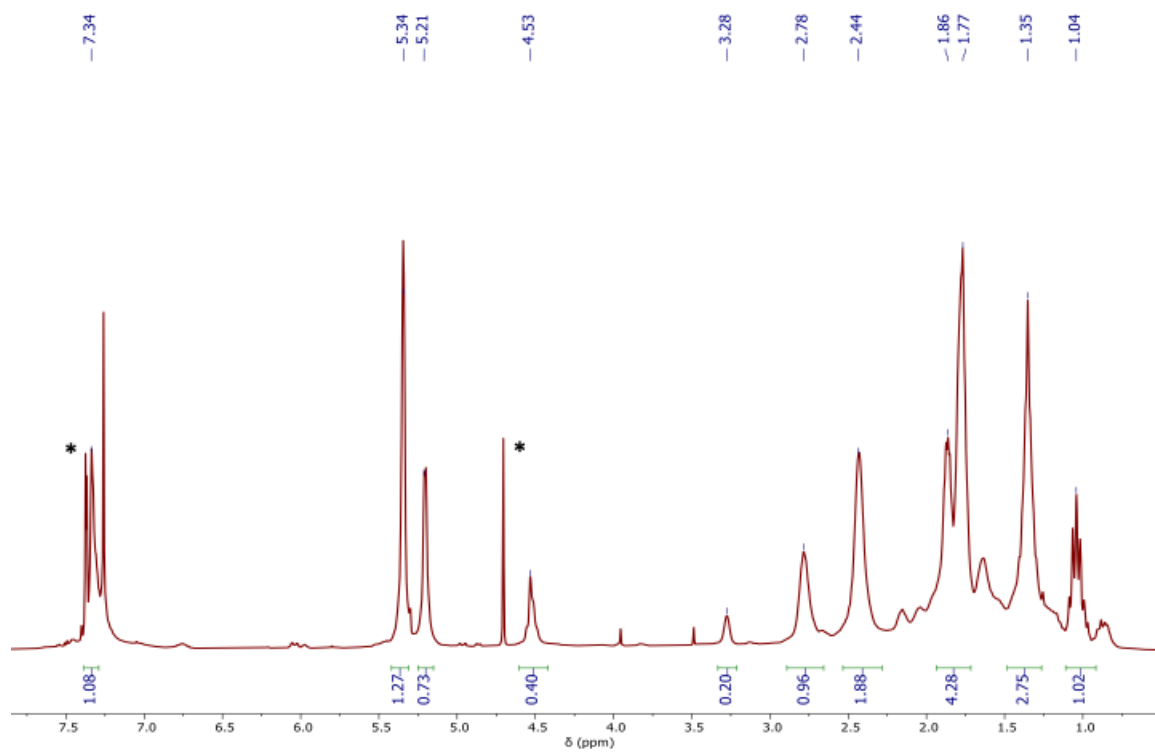


Figure 2.41. Representative ^1H NMR of hydroetherification (BnOH) of 2.1 in CDCl_3 (* denotes residual BnOH $\delta=4.6$ and 7.2-7.4 ppm).

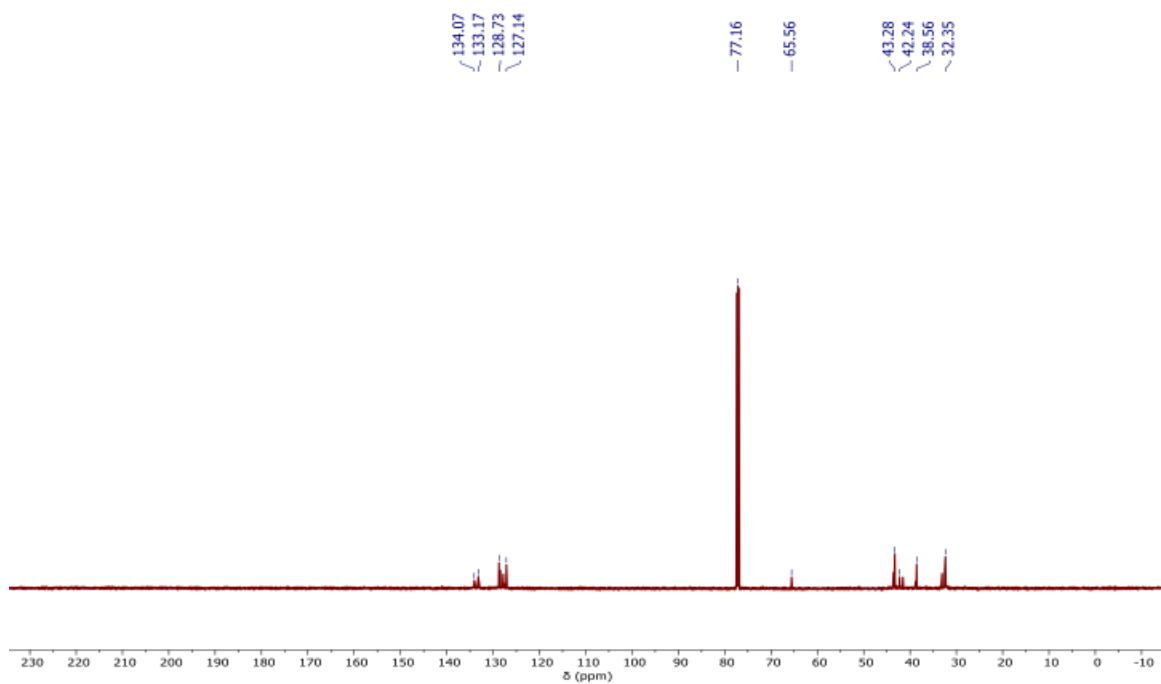


Figure 2.42. Representative ¹³C NMR of hydroetherification (BnOH) of 2.1 in CDCl₃.

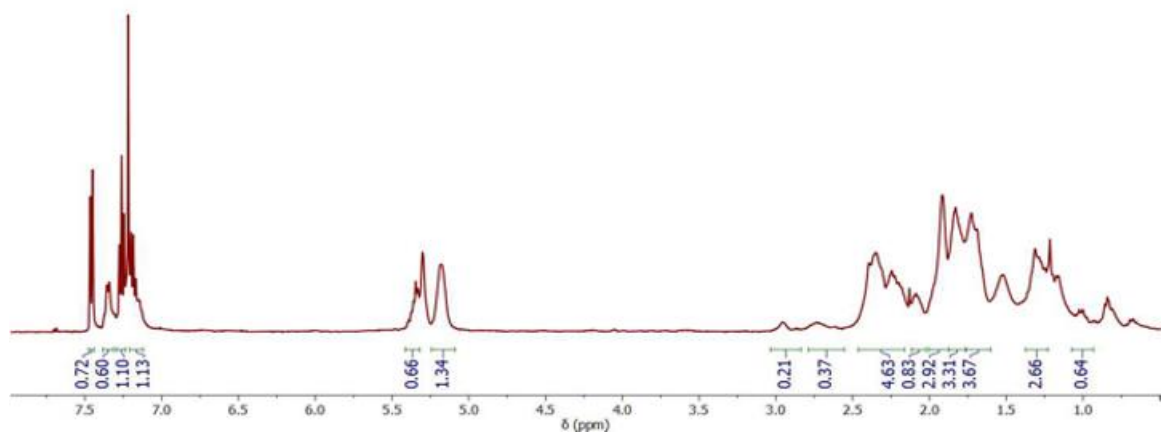


Figure 2.43. Representative ¹H NMR of hydrothioetherification (PhSH) of 2.1 in CDCl₃.

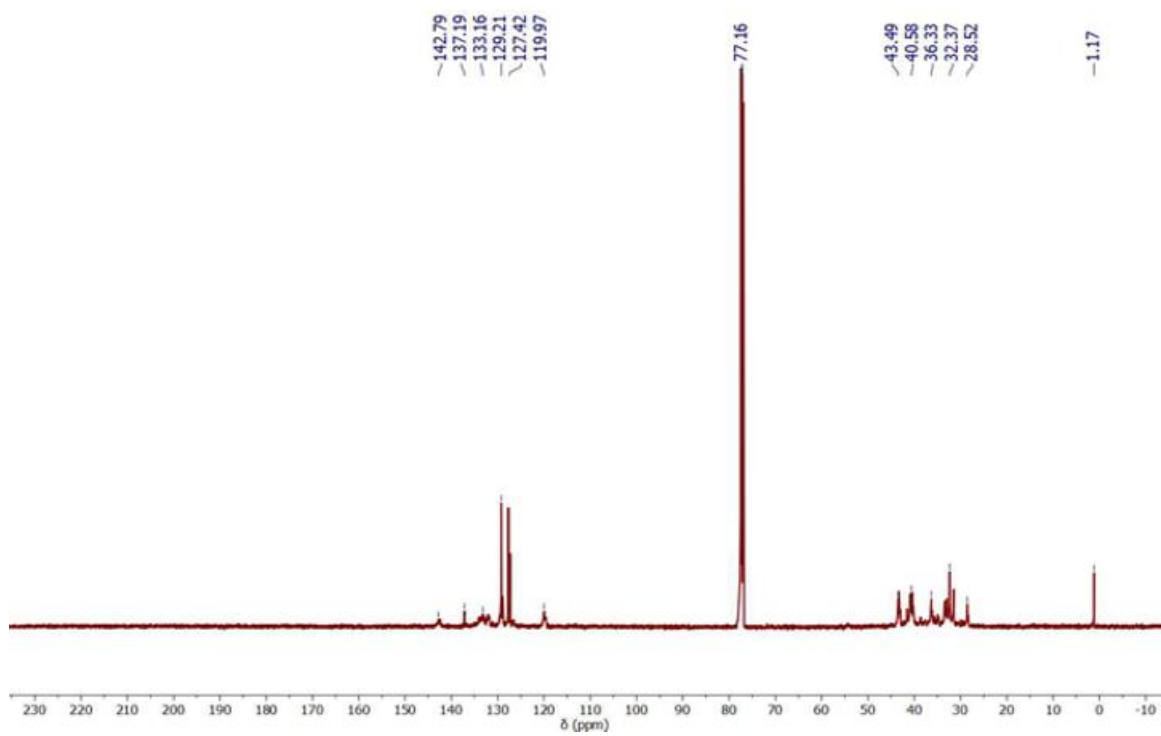


Figure 2.44. Representative ^{13}C NMR of hydrothioetherification (PhSH) of 2.1 in CDCl_3 .

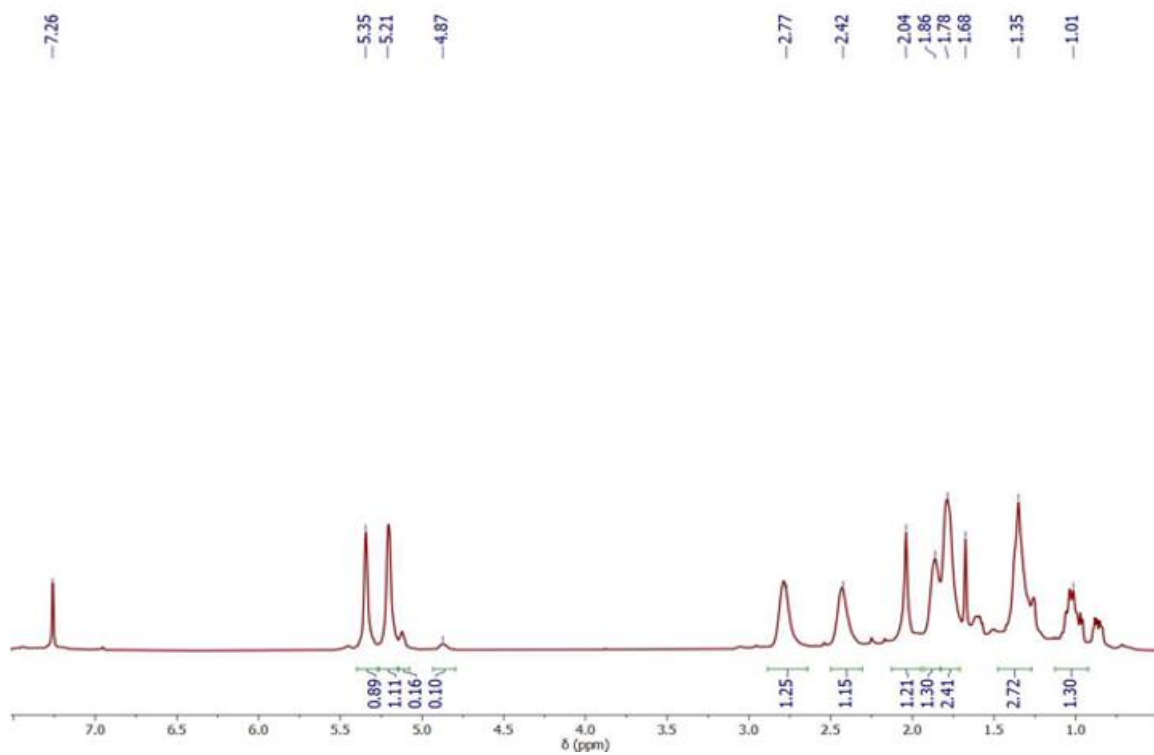


Figure 2.45. Representative ^1H NMR of hydrocarboxylation (AcOH) of 2.1 in CDCl_3 .

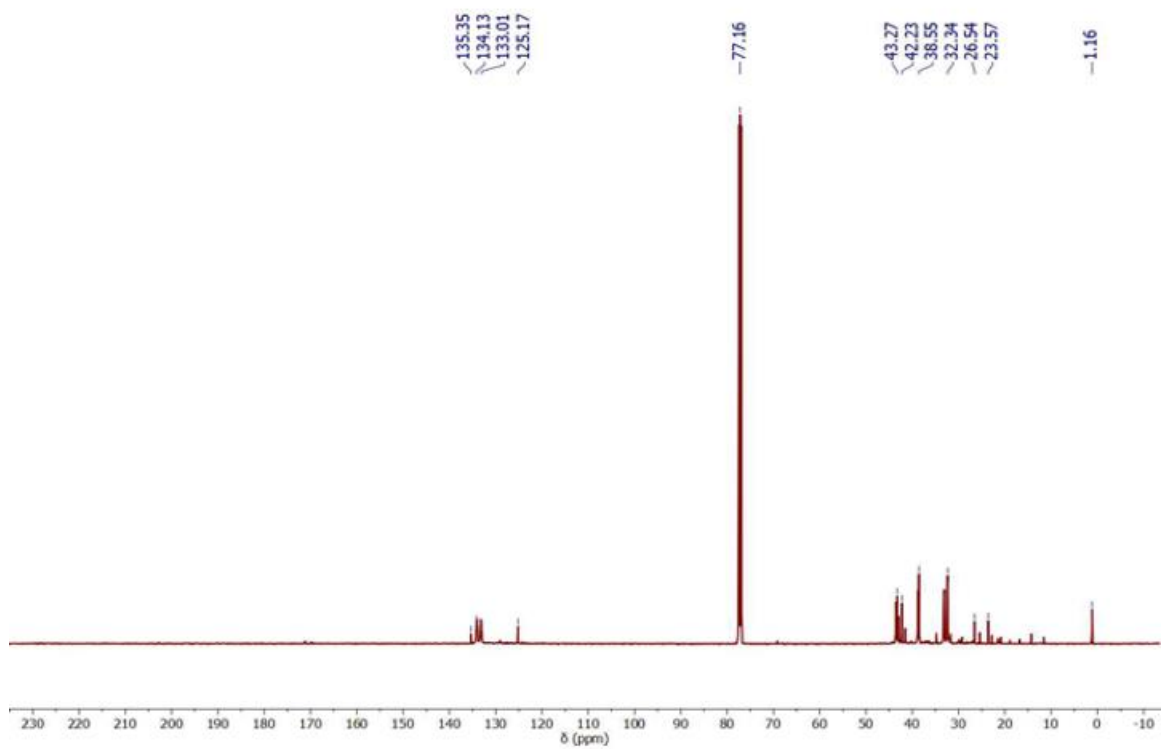


Figure 2.46. Representative ^{13}C NMR of hydrocarboxylation (AcOH) of 2.1 in CDCl_3 .

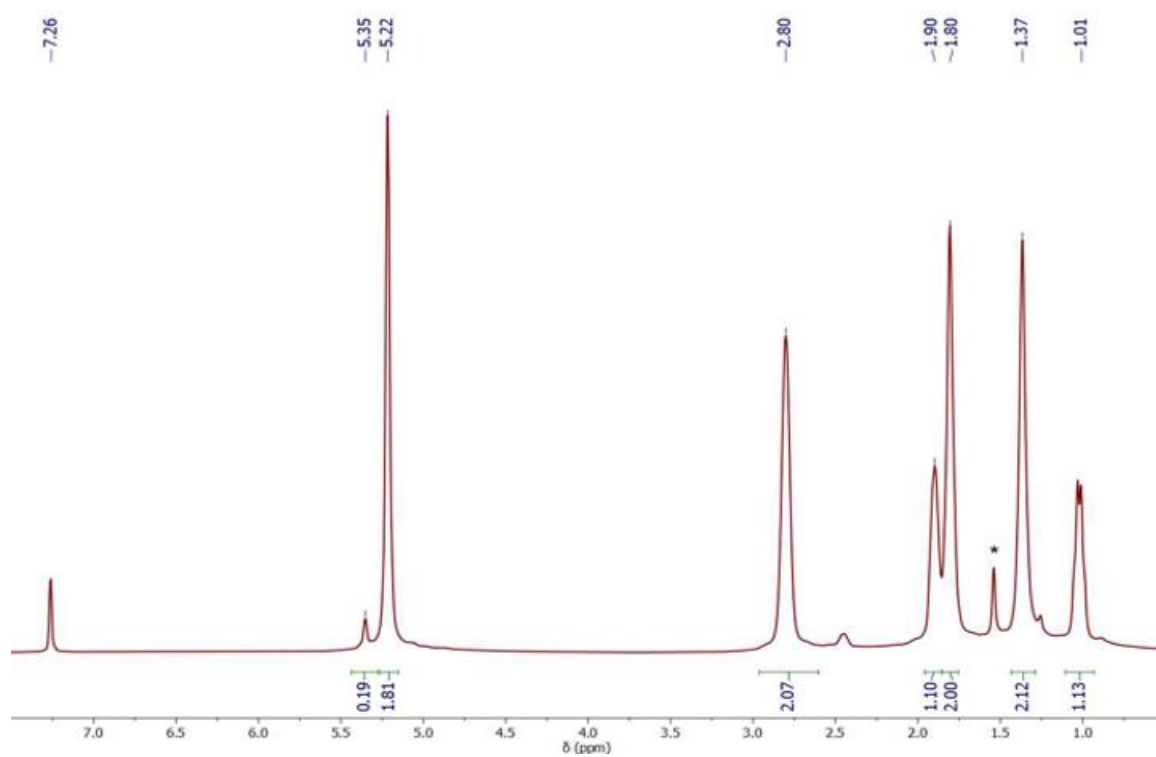


Figure 2.47. ^1H NMR of product from the control experiment - 2.2, - $(\text{PhS})_2$ (Table 2.1)

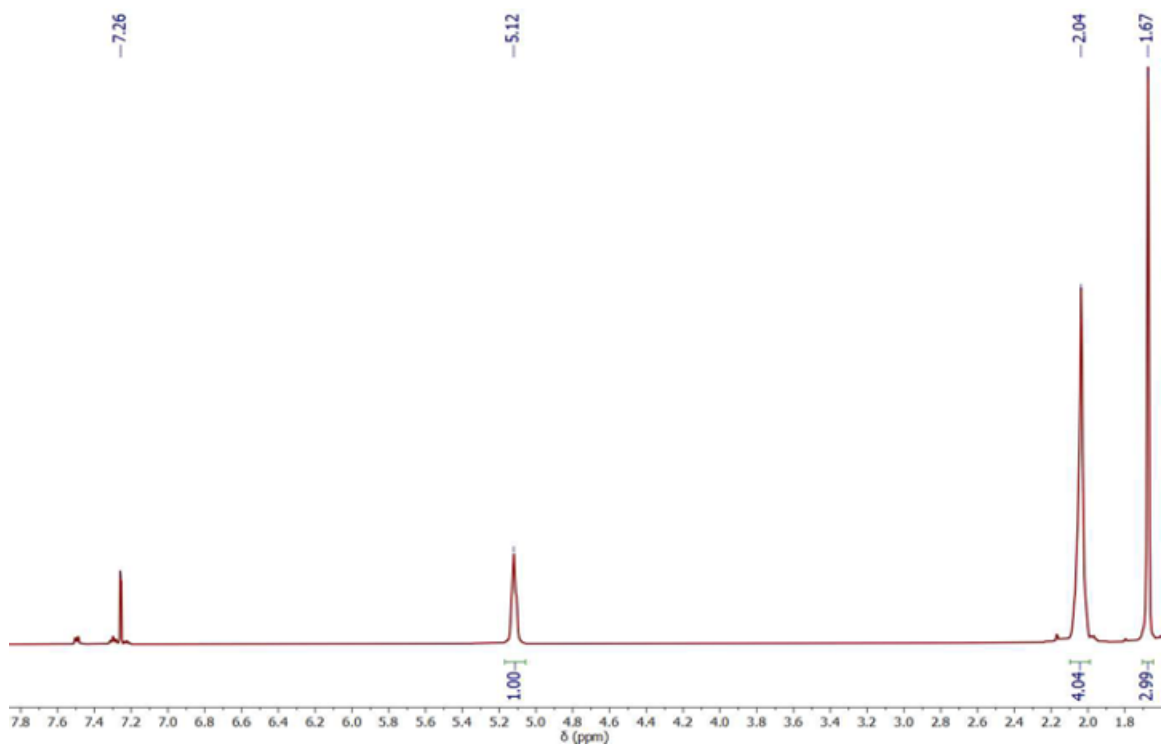


Figure 2.48. Representative ^1H NMR of the product from photoediting (1 h) of 2.4 in CDCl_3 .

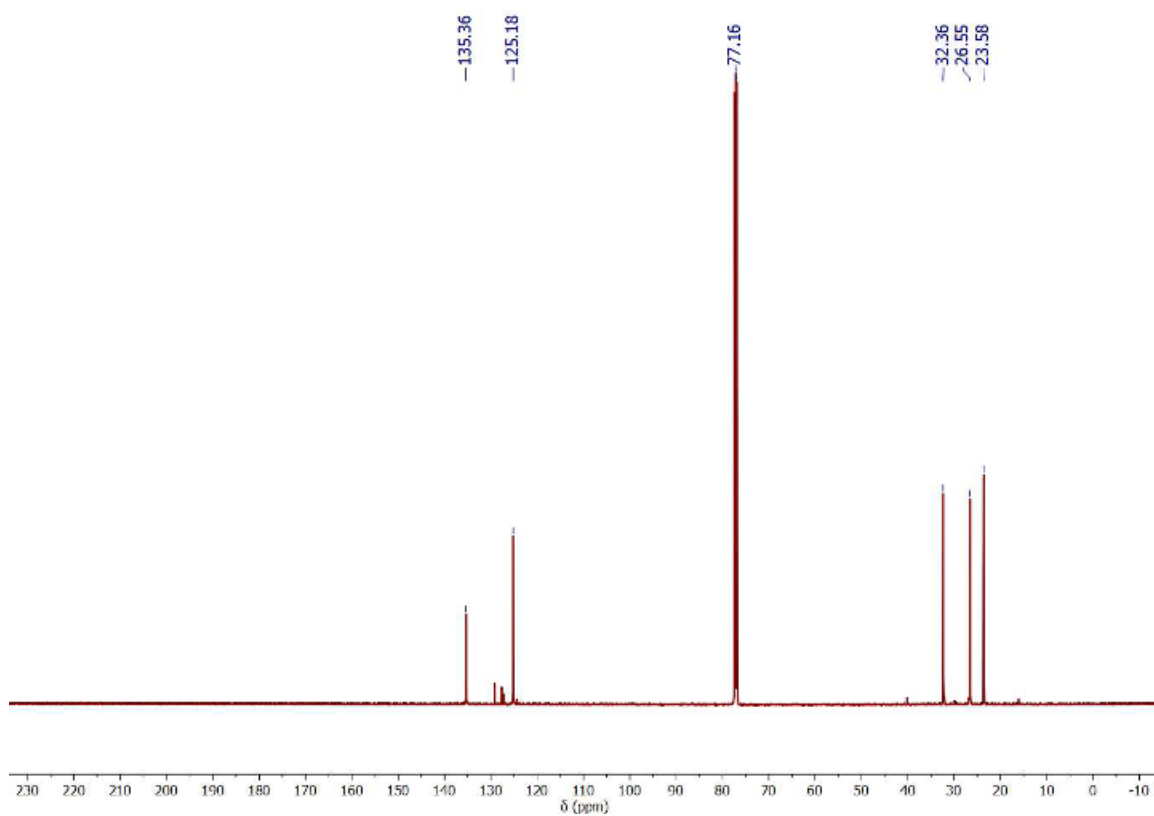


Figure 2.49. Representative ^{13}C NMR of the product from photomodification (1 h) of 2.4 in CDCl_3 .

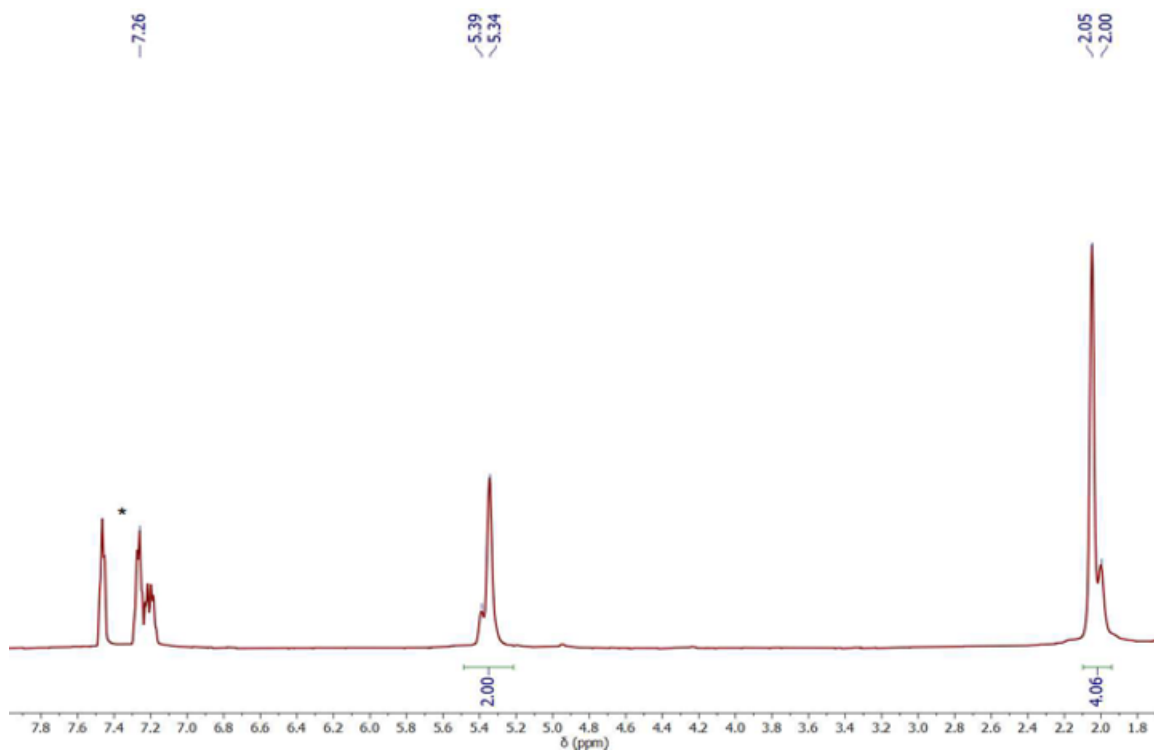


Figure 2.50. Representative ^1H NMR of the product from photomodification (1 h) of 2.5 in CDCl_3 (*denotes diphenyl disulfide $\delta = 7.3, 7.5$ ppm).

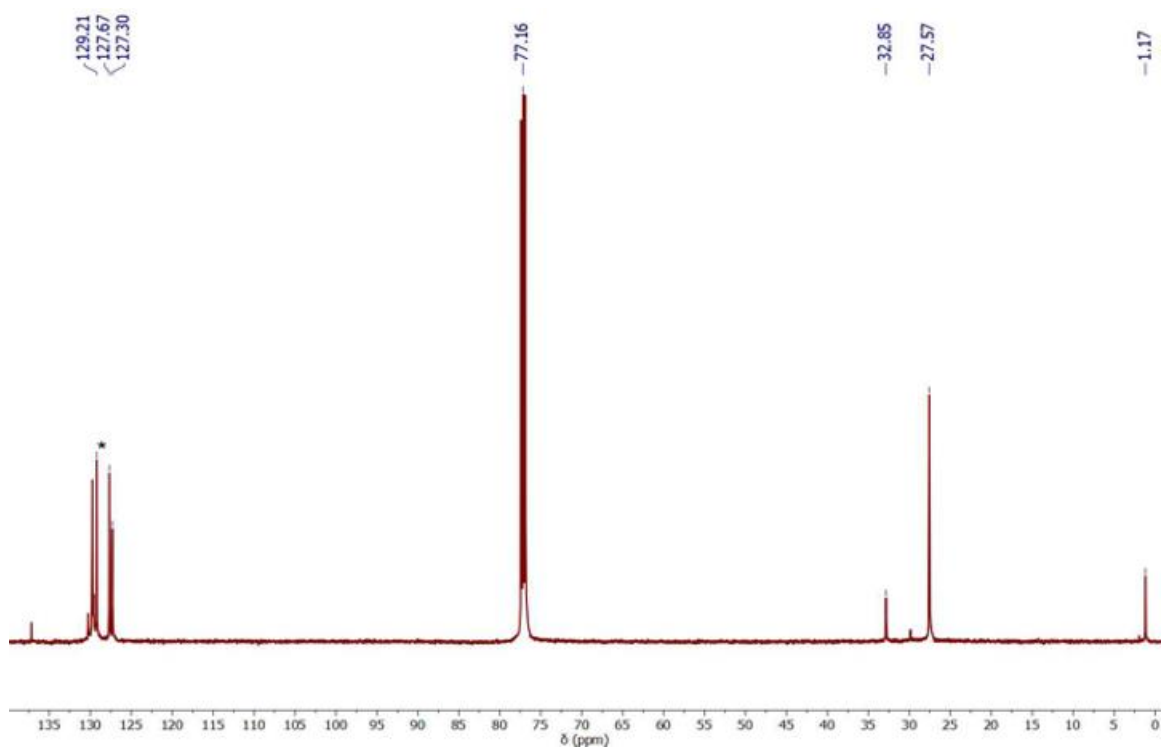


Figure 2.51. Representative ^{13}C NMR of the product from photomodification (1 h) of 2.5 in CDCl_3 .

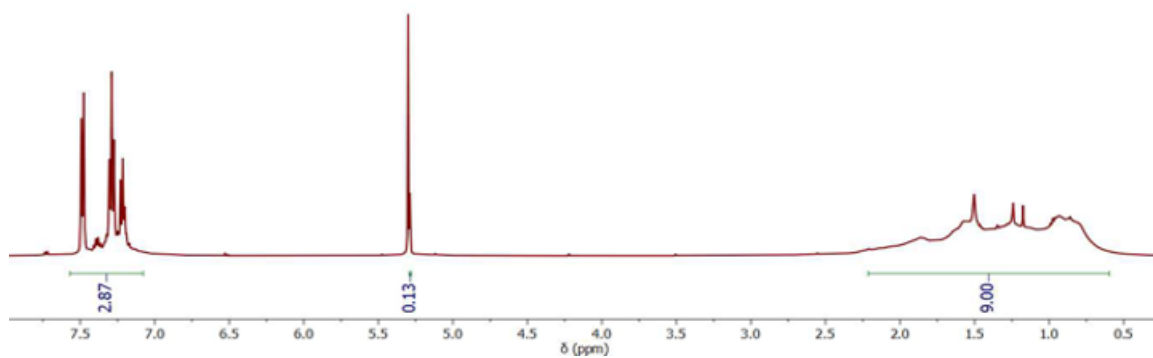


Figure 2.52. Representative ^1H NMR of the product from prolonged photomodification (96h) of 2.4 in CD_2Cl_2 .

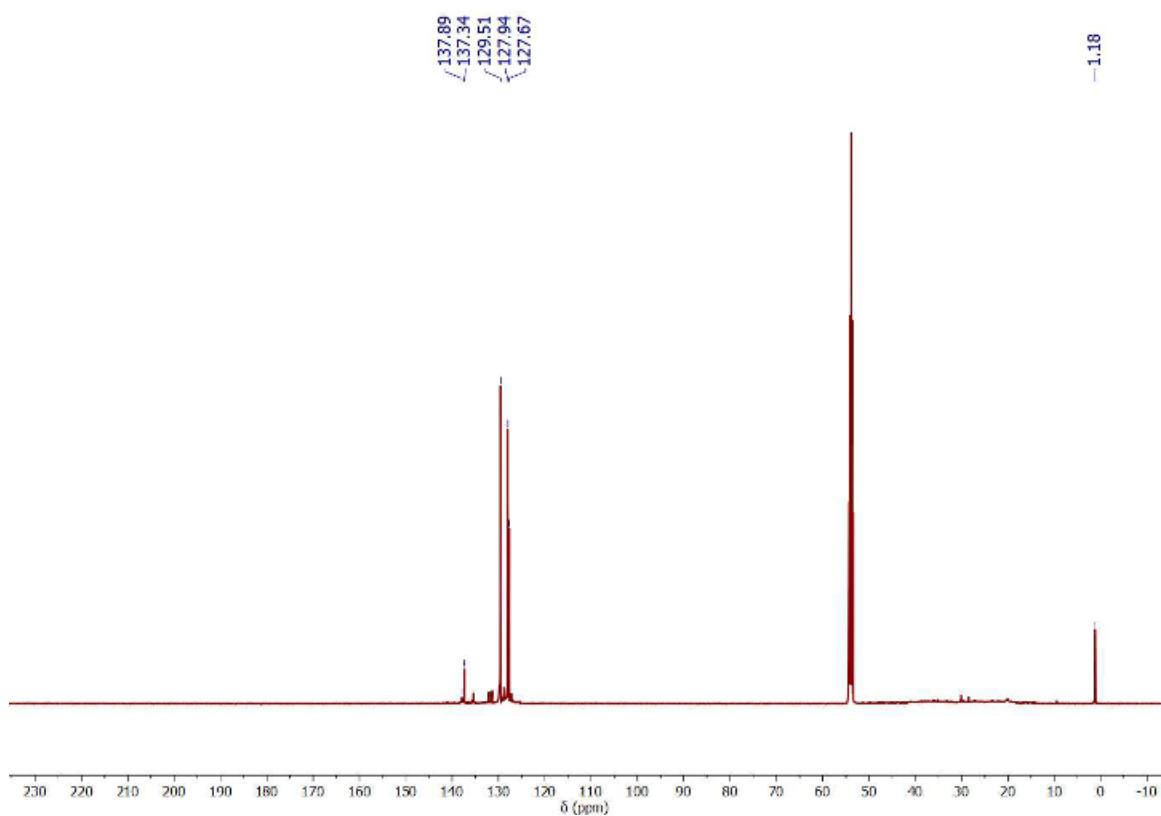


Figure 2.53. Representative ^{13}C NMR of the product from prolonged photomodification (96 h) of 2.4 in CD_2Cl_2 .

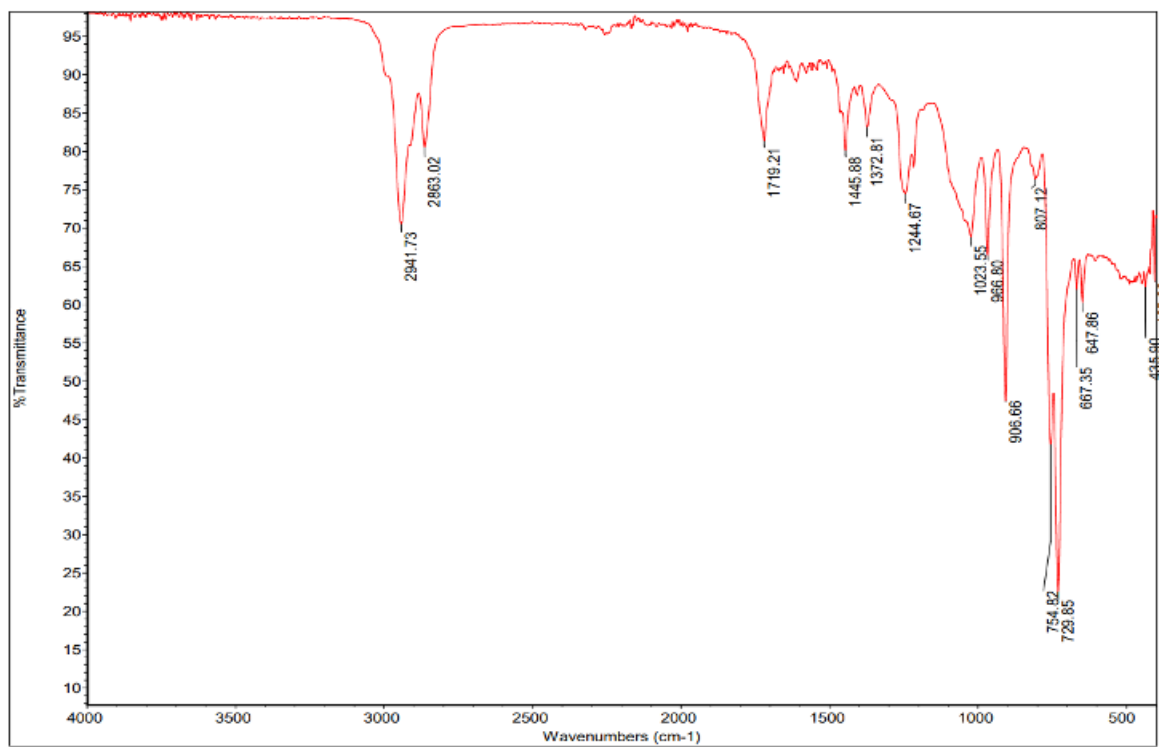


Figure 2.54. IR Spectra of the product of hydrocarboxylation of 2.1. Ester stretch at 1791 cm^{-1} .

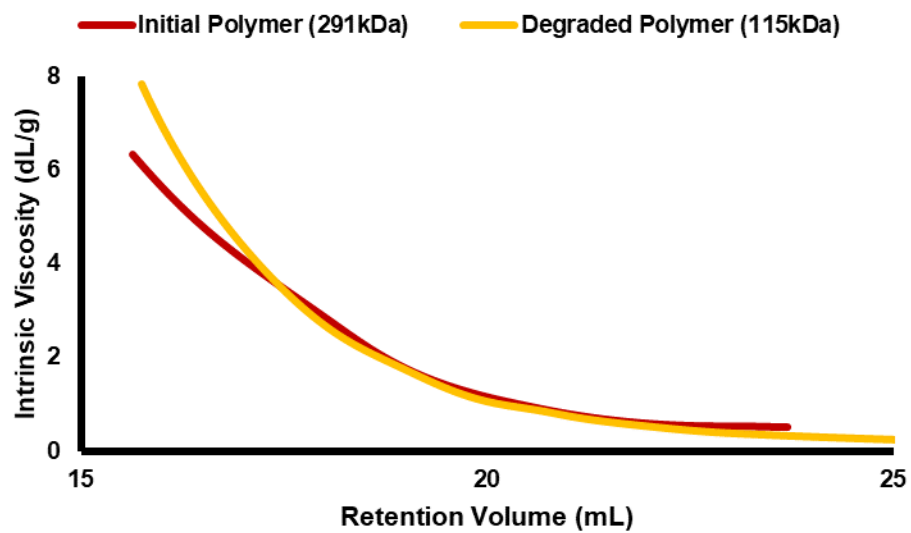


Figure 2.55. Mark-Houwink Plot of polymer before and after degradation.

**CHAPTER THREE : HYDRDROGEN BONDING INFLUENCED
MODIFICATION OF POLYVINYL CHLORIDE**

3.1 Abstract

The chlorinated backbone of the commonly used commodity polymer PVC provides a potentially reactive site for substitution chemistry. We investigated the use of urea,³¹ thiourea,³⁵ and squaramide⁶² derivatives in hydrogen bond donor (HBD) catalysis to encourage nucleophilic substitution on PVC in mild, metal-free environments.

Successful small-molecule transformations in which HBDs activate electrophiles through directed, noncovalent contacts served as the model for this strategy.³² There was little discernible substitution or chain functionalization despite a thorough screening of HBD catalysts, solvents, temperatures, and nucleophiles (such as amines, thiols, and carboxylates). Strongly basic or hot circumstances caused PVC to degrade or discolor, and most of the time, polymer recovery revealed little structural or spectral change (as verified by NMR). The unsatisfactory result was probably caused by the C–Cl bond's limited accessibility, relatively low reactivity in neutral circumstances, and potential interference by plasticizers or additives.

3.2 Introduction

PVC products are increasingly used in construction, particularly for exterior applications including window profiles, cladding structures, and siding, thanks to their low cost and high performance.^{63,64} However, the capacity of PVC products to resist photodegradation over extended periods of sunshine exposure will determine whether they are ultimately accepted by users for use in outdoor building applications.⁶⁴ There has been introduction of a generalized method for photoredox-mediated dehalogenation processes by Stephenson and colleagues with N,N-diisopropylethylamine serving as a sacrificed

electron donor for the reductive quenching of the excited state $^*Ru(bpy)_3^{2+}$ (Photocatalyst) species.⁶⁵ Anne J. McNeil group reported waste generated from PVC used as the source of chlorine in the electrolysis reaction to degrade PVC.⁷ MacMillan and coworkers have shown that despite difficulty in activating alkyl chlorides (Csp^3-Cl), cross coupling of an aryl chloride and an alkyl chloride is made possible using an iridium photocatalyst ($Ir(ppy)_2(dtbbpy)(PF_6)$), a silane reagent, nickel catalyst, *t*-amyl alcohol.⁶⁶ So their scheme will be employed with the possible chemical upcycling of PVC. It was hypothesized that the addition of a heteroatom to the silane reagent could significantly enhance the polarity of the C-Cl bonds and thereby significantly reduce the energy barrier for the abstraction of chlorine atom⁶⁶ by MacMillan and coworkers. This was the main drive for the successful cross-coupling. **Figure 3.1** demonstrates the use of thioureas in the world of macromolecules.

But there have been significant benefits that make hydrogen bonding-induced polymer functionalization a desirable approach for the creation and alteration of cutting-edge materials.^{31,32,35,62} Its capacity to operate in mild, metal-free environments (aligning well with green chemistry principles), frequently at room temperature, and without the requirement for outside energy inputs like light or power is one of its main advantages. This lowers the possibility of chain scission or polymer degradation and makes it extremely compatible with sensitive functional groups. Hydrogen bonding, as opposed to radical-based techniques, permits extremely directed and selective interactions, enabling accurate functionalization at certain locations along the side chains or polymer backbone.³² Additionally, hydrogen bonds are reversible and dynamic, which opens the

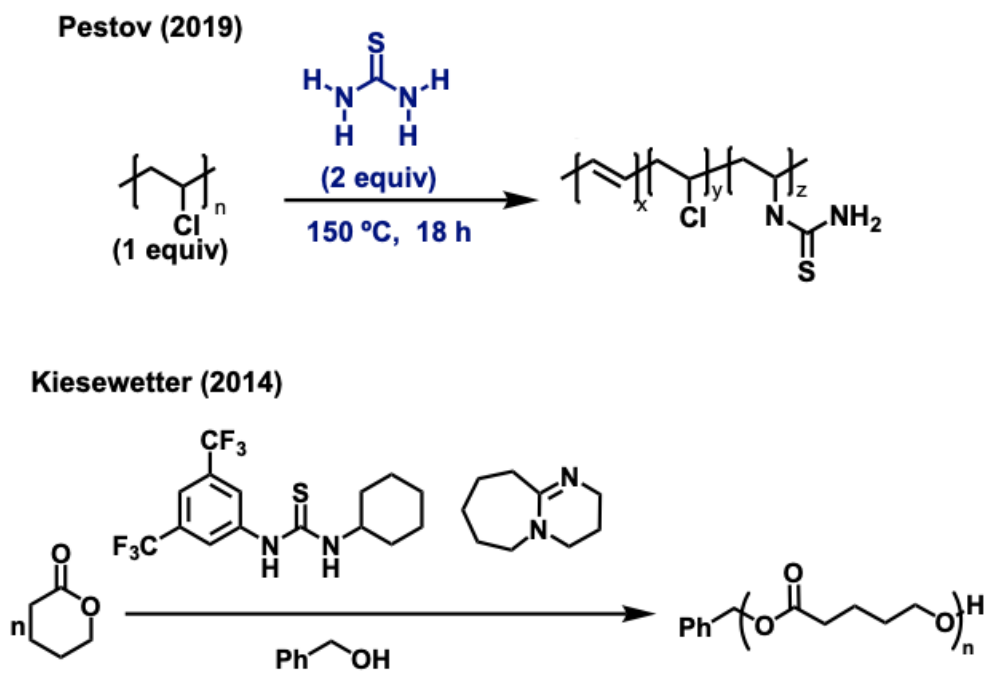


Figure 3.1. Hydrogen Bonding Catalysis Chemistries on Macromolecules.

door to self-healing materials, stimuli-responsive systems, and recyclable networks.⁶⁷ Because it typically involves small organic molecules (e.g., urea, thiourea, squaramides) as catalysts or templates. These features collectively make hydrogen bonding an ideal tool for sustainable polymer chemistry, particularly in the fields of supramolecular materials, bio-compatible systems, and precision post-polymerization modification. We posited that the interaction of PVC with hydrogen bonding donors will make the chlorine motifs in PVC good leaving group to make drive towards the SN1 mechanism. Other than successful substitution (polymer functionalization) we wanted to further investigate enantioselectivity by employing chiral catalysts.

3.3 Conclusions

We could not demonstrate significant hydrogen bonded assisted substitution conditions (especially since eliminations could have occurred) suited to alter different PVC substrates. This polymer modification however still shows promise for the functionalization of PVC.

3.4 Acknowledgements

For assistance with substitution experiments, I thank Seth Taylor.

3.5 Results and Discussion

3.5.1 General Materials and Methods

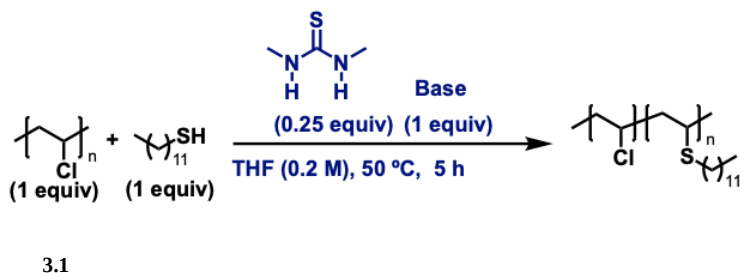
Unless otherwise noted, solvents were dried on an MBraun solvent purification system with 3Å molecular sieves and degassed via three freeze-pump-thaw cycles. PVC (purified by precipitation from methanol) were purchased from Sigma. All other reagents and materials were obtained from commercial sources and used without further purification

except the hydrogen bonding catalysts. Oxygen and water sensitive manipulations were performed in a N₂ filled MBraun glovebox. ¹H spectral data were collected on a Bruker 500 MHz NMR.

3.5.2 Initial Reaction Condition Optimizations

3.5.2.1 Thioetherification of 3.1 with dimethylthiourea and dodecanethiol

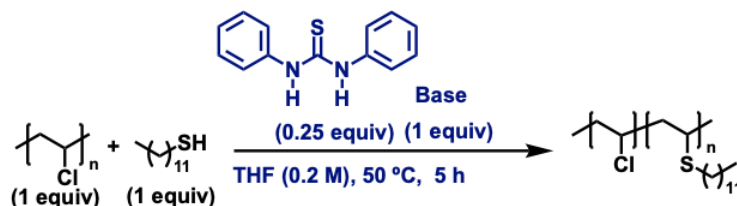
In a N₂ filled glovebox, a 2-dram vial was charged with THF (5.0 mL) solution of **3.1** (70mg, 1.0mmol), Mesitylene (140 μ L, 1.0mmol), K₂CO₃ (139mg, 1.0mmol), dimethylthiourea (26mg, 0.25mmol) and a Teflon stir bar. The vial was tightly sealed with a septum, removed from the glovebox. The thiol (250 μ L, 0.067 mmol) was added under a positive flow of N₂ by being taken up in a gas-tight syringe and the needle inserted into septa-capped 2-dram vial to protect from air exposure. 0.5mL aliquot was taken for NMR analysis was taken up in the same manner. The pierced septum was sealed with grease immediately. The reaction mixture was warmed to 50 °C and heated in a sand bath for 5 hours under static N₂ with stirring according to **Scheme 3.1**. Afterwards another 0.5mL aliquot was taken for NMR analysis. Representative spectral data collection showed a methine signal (δ = 3.5-4.3 ppm) suggesting ~5% conversion to the product as shown in (**Table 3.1**).



Scheme 3.1. Thioetherification of 3.1.

3.5.2.2 Thioetherification of 3.1 with diphenylthiourea and dodecanethiol

In a N₂ filled glovebox, a 2-dram vial was charged with THF (5.0 mL) solution of **3.1** (61 mg, 1.0 mmol), Mesitylene (140 μ L, 1.0 mmol), K₂CO₃ (138 mg, 1.0 mmol), diphenylthiourea (57 mg, 0.25 mmol) and a Teflon stir bar. The vial was tightly sealed with a septum, removed from the glovebox. The dodecanethiol (250 μ L, 0.067 mmol) was added under a positive flow of N₂ by being taken up in a gas-tight syringe and the needle inserted into septa-capped 2-dram vial to protect from air exposure. 0.5 mL aliquot was taken for NMR analysis was taken up in the same manner. The pierced septum was sealed with grease immediately. The reaction mixture was warmed to 50 °C and heated in a sand bath for 5 hours under static N₂ with stirring according to **Scheme 3.2**. Afterwards another 0.5 mL aliquot was taken for NMR analysis. Representative spectral data collection showed a methine signal (δ = 3.5-4.3 ppm) suggesting ~5% conversion to the product as shown in (**Table 3.1**).

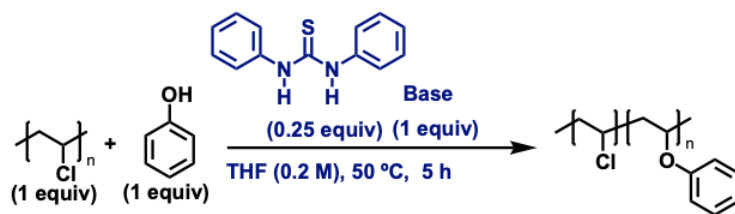


Scheme 3.2. Thioetherification of 3.1.

3.5.2.3 Etherification of 3.1 with diphenylthiourea and phenol

In a N₂ filled glovebox, a 2-dram vial was charged with THF (5.0 mL) solution of **3.1** (62.5 mg, 1.0 mmol), Mesitylene (140 μ L, 1.0 mmol), K₂CO₃ (138 mg, 1.0 mmol), diphenylthiourea (57 mg, 0.25 mmol), phenol (95 mg, 1.0 mmol) and a Teflon stir bar. The vial was tightly sealed with a septum, removed from the glovebox. Under a positive flow

of N₂ by a gas-tight syringe, the needle was inserted into the septa-capped 2-dram vial to take 0.5mL aliquot for NMR analysis. The pierced septum was sealed with grease immediately. The reaction mixture was warmed to 50 °C and heated in a sand bath for 5 hours under static N₂ with stirring according to **Scheme 3.3**. Afterwards another 0.5mL aliquot was taken for NMR analysis. Representative spectral data collection showed a methine signal ($\delta = 3.5\text{--}4.3$ ppm) suggesting 0% conversion to the product as shown in (**Table 3.1**).

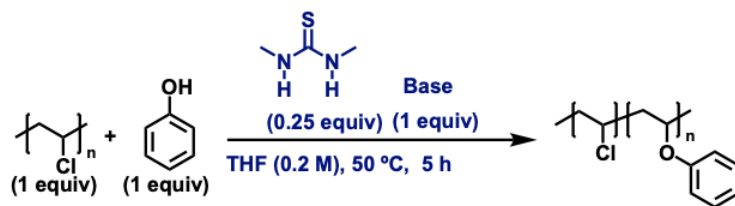


Scheme 3.3. Etherification of 3.1.

3.5.2.4 Etherification of 3.1 with dimethylthiourea and phenol

In a N₂ filled glovebox, a 2-dram vial was charged with THF (5.0 mL) solution of **3.1** (62.5mg, 1.0mmol), Mesitylene (140 μ L, 1.0mmol), K₂CO₃ (139mg, 1.0mmol), dimethylthiourea (26mg, 0.25mmol), phenol (94mg, 1.0mmol) and a Teflon stir bar. The vial was tightly sealed with a septum, removed from the glovebox. Under a positive flow of N₂ by a gas-tight syringe, the needle was inserted into the septa-capped 2-dram vial to take 0.5mL aliquot for NMR analysis protect from air exposure. The pierced septum was sealed with grease immediately. The reaction mixture was warmed to 50 °C and heated in a sand bath for 5 hours under static N₂ with stirring according to **Scheme 3.4**. Afterwards another 0.5mL aliquot was taken for NMR analysis. Representative spectral data

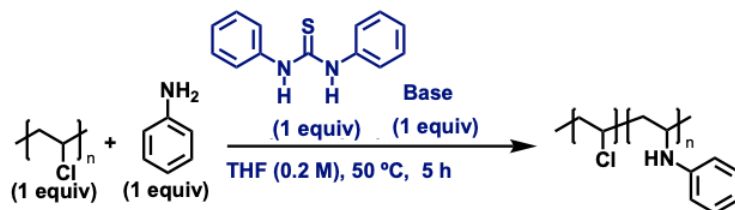
collection showed a methine signal ($\delta = 3.5\text{--}4.3$ ppm) suggesting 20% conversion to the product as shown in (**Table 3.1**).



Scheme 3.4. Etherification of 3.1.

3.5.2.5 Amination of 3.1 with diphenylthiourea and aniline

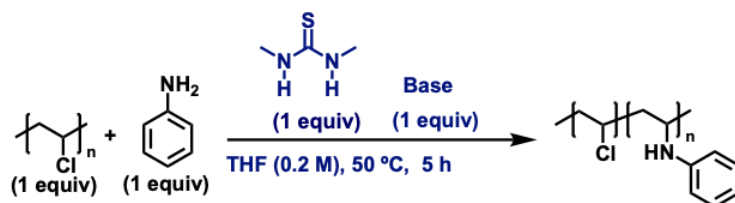
In a N₂ filled glovebox, a 2-dram vial was charged with THF (5.0 mL) solution of **3.1** (63mg, 1.0mmol), Mesitylene (140 μ L, 0.8 mmol), K₂CO₃ (138mg, 1.0mmol), diphenylthiourea (228mg, 1.0mmol) and a Teflon stir bar. The vial was tightly sealed with a septum, removed from the glovebox. The aniline (96 μ L, 1.0mmol) was added under a positive flow of N₂ by being taken up in a gas-tight syringe and the needle inserted into septa-capped 2-dram vial to protect from air exposure. 0.5mL aliquot was taken for NMR analysis was taken up in the same manner. The pierced septum was sealed with grease immediately. The reaction mixture was warmed to 50 °C and heated in a sand bath for 5 hours under static N₂ with stirring according to **Scheme 3.5**. Afterwards another 0.5mL aliquot was taken for NMR analysis. Representative spectral data collection showed a methine signal ($\delta = 3.5\text{--}4.3$ ppm) suggesting 0% conversion to the product as shown in (**Table 3.1**).



Scheme 3.5. Amination of 3.1.

3.5.2.6 Amination of 3.1 with dimethylthiourea and aniline

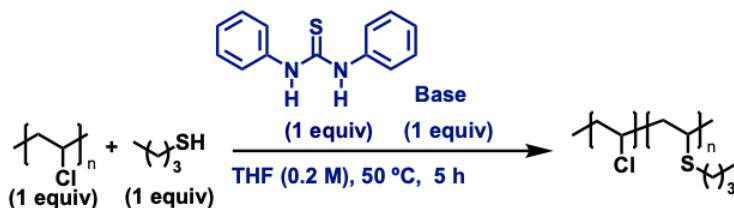
In a N₂ filled glovebox, a 2-dram vial was charged with THF (5.0 mL) solution of **3.1** (62mg, 1.0mmol), Mesitylene (140 μ L, 1.0 mmol), K₂CO₃ (145mg, 1.0mmol), dimethylthiourea (108mg, 1.0 mmol) and a Teflon stir bar. The vial was tightly sealed with a septum, removed from the glovebox. The aniline (96 μ L, 1.0mmol) was added under a positive flow of N₂ by being taken up in a gas-tight syringe and the needle inserted into septa-capped 2-dram vial to protect from air exposure. 0.5mL aliquot was taken for NMR analysis was taken up in the same manner. The pierced septum was sealed with grease immediately. The reaction mixture was warmed to 50 °C and heated in a sand bath for 5 hours under static N₂ with stirring according to **Scheme 3.6**. Afterwards another 0.5mL aliquot was taken for NMR analysis. Representative spectral data collection showed a methine signal (δ = 3.5-4.3 ppm) suggesting 0% conversion to the product as shown in (**Table 3.1**).



Scheme 3.6. Amination of 3.1.

3.5.2.7 Thioetherification of 3.1 with diphenylthiourea and butanethiol

In a N₂ filled glovebox, a 2-dram vial was charged with THF (5.0 mL) solution of **3.1** (63mg, 1.0mmol), Mesitylene (140 μL, 1.0mmol), K₂CO₃ (136mg, 1.0mmol), diphenylthiourea (211mg, 1.0mmol) and a Teflon stir bar. The vial was tightly sealed with a septum, removed from the glovebox. The butanethiol (100 μL, 1.0 mmol) was added under a positive flow of N₂ by being taken up in a gas-tight syringe and the needle inserted into septa-capped 2-dram vial to protect from air exposure. 0.5mL aliquot was taken for NMR analysis was taken up in the same manner. The pierced septum was sealed with grease immediately. The reaction mixture was warmed to 50 °C and heated in a sand bath for 5 hours under static N₂ with stirring according to **Scheme 3.7**. Afterwards another 0.5mL aliquot was taken for NMR analysis. Representative spectral data collection showed a methine signal (δ = 3.5-4.3 ppm) suggesting ~11% conversion to the product as shown in (**Table 3.1**).

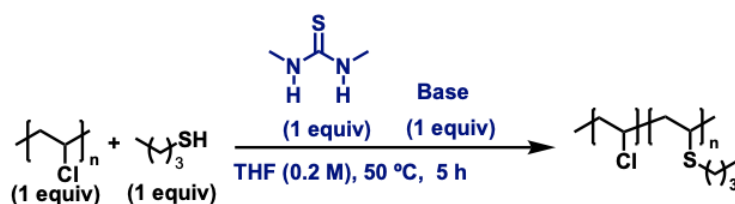


Scheme 3.7. Thioetherification of 3.1.

3.5.2.8 Thioetherification of 3.1 with dimethylthiourea and butanethiol

In a N₂ filled glovebox, a 2-dram vial was charged with THF (5.0 mL) solution of **3.1** (61mg, 1.0mmol), Mesitylene (140 μL, 1.0mmol), K₂CO₃ (139mg, 1.0mmol), dimethylthiourea (104mg, 1.0 mmol) and a Teflon stir bar. The vial was tightly sealed with a septum, removed from the glovebox. The butanethiol (100 μL, 1.0 mmol) was

added under a positive flow of N₂ by being taken up in a gas-tight syringe and the needle inserted into septa-capped 2-dram vial to protect from air exposure. 0.5mL aliquot was taken for NMR analysis was taken up in the same manner. The pierced septum was sealed with grease immediately. The reaction mixture was warmed to 50 °C and heated in a sand bath for 5 hours under static N₂ with stirring according to **Scheme 3.8**. Afterwards another 0.5mL aliquot was taken for NMR analysis. Representative spectral data collection showed a methine signal (δ = 3.5-4.3 ppm) suggesting ~5% conversion to the product as shown in (**Table 3.1**).

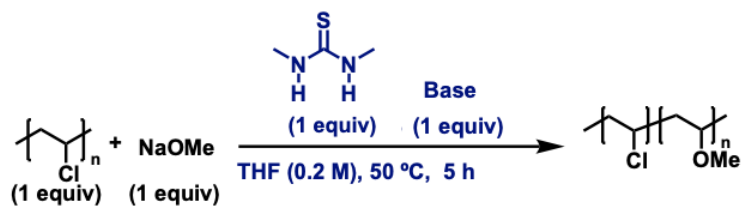


Scheme 3.8. Thioetherification of 3.1.

3.5.2.9 Etherification of 3.1 with dimethylthiourea and NaOMe

In a N₂ filled glovebox, a 2-dram vial was charged with THF (5.0 mL) solution of **3.1** (69 mg, 1.0mmol), Mesitylene (140 μ L, 1.0mmol), K₂CO₃ (138mg, mmol), NaOMe (56mg, 1.0mmol), dimethylthiourea (104 mg, 1.0mmol) and a Teflon stir bar. The vial was tightly sealed with a septum, removed from the glovebox. Under a positive flow of N₂ by a gas-tight syringe, the needle was inserted into the septa-capped 2-dram vial to take 0.5mL aliquot for NMR analysis protect from air exposure. The pierced septum was sealed with grease immediately. The reaction mixture was warmed to 50 °C and heated in a sand bath for 5 hours under static N₂ with stirring according to **Scheme 3.9**. Afterwards another 0.5mL aliquot was taken for NMR analysis. Representative spectral data

collection showed a methine signal ($\delta = 3.5\text{-}4.3$ ppm) suggesting ~12% conversion to the product as shown in (Table 3.1) .

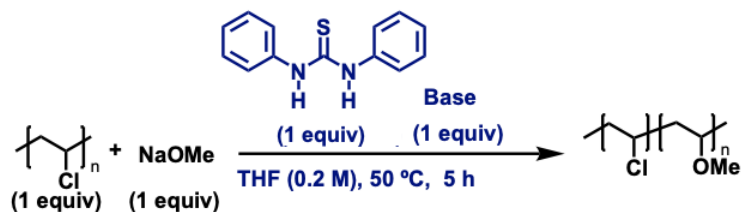


Scheme 3.9. Etherification of 3.1.

3.5.2.10 Etherification of 3.1 with diphenylthiourea and NaOMe

In a N₂ filled glovebox, a 2-dram vial was charged with THF (5.0 mL) solution of **3.1** (63mg, 1.0 mmol), Mesitylene (140 μ L, 0.8 mmol), K₂CO₃ (143mg, 1.0 mmol), NaOMe (62mg, 1.0 mmol), diphenylthiourea (230mg, 1.0 mmol) and a Teflon stir bar. The vial was tightly sealed with a septum, removed from the glovebox. Under a positive flow of N₂ by a gas-tight syringe, the needle was inserted into the septa-capped 2-dram vial to take 0.5mL aliquot for NMR analysis protect from air exposure. The pierced septum was sealed with grease immediately. The reaction mixture was warmed to 50 °C and heated in a sand bath for 5 hours under static N₂ with stirring according to **Scheme 3.10**.

Afterwards another 0.5mL aliquot was taken for NMR analysis. Representative spectral data collection showed a methine signal ($\delta = 3.5\text{-}4.3$ ppm) suggesting ~7% conversion to the product as shown in (Table 3.1)



Scheme 3.10. Etherification of 3.1.

APPENDIX

Table 3.1. Substitution experiments and conversions (results).

Entry	Oxygen and water free conversions (Averages of two runs)
3.5.2.1	5.4%
3.5.2.2	4.7%
3.5.2.3	0.0%
3.5.2.4	20.0%
3.5.2.5	0.0%
3.5.2.6	0.0%
3.5.2.7	10.9%
3.5.2.8	5.5%
3.5.2.9	12.6%
3.5.2.10	7.0%

CHAPTER FOUR : CONCLUSIONS AND OUTLOOK

With high rise in polymer production, there is the need and avenue to explore and develop strategies that can provide necessary modifications for various reasons most notably plastic waste treatment via chemical upcycling. Our work shows that, in mild, metal-free conditions, photoredox catalysis may efficiently break down polyalkenamers (such as polynorbornene, polyisoprene, and polybutadiene) into valuable hydrocarbon compounds. We used visible-light photocatalysis to create radical cations by single-electron oxidation of the olefinic backbone, building on earlier work that used electrochemical techniques. This led to nucleophile trapping for functionalization and β -scission for degradation. The approach demonstrated its usefulness for sustainable polymer modification by proving effective in ambient settings, including sunlight, and producing wax-like, upcycled materials after longer reaction periods. Degradation and functionalization of Polyalkenamer demonstrated by us shows unique architectures can be accessed via photoredox reactions. We believe this presents a new opportunity to investigate new strategies of modifying polyolefins since they make up a huge percentage of polymers produced and explore untapped chemical space in polymerization and polymer modifications.

Better hydrogen bonding conditions can be sought after or investigated for PVC modification or other halogen containing polymers by activating the C-X bond by combining Hydrogen bond donors and photoredox systems since there were minimal significant conversions.

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VITA

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