Rapid Water Tolerant Cationic RAFT Photopolymerization

by

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ABSTRACT

In the search for ever more sustainable manufacturing techniques, additive manufacturing through light driven 3D printing processes is growing rapidly as a field, specifically the production of "living" materials which can be repaired and or reprocessed through the reactivation of polymer chain ends. Currently research in the production of these living materials is largely focused on radical polymerization methods. Cationic polymerizations have been developed for this purpose, although there is still much work to be done. This work seeks to explore a transition-metal free system to produce living materials through cationic reversible addition fragmentation chain-transfer (C-RAFT).

Cationic polymerization is known for its rapid propagation. This is due to the highly reactive active center which also readily reacts with nucleophiles in unwanted chain transfer reactions. For this reason, reagents in living cationic polymerizations are subject to rigorous purification steps involving the distillation of monomer and solvent, freeze—pump—thaw cycles, and running the reaction under an inert environment[1]. These restrictions make living cationic polymerizations unattractive for 3D printing processes. New systems for rapid water tolerant C-RAFT photopolymerization will provide for new materials to be produced through this more sustainable manufacturing process.

In this work, living cationic polymerization of isobutyl vinyl ether (IBVE) is achieved using a synthesized cationic RAFT agent and an initiating system consisting of camphorquinone (CQ), ethyl 4-(dimethylamino)benzoate, and iodonium salt HNu-254. Molecular weights of 12 kg/mol are achieved with a dispersity of 1.4. The polymerization mechanism is probed and shows rapid kinetics consistent with living polymerizations in addition to photo-controllability as indicated by light on-off experiments. Chain extension experiments display re-activation of the trithiocarbonate chain end. This feature is then used to produce block-copolymers using ethyl vinyl ether and cyclohexyl vinyl ether.

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[1] Goethals et al, *Carbocationic Polymerizations*

ACKNOWLEDGMENTS

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CHAPTER 1

INTRODUCTION

Photo-controlled polymerization mechanisms are easily transferred to 3D printing applications which leverage the spatial and temporal control of light to "print" products from a resin often consisting of monomer, crosslinker, and a photo-controlled initiating system[2]. The additional use of RAFT agents in these processes produce living materials which can be easily repaired or reprocessed through chain end reactivation. Chen et al demonstrated how the incorporation of trithiocarbonate iniferters in polymer gels allows for the radical insertion of new monomer and or crosslinker units at the location of these iniferters. This allows the properties of the original "parent" gel to be changed as new units are inserted throughout the network to create a unique "daughter" gel. In addition to the creation of "daughter" gels this also allows facile healing of damaged gels and welding of separate gels. While the properties of these gels are interesting, much more research must be done before they can be applied to additive manufacturing processes. Currently the process is slow and uses a glovebox making it unattractive for 3D printing[3]. Zhang et al made headway against both of these challenges with an oxygen tolerant radical PET-RAFT 3D printing process. Unlike Chen's work with a trithiocarbonate iniferter, Zhang uses a traditional RAFT agent in their production of crosslinked materials. As the product is not a gel, insertion of monomer units throughout the network is not achieved. However, the object's surface is modified through reactivation of the trithiocarbonate chain ends. Furthermore, the use of a tertiary amine in the PET-RAFT process provides an oxygen scavenging pathway allowing these polymerizations to take place under ambient conditions. Printing speeds of 1.2 cm/hr can be achieved with this mechanism[4].

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[2] Jung et al, *Designing with Light: Advanced 2D, 3D, and 4D Materials*

[3] Chen et al, *Living Additive Manufacturing: Transformation of Parent Gels into Diversely Functionalized Daughter Gels Made Possible by Visible Light Photoredox Catalysis* 124-134

[4] Zhang et al, *A Versatile 3D and 4D Printing System through Photocontrolled RAFT Polymerization*

These living materials which utilize RAFT agents or similar trithiocarbonate species can be easily repaired or reprocessed to produce more functional materials. This allows the life of such materials to be extended and thereby reduces plastic waste. In the current state, the production of these living materials is inhibited by their slow polymerization rate. Additionally, the materials being investigated for these processes are by and large those which can be produced through a radical mechanism due to the commercial availability of RAFT agents and the tolerant nature of the polymerization. Cationic polymerizations on the other hand are very sensitive to small amounts of nucleophilic impurities such as water due to the high reactivity of the propagating cation. This leads to premature termination of propagating chains as shown in Figure 1. For this reason, great effort is taken to purify reagents when attempting controlled polymerizations. Monomers and solvents are distilled, and reactions are run under an inert atmosphere to prevent such termination reactions[1].
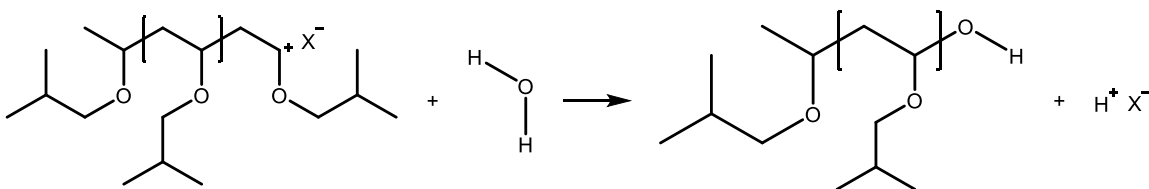
Figure 1. Mechanism for Chain Transfer by Water[5].

Cationic polymerizations are used to produce a variety of materials from monomers including epoxides, vinyl ethers, cyclic ethers, and lactones[6]. Polyisobutylene, butyl rubber (copolymer of isobutylene and isoprene), and polybutene (copolymer of isobutylene and other butenes) are also produced through cationic polymerizations[7]. A cationic RAFT (C-RAFT) polymerization without strict purification steps and tolerant to nucleophilic impurities would encourage its use in 3D printing processes. This would add to the types of products which can

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[1] Goethals et al, *Carbocationic Polymerizations*

[5] Polymer Database. "Chain Transfer Reactions in Cationic Polymerization".

[6] Michaudel et al, *Cationic Polymerization: From Photoinitiation to Photocontrol* 9798-9808

[7] Roy et al, *Cationic Polymerization of Nonpolar Vinyl Monomers for Producing High Performance Polymers*

be produced through this more sustainable route. The first step towards the incorporation of cationic RAFT for additive manufacturing is the rapid production of living polymers. Additionally, the production of such polymers without the strict conditions typically associated with C-RAFT will further encourage the incorporation of these chemistries into more sustainable 3D printing processes. This work aims to investigate C-RAFT under mild conditions without rigorous purification of reagents.

To achieve controlled cationic polymerizations, researchers have carefully selected counterions which interact with the active center to give an equilibrium between an active propagating species and a covalently bonded dormant species. The I_2 catalyzed system was one of the first controlled polymerizations to give a narrow molecular weight distribution and revealed the importance of this equilibrium[1,8]. From this, base assisted systems were developed using a Lewis base and a strong Lewis acid initiator in nonpolar solvents. Nonpolar solvents are used as they will not interrupt the equilibrium interactions involving the Lewis base and the propagating cation. Ethylaluminum dichloride was a commonly used Lewis base for the living polymerization of isobutyl vinyl ether (IBVE) from its adduct with hydrochloric acid. It was later discovered that $FeCl_3$ and $SnCl_4$ systems polymerize from the same adduct using ethyl acetate as a solvent on the order of 10^3 times faster[9].

More recently researchers have experimented with the counterion to not only achieve living polymerizations, but additionally allow them to occur in the presence of small amounts of moisture. Tight ion pairings between the propagating cation and the corresponding counterion have been found to protect growing polymer chains from nucleophiles. It was hypothesized by Kottisch et al that a propagating chain in equilibrium between a salt and a covalently bonded species would selectively incorporate monomer species as opposed to nucleophiles, which would

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[1] Goethals et al, *Carbocationic Polymerizations*

[8] Miyamoto et al, *Synthesis of Monodisperse Living Poly(vinyl ethers) and Block Copolymers by the Hydrogen Iodide/Iodine Initiating System* 2228-2230

[9] Aoshima et al, *A Renaissance in Living Cationic Polymerization* 5245-5287

terminate the growing chain. Using pentacarbomethoxycyclopentadiene as the organic acid

initiator they were able to achieve controlled polymerizations of vinyl ethers without rigorous

purification of their starting materials[10]. Further experimentation found that hydrogen bond donors

can be incorporated in this system to tune the basicity of the counterion and therefore augment

the rate of polymerization[11]. Li et al took inspiration from this work and the work of Kamigaito's

group, to produce a moisture tolerant C-RAFT polymerization[12]. Kamigaito's group synthesized a

specific C-RAFT agent to polymerize vinyl ethers in a living fashion[13]. The incorporation of a

RAFT agent allows chain end reactivation for the formation of block copolymers[14]. Li et al had

already produced a water tolerant, living polymerization of IBVE using manganese carbonyl as a

photocatalyst[15]. With more work, Li et al was able to utilize the same manganese carbonyl

catalyst to produce a C-RAFT agent in situ from commercially available reagents. Similar to

Kamigaito's group the C-RAFT agent allows re-activation of chain ends to produce block

copolymers[12].
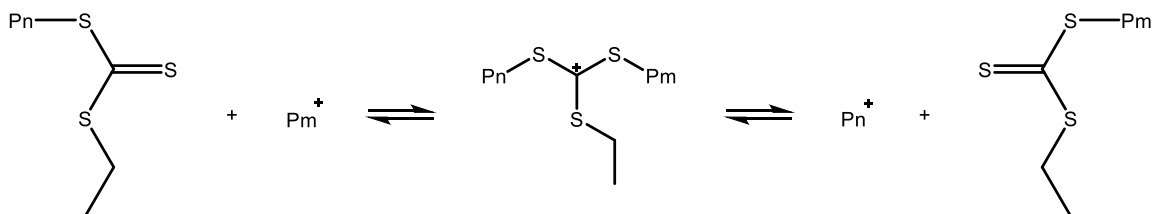
Figure 2. Cationic RAFT Mechanism as proposed by Kamigaito et al[13].

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[10] Kottisch et al, *Controlled Cationic Polymerization: Single-Component Initiation under Ambient Conditions* 10605-10609

[11] Kottisch et al, *Hydrogen Bond Donor Catalyzed Cationic Polymerization of Vinyl Ethers* 4535-4539

[12] Li et al, *Manganese Carbonyl Induced Cationic Reversible Addition-Fragmentation Chain Transfer (C-RAFT) Polymerization under Visible Light* 2724-2731

[13] Uchiyama et al, *Cationic RAFT Polymerization Using PPM Concentrations of Organic Acid* 1944-1948

[14] Guerre et al, *Combination of Cationic and Radical RAFT Polymerizations: A Versatile Route to Well-Defined Poly(ethyl vinyl ether)-block-poly(vinylidene fluoride) Block Copolymers* 393-398

[15] Li et al, *Visible Light Induced Controlled Cationic Polymerization by: In Situ Generated Catalyst from Manganese Carbonyl*

Zhao et al took this research to the next step with their development of a C-RAFT system for 3D printing. This group utilized a dithiocarbamate C-RAFT agent in conjunction with an iodonium salt initiator and an iron catalyst. With this system they were able to print objects using near-infrared light with a stereolithographic 3D printer under ambient conditions without rigorous purification of their starting materials. Printed materials displayed chain end functionality as surface properties were modified with additional monomers[16].

Even with these advances there is still much work to be done to incorporate cationic RAFT into additive manufacturing processes. Both Kottisch's and Li's work have shown rapid polymerization. Zhao et al advanced the field with implementation of their C-RAFT system in a 3D printing process. This work seeks to add to the systems which are capable of 3D printing living materials through a cationic mechanism. Unlike the previous works mentioned this work utilizes a transition-metal free system opting for camphorquinone as a photosensitizer. In this investigation C-RAFT is performed using S-1-isobutoxylethyl-S'-ethyltrithiocarbonateas as a C-RAFT agent, IBVE, and an initiating system composed of (1S)-(+)-Camphorquinone (CQ), ethyl 4-(dimethylamino)benzoate (EDMAB), and iodonium salt HNu-254. The mechanism by which these species interact is investigated as well as the ability of the C-RAFT agent to control the polymerization without rigorous purification and under ambient conditions. Kinetic studies are done to explore the photo-controllability of the reaction as well as chain extension experiments to verify chain end reactivation. Research is done to determine the ability to produce block copolymers using cationic polymerizable monomers.

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[16] Zhao et al, *Photoinduced Free Radical Promoted Cationic RAFT Polymerization toward "Living" 3D Printing* 1315-1320

CHAPTER 2

RESULTS AND DISCUSSION

Formulations for Table 1 entries 1-10 were prepared in oven dried 7 ml glass vials with stir bars. All samples included 1.0 mL of isobutyl vinyl ether and 1.5 mL of dichloromethane as solvent. S-1-isobutoxylethyl-S'-ethyltrithiocarbonate is used as the C-RAFT agent. 2-(butylthiocarbonothioylthio) propanoic acid (BTPA) is a radical RAFT agent tested for comparison. For each formulation a dry and non-dry sample was prepared. The non-dry samples had no purification steps while the dry samples were dried with 3 Å molecular sieves prior to light irradiation. After irradiation for the designated time, the reactions were quenched with 200 μl of methanol. Aliquots were taken from each sample for analysis with proton nuclear magnetic resonance (HNMR) and size exclusion chromatography (SEC). The rest was precipitated twice in methanol and again analyzed with HNMR and SEC.

Table 1. Polymerizations of Isobutyl Vinyl Ether and Corresponding SEC Data

Entry	IBVE:EDMAB:CQ:HNu-254	RAFT Agent (molar equivalent)	M_n Dry (kg mol$^{-1)}$)	M_w/M_n Dry	M_n Non-Dry (kg mol$^{-1)}$)	M_w/M_n Non-dry
1	100:0:0.1:0	C-RAFT (1)	-	-	-	-
2	100:0:0.1:0	C-RAFT (1)	-	-	-	-
3	100:0.086:0.1:0	C-RAFT (1)	-	-	-	-
4*	100:0.086:0.1:0.052	C-RAFT (1)	12.0	1.36	11.8	1.29
5*	100:0:0.1:0.052	C-RAFT (1)	11.5	1.32	13.8	1.37
6	100:0:0:0	C-RAFT (1)	-	-	-	-
7*	100:0.086:0.1:0.052	None	22.6	2.40	15.6	1.78
8	100:0.086:0.1:0.052	BTPA (1)	N/A	N/A	19.7	3.52
9	100:0.0086:0.01:0.0052	C-RAFT (1)	N/A	N/A	11.1	1.50
10	100:0.086:0:0.052	C-RAFT (1)	N/A	N/A	12.1	1.58

*indicates SEC data was taken after polymer product was precipitated twice in methanol

-indicates no polymer was formed

N/A indicates polymerization was not attempted

Both HNMR and SEC data from the initial experiment indicate that the iodonium salt, HNu-254, is required for polymerization as only those formulations which contained HNu-254 polymerized. Polymerization proceeded under 450 nm blue light in the absence of EDMAB and CQ. The C-RAFT agent is also shown to have a significant effect on the product's dispersity (Đ). Polymer samples produced in the presence of the C-RAFT agent (Table 1, entries 4,5,9,10) all showed a degree of control not seen from samples polymerized in the absence of the C-RAFT agent (Table 1, entry 7), or in the presence of a commercially available radical RAFT agent (Table 1, entry 8). Drying the resins does not appear to have a large effect on the purified polymers. It should be noted that SEC of the unpurified samples containing the C-RAFT agent show a broader molecular weight (Đ=1.63) for the non-dry samples than for the dry samples(Đ=1.56). This shows the polymerizations to only be tolerant of impurities as the molecular sieves have a small effect on the polymerization. Drying also affects formulations without the C-RAFT agent as shown in Table 1 entry 7. In this case the drying process noticeably increases the molecular weight. This showcases the negative chain transfer effects of moisture on the cationic polymerization process.

The role of each species was investigated through kinetic studies. Table 1, entries 4,5,7,9, and 10 were polymerized under non-dry conditions with aliquots taken at specific timepoints. Samples were then analyzed using HNMR with benzene as an internal standard. These studies determined that while CQ and EDMAB are not required for polymerization, they have a significant effect on the rate. Table 1 entry 4, which contains the C-RAFT agent and all three components of the initiating system, achieves full monomer conversion in 6 minutes, whereas Table 1 entry 5, which lacks EDMAB, only reaches 95% conversion after 2 hours of irradiation. The kinetics of entry 10 were not explored in depth although no polymerization occurred in the first 12 minutes of irradiation. With this finding it was determined that the mechanism by which IBVE polymerizes in the absence of CQ is negligible compared to the mechanism which employs CQ. Table 1 entries 4 and 7 polymerize at similar rates. For this reason, it is believed that the C-RAFT agent does not play a significant role in initiation.

Unsurprisingly Table 1 entry 9, which includes CQ, EDMAB, and HNu-254 at 1/10th of the standard concentrations, showed very slow polymerization with no conversion through the first 3 hours of irradiation. Entry 9 achieved a monomer conversion of 84% only after 24 hours of irradiation.

Literature supports these results and the roles of CQ, EDMAB, and HNu-254. Iodonium salts such as HNu-254 are known to initiate cationic polymerization on their own when irradiated with UV light according to Figure 3[17]. It is believed that the lack of visible light absorption by HNu-254 is what causes the reduced polymerization rate. Camphorquinone acts as a photosensitizer capable of absorbing visible blue light. As shown in Figure 4, monomer reduces camphorquinone in its excited state to a ketyl radical which then interacts with an iodonium salt to regenerate camphorquinone and produce a proton capable of polymerizing IBVE[18]. Figure 5 displays the most rapid polymerization mechanism in which EDMAB is included along with CQ and HNu-254. In this mechanism CQ is reduced by EDMAB. The oxidized EDMAB then undergoes a hydrogen transfer to produce a proton. CQ is regenerated through its oxidation by the iodonium salt[19].

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[17] Crivello et al, *Visible and Long-Wavelength Photoinitiated Cationic Polymerization* 343-356

[18] Cook et al, *Photopolymerization of Vinyl Ether Networks using an Iodonium Initiator-The Role of Photosensitizers* 5474-5487

[19] Oxman et al, *Evaluation of Initiator Systems for Controlled and Sequentially Curable Free-Radical/Cationic Hybrid Photopolymerizations* 1747-1756
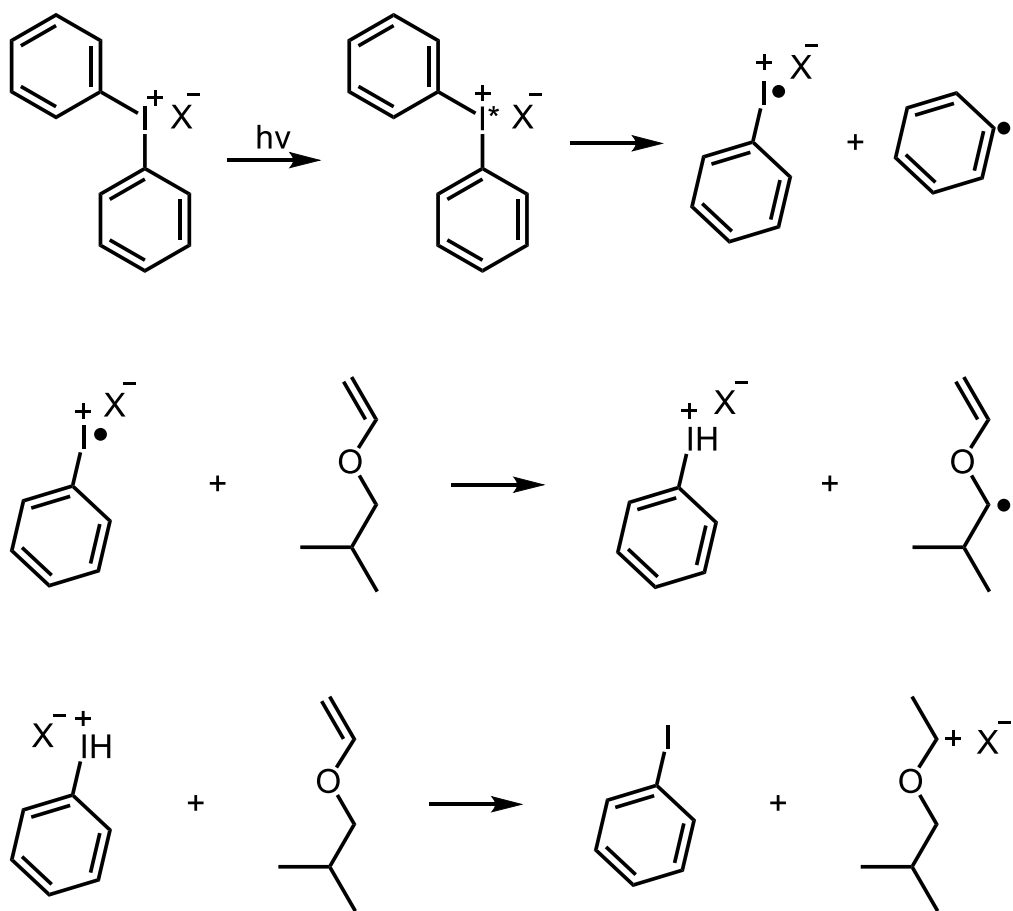
Figure 3. Polymerization of IBVE via an Iodonium Salt[17]

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[17] Crivello et al, *Visible and Long-Wavelength Photoinitiated Cationic Polymerization* 343-356
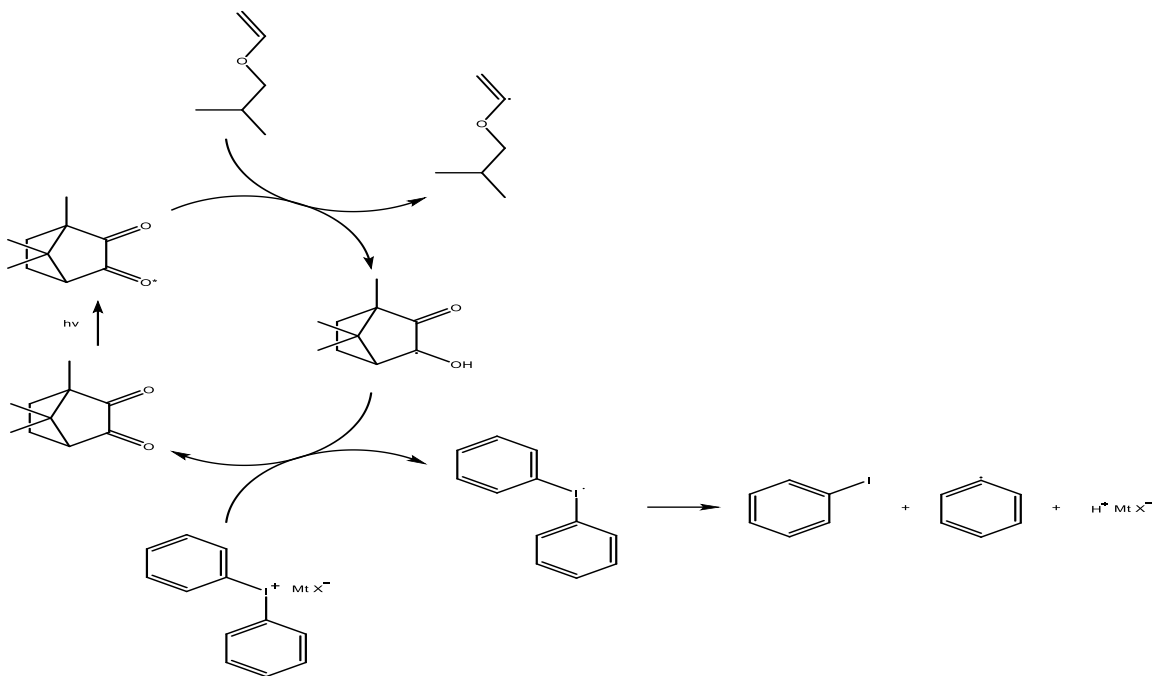
Figure 4. Initiation of Cations utilizing an Iodonium Salt with aid from Camphorquinone[18]

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[18] Cook et al, *Photopolymerization of Vinyl Ether Networks using an Iodonium Initiator-The Role of Photosensitizers* 5474-5487
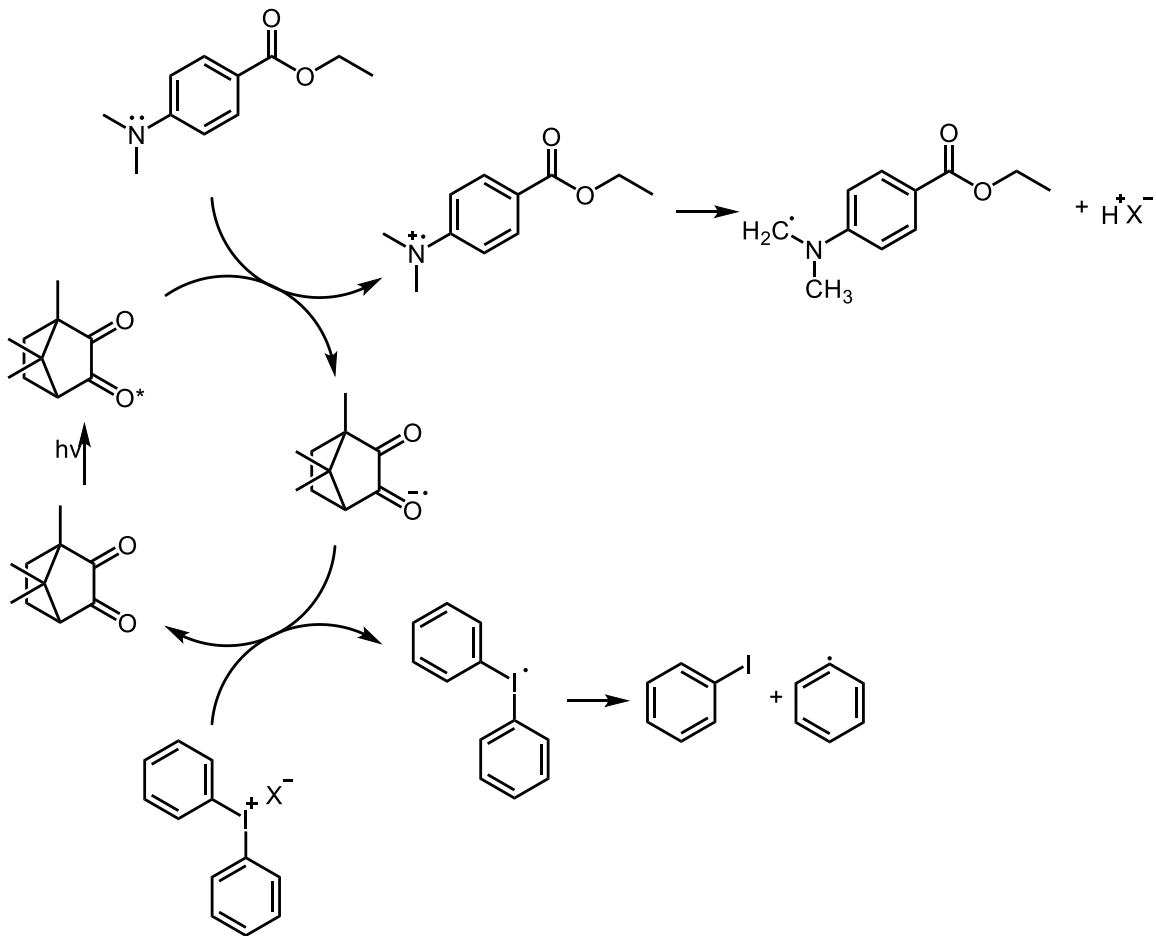
Figure 5. Initiation of Cations utilizing an Iodonium Salt with aid from Camphroquinone and Ethyl 4-(Dimethylamino)Benzoate[19]

It should be noted that all these mechanisms produce radicals which undergo various termination reactions or alternatively can interact with HNu-254 to produce more cations. These radicals are also capable of initiating radical polymerization when an appropriate monomer is used, such as methyl acrylate. In the case of IBVE, radical polymerization is not an option. An attempt to polymerize IBVE using 2,2-Dimethoxy-2-phenylacetophenone as a radical initiator showed no polymer formation after 16.5 hours of irradiation by 365 nm light. This supports the polymerization of IBVE as one achieved through a cationic mechanism.

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[19] Oxman et al, *Evaluation of Initiator Systems for Controlled and Sequentially Curable Free-Radical/Cationic Hybrid Photopolymerizations* 1747-1756

In addition to determining the roles of each species the kinetic data for the full system was used to produce Figure 5. The linear plot of $\text{Ln}[M_0/M_t]$ vs time indicates a constant cation concentration indicative of living polymerizations.
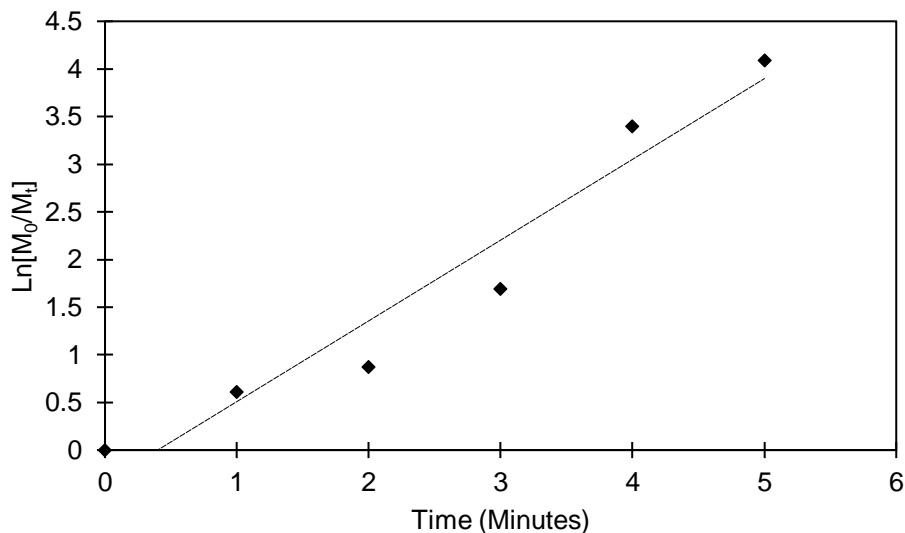
Figure 6. Plot of $\text{Ln}[M_o/M_t]$ vs Time

Photo-controllability was then tested using light on-off experiments. The IBVE was polymerized with and without the C-RAFT agent. Samples were produced and irradiated while stirring with 450 nm light (82 lux) for 2 minutes followed by a 4 minute dark period and finally another 2 minutes of irradiation. Figure 8 clearly shows the system has on/off behavior consistent with a photo-controlled polymerization. Polymerization occurs when irradiated and stops during dark periods. This is shown to be a feature of the C-RAFT agent as formulations without the C-RAFT agent show continued polymerization during the dark periods (Figure 9).
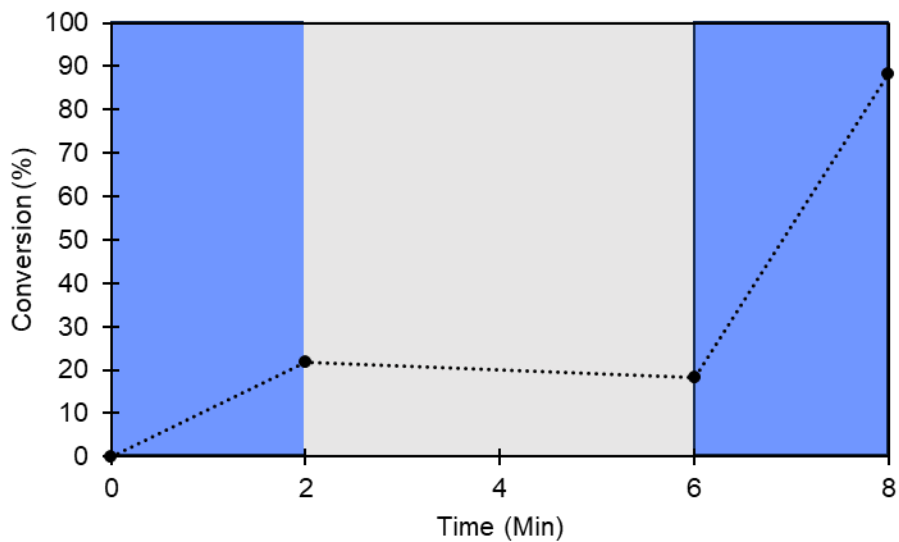
Figure 7. Light On-Off Experiment Utilizing C-RAFT Agent
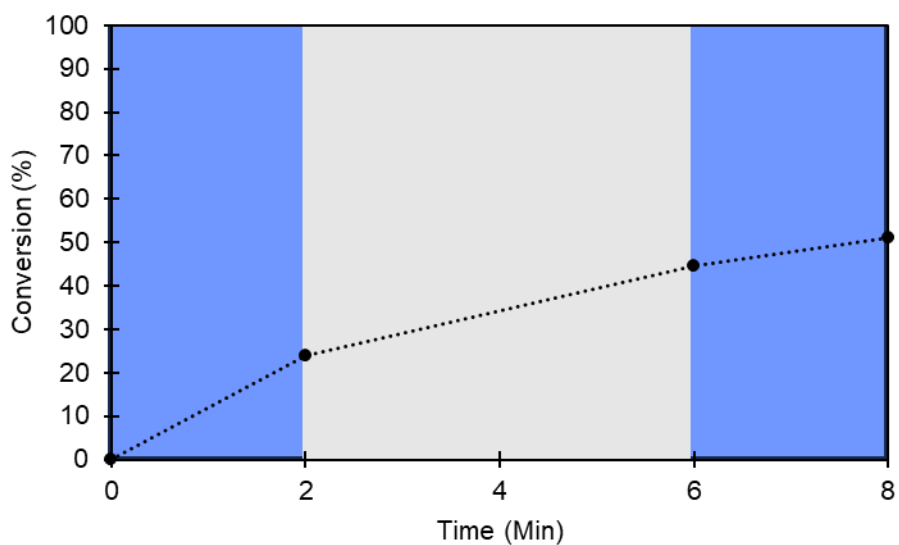
Figure 8. Light on-off experiment without C-RAFT agent

After establishing the polymerization was photo-controlled, the system was tested for reactivation of the trithiocarbonate chain ends. The polymers produced in Table 1 (entries 4, 5, and 7) were used to produce the extended polymers in Table 2 (entries 4E, 5E, and 7E). Polymer was combined with monomer and the initiating components in the ratio PolyIBVE:IBVE:EDMAB:CQ:HNu-254:: 0.25:100:0.086:0.1:0.052. DCM was used as a solvent at

150 vol% of the monomer. Just as with the initial experiment, dry samples were dried using 3 Å

molecular sieves prior to irradiation. Non-dry samples had no purification steps. Samples were

irradiated with blue 450 nm light (82 Lux) while stirring for 2.5 hours.

Table 2. Chain Extension of Isobutyl Vinyl Ether

Entry	IBVE:EDMAB:CQ:HNu-254	RAFT Agent (molar equivalent)	M_n Dry (kg mol$^{-1)}$)	Đ Dry	M_n Non-dry (kg mol$^{-1)}$)	Đ Non-dry
4	100:0.086:0.1:0.052	C-RAFT (1)	12.0	1.36	11.8	1.29
4E	100:0.086:0.1:0.052	None	25.3	2.54	24.7	2.54
5	100:0:0.1:0.052	C-RAFT (1)	11.5	1.32	13.8	1.37
5E	100:0.086:0.1:0.052	None	27.2	2.52	24.7	2.50
7	100:0.086:0.1:0.052	None	22.6	2.40	15.6	1.78
7E	100:0.086:0.1:0.052	None	26.2	2.03	20.1	1.74

Table 2 entries 4E and 5E, in which the C-RAFT agent was incorporated in the original

polymer, display an increase in molecular weight after extension compared to Table 2 entry 7E,

which shows little increase in molecular weight. SEC traces comparing non-dry data for entries

4E and 5E with 7E (Figure 6) reveals that not only was there an increase in molecular weight with

these samples, but the increase is greater than what is seen when IBVE is polymerized without

chain extension as in the case of 7E. This indicates that polymer chain ends were successfully re-

activated.
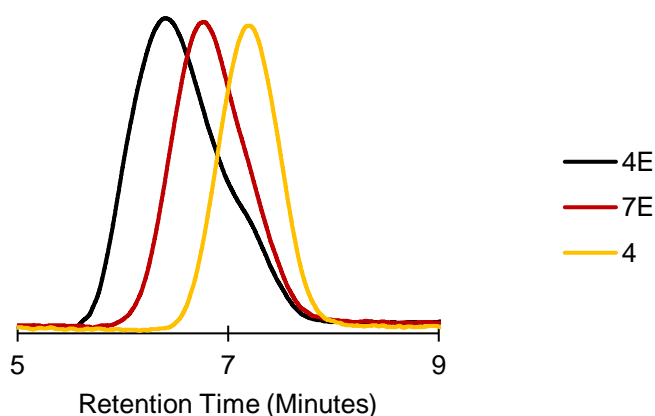
Figure 9. Low Angle Light Scattering SEC Traces of Non-Dry Chain Extension Experiment

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This same extension beyond the molecular weights achieved with the 7E control is also seen in the dry samples although not to the same extent (Figure 7). Attempting a second extension of the already extended polymers yielded no further increases. It is hypothesized that once polymer chains reach a certain size, smaller growing chains begin to out-compete the larger ones for monomer addition. As shown in Figure 5, the initiation processes does not necessarily interact directly with the trithiocarbonate chain ends. In the case of the extension experiments, this leads to uncontrolled growth in addition to chain extension. This limits the ability of the dried samples to extend further past the larger molecular weights seen from entry 7E. Other works with poly isobutyl vinyl ether have indicated this same difficulty in achieving controlled polymerizations above 20 kg/mol[10]. Figures 6 and 7 present a shoulder on the extended polymers at the location of the polymer pre-extension. This is likely caused by polymer formed independently of the C-RAFT agent.
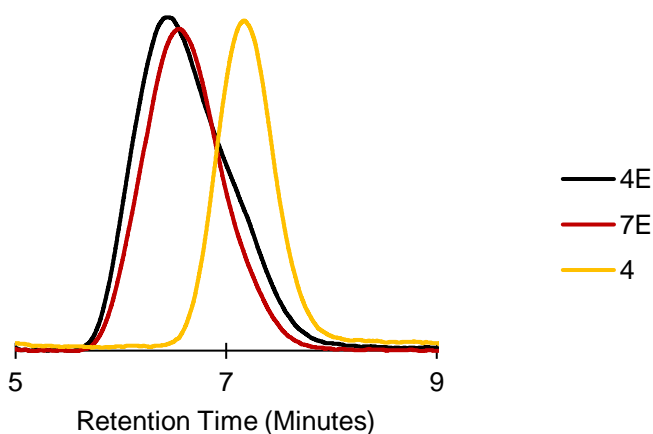

Figure 10. Low Angle Light Scattering SEC Traces of Dry Chain Extension Experiment

[10] Kottisch et al, *Controlled Cationic Polymerization: Single-Component Initiation under Ambient Conditions* 10605-10609

Reactivation of chain ends for the formation of block co-polymers were investigated using cyclohexyl vinyl ether (CVE) and ethyl vinyl ether (EVE) with IBVE. Formulations of CVE, EVE, and IBVE were produced using the standard formulation of monomer:EDMAB:CQ:HNu-254:C-RAFT agent::100:0.086:0.1:0.052:1 and DCM as solvent. SEC data shows that the C-Raft agent only controls IBVE. EVE and CVE show little to no control under these conditions. Despite not being controlled they were still tested to determine if the C-RAFT agent was incorporated into the polymer. All polymers except EVE were precipitated twice in methanol and tested for block co-polymer formation.

Table 3. Block Copolymers

Attempted Polymer	M_n (kg mol^{-1})	M_w/M_n
IBVE	12.0	1.28
*IBVE C	16.7	1.57
IBVE-CVE	20.7	2.50
*IBVE C-CVE	12.6	1.93
IBVE-EVE	14.4	1.48
*IBVE C-EVE	19.8	1.67
CVE	16.5	2.20
*CVE C	13.8	2.05
CVE-IBVE	20.0	2.21
*CVE C-IBVE	16.9	1.76
EVE	9,1	1.63
*EVE C	11.4	2.84
EVE-IBVE	20.5	2.00
*EVE C-IBVE	15.0	2.11

*Indicates control sample for comparison and was not formulated with the C-RAFT agent.

IBVE shows evidence of extension with CVE (Figure 10) whereas CVE shows no extension with IBVE. CVE is a bulkier monomer which has been hypothesized by other groups to

interfere with growing chain ends[11]. It is believed that in this system, this sterically challenging

monomer leads to poor chain end fidelity. IBVE on the other hand maintains chain end fidelity.

These chain ends are believed to be re-activated during the extension process with CVE,

although they are not believed to be maintained throughout the polymerization.
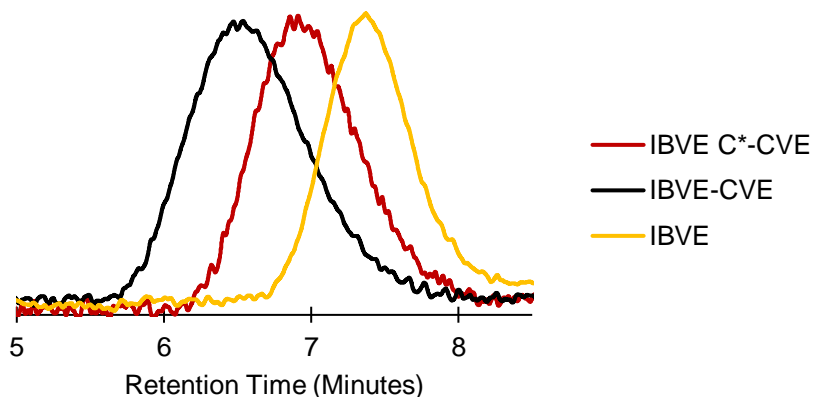
Figure 11. Low Angle Light Scattering SEC Traces of Block Copolymer Extension

      Chain extension is understood to occur when polymer formed using the C-RAFT agent is

extended with additional monomer to molecular weights larger than both the original polymer and

the control sample in which the C-RAFT agent is never used. This standard makes it clear which

polymers underwent chain extension, however it does not prove that a polymer did not undergo

the chain extension. Often SEC traces show an increase in molecular weight from the original

polymer which can't confidently be attributed to the C-RAFT agent due to it not producing

molecular weights larger than the control sample. More work must be done to verify the results in

these cases. This standard also favors the extension of smaller polymers as larger ones become

more difficult to extend as previously mentioned.

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[11] Kottisch et al, *Hydrogen Bond Donor Catalyzed Cationic Polymerization of Vinyl Ethers* 4535-4539

CHAPTER 3

CONCLUSION

This work has demonstrated the living, cationic polymerization of isobutyl vinyl ether using a synthesized cationic RAFT agent. This polymerization is achieved without rigorous purification of reagents. Although controlled polymerizations are achieved the results indicate the mechanism is merely tolerant and not wholly unaffected by impurities. Drying the polymer resin with 3 Å molecular sieves before irradiation shows an increase in control of the raw, unpurified polymer. Larger molecular weights are also achieved when formulations without a C-RAFT agent are dried.

Kinetic studies of the system are supported by literature on the roles of camphorquinone as a photosensitizer, ethyl 4-(dimethylamino)benzoate as an accelerator, and HNu-254 as an initiator. Propagation is consistent with living polymerizations and is photo-controlled. SEC data indicates the polymer chain ends can be successfully re-activated for the formation of block copolymers. More research is needed to confirm chain end fidelity in the production of these copolymers.

The rapid photo-induced polymerization shows this system has potential to be used in light driven 3D printing applications. The incorporation and reactivation of the cationic raft agent make this system a strong candidate to produce living materials. More research must be done in this area to determine chain end fidelity and chain end reactivation in crosslinked materials. Photo-control also makes this system a potential candidate for multi-material 3D printing. Through the use of a transition-metal free system this research is a step towards the more sustainable production of cationic polymerized materials.

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APPENDIX A

MATERIALS AND METHODS

Materials: Isobutyl vinyl ether (IBVE) (99% Sigma Aldrich), ethyl vinyl ether (>98.0% TCI), methyl acrylate (99%, Sigma Aldrich), and cyclohexyl vinyl ether (>98.0%, TCI) were filtered through a plug of activated basic aluminum oxide (activated, basic, Brockmann I, Sigma Aldrich) to remove KOH inhibitor prior to use unless otherwise noted. (1S)-(+)-Camphorquinone (99% Sigma Aldrich), Ethyl 4-(Dimethylamino)benzoate (98.0+% TCI), and 2,2-dimethoxy-2-phenylacetophenone (98.0+%, Fisher Scientific) were used as received. [4-[Octyloxy]phenyl]phenyliodonium hexafluoroantimonate (H-Nu 254) was purchased from Spectra Photopolymers and used as received. Ethyl mercaptan (>98.0% TCI) was distilled prior to use and stored at (4.5 °C). Carbon disulfide (≥99.9% Sigma Aldrich) was distilled and stored at (-19.7 °C) prior to its use in the synthesis of S-1-isobutoxylethyl-S'-ethyltrithiocarbonate. In the synthesis of 2-(butylthiocarbonothioyl) propionic acid, carbon disulfide was used as received. Sodium hydride (57-63% oil dispersion, Fisher Scientific), sodium bicarbonate (Fisher Scientific), sodium sulfate (anhydrous, 99%, Fisher Scientific), sodium hydroxide (anhydrous, ≥98%, Sigma Aldrich), calcium hydride (Powder, 0-2 mm, ≥90% (gas volumetric), Sigma Aldrich) 1-butanethiol (99% Sigma Aldrich), 2-bromopropionic acid (99% Sigma Aldrich) were all used as received. Hexanes (≥98.5%, Spectrum Chemical), n-hexane (≥95%, Sigma Aldrich), diethyl ether (≥99.7% Sigma Aldrich), hydrochloric acid (37% aqueous, 12 M, Sigma Aldrich), benzene (anhydrous, 99.8%, Sigma Aldrich), dichloromethane (≥99.5%, Sigma Aldrich), methanol (≥99.8%, VWR Chemicals), and isopropanol (≥99.5%, Sigma Aldrich) were used as received.

Synthesis of Synthesis of S-1-isobutoxylethyl-S'-ethyltrithiocarbonate: The cationic chain transfer agent S-1-isobutoxylethyl-S'-ethyltrithiocarbonate was synthesized according to a modified literature procedure[20]. An oven dried round bottom flask equipped with an oven dried stirbar was charged with sodium hydride (60%, 1.00 g, 25.0 mmol, 1.0 equiv) sealed with a septum cap and purged with nitrogen. The sodium hydride was washed with hexanes, which had been dried over 3 Å molecular sieves. Diethyl ether (10.0 mL), which had been dried over 3 Å molecular sieves, was added and the mixture was cooled to 0 °C. Distilled ethanethiol (1.85 mL,

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[20] Kottisch et al, *Cationic Polymerization of Vinyl Ethers Controlled by Visible Light* 15535-15538

25.0 mmol, 1.0 equiv) was added dropwise over 10 minutes at 0 °C. A syringe needle was used to alleviate pressure buildup during this addition. The suspension was stirred at room temperature for 10 minutes, then cooled again to 0 °C before distilled carbon disulfide (1.65 mL, 27.5 mmol, 1.1 equiv) was added dropwise over 10 minutes at 0 °C again using a syringe needle to relieve pressure. The resulting thick yellow suspension was stirred at room temperature for 2 hours. A separate oven-dried flask and stir bar containing a solution of aqueous hydrochloric acid (2.29 mL, 12.0 M, 27.5 mmol, 1.1 equiv) and 11.5 mL diethyl ether was cooled to -78 °C and isobutyl vinyl ether (3.26 mL, 25.0 mmol, 1.0 equiv), which had been distilled over calcium hydride and stored at -19.7 °C, was added dropwise. The solution was stirred at –78 °C for 1 hour, then warmed to 0 °C over 30 minutes. Subsequently, the organic layer of this cold solution was added dropwise to the suspension of sodium ethyl trithiocarbonate over 30 minutes using a syringe occasionally to relieve pressure buildup. The resulting mixture was stirred at room temperature for 2 hours, then diluted with diethyl ether (10 mL) and quenched with saturated sodium bicarbonate solution (10 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic phases were washed with water (10 mL), brine (10 mL), then diluted with hexanes (40 mL), dried over sodium sulfate, and evaporated to dryness in vacuo. Column chromatography (SiO2, hexanes) provided S-1-isobutoxylethyl-S'-ethyltrithiocarbonate as a yellow oil (0.77mg, 13%). The spectroscopic data for this compound was consistent with those reported in the literature[20].

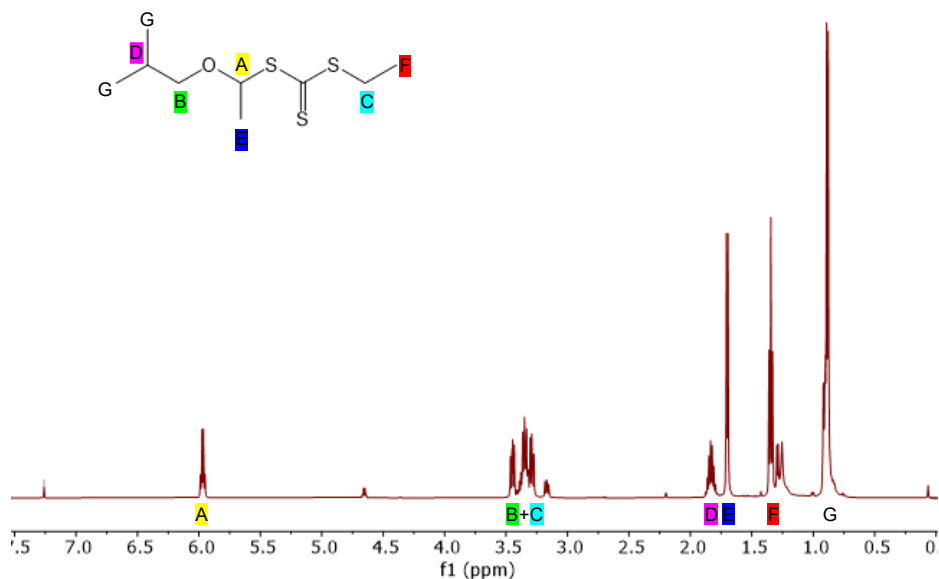[20] Kottisch et al, *Cationic Polymerization of Vinyl Ethers Controlled by Visible Light* 15535-15538

Figure 12. H-NMR Spectrum for S-1-Isobutoxylethyl-S'-Ethyltrithiocarbonate with Peak Assignments (CDCl₃)

Synthesis of 2-(butylthiocarbonothioylthio) propanoic acid: 2-(butylthiocarbonothioylthio) propanoic acid (BTPA) was synthesized according to a literature procedure[21]. Specifically, 1-butanethiol (40 mmol), 6.5 mL of 25% sodium hydroxide in deionized water (41 mmol), and 2.7 mL of carbon disulfide (45 mmol) were combined in 6.0 mL of water and stirred for 30 minutes. The flask was transferred to an ice bath where 3.7 mL of 2-bromopropionic acid (41 mmol) was added slowly with 6.0 mL of 25% sodium hydroxide in deionized water (38 mmol). The mixture was stirred at room temperature for 21 hours. 2-(butylthiocarbonothioyl) propionic acid was precipitated from solution with 10.0 mL of 10 M HCl and extracted into hexanes. The organic fraction was evaporated to dryness in vacuo to yield an opaque yellow solid. Solids were recrystallized in hexanes and filtered to yield the final product (7.6 g, 80%). The spectroscopic data for this compound was consistent with those reported in the literature[21].

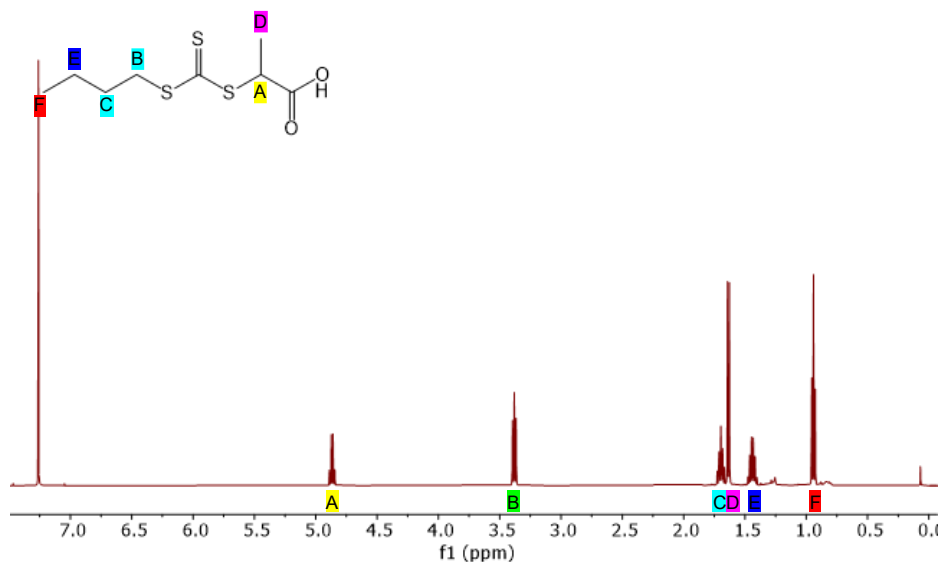[21] Niu et al, *Engineering Live Cell Surfaces with Functional Polymers via Cytocompatible Controlled Radical Polymerization* 537-545

Figure 13. H-NMR Spectrum for 2-(Butylthiocarbonothioylthio) Propanoic Acid with Peak Assignments (CDCl₃)

General Procedure for synthesis of poly (isobutyl vinyl ether): A 7 mL oven dried flask was charged with an oven dried stir bar, 1000 µl isobutyl viny ether (7.7 mmol, 100 equiv), 500 µl stock solution of camphorquinone in dichloromethane (7.7 µmol, 15.3 mmol L⁻¹, 0.1 equiv), 500 µl stock solution of ethyl 4-(dimethylamino)benzoate in dichloromethane (6.6 µmol, 13.2 mmol L⁻¹, 0.086 equiv), 500 µl stock solution of HNu-254 in dichloromethane (4.0 µmol, 7.9 mmol L⁻¹, 0.052 equiv), and 18.0 µl of S-1-isobutoxylethyl-S'-ethyltrithiocarbonate (0.077mmol, 1 equiv). The vial was vortexed for 10 seconds and then irradiated with blue light (450 nm) while stirring for the desired amount of time before being quenched with 200 µl of methanol. Polymer can be further purified through precipitation in methanol.
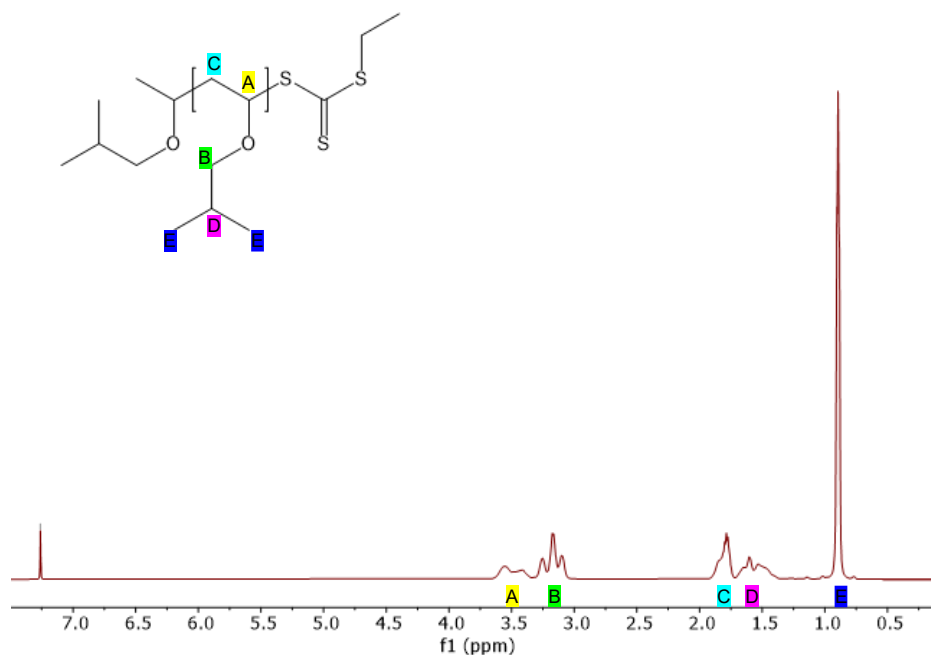
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Figure 14. H-NMR Spectrum of Purified Poly(Isobutyl Vinyl Ether) with Peak Assignments (CDCl₃)

General Procedure for synthesis of poly(ethyl vinyl ether): A 7 mL oven dried flask was charged with an oven dried stir bar, 737 µl ethyl viny ether (7.7 mmol, 100 equiv), 369 µl stock solution of camphorquinone in dichloromethane (5.7 µmol, 15.3 mmol L⁻¹, 0.074 equiv), 369 µl stock solution of ethyl 4-(dimethylamino)benzoate in dichloromethane (4.9 µmol, 13.2 mmol L⁻¹, 0.064 equiv), 369 µl stock solution of HNu-254 in dichloromethane (2.9 µmol, 7.9 mmol L⁻¹, 0.038 equiv), and 18.0 µl of S-1-isobutoxylethyl-S'-ethyltrithiocarbonate (0.077mmol, 1 equiv). The vial was vortexed for 10 seconds and then irradiated with blue light (450 nm) while stirring for the desired amount of time before being quenched with 200 µl of methanol.

26
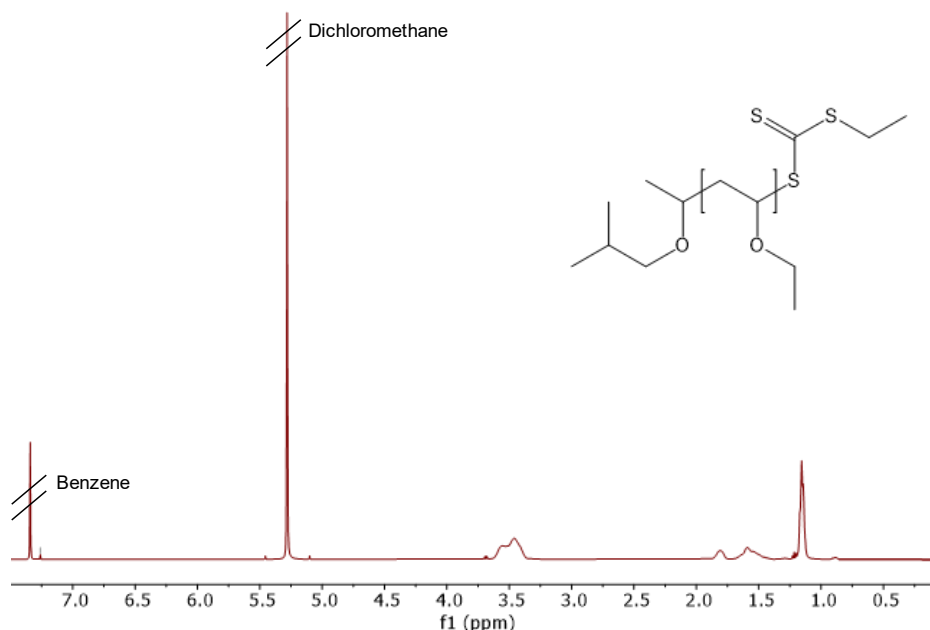
Figure 15. H-NMR Spectrum of Purified Poly(Isobutyl Vinyl Ether) (CDCl$_3$)

General Procedure for synthesis of poly(cyclohexyl vinyl ether): A 7 mL oven dried flask was charged with an oven dried stir bar, 1086 μl cyclohexyl viny ether (7.7 mmol, 100 equiv), 500 μl stock solution of camphorquinone in dichloromethane (7.7 μmol, 15.3 mmol L^{-1}, 0.1 equiv), 500 μl stock solution of ethyl 4-(dimethylamino)benzoate in dichloromethane (6.6 μmol, 13.2 mmol L^{-1}, 0.086 equiv), 500 μl stock solution of HNu-254 in dichloromethane (4.0 μmol, 7.9 mmol L^{-1}, 0.052 equiv), and 18.0 μl of S-1-isobutoxylethyl-S'-ethyltrithiocarbonate (0.077mmol, 1 equiv). The vial was vortexed for 10 seconds and then irradiated with blue light (450 nm) while stirring for the desired amount of time before being quenched with 200 μl of methanol. Polymer can be further purified through precipitation in methanol.
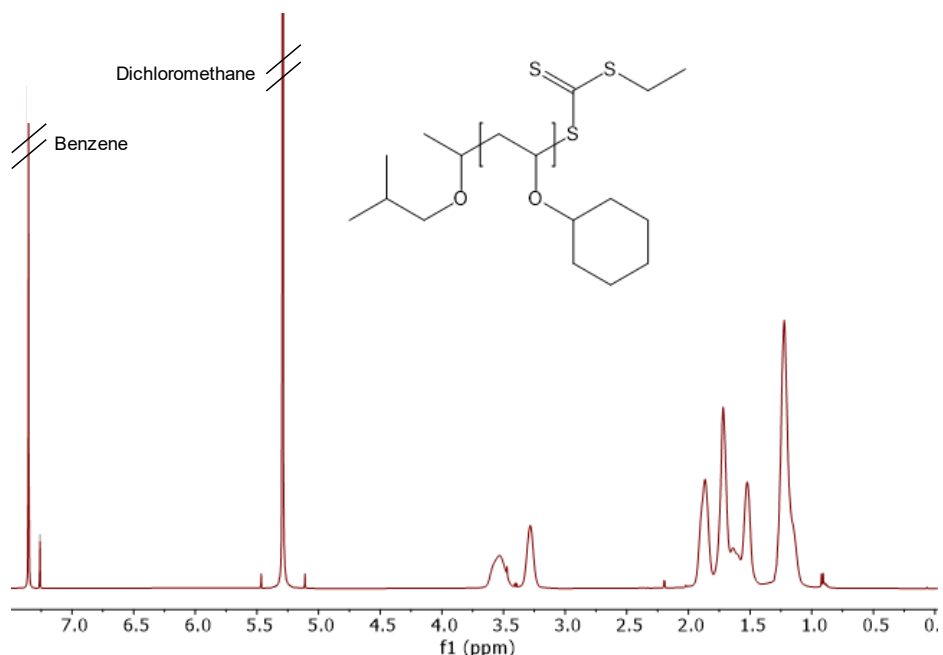
27

Figure 16. H-NMR Spectrum of Purified Poly(Cyclohexyl Vinyl Ether) (CDCl₃)

Procedure for chain extension of poly(isobutyl vinyl ether): Stock solution of camphorquinone in dichloromethane (15.3 mmol L⁻¹, 0.1 equiv), stock solution of ethyl 4-(dimethylamino)benzoate in dichloromethane (13.2 mmol L⁻¹, 0.086 equiv), stock solution of H-Nu 254 in dichloromethane (5.1 mg mL⁻¹, 0.052 equiv), and isobutyl vinyl ether (100 equiv) were added to purified poly isobutyl vinyl ether (0.25 equiv) agent in a 7ml oven dried glass vial. The vial was sonicated and vortexed to ensure polymer dissolved into the solution and an oven dried stir bar was added. The vial was irradiated with 450 nm blue light while stirring. After the desired amount of time the reaction was quenched with methanol. Polymer can be further purified through precipitation in methanol.

Polymerization of poly(ethyl vinyl ether-b-isobutyl vinyl ether): Stock solution of camphorquinone in dichloromethane (15.3 mmol L⁻¹, 0.1 equiv), stock solution of ethyl 4-(dimethylamino)benzoate in dichloromethane (13.2 mmol L⁻¹, 0.086 equiv), stock solution of H-Nu 254 in dichloromethane (7.9 mmol L⁻¹, 0.052 equiv), and isobutyl vinyl ether (100 equiv) were added to poly ethyl vinyl ether (0.25 equiv) in a 7ml oven dried glass vial. The vial was sonicated and vortexed to ensure polymer dissolved in to the solution and an oven dried stir bar was added. The vial was irradiated with 450 nm blue light while stirring. After the desired amount of time the

28

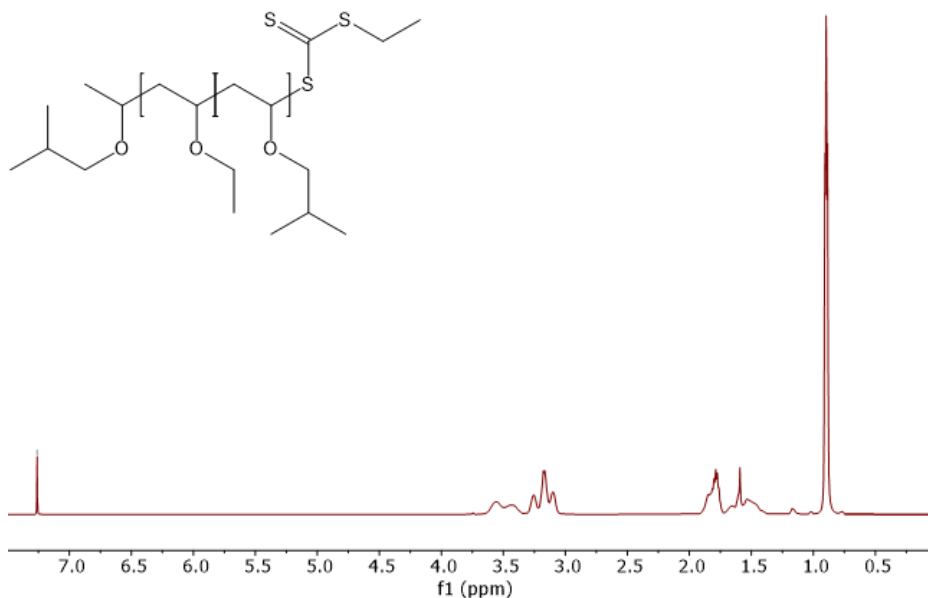
Polymerization of poly(ethyl vinyl ether-b-isobutyl vinyl ether): Stock solution of camphorquinone in dichloromethane (15.3 mmol L^{-1}, 0.1 equiv), stock solution of ethyl 4-(dimethylamino)benzoate in dichloromethane (13.2 mmol L^{-1}, 0.086 equiv), stock solution of H-Nu 254 in dichloromethane (7.9 mmol L^{-1}, 0.052 equiv), and isobutyl vinyl ether (100 equiv) were added to poly ethyl vinyl ether (0.25 equiv) in a 7ml oven dried glass vial. The vial was sonicated and vortexed to ensure polymer dissolved in to the solution and an oven dried stir bar was added. The vial was irradiated with 450 nm blue light while stirring. After the desired amount of time the

reaction was quenched with methanol. Polymer can be further purified through precipitation in methanol.


Figure 17. H-NMR Spectrum of Poly(EVE-b-IBVE) showing excess Poly(IBVE) homopolymer (CDCl$_3$)

Polymerization of poly(isobutyl vinyl ether-b-cyclohexyl vinyl ether): Stock solution of camphorquinone in dichloromethane (15.3 mmol L^{-1}, 0.1 equiv), stock solution of ethyl 4-(dimethylamino)benzoate in dichloromethane (13.2 mmol L^{-1}, 0.086 equiv), stock solution of H-Nu 254 in dichloromethane (7.9 mmol L^{-1}, 0.052 equiv), and cyclohexyl vinyl ether (100 equiv) were added to purified poly isobutyl vinyl ether (0.25 equiv) in a 7ml oven dried glass vial. The vial was sonicated and vortexed to ensure polymer dissolved in to the solution and an oven dried stir bar was added. The vial was irradiated with 450 nm blue light while stirring. After the desired amount of time the reaction was quenched with methanol. Polymer can be further purified through precipitation in methanol.
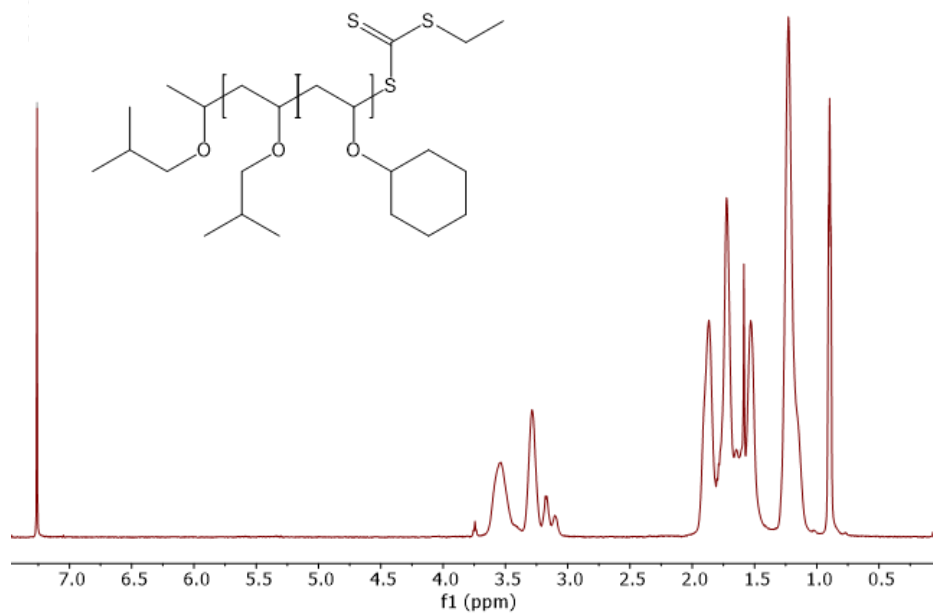
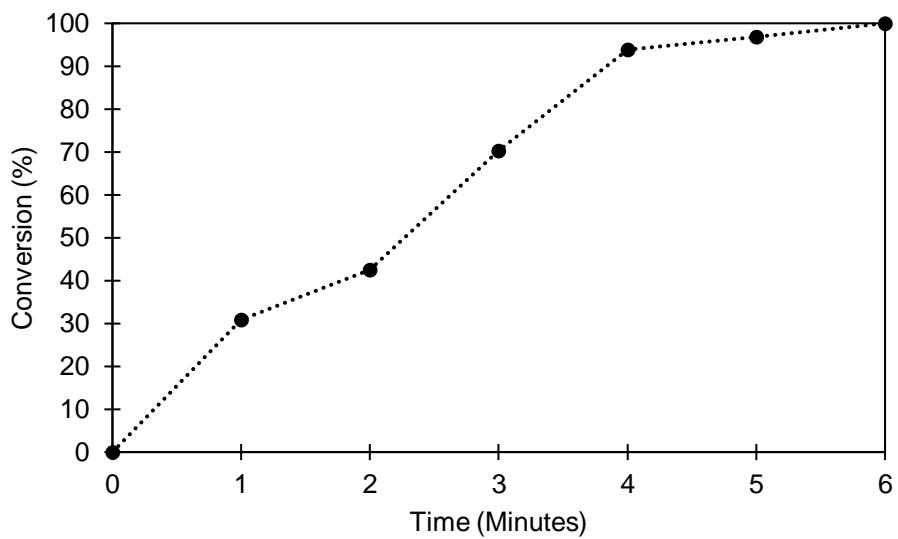Figure 18. H-NMR Spectrum of Poly(IBVE-b-CVE) (CDCl₃)

APPENDIX B

KINETIC DATA

Figure 19. Conversion of Isobutyl Vinyl Ether vs Time with C-RAFT Agent

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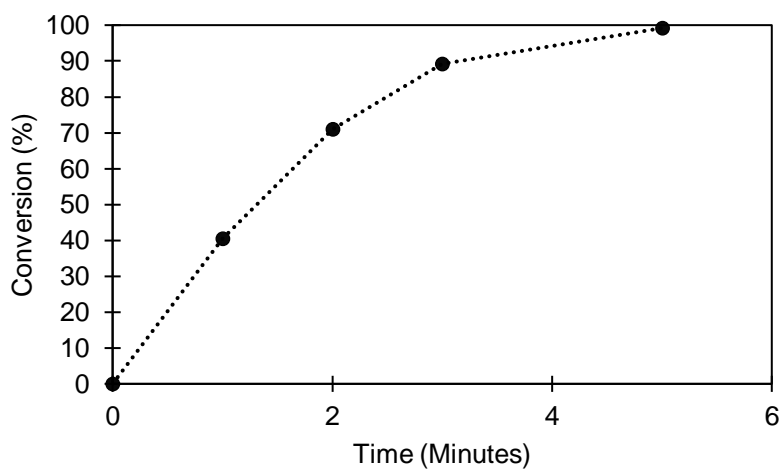
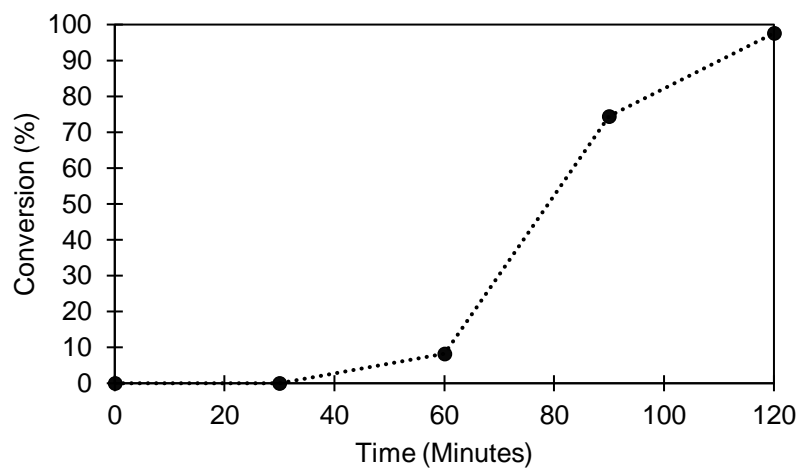Figure 20. Conversion of Isobutyl Vinyl Ether vs Time sans C-RAFT Agent

Figure 21. Conversion of Isobutyl Vinyl Ether vs Time Sans EDMAB
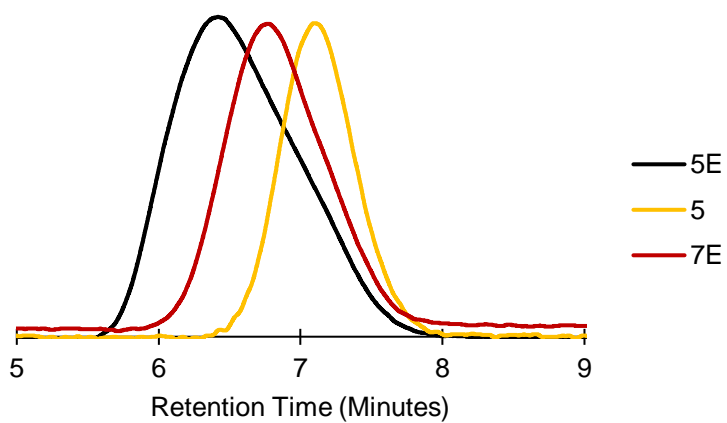
APPENDIX C

SEC DATA
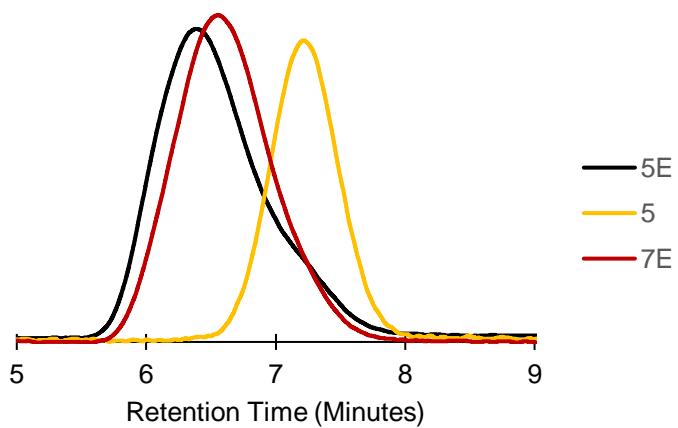
Figure 22. Non-Dry Chain Extension of Isobutyl Vinyl Ether

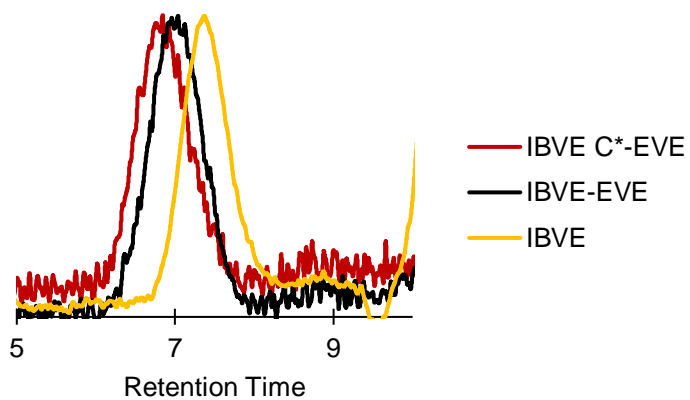Figure 23. Dry Chain Extension of Isobutyl Vinyl Ether
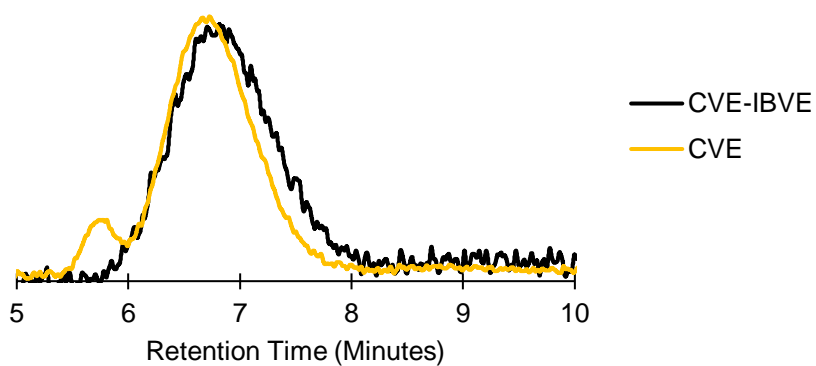
Figure 24. Attempted Poly(IBVE-b-EVE) Copolymer Extension

Figure 25. Attempted Poly(CVE-b-IBVE) Copolymer Extension