THE PENNSYLVANIA STATE UNIVERSITY
SCHREYER HONORS COLLEGE

DEPARTMENT OF CHEMISTRY

NITROXIDE MEDIATED "LIVING" POLYMERIZATION OF ACRYLATES AND
ALKENES

PAUL E. CHIARULLI
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Reviewed and approved* by the following:

Ayusman Sen
Distinguished Professor of Chemistry
Thesis Supervisor

Kenneth S. Feldman
Professor of Chemistry
Honors Adviser

Alan Benesi
Director of the NMR Facility
Faculty Reader

* Signatures are on file in the Schreyer Honors College.

Abstract

Although a large body of research has focused on the "living" free radical RAFT or ATRP methods for the copolymerization of nonpolar alkenes and polar vinyl monomers, much less is related to nitroxide mediated (NMP) polymerization. The copolymerization of butyl acrylate with the alkenes 1-decene and 1-octene was investigated using a "living" free radical methodology with the nitroxide TIPNO presented by Benoit, et al. Additionally, Al_2O_3 was utilized to determine the efficacy of Lewis acids in increasing polymerization rate and alkene incorporation outside of uncontrolled radical methods. The polymers synthesized showed a mostly linear relationship between M_n and monomer conversion as well as fairly low polydispersity indices, providing evidence for "living" character of the polymerization.

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Chapter 1: Introduction

Free Radical Polymerization

       Although a large number of synthetic pathways exist for the bonding of monomers to form polymer chains, addition polymerization remains the most industrially important process (in terms of volume produced) for the creation of polymers—responsible for such ubiquitous materials as polyethylene, polystyrene, polypropylene, poly(vinyl chloride), poly(tetrafluoroethylene), and others.[1] In contrast to condensation polymerization, in which difunctional monomers react with the loss of water or other small molecule, addition polymerization is a process by which unsaturated monomers form long chains through the reaction of an activated monomer intermediate with the unactivated form. The three major types of addition polymers—anionic, cationic, and free radical—are differentiated based on the type of activated monomer formed (anion, cation, and radical, respectively). Free radical polymerization is one of the easiest methods of addition polymerization, generally requiring much less stringent reaction conditions than other syntheses.[2]

       Free radical polymerization can be described by three distinct steps: initiation, propagation, and termination. Chain transfer, though not always desirable, is another process important to polymer growth (see Figure 1).[3]

Initiation:
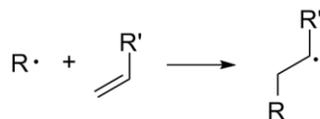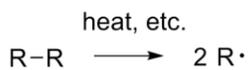
Propagation:
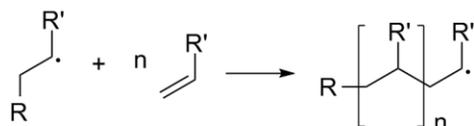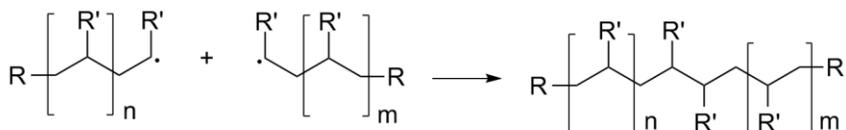
Termination:

Chain Transfer:
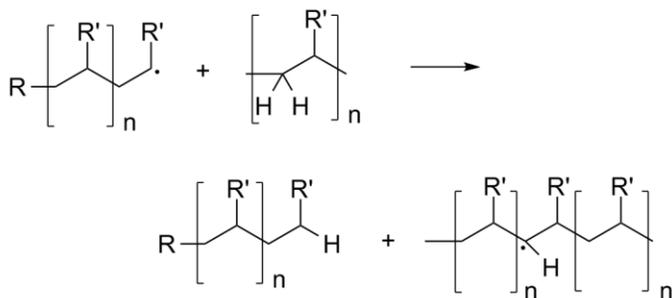
Figure 1. Initiation, Propagation, Termination, and Chain Transfer Processes

In initiation, the monomer of interest is treated with an initiator. The application of heat,

radiation, redox reagents, etc. causes the homolysis of a specific labile bond in the initiator,

resulting in useful free radicals.[1] Initiators used for free radical polymerization are often

multiply-substituted about the bond of interest in order to give the most stable radicals. For

example, commonly used symmetric aliphatic azo initiators (e.g., 2,2'-azobisisobutyronitrile

"AIBN," dimethyl 2,2'-azobisisobutyrate "MAIB") produce resonance stabilized tertiary radicals

upon decomposition. These initiator radicals subsequently attack monomer molecules, forming

activated monomer radicals.[4] It should also be noted that an activated species can be generated

straight from the monomer, without an initiator intermediary, but this has only been

demonstrated conclusively in the case of styrene.[5]

In the propagation step, the newly activated monomer radical reacts rapidly with an

unactivated monomer to form an activated dimer. In turn, the dimer reacts with another

unactivated monomer, resulting in a chain reaction that continues until the activated

macromolecule encounters either a species capable of causing termination/chain transfer or all

unactivated monomer is consumed.[1] For a high molecular weight polymer to be formed, the

propagation step must occur at a higher rate than competing reactions (i.e., termination, chain

transfer).[4]

Chain termination is the process by which actively growing chains are halted and

deactivated through radical recombination of two macroradicals (depicted in Figure 1) or

disproportionation. During the latter process, a hydrogen radical is transferred from one chain

end to another, producing saturated and unsaturated ends. In both cases, the polymer chain(s) are

"dead," as no more addition can occur to the deactivated form.[5]

Chain transfer occurs when the active end of a propagating radical reacts with a transfer

agent to give a terminated polymer and another active radical. As a result, the number of

polymer molecules increases, while the degree of polymerization decreases. Most commonly,

chain transfer occurs when one growing chain attacks another, abstracting a hydrogen atom,

terminating the original chain and producing a new active site. Branching occurs when the

attack takes some distance from the chain end of the other polymer.[3] However, chain transfer

can also occur with solvent, initiator, impurity, or another additive acting as the chain transfer

agent. As such, choosing an appropriate solvent system and initiator is very important for creating polymers of high molecular weight.[1]

The major disadvantage of traditional free radical polymerizations is a general lack of control over the polymer product. As different initiator molecules decompose at different rates, some chains begin to propagate before others, leading to very broad molecular weight distributions. Moreover, free radicals are extremely reactive and undergo frequent chain transfer reactions via hydrogen abstraction from initiator, solvent, polymer, or other monomer molecules. Thus, free radical polymerizations tend to result in highly branched, polydisperse materials. Additionally, it is difficult to control individual chain length due to somewhat random chain terminations.[2] However, a number of methods, called "living" polymerizations, have been introduced to provide greater control over polymer properties.

"Living" Polymerization

Controlled, or "living" polymerizations are termed as such because they tend to give linear polymer chains that remain active after all monomer has been incorporated.[6] Although there are many different types of "living" polymerizations, they share certain general characteristics. In a living procedure, the initiation process is faster than the rate of propagation, giving very uniform chain lengths and narrow molecular weight distributions (i.e., ratio of weight average to number average molecular weight, M_w/M_n, close to 1).[7] Furthermore, since each initiator molecule begins only one chain, the experimenter may control chain length by modifying the amount of initiator or the amount of monomer present. Again, as the chains are not deactivated to a significant extent by termination processes, they remain active after all monomer has been consumed. At this point, additional monomer may be added to create longer

chains, or a different monomer may be applied to create a new diblock copolymer. Similarly, useful functionality can be easily added at a chain terminus.[3]

Previously, the only available "living" procedures for creating well-defined, controlled polymers were anionic[8-9] and cationic polymerizations.[10-11] Though these techniques give polymers with low polydispersities and functionalized ends, they are nonetheless unsuitable for large-scale use due to their extremely stringent reaction conditions. Water and oxygen must be completed excluded from the polymerization (chain ends are highly reactive with hydroxyl moieties), and ultrapure reagents must be used.[12] Moreover, the anion or cation chain ends are not compatible with a wide variety of functionalized vinylic monomers (a monomer class easily polymerized via less controllable traditional radical techniques).[13] More recently, living free radical systems have been developed extensively for their greater versatility and ease of application.[12]

"Living" Free Radical Polymerization

The general strategy for controlling radical polymerization is similar among different types of "living" free radical polymerizations. A mediating radical species is introduced which acts to reversibly terminate propagating chains. The key idea is to mitigate the effects of chain terminations by temporarily converting a majority of propagating chains into a dormant form. With a very low concentration of reactive chain ends, irreversible termination or chain transfer processes are minimized.[13]
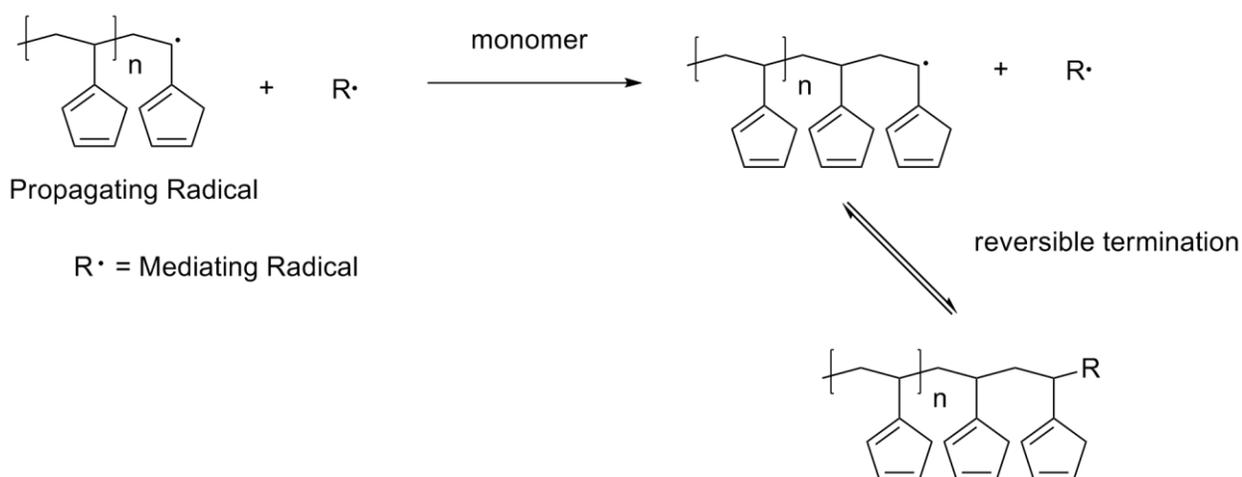
Figure 2. An Example of a Living Polymerization with a Generalized Mediating Radical

Three major processes have emerged as the most important methods of "living" free radical polymerization: Atom Transfer Radical Polymerization (ATRP), Reversible Addition Fragmentation/Transfer (RAFT), and Nitroxide Mediated Polymerization (NMP). ATRP involves the use of a halogenated species along with a transition metal complex catalyst. Initially, the metal abstracts the halogen, creating a radical initiator that can interact with the monomer to form the propagating chains. In turn, the propagating chains are reversibly terminated by transfer of the halogen to the propagating species. As such, the majority of chains are relegated to the dormant state, and "living" character of the growing chains is achieved.[14-15] Significantly, the ATRP methodology has been shown to be successful with a large number of different transition metals.[16] RAFT relies upon the addition of a reversible chain transfer agent (usually a thiocarbonylthio compound) to a free radical polymerization. This RAFT "agent" interacts with propagating chains, reversibly terminating them and producing a dormant state.[17-18] NMP is potentially the simplest of the three, as it often requires only the addition of a single reagent (an alkoxyamine) to initiate polymerization. The absence of added metal complexes, as in ATRP, leads to easier purification and higher functional group tolerance.[19]

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Nitroxide Mediated "Living" Polymerization

Of the many different classes of compounds tested for their versatility as mediating

radicals in "living" free radical polymerizations, nitroxides have proven to be the most successful

by far.[13] Initial research centered around the nitroxide 2,2,6,6-tetramethylpiperidinoxy

(TEMPO). Moad and Rizzardo discovered that under appropriate conditions, TEMPO could act

as a trap to radicals created from vinylic monomers. Today, however, TEMPO has limited use in

true living polymerization and is largely limited to styrene-based systems.[20-21]

Later, the development of new unimolecular initiators, termed alkoxyamines, provided

much needed flexibility in classes of monomer that could be successfully polymerized. Upon

heating, the alkoxyamine decomposes through homolysis of the thermolytically unstable C-O

bond, giving an initiating radical and a nitroxide radical.[13]

1   **2**
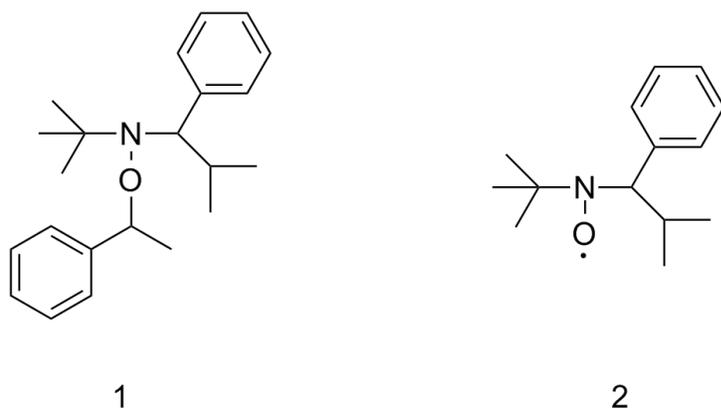
Figure 3. The Alkoxyamine 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane and Its

Homolytic Product Nitroxide, TIPNO

N-*tert*-butyl-N-(1-phenyl-2-methylethylyl)nitroxide, or TIPNO, introduced by Benoit et al., is

one of the most important nitroxides utilized in NMP (Figure 3). The TIPNO-alkoxyamine

system has proven amenable to a wide range of vinylic monomers, including acrylates, acrylic

acid, 1,3-dienes, acrylonitrile, and acrylamides, successfully surmounting some of the limitations

associated with TEMPO.[22] Furthermore, TIPNO has been shown to be better than TEMPO at controlling the polymerization of styrenic monomers.[23]

Nitroxide mediated polymerization with alkoxyamines occurs through what Fischer terms the Persistent Radical Effect (Figure 4).[24] Upon heating, the alkoxyamine dissociates into the nitroxide TIPNO and a radical initiator. If monomer is not present in solution, the initiator radicals will eventually be lost to self-termination reactions (importantly, the nitroxide does not self-terminate). In the presence of monomer M, the initiator will convert monomer molecules to activated monomer radicals. Accordingly, these propagating monomer radicals may be reversibly terminated to a dormant state upon interaction with nitroxide, and the majority of radicals will remain dormant throughout the reaction. Thus, polymeric radical self-termination is almost completely eliminated when sufficient nitroxide is present.[25-26]
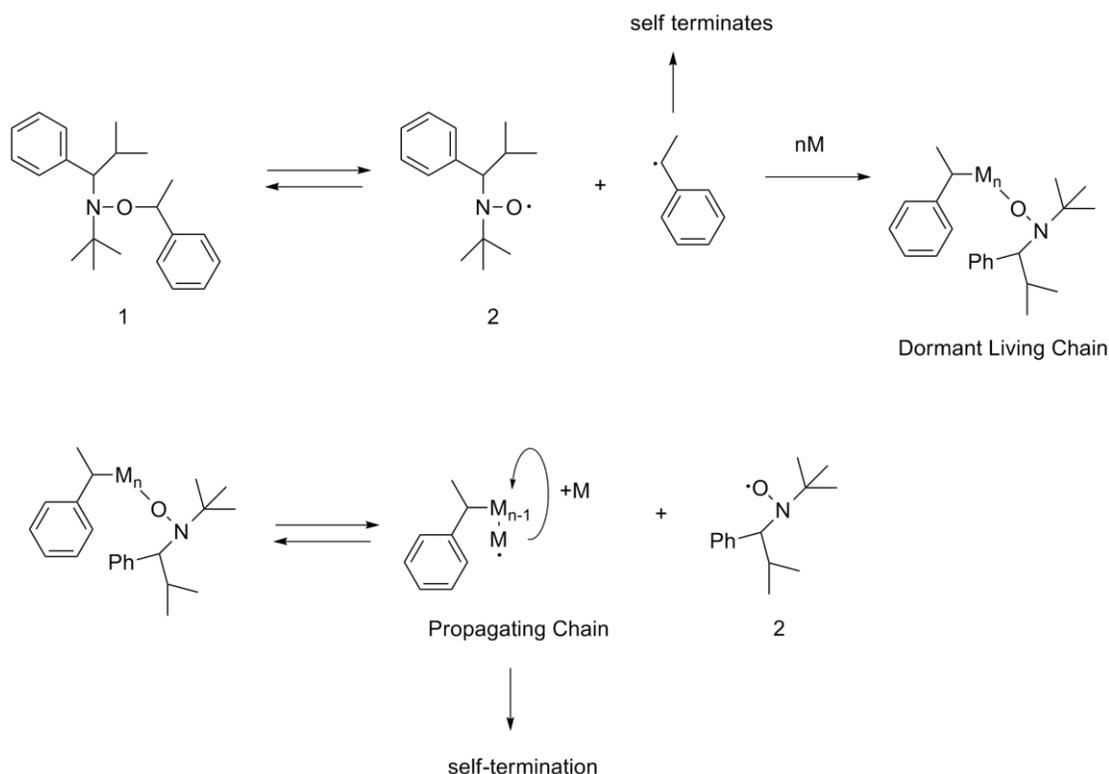
Figure 4. Nitroxide Mediated Living Polymerization

Benoit et al. improved slightly upon this general scheme by noting that small amounts of free nitroxide added prior to polymerization brought about noticeable decreases in the rates of polymerization, offering much better control over the process. Also, lower polydispersities were obtained with this method for polymers synthesized from a variety of monomers.[19] Still, the polymers reported were generally homopolymers or copolymers of two different vinylic monomers. Much less research has focused on the copolymerization of polar and nonpolar monomers using NMP procedures.

Polymerization of Polar Vinyl Monomers and Nonpolar Alkenes

The copolymerization of nonpolar olefins with polar vinyl monomers has been an area of significant research interest in the past decade due to the wide range of polymer properties that can be obtained. There are numerous advantages to incorporating polar functional groups into a nonpolar material, as polar groups influence important polymer properties, such as miscibility, adhesion, solvent resistance, toughness, and surface properties.[27-28] As mentioned previously, polar vinyl monomers, like acrylates, readily polymerize through traditional free radical mechanisms. In contrast, alkenes generally undergo metal catalyzed coordination-insertion polymerization (i.e., with Ziegler-Natta catalysts), and only undergo radical polymerizations under very harsh conditions.[29] Early efforts by Logothetis et al. to reconcile these differences and copolymerize the two monomer classes involved the use of strong Lewis acids that complex with the ester of the acrylate. In turn, the complex forms a copolymer with the alkene upon addition of a radical initiator.[30] Later work by Liu and Elyashiv, et al. demonstrated the viability of a copper-mediated atom transfer radical polymerization in the synthesis of methyl acrylate and 1-alkene copolymers.[31-32] Subsequent ATRP methods have resulted in the successful polymerization of 1-octene and methyl methacrylate.[33]

With regard to nitroxide-mediated living polymerizations, however, less work has been done on polar/nonpolar copolymer systems. Rather, much research has examined homopolymers of acrylates or copolymers of styrene and other vinylic monomers.[34-35]

Lewis Acids in Polymerization

In discussing the copolymerization of acrylates and 1-alkenes, it is important to further examine the contribution of Lewis acids to the process. When traditional free radical polymerization of acrylates and alkenes is attempted, random acrylate copolymers in low yields are generally obtained. However, in the presence of simple Lewis acids, there is a significant increase in both the polymerization rate and alkene incorporation.[36] The major reason for these increases is that the coordination of the Lewis acid with the carbonyl of acrylate monomer reduces the electron density of the conjugated double bond. Accordingly, the electron-rich, nucleophilic propagating radical of the 1-alkene is much more likely to attack the now electrophilic, Lewis-acid coordinated acrylate monomer (and vice versa).[37]
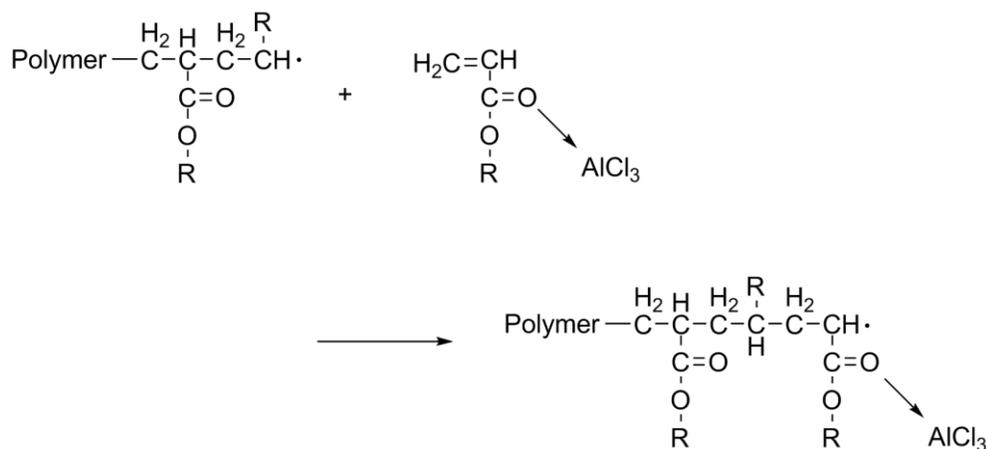

Figure 5. Lewis Acid Coordination with Polymer

The Lewis acid coordination effect has been shown to be applicable to a number of acrylates (most notably methyl methacrylate) and a wide range of 1-alkenes.[38] Still, it remains to be seen if this methodology will be beneficial to a living nitroxide mediated polymerization.

Experimental Overview

Although nitroxide-mediated polymerization of polar vinyl monomers and alkenes has been attempted previously, the vinylic monomers used have generally been methyl acrylate or norbornene derivatives.[39-40] Furthermore, as was stated previously, the addition of Lewis acid has not been attempted with this methodology to increase the polymerization rate and nonpolar alkene incorporation.

In this experiment, copolymers of butyl acrylate with the alkenes 1-decene and 1-octene were created through nitroxide polymerization with alkoxyamine **1** and nitroxide **2** in order to demonstrate the efficacy of the NMP methodology on the copolymerization of these monomers.
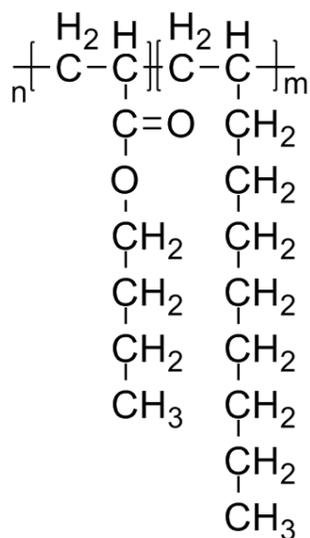
Figure 6. General Formula of Expected Random Copolymer of Butyl Acrylate/1-Decene

The distribution of molecular weights obtained will be compared to the number of moles of monomer converted in order to determine the extent of the living character of the polymerization. Polydispersity indices of each polymer were also evaluated. Moreover, the effect of the addition of the Lewis acid Al_2O_3 on butyl acrylate/1-decene living copolymers was tested to examine any possible changes in polymerization rate or alkene incorporation. The

effects of Lewis Acid addition have not been extensively researched with regard to nitroxide mediated polymerization.

Chapter 2: Experimental

General Considerations

All chemicals were obtained from Sigma Aldrich unless otherwise stated. Butyl acrylate (99%),

1-decene (97%), and 1-octene (98%) were passed over a basic alumina column to remove any

inhibitors and impurities. The monomers, along with trichloroethylene (TCE, 99%), were

distilled over calcium hydride, pump-freeze-thaw degassed with liquid nitrogen, and stored

under N_2. Aluminum Oxide (puriss., 98%) was used as received. The alkoxyamine 2,2,5-

trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane, **1**, was synthesized according to procedure

presented by Benoit, et al.[19] ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.5-7.1 (m, 20H), 4.90 (q, 2H J = 6.5

Hz), 3.41 (d, 1H, J = 10.8 Hz), 2.35 (m, 2H), 1.62 (d, 3H, J = 6.8 Hz), 1.31 (d, 3H, J = 6.3 Hz),

0.77 (s, 9H), 0.54 (d, 3H, J = 6.5 Hz). Similarly, the nitroxide N-tert-butyl-N-(1-phenyl-2-

methylethylyl)nitroxide, **2**, was synthesized from procedure from Benoit, et al.[19] ^{1}H NMR (300

MHz, CDCl$_3$) δ 7.60 (m, 5H), 3.41 (d, 1H, J = 6.5 Hz), 2.28 (m, 1H), 1.44 (s, 9H), 1.20 (d, 6H, J

= 6.8 Hz), 0.97 (s, 9H), 0.58 (d, 6H, J = 6.8 Hz).

Instrumentation

Gas chromatography was performed on an Agilent 5890 Series II GC with a Restek RTX-5

capillary column and FID detector. The injector temperature was set to 250 °C. Samples were

first heated from 40 °C to 120 °C with a ramp rate of 5 °C/min and then subsequently from 120

°C to 250 °C with a rate of 15 °C/min. Molecular weights and molecular weight distributions

were determined on a Shimadzu gel permeation chromatography (GPC) chromatograph

containing a three-column bed (Styragel HR 7.8 x 300 mm columns with 5 μm bead size), a

Shimadzu RDI-10A differential refractometer, and a Shimadzu SPD-10A tunable absorbance

detector (254 nm). Samples were run in THF with a flow rate of 1 mL/min at 35 °C and

calibrated against polystyrene standards. EZSTART 7.2 software was utilized for data analysis.

NMR spectra were taken on a Bruker 300-DPX spectrometer at ambient temperature (^{1}H NMR,

300 MHz). Centrifugation of samples was performed on an Eppendorf 5000 series centrifuge.

General Procedure for NMP Polymerization of Acrylate and Alkene Monomers

In an N_2-filled glovebox, a desired amount of 1-alkene and butyl acrylate (see Table 1) were

combined with TCE (0.5 g, 3.8 mmol), **1** (0.1 g, 0.306 mmol), **2** (6.7 mg, 0.0306 mmol), and

approximately 5 mL of dry chlorobenzene in a 20 mL scintillation vial. Al_2O_3 (0.4 g, 3.9 mmol)

was added where applicable. The vial was sealed and allowed to stir for 72 h at 120 °C. A small

amount of the solution mixture was removed at each of 0 h, 2 h, 4 h, 6.5 h, 9.5 h, 24 h, and 48 h

and subsumed in methanol to stop polymerization and to allow for accurate GC and GPC

analysis. Polymer samples in methanol were precipitated with a small amount of H_2O and

collected by centrifugation at 3000 rpm for 7 min. Samples were transferred with

dichloromethane and dried under high vacuum overnight.

Sythesis of Poly(Butyl Acrylate) and Block Copolymer to Demonstrate "Living" Character

In an N_2-filled glovebox, butyl acrylate (3.20 g, 25 mmol) was combined with **1** (32.5 mg, 0.1

mmol) and **2** (1.1 mg, 5 μmol) in a 20 mL scintillation vial. The vial was sealed and allowed to

stir for 16 h at 125 °C. The liquid product was precipitated with methanol and collected by

centrifugation at 8000 rpm for 8 min. The sample was transferred with dichloromethane and

dried under high vacuum overnight to give Poly(Butyl Acrylate) as a clear, viscous product. ^{1}H

NMR (300 MHz, CDCl$_3$) δ 4.05 (s, 2H), 1.5 (m, 10H). A portion of the butyl acrylate obtained

(0.2 g, 8.5 μmol) was transferred back to the glovebox to serve as the starting block. To this

mixture, butyl acrylate (0.256 g, 2.0 mmol) and 1-decene (1.0 mmol) were added. The reaction

mixture was sealed and allowed to stir for 8 h at 125 °C. The product was precipitated with

methanol, centrifuged at 8000 rpm for 8 min, collected with dichloromethane, and allowed to dry under high vacuum overnight to afford a clear solid product. The polymer was analyzed via gel permeation chromatography; molecular weight distribution traces were compared between the original Poly(BA) and the presumed block copolymer to determine success of the polymerization.

Chapter 3: **Results and Discussion**

Table 1 displays the ratios and identities of acrylate and alkene monomers used in each trial, as well as the data obtained, via GC and GPC analysis, on the conversion of butyl acrylate monomer, the number average molecular weights, and the polydispersity indices of the final polymers. In addition, the percent olefin/alkene incorporation into each polymer, obtained from ^{1}H NMR data as described below, is listed.

Table 1. Proportions and Identities of Reagents Used and Polymer Data[a]

| Olefin Monomer	Butyl Acrylate (g)	Al_2O_3 (g)	BA Converted (%)	M_n (10^3)[b]	M_w/M_n[b]	Olefin Incorporation (%)
1-Decene (1.1 g)	2.5	0	33	4.9	1.23	11.4
1-Decene (1.1 g)	2.5	0.4	44	5.2	1.27	12.0
1-Decene (2.0 g)	1.5	0	56	4.6	1.42	19.9
1-Octene (1.1 g)	2.5	0	42	4.6	1.42	11.8

[a]Conditions: TCE, 0.5 g; **1** 0.1 g; **2** 6.7 mg; chlorobenzene 5 mL; 120 °C; 72 h.

[b]By GPC relative to polystyrene standards. M_n is the number-average molecular weight; M_w is the weight-average molecular weight; PDI (Polydispersity Index) = M_w/M_n

Butyl Acrylate conversion percentages were found using areas under the curve of gas chromatographs at different time intervals during polymer formation. For each time period, the butyl acrylate peak area was divided by the area of the TCE standard. The differences between the initial result (with all monomer present), at 0 h, and subsequent results were used to calculate the percentage conversion at each time interval. The percentage listed in Table 1 is that calculated for the final polymer product at 72 h. As expected, copolymer number three on the list, with a higher ratio of decene to butyl acrylate, shows a higher acrylate conversion percentage, correlating with higher decene conversion.

The polydispersities listed for all the polymers in the table are somewhat high for "living" polymerizations, but they are nonetheless below the theoretical lower limit of a traditional radical polymerization, 1.5. It is likely, then, that the polymers have some living character.

Figure 7 depicts the relationship of molecular weights and polydispersity with the moles of butyl acrylate converted for the 2.5 g BA/1.1 g 1-decene copolymer. The linear increase in M_n along with the moles of monomer converted is characteristic of straight, nonbranching propagating chains and thus provides evidence of living character. If the polymerization were not living, the M_n plot would be much more skewed from random chain transfers and terminations. Additionally, the polydispersity index, M_w/M_n, begins low and stays much the same as more moles of monomer are converted. In an uncontrolled polymerization, chain lengths tend to become more unequal from branching during polymerization and PDI increases.
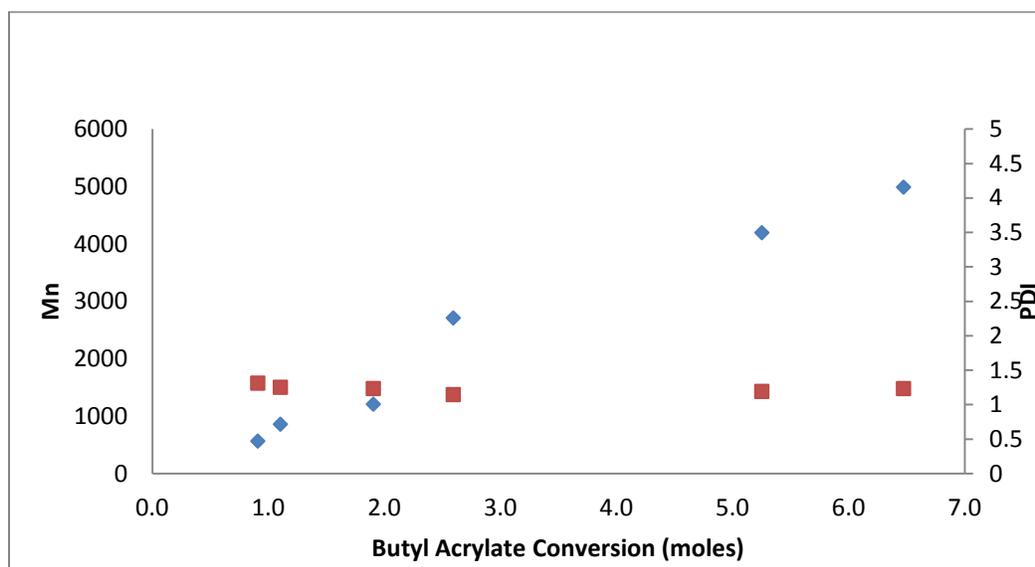

Figure 7. Dependence of Molecular Weight and Polydispersity on Moles of Butyl Acrylate Converted[a]

[a]Conditions: BA, 2.5 g; 1-decene, 1.1 g; TCE, 0.5 g; **1** 0.1 g; **2** 6.7 mg; chlorobenzene 5 mL; 120 °C.

Figure 8 is a kinetic plot of the natural log of butyl acrylate monomer concentration at time zero over the concentration of the monomer at a specific later time. As butyl acrylate

monomer is used up (M decreases) via incorporation into the polymer, $Ln(M_0/M)$ increases. The

linearity of the increase indicates that the copolymerization follows first order kinetics (i.e., rate

dependent only on the concentration of the monomer in question), a criterion for living

polymerization.
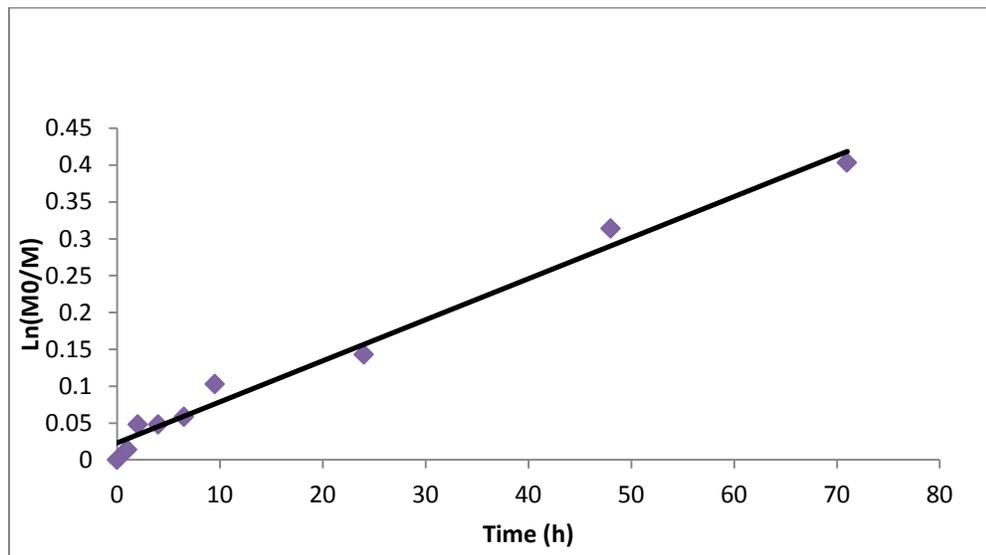
Figure 8. $Ln([M]_0/[M])$ (where $[M]_0$ is the initial monomer concentration and $[M]$ is the

monomer concentration) Vs. Reaction Time for the Copolymerization of BA/1-Decene[a]

[a]Conditions: BA, 2.5 g; 1-decene, 1.1 g; TCE, 0.5 g; **1** 0.1 g; **2** 6.7 mg; chlorobenzene 5 mL; 120 °C.

Figure 9 shows a ^{1}H NMR spectrum of the 2.5 g BA/1.1 g 1-decene copolymer.

$$\frac{Decene}{BA} = \frac{(12.566-10)/20}{1} = 0.1283$$

$$\% \, BA = \frac{1}{1.1283} = 0.886$$
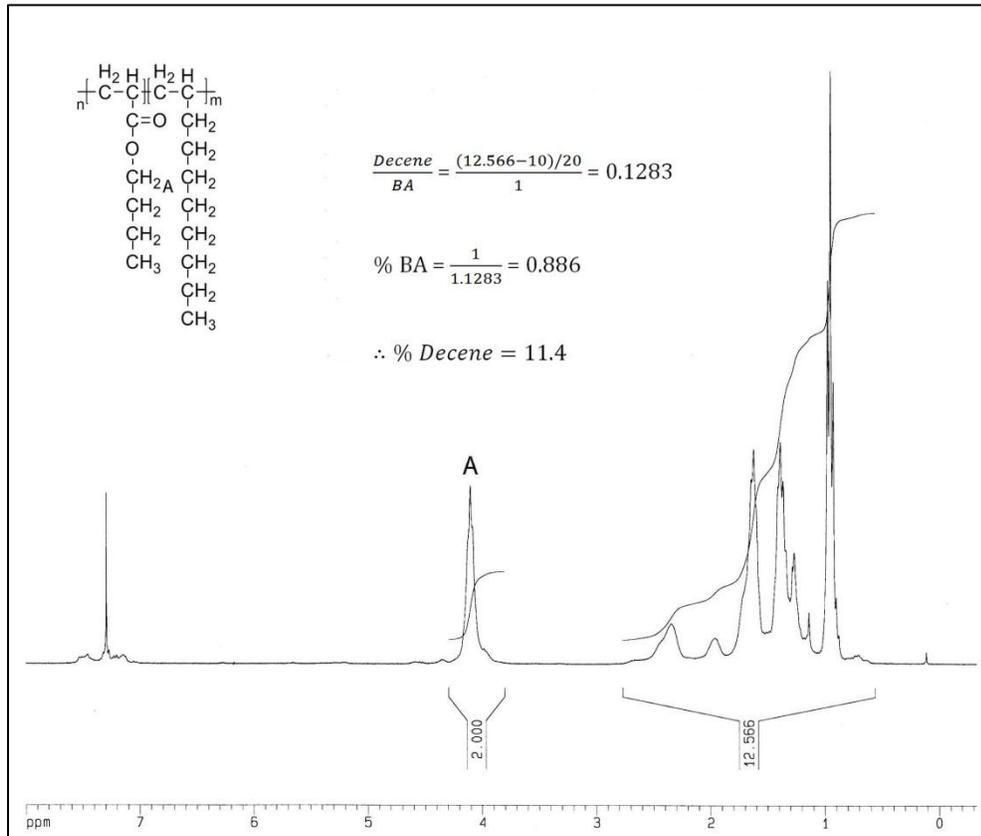
$$\therefore \% \, Decene = 11.4$$

Figure 9. ^{1}H NMR Spectrum of BA/1-Decene Copolymer[a]

[a]Conditions: BA, 2.5 g; 1-decene, 1.1 g; TCE, 0.5 g; **1** 0.1 g; **2** 6.7 mg; chlorobenzene 5 mL; 120 °C.

The composition of each copolymer—specifically the 1-alkene incorporation—was determined by comparing, using ^{1}H NMR, the integrations of the methoxy protons vs. all other aliphatic protons in the polymer. As seen in Figure 9, the downfield resonance close to 4 ppm was characterized as representing the two methoxy protons of the butyl acrylate subunits and was calibrated to 2.0. The rest of the protons between the acrylate and alkene units of the polymer are represented by the upfield multiplet (in this case, integration = 12.566). Therefore, the ratio of decene to butyl acrylate can be described by the quantity of the total integration of the area (12.566) minus the non-methoxy butyl acrylate protons (10) divided by the total number of decene protons (20). The number obtained from this calculation is the fractional number of

decene protons per butyl acrylate proton in the polymer. Accordingly, the percentage of decene in the polymer is one minus butyl acrylate protons/total protons (or the percent BA).

In this case, the calculated 1-decene incorporation was 11.4 percent. This is not an insignificant percent, as butyl acrylate propagating radicals and butyl acrylate monomers tend to to react over butyl acrylate propagating radicals and alkene monomers. Again, acrylate monomers have been shown previously to be highly reactive in traditional radical procedures whereas 1-alkene monomers are nonreactive. Hence, an incorporation of 11.4% alkene into the polymer using a radical procedure is a success.

Figure 10 represents a plot of the dependence of molecular weight and polydispersity on moles of butyl acrylate converted for the copolymer of 2.5 g BA/1.1 g 1-decene with added Lewis Acid. The plot similarly shows a low, non-increasing PDI and a linearly increasing molecular weight with moles of monomer converted. Again, both are indicative of living character.
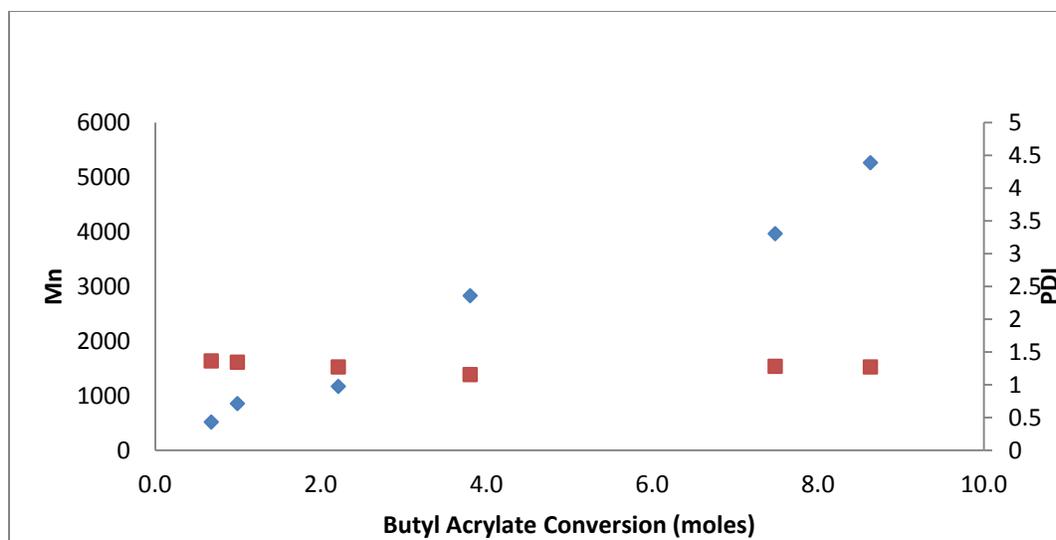
Figure 10. Dependence of Molecular Weight and Polydispersity on Moles of Butyl Acrylate Converted[a]

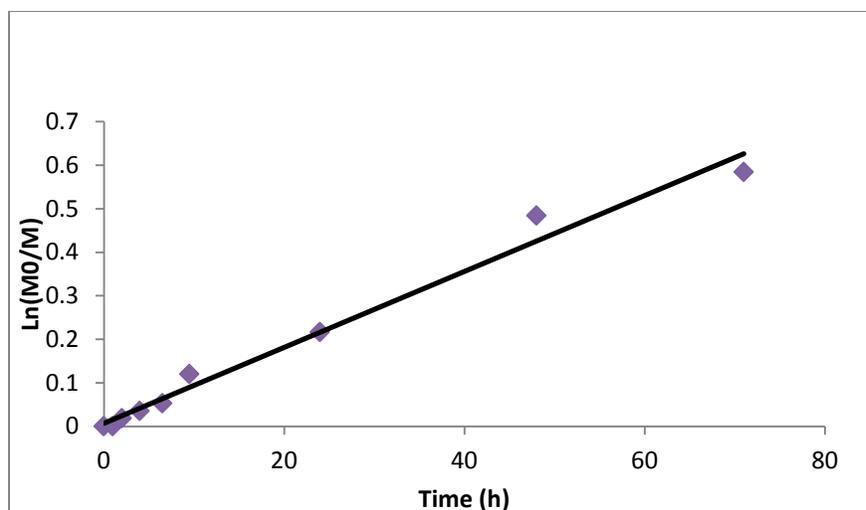[a]Conditions: BA, 2.5 g; 1-decene, 1.1 g; Al$_2$O$_3$, 0.4 g; TCE, 0.5 g; **1** 0.1 g; **2** 6.7 mg; chlorobenzene 5 mL; 120 °C.

Interestingly, Figure 11 is a kinetic plot that provides evidence of living character for reasons cited previously. However, Figure 11 differs from Figure 8 in that it shows a butyl acrylate concentration that decreases more rapidly (i.e., ln(M$_0$/M) increases faster) compared to the first polymer. Thus, the slope of Figure 8 is 5.6 x 10^{-3} h^{-1}, while the slope of Figure 11 is 8.7 x 10^{-3} h^{-1}. As such, the final value of Ln(M$_0$/M) is larger for the BA/decene polymer with added Lewis acid (around 0.6 vs. 0.4). One can infer, then, that the addition of Lewis acid increases the rate of polymerization, as with traditional uncontrolled radical polymerizations.

Figure 11. Ln($[M]_0/[M]$) (where $[M]_0$ is the initial monomer concentration and $[M]$ is the monomer concentration) Vs. Reaction Time for the Copolymerization of BA/1-Decene with Lewis Acid[a]

[a]Conditions: BA, 2.5 g; 1-decene, 1.1 g; Al$_2$O$_3$, 0.4 g; TCE, 0.5 g; **1** 0.1 g; **2** 6.7 mg; chlorobenzene 5 mL; 120 °C.

The increased rate of reaction can be explained using FMO-based arguments regarding radical addition selectivity. In general, alkyl radicals reacting with alkenes can display either nucleophilic or electrophilic character, depending on the nature of substituent groups on the molecules. When electron withdrawing groups are present in the radical species, the energy of the Singly Occupied Molecular Orbital (SOMO) is decreased, allowing for greater interaction with the alkene Highest Occupied Molecular Orbital (HOMO). Thus, the radical can be described as having more electrophilic character.[41] In this case, the acrylate radicals display more electrophilic character from the electron withdrawing effects of the ester.

As was previously discussed, the coordination of the Lewis Acid with carbonyl of the acrylate monomer reduces the electron density of conjugated double bond and subsequent radical species. Therefore, the SOMO of the Lewis Acid coordinated acrylate radical is further lowered

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in energy and can interact more strongly with the alkene HOMO than that of the uncoordinated acrylate radical. The increased rate of polymerization is the observable effect of this interaction.

The ^{1}H NMR spectrum of the Lewis Acid mediated copolymer is represented by Figure 12. The 1-decene incorporation percent is calculated in the aforementioned manner. The percentage obtained, 12.0, is only marginally (negligibly) higher than that for the copolymer synthesized without Al_2O_3 (11.4%). That there is little difference between the two values for incorporation may be due to the interference of the coordination between the acrylate ester and the Lewis Acid by the nitroxide or nitroxide-bound dormant chain.

$$\frac{Decene}{BA} = \frac{(12.725-10)/20}{1} = 0.13625$$

$$\% \ BA = \frac{1}{1.13625} = 0.880$$

$$\therefore \% \ Decene = 12.0$$

Figure 12. 1H NMR Spectrum of BA/1-Decene Copolymer with Added Lewis Acid, Al_2O_3[a]

[a]Conditions: BA, 2.5 g; 1-decene, 1.1 g; Al_2O_3, 0.4 g; TCE, 0.5 g; **1** 0.1 g; **2** 6.7 mg; chlorobenzene 5 mL; 120 °C.

Figure 13 depicts the dependence of molecular weight and PDI on the moles of acrylate monomer converted for the 1.5 g BA/2.0 g 1-decene copolymer. Although the relationship between molecular weight and BA conversion is not quite as linear as in the previous examples, it nonetheless likely shows some living character.
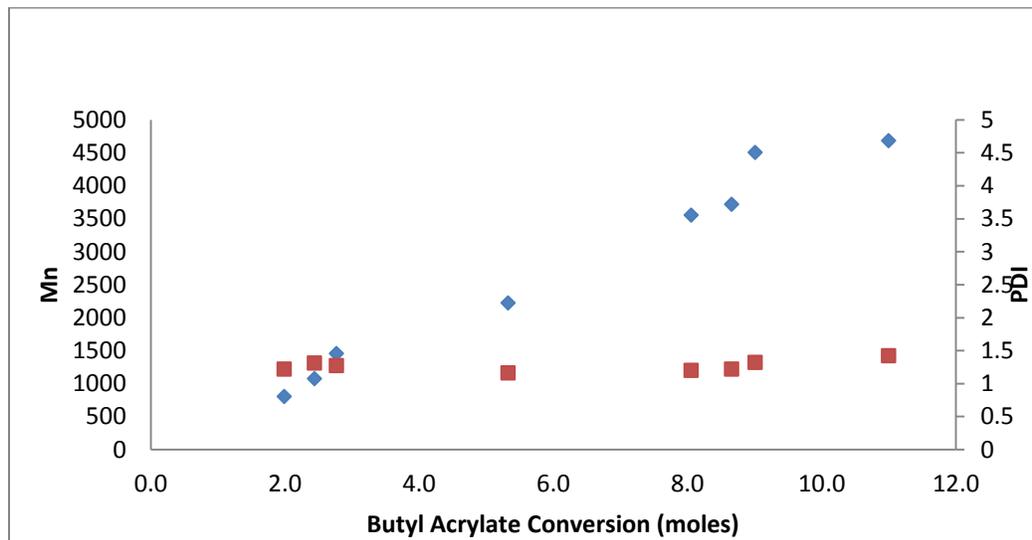
Figure 13. Dependence of Molecular Weight and Polydispersity on Moles of Butyl Acrylate Converted[a]

[a]Conditions: BA, 1.5 g; 1-decene, 2.0 g; TCE, 0.5 g; **1** 0.1 g; **2** 6.7 mg; chlorobenzene 5 mL; 120 °C.

A kinetic plot of the natural log of the initial butyl acrylate concentration divided by the present concentration vs. time is presented in Figure 14. This plot is linear, displaying first order kinetics and living character. Here, the butyl acrylate concentration decreases much more rapidly compared to the initial polymer, with an $Ln(M_0/M)$ of 0.6 after only 30 h. The reason for this observation may be that the incorporation of BA into the polymer is occurring at roughly the same absolute rate as the 2.5 g BA/1.1 g 1-decene copolymer. However, because there is much less initial acrylate in the feed, it decreases proportionally much faster.
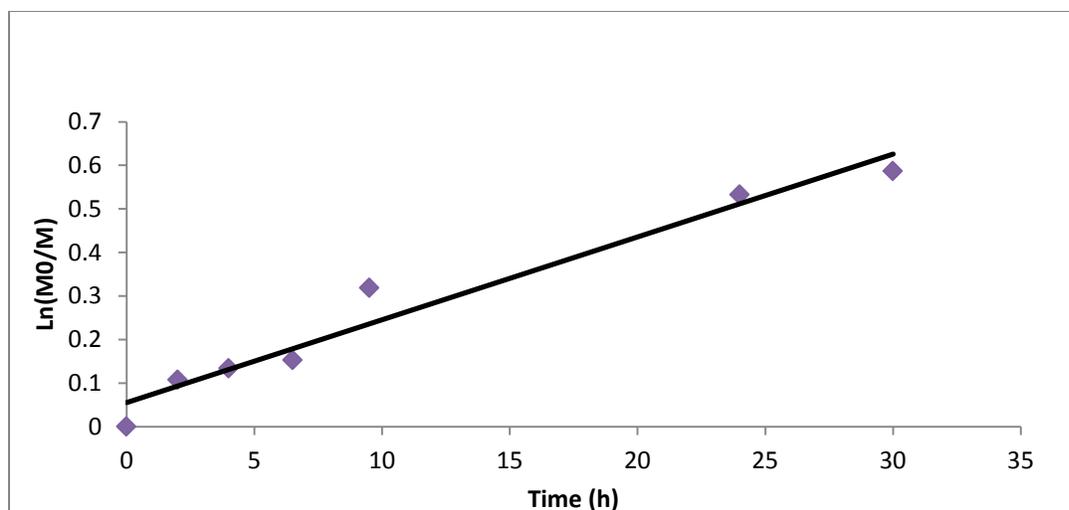
Figure 14. Ln($[M]_0$/[M]) (where $[M]_0$ is the initial monomer concentration and [M] is the

monomer concentration) Vs. Reaction Time for the Copolymerization of BA/1-Decene[a]

[a]Conditions: BA, 1.5 g; 1-decene, 2.0 g; TCE, 0.5 g; **1** 0.1 g; **2** 6.7 mg; chlorobenzene 5 mL; 120 °C.

Figure 15 depicts the 1H NMR spectrum of the 1.5 g BA/2.0 g 1-decene copolymer.
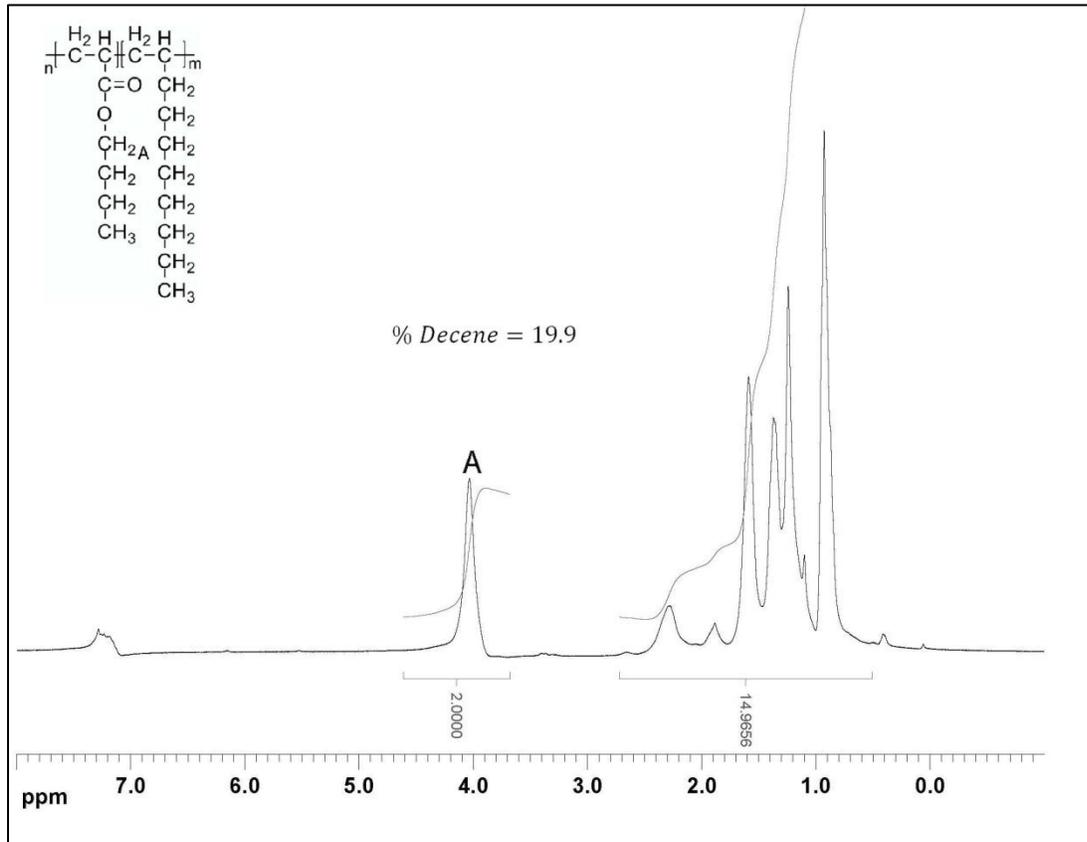
Figure 15. ^{1}H NMR Spectrum of BA/1-Decene Copolymer[a]

[a]Conditions: BA, 1.5 g; 1-decene, 2.0 g; TCE, 0.5 g; **1** 0.1 g; **2** 6.7 mg; chlorobenzene 5 mL; 120 °C.

A large increase in 1-decene incorporation can be seen in Figure 15 as compared to that of the original monomer. As has been stated previously, acrylates are much more reactive in traditional radical polymerization than alkenes. Therefore, acrylate propagating radicals should react preferentially with acrylate monomers over olefin monomers in this system. However, when there is less BA and greater 1-decene monomer present, the incorporation of decene into the polymer is increased.

Since poly(1-Decene) does not form to a significant extent under these radical conditions, it stands to reason that the 1-decene incorporation in the copolymer can be increased further by using higher proportions of 1-decene in the monomer feeds. More experiments should be

performed to determine the monomer ratio for achieving the best alkene incorporation while keeping molecular weight acceptably high.
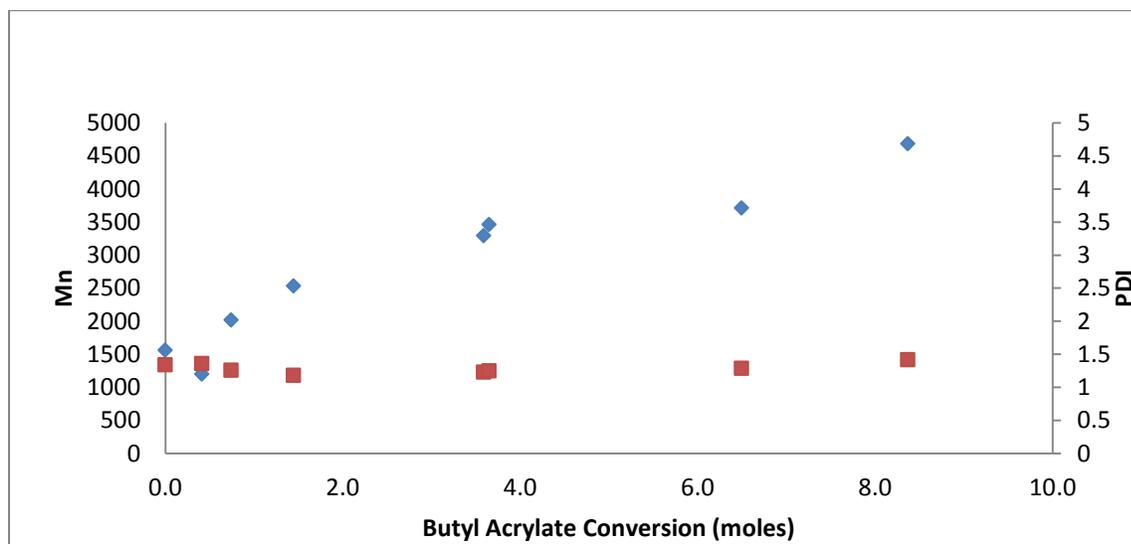
Figure 16. Dependence of Molecular Weight and Polydispersity on Moles of Butyl Acrylate Converted[a]

[a]Conditions: BA, 2.5 g; 1-octene, 1.1 g; TCE, 0.5 g; **1** 0.1 g; **2** 6.7 mg; chlorobenzene 5 mL; 120 °C.

Figure 16 represents the dependence of the MW and PDI on the moles of butyl acrylate monomer converted. In this case, the plot is slightly less linear than the initial 1-decene polymer plot, although it may still exhibit some living character. Moreover, although the polydispersity remains low throughout the polymerization, it is still somewhat high at the outset. Nevertheless, there doesn't seem to any objective reason, per se, why 1-octene would be less suitable for nitroxide mediated living polymerization than 1-decene. Therefore, any deviations from linearity more so than those found in the first 1-decene polymer plot can likely be attributed to experimental error.
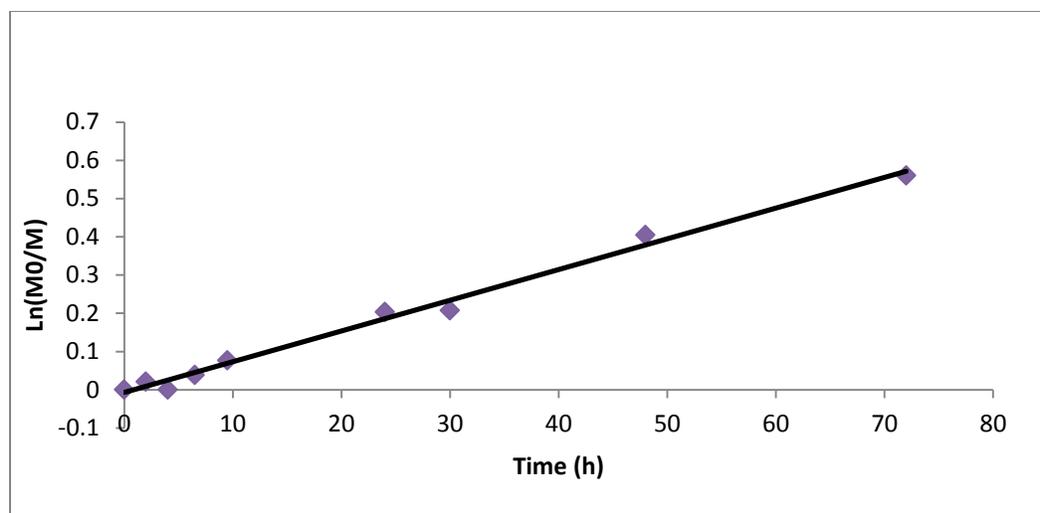
Figure 17. Ln($[M]_0/[M]$) (where $[M]_0$ is the initial monomer concentration and $[M]$ is the monomer concentration) Vs. Reaction Time for the Copolymerization of BA/1-octene[a]

[a]Conditions: BA, 2.5 g; 1-octene, 1.1 g; TCE, 0.5 g; **1** 0.1 g; **2** 6.7 mg; chlorobenzene 5 mL; 120 °C.

Intriguingly, the polymerization rate (as related to the rate of disappearance of butyl acrylate) is higher for the general 1-octene/butyl acrylate copolymer compared to the general 1-decene/butyl acrylate copolymer (in fact, the rate is similar to that obtained from the copolymerization of 1-decene/BA with Lewis acid). The reasons for this increase are not especially clear and, again, may be attributable to experimental error.

$$\frac{Octene}{BA} = \frac{(12.1417-10)/16}{1} = 0.134$$

$$\% \, BA = \frac{1}{1.134} = 0.882$$
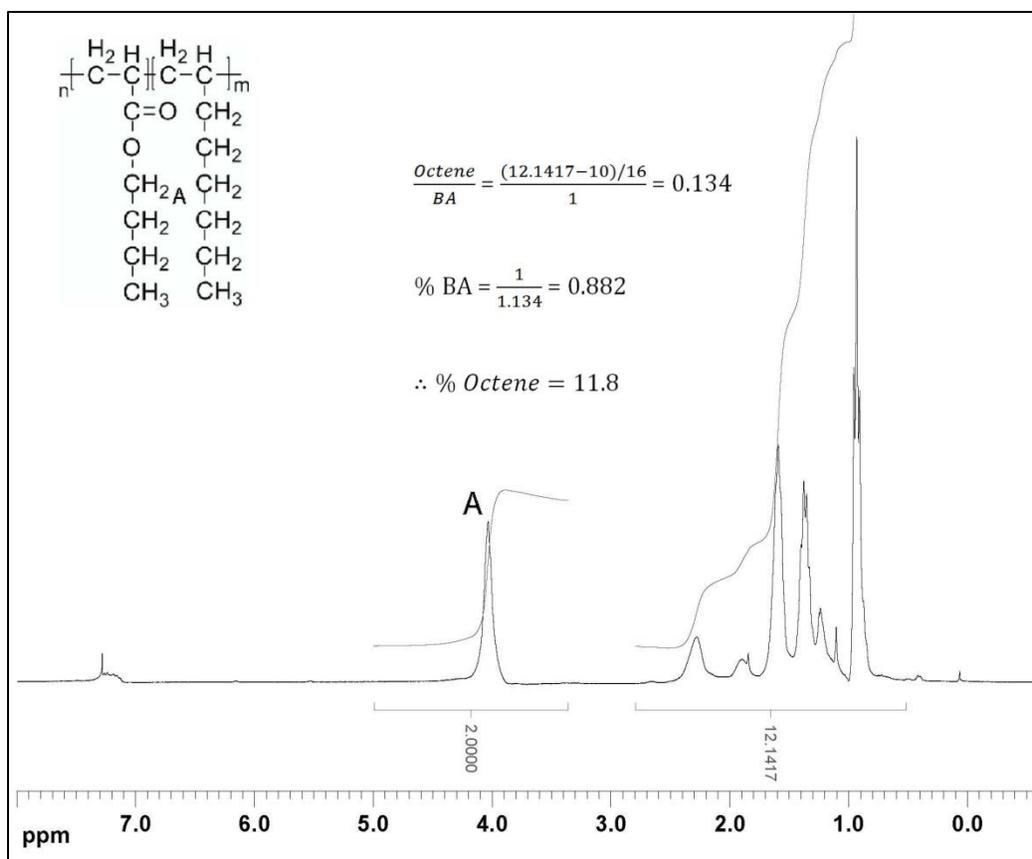
$$\therefore \% \, Octene = 11.8$$

Figure 18. ^{1}H NMR Spectrum of BA/1-Octene Copolymer[a]

[a]Conditions: BA, 2.5 g; 1-octene, 1.1 g; TCE, 0.5 g; **1** 0.1 g; **2** 6.7 mg; chlorobenzene 5 mL; 120 °C.

Again, the 1-alkene incorporation described in Figure 18 is comparable to those obtained with 1-decene copolymers. The procedure for calculating the percentage of octene in the copolymer remains roughly the same, although the octene contribution to the aliphatic resonances must be divided by 16 rather than 20, as 1-octene has four fewer protons than 1-decene. The alkene incorporation rate between the BA/octene and analogous BA/decene copolymers is likely similar because the physical size difference between the two polymers is small enough that it has little or no impact on the incorporation.

In conclusion, the evidence presented suggests that the "living" radical polymerization method using TIPNO as the mediating nitroxide has been successfully applied to a copolymerization of acrylates and alkenes. This system provides a method for synthesizing

various acrylates and alkenes with strong control over the polymer product and acceptably high alkene incorporation. Most of the polymers synthesized had strong linear relationships between their molecular weights and monomer conversions. Furthermore, this research provides evidence that the Lewis acids used to increase polymerization rate and alkene incorporation in traditional uncontrolled radical polymerization methods are ineffective or only marginally effective in this system.

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Paul Chiarulli
17 Chapel Ridge Rd.
Pittsburgh, PA 15238
pec5019@psu.edu

Education:
  The Pennsylvania State University, Schreyer Honors College
    University Park, PA 16802
    Bachelor of Science Degree in Chemistry, Fall 2010
    Minor in Art History
    Honors in Chemistry
    Thesis Title: Nitroxide Mediated "Living" Polymerization of Acrylates and Alkenes
    Supervisor: Ayusman Sen

Related Projects:
  Synthesis of (E)-(2'-acetoxyethyl)-3,4,5-trimethoxycinnamate (Fall 2008)
      ▪ Designed a concise synthesis of an isolated natural product cinnamic ester
      ▪ Utilized an inexpensive cinnamic acid starting material
  Organometallic Catalyst Syntheses (Summer-Fall 2008)
      ▪ Helped synthesize palladium catalysts for the copolymerization of ethylene and carbon monoxide

Work/Volunteer Experience:
  Sen Research Group (June 2008-2010)
      ▪ The Pennsylvania State University
      ▪ Undergraduate Researcher
      ▪ Synthesized acrylate/alkene copolymers using traditional radical and "living" pathways
      ▪ Made use of GC, GPC, and NMR apparatuses for synthetic analyses
  Hartley Ecology Research Group (June-August 2009)
      ▪ University of Sussex, Sussex, United Kingdom
      ▪ Investigated mycorrhizal effects on silica-based plant defenses
      ▪ Calibrated and operated an XRF spectrophotometer for analysis of plant samples
  Chau Hiix Archaeological Project (June 2007)
      ▪ Belize, Central America
      ▪ Excavator, Lithics Analyst
      ▪ Aided in excavations of Mayan dig sites
      ▪ Facilitated lithic (e.g. stone tool) analysis

Notable Honors and Activities:
  Phi Beta Kappa Honors Society (inducted 2010)
      ▪ Membership awarded for high intellectual achievement in the liberal arts and sciences
  Amnesty International Penn State (2007-2010)
      ▪ Various officer positions