POLYPROPYLENE THERMOSETS BY FUNCTIONAL NITROXYL-MEDIATED RADICAL CROSSLINKING

by

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Abstract

New chemistry for preparing polypropylene (PP) thermosets is described, wherein radical degradation suffered during conventional peroxide treatment is overcome using a nitroxyl additive bearing a polymerizable functional group. A small amount of 4-vinylbenzoic-2,2,6,6-tetramethylpiperidin-N-oxyl (VBTEMPO) is used to trap peroxide-derived, alkyl radical intermediates during the early stages of the modification process, yielding a macromonomer derivative *in situ* that crosslinks in the later stages through side-chain oligomerization. This process has proven capable of producing thermosets with gel contents in excess of 90%, while providing the induction period needed to shape the formulation before it rendered thermoset. Control over PP crosslinking dynamics and yields have been gained by appropriate selection of peroxide initiator, polymerizable functional structure, and additional cure formulation components. The thesis concludes with preliminary assessments of the stability of PP-derived alkoxyamines, and their potential to confer oxidative stability to a thermoset.

Acknowledgements

I'd like to thank my supervisor Dr. J. Scott Parent for his continuous guidance and support throughout my degree and valuable advice concerning life, perspectives, and responsibilities. I would also like to thank all my lab mates, especially Christopher Twigg, Michael Bodley, and Stu Bacon for their time and patience working with me. I extend a special gratitude for all other co-workers and friends I spent time with inside and outside of the lab, who truly made my time here enjoyable and memorable. After nearly six years attending Queen's University I can honestly say that the experiences here have changed me into the person I am today, as I try to continue to grow and learn from all things in life every day. Last but not least, I extend my sincerest thanks for my parents and sister who have been there for me since day one, there's no way I could have done any of this without them.

Table of Contents

Abstract ii

Acknowledgements iii

Chapter 1 : Introduction 1

1.1 Crosslinking Fundamentals 1

1.2 Peroxide Initiated Curing: Dynamics and Yields 2

1.3 Nitroxyl Mediated Curing 7

1.4 Scissionable Polymers 12

1.5 Alkoxyamine Stability 13

1.6 Anti-oxidative Abilities of Alkoxyamines and Nitroxyls 15

1.7 Research Objectives 18

Chapter 2 : Functionalized TEMPO- Mediated PP Curing 19

2.1 Introduction 19

2.2 Materials and Methods 20

2.2.1 Materials 20

2.2.2 Instrumentation and Analysis 23

2.3 Results and Discussion 23

2.3.1 VBTEMPO Dynamics and Yields 23

2.3.2 Influence of Peroxide Initiator 31

2.3.3 Influence of Monomer Structure 32

2.3.4 Synergy with Multifunctional Monomers 35

2.4 Conclusion 37

Chapter 3 : Alkoxyamine Instability and its Implications for PP Modification and Oxidative Stabilization 38

3.1 Introduction 38

3.2 Materials and Methods 40
3.2.1 Materials 40
3.2.2 Thermal Decomposition Model Compound 41
3.2.3 Thermal Decomposition $PP_{atactic}$-g-TEMPO 42
3.2.4 Accelerated PP Oxidation 43
3.3 Results and Discussion 44
3.3.1 Alkoxyamine Stability 44
3.3.2 Accelerated Oxidation of PP-g-TEMPO 51
3.4 Conclusion 53
Chapter 4 : Conclusions and Future Work 55
4.1 Conclusions 55
4.2 Future Work 56
References 58
Appendix A: Characterization of new functionalized nitroxyls 66
VBTEMPO (1a) ^{1}HNMR 66
VBATEMPO (2) ^{1}HNMR 67

List of Figures

Figure 1: Crosslinking of polymer chains to form a continuous network. 1

Figure 2: Dynamics of peroxide-initiated macromonomer crosslinking ([DCP] = 18 μmole/g) [17]. 6

Figure 3: Molecular structures of free TEMPO and AOTEMPO 9

Figure 4: DCP- initiated LLDPE crosslinking with and without AOTEMPO ([DCP] = 55.6 μmole/g; a. Storage modulus, G'; b. Cure rate dG'/dt) [16]. 10

Figure 5: Influence of nitroxyl trapping ratio on PP modification dynamics (a. TEMPO; b. VBTEMPO; [DCP] = 74 μmol/g). 27

Figure 6: Influence of peroxide initiator on VBTEMPO, PP cure dynamics ([DC] = 74 μmole/g; [L-101 = 39 μmole/g]). 32

Figure 7: Influence of polymerizable functional group on PP cure dynamics (a. TR=0.50; b. TR=0.75; [DCP] =74 μmole/g). 34

Figure 8: Influence of co-agent a. DVB with VBTEMPO and b. TMPTA with AOTEMPO on DCP-initiated PP Cure dynamics and yields ([DCP] = 74 μmole/g). 36

Figure 9: Labelled ^{1}H NMR of 4-TEMPO-2,4,6-trimethyl heptane (2) i) before and ii) after 60 min. at 100°C. Solvent d-DSMO. 46

Figure 10: ^{1}H NMR spectra of model compound disproportionation products (bottom), prior to any thermal treatment PP-g-BzOTEMPO (middle), and thermally treated PP-g-BzOTEMPO (top). Solvent $CDCl_3$. 49

Figure 11: Accelerated oxidation of PP-g-TEMPO films (100°C; P_{O2} = 5 bar; [DCP] = 74 μmole/g). 52

Figure 12: ^{1}H NMR spectrum of VBTEMPO (1a) aromatic/alkene region. Solvent $CDCl_3$. 67

Figure 13: ^{1}H NMR spectrum of VBTEMPO (1a) aromatic/alkene region. Solvent $CDCl_3$. 69

List of Abbreviations

AOTEMPO - 4-acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl

BDE - Bond Dissociation Enthalpy

Bu_3SnH - tributyltin hydride

BzOTEMPO - 4-benzoate-2,2,6,6-tetramethylpiperidine-N-oxyl

C – Carbon

C-H – carbon-hydrogen bond

C=C – carbon-carbon double bond

C=O – carbonyl

δ – chemical shift

d-DMSO – deuterated dimethyl sulfoxide

DVB – divinylbenzene

FT-IR - Fourier-transform-infra-red spectrometry

G' – storage modulus

^{1}H NMR – proton nuclear magnetic resonance

h – hours

H – Hydrogen

H-abs - Hydrogen atom abstraction

IIR - poly(isobutylene-co-isoprene)

J_x – coupling constant

k_d - first-order rate constant for peroxide decomposition

LLDPE – linear low density polyethylene

min – minutes

mp – mlething point

MW – molecular weight

L-101 - 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane

L-231 - 1,1-Bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane

N – Nitrogen

N_2 – nitrogen gas

NMR – nuclear magnetic resonance

O – oygen

PE – Polyethylene

PIB – polyisobutylene

PP – Polypropylene

ppm – parts per million

1° - primary

R – R group substituent

ROOH – hydroperoxides

2° - secondary

TEMPH - 2,2,6,6-tetranethylpiperidine

TEMPO - 2,2,6,6-tetramethylpiperidine-N-oxyl

TEMPOH - 4-hydroxy-2,2,6,6-tetramethylpiperdin-1-oxyl

TEMPOR - 1-alkoxy-2,2,6,6-tetramethyl-4-piperidine

3° - tertiary

t_{ind} – induction time

$t_{1/2}$ – half life

TLC - thin-layer chromatography

TMIO - 1,1,3,3-tetramethylisoindolin-2-oxyl

TMPTA - trimethylolpropane triacrylate

TR – trapping ratio

VBTEMPO - 4-vinylbenzoic-2,2,6,6-tetramethylpiperidin-N-oxyl

List of Schemes

Scheme 1: Idealized reaction mechanism for peroxide initiated curing of polyethylene (PE). 3

Scheme 2: Idealized reaction mechanism for AOTEMPO-mediated LLDPE curing. 11

Scheme 3: β-chain scission mechanism of tertiary radicals in PP. 12

Scheme 4: Main reactions that a polystyrene-TEMPO Adduct can make at high temperatures: (a) Reversible Dissociation; (b) Decomposition (β-H-abs); (c) Bialkyl Combination (Termination) [30]. 14

Scheme 5: Formation on unsaturation and hydroxylamine in TEMPO grafted PP during processing conditions. 15

Scheme 6 : Simplified Denisov Cycle [36]. 17

Scheme 7: Idealized three phase mechanism for VBTEMPO-mediated PP crosslinking. 25

Scheme 8: Disproportionation of 4-TEMPO-2,4,6-trimethyl heptane (2). 45

Scheme 9: Potential products of nitroxyl trapping of PP-derived macroradicals. 48

Scheme 10: Speculative formation of allylic alkoxyamines in PP at slow grafting conditions. 50

Scheme 11: Molecular structure of VBTEMPO (1a) with ^{1}H labeling corresponding to ^{1}HNMR. 66

Scheme 12: Molecular structure of VBATEMPO (2) with ^{1}H labeling corresponding to ^{1}HNMR. 68

List of Tables

Table 1: PP-bound alkoxyamine content as a function of time at various decomposition temperatures. 47

Chapter 1: Introduction

1.1 Crosslinking Fundamentals

Chemical modification of polyolefins is a class of industrial processes that are used widely to improve thermomechanical properties. A key example is peroxide crosslinking, which transforms a thermoplastic material into a thermoset derivative, thereby improving properties such as heat distortion temperature, chemical resistance and elasticity [1]. While the polymer chains in a thermoplastic can snake through their entanglements when subjected to a static load, the crosslinked network of polymer chains in a thermoset resist these stress relaxation processes (Figure 1). The result is an article that is much more creep resistant [2].

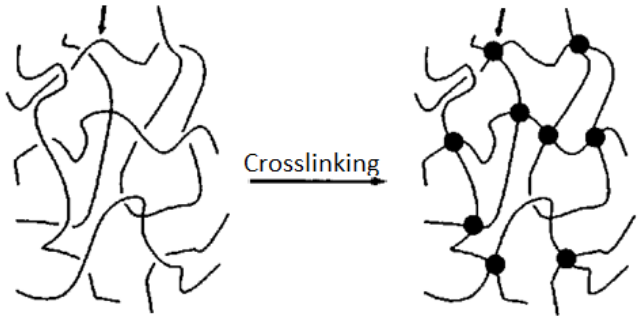


Figure 1: Crosslinking of polymer chains to form a continuous network.

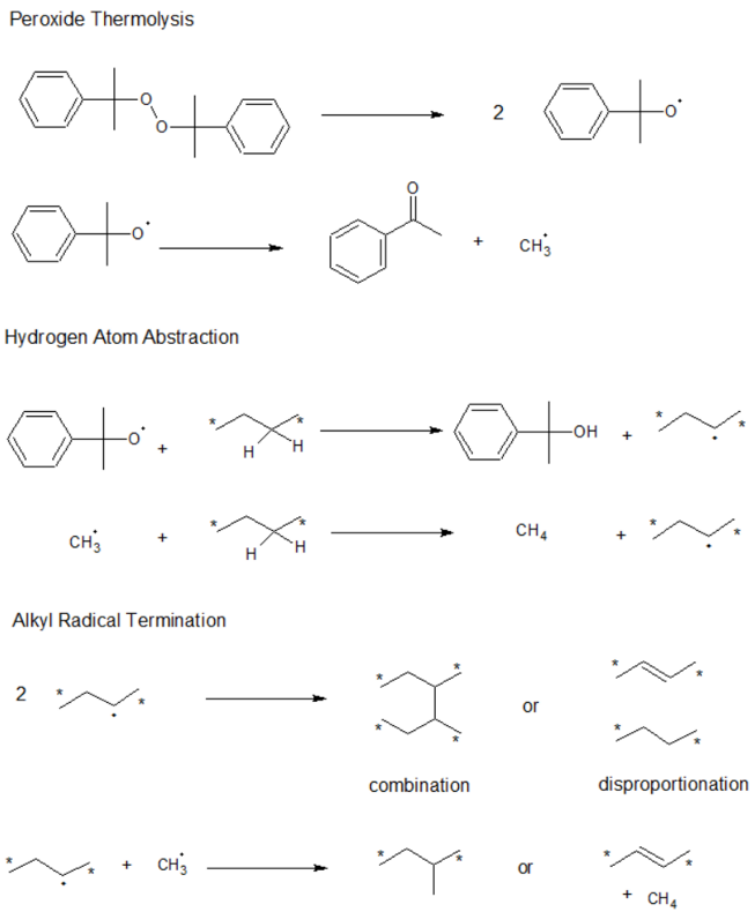
Crosslinking processes, also known as vulcanization or curing, employ a wide range of ionic and radical chemistry, the selection of which depends on the polymer structure and the specific field of use. Sulfur cures of unsaturated polymers are widely used to produce elastomeric thermosets with exceptional dynamic properties and flex fatigue resistance. These desirable properties stem from the labile nature of the polysulfide bonds that comprise the polymer network, but it also compromises heat resistance of sulfur-cured products [3] [4]. In addition, sulfur-based

formulations generally require organic accelerators and zinc complexes to improve crosslinking rates and yields, which leave objectionable byproducts in the crosslinked article.

An alternate technology that does not produce toxic cure residues is based on peroxide-initiated radical chemistry. The crosslink network generated by these formulations is comprised of carbon-carbon bonds that demonstrate remarkable temperature and creep resistance, making them ideal for severe service applications such as engine mounts and organic fluid delivery systems. Furthermore, this chemistry can engage both saturated and unsaturated polymers, unlike sulfur crosslinking that can only affect materials containing unsaturation (C=C) [1].

1.2 Peroxide Initiated Curing: Dynamics and Yields

Radical crosslinking processes feature thermolysis of peroxide bonds when the formulation is heated, giving alkoxy radical intermediates. Hydrogen-atom abstraction (H-abs) from the polymer generates alcohol and the required macroradicals [5], whose termination by combination produces the desired crosslink (Scheme 1). The process has no kinetic chain character, meaning the number of carbon-carbon (C-C) crosslinks cannot exceed the number of moles of initiator in the formulation, and the crosslink density of the product scales linearly with the peroxide loading. Inefficiencies arise from H-atom transfer rates of alkoxyl radicals and the macroradical termination preferences for combination versus disproportionation [6].



Scheme 1: Idealized reaction mechanism for peroxide initiated curing of polyethylene (PE).

The dynamics of peroxide cures are dictated by the rate of peroxide thermolysis at the specific reaction temperature. This stems from the transient nature of radical intermediates whose diffusion-controlled termination rate constants are on the order of 10^{8}-10^{9} $M^{-1}s^{-1}$, calculated from model compounds in solution [7], result in lifetimes on the order of milliseconds. Since peroxide breakdown is much slower, it serves as the rate determining step [8]. Peroxide decomposition is a

first order reaction, meaning that crosslinking rates are highest in the initial stages, and decline exponentially toward zero as the initiator is consumed.

The central role of H-abs in polyolefin crosslinking has motivated careful studies of its efficiency and regioselectivity. Direct measurement of peroxide by-products is a simple means of assessing the H-atom transfer reactivity of a given polymer. For example, decomposition of dicumyl peroxide (DCP) in a hydrocarbon will generate cumyl alcohol and acetophenone as byproducts of H-abs and cumyloxyl fragmentation, respectively (Scheme 1) [9]. Since the rate of cumyloxyl scission to methyl radical and acetophenone is relatively constant in a non-polar medium, it can serve as a "radical clock" through which different polymer reactivity is gauged. The abstraction efficiency (AE), defined as the fraction of cumyloxy radicals that abstract a hydrogen atom follows from Equation 1 [10].

$$AE = \frac{\text{OH}}{\text{O} \quad + \quad \text{OH}} \qquad (1)$$

High AE values are indicative of reactive H-atom donors, and they differ significantly between various polyolefins. For example, Garrett et al. measured the abstraction efficiency for DCP acting at 160 °C on polyethylene (PE), polypropylene (PP) and polyisobutylene (PIB), reporting values of 0.56, 0.37, and 0.17, respectively [11]. These data are remarkable, in that the highest AE was found for the PE system, which presents only secondary C-H bonds for H-atom transfer, whereas PP provides an abundance of tertiary C-H bonds. Based on bond dissociation enthalpies,

it is expected that PP would be the more reactive hydrocarbon. This is evidence of the importance of steric effects in H-atom transfer chemistry [11] [12]. It is now generally accepted that reaction of secondary C-H bonds within PP and PIB is sterically encumbered by adjacent functionality, leading to reduced AE values than observed for PE.

The use of additives called coagents to enhance the extent of polyolefin crosslinking is a common industrial practice. These organic compounds feature multiple allylic, acrylic, styrenic, or maleimide groups [13] [14] that are designed to functionalize the polymer by C-H bond addition, and oligomerize to produce an extensive crosslink network [15]. Their effectiveness depends to a great extent on their polymer grafting efficiency, since they can only contribute to the crosslink network if bound to polymer chains. This grafting process involves macroradical addition to the C=C functionality, and can be followed by further monomer addition and/or H-abs from the polymer to terminate the graft while regenerating a polymer macroradical [16]. Since this process involves macroradical generation, it is most effective on polymers that are good H-atom donors. This presents a challenge for coagent-assisted polypropylene modifications, since PP is not particularly reactive with respect to H-atom transfer.

One means of overcoming the limited grafting potential of some polyolefins involves introducing macromonomer functionality using ionic chemistry. This has been demonstrated on isobutylene-rich elastomers wherein pendant acrylic, styrenic and maleimide groups were introduced by bromide displacement from halogenated poly(isobutylene-co-isoprene) (IIR) using the requisite carboxylate nucleophile [17]. Dakin et al. used this strategy to produce macromonomers that

cured rapidly and extensively when heated with a small amount of peroxide initiator. The cure extent varied with functional group structure, as illustrated in Figure 2 [17].

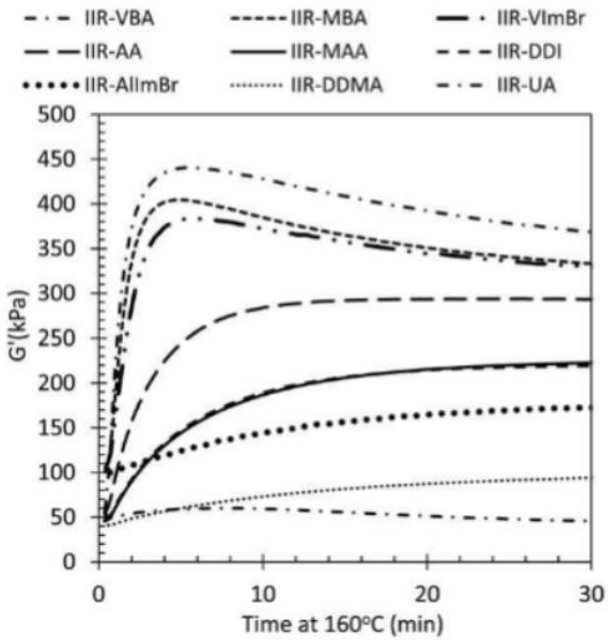


Figure 2: Dynamics of peroxide-initiated macromonomer crosslinking ([DCP] = 18 µmole/g) [17].

The cure dynamics data plotted in this figure are typical of most modern research in crosslinking chemistry. The evolution of a crosslinked network is monitored by measuring the dynamic storage modulus (G') of the formulation. Crosslinking restricts chain segment mobility, increasing polymer elasticity in proportion to the polymer network density. Therefore, G' measurements recorded at a fixed temperature, frequency, and shear strain amplitude provide real-time data on the cure extent [9]. The data plotted in Figure 2 show that a macromonomer bearing vinylbenzoate groups (IIR-VBA) produced the highest crosslink density of all the materials tested, superior to that of acrylate (IIR-AA) and vinyl imidazolium (IIR-VImBr)

functionality. While this approach to macromonomer synthesis is effective, it requires a starting material that bears a suitable electrophile. Moreover, these macromonomers crosslink very rapidly, which can be problematic for compression molding operations that require the material to assume the shape of the mold before being rendered thermoset. Therefore, chemistry that introduces macromonomer functionality from a PP homopolymer is a persistent need, as is a formulation whose cure dynamics and yields can be tailored to suite a given polymer processing operation.

Gel content measurements are a widely-reported measure of crosslink density in the thermoset literature. Gel content is defined as the weight percent of material that cannot be extracted from a sample, with linear polymers giving a zero value, and completely crosslinked thermosets yielding 100% gel. It is a measurement that is easy to acquire, readily interpreted, and sensitive when the degree of crosslinking is relatively low. Once gel contents reach 100%, the value remains unchanged even as the crosslink density increases. As such gel contents are complementary to storage modulus data, and both are used in the present study.

1.3 Nitroxyl Mediated Curing

Nitroxyls are considered to be "stable" radicals in that pure samples are stable indefinitely. Originally developed for fundamental research as traps for carbon-centered radicals [16], they found application in the polymer field as the cornerstone reagent of "controlled radical polymerization" processes. They react at the diffusion limit by combination with alkyl radicals to produce alkoxyamines whose thermal stability varies widely with alkyl substituent structure [18]

[19] [20]. In controlled radical polymerization, alkoxyamine thermolysis is required as a means of maintaining a small steady-state population of propagating macroradicals. However, in the context of polyolefin crosslinking, the goal is to trap alkyl macroradicals irreversibly. In so doing, all macroradical reactivity is suppressed to provide an induction period during which polymer molecular weight is unchanged. If the nitroxyl bears a functional group, then macroradical trapping also introduces pendant functionality to the polymer during the induction period.

The length of the induction period is a simple function of the first-order rate constant for peroxide decomposition (kd) and the nitroxyl concentration relative to the initiator concentration [20]. Assuming that peroxide thermolysis is not affected by the presence of nitroxyl, that carbon-centered radical trapping is rapid, and the resulting alkoxyamines are stable, the induction time can be predicted using:[20]

$$t_{ind} = -\frac{1}{k_d}\ln\left[1 - \frac{[Nitroxyl]}{n[Initiator]_0}\right] \quad (2)$$

in which n is the number of radicals formed per initiator molecule (n=2 for DCP). The ratio of nitroxyl to initiator-derived radicals is known as the trapping ratio (TR, Equation 3).

$$TR = \frac{[Nitroxyl]}{n[Initiator]_0} \quad (3)$$

A formulation with TR=0 contains no nitroxyl, while one with TR=1 has a sufficient radical trap population to quench all the initiator charged to the formulation.

2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) is an inexpensive, readily-available nitroxyl that is used widely in controlled radical polymerization research. Studies of its effect on peroxide cures of linear low density polyethylene (LLDPE) have demonstrated its ability to delay the cure onset to a predictable induction period. However, trapping alkyl macroradicals as alkoxyamines prohibits their combination to form crosslinks, resulting in depressed cure yields that scale with trapping ratio [21]. This inherent tradeoff between induction delay and crosslink density motivated research reported by Hyslop et al., in which nitroxyls bearing a polymerizable functional group, including 4-acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl (AOTEMPO), were employed as additives for LLDPE cure formulations [20] (Figure 3).

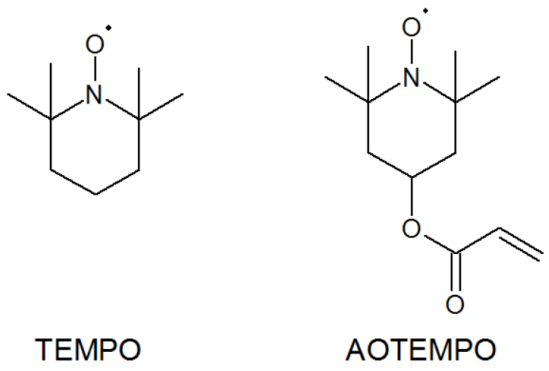


Figure 3: Molecular structures of free TEMPO and AOTEMPO

Figure 4 includes plots of storage modulus measurements illustrating the dynamics and yields of DCP-initiated LLDPE cures formulations with and without AOTEMPO. While the DCP-only cure produced typical first-order dynamics beyond an initial sample heat up period, the use of AOTEMPO at a TR of 0.50 provided an induction period that was consistent with Equation 2. More importantly, this induction delay was not accompanied by a loss in the extent of

crosslinking. At the end of the induction phase of the process, radical oligomerization of polymer-bound acrylate functionality produced multiple crosslinks from the residual peroxide initiator, thereby recovering crosslinks lost to nitroxyl trapping of polymer macroradicals.

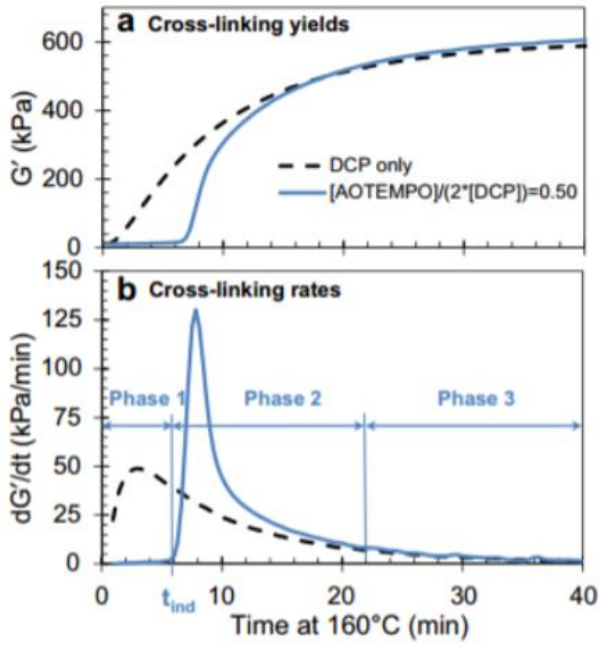
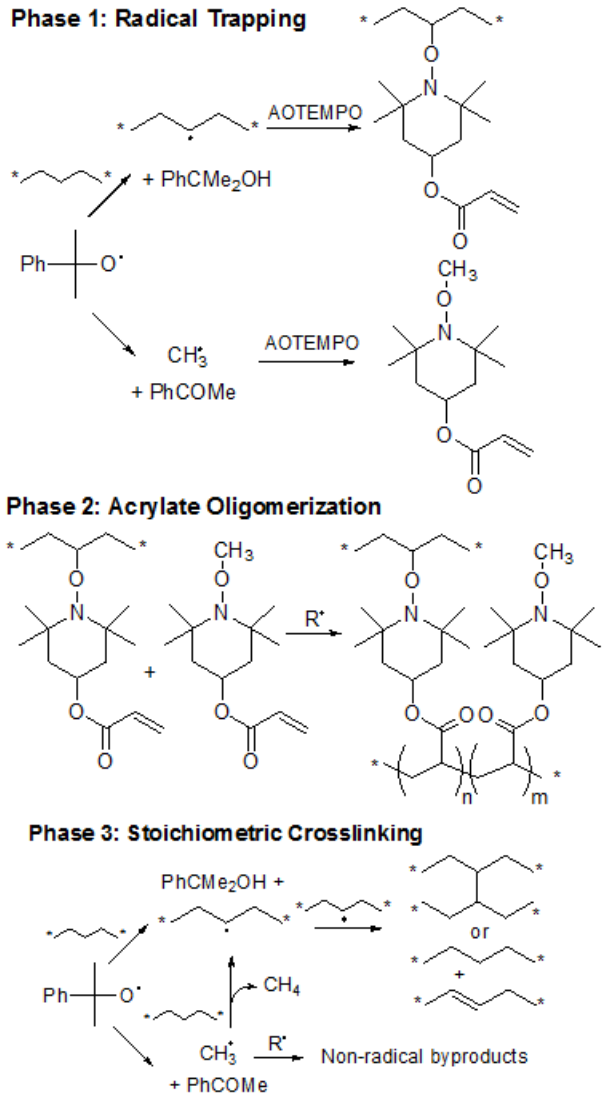


Figure 4: DCP- initiated LLDPE crosslinking with and without AOTEMPO ([DCP] = 55.6 µmole/g; a. Storage modulus, G'; b. Cure rate dG'/dt) [16].

Scheme 2 is an idealized mechanism for an AOTEMPO-mediated LLDPE cure illustrating the three phases in Figure 4b [16]. During phase 1, peroxide-derived macroradicals and methyl radicals are quenched rapidly by nitroxyl to produce alkoxyamines. This phase persists until all nitroxyl is consumed, and is characterized by a constant storage modulus.



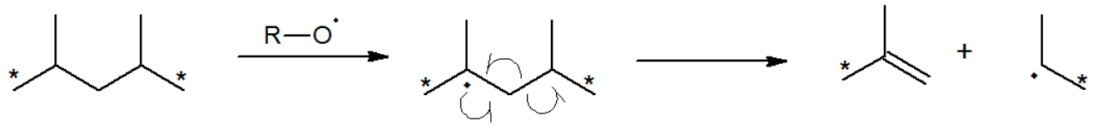
Scheme 2: Idealized reaction mechanism for AOTEMPO-mediated LLDPE curing.

Phase 2 is demarked by a rapid increase in G' due to oligomerization of acrylate functionality as well as conventional macroradical combination. This relatively short-lived stage proceeds until all polymerizable functionality is converted, where after the cure progresses by macroradical

combination alone (Phase 3). This three-phase cure process is effective for ethylene rich polyolefins that crosslink efficiently when treated with peroxide alone. However, it has proven to be ineffective for highly unsaturated polymer such as polybutadiene [22], and has not been applied systematically to polyolefins that do not crosslink under the action of peroxides, as these suffer extensive molecular weight degradation.

1.4 Scissionable Polymers

Whereas macroradical combination is the dominant molecular weight altering reaction in ethylene-rich polymers, macroradical cleavage dominates chemical modification of propylene rich materials. Scheme 3 illustrates the tertiary alkyl radical fragmentation process that is responsible for severe losses in melt viscosity when PP is heated with peroxide alone. Note that this reaction does not terminate macroradical intermediates and, as such, has a chain character wherein one initiation event can produce several scission occurrences [23] [24].



Scheme 3: β-chain scission mechanism of tertiary radicals in PP.

One of the challenges in overcoming tertiary macroradical scission stems from the regioselectivity of H-atom abstraction from the polymer. Although PP provides primary,

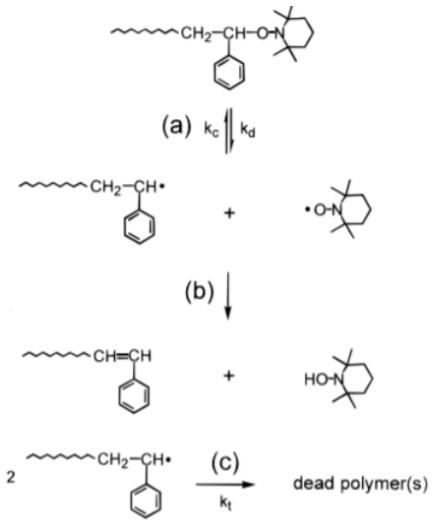
secondary and tertiary C-H groups, H-atom transfer from the latter is preferred [11], increasing the proportion of the problematic radical intermediate. This promotes chain scission relative to macroradical combination to the point that PP cannot be cured extensively using conventional radical chemistry.

Numerous attempts have been made to affect a PP cure, with strategies relying on coagents to boost crosslinking rates or on orthogonal silane moisture-curing chemistry to build molecular weight without the involvement of macroradical intermediates. Chodak et al. reported that the use of p-benzoquinone as a coagent in conjunction with various initiators is capable of modest gel content. However, they speculate that PP fragmentation is not fully inhibited, as quinone reacts with end macroradicals to form the polymer network [25]. Peroxide-initiated addition of trimethoxysilane functionality to PP through the grafting of methacryloylpropyltrimethoxysilane produced a derivative that moisture-cured to gel contents on the order of 30% [26]. Therefore, a one-pot curing process that can generate high gel fractions from modest reagent loadings remains an active field of research.

1.5 Alkoxyamine Stability

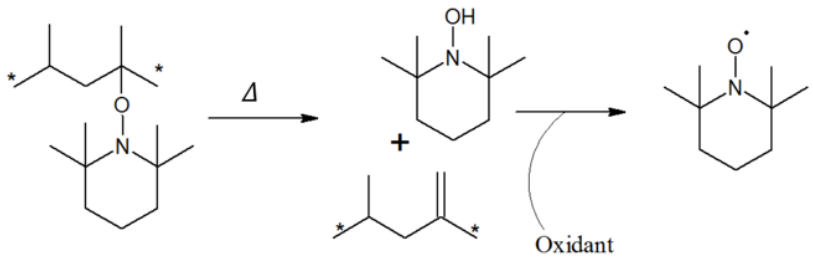
Equation 2 assumes that alkyl radical trapping via nitroxyls is not only fast relative to all other reactivity in the system, but is also irreversible. Primary and secondary alkoxyamines have been studied in the context of both model compounds and polymer-bound systems. The results show that under processing conditions, primary and secondary alkoxyamines are stable as heating model alkoxyamines showed no evidence of degradation [27] [20].

Acrylic and benzylic radicals are resonance-stabilized, making their corresponding alkoxyamines more labile toward thermolysis than un-activated primary and secondary alkyl radicals encountered in polyolefin modifications [28]. Beyond thermolysis to a carbon-centered radical + nitroxyl, the alkoxyamines produced from acrylic and benzylic compounds are prone to disproportionation to olefin + hydroxylamine [29] [30] [31]. The mechanism for this alkoxyamine decomposition is not well understood. Ohno et al. suggest that disproportionation occurs by alkoxyamine thermolysis followed by H-atom abstraction adjacent from the carbon-centered radical by nitroxyl (Scheme 4). In contrast, Ananchenko et al. propose a non-radical alkene elimination. They showed that the non-radical reaction extent has a strong dependence on nitroxide, with special attention drawn to steric effects of nitroxide substituents, and the carbon-centered radical species [31].



Scheme 4: Main reactions that a polystyrene-TEMPO Adduct can make at high temperatures: (a) Reversible Dissociation; (b) Decomposition (β-H-abs); (c) Bialkyl Combination (Termination) [30].

Given the central role of tertiary macroradicals in a PP modification, the stability of their alkoxyamines is a key concern. Garrett et al. noted a small extent of tertiary alkoxyamine disproportionation when their model compound was heated to 160 °C for 10 min [11]. The impact of this side reaction on PP modification reaction outcomes is difficult to predict given available information. As shown in Scheme 5, disproportionation to olefin + hydroxylamine would likely be followed by oxidation of the latter to regenerate the nitroxyl. If this occurs to an appreciable extent, then the recycling of nitroxyl during phase 1 of the process could generated unsaturation in the polymer backbone, prolong the induction period, and shift the effective trapping ratio beyond that dictated by a 1:1 trapping stoichiometry.



Scheme 5: Formation on unsaturation and hydroxylamine in TEMPO grafted PP during processing conditions.

The presence of a tertiary alkoxyamine complicates the process providing potential side effects to nitroxyl-mediated, peroxide initiated curing chemistry of PP.

1.6 Anti-oxidative Abilities of Alkoxyamines and Nitroxyls

Polymer oxidation is a radical process that can severely limit the lifespan of consumer goods by affecting their chemical structure and resulting mechanical properties [32]. Slow photolysis or

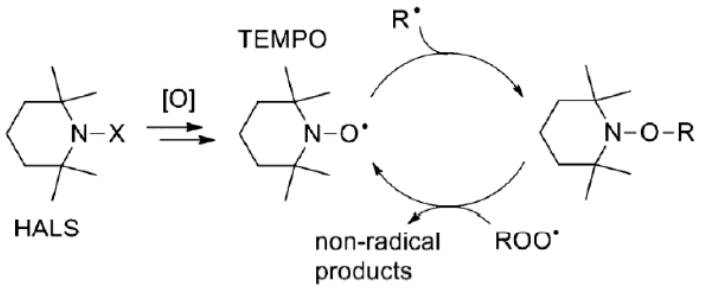
thermolysis of C-H and C-C bonds can generate carbon-centered macroradicals whose combination can crosslink the material to the point of brittleness, and whose disproportionation introduces C=C unsaturation that can lead to discoloration and heightened oxidation sensitivity. Interaction of macroradicals with atmospheric oxygen dramatically accelerates these changes, as hydroperoxide (ROOH) generation drives an autoaccelerating oxidation sequence that greatly amplifies radical populations [33].

Gisjman et al. suggest that PP oxidations proceed through two phases, the first being an autocatalytic sequence wherein hydroperoxides (ROOH) are accumulated [34]. During this stage, the oxidation rate is controlled by ROOH decomposition. The second phase involves a preferential oxidation of the previous oxidation products to peracids due to restricted mobility [32]. Since PP degradation is heterogeneous, the local degree of oxidation is higher compared to the overall oxidation level, as such it is expected that the secondary oxidation occurs from interactions from the first oxidation phase products [35]. After primary oxidation products are formed from ROOH accumulation, they are subsequently oxidized to the much faster decomposing peracids which accounts for the increase in oxidation rate rather than accumulation of hydroperoxides [35].

Irrespective of their specific mechanism, changes in molecular weight distribution are accompanied by oxidation products such as ketones, aldehydes and carboxylic acids. Therefore, the extent of PP oxidation can be monitored by Fourier-transform-infra-red (FT-IR) spectrometry, using the absorbance carbonyl resonances to determine changes in the concentration of oxidation

products. Comparing the carbonyl peaks relative to aliphatic CH_2 stretching, wagging, or rocking peaks, which will remain unchanged regardless of oxidation extent, provides quantitative data that can be used to assess the efficacy of different antioxidants.

2,2,6,6-tetranethylpiperidine (TEMPH) and its oxidized derivatives comprise a well-established class of antioxidants known as hindered amine light stabilizers (HALS) [36]. Although mechanistic details of the activation of TEMPH and alkoxyamines is lacking, many have cited the Denisov cycle that is illustrated in Scheme 6 [36]. TEMPO is a central feature of these mechanisms, as it acts in a conventional sense by combination with alkyl radical intermediates. Of particular interest is the proposed reaction between alkoxyamine and peroxyl to regenerate TEMPO, given that nitroxyl-mediated polyolefin modifications produce alkoxyamine as a matter of course. If they are activated by oxidation reaction intermediates during their service life, polymer-bound alkoxyamines may exhibit antioxidant properties. Functional nitroxyls would then provide unique control over polyolefin cure dynamics and yields, while boosting the oxidative resistance of the resulting thermosets.



Scheme 6 : Simplified Denisov Cycle [36].

1.7 Research Objectives

This thesis summarizes investigations of PP crosslinking by peroxide-initiated reactions of functional nitroxyl additives, which explore the influence of C=C functionality before examining their synergy with multi-functional acrylic and styrenic coagents (Chapter 2). These studies are extended to a preliminary assessment of tertiary alkoxyamine instability with respect to disproportionation, and the potential for improved oxidative stability amongst nitroxyl-grafted PP (Chapter 3).

Chapter 2: Functionalized TEMPO- Mediated PP Curing

2.1 Introduction

Chemically modifying polyolefins by peroxide-initiated radical chemistry is widely used to affect desirable changes in polymer composition and/or architecture [37] [38]. Radical-mediated grafting of monomers such as maleic anhydride and vinyl trialkoxysilanes yield derivatives that bond to high surface energy components of polymer blends and composites [39], while radical crosslinking of ethylene-rich materials produces thermoset derivatives with greatly improved thermomechanical properties [40] [3]. These processes are generally conducted solvent-free in conventional melt processing devices, without complications derived from atmospheric moisture or oxygen [41]. Unfortunately, the scope of this synthetic approach is often limited by the transient nature of radical intermediates, and an inability to control radical reaction dynamics and yields.

Notwithstanding a widespread interest in isotactic polypropylene (PP) thermosets, there remains a need for efficient radical chemistry to crosslink this polyolefin. At the melt temperatures required to process PP, tertiary macroradical fragmentation affects molecular weight to a greater extent than radical-radical combination, causing a net reduction in molecular weight when the material is heated with peroxide alone [42]. Attempts to graft trifunctional monomers such as trimethylolpropane triacrylate (TMPTA) have also met with limited success, since C-H bond addition yields are uncompetitive with chain scission. As a result, these products possess bimodal molecular weight and branching distributions, and very low gel fractions.

A standard route to thermosetting polyolefins involves introducing functional groups that crosslink the polymer by C=C oligomerization, as opposed to backbone macroradical combination. Key examples are isobutylene-rich elastomers containing pendant acrylic or styrenic functionality, whose radical oligomerization outcompetes radical chain cleavage, yielding a thermoset whose crosslink density scales with polymer-bound monomer content [17]. However, our recent studies of functional nitroxyl chemistry suggests an alternate route to a macromonomer-based PP thermoset, wherein peroxide initiates a seamless sequence of C=C functional group grafting to the polyolefin, followed by oligomerization of polymer-bound monomer.

In this chapter small amounts of 4-vinylbenzoic-2,2,6,6-tetramethylpiperidin-N-oxyl (VBTEMPO) is used in peroxide initiated formulations to reveal the unique dynamics and yields of PP homopolymer crosslinking. These results are extended to alternate C=C functionality before examining the synergy between functional nitroxyls and multi-functional acrylic and styrenic monomers.

2.2 Materials and Methods

2.2.1 Materials

Polypropylene (PP, M_n= 166,000 g/mole, M_w = 580,000 g/mol; MFI = 0.5g/10 min), dicumyl peroxide (DCP, 99%), 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO, 99%), 4-hydroxy-2,2,6,6-tetramethylpiperdin-1-oxyl (TEMPOH, 97%), 4-vnylbenzoic acid (VBA, 97%), 4-(dimethylamino)pyridine (DMAP, 99%), *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (EDC*HCl, ≥98%) 4-amino-TEMPO (97%), acryloyl chloride (≥97%),

methacryloyl chloride (97%), crotonoyl chloride (90%), cinnamoyl chloride (98%), triethylamine (≥99.5%), butylated hydroxytoluene (BHT, ≥99%), Luperox 101, 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane (L-101, 90%), divinylbenzene (90%), and trimethylpropane triacrylate (TMPTA) were used as received from Sigma-Aldrich. 2,5-Dimethyl-2,5-di(t-butylperoxy)hexyne-3 (L-130, 56%) was used as received from Alf Atochem. Synthesis of 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl **(1c)**, 4-cinnamoyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl **(1d)**, and 4-crotonoyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl **(1e)** was done according to previously reported methods [20].

4-Vinylbenzoyloxy- 2,2,6,6-tetramethylpiperidine-N-oxyl (VBTEMPO) (1a) 4-(Dimethylamino) pyridine (0.122 g, 0.998 mmol) was added to a solution of 4-vinylbenzoic acid (0.742 g, 5.01 mmol), TEMPOH (0.856 g, 4.99 mmol), and *N*-(3-Dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (1.054 g, 5.5 mmol) in dichloromethane (15 mL), and the mixture was stirred at room temperature for 20 h after heating to reflux for 4 h under N_2. The resulting solution was washed with dilute HCl_{aq} (1x10 ml) and brine (4x10 mL), then dried (Na_2SO_4) before removing solvent under vacuum, yielding orange crystals that were recrystallized from hexanes. Yield: 57%; mp 78-79 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm,): 8.04 (2H, aromatic ortho, m), 7.53 (2H, aromatic meta m,), 6.83 (1H, dd, $J_{1\,(Trans)}$ =15 Hz, $J_{2\,(Cis)}$ = 10 Hz), 5.94 ($1H_{trans}$, d, J_1 = 15 Hz), 5.45 ($1H_{cis}$, d, J_1 = 10 Hz), 2.50-0.80 (17 H, unidentifiable due to radical nature of molecule). FT-IR (thin film, cm^{-1}): 1710 (C=O). HRMS-EI (m/z): calcd for $C_{18}H_{24}NO_3$, 302.1756, found 302.1751.

4-Acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl (AOTEMPO) (1b) A solution of triethylamine (706 mg, 0.97 mL, 6.98 mmol) in benzene (12.0 mL) was added dropwise to a

solution of TEMPOH (0.688 g, 4.40 mmol) in benzene (10.0 mL). Acryloyl chloride (0.374 g, 340 μL, 4.16 mmol) in benzene (7.0 mL) was added dropwise from an addition funnel at room temperature, under N_2 with stir. The progress of the reaction was monitored by thin-layer chromatography (TLC). The reaction mixture was stirred at room temperature for 20 h before the second portion of Acryloyl chloride (0.188 g, 170 μL, 2.08 mmol) in benzene (3.5 mL) was added dropwise. The reaction mixture was stirred at room temperature for 1 h or until TLC reveled complete conversion of TEMPOH. The resulting solution was filtered before removing solvent under vacuum, yielding orange crystals that were recrystallized from cyclohexane. Yield: 76%; mp 100-102 °C; lit. 102-104 °C.

4-Vinylbenzamide-2,2,6,6-tetramethylpiperidine-N-oxyl (VBATEMPO) (2) *N*-(3-Dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (1.054 g, 5.5 mmol) was added to a solution of 4-vinylbenzoic acid (0.742 g, 5.01 mmol) and 4-Amino-TEMPO (0.855 g, 4.99 mmol) in dichloromethane (15 mL), and the mixture was stirred at room temperature for 16 h after heating to reflux for 3 h under N_2. The resulting solution was washed with dilute HCl_{aq} (1x10 mL) and brine (4x10 mL), then dried (Na_2SO_4) before removing solvent under vacuum, yielding pale orange powdery crystals that were recrystallized from 9:1 Benzene: Hexanes. Yield: 58%; mp 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm,): 7.64 (2H, aromatic ortho, m,), 7.41 (2H, aromatic meta, m), 7.07 (1H, amide, broad s,), 6.70 (1H, dd, $J_{1\ (Trans)}$ =16 Hz, $J_{2\ (Cis)}$ = 12 Hz), 5.78 ($1H_{trans}$, d, J_1 = 16 Hz), 5.30 ($1H_{cis}$, d, J_1 = 12 Hz), 0.80 – 2.0 (17H). FT-IR (thin film, cm^{-1}): 1630 (C=O) HRMS-EI (m/z): calcd for $C_{18}H_{25}N_2O_2$, 301.1916, found 302.1921.

2.2.2 Instrumentation and Analysis

^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker AVANCE – 400 and 500 spectrometers in $CDCl_3$. High resolution mass spectrometry was conducing using a Waters/ Micromass GCT-TOF mass spectrometer operating under electron impact mode. PP thermosets were prepared by coating ground polymer (5 g) with an acetone solution of the specified initiator and nitroxyl, mixed by hand and allowed to dry. Samples were crosslinked using the Advanced Polymer Analyzer 2000 (Alpha Technologies) equipped with biconical plates, operating with a 3° arc (strain amplitude) at a frequency of 1 Hz at various temperatures. Gel contents were measured according to ASTM D 2765-01. A weighed sample was enclosed in 120 –mesh stainless steel cloth, and extracted with boiling xylenes that contained BHT to mitigate polymer oxidation. Extraction was continued for 4 h, after which the sample was dried to constant weight, and the gel content reported as a percent of mass retained from the original sample.

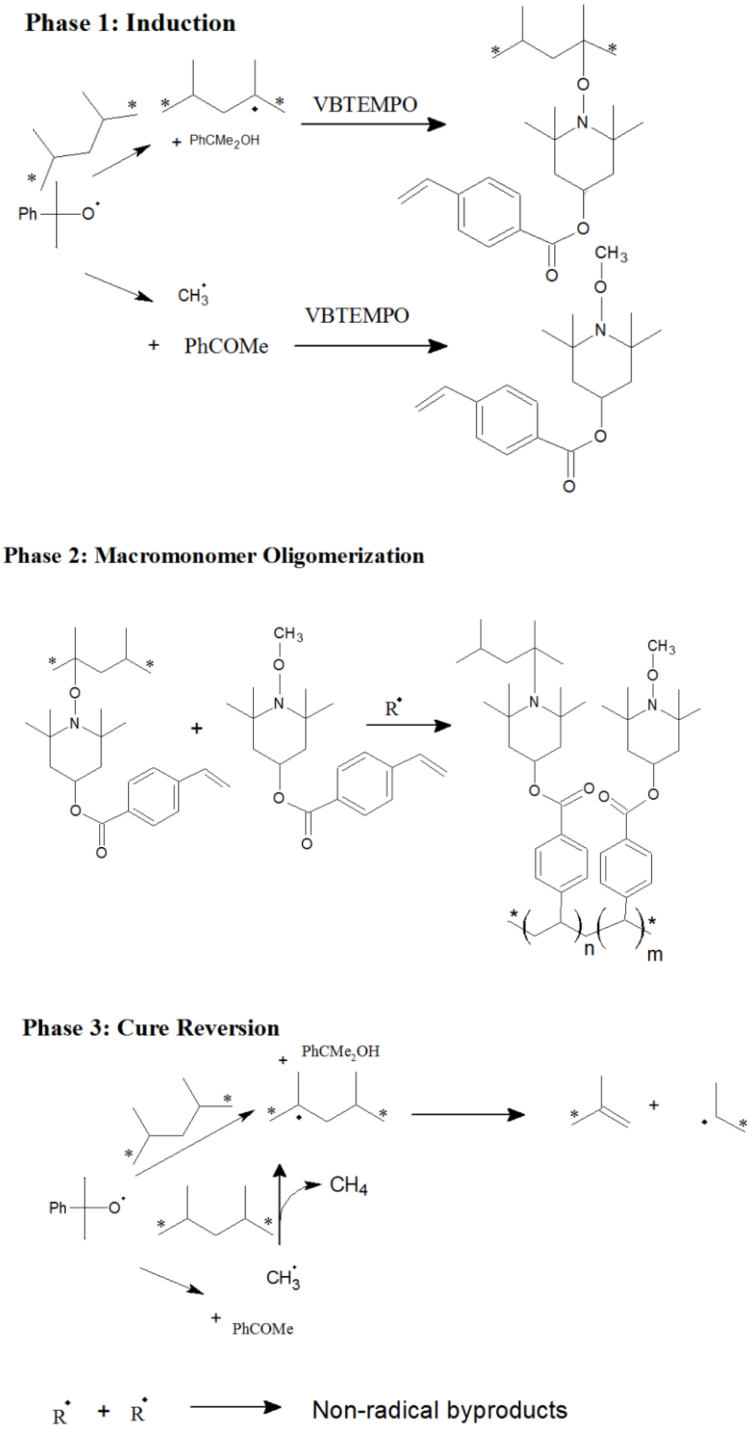
2.3 Results and Discussion

2.3.1 VBTEMPO Dynamics and Yields

The crosslink yield that is needed to produce a serviceable thermoset depends on the targeted polymer network density, the molecular weight distribution of the starting material, and the prevalence of complicating side reactions. Polyethylene crosslinking is a relatively simple stoichiometric process involving H-atom transfer to initiator-derived radicals, followed by combination of the resulting macroradicals. The efficacy of a given formulation is affected by the abstraction efficiency of the peroxide acting upon the polymer, and the proportion of macroradical termination by combination versus disproportionation [43]. As described above, PP

modifications are complicated by tertiary alkyl macroradical fragmentation, a chain reaction process that competes effectively with macroradical combination, resulting in a net loss of molecular weight (MW) when the polyolefin is heated with peroxide alone.

Scheme 7 illustrates an idealized functional nitroxyl process, comprised of a three phase sequence: radical trapping, macromonomer crosslinking, and cure reversion for PP.



Scheme 7: Idealized three phase mechanism for VBTEMPO-mediated PP crosslinking.

During the trapping phase, the material's MWD is unchanged, owing to rapid quenching of carbon-centered radicals, both methyl and polymeric alkyl, by combination with nitroxyl. Note that previous model compound studies have demonstrated that functional nitroxyls trap alkyl radicals by combination as opposed to C=C bond addition, due to differences in bimolecular rate constants that are several orders of magnitude [19]. The yield of polymer-bound alkoxyamine generated during this phase is dependent on the H-atom AE of cumyloxyl acting upon PP, which at 165^{o}C is approximately 37% [11], meaning that this percentage of the nitroxyl in the formulation will produce the desired alkoxyamine. Of course, this upper limit on macromonomer functional group content requires all alkoxyamine regioisomers to be thermally stable, an assumption that is examined in detail in the model compound section of this work.

The complete conversion of nitroxyl functionality to alkoxyamines marks the end of the induction period. During phase 2 of the process, residual peroxide initiates monomer oligomerization and chain scission concurrently, the balance of which dictates crosslink density. Note that only as much peroxide as is needed to convert polymer-bound monomer is desired, since phase 3 of the process, cure reversion, involves unabated PP degradation. This requires careful consideration of the relative amounts of peroxide and nitroxyl, hereafter referred to as the trapping ratio, TR = [nitroxyl]/(2*[DCP]), which represents the fraction of initiator-derived radicals that can be quenched by nitroxyl, assuming a 1:1 trapping stoichiometry. A formulation with TR=0.00 is a peroxide-only reaction, while one with TR=1.00 may be expected to produce an indefinite induction period.

The rheology data presented in Figure 5 demonstrates these principles using time-resolved measurements of the dynamic storage modulus (G') at fixed temperature, frequency, and shear strain amplitude [9]. Efficient stress relaxation in uncrosslinked polymer melts produces a relatively inelastic, low G' response to an oscillating shear deformation. Chain coupling yields a covalent network that restricts polymer segment mobility, thereby raising G' as network densities increase. The data plotted in Figure 5 were recorded for PP melt formulations containing 74 µmoles DCP per gram of polymer, acting in combination with varying amounts of a nitroxyl additive.

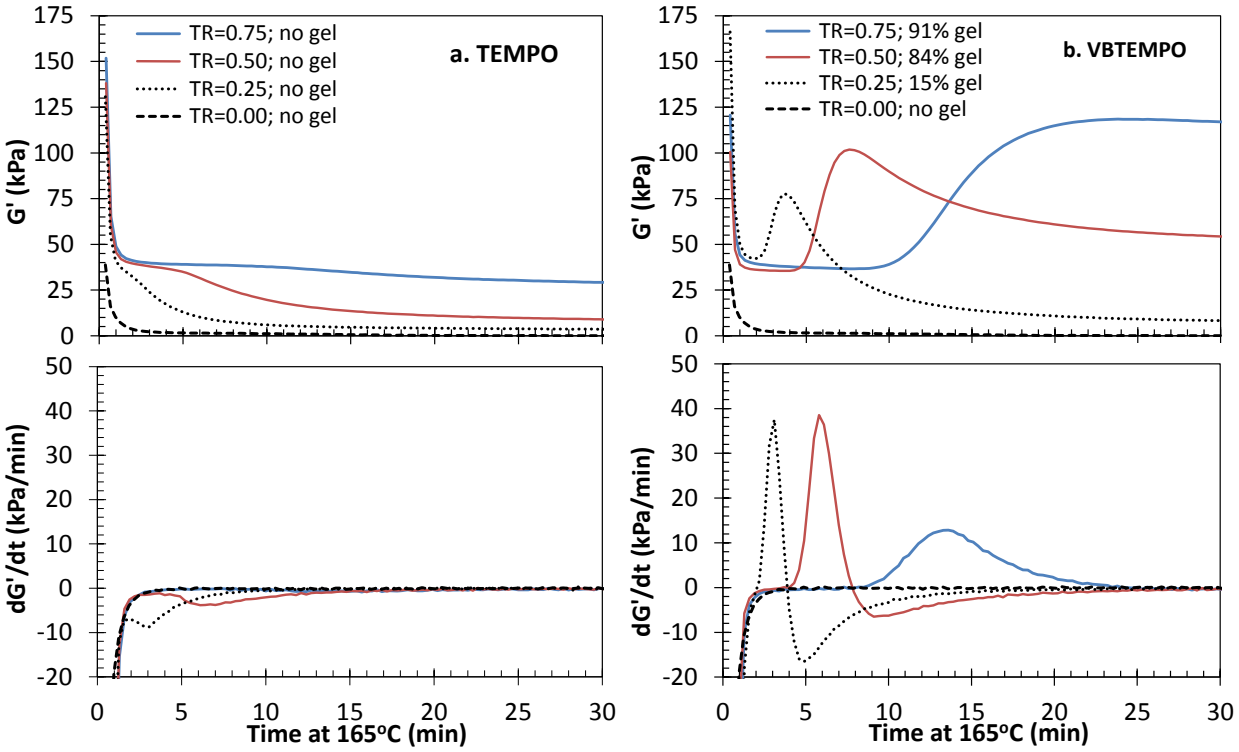


Figure 5: Influence of nitroxyl trapping ratio on PP modification dynamics (a. TEMPO; b. VBTEMPO; [DCP] = 74 µmol/g).

Control experiments involving TEMPO (Figure 5a) demonstrate the susceptibility of PP to radical degradation [23], and the extent to which this nitroxyl can mitigate chain scission. Melting of the thermoplastic causes G' to decrease during the first 1.2 min of the process, after which peroxide-initiated chain scission is responsible for any observed G' losses. In the absence of nitroxyl, molecular weight degradation was extensive enough to lower G' to the measurement limit of the instrument. However, applying TEMPO at a TR of 0.75 produced a stable storage modulus for approximately 8 min, after which PP degradation proceeded unabated.

A simple equation for the duration of the induction period (t_{ind}) as a function of intitiator half-life ($t_{1/2}$) and nitroxyl trapping ratio (TR) applies when peroxide thermolysis is a first-order decomposition process, and the trapping of alkyl radicals by nitroxyl is rapid and irreversible [44].

$$t_{ind} = -\frac{1}{k_d}\ln\left[1 - \frac{[Nitroxyl]}{n[Initiator]_0}\right] \quad (2)$$

Using $t_{1/2}$ = 3.4 min for DCP at 165°C [45], the induction periods for TR=0.25, 0.50, and 0.75 are 1.4 min, 3.4 min and 6.7 min, respectively, which are in good agreement with experimental values corrected for the time required to melt the formulation in the rheometer cavity (Figure 5). This predictable induction time can be of considerable practical value, since it allows the material to be shaped and undergo complete stress relaxation before being rendered thermoset.

The ability of small amounts of VBTEMPO to control the dynamics and yields of PP crosslinking is demonstrated by the data plotted in Figure 5b. The storage modulus rate plots, dG'/dt, generated by numerical differentiation of G' versus time data, best illustrates the transitions

between each phase of the crosslinking process: trapping, oligomerization, and reversion. The induction period is defined by $dG'/dt \approx 0$, since the efficient alkyl radical trapping by nitroxyl inhibits any change in MW. Phase 2 is characterized by $dG'/dt > 0$, wherein the co-oligomerization of polymer-bound monomer with methyl-alkoxyamine outweighs macroradical scission to generate the desired polymer network. Crosslinking by C=C oligomerization and backbone cleavage are not necessarily orthogonal reactions. Ciardelli has noted that the presence of monomer establishes a radical population that differs from a peroxide-only formulation [9]. In the present case, propagating benzylic radical intermediates arising from VBTEMPO may divert radical populations away from the tertiary alkyl macroradicals that are responsible for chain scission. Phase 3 of the process, reversion, is defined by $dG'/dt < 0$, during which any crosslinking produced by residual macromonomer is overwhelmed by the β-scission of tertiary macroradicals.

The observed influence of TR on the duration and intensity of each phase highlights the need to optimize formulations in order to meet crosslink density and t_{ind} targets. Increasing TR raises the concentration of polymer-bound monomer that is produced in phase 1, thereby establishing a more favorable balance between crosslinking and degradation during phase 2. Higher TR values also reduce the amount of residual peroxide remaining once all macromonomer functionality is converted, thereby reducing undesirable cure reversion in phase 3. However, an excessive TR may not provide sufficient initiator to convert C=C to crosslinks, effectively "short-shooting" the oligomerization process.

The results plotted in Figure 5b are remarkable in terms of the control that can be imposed on a PP modification process, both in terms of dynamics and yields. Whereas the treatment of PP with peroxide alone produced no gel in the product, inclusion of VBTEMPO at a fraction of the DCP loading gave a gel content of 91%. This is a remarkable result, in that no other one-pot radical reaction has produced such an extensive crosslink density from a PP hompolymer. A closer analysis of this experiment is informative. The formulation provided [DCP]= 74 μmole/g to generate 148 μmole radicals/g of polymer, and [VBTEMPO]= 111 μmole/g to trap alkyl radicals during phase 1 of the process. The H-atom abstraction efficiency of cumyloxyl from PP at 165°C is 0.37, meaning that 37% of cumyloxy radicals abstract an H-atom from the polymer to produce a macroradical, and 63% fragment to methyl radical + acetophenone. Therefore, the expected concentration of polymer-bound VBTEMPO at the end of the induction period is 111 μmole/g * 0.37 = 41 μmole/g. Given that the PP starting material had a M_n = 166,000 g/mole, this amounts to ***~7 VBTEMPO groups per PP chain***, with an average molecular weight between functional groups of about 23,000 g/mole. This level of polymer functionalization is sufficient to render most conventional polymers completely thermoset, and the reaction did, indeed, incorporate 91 wt% of the polymer in the gel fraction.

While vinylbenzoate functionality is clearly capable of crosslinking PP, chain scission is also influential. Consider the TR=0.5 VBTEMPO formulation illustrated in Figure 5b. This reaction generated a peak G' of 102 kPa which declined to 54 kPa during the following phase 3 reversion. Notwithstanding this loss of crosslink density, the gel content of the final product was 84%, not far from that observed for the TR=0.75 formulation. This indicates that scission of an established

polymer network reduces its network density (and by extension, its storage modulus) without substantially affecting molecular weight, since most fragments remain fixed to the network through alternate covalent bonds. However, chain fragments that are not functionalized with VBTEMPO are released, making it difficult for this cure chemistry to produce fully gelled products.

2.3.2 Influence of Peroxide Initiator

The efficiency of H-atom abstraction by peroxide-derived radicals governs the amount of polymer-bound VBTEMPO functionality introduced during phase 1 of the cure process. As such, selecting an initiator requires consideration not only of the peroxide thermolysis rate, but the macroradical yield it can generate at the reaction temperature. Figure 6 illustrates the dynamics and yields of VBTEMPO cure formulations involving DCP and 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (L-101), the latter generating four alkoxy radicals per molecule, two t-butoxy and two dimethylalkoxy radicals. When compounded with PP and VBTEMPO at equivalent total radical loadings, L-101 provided longer induction periods, owing to the lower rate of L-101 decomposition, and higher crosslink densities.

Differences in cure yield are attributed to H-abs efficiency generated by t-butoxy and cumyloxy radicals [46] [47]. Watanabe et al. have shown that DCP thermolysis at 140°C in cyclohexane provides an H-atom abstraction efficiency of 54%, whereas di-tert-butyl peroxide under identical conditions provides gives a value of 72% [48]. This disparity is large enough to account for the observed superiority of L-101, given that PP macroradicals are required to produce polymer-

bound monomer functionality, while methyl radical generation produces free alkoxyamine that cannot contribute directly to crosslink density [49] [50].

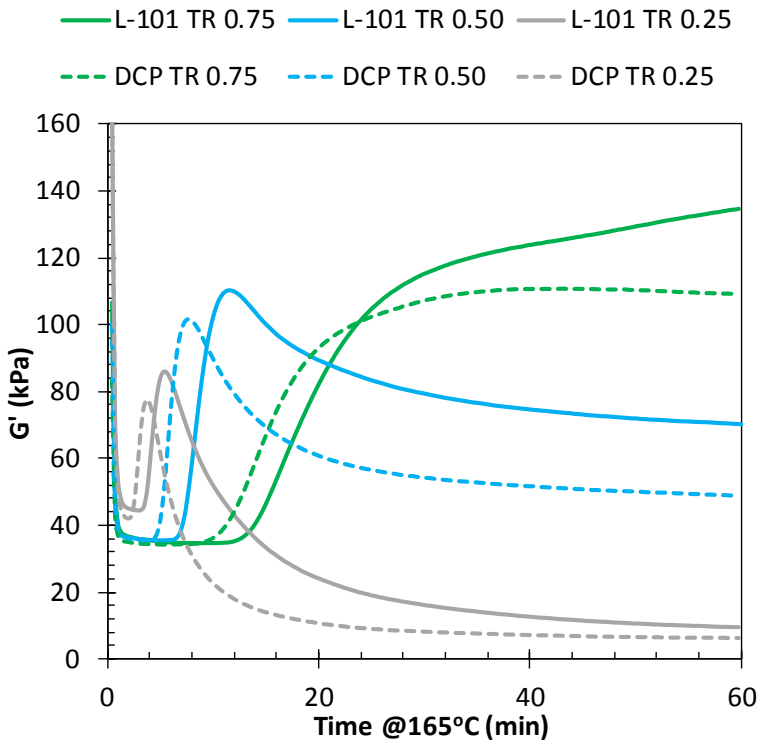


Figure 6: Influence of peroxide initiator on VBTEMPO, PP cure dynamics ([DC] = 74 µmole/g; [L-101 = 39 µmole/g]).

2.3.3 Influence of Monomer Structure

Our focus on vinyl benzoate functionality stemmed from research on isobutylene-rich macromonomers that can be prepared by ionic reactions of a halogenated starting material, thereby obviating phase 1 of the nitroxyl-mediated process. When heated with a peroxide initiator, these elastomers react through a progression analogous to phase 2 (oligomerization) and phase 3 (reversion) of the present system. These previous studies showed activated styrenics to

be superior to standard acrylates [17], a trend that is borne out by the functional nitroxyls examined in this work. The rheological data plotted in Figure 7 demonstrate the following order of reactivity: vinyl benzoate > vinyl benzamide > acrylate > crotonate > methacrylate > cinnamate. While propagation rate constants for acrylates at moderate temperatures are generally greater than those reported for styrenics [51], vinyl benzoate reactivity likely benefits from the electron withdrawing effect of the para-ester group, as reported for comparisons of dodecyl-4-vinyl benzoate and styrene polymerizations [52].

As described above, the amount of nitroxyl grafted to PP is a function of the macroradical yield generated in phase 1. Therefore, each formulation using a trapping ratio of 0.50 should produce about 27 μmole of bound monomer/ g·polymer (Figure 7a), while those using a trapping ratio of 0.75 (Figure 7b) should produce 41 μmole/g·polymer. Since these yields are independent of the C=C functional group structure, each formulation has the **potential** to build the same network density, if it can oligomerize its polymer-bound monomer quantitatively. The data plotted in Figure 7 show that this potential is not enough, and that kinetic reactivity is paramount to producing a PP thermoset. That is, the rate of network creation by pendant C=C group activation must exceed that of network cleavage by backbone macroradical scission.

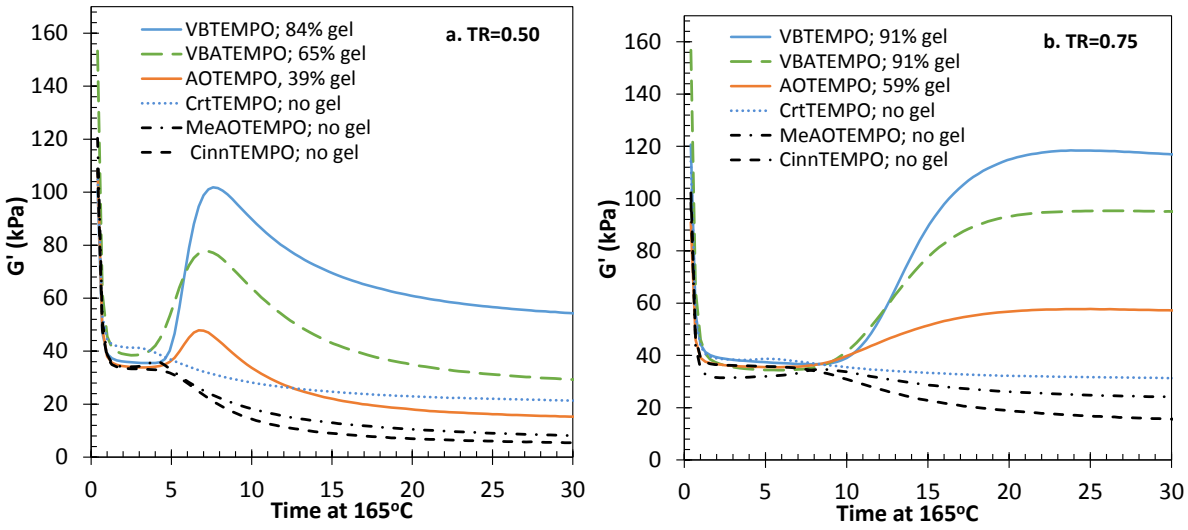


Figure 7: Influence of polymerizable functional group on PP cure dynamics (a. TR=0.50; b. TR=0.75; [DCP] =74 µmole/g).

An unreactive system such as MeAOTEMPO, for which polymer degradation is competitive with C=C oligomerization, generates chain fragments whose low molecular weight makes them more difficult to bring up to, and beyond, the gel point [53]. As such, even if sufficient peroxide is available to convert polymer-bound monomer during phase 2, the result is a low crosslink density. On the other hand, a reactive system such as VBTEMPO, for which crosslinking is kinetically favored, produces highly branched architectures whose molecular weight is relatively insensitive to chain scission. Once the crosslink density exceeds the gel point, scission will lower crosslink density / storage modulus without affecting gel contents, since the chain fragments are retained by the extensive polymer network. Therefore, development of nitroxyls for PP crosslinking should focus on kinetically reactive functionality that can establish a high crosslink density using a minimal amount of initiator. Not only will these systems generate more robust,

extensive polymer networks, they will support higher trapping ratios and incur less phase 3 reversion.

2.3.4 Synergy with Multifunctional Monomers

The peroxide-initiated grafting of multifunctional coagents such as trimethylolpropane triacrylate (TMPTA) has been studied widely as a means of improving the crosslink density of ethylene-rich thermoset formulations [53]. Ideally, macroradical addition to acrylate introduces polymer-bound monomer, which can support polyolefin crosslinking by repeated grafting and/or oligomerization. Unfortunately, acrylate grafting yields to PP are low, given the low abstraction efficiency of peroxides acting on this material, and the preference of acrylate for homopolymerization versus grafting. As a result, PP-g-TMPTA products have bimodal molecular weight and branching distributions comprised of low MW linear polymer and a small population of hyperbranched chains [54].

The functional nitroxyl approach adopted in this work overcomes the main deficiency of a multifunctional monomer by producing polymer-bound monomer by trapping macroradicals by nitroxyl combination as opposed to C=C addition. The macromonomer generated during phase 1 can copolymerize with coagent during phase 2, thereby raising the branching extent of the polymer network. This is demonstrated in Figure 8 for styrenic and the acrylic systems. Note the ineffectiveness of divinylbenzene (DVB) and TMPTA acting alone on PP, as only gel-free products of low storage modulus were observed.

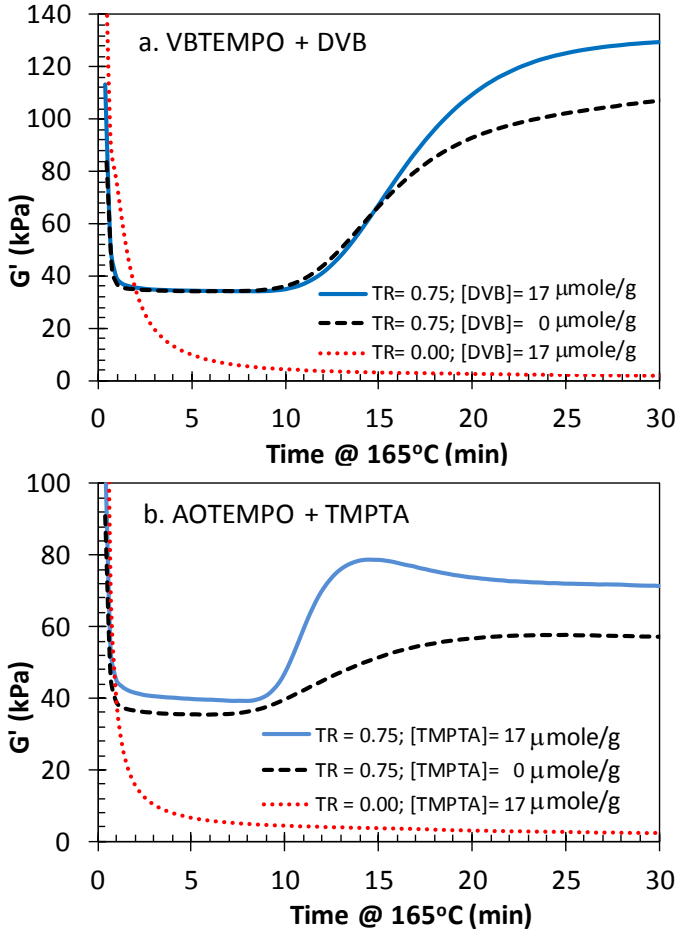


Figure 8: Influence of co-agent a. DVB with VBTEMPO and b. TMPTA with AOTEMPO on DCP-initiated PP Cure dynamics and yields ([DCP] = 74 µmole/g).

In contrast, the inclusion of a small amount of co-agent improved the yields achieved with VBTEMPO and AOTEMPO. This synergy provides a simple method of meeting a targeted crosslink density while minimizing peroxide and functional nitroxyl loadings.

2.4 Conclusion

Presented here is a one-pot, peroxide-initiated, delayed-onset curing chemistry for PP homopolymers. The chemistry bears dependency of the kinetic reactivity of the polymerizable functional group associated with the nitroxyl trapping agent. In order to form a high gel-content thermoset the reactivity of the functional group must out compete PP β-chain scission. Induction time and G' yield can be controlled via the choice of peroxide initiator due to differences in thermolysis rates and H-abs abilities. Another dimension which can control G' yield is the variation in polymerizable functional group. If lower yields or gel contents are desirable than the C=C functional group can be selected to influence the desired yields. Finally nitroxyl loadings can be reduced to create a more economically feasible formulation via the use of cheaper co-agents, which synergize well with mimicked pendant nitroxyl polymerizable functional groups.

Chapter 3: Alkoxyamine Instability and its Implications for PP Modification and Oxidative Stabilization

3.1 Introduction

Literature reports of nitroxyl chemistry in the polymer field are dominated by controlled radical polymerization of acrylic and styrenic monomers, in which reversible trapping of propagating macroradicals provides pseudo-living reaction conditions [29] [30] [31]. The resulting polymers can have narrow molecular weight distributions, and the potential exists to prepare block copolymers in ways that cannot be realized by conventional radical polymerization. In these systems, alkoxyamine thermolysis is central to the process, as it sustains a radical concentration that is sufficient for slow polymer chain growth, but small enough to suppress termination by radical combination.

Careful studies of this polymerization technology have demonstrated alternate alkoxyamine decomposition pathways, including disproportionation to olefin + hydroxylamine [30] [31]. The latter is readily oxidized to nitroxyl by oxygen and/or initiator-derived radical intermediates. This side-reaction leads to "dead" polymer chains that can no longer grow, and releases free nitroxyl that quenches further polymerization by shifting the alkoxyamine thermolysis equilibrium toward the dormant state.

In the context of PP modification, alkoxyamine instability is generally undesirable, since the objective is to quench alkyl macroradicals irreversibly to introduce polymer-bound,

polymerizable functionality. Oligomerization of these macromonomer groups is expected to occur only after all nitroxyl is consumed. Therefore, the conversion of vinylbenzoate groups to crosslinks is not expected to be a "controlled radical polymerization", but a conventional radical process. Research on the primary, secondary and tertiary aliphatic alkoxyamines of present interest is scant. Nitroxyl exchange studies described by Scott et al. showed that secondary alkoxyamines do not cleave to TEMPO + R· significantly over 5 hours at 160°C, but suffer a small extent of disproportionation (<20%) over this time scale [27]. Given the relatively short duration of PP+VBTEMPO modifications, this information suggests that the secondary alkoxyamines (and primary alkoxyamines by extension) generated in the PP system are sufficiently robust that their instability can be ignored without introducing significant error to the analysis.

Based upon available information, the same assumption cannot be justified for tertiary alkoxyamines. In the course of a study of H-atom transfer reactions of PP and its model compounds, Garrett et al. noted the disproportionation of 2-(2,4-dimethylpentan-2-yloxy)-1,1,3,3-tetramethylisoindoline, a tertiary alkoxyamine derived from 1,1,3,3-tetramethylisoindolin-2-oxyl (TMIO). While the extent of decomposition was limited to a few percent over 10 min at 160°C [11], it is enough to raise concerns for the VBTEMPO reactions of present interest. This has motivated the study of tertiary alkoxyamines derived from TEMPO, with particular emphasis on disproportionation and the complications that might arise for a PP crosslinking process.

A closely related issue centers on the potential for alkoxyamines to stabilize PP against polymer oxidation. Amongst a broad class of stabilization agents commonly referred to as hindered amine

light stabilizers (HALS), are 1-alkoxy-2,2,6,6-tetramethyl-4-piperidines (TEMPOR) that are marketed under the Tinuvin trade name. The mechanisms through which these compounds are activated under oxidation conditions remain unresolved, but their efficacy is well documented [36]. Given that TEMPO-derived alkoxyamines of PP are produced in the course of a VBTEMPO-mediated cure, the ability of this polymer bound functionality to stabilize PP against oxidative degradation is a point of interest, and was tested by preliminary experiments.

3.2 Materials and Methods

3.2.1 Materials

Atactic polypropylene (MW = 10,000 g/mol) was received from Scientific Polymer Products Inc. and was subjected to hydrogenation over platinum. Polypropylene (M_n= 166,000 g/mole, M_w = 580,000 g/mol; MFI = 0.5g/10 min), dicumyl peroxide (DCP, 99%), Luperox 231, 1,1-Bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane (L-231, 92%), 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO, 99%) Lithium bromide (≥99%), Hydrobromic acid (≥48% Aq), Tributyltin hydride (Bu_3SnH, 97%), Tetrabutylammonium bromide (≥98%), 4-Hydroxy-TEMPO benzoate (BzOTEMPO,97%), Hexanes (98%), Acetone (99%), and Xylenes (99%) were used as received from Sigma-Aldrich. 2,4,6-Trimethyol-4-heptanol (97%) was used as received from Alfa Aesar.

4-Bromo-2,4,6-trimethyl heptane (1) 2,4,6-trimethyl-4-heptanol (0.617 g, 3.90 mmol) was added to a mixture of lithium bromide (0.508 g, 5.85 mmol) and 48% hydrobromic acid $_{Aq}$ (882

μL, 7.8 mmol) at 0 °C with vigorous stirring for 16-20 h and was allowed to warm to room temperature. Ice water (2.0 mL) was added to the resulting two-phase mixture and the organic layer was extracted with ether (3X3 mL). Ethers were combined and washed with ice water (2X5 mL) then dried (Na_2SO_4) before reducing under vacuum yielding a clear colorless liquid. Yield 73%, purity 34%. **1** was not further purified as the alkene elimination products did not interfere in the next steps.

4-(2,2,6,6-Tetramethylpiperidine)-2,4,6-trimethyl heptane (2): 4-Bromo-2,4,6-tetramethyl heptane **(1)** (0.291 g, 1.32 mmol) and TEMPO (0.608 g, 3.95 mmol) were dissolved under N_2 in benzene (15 mL) at room temperature with stir. Bu_3SnH (610 μL, 2.30 mmol) was added in three portions in 60 min intervals. After complete addition, stirring continued for 14 h. Removal of solvent via vacuum and purification by column chromatography (Ethyl Acetate: Hexanes =1:10) afforded **(2)** 60.6 mg (15.7 %). ^{1}H NMR (400 MHz, d-$DMSO_3$, δ, ppm,): 1.78 (2H, m) 1.69-1.64 (2H, dd, axial -C**H$_a$**H$_e$C(ON-)CC**Ha**H$_e$-, $J_{a,a}$= 16 Hz, $J_{a,e}$ = 8 Hz) 1.54-1.46 (6H, m) 1.40-1.33 (2H, m) 1.27 (3H, s)1.09 (6H, s), 1.06 (6H, s) 0.95 (12H, d, J_1 = 8 Hz). HRMS-EI (m/z): calcd. for $C_{19}H_{39}NO$, 297.5191, found 298.3096.

3.2.2 Thermal Decomposition Model Compound

A solution of the compound 4-TEMPO-2,4,6-trimethyl heptane **(2)** in d-DMSO was purged with N_2 and heated to 100 °C for one hour. The solution was cooled and analyzed by ^{1}H NMR.

2,4,6-Trimethyl-3-heptene (Z Isomer) (3a): 2 in d-DMSO was heated to 100 °C for 1 hour. Thermal degradation products were not separated or purified. ^{1}H NMR (400 MHz, d-DMSO$_3$, δ, ppm,) 4.98 (1H, d, (-C(CH$_3$)=C**H**(CH$_3$)$_2$), J_1 = 8 Hz), 2.47 (1H, m, ((CH$_3$)$_2$C**H**C=CH-) under d-DMSO peak), 1.77 (2H, d, ((CH$_3$)$_2$CHC**H**$_2$C(CH$_3$)=CH-), J_1 = 8 Hz), 1.65 (1H, m, ((CH$_3$)$_2$C**H**CH$_2$-)), 1.54 (3H, s, (CH$_2$C(C**H**$_3$)=CH-)), 0.91 (6H, d, ((C**H**$_3$)$_2$CHC=C(CH$_3$)-), J_1 = 8 Hz), 0.82 (6H, d, ((C**H**$_3$)$_2$CHCH$_2$C(CH$_3$)=CH-), J_1 = 8 Hz).

2,4,6-Trimethyl-3-heptene (E Isomer) (3b): 2 in d-DMSO was heated to 100 °C for 1 hour. Thermal degradation products were not separated or purified. ^{1}H NMR (400 MHz, d-DMSO$_3$, δ, ppm,) 4.91 (1H, d, (-C(CH$_3$)=C**H**(CH$_3$)$_2$), J_1 = 8 Hz), 2.47 (1H, m, ((CH$_3$)$_2$C**H**C=CH-) under d-DMSO peak), 1.77 (2H, d, ((CH$_3$)$_2$CHC**H**$_2$C(CH$_3$)=CH-), J_1 = 8 Hz), 1.65 (1H, m, ((CH$_3$)$_2$C**H**CH$_2$-)), 1.54 (3H, s, (CH$_2$C(C**H**$_3$)=CH-)), 0.91 (6H, d, ((C**H**$_3$)$_2$CHC=C(CH$_3$)-), J_1 = 8 Hz), 0.82 (6H, d, ((C**H**$_3$)$_2$CHCH$_2$C(CH$_3$)=CH-), J_1 = 8 Hz).

2,6-Dimethyl-4-methyleneheptane (3c): 2 in d-DMSO was heated to 100 °C for 1 hour. Thermal degradation products were not separated or purified. ^{1}H NMR (400 MHz, d-DMSO$_3$, δ, ppm,) 4.70 (2H, s, (**H**$_2$C=C-)), 1.84 (4H, d, ((CH$_3$)$_2$CHC**H**$_2$-)$_2$ J_1 = 8Hz), 1.70 (2H, m, ((CH$_3$)$_2$C**H**CH$_2$-)$_2$, 0.85 (12H, d, ((C**H**$_3$)$_2$CHCH$_2$-)$_2$, J_1 = 8Hz).

3.2.3 Thermal Decomposition PP$_{atactic}$-g-TEMPO

Hydrogenated atactic-PP (9.0 g) was added to a two-neck round bottom flask and submerged in an oil bath at 110 °C and allowed to melt (~10 min.). BzOTEMPO (1.236 g, 4.47 mmol) was mixed for 10 min before adding L-231 (0.4902 g, 1.621 mmol). Once thoroughly mixed, the solution was cooled to room temperature and freeze-thaw degassed 3 times with N_2. The

deoxygenated solution was heated to 110 °C for 350 min. (3.2 half-lives). The graft modified PP was purified by dissolution precipitation using xylenes/acetone, followed by hexanes/acetone, and dried under vacuum. ^{1}H NMR spectrum integration of the aromatic resonances derived from BzOTEMPO relative to an internal standard provided the initial alkoxyamine concentration bound to the polymer. The integrated peaks were normalized relative to actual protons present in the compound. Then a ratio was used between signals from the internal standard and the bound labeling group, with a known amount of internal standard to calculate the amount of grafted nitroxyl.

Thermal decomposition experiments were then conducted on portions of the initial grafted PP under N_2 at various temperatures for a series of time lengths. Finally post thermal decomposition samples were then purified as mentioned above and ^{1}H NMR was taken again to detect changes in bound nitroxyl concentration.

3.2.4 Accelerated PP Oxidation

PP isotactic was grafted using TEMPO and DCP following the same techniques described in chapter 2 for the PP thermosets. The PP was then purified via dissolution/precipitation (xylenes/acetone). Thin films were hot pressed at 165 °C for 20-60 seconds. The resulting films were charged to an auto-clave and maintained at 100 °C under 5 bar of pure O_2. Films were analyzed by FT-IR spectroscopy prior to and post regular time intervals (~12 hours) of oxidation. The carbonyl region peak of absorbance used for detecting oxidation was at 1732 cm^{-1}, and was normalized for film thickness using a CH_2 wagging peak at 1165 cm^{-1}. The carbonyl index

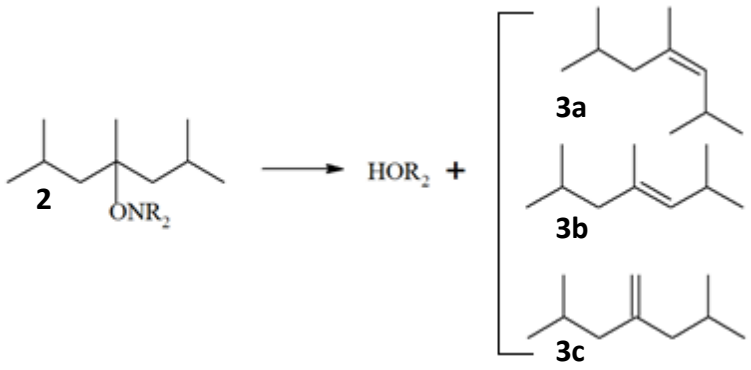
($A_{1732cm-1}/A_{1165cm-1}$), was used as a measure of PP oxidation to compare the effects of alkoxyamines relative to additive-free controls.

3.3 Results and Discussion

3.3.1 Alkoxyamine Stability

Detailed analysis of chemically modified polymers is complicated by their low functional group content and the inability to isolate products by conventional laboratory separation methods. Model compounds are useful in this regard, as they can provide unambiguous information on product structure, if not quantitative reaction rate data for a polymer melt process. A tertiary alkoxyamine, 4-TEMPO-2,4,6-trimethyl heptane (**2**), was prepared by bromination of 2,4,6-trimethyl-4-heptanol **(1)**, followed by regioselective conversion to the target molecule via Bu_3SnH and excess TEMPO.

Heating the alkoxyamine **(2)** in deuterated dimethyl sulfoxide (d-DMSO) to 100°C for 60 min. yielded a mixture of disproportionation products (Scheme 8). ^{1}H NMR spectrum integration (Figure 9ii) showed that 85% of the starting material was converted during this treatment to give Z-2,4,6-trimethyl-3-heptene (**3a**, 4%), E-2,4,6-trimethyl-3-heptene (**3b**, 53%), and 2,6-dimethyl-4-methyleneheptane (**3c**, 42%). The mechanism of this decomposition, whether radical-mediated [29] [30]or ionic [31] [55], is presently unknown. Nevertheless, the extent of tertiary alkoxyamine disproportionation at 100°C is concerning, given that PP modifications must be conducted above the 160°C melting point of the polymer.



Scheme 8: Disproportionation of 4-TEMPO-2,4,6-trimethyl heptane (2).

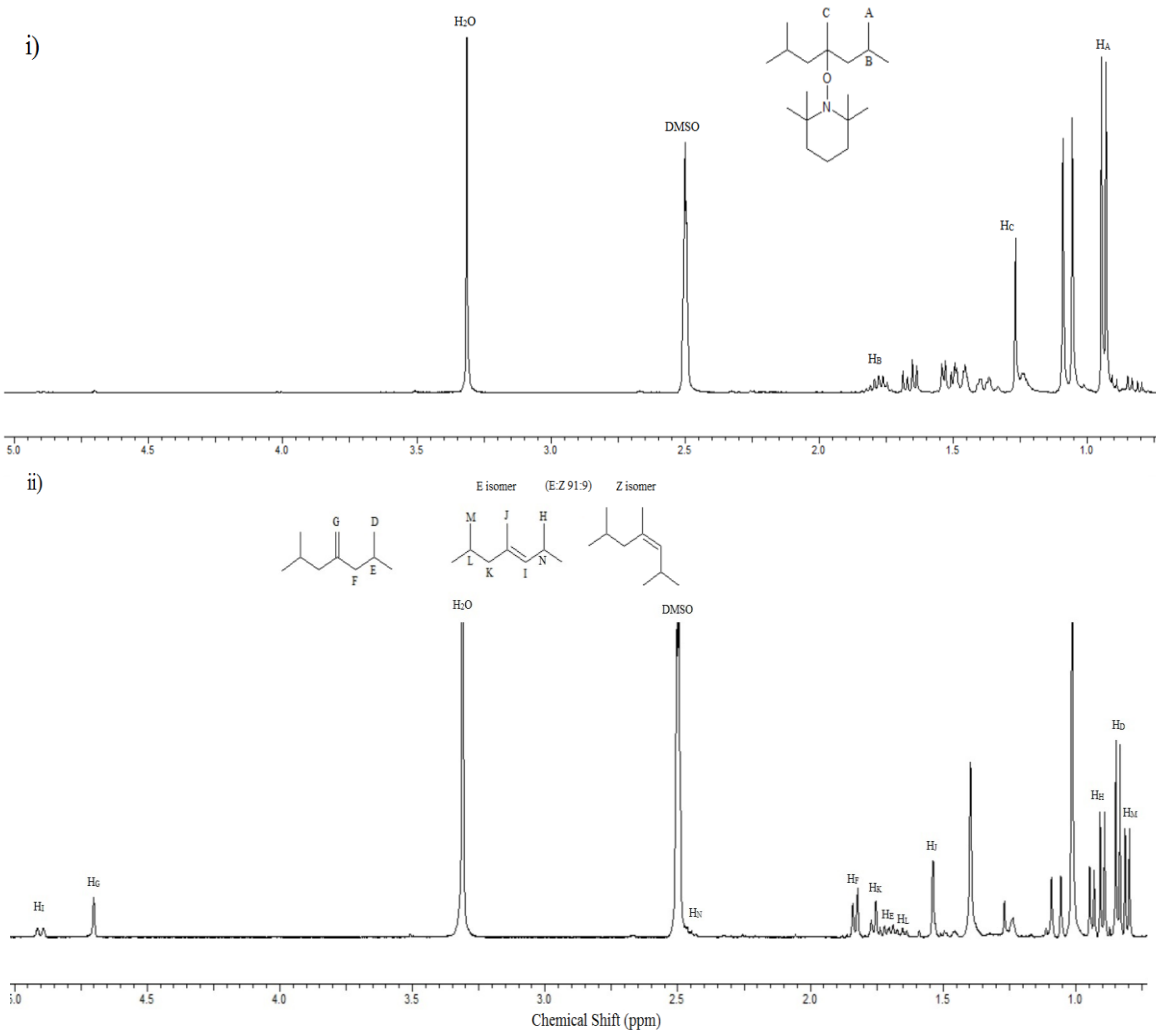


Figure 9: Labelled ^{1}H NMR of 4-TEMPO-2,4,6-trimethyl heptane (2) i) before and ii) after 60 min. at 100°C. Solvent d-DSMO.

While useful for identifying the structure of potential reaction products, model compound reaction rates and yields must be interpreted with caution. This is particularly true in the present case, given that the model decomposition was conducted in a polar, aprotic solvent (DMSO), in contrast to PP modifications where the non-polar hydrocarbon is the reaction medium. This

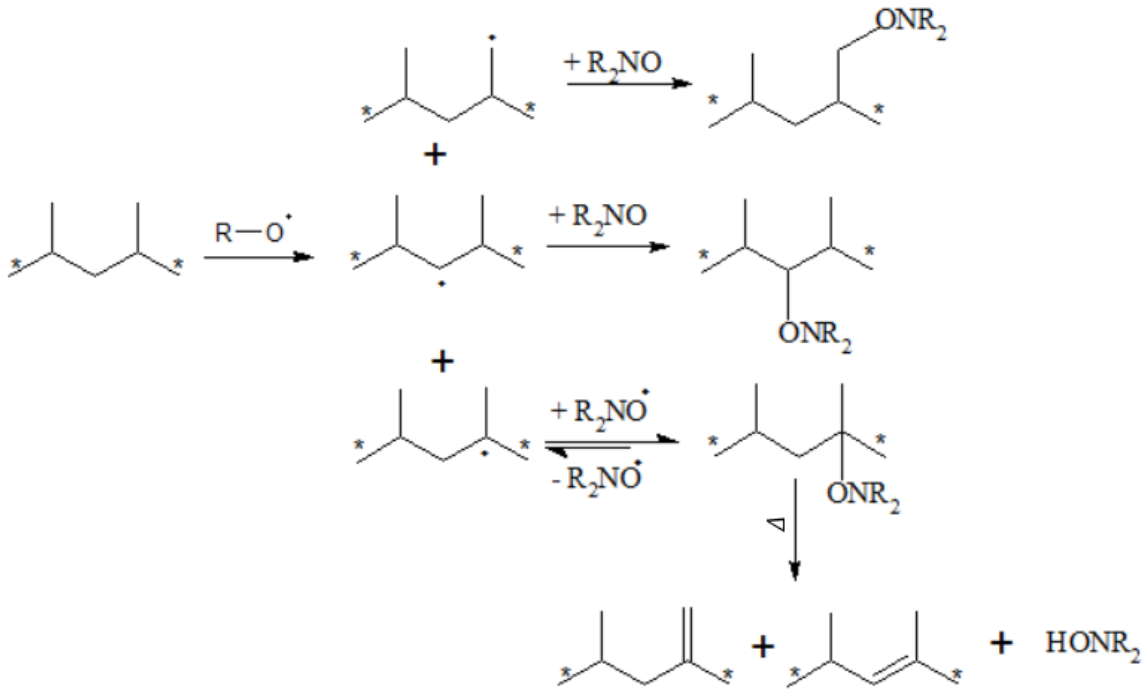
motivated a study of alkoxyamine stability with in graft-modified PP. To this end, low molecular weight, atactic polypropylene was treated with peroxide and benzoated hydroxyTEMPO (BzOTEMPO) to produce polymer-bound alkoxyamine functionality, and purified to remove residual peroxide and/or nitroxyl derived byproducts. ^{1}H NMR spectrum integration of the starting material as well as purified samples isolated after heating PP-g-BzOTEMPO for specific intervals generated the data listed in Table 1.

Table 1: PP-bound alkoxyamine content as a function of time at various decomposition temperatures.

Temperature (°C)	Time (min)	BzOTEMPO content (μmole/g·PP)
100	0	57
	30	50
	120	48
165	0	57
	10	52
	20	47
	30	42
	120	37
185	0	57
	30	40
	120	37

The observed losses in alkoxyamine content from PP-g-BzOTEMPO were significant for all three of the temperatures studied, suggesting that disproportionation may contribute to VBTEMPO-based PP cure formulations. A two-hour exposure to 100°C resulted in a 16% decline in polymer-bound alkoxyamine concentration, far less than expectations based on the model compound reaction, but highly relevant to accelerated oxidation tests (see below). Data acquired

at 165 °C relate to the VBTEMPO formulations described in Chapter 2, which operate on a 30-minute timeframe. Over this timescale, PP-g-BzOTEMPO lost 35% of its alkoxyamine content. Note that this decline did not follow a first-order decomposition toward zero concentration, but plateaued around 37 μmole/g·PP. This is likely due to the presence of primary, secondary and tertiary alkoxyamines in the sample, with only the latter being appreciably unstable toward disproportionation (Scheme 9).



Scheme 9: Potential products of nitroxyl trapping of PP-derived macroradicals.

Although the integration of aromatic resonances within ^{1}H-NMR spectra provided a quantitative measure of the extent of alkoxyamine decomposition, ascertaining the structure of the olefinic byproducts unambiguously proved to be difficult. Comparing the ^{1}H NMR of the degraded model

compound to that of the degraded grafted PP reveals that similar by-products were found in both experiments (Figure 10). The resonance of interest is δ=4.71 ppm arising from vinyl unsaturation akin to model compound **3c**, with only small evidence of the internal olefins **3a,b** apparent in the spectrum.

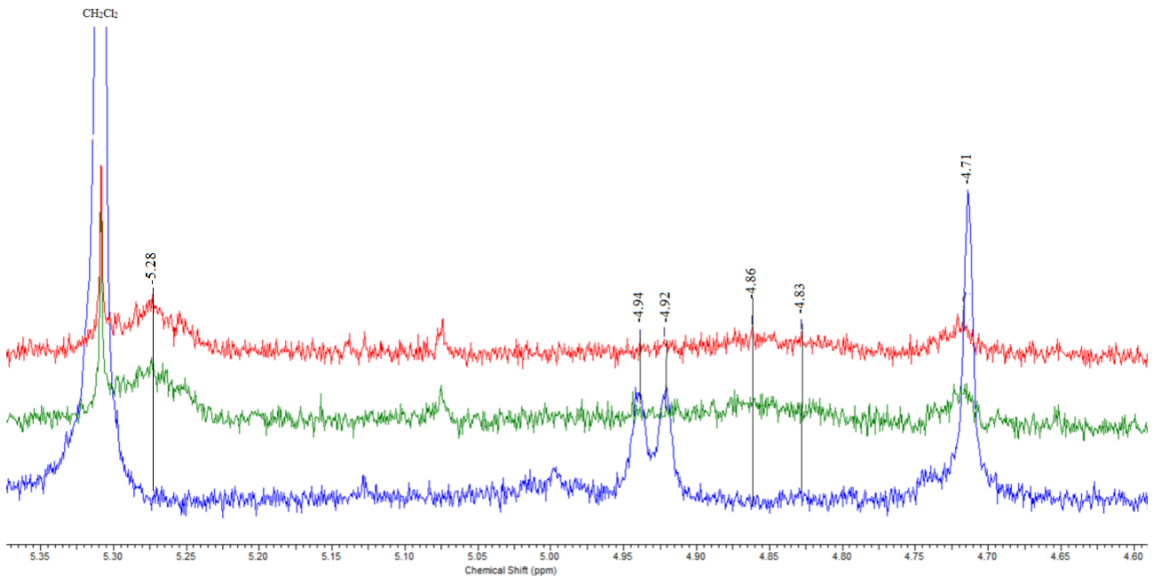
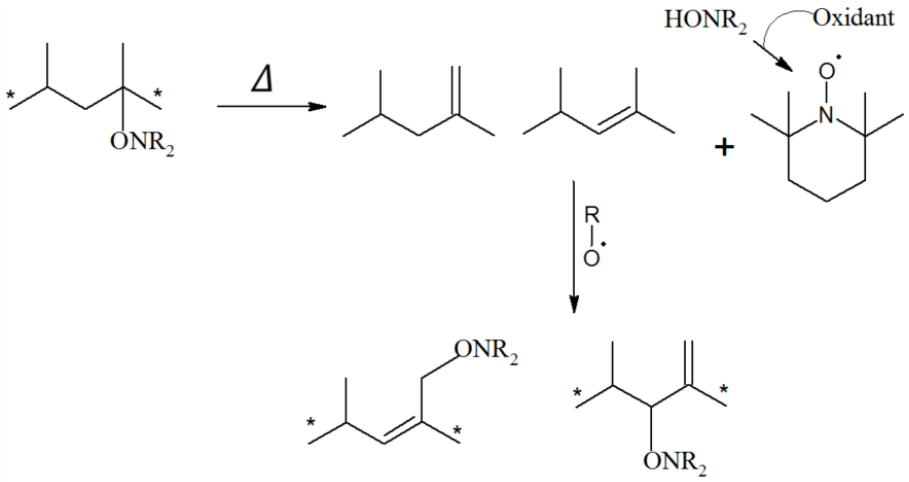


Figure 10: ^{1}H NMR spectra of model compound disproportionation products (bottom), prior to any thermal treatment PP-g-BzOTEMPO (middle), and thermally treated PP-g-BzOTEMPO (top). Solvent $CDCl_3$.

Comparing the pre and post thermal treated PP-g-BzOTEMPO ^{1}HNMR unfortunately does not reveal the formation of any obvious decomposition by-products. As such speculation regarding regioselective thermal decomposition of the alkoxyamines is not conclusive, especially since primary and secondary decomposition products would be indistinguishable in ^{1}H NMR. The resonance at δ = 5.28 ppm only shows up for the PP-g-BzOTEMPO experiments and provides another region of uncertainty with respect to PP nitroxyl-mediated chemistry. The downfield shift of this alkene peak can rise from α-alkoxyamine functionality, bearing analogous allylic

alkoxyamine ^{1}H NMR shifts seen in work done by Scott et al. [27]. Integrating the peak at 5.28 ppm and comparing it to the aromatic peaks from the BzOTEMPO suggests that is possible for a significant amount alkoxyamines to end up in an allylic position instead of the expected aliphatic position in our PP-grafting formulation. The confirmation of generating unsaturation in the polymer backbone with suspected cyclic activity of TEMPO provides the necessary components for producing allylic alkoxyamines (Scheme 10).



Scheme 10: Speculative formation of allylic alkoxyamines in PP at slow grafting conditions.

A more robust experiment is needed to detect the thermal decomposition by-products of PP alkoxyamines as there are further complications to this nitroxyl-mediated peroxide chemistry than anticipated.

3.3.2 Accelerated Oxidation of PP-g-TEMPO

While the commercial application of primary alkoxyamines as polymer antioxidants is widespread, their mechanism remains the subject of active speculation. It is generally agreed that conversion to nitroxyl is required, leading to a chain breaking donor antioxidant process wherein nitroxyl quenches alkyl radicals by combination [36]. However, the pathway by which a primary alkoxyamine is transformed into a nitroxyl is unclear. In the case of VBTEMPO-modified PP thermosets, there exist primary, secondary and tertiary alkoxyamines, the latter being demonstrated as labile at temperatures above 100°C. The potential therefore exists for PP-g-TEMPO to exhibit better oxidative resistance than its parent material.

This potential was examined by exposing thin, freestanding films of PP and its derivatives to accelerated oxidation conditions (5 atm of pure oxygen and 100°C) for upwards of 15 days, and measuring the extent of oxidation by transmittance FT-IR spectroscopy. The control sample was purified isotactic PP, to which two purified PP-grafted-TEMPO (PP-g-TEMPO) derivatives were compared. The first derivative contained on the order of 28 μmole/g·PP of polymer-bound TEMPO, while the second contained about 41 μmole/g·PP of polymer-bound TEMPO. One film of each material was subjected to identical oxidation conditions in the same autoclave, and removed periodically for analysis of the growth of carbonyl (C=O) resonances in the FT-IR spectrum. Using peak heights measured in absorbance mode, the carbonyl index (CI) of each polymer was monitored over time and plotted in Figure 11.

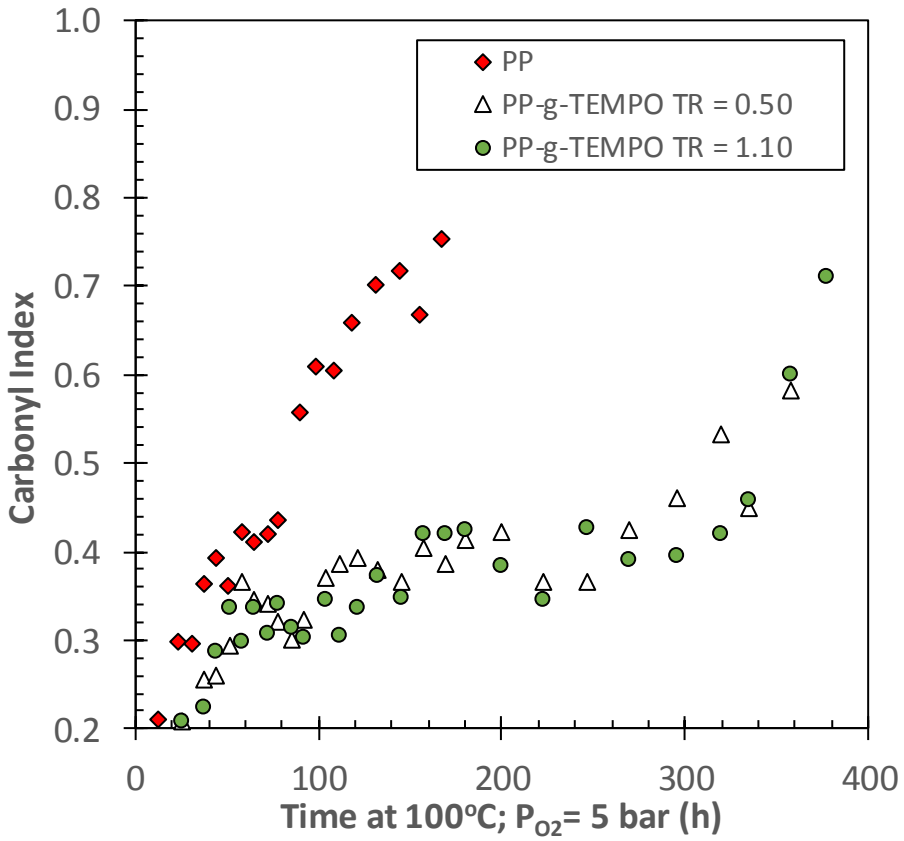


Figure 11: Accelerated oxidation of PP-g-TEMPO films (100°C; P_{O2} = 5 bar; [DCP] = 74 µmole/g).

The control sample oxidized almost immediately and became brittle to the point where the sample crumbled after 166.5 hr in the accelerated aging environment. However, PP-g-TEMPO materials showed reduced oxidation activity for more than 335 hr before failing mechanically in the same manner.

The enhanced stability is a confirmation of antioxidant activity of TEMPO-based alkoxyamines of PP at 100 °C, and may be attributed to the tertiary alkoxyamine instability documented above.

Via the possible decomposition products of tertiary alkoxyamine (hydroxylamine + olefin), literature shows that transformation of hydroxylamines are effective antioxidants [56]. Conversion of hydroxylamine to nitroxyl provides the above discussed antioxidant behaviour through macroradical trapping [36] [56]. The tertiary alkoxyamine instability at 100 °C greater clouds the speculation though as to how alkoxyamines in polyolefins act as an antioxidant. Detecting the stabilizing capacity differences between thermally stable and unstable alkoxyamines is not differentiable at these conditions. It should be noted, however, that antioxidant protection at ambient temperatures is required for consumer good applications. Unfortunately, a room temperature study using 6 bar of O_2 was run for 40 weeks, but demonstrated no oxidation activity in the control material or the PP-g-TEMPO samples. Suggestions for further studies in this area can be found in the following chapter.

3.4 Conclusion

The tertiary alkoxyamine functionality generated by TEMPO-based PP modification chemistry is susceptible to disproportionation at elevated temperatures. It is likely that the disproportionation is regioselective in that after long periods of time (2 h) in a decomposition environment there appears to be a plateau in loss of alkoxyamine. This suggests that some alkoxyamine regioisomers are more stable than other sites in PP, with the latter likely being the tertiary site. There also exists potential for allylic alkoxyamines to form considering the cyclic nature of TEMPO and generation of polymer backbone unsaturation, resulting from tertiary-alkoxyamine stability. Since products of decomposition could not be quantitatively analyzed, determining the regioisomers of alkoxyamine decomposition and post thermal treatment stable alkoxyamine positions with complete certainty was not possible.

TEMPO-g-PP contains antioxidative capacities in an accelerated oxidation environment at 100 °C compared to its parent material. The debate of thermally stable alkoxyamines (primary and secondary) contributing greater capacity as antioxidants compared to process liberated nitroxyl (thermally treated tertiary alkoxyamine) is still unanswered as ambient temperature oxidation experiments revealed no oxidation in samples with and without grafted nitroxyl.

Chapter 4: Conclusions and Future Work

4.1 Conclusions

New chemistry for preparing PP thermosets is described, wherein radical degradation suffered during conventional peroxide treatment is overcome using a nitroxyl additive bearing a polymerizable functional group. This chemistry heavily bears dependency of the kinetic reactivity of the polymerizable functional group associated with the nitroxyl trapping agent. G' yields and gel content extents can be controlled by selecting polymerizable functionalities with varying degrees of reactivity that will face different outcomes when competing with peroxide induced β-chain scission. Control of crosslink density yields and induction times is possible via the choice of peroxide initiator due to differences in thermolysis rates and H-abs abilities. In an industrial application there is room for economically optimizing formulations with the use of coagents, as their synergy with functionalized nitroxyls can achieve competitive crosslink yields with reduced nitroxyl and initiator loadings.

The tertiary alkoxyamine functionality generated by TEMPO-based PP modification chemistry is unstable at elevated temperatures. While instability does exists, some of the alkoxyamine regioisomers exhibit stable behavior as after thermally treating samples for 2 h losses in alkoxyamine concentrations appeared to plateau. The products of alkoxyamine thermal instability were inconclusive except for the detection of unsaturation. The fate of alkoxyamine stability can result in unsaturation which provides allylic sites not present in the parent material. If TEMPO is catalytic in processing conditions than it is possible that allylic alkoxyamines form giving rise to

alternative polymer reactivity compared to the previously assumed strictly aliphatic alkoxyamines in PP nitroxyl-mediated curing.

Stabilizing capacities of TEMPO-g-PP in an accelerated oxidation environment were observed compared to its parent material. The mechanism of alkoxyamines acting as antioxidants remains a mystery as thermally accelerated oxidation experiments cloud the results due to inherent alkoxyamine thermal stability behavior.

4.2 Future Work

It may be desirable to extend the one-pot peroxide curing chemistry to other scissionable polymers such as PIB. Curing PIB has not been successful in the past due to its low macroradical yields. Though the effectiveness of this chemistry does scale with increasing macroradical yields in the polymer, perhaps an even more reactive polymerizable group could out-compete chain scission reactions even with very small macromonomer yields. A functionalized nitroxyl bearing multi-polymerizable groups comparable to the ones tested here have the **potential** to provide the greater kinetic reactivity required for a PIB cure.

To detect the regioisomers of alkoxyamine functionality a more robust model compound method should be employed. Such a method could include formation of a model compound bearing all alkoxyamine regioisomers with quantification of yields at each site. Followed by decomposition and subsequent quantification of remaining alkoxyamine yields at each respective site. This experiment could be conducted using gas chromatography techniques as long as each

alkoxyamine bears a unique detection response factor. Also it would be of interest quantify the existence of allylic alkoxyamines and compare their concentration to that of aliphatic. Such techniques as nitroxyl exchange experiments could give light regarding allylic alkoxyamine populations in PP.

Regarding alkoxyamine capacity to act as oxidation stabilizers, an ambient condition experiment is necessary. The goal would be to accelerate oxidation rates without using thermal energy as the source. Perhaps oxidation could be accelerated via photolysis at room temperature, assuming the photolytic process does not have an effect on alkoxyamine stability. Inferences between thermally stable and unstable alkoxyamine antioxidant capacity could also be evaluated by comparing oxidation extents between formulations with PE and PP. This would be useful since PE is known to have relatively more thermally stable alkoxyamines compared to that of the PP system, helping to assess stability effects of alkoxyamine on antioxidation capacities.

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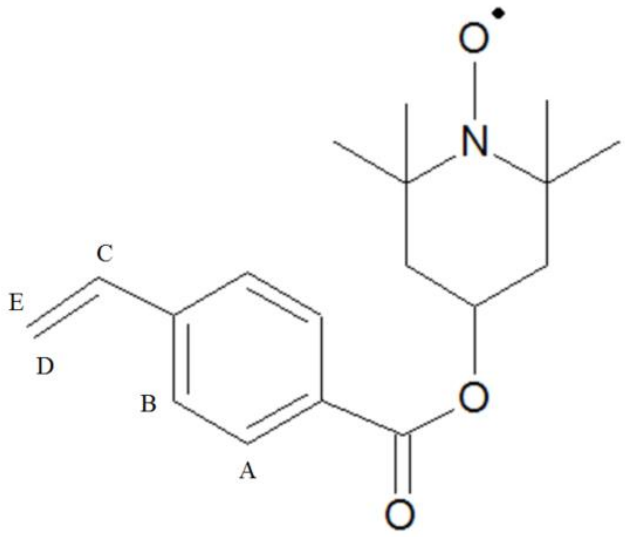
Appendix A: Characterization of new functionalized nitroxyls

VBTEMPO (1a) ^{1}HNMR

Scheme 11 shows the molecular structure of VBTEMPO (1a) with labeled protons that were detectable using ^{1}HNMR.



Scheme 11: Molecular structure of VBTEMPO (1a) with ^{1}H labeling corresponding to ^{1}HNMR.

The corresponding ^{1}H NMR spectrum for the labeling in Scheme 11 can be seen in Figure 12.

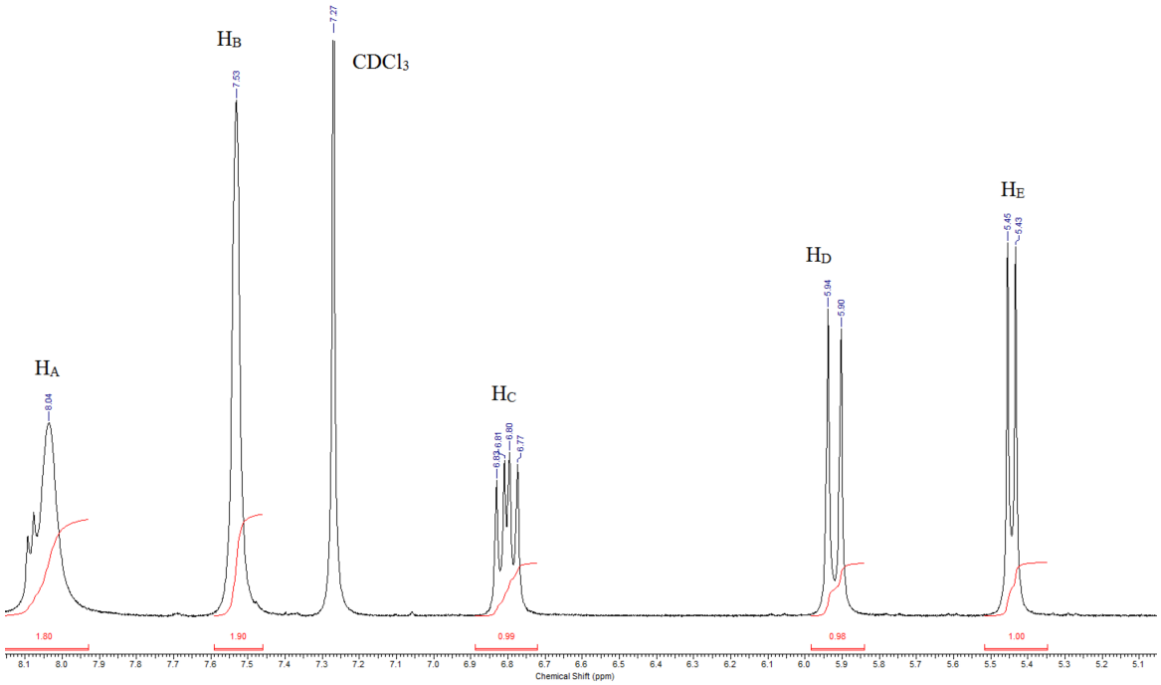
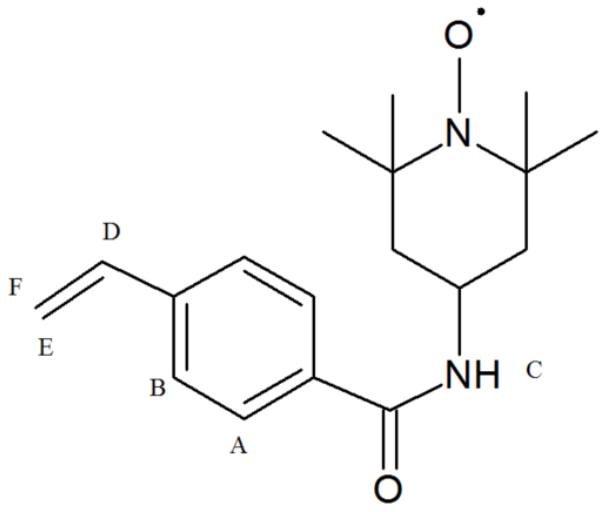


Figure 12: ^{1}H NMR spectrum of VBTEMPO (1a) aromatic/alkene region. Solvent $CDCl_3$.

Only the aromatic/alkene region has been shown here as the radical nature of the nitroxyl made ^{1}H NMR characterization not possible for the aliphatic region of the spectrum. The characterization of these peaks can be seen in the materials section of Chapter 2.

VBATEMPO (2) ^{1}HNMR

Scheme 12 shows the molecular structure of VBATEMPO (2) with labeled protons that were detectable using ^{1}HNMR.



Scheme 12: Molecular structure of VBATEMPO (2) with ^{1}H labeling corresponding to ^{1}HNMR.

The corresponding ^{1}H NMR spectrum for the labeling in Scheme 12 can be seen in Figure 13.

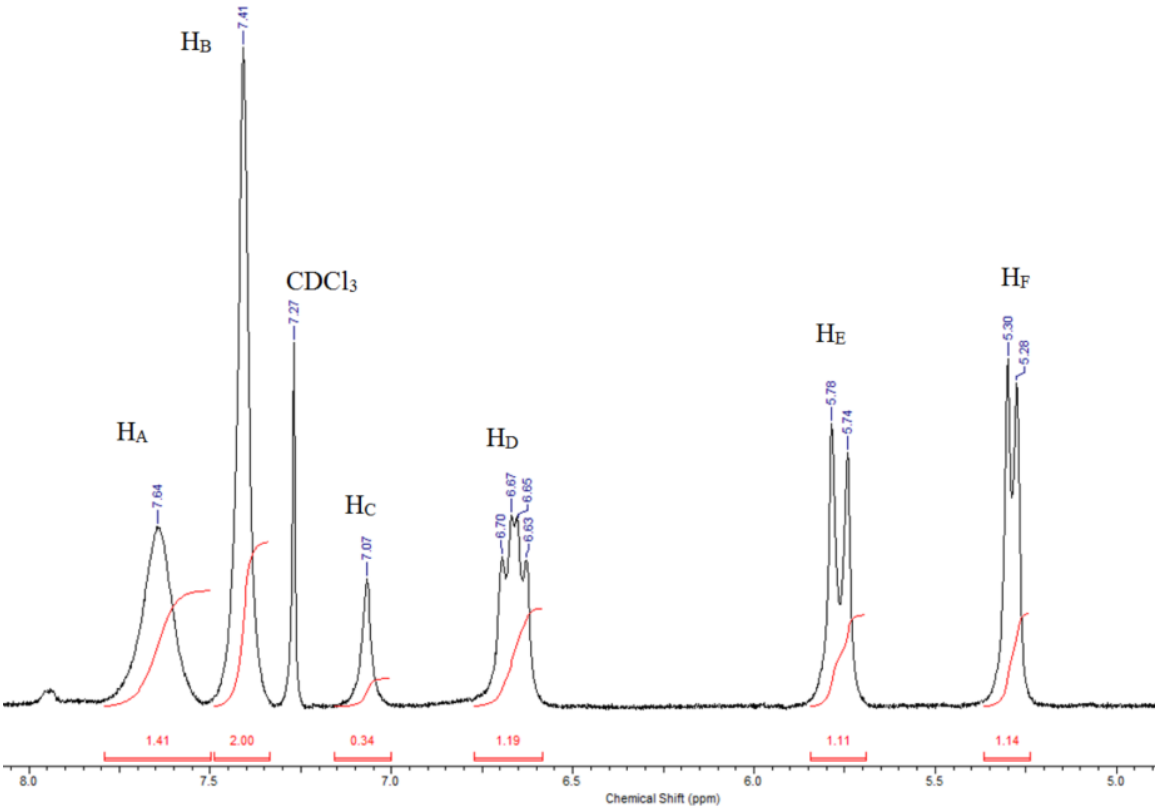


Figure 13: ^{1}H NMR spectrum of VBTEMPO (1a) aromatic/alkene region. Solvent $CDCl_3$.

Only the aromatic/alkene region has been shown here as the radical nature of the nitroxyl made ^{1}H NMR characterization not possible for the aliphatic region of the spectrum. The characterization of these peaks can be seen in the materials section of Chapter 2.