ADDITIVE EFFECTS ON MELT-STATE MODIFICATION OF COMMODITY POLYOLEFINS

by

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Abstract

In this work, melt-state peroxide mediated crosslinking of butyl rubber (IIR) and linear low density polyethylene (LLDPE) was used to determine additive effects, as well as the effect of higher isoprene content on the extent of crosslinking. Grafting of vinyltriethoxysilane (VTEOS) to polymer and hydrocarbon substrate was used to determine the effects of unsaturation and additives on radical intermediates.

Grafting of VTEOS to butyl rubber (melt-state) was sensitive to isoprene content. Higher isoprene improved the rate of combination relative to chain scission because of resonance stabilization of allylic macroradical intermediates. Graft yields for IIR were lower than those of poly(isobutylene) homopolymer, because unsaturation dramatically increased the relative rate of degradative chain transfer.

Higher reactivity of high isoprene rubber was employed to graft acrylated radical traps that combine with polymer macroradicals and subsequently oligomerize. This occurred in appreciable quantities, giving a modest crosslinked network that was less prone to stress relaxation, compared to poly(isobutylene).

The effects of several antioxidants on peroxide crosslinking of LLDPE and grafting of VTEOS to cyclohexane were assessed. All but the hindered amine 2,2,6,6-tetramethylpiperidine (TEMPH) were found to affect peroxide cures and graft addition. TEMPH survived grafting reactions, as well as DCP-only crosslinking reactions in cyclohexane in the absence of oxygen, while 1,2,2,6,6-pentamethylpiperidine (TEMPMe) did not.

High molecular weight hindered amine suppressed oxidative degradation in LLDPE films for 16 days, quantitatively as well as BHT (industry standard). Thus, hindered amine 2,2,6,6-tetramethylpiperidine (TEMPH) was selected as an ideal latent antioxidant, and this was explained by the requirement of oxidative activation to form a reactive nitroxyl for radical scavenging. Activation mechanisms were reviewed, the most likely being the formation of a tetramethylpiperinyl radical intermediate before oxidation to generate nitroxyl.

Co-Authorship

Chapters 2 and 3 have been included in manuscript format for submission. As such, the work presented in Chapter 2 includes research originally done by Brian Molloy: functionalized nitroxyl effects on the crosslinking of PIB (Figure 6), and G’ measurements of IIR reacted with DCP (Figure 7a), which were repeated and confirmed by me. This work also includes polymer abstraction efficiencies for high isoprene IIR and PIB determined by Elena Mueller (Table 1), as well as synthesis and stability testing of 2,2,4,8,8-pentamethyl-4-nonene-g-TEMPO allylic alkoxyamines performed by Anca Penciu (Section 2.3.3, Figure 5A). I would like to thank all of them for their contributions, as well as for allowing me to include this data in my thesis. I would also like to thank Dr. J. Scott Parent for helping me write this manuscript. All other data and written work appearing in the following Chapters is original to this thesis unless otherwise referenced.

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Table of Contents

Chapter 1 Introduction and Literature Review 1

1.1 Melt-State Peroxide Modification of Poly(ethylene) 1

1.2 Melt-State Peroxide Modification of Poly(isobutylene-co-isoprene). 8

1.3 Nitroxyls used as Scorch Protectants 12

1.4 LLDPE Oxidative Degradation and Effective Antioxidants. 16

1.5 Research Objectives 27

1.6 Literature Cited 28

Chapter 2 Peroxide-initiated Chemical Modification of Poly(isobutylene-co-isoprene) 33

2.1 Abstract. 33

2.2 Introduction. 34

2.3 Experimental Section. 36

2.3.1 Materials. 36

2.3.2 Instrumentation and Analysis 37

2.3.3 Synthesis of Allylic Alkoxyamines 2a:2b:2c. 37

2.3.4 PMN model compound study. 38

2.3.5 Polymer H-Atom Abstraction Efficiency 38

2.3.6 Polymer H-Atom Abstraction Regioselectivity. 39

2.3.7 Vinyltriethoxysilane melt state grafting. 39

2.3.8 Vinyltriethoxysilane solution grafting. 39

2.3.9 Cure Rheology. 40

2.4 Results and Discussion. 40

2.4.1 Abstraction Efficiency. 40

2.4.2 Regioselectivity of H-atom transfer. 42

2.4.3 Peroxide-initiated Polymer Modifications. 46

2.4.4 Vinyltriethoxysilane graft yields 48

2.4.5 AOTEMPO-mediated Cross-linking. 51

2.5 Conclusions. 54

2.6 Literature Cited. 55

Chapter 3 Peroxide-initiated Modification of Polyolefins 58

3.1 Abstract. 58

3.2 Introduction. 60

3.3 Experimental Section. 64

3.3.1 Materials. 64

3.3.2 Instrumentation and Analysis. 64

3.3.3 Cure Rheology. 65

3.3.4 Vinyltriethoxysilane grafting. 65

3.3.5 Hindered Amine Conversion Study. 66

3.3.6 Polymer Oxidation. 66

3.4 Results 66

3.4.1 Peroxide-initiated LLDPE Crosslinking. 66

3.4.2 Effective Concentration of Latent AO’s. 71

3.4.3 Peroxide-initiated Grafting of VTEOS. 72

3.4.4 LLDPE oxidation. 74

3.5 Discussion. 74

3.6 Conclusions. 82

3.7 Literature Cited 84

Chapter 4 Conclusions and Future Work 88

4.1.1 H-atom Transfer Yields and Regioselectivity 88

4.1.2 In Search of a Latent Antioxidant 89

4.2 Future Work. 91

List of Figures

Figure 1. Dynamics of LLDPE crosslinking and DCP thermolysis... 4
Figure 2. Dynamics of peroxide-initiated IIR-g-AA crosslinking 10
Figure 3. Influence of AOTEMPO on peroxide-initiated LLDPE cure dynamics and yields 13
Figure 4. 1H NMR with expanded regions showing: A) 2,2,4,8,8-pentamethyl-4-nonene B) IIR-5.8 41
Figure 5. 1H NMR showing TEMPO-trapped radical derived from H-atom donation to cumyloxyl 43
Figure 6. Dynamics of DCP-initiated polymer modification 47
Figure 7. Dynamics of PIB and IIR-5.8 modifications using different trapping ratios 53
Figure 8. Cure dynamics for DCP-initiated LLDPE crosslinking with different additives 68
Figure 9. DCP-initiated LLDPE crosslinking yields.. 69
Figure 10. VTEOS conversion in cyclohexane 73
Figure 11. Oxidation of LLDPE films 74

List of Tables

Table 1. DCP abstraction efficiency and VTEOS conversion 42

Table 2. VTEOS conversion in cyclohexane + cyclohexene mixtures[a] 50

Table 3. Additive structures with additive effects on: a. modulus changes for peroxide-initiated melt-crosslinking of LLDPE, and b. conversion of VTEOS grafted to cyclohexane 70

Table 4. ΔG’ for DCP crosslinking of LLDPE with additives 71

List of Schemes

Scheme 1. High temperature peroxide initiation and H-atom abstraction/disproportionation 2
Scheme 2. Stoichiometric radical mediated crosslinking of PE 3
Scheme 3. Radical mediated grafting of VTEOS to PE (modified from Parent and coworkers) 6
Scheme 4. β-scission and combination of PIB macroradicals 8
Scheme 5. BIIR substitution reaction producing IIR-g-AA 9
Scheme 6. Peroxide-mediated competing acrylate oligomerization and β-scission of IIR-g-AA 10
Scheme 7. Functionalized and unfunctionalized nitroxyls of the type 2,2,6,6-tertramethylpiperidin-1-oxyl 12
Scheme 8. Peroxide-mediated competing acrylate oligomerization and β-scission of IIR-g-AA 14
Scheme 9. Radical chain oxidation 16
Scheme 10. Hydroperoxide reactions involved in thermal oxidation of PE 17
Scheme 11. Irgaphos168 decomposition of hydroperoxide and peroxy radicals 20
Scheme 12. Summary of primary antioxidant mechanism of BHT 21
Scheme 13. Vitamin E oxidation products and pathways for product formation in peroxyl radical scavenging 22
Scheme 14. Simple Denisov Cycle 23
Scheme 15. Proposed catalytic role of TEMPH in oxidative stabilization of polypropylene 24
Scheme 16. Amine regeneration from alkoxyamine 25
Scheme 17. Cumyloxy fragmentation and H-atom abstraction 35
Scheme 18. Potential H-atom abstraction products of PMN 44
Scheme 19. Regioselectivity of H-atom abstraction from PMN 46
Scheme 20. Simultaneous degradation and cross-linking of IIR 48
Scheme 21. Radical-mediated grafting of VTEOS to cyclohexane 49
Scheme 22. AOTEMPO-mediated reactions of PIB 52
Scheme 23. Peroxide-initiated crosslinking of polyethylene 61
Scheme 24. Graft propagation sequence for VTEOS addition to a polyolefin 61
Scheme 25. Radical oxidation with potential antioxidant interactions 62
Scheme 26. TEMPH aminyl radical activation, adapted from Gryn'ova and coworkers 78
Scheme 27. Simplified hydroperoxide 2 step reaction with secondary amine to produce nitroxyl 79

List of Abbreviations

δ – chemical shift
µmol – micromoles
AE – abstraction efficiency
AO –antioxidant
AOTEMPO – 4-acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl free radical
BDE – bond dissociation energy
BHT – butylated hydroxytoluene
BIIR- brominated poly(isobutylene-co-isoprene)
Bu$_4$NOH – tetrabutylammonium hydroxide
CDCl$_3$ – deuterated chloroform
DCP – dicumyl peroxide
eq. - equivalents
g – grams
G’ – storage modulus
GC – gas chromatography
h – hours
HAS – hindered amine stabilizer
HALS – hindered amine light stabilizer
H-atom – hydrogen atom
Hz - Hertz
IIR – poly(isobutylene-co-isoprene)
IIR-g-AA – acrylate derivative of BIIR
IP – isoprene
Kg - kilograms
kPa – kilopascals
L231 – Luperox/Lupersol 231 - 1,1-Bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane
min - minutes
mL - milliliters
mmHg – millimeters of mercury
mmol - millimoles
mol - moles

MPa – megapascals

MFI – melt flow index

NMR – nuclear magnetic resonance

OTEMPOS - Bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate

PE – poly(ethylene)

PIB – poly(isobutylene)

PMN -2,2,4,8,8-pentamethyl-4-nonene

ROOR - peroxide

rpm – revolutions per minute

TEMP· - 2,2,6,6-tetramethylpiperidinyl radical

TEMPH – 2,2,6,6-tetramethylpiperidine

TEMPHS - Bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate

TEMPMe – 1-2,2,6,6-pentamethylpiperidine

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

TMP – 2,2,4,4-tetramethylpentane

UHMWPE – ultra-high molecular weight poly(ethylene)

UV – ultraviolet

VTEOS - vinyltriethoxysilane

Chapter 1

Introduction and Literature Review

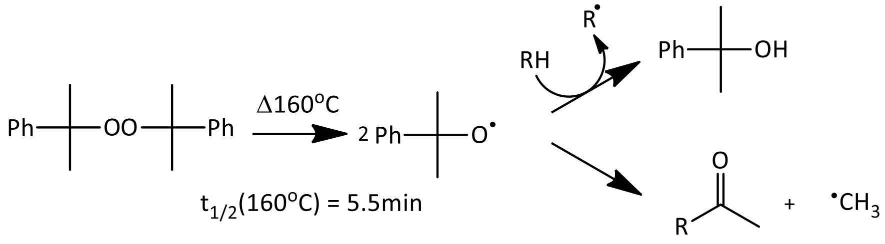
1.1 Melt-State Peroxide Modification of Poly(ethylene)

Poly(ethylene) (PE) is a relatively inexpensive commodity polyolefin that has a high chemical resistance and low electrical conductivity. It is a highly crystalline long chain aliphatic material and has a melting temperature normally between 108-132°C for commercial polymers.[1] PE tends to have no volatile or extractable plastisizers when compared with other polymers such as poly(vinylchloride) and has no effective solvent at room temperature. There are many different types of PE, and each has its own specific characteristics. Being competitive with LDPE (low density poly(ethylene)), LLDPE (linear low density poly(ethylene)) has found applications where high toughness, tensile strength, elongation at break, and puncture resistance are required such as for kitchen utensils, low-voltage wire and cable insulation, and stretch film. LLDPE shows reduced environmental stress cracking and improvement in deformation resistance when compared with LDPE of similar density and melt flow index (MFI).[1]

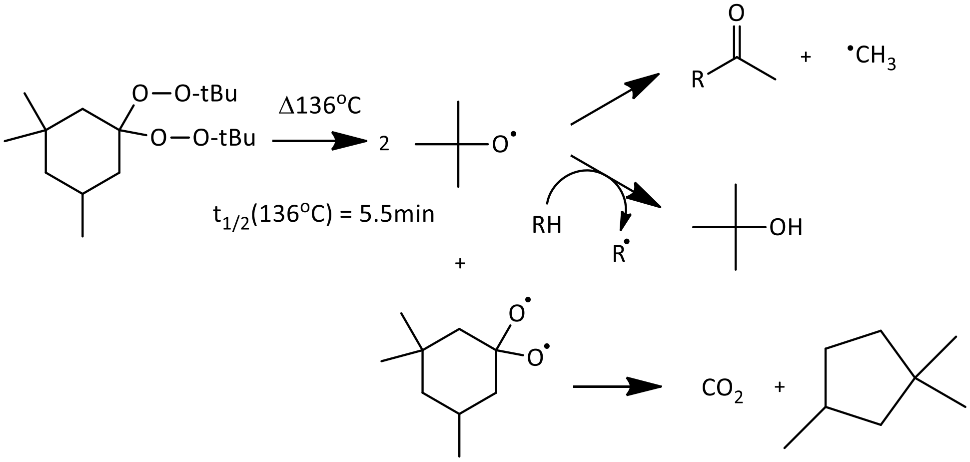
PE as an unmodified homopolymer has a limited range of applications because it is unreactive toward organic fillers and will undergo softening above approximately 110°C. Modification of plastics and elastomers to produce value added materials is common practice in the polymer industry. Polyolefins such as PE can be processed in the melt state, where they undergo chemical modification and architectural changes to produce thermoset or grafted products.[2] Melt processing of a plastic can be done during compression molding, reactive extrusion, or sintering, where the plastic has time to be shaped before initiators activate polymer chains for combination (crosslinking), cleavage (controlled degradation), or addition (grafting). Peroxide mediated crosslinking of LLDPE improves resistance to stress relaxation and creep, as well as giving a higher resistance to thermal decomposition and wear.[3] Modification using peroxides must be carried out at temperatures high enough to adequately reduce melt viscosities and decompose peroxides. Depending on the peroxide used, it will decompose readily at different temperatures and it can have a substantially different effect on polymer reactivity.[4] In general, peroxides react by abstracting an H-atom (hydrogen atom) from the polymer backbone after thermolysis (Scheme 1).

Scheme 1. High temperature peroxide initiation and H-atom abstraction/disproportionation

Bis(1-methyl-1-phenylethyl)peroxide (DCP) thermal decomposition



1,1-bis(t-butylperoxy)-3,5,5-trimethylcyclohexane (L231) thermal decomposition

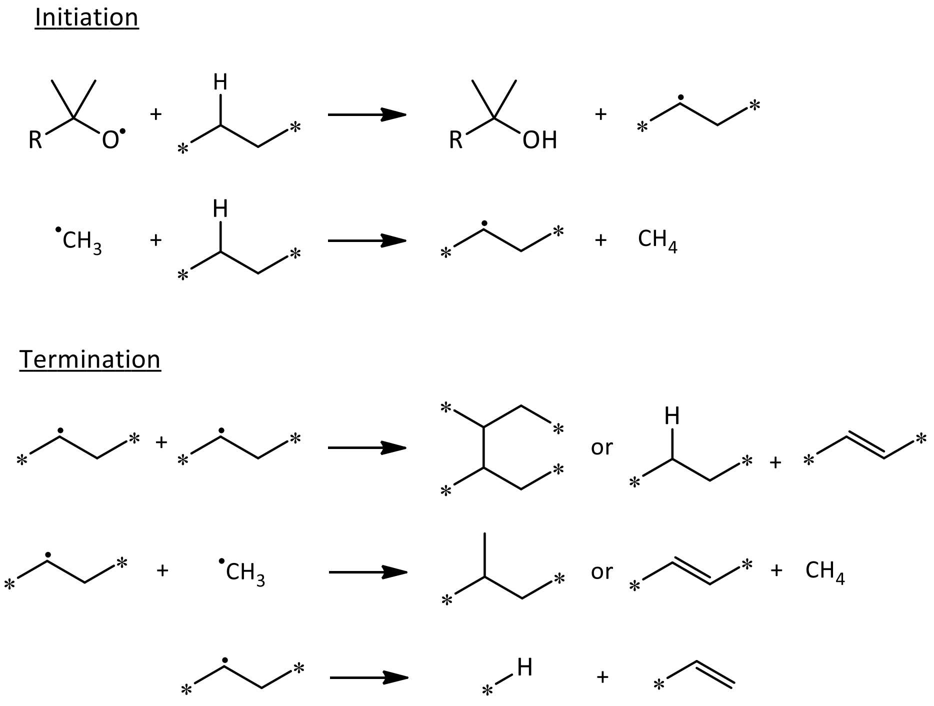


The reactivity of a polymer towards H-atom transfer determines the extent of modification that can occur. In polymer systems that are poor H-atom donors, peroxides such as DCP and L231

(Scheme 1) have a higher propensity to fragment to produce a ketone and methyl radical that is much less likely to abstract an H-atom from a saturated polyolefin.[5] The fragmentation process has been shown to be a function of only temperature in non-polar media such as LLDPE,[6] where higher temperatures result in more disproportionation.[7] Thus, a lower cure temperature could be used to initiate L231 and limit the β-scission of alkoxy radicals.[8] The half-life of DCP at 160°C is 5.5 min, meaning that after 5.5 min, approximately 50% of the dialkylperoxide will have undergone thermolysis to produce alkoxy radicals. The same half-life for L231 is achieved at 136°C, meaning that at a much lower temperature it is possible to achieve radical modification with less disproportionation.

For peroxide crosslinking of a saturated polyolefin such as LLDPE, alkyl macroradicals generated by H-atom abstraction either combine to form a crosslink, or disproportionate to yield unsaturation (Scheme 2).[9]

Scheme 2. Stoichiometric radical mediated crosslinking of PE



Termination via combination gives rise to increases in the molecular weight of the polymer, while decreasing stress-relaxation and creep. In order to gain insight into the rate, extent and dynamics of crosslinking reactions, changes to the elastic storage modulus (G') are monitored using a controlled strain rheometer, and these changes are proportional to changes in crosslink density (assuming fixed temperature, frequency, and rate of shear).[10] G' is used to represent elastically stored energy in the polymer, and this elasticity increases proportionally with crosslink density. Changes in G' resulting from crosslinking initiated by DCP or L231 are stoichiometric and first order with respect to peroxide thermolysis (Figure 1).[11] Alkyl radicals terminate quickly relative to peroxide thermolysis, and a pseudo steady-state radical concentration is observed.[8,12]

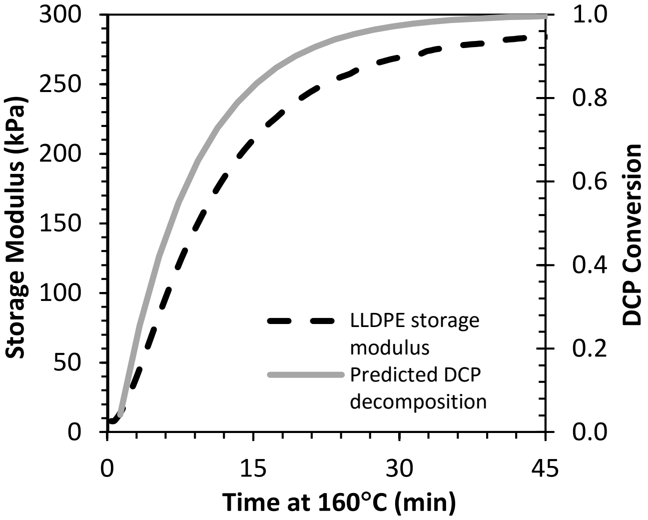
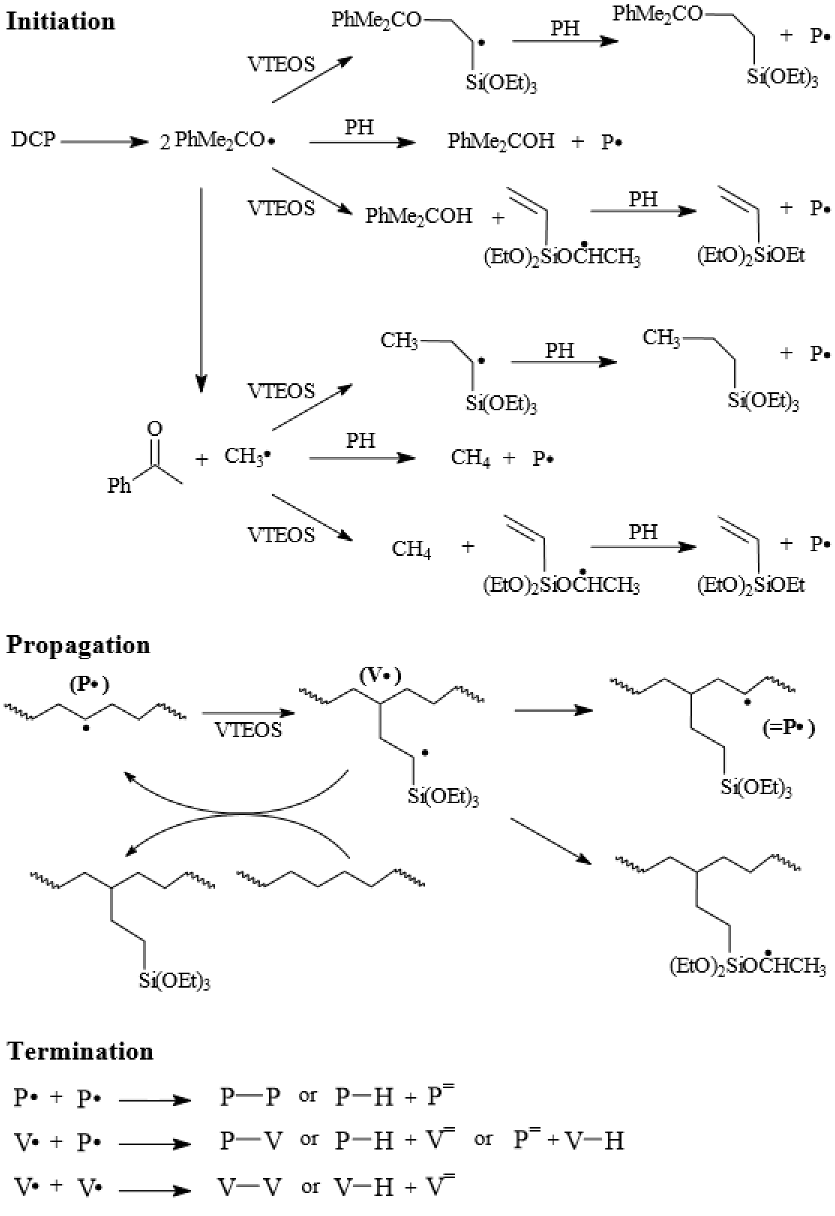


Figure 1. Dynamics of LLDPE crosslinking and DCP thermolysis[11]

Crosslinking dynamics clearly shadow peroxide decomposition, demonstrating the dependence of crosslinking rate on thermal decomposition. Dicumyl peroxide decomposition is unimolecular in character, so relative post-reaction concentrations of cumyl alcohol (resulting from H-atom abstraction) and acetophenone (resulting from β-scission) can be used to estimate the extent of H-atom abstraction compared to β-scission. This value has come to be known as abstraction efficiency (AE = [cumyl alcohol]/[cumyl alcohol + acetophenone]),[13] and is reported to be about 70% in cyclohexane[8] and 56% in PE.[7]

Conventional peroxide initiation is also used extensively to graft modify PE with vinylsilanes.[8] The grafting of vinyltriethoxysilane (VTEOS) to PE produces a moisture crosslinkable derivative that can undergo a thermosetting reaction after the production phase.[14] The dominant mechanism of grafting, as well as influences of peroxide loading and monomer concentration on reaction dynamics and yields have been thoroughly investigated.[15,16] Grafting VTEOS to polyolefin or a hydrocarbon substrate yields a closed reaction sequence where vinylsilane preferentially adds a single graft per site (Scheme 3).[17]

Scheme 3. Radical mediated grafting of VTEOS to PE (modified from Parent and coworkers)[16]



Scheme 3 is a detailed summary of grafting reaction intermediates in PE. The dominant reaction pathway considered involves initiation of polymer, addition to vinyl monomer, and H-atom transfer to quench the grafted monomer radical. Addition is expected to occur on the non-substituted end of the vinyl monomer due to steric effects of the trialkoxysilane. Intermolecular

H-atom abstraction is preferred in the production of uniformly grafted polymer chains, allowing the radical to continue to propagate.

Alkoxy radicals that encounter vinyl monomer may abstract from the monomer leading to a similar addition/transfer reaction, or oligomerize the monomer. Since single grafts are predominant, oligomerization is not favored and radical propagation from chain transfer dominates. Methyl radical addition to vinyl monomer is favored over abstraction, thus β-scission of alkoxy radicals leads directly to the formation of small monomer-derived molecules.[8,18] Alkoxy radicals do not prefer addition to the monomer, and this reaction can be essentially disregarded.

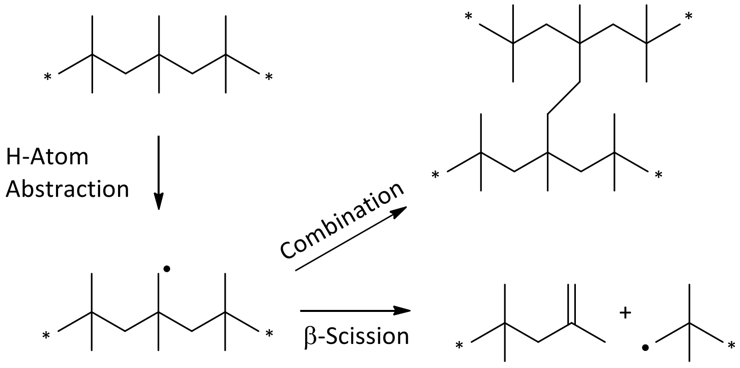
Post graft-modification, silane crosslinking can be done in the presence of water and an organic transition metal catalyst.[19] A hydrolysis/condensation type reaction occurs to produce Si-O-Si covalent bonds. This process produces silane crosslinked PE that is somewhat more susceptible to degradation than direct peroxide crosslinking,[20] however its advantages lie in post-production processing.

Model hydrocarbons have previously been used for the purpose of gaining additional insight into the reactivity of vinytrialkoxysilanes.[8,21] This thesis will primarily focus on grafting reactions involving vinyltriethoxysilane and cyclohexane initiated by DCP. Grafting vinyl monomer to cyclohexane is used in the context of additive effects on graft yields, rather than using the reactions to determine intrinsic properties. Additive effects on graft yields in model hydrocarbons have been investigated before, as incorporation of additives including polymer stabilizers usually occurs before or during radical modifications because of the extreme conditions experienced by the polymer.[22]

1.2 Melt-State Peroxide Modification of Poly(isobutylene-co-isoprene).

Another polyolefin of industrial interest is poly(isobutylene) (PIB). PIB is an amorphous elastomer that has low gas permeability as well as excellent thermal and oxidative stability owing to the high bond dissociation energy (BDE) of accessible methyl groups.[23] PIB also has a low glass transition temperature and low crystallinity and these features cause the polymer to undergo stress relaxation and deform under applied force. It has a very limited number of applications without further modification, and as such, developing a thermoset using peroxides has been attempted. Unfortunately the low reactivity of PIB with respect to H-atom donation to cumyloxy and *t*-butoxy radical intermediates ensures that they undergo significantly more disproportionation than in LLDPE. In addition to this, isobutylene macroradicals undergo β-scission to cleave the polymer backbone (Scheme 4).

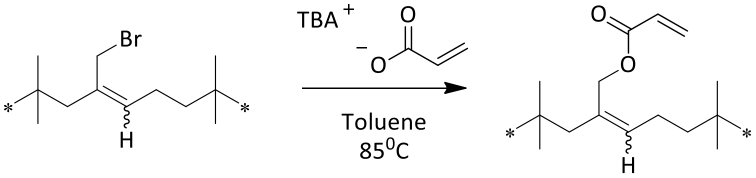
Scheme 4. β-scission and combination of PIB macroradicals



Chain scission proceeds unabated as a result of macroradicals derived from peroxide modification, which drives the molecular weight of the polymer down. In contrast to PIB, poly(isoprene) is highly reactive towards peroxide modification and can form a strong thermoset from the addition of a relatively small amount of DCP.[24] Thus, increased reactivity towards alkoxy radicals can be achieved while still retaining the desirable properties of PIB by copolymerizing small amounts (~2 mol %) of isoprene with isobutylene to make poly(isobutylene-co-isoprene) (IIR).[25,26] IIR has come to be known as butyl rubber and is ideal for use in tire inner tubes, where sufficient isoprene content enables sulfur vulcanization to develop a thermoset.[27] Despite the widespread use of sulfur vulcanization, peroxide crosslinking generates thermosets with superior thermal stability.[4] Increased reactivity of IIR towards H-atom donation to peroxide derived radicals can recover MW losses from competing β-scission of isobutylene radicals, however it is insufficient on its own to generate a thermoset.[28]

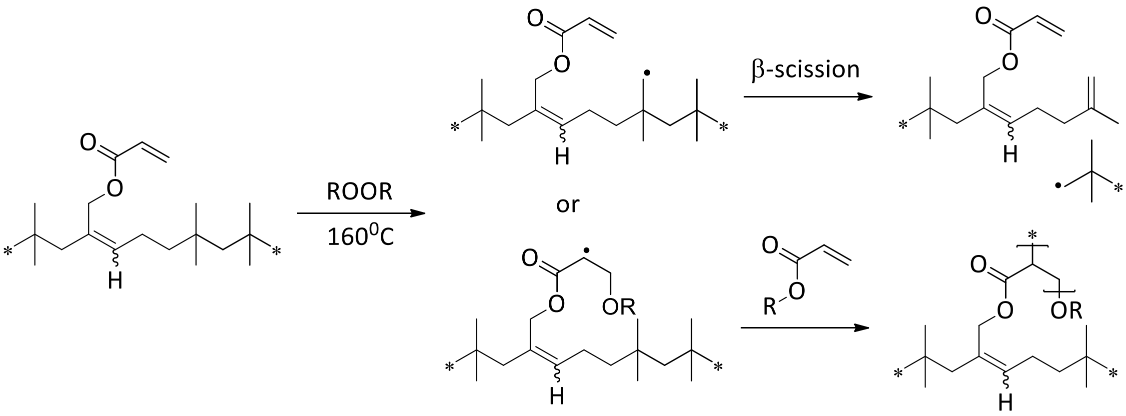
Since IIR containing small amounts of isoprene is not amenable to peroxide modification, cure reactivity can be greatly improved by the halogenation of isoprene unsaturation. More specifically, this is done by the introduction of bromine functionality to create brominated IIR (BIIR).[29] By introducing bromine functionality to the copolymer, subsequent reactions that displace this halogen can occur, such as the substitution of an acrylate to produce a reactive macromonomer derivative poly(isobutylene-co-isoprene)-graft-acrylic acid (IIR-g-AA) (Scheme 5).[30,31]

Scheme 5. BIIR substitution reaction producing IIR-g-AA



Acrylate functionalized IIR can be reacted with peroxides to overcome β-scission because of the non-stoichiometric nature of acrylate oligomerization (Scheme 6).[32] Reaction of IIR-g-AA with DCP has been found to generate a modest thermoset at 170°C (Figure 2).[30] One of the major drawbacks of this reaction, however, was found to be scorch.[31]

Scheme 6. Peroxide-mediated competing acrylate oligomerization and β-scission of IIR-g-AA



Highly reactive functionality has a tendency to reach cure completion too quickly, before molding or shaping can occur, or before peroxide radicals are consumed. This is the effect known as scorch. Scorch is observed in peroxide crosslinking of IIR-g-AA as cure reversion occurs, causing a drop in G' after a maximum is reached (Figure 2, 18.5 µmole/g DCP).

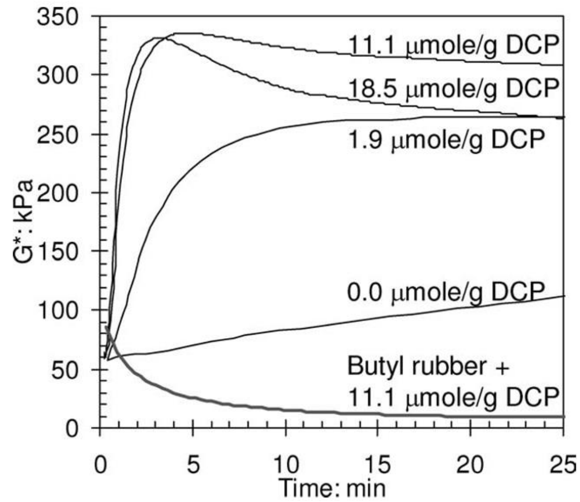


Figure 2. Dynamics of peroxide-initiated IIR-g-AA crosslinking (0.15mmole/g acrylate; 170C)[30]

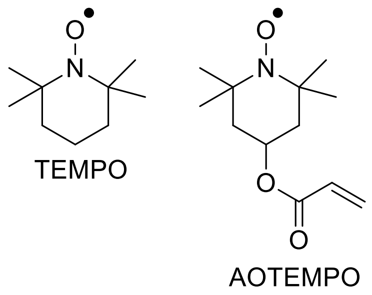
Figure 2 shows DCP activation of IIR-g-AA proceeding quickly at the onset of the cure. After 3 minutes, cure reversion occurs where there is a noticeable loss of G'. Cure reversion occurs when acrylate functionality is consumed before the peroxide has finished initiating, letting polymer chain scission run unabated, as was the case in PIB. As mentioned previously, changes in G' reflect changes in the polymer architecture, where sustained increases are inherent to crosslink formation and increased storage of elastic energy.

Returning to the dilemma of unfuntionalized IIR crosslinking, more information about H-atom abstraction regioselectivity from IIR could be used to rationalize how isoprene content affects the low abstraction efficiency of PIB. ^{1}H NMR (nuclear magnetic resonance) spectroscopy is a useful tool for analysis of molecular structures, as chemical shift (ppm) from a reference value of 0 for tetramethylsilane is unique to each atom's environment. ^{1}H NMR analysis of IIR has showed that 2,2,4,8,8-pentamethyl-4-nonene (PMN) is consistent with the overwhelmingly predominant olefin in the polymer, giving a reason to attempt to study its H-atom donation reactivity. This compound has been used as a model for IIR halogenation,[33,34] as well as the thermal stability and nucleophilic substitution chemistry of brominated IIR.[35,36] In this thesis, ^{1}H NMR spectra of abstraction products originating from reaction of PMN with DCP may give insight into H-atom abstraction regioselectivity. This topic is covered in more detail in Chapter 2.

1.3 Nitroxyls used as Scorch Protectants

Peroxide crosslinking transforms a thermoplastic into a thermoset product that generally has a particular shape in accordance with its intended use. Once crosslinking has occurred, the thermoset is essentially unprocessable. The cure should not reach completion before a final shape is achieved, or all of the peroxide is decomposed. Scorch occurs when thermosetting proceeds too quickly from the onset of crosslinking. In order to prevent scorch, a nitroxy radical trap such as 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO - Scheme 7) can be used to trap alkyl macroradicals in the early stages of the cure, suppressing macroradical combination. Nitroxyls typically react only with carbon-centered radicals at the diffusion limit of bimolecular reaction velocities.[37]

Scheme 7. Functionalized and unfunctionalized nitroxyls of the type 2,2,6,6-tertramethylpiperidin-1-oxyl



The same maximum change in G’ cannot be achieved for DCP or L231 initiated LLDPE cures due to trapping of macroradicals by TEMPO. One way to overcome this is to add acrylate functionality to the TEMPO molecule. Addition of acrylate functionalized nitroxyl (AOTEMPO - Scheme 7) recovers G’ losses through functionalized acrylate oligomerization.[38] This oligomerization occurs several orders of magnitude slower than radical trapping, giving a pronounced induction period (Figure 3).[39]

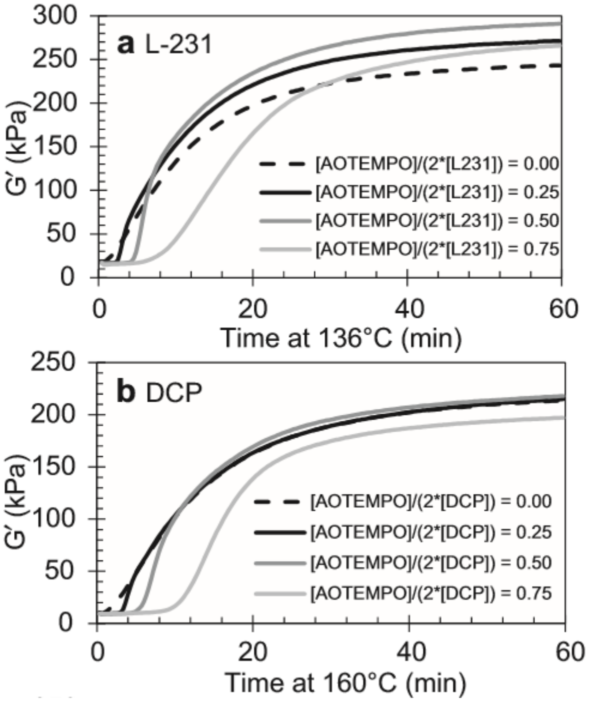


Figure 3. Influence of AOTEMPO on peroxide-initiated LLDPE cure dynamics and yields (a. [L231] = 18.5 µmole/g, b. [DCP] = 18.5 µmole/g)[39]

The induction time follows a relationship based on relative peroxide and nitroxyl loadings, described by Equation (1, where k_d is the first-order rate constant for peroxide thermolysis at the reaction temperature.

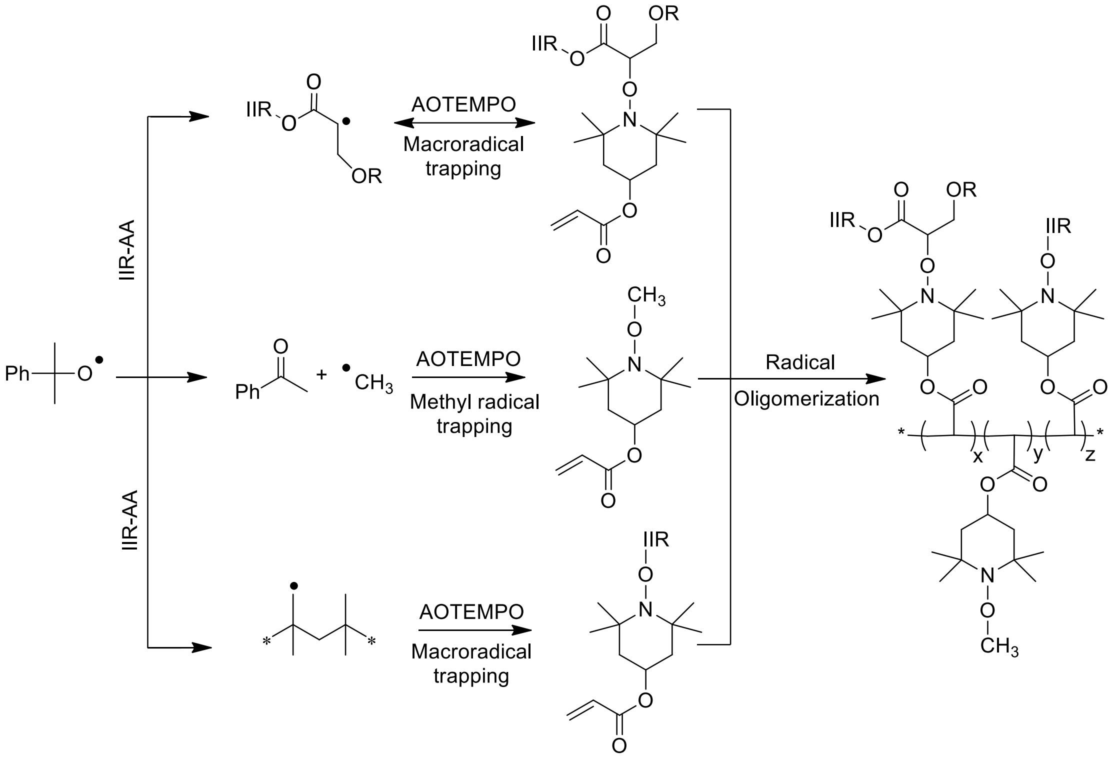
$$t_{ind} = -\frac{1}{k_d} ln\left[1 - \frac{[nitroxyl]_o}{2[ROOR]_o}\right] \tag{1}$$

This expression contains what is known as the molar trapping ratio, which is the fraction of initiator-derived radicals that can be trapped by any particular additive (Equation (2).

$$Trapping\ Ratio = \frac{[additive]_o}{2[ROOR]_o} \approx \frac{n_{additive}}{2n_{ROOR}} \tag{2}$$

Similarly to how AOTEMPO can be used to suppress LLDPE crosslinking, it can be used to suppress acrylate oligomerization in IIR-g-AA, which occurs quickly at the onset and undergoes cure reversion after a certain period of time with sufficient peroxide loading.[31] Oligomerization of acrylate functionality occurs more slowly, and again an induction time is observed, however it is significantly longer than predicted by Equation (1. Trapping and oligomerization in a DCP initiated IIR-g-AA cure is thought to occur according to Scheme 8.

Scheme 8. Peroxide-mediated competing acrylate oligomerization and β-scission of IIR-g-AA



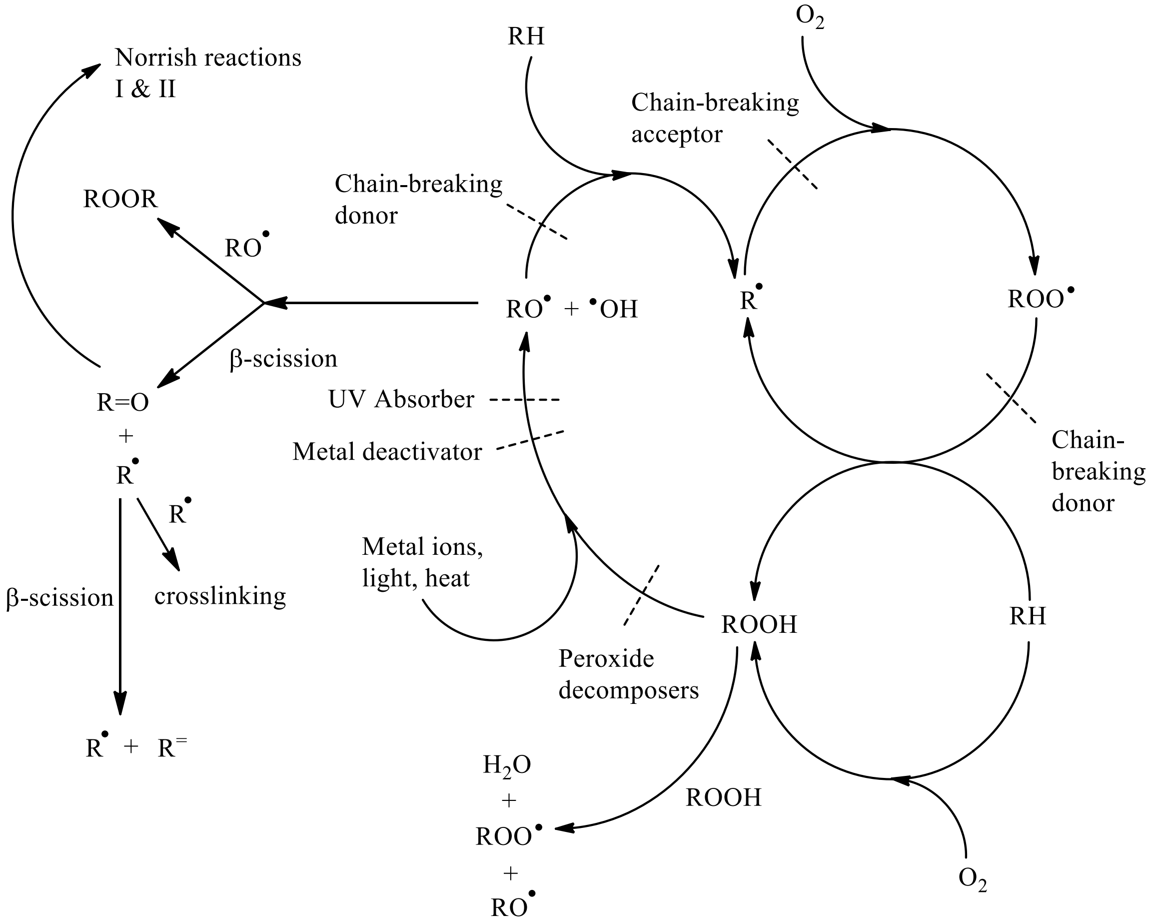
The lengthening of the induction time was unexpected considering that AOTEMPO should not affect first-order decomposition of dicumylperoxide.[40] The difference in reactivity was explained by alkoyxamine dissociation and regeneration playing a role in longer induction times.[31] The accuracy of Equation (1) is dependent on the stability of the alkoxyamine generated during nitroxy trapping. Methyl radicals are readily trapped by nitroxyls, and the corresponding methyl-alkoxyamines are stable at high temperatures.[41,42] However, the thermal stability of the other alkoxyamines formed from macroradical trapping is questionable at higher temperature. Bond dissociation and nitroxyl regeneration occur in small quantities in a similar trapping scenario with poly(methylmethacrylate).[43]

Living radical polymerizations rely on the dissociation of the O-R bond occurring slowly at high temperatures, freeing an alkyl macroradical capable of reaction.[44] A poly(butadiene) model compound (3-heptene) allyl radical has been trapped by TEMPO and dissociated at temperatures well below 160°C.[45] Disproportionation occurs at a lower rate with cyclooctene-TEMPO alkoxyamines at 100°C. With this in mind, trapping of a model compound for IIR by TEMPO after reaction with alkoxy radicals could give insights into H-atom abstraction regioselectivity, but dissociation and rearrangement, or disproportionation of the alkoxyamine at 160°C may be significant.

1.4 LLDPE Oxidative Degradation and Effective Antioxidants.

Polyolefins undergo oxidative degradation through radical mediated reactions which can seriously affect the mechanical and aesthetic properties of the polymer. Degradation of polyolefins can be initiated by any type of energy sufficient to break the carbon-hydrogen or carbon-carbon bond along the polymer backbone to produce unstable carbon-centered radicals (R·). It tends to happen at weak points such as unsaturated bonds or tertiary carbons.[46] In the absence of oxygen, the macroradicals terminate to form crosslinks or unsaturation, but in the presence of oxygen they react quickly to form peroxy radicals (ROO·) (Scheme 9).[47]

Scheme 9. Radical chain oxidation



If a peroxy radical is formed, it can abstract a labile hydrogen atom from another carbon to form a hydroperoxide (ROOH). The process becomes autocatalytic when the hydroperoxide decomposes into two radicals: alkoxy (RO·) and hydroxy (HO·). This process is catalyzed by sufficient thermal energy, high energy radiation (ultra-violet), or residual transition metals from polymerization.[48] As a result of H-atom abstraction by peroxy radicals, polymer embrittlement can occur if polymer bound radicals terminate by combination, or oppositely, polymer softening can occur if radicals disproportionate leading to chain scission. In the absence of inhibitors, the chain reaction follows unimolecular hydroperoxide decomposition and is terminated by bimolecular reactions of two radicals resulting in the dependence of oxidation rate on initiation (Scheme 10). Termination of peroxy radicals can occur by bimolecular interaction to yield a non-radical ketone, alcohol, and O_2.[49]

Scheme 10. Hydroperoxide reactions involved in thermal oxidation of PE (modified from Gugumus)[50]

Initiation / Branching

$POOH + PH \rightarrow PO^{\bullet} + H_2O + P^{\bullet}$

$POOH + PH \rightarrow P = O + H_2O + PH$

$POOH + POOH \rightarrow PO_2^{\bullet} + H_2O + PO^{\bullet}$

$POOH + POOH \rightarrow POOH + P = O + H_2O$

Termination

$PO_2^{\bullet} + PO_2^{\bullet} \rightarrow P = O + POH$

$PO_2^{\bullet} + PO_2^{\bullet} \rightarrow POOP + O_2$

Propagation

$PO^{\bullet} + PH \rightarrow POH + P^{\bullet}$

$PO^{\bullet} \rightarrow (P = O)_{aldehyde} + P^{\bullet}$

$P^{\bullet} + O_2 \rightarrow PO_2^{\bullet}$

$PO_2^{\bullet} + PH \rightarrow POOH + P^{\bullet}$

$PO_2^{\bullet} + POOH \rightarrow POOH + {}^{\bullet}POOH$

${}^{\bullet}POOH \rightarrow P = O + {}^{\bullet}OH$

${}^{\bullet}OH + PH \rightarrow H_2O + P^{\bullet}$

Thermal oxidation of LLDPE results in the formation of peroxy radicals, which can abstract a hydrogen and subsequently cleave to perpetuate the cycle of oxidative degradation.[51,52] LLDPE oxidation can be quantified using Fourier-transform-infra-red (FT-IR) spectrometry by measuring the absorbance of carbonyl containing compounds (ketonic and other carbonyl containing moieties that absorb between 1550 cm^{-1} and 1850 cm^{-1}).[53,54] The absorbance is measured relative to absorbance of the CH_2 symmetric stretching in the polymer (2750 cm^{-1} to 2875 cm^{-1}). This value can be called the carbonyl index (Equation (3)).[55,56,57]

$$\text{Carbonyl Index} = \frac{A_{1725cm^{-1}}}{A_{2812cm^{-1}}} \qquad (3)$$

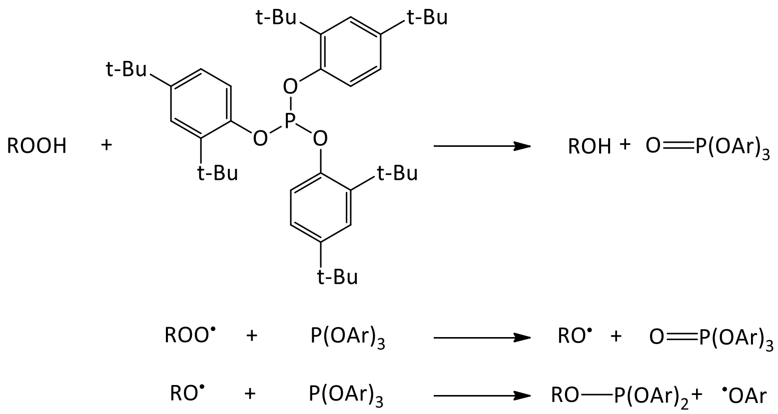
The change in this carbonyl index can be used to quantify relative effects of oxidative environments and different additives on the extent of oxidation resulting in carbonyl compounds.[54,58] When examining a typical FT-IR transmission spectra of PE, strong absorbance can be seen in the region 3000-2800 cm^{-1}, correlating to the CH_2 stretching frequency, and medium absorbance observed between 1550 cm^{-1} and 1400 cm^{-1} from CH_2 bending. Another smaller absorbance is also observable at 750-650 cm^{-1} (rocking).

Since PE is a semi-crystalline polymer, oxidation has been shown to take place quickly in amorphous domains of the polymer, where impurities (including additives) are accumulated.[59] Oxidation is expected to take place quickly in these domains owing to high local concentrations of oxidants as well as more rapid diffusion. At higher temperatures and partial pressures of oxygen however, oxidation products are not as likely to amass in local amorphous domains, and oxidations takes place more uniformly across amorphous boundaries.[50]

Whether the polymer undergoes hardening from crosslinking, or softening due to chain scission, unwanted radical chemistry can be interrupted by antioxidants (AO). In general, antioxidants are considered to be any compound that inhibits the formation of oxidative radicals. An ideal antioxidant would function at the diffusion limit, reacting immediately with any peroxy radical that it encountered. This is not readily observed in most stabilizers, however. It is necessary for any AO added to be able to quench the radicals produced through oxidative degradation in order to stabilize the polymer. There are many different types of antioxidants, but only a limited number of them will be mentioned, since the goal of this work is not to summarize all antioxidants, but rather to find a latent one.

Preventative antioxidants act in a way to prevent the initiation of radical pathways involved in oxidation. One way to achieve this is to stop the decomposition of peroxides into active radicals that propagate the oxidation cycle.[60] Metal ion deactivators act by inhibiting metal ion catalyzed peroxide decomposition. These metal ions are, presumably, left over catalysts from polymerization reactions. Peroxide decomposers, on the other hand, promote the decomposition of hydroperoxides to stable products before they can cleave to form oxidizing radicals. One such decomposer is the aryl phosphite. An aryl phosphite such as tris(2,4-di-tert-butylphenyl)phosphite (Irgaphos168), functions as an antioxidant by decomposing hydroperoxides to yield phosphates and alcohols,[61] as well as trapping peroxyl radicals to form phosphates and alkyl aryl phosphites (Scheme 11).[62] At higher temperatures they have been found to become more reactive than phenolic antioxidants through hydrolysis to form phenols, hydrogen phosphites and phosphonites.[62]

Scheme 11. Irgaphos168 decomposition of hydroperoxide and peroxy radicals

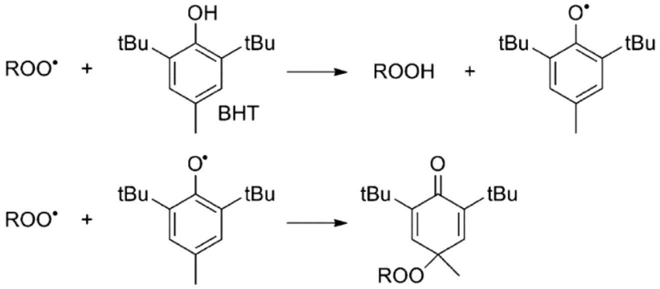


Organic sulfides are another type of preventative peroxide decomposer. Sulfoxides and thiosulfinates arise from mono- and di-sulfides as they react with hydroperoxides, and are the main agents responsible for organic sulfide inhibition of oxidation.[60] These sulfides do not interact to prevent oxidation when peroxide decomposition is not involved.

Another large class of preventative antioxidants is commonly known as UV absorbers.[63] These react by absorbing harmful UV radiation, and undergoing internal H-atom transfer to quench exited triplet states.[64] These are not examined extensively, since during thermal oxidation UV radiation should play a negligible role in polymer oxidation.

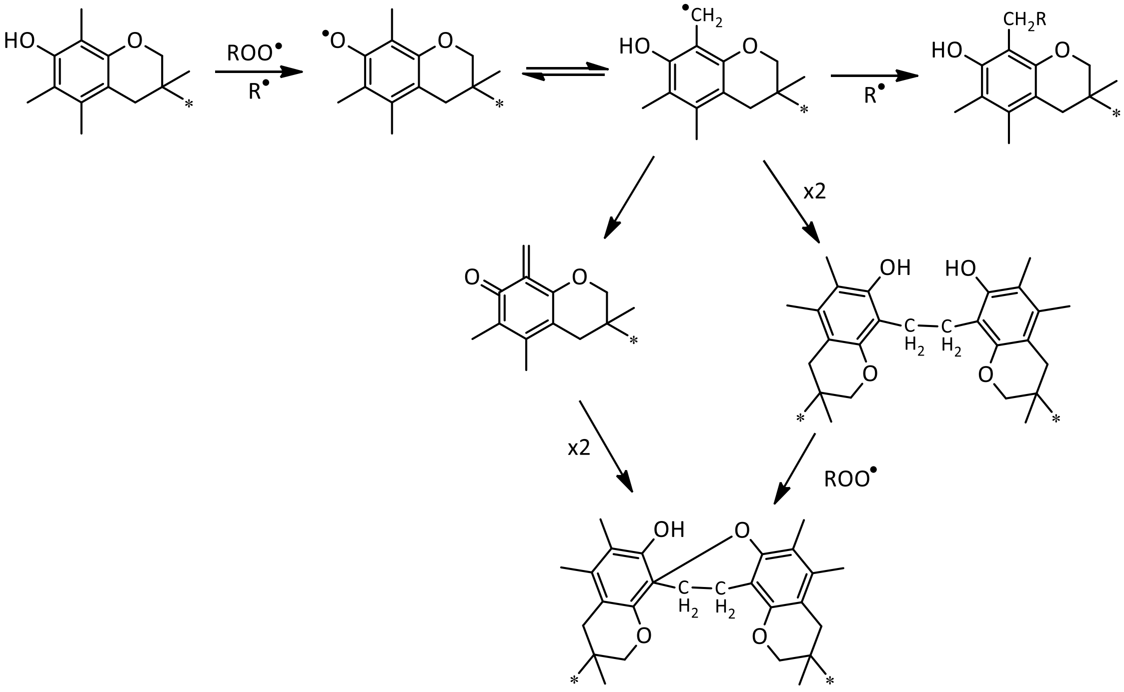
Chain breaking antioxidants interrupt the oxidation cycle by donating H-atoms, or accepting and trapping radical populations. One of the most common types of antioxidants for oxidative stabilization is the hindered phenolic antioxidant (a chain breaking donor and acceptor). In polyolefin applications, the best examples are 3,5-di-tert-4-butylhydroxytoluene (BHT) and α-tocopherol (Vitamin E).[52] Hindered phenolic AO’s are a type of sacrificial antioxidant that interfere in the propagation of radicals by donating an H-atom and breaking the cycle.[47,65,66] Phenoxy radicals are formed in the primary reaction step. The second step of radical quenching involves the formation of an adduct with a peroxy radical, and thereafter transformations depend on the local concentration of phenoxyls and co-reactants such as peroxy radical intermediates and oxygen.[65,67] BHT is known to stabilize at least 2 radicals (Scheme 12) per molecule, however that rating is only valid at temperatures below 100°C, above which BHT losses its propensity to stabilize the second peroxy radical.[68]

Scheme 12. Summary of primary antioxidant mechanism of BHT (modified from Gryn'ova and coworkers)[68]



Another phenolic antioxidant, vitamin E, is a potent sacrificial antioxidant with a rate constant for peroxy radical trapping calculated to be 32 x 10^5 $M^{-1}s^{-1}$, compared to that of BHT, with a rate constant calculated to be 0.14 x 10^5 $M^{-1}s^{-1}$.[69] Vitamin E has a well-established mechanism of AO activity, and it is capable of quenching more than twice its molar quantity in radicals generated in the system.[70] It has been shown to be more potent than BHT in melt stabilization and it can be expected to have negligible detrimental effects to biological systems.[71,72] Recently, vitamin E has been analyzed for use as a biocompatible antioxidant for ultra-high molecular weight poly(ethylene) (UHMWPE) stabilization and was found to be effective at low concentrations (as low as 0.05%).[73,74,75] The primary mechanism of stabilization is hydrogen atom abstraction (by macroradical or peroxy radical) from the OH of vitamin E.[73] Aside from H-atom donation, vitamin E forms various complexes with peroxyl radicals (Scheme 13).[70]

Scheme 13. Vitamin E oxidation products and pathways for product formation in peroxyl radical scavenging

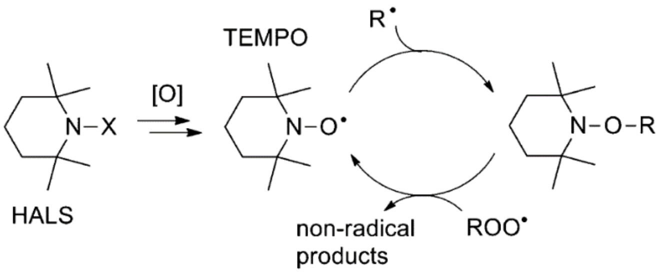


As a free radical scavenger, vitamin E can prolong the lifetime of articles made from UHMWPE by a factor of more than 2.5 times, and when compared with traditional antioxidants (eg. Irgarox 1010 – high molecular weight BHT equivalent), it was found to be the most effective stabilizer for UHMWPE in a highly oxidative environment.[76]

For AOs that incorporate H-atom donation resulting in a stabilized radical, lowering the BDE of the O-H bond below that of a ROO-H bond (88 kcal/mol) is necessary for H-atom transfer.[69] The resulting radical product must also be stabilized such that it does not enter into the radical chain oxidation cycle. Ideally the bond energy would be so low that it could react at the diffusion limit without activating direct reactions with O_2. However, lowering the BDE is not sufficient for increasing H-atom donation rates to peroxy radicals, and it has been suggested that this is due to a difference in the mechanism of H-atom abstraction from C-H, O-H, and N-H bonds in aryl stabilizing agents.[69] Diarylamines are capable of H-atom donation to quench peroxy radicals and are commonly used in rubber-based applications, where discoloring stabilizers are acceptable.[77] They are extremely effective antioxidants that react quickly with peroxy radicals to produce stabilized radicals. Although they are good process stabilizers, much like vitamin E, they will react with alkoxy radicals making them a poor choice for a potential latent antioxidant.

Since the discovery of their usefulness as radical trapping antioxidants in the early 1970s, hindered amine stabilizers (HAS) such as 2,2,6,6-tetramethylpiperidine (TEMPH) and its derivatives, have become an important class of stabilizer.[78,79,80] They can be effective radical scavenging antioxidants at low concentrations and high temperatures, even though they do not absorb UV radiation or directly decompose hydroperoxides. This is because they have a method of cyclic regeneration that will increase the factor of inhibition well above that of other antioxidants, taking part in a mechanism that is still a topic of debate (Scheme 14).[68,69]

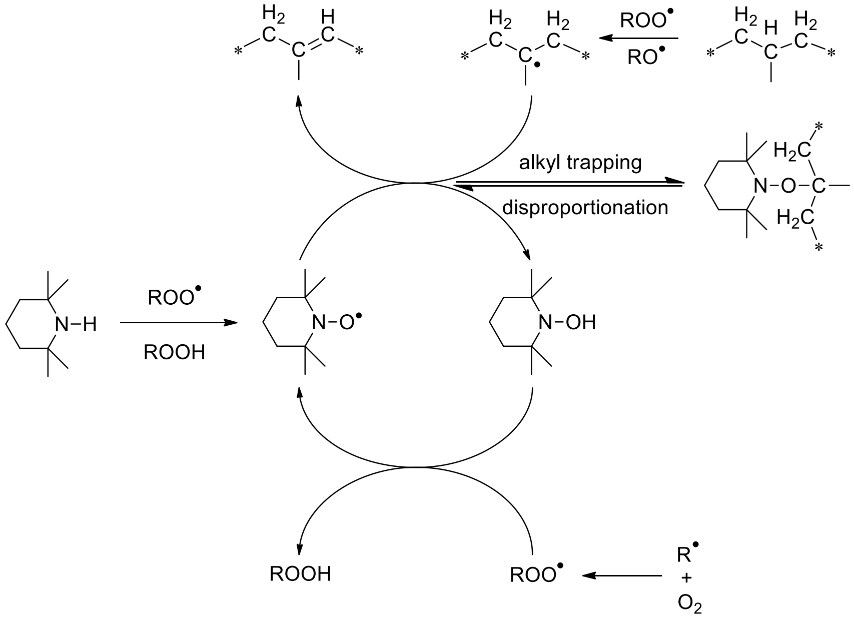
Scheme 14. Simple Denisov Cycle



With this in mind, there have been many studies examining the mechanism of HAS stabilization and the regenerative processes that they undergo.[81,82,83,84] It is generally assumed that hindered amines are readily oxidized to form nitroxyls, since the amines themselves are not efficient process stabilizers.[85,86,87] The mechanism of nitroxyl radicals differs from that of other antioxidants in that it directly traps carbon-centered radicals at the diffusion limit, and not oxygen-centered radicals.[37] The effectiveness is thus dictated by the competitive rate of nitroxyl trapping relative to oxygen addition to alkyl radicals. Reaction of alkyl radicals with oxygen to form peroxy radicals occurs near the diffusion limit, with rate constants on the order of 10^8-10^9 M^{-1} s^{-1}.[64] This is similar to the rate of alkoxyamine formation by radical trapping as mentioned above. Slower oxygen diffusion through solid-state polymer may allow a chance for alkoxyamine formation to outcompete oxidation of alkyl radicals.[64] This does not account for regenerations of nitroxyl, however, and this is factor required for high stabilization capacity. A commonly published mechanism of cyclic regeneration includes hydroxylamine formation and alkyl radical trapping and disproportionation (

Scheme 15).[64,86]

Scheme 15. Proposed catalytic role of TEMPH in oxidative stabilization of polypropylene



This scheme is founded based on analysis of unsaturation increases resulting (presumably) from NO-R bond dissociation from polypropylene under oxidative conditions.[86] Formation of unsaturation due to disproportionation in model compounds of PE has been studied previously, and nitroxyl formation from this process would support a method of regeneration analogous to that in Scheme 15. Regeneration in the presence of nitroxide from alkoxyamine containing a β-hydrogen can occur by abstraction of this atom and subsequent formation of an aminyl radical and ketone by N-OR bond cleavage.[68]

Recent publications have reviewed methods of stabilization and regeneration of HAS, but a mechanism remains only speculative.[68,69] It has been discovered that amine is regenerated and is involved in the intermediary steps. A scheme has been suggested for nitroxyl regeneration involving alkyl groups without a β-hydrogen similar to the one in Scheme 15 by Gryn'ova and coworkers, however no direct route to amine formation was proposed.[68] A relatively obvious mechanism of aminyl radical formation involves H-atom abstraction from the polymer and subsequent scission of the N-O bond (Scheme 16).

Scheme 16. Amine regeneration from alkoxyamine[69]

$$\mathrm{ROO^{\bullet} + TEMPOCHRR' \rightarrow ROOH + [TEMPOC^{\bullet}(R)(R')]}$$

$$\mathrm{[TEMPOC^{\bullet}(R)(R')] \rightarrow TEMP^{\bullet} + C(O)RR'}$$

$$\mathrm{TEMP^{\bullet} + XH \rightarrow TEMPH + X^{\bullet}}$$

While it is important to have a general understanding of possible mechanisms of regeneration, this does not identify a method of activation. The discussion of Chapter 3 is mostly devoted to plausible activation mechanisms of the hindered amine. For applications of peroxide cures and alkoxyvinylsilane grafted polyolefins requiring high temperature aging performance, antioxidants are added to the polymer prior to processing. Chain breaking donor antioxidants BHT and vitamin E can be expected to significantly affect crosslinking and grafting reactions by donating labile hydrogen atoms to chain propagating alkoxy or alkyl radicals.[88] Chapter 3 will examine each of the antioxidants mentioned as potential candidates for additives that are latent with respect to radicals generated from dialkylperoxide decomposition.

1.5 Research Objectives

1. Determine effects of higher isoprene content on peroxide mediated crosslinking and grafting yields in IIR
2. Determine the regioselectivity of H-atom abstraction from IIR in the presence of cumyloxy radicals at processing conditions
3. Quantify effects of antioxidants on radical mediated crosslinking of LLDPE and grafting of VTEOS to cyclohexane
4. Identify an antioxidant that hinders oxidative degradation, but survives crosslinking and grafting reactions

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Chapter 2

Peroxide-initiated Chemical Modification of Poly(isobutylene-co-isoprene):

H-atom Transfer Yields and Regioselectivity

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2.1 Abstract.

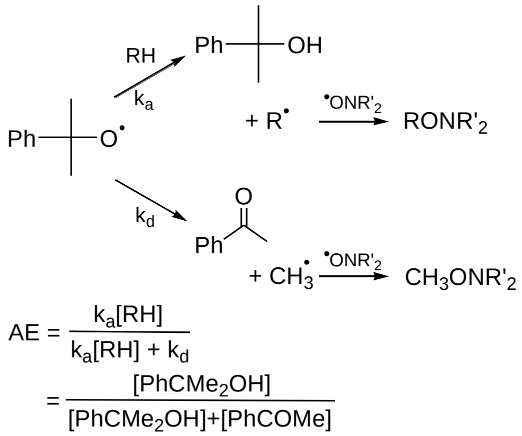
The yield and regioselectivity of H-atom abstraction by cumyloxy radicals from poly(isobutylene-co-isoprene) (IIR) are quantified and discussed in the context of cross-linking/degradation outcomes and vinyltriethoxysilane (VTEOS) graft yields. Studies of IIR materials with different isoprene contents, coupled with radical trapping experiments, show that H-atom abstraction from the allylic functionality provided by isoprene mers is responsible for the heightened H-atom transfer reactivity of IIR relative to poly(isobutylene). Resonance stability of the resulting allyl macroradical intermediates, coupled with their preference for termination by combination, makes IIR materials of high isoprene content less prone to peroxide-initiated chain scission. However, heightened reactivity toward cumyloxy radicals does not translate into improved yields of VTEOS grafting. In fact, monomer addition yields decline sharply with increasing unsaturation content, presumably due to the low rate of allyl radical addition to VTEOS as well as the inhibitory effect of H-atom transfer between alkyl macroradicals and allylic hydrogen. Knowledge of H-atom transfer reactivity is extended to the development of a new approach to IIR cross-linking that involves acrylate-functionalized nitroxyl additives.

2.2 Introduction.

Peroxide-initiated radical chemistry is used extensively to improve polyolefin properties by modifying their chemical composition and/or architecture.[1,2] Key examples include cross-linking to generate thermoset products,[3] and grafting of anhydride and trialkoxysilane functionality to produce reactive derivatives for use in adhesive, blend, and composite formulations.[4] Since these processes can be conducted solvent-free using conventional polymer processing equipment, they can be cost effective as long as reaction yields are sufficiently high.[5]

Most radical-mediated polyolefin modifications involve macroradical generation by H-atom donation to peroxide-derived radicals.[6] Where changes in polymer architecture are desired, as is the case for controlled degradation[7] and cross-linking processes,[8] H-atom abstraction yields macroradical intermediates whose subsequent β-scission and/or combination gives rise to desired changes in molecular weight and branching distributions. Graft modification with vinyltrialkoxysilanes also involves macroradical production, followed by a closed reaction sequence of macroradical addition to monomer and H-atom abstraction by the resulting monomer-derived radical intermediate.[9] A complete understanding of all H-atom transfer reactions involved in polyolefin modifications is, therefore, a formidable challenge, especially when the polymer presents multiple H-atom donors.

Scheme 17. Cumyloxy fragmentation and H-atom abstraction



A simple means of assessing the reactivity of an H-atom donor is to quantify the byproducts of peroxide initiator decomposition. Thermolysis of dicumyl peroxide (DCP) in non-polar media yields cumyloxy intermediates, whose fragmentation to acetophenone and a methyl radical depends only on temperature.[10] Therefore, this process can serve as a control reaction to determine the relative rate of H-atom abstraction from a hydrocarbon to produce cumyl alcohol and corresponding carbon-centered radicals (Scheme 17). We have recently reported abstraction efficiency (AE = [cumyl alcohol]/([cumyl alcohol]+[acetophenone]) measurements at industrially-relevant temperatures, demonstrating a wide range of H-atom donor reactivity amongst polyolefins of commercial interest.[11] This approach has also been used to study cumyloxyl abstraction from saturated hydrocarbons and alkylated aromatics,[12,13] as well as t-butoxyl reaction with a number of polymers.[14]

We applied this methodology to a series of homopolymers, and discovered a decline in H-atom donor reactivity from polyethylene (HDPE, AE=56%) to polypropylene (PP, AE=35%) to polyisobutylene (PIB, AE = 17%).[11] The low reactivity of PIB results in graft modification yields that are well below those achieved for most commercial polyolefins, and the high peroxide initiator loadings needed to support these reactions increase production costs and raise initiator byproduct concentrations to undesirable levels.[15] One approach to remedying this deficiency is to employ a random copolymer, poly(isobutylene-co-isoprene) (IIR) containing residual C=C unsaturation that supports conventional sulfur vulcanization chemistry[16] and affects its response to peroxide initiators.[17] Commercial grades of IIR contain approximately 2 mole % isoprene, but materials containing up to 6 mole % have been prepared in the hope of improving the scope of applicable modification chemistry.[18] This report provides AE data for IIR materials of varying isoprene content, and rationalizes the observed data using regioselectivity studies involving appropriate model compounds. The results are used to account for the response of IIR to peroxide-initiated degradation and vinyltriethoxysilane grafting, and knowledge of the reactivity is used to study a new cross-linking strategy involving acrylate-functionalized nitroxyls.

2.3 Experimental Section.

2.3.1 Materials.

The following materials were used as received from Sigma-Aldrich (Oakville, Ontario): Dicumyl peroxide (DCP, 98%), 1,1-Bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane (L231, 92%), 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO, 99% purified by sublimation), copper powder (99%), copper (II)bromide (99%), N,N,N',N',N"-pentamethyldiethylenetriamine (PMDETA , 99%), benzene (>99%), 2,6-ditertbutyl cresol (99%), vinyltriethoxysilane (VTEOS, 97%), anhydrous cyclohexane (99.5%) and cyclohexene (>99%). Activated acidic alumina (Anachemia, 80-200 mesh) was used as received. Toluene (≥ 99.5%) and acetone (≥ 99.5%) were used as received from Fisher Scientific (Ottawa, Ontario). Brominated butyl rubber (BB2030) was used as supplied by Lanxess Inc. (Sarnia, Ontario). Polyisobutylene (PIB, M_w = 85,000 g/mol and M_w = 400,000 g/mol; Scientific Polymer Products and Sigma Aldrich), was purified by dissolution/precipitation (hexanes/acetone), as were IIR-2.8 (isoprene content ~ 0.35mmol/g), IIR-4.2 (isoprene content ~ 0.71mmol/g) and IIR-5.8 (isoprene content ~ 1.01 mmol/g) that were provided by LANXESS Inc. (Sarnia, ON). 2,2,4,8,8-pentamethyl-4-nonene (PMN), brominated 2,2,4,8,8,-pentamethyl –4-nonene (BPMN)[19] and 4-acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl (AOTEMPO)[20] were prepared as previously described.

2.3.2 Instrumentation and Analysis.

Analysis of cumyl alcohol and acetophenone was conducted with a Hewlett Packard 5890 series II gas chromatograph equipped with a Supelco SPB-1 microbore column using 2 mL/min of helium as carrier gas. Injector and detector temperatures were held at 225 °C and 300 °C, respectively, with the oven temperature starting at 40 °C for 6 min, ramping to 150 °C at 10 °C/min, ramping to 280 °C at 12 °C/min, and holding for 15 min. ^{1}H-NMR spectra were recorded in $CDCl_3$ using a Bruker AC-400 spectrometer, with chemical shifts reported in ppm relative to chloroform (δ 7.24). Rheological tests for the change in dynamic storage moduli were recorded in a controlled strain rheometer (Advanced Polymer Analyzer 2000, Alpha Technologies) equipped with biconical disks and operating at 1 Hz and 3° arc.

2.3.3 Synthesis of Allylic Alkoxyamines 2a:2b:2c.

A mixture of alkoxyamines was prepared according to the method described by Matyjaszewski *et al.*[21] BPMN (0.0498 g, 0.18 mmole) was combined with TEMPO (0.0488g, 0.3 mmole), $CuBr_2$ (0.0049g, 0.025 mmole), copper powder (0.0193g), PMDETA (0.020 g, 0.075 mmole) and benzene (3 ml). The mixture was freeze/thaw degassed and heated to 70°C under vigorous agitation for 5 hours under nitrogen. The resulting solution was purified by flash chromatography (alumina, hexanes eluent), yielding the desired product as a pale yellow oil in 72% yield. ^{1}H NMR, COSY, HSQC and NOE analyses as well as mass spectrometry analysis confirmed the desired product, **2** as a mixture of E,Z-endo and exo isomers. Mass spectrometry: required for $C_{23}H_{45}ON$ (C.I., M-H$^+$): m/e 351.35; found: m/e 350.34. ^{1}HNMR ($CDCl_3$) downfield assignments: **2a**: 5.14 (s, 1H, exo CH=), 4.93 (s, 1H, exo CH=), 4.15-4.11 (dd, 1H, exo CH); **2b**: δ 5.50 (t, 1H, E CH=), 4.18 (s, 2H, E CH_2-); **2c**: 5.23 (t, 1H, Z CH=), 4.27 (s, 2H, Z CH_2-).

The thermal stability of **2a:2b:2c** was tested by dissolving a 20:70:10 mixture (5 mg, 0.014 mmole) in C_6D_6 (0.5 ml) and deoxygenating by freeze/thaw degassing before sealing under N_2 and heating to 144°C for 40h. No new compounds were observed, but the isomer distribution shifted to 3:39:58. Stability in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BHT) was tested by mixing **2a:2b:2c** (10 mg, 0.028 mmole), BHT (100 mg, 0.45 mmole) and C_6D_6 (0.5 ml), freeze/thaw degassing the solution, and heating to 144°C under N_2. ^{1}H-NMR analysis showed complete loss of starting material after 21 hours.

2.3.4 PMN model compound study.

PMN (0.1534 g, 0.781 mmol) was combined with DCP (0.0076 g, 0.028 mmol) and TEMPO (0.0109 g, 0.070 mmol) in a 0.3mL Wheaton vial and internally stirred at 160 ^{0}C for 38 min in an oil bath. The resulting mixture was analyzed for initiator byproduct concentrations using gas chromatography, and for alkoxyamine concentrations by ^{1}H NMR analysis. ^{1}HNMR ($CDCl_3$) downfield assignments: 1° allylic alkoxyamines **2b**: δ 4.18 (s, 2H, E CH_2-) and **2c**: 4.27 (s, 2H, Z CH_2-); 1° alkyl alkoxyamine **2d:** δ 3.60 (s, 2H, CH_2-).

2.3.5 Polymer H-Atom Abstraction Efficiency.

DCP (0.010 g, 0.037 mmol) was added to Elastomer (0.500 g) in a laboratory mixing molder for 38min at 160°C. The resulting mixture was dissolved in toluene (3 ml) and the polymer recovered by precipitation from acetone (25 ml).The toluene/acetone solution containing initiator byproducts was analyzed by GC.

2.3.6 Polymer H-Atom Abstraction Regioselectivity.

IIR-5.8 (0.500 g) was flattened and DCP (0.025 g, 0.092 mmol), TEMPO (0.348 g, 0.223 mmol) were dissolved in a minimal amount of acetone and dispersed on the surface. After the acetone had evaporated, the elastomer was rolled and placed in a laboratory mixing molder where it was mixed at 60 rpm for 38 min at 160 °C. The resulting mixture was dissolved in toluene (3 ml) and the polymer recovered by precipitation from acetone (25 ml). This purification step was repeated a second time and a portion (10 mg) of both the original sample and the dry purified sample were dissolved in $CDCl_3$ for ^1H NMR analysis.

2.3.7 Vinyltriethoxysilane melt state grafting.

Elastomer (40 g) was mixed with VTEOS (2.00 g, 10.5 mmol) and DCP (0.0800 g, 0.296 mmol) in a Haake Rheomix 600 internal batch mixer for 10 minutes at 50^0C. The resulting master batch showed no evidence of silane conversion by ^1H NMR analysis. Samples (5.00 g) were reacted in the melt-sealed cavity of the rheometer for 60 min at 160 ^{0}C. VTEOS conversion was determined by ^1H-NMR by integrating the region of vinyl group resonances (5.8–6.2 ppm, m, 3H) relative to those produced by $–CH_2-$ groups of the ethoxy substituents (3.8 ppm, q, 6H). Reported data are the average of 3 replicates.

2.3.8 Vinyltriethoxysilane solution grafting.

DCP (0.010 g, 0.037 mmol) and cyclohexene (none, 1.5, 3.0, 6.1, or 9.1 mmol) were added to cyclohexane (5.00 g, 59 mmol) in a 10 mL stainless steel reaction vessel. The vessel was degassed three times and pressurized to 1380 kPa (200psi) with nitrogen. The vessel was stirred internally by magnetic stir bar in an oil bath at 160°C for 60 min. A portion (0.100 mL) of the product was analyzed before and after the reaction for the conversion of VTEOS by ^1H-NMR.

2.3.9 Cure Rheology.

Elastomer (5.00 g) was sheeted in a two-roll mill, coated with an acetone solution containing DCP (0.050 g, 0.19 mmol) and the required amount of AOTEMPO (none, 0.093, 0.19, 0.37, or 0.56 mmol) and allowed to air dry. The resulting films were milled and cured within the cavity of the controlled strain rheometer.

2.4 Results and Discussion.

2.4.1 Abstraction Efficiency.

Whereas the structure of high molecular weight PIB is simple, with only trace amounts of vinylidene end groups in the polymer, IIR materials containing high isoprene contents are more complex. Raising the diene content not only raises the amount of conventional 1,4-addition product, it increases the population of isoprene diads and the yield of isoprene-derived oligomers (which were removed by purification).[22] Figure 4 provides enlarged downfield ^{1}H-NMR spectra for: A) 2,2,4,8,8-pentamethyl-4-nonene, and B) IIR containing 5.8 mol% isoprene (IIR-5.8). These data confirm that isoprene incorporation in IIR proceeded overwhelmingly by 1,4-addition, and that the radical chemistry of IIR-5.8 should be dominated by the allylic H-atom reactivity provided by this functional group. It should be noted that high IP grades of IIR contain a very small amount (≤0.11 mol%) of incorporated divinylbenzene, used to offset molecular weight losses to chain transfer during the cationic polymerization.[18] At this level, the presence of benzylic H-atom functionality is not expected to be significant.

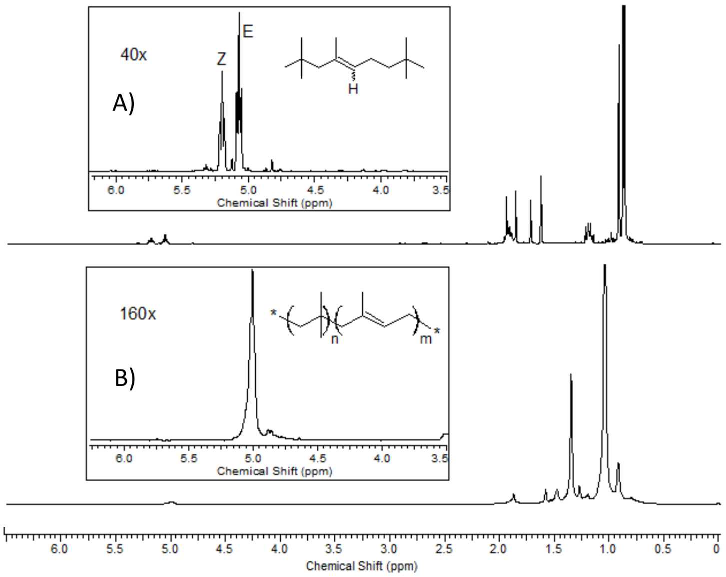


Figure 4. 1H NMR with expanded regions showing: A) 2,2,4,8,8-pentamethyl-4-nonene B) IIR-5.8

Table 1 provides AE values for PIB and IIR materials of different isoprene contents, which demonstrate the extent to which H-atom donor reactivity is affected by incorporating more diene in the copolymer. Given that AE is the fraction of cumyloxy radicals that abstract an H-atom from the hydrocarbon as opposed to fragmenting to a methyl radical and ketone, higher numbers reflect heightened kinetic reactivity. AE increased from 0.17 for PIB to 0.31 for IIR containing 5.8 mole % isoprene. Note that 2,2,4,4-tetramethypentane (TMP), a model compound for the isobutylene mers in PIB and IIR, provided an AE = 0.18, whereas 2,2,4,8,8-pentamethyl-4-nonene (PMN), a model compound for the isoprene mers in IIR, provided an AE = 0.56.

Table 1. DCP abstraction efficiency and VTEOS conversion

Polymer/Hydrocarbon	AE[a]	VTEOS Conversion[b]
Polyisobutylene	0.17	0.27
IIR-2.8% isoprene	0.22	0.17
IIR-4.2% isoprene	0.28	0.14
IIR-5.8% isoprene	0.31	0.10
2,2,4,4–Tetramethylpentane	0.18	---
2,2,4,8,8-Pentamethyl-4-nonene	0.56[c]	---

a. [DCP] = 2 wt%, 160°C, 38 min.
b. [DCP] = 0.2 wt%, [VTEOS] = 5 wt%, 160°C, 60 min.
c. [DCP] = 5 wt%, 160°C, 38 min.

While it is clear that IIR containing high amounts of isoprene provides greater macroradical yields from DCP, knowledge of the regioselectivity of hydrogen atom abstraction is needed to understand its implications for polymer modification chemistry. Allylic positions provided by residual C=C unsaturation in IIR have been implicated by Loan,[17] who noted the low bond dissociation energy of allylic C-H bonds. This is recognition of the enthalpic contribution to the transition state energy, but recent research has highlighted the importance of entropic barriers, wherein steric effects play a key role in determining the rate of H-atom transfer.[11] This is illustrated clearly by PIB, whose reactivity is restricted to methyl groups due to steric hindrance imposed by quaternary carbons adjacent to methylene groups. The allylic functionality within IIR may suffer from similar steric effects imposed by adjacent isobutylene mers. The following section describes the regioselectivity of H-atom transfer from IIR, after which consequences for degradation/cross-linking and grafting chemistry are explored.

2.4.2 Regioselectivity of H-atom transfer.

We have previously reported on the selectivity of H-atom abstraction from PIB, wherein a nitroxyl was used to trap carbon-centered radicals produced from a model hydrocarbon, 2,2,4,4-

tetramethylpentane (TMP).[11] This use of alkoxyamine distributions to define the radical population generated by a peroxide initiator has been applied successfully to closely related systems.[23] In the case of PIB/TMP, steric inhibition imposed by quaternary carbons on adjacent methylene groups resulted in negligible reactivity at the secondary position. Reactivity is essentially entropy-controlled, with H-atom transfer restricted to sterically accessible methyl groups. Heating PIB with DCP and excess TEMPO gave the graft-modified product, PIB-g-TEMPO, whose ^{1}H-NMR spectrum is provided in Figure 5C. As expected, it shows clear evidence of a primary alkoxyamine, with little sign of the analogous secondary alkoxyamine stemming from methylene group activation.

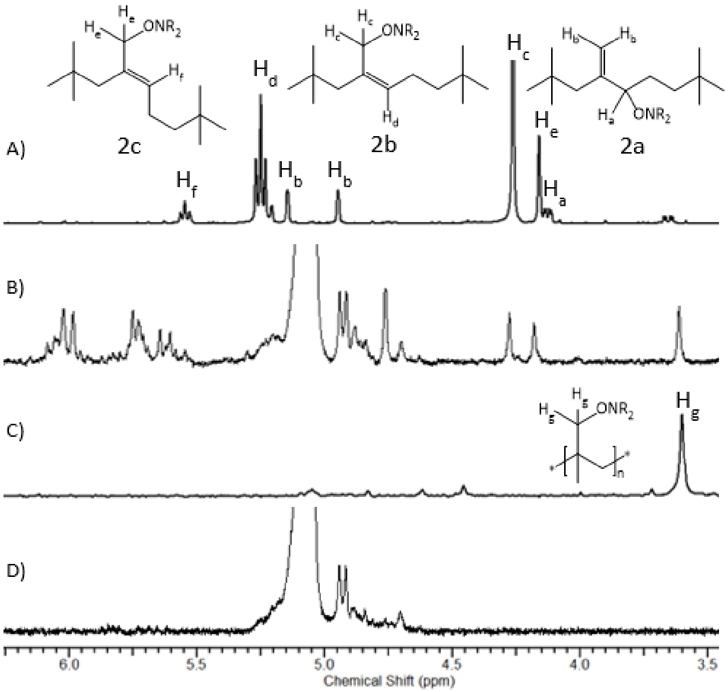
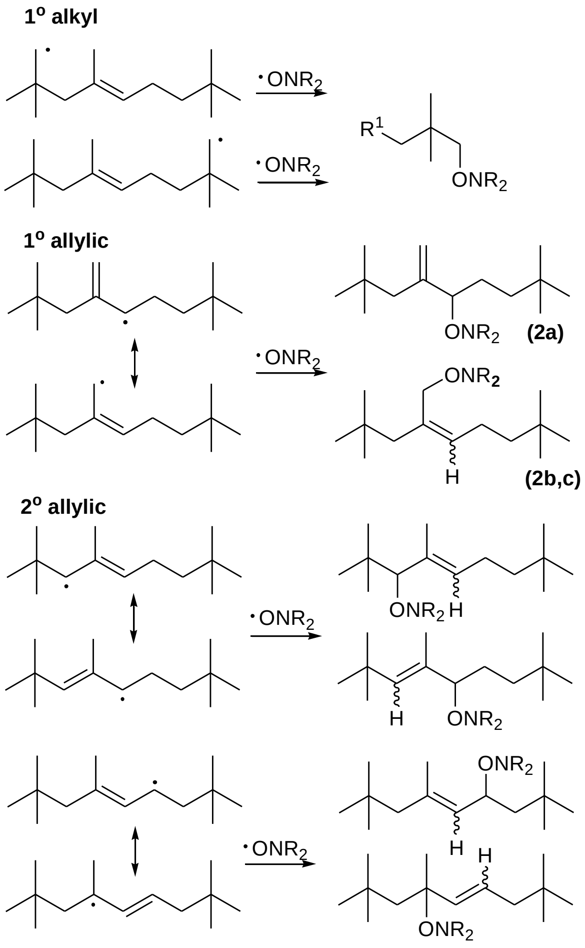


Figure 5. 1H NMR showing TEMPO-trapped radical derived from H-atom donation to cumyloxyl: A) 5-bromo-2,2,4,8,8-pentamethyl-4-nonene B) IIR-5.8-g-TEMPO C) PIB-g-TEMPO D) Unreacted IIR-5.8.

The ^{1}H-NMR spectrum of IIR-g-TEMPO, generated by reacting IIR-5.8 with DCP and TEMPO, shows the same primary alkoxyamine functionality found in PIB-g-TEMPO, indicating that H-atom abstraction from methyl groups is a significant reaction pathway (Figure 5B). Further downfield in the ^{1}H-NMR spectrum is evidence of the complexity of allylic H-atom abstraction chemistry, as a wide range of regio and stereoisomers can be generated from isoprene mers.

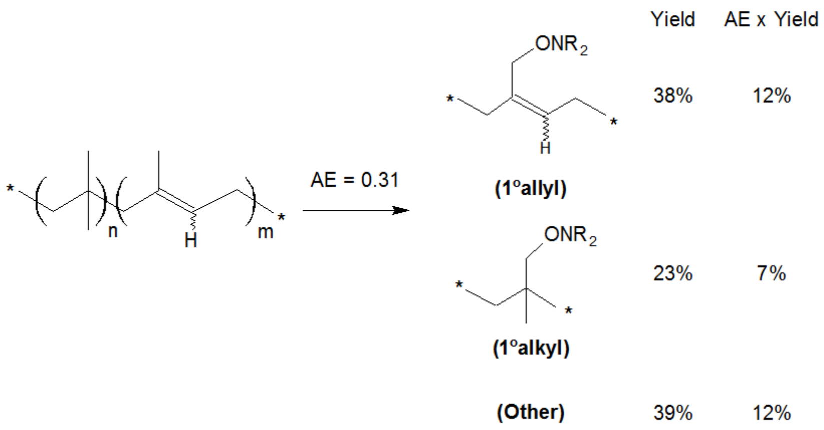
Scheme 18. Potential H-atom abstraction products of PMN



Scheme 18 illustrates potential H-atom transfer reactions for cumyloxyl acting upon the model compound, PMN. Abstraction from methyl groups produces robust secondary alkoxyamines that are easily quantified by the same downfield ^{1}H-NMR singlet generated by PIB and TMP. The primary allylic position yields three allylic alkoxyamines; an exomethylene isomer (**2a**) as well as E,Z-isomers of the trisubstituted olefin (**2b**,**c**). We prepared an authentic sample of these compounds by halogen abstraction from brominated PMN (BPMN) using CuBr with an appropriate ligand at 70°C. Trapping of the resulting allylic radicals with TEMPO produced **2a:2b:2c** in a 20:70:10 ratio. More importantly, it provided ^{1}H-NMR data needed to characterize H-atom abstraction from the primary allylic position within IIR-g-TEMPO (Figure 5B). The thermal stability of these alkoxyamines was tested by heating the 20:70:10 mixture of **2a**:**2b**:**2c** to 145°C for 44 hours. This shifted the isomer distribution to 3:39:58 without generating new products. Therefore, the total yield of **2a,b,c** is a reliable measure of H-atom abstraction from the primary allylic position, but rearrangement to more stable olefins shifts isomer distributions from initial values. Indeed the ^{1}H-NMR spectrum of IIR-g-TEMPO, which was prepared at 160°C, shows little of the exomethylene isomer.

Abstraction from secondary allylic C-H groups is expected to yield additional allylic alkoxyamines. However, the expected allylic heteroatom resonances in the ^{1}H-NMR spectrum are lacking, with only conjugated dienes apparent in the downfield region, as well as a doublet at 4.8ppm arising from polymer bound cyclic oligomers (Figure 5B/D).[22] Note that H-atom abstraction from the 3-position is unlikely, due to steric effects from the adjacent t-butyl substitutent (Scheme 18). The 6-position is less unencumbered, but it yields a tertiary allylic alkoxyamine of questionable thermal stability.[24,25] Alkoxyamine disproportionation to conjugated diene is possible under the conditions used in this work. However, we observed similar products when PMN was treated with DCP in the absence of TEMPO (not shown), suggesting that allyl radical intermediates are capable of generating conjugated dienes without assistance from the nitroxyl.

Scheme 19. Regioselectivity of H-atom abstraction from PMN



A material balance on IIR-g-TEMPO alkoxyamines accounted for 61% of the cumyl alcohol generated by reaction of cumyloxyl with the polymer, with the remaining 39% unaccounted for, but presumably originating from secondary allylic H-atom abstraction (Scheme 19). Note that the product of the alkoxyamine yield and the abstraction efficiency gives the percent of cumyloxy radicals that abstract from a specific site. Despite being present in far greater quantity, primary alkyl groups accounted for just 7% of the abstraction yield, while primary allylic groups accounted for 12%. The heighted reactivity of the allylic position is consistent with expectations based upon its low C-H bond dissociation energy, since steric/entropic effects are equivalent for the two functional groups.

2.4.3 Peroxide-initiated Polymer Modifications.

Equipped with a better understanding of H-atom donation by the unsaturation within IIR, our attention turned to the effect of an allyl radical populations on the outcome of peroxide-initiated polymer modifications. Figure 6 illustrates the dynamic storage modulus (G') of PIB and IIR materials containing 2.8, 4.2, and 5.8 mol% isoprene, when the polymers were mixed with DCP and heated to 160°C. These measurements were recorded at a fixed strain amplitude, and oscillation frequency, such that G' losses reflected declines in molecular weight owing to macroradical cleavage.[26] The data clearly demonstrate the susceptibility of PIB to radical degradation,[27] and the extent to which small amounts of isoprene can mitigate chain scission. These observations are consistent with solvent swelling data acquired by Loan, who showed that 2.8% isoprene content was sufficient to yield an IIR copolymer that does not degrade substantially when treated with DCP at 140°C.[17] Given that chain scission is accelerated by increased temperature, the threshold we observed at 160°C was 4.2% isoprene.

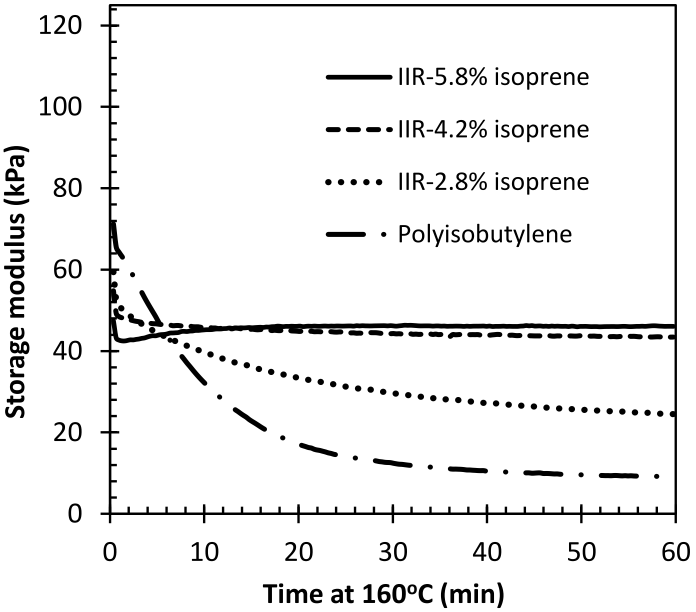
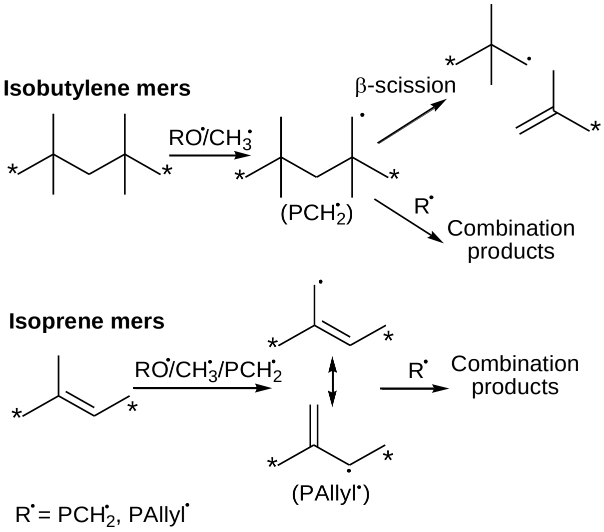


Figure 6. Dynamics of DCP-initiated polymer modification ([DCP] = 37 µmole/g)

A skeletal mechanism that accounts for this rheology data is illustrated in Scheme 20. As described above, H-atom donation by PIB is regioselective for methyl groups, giving primary alkyl macroradicals that can cleave to produce a vinylidene end group and another primary radical.[28] This intermediate has several fates: it can continue to fragment to yield isobutylene, it can engage in H-atom transfer to produce alternate macroradicals, and it can terminate by combination. The storage modulus data plotted in Figure 6 show that macroradical fragmentation is competitive with termination by combination, resulting in a net loss of molecular weight.

Scheme 20. Simultaneous degradation and cross-linking of IIR

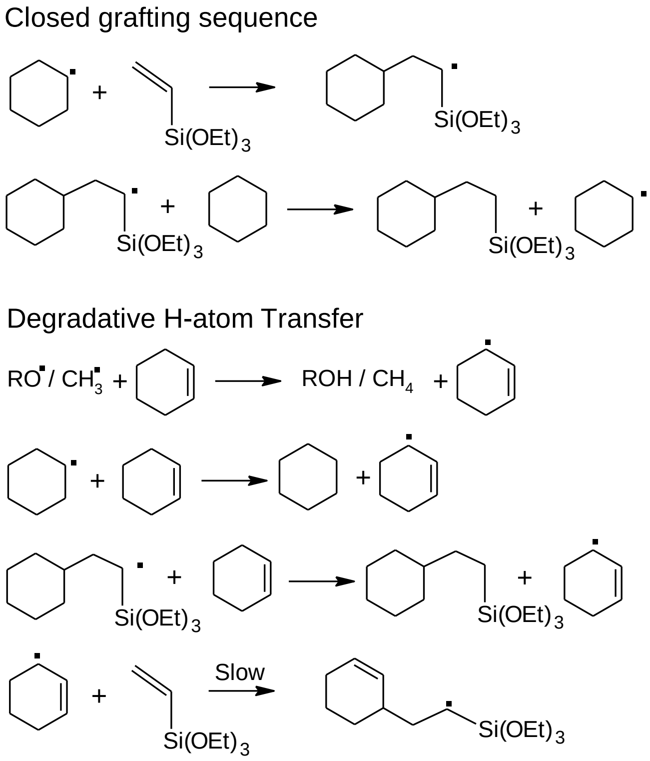


Our abstraction efficiency and regioselectivity studies have demonstrated the reactivity of allylic C-H bonds in H-atom transfer. The resonance-stabilized allylic macroradicals terminate exclusively by combination[29] and, apparently do not fragment as readily and primary alkyl macroradicals. As such, the balance between macroradical fragmentation and combination is shifted toward the latter, such that the storage modulus is substantially unaffected by peroxide-initiated modification. Note that isoprene mers not only improve peroxide abstraction efficiencies, they may serve as H-atom donors to primary alkyl radicals, thereby quenching the source of backbone fragmentation. The net result is an IIR material containing 5.8 mol% isoprene whose storage modulus left nearly unchanged by DCP after 60 min at 160°C (Figure 6).

2.4.4 Vinyltriethoxysilane graft yields

Peroxide-initiated addition of monomers such as vinyltriethoxysilane (VTEOS) is commercial technology for preparing functional polyolefins[30] that has not been developed for PIB and IIR elastomers.[31] VTEOS is also a convenient reagent for careful experimental work, since it has good solubility in polyolefins, and it has a very low propensity to homopolymerize.[32,33] Vinylsilane conversion to multiple single grafts occurs through a closed sequence involving macroradical addition to VTEOS, followed by H-atom transfer to the resulting monomer-derived alkyl radical (Scheme 21).[9,34,35,36] As such, heightened reactivity of a polymer toward H-atom abstraction can, by improving macroradical yields and improving the efficiency of the propagation sequence, translate into improved VTEOS conversions. This trend has been demonstrated for saturated polyolefins such as polyisobutylene, polypropylene, polyethylene and polyethylene oxide, for which AE and VTEOS conversion are strongly correlated.[11]

Scheme 21. Radical-mediated grafting of VTEOS to cyclohexane



The data listed in Table 1 show that this relationship does not hold for the IIR system, as the higher AE values gained by introducing unsaturation to the polymer were accompanied by sharp declines in VTEOS graft yields. Whereas PIB gave a VTEOS conversion of 0.27, IIR containing 5.8 mol% isoprene provided just 0.10, despite having nearly twice the peroxide AE. This is attributed to two factors; the quenching of propagating alkyl radicals by allylic H-atom transfer,[37] and the slow rate of allyl radical addition to VTEOS. These concepts were derived from a series of small molecule studies, described below. It should be noted that G' losses in grafting reactions still reflected those of radical crosslinking reactions, indicating competitive β-scission of isobutylene.

Table 2 summarizes the outcome of DCP-initiated VTEOS additions to cyclohexane + cyclohexene mixtures. Under conditions similar to our IIR modification experiments, a cyclohexane solution containing 263 µmole/g of VTEOS and 7.4 µmole/g of DCP gave a monomer conversion of 0.98. This corresponds to a peroxide yield of 16.3 mol/mol, meaning that 16.3 moles of VTEOS were consumed per mole of cumyloxy radicals derived from DCP thermolysis. This is evidence of a chain reaction propagating through the closed grafting sequence illustrated in Scheme 21.

Table 2. VTEOS conversion in cyclohexane + cyclohexene mixtures[a]

Mole % cyclohexene	VTEOS Conversion	Peroxide Yield (mol/mol)
0.0	0.98	16.3
2.6	0.19	3.4
5.1	0.12	2.1
10.2	0.02	0.4
15.3	trace	≈ 0.0

a. [DCP] = 7.4 µmole/g, [VTEOS] = 263 µmole/g, 160°C, 60 min.

The peroxide yield in cyclohexane is reasonable and similar to values obtained in a previous study on grafting VTEOS to LLDPE and tetradecane.[38] Charging 2.6 mole% cyclohexene to the reaction mixture lowered the VTEOS conversion to 0.19, while 15.3 mole% cyclohexene quenched the reaction entirely. Degradative chain transfer is a term used in polymerization literature when a compound engages propagating macroradicals in an atom transfer process (H-atom or halogen) to yield a transient radical that does not undergo rapid monomer addition.[32,36,39] In the present context, allylic H-atom transfer to initiator-derived and propagating alkyl radicals quenches graft propagation, since the rate of allyl radical addition to VTEOS is uncompetitive with radical termination.[40] The greater the isoprene content in the IIR copolymer, the more degradative chain transfer is incurred during a VTEOS graft modification.

2.4.5 AOTEMPO-mediated Cross-linking.

None of the IIR copolymers examined in this work cross-linked under the action of DCP alone, but isobutylene-rich elastomers bearing polymerizable pendant groups are known to cure extensively when heated with small amounts of peroxide initiator.[41] For example, halide displacement from brominated butyl rubber (BIIR) with tetrabutylammonium acrylate produces a macromonomer derivative that cross-links rapidly to a high cure extent.[42,43] This synthetic approach involves IIR halogenation, followed by nucleophilic substitution, with both reactions being conducted in solution. These acrylate-based macromonomers contain on the order of 150 µmole of acrylate functionality per gram of polymer, which when compounded with 11 µmole of DCP /g polymer, provided a change in storage modulus of $\Delta G' = G'_{max} - G'_{min}$ = 250 kPa at 160°C, albeit with a tendency to cure too rapidly at the onset.

A one-step, solvent-free approach uses an acrylate functionalized nitroxyl (AOTEMPO) in an otherwise conventional peroxide cure formulation (Scheme 22).[44] Based on previous studies of AOTEMPO-mediated polyethylene crosslinking,[45] PIB and IIR processes should demonstrate three phases: radical trapping, oligomerization/degradation, and cure reversion. Chain scission during the induction phase is suppressed by macroradical quenching by nitroxyl. Upon complete AOTEMPO consumption, oligomerization of polymer-bound acrylate groups will crosslink the polymer, hopefully faster than accompanying macroradical scission, leading to a significant cure extent. Cure reversion is expected if all acrylate macromonomer functionality is consumed prior to complete peroxide consumption, leaving backbone degradation to proceed unabated.

Scheme 22. AOTEMPO-mediated reactions of PIB

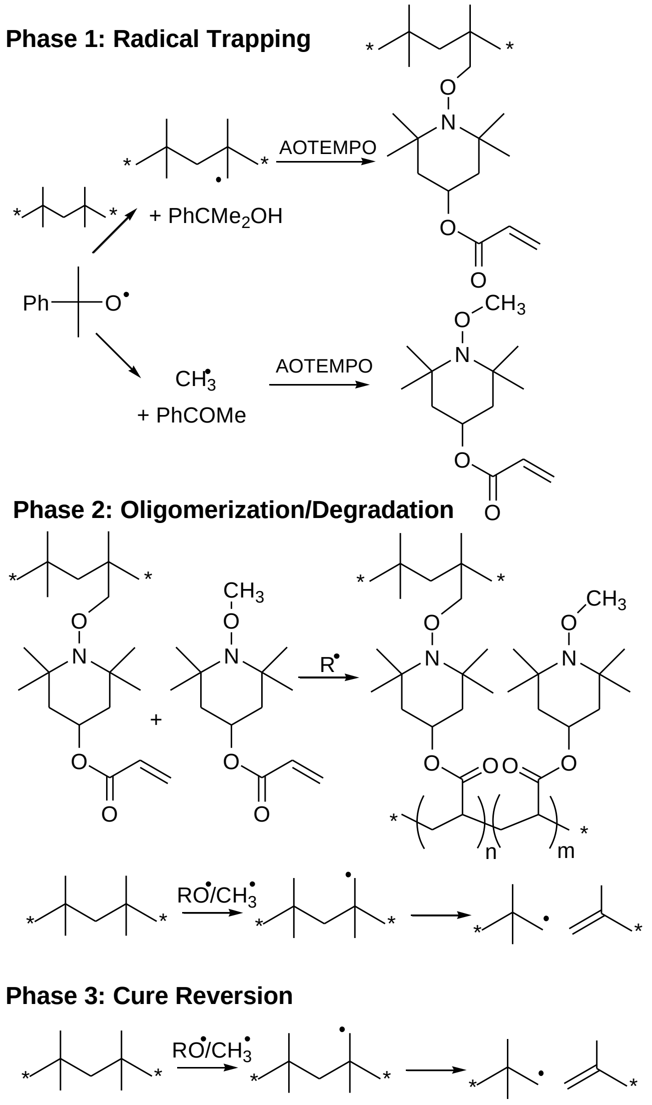


Figure 7a provides cure rheology data for PIB formulations containing different AOTEMPO concentrations, expressed in terms of the trapping ratio, ([AOTEMPO]/(2*[DCP])), which represents the fraction of initiator-derived radicals quenched by the nitroxyl. Note that a value of 1.0 can quench all radical activity, stunting the oligomerization phase of the process, while a low trapping ratio can leave an excessive amount of residual peroxide beyond the oligomerization phase, resulting in cure reversion. The data show that, irrespective of the amount of AOTEMPO employed, no cure could be generated for PIB (Figure 7a).

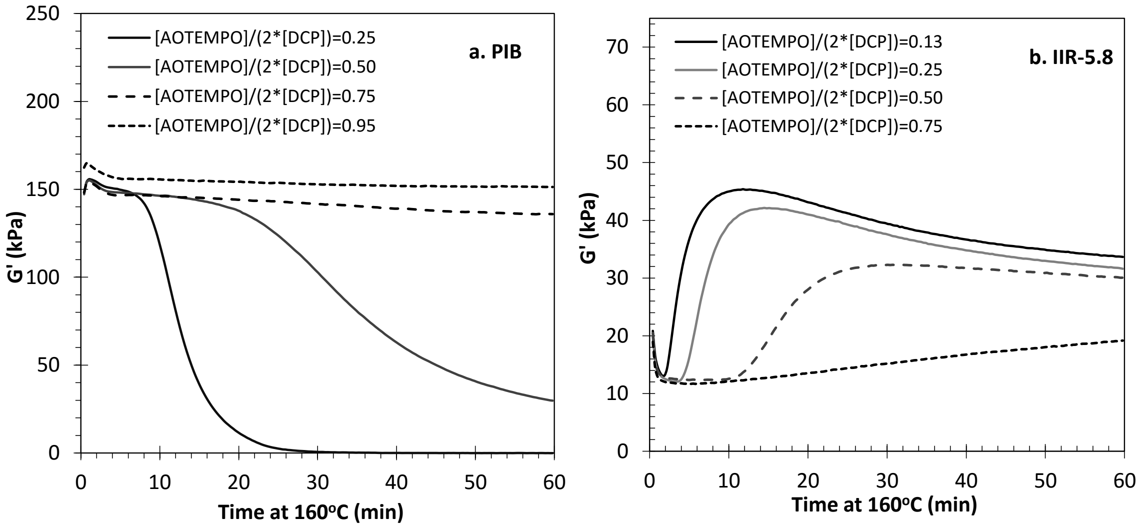


Figure 7. Dynamics of PIB and IIR-5.8 modifications using different trapping ratios (a. [DCP] = 74 µmole/g, 160°C)

The failure of AOTEMPO to provide a net increase in G' is the result of an inadequate macromonomer oligomerization phase. There is clear evidence of an induction period, during which macroradical trapping generates macromonomer functionality. However, the low abstraction efficiency for PIB (AE=0.17, Table 1) means that most AOTEMPO is converted to methyl alkoxyamine, as opposed to polymer-bound alkoxyamine. Given that phase 2 of the process involves simultaneous chain scission and macromonomer oligomerization, the concentration of polymer-bound acrylate groups is insufficient to support a competitive cure process, and no net crosslinking is achieved.

High isoprene grades of IIR present a potential solution to the AOTEMPO performance deficiency, as they provide higher abstraction efficiencies than PIB. Higher macroradical yields translate into improved polymer-bound acrylate concentrations that, in turn, support a more rapid and extensive cross-link network formation. The data plotted in Figure 7b show some promise. A trapping ratio of 0.25 provided a distinct induction period, followed by a pronounced oligomerization phase, and then mild cure reversion. However, the cure extent was just ΔG'= 30 kPa at 160°C, well below that generated by the aforementioned acrylated BIIR, thereby highlighting the need for further advancement of the functional nitroxyl approach. The performance of the functionalized nitroxyl may be increased by changing the functional group to a more reactive 4-vinylbenzoic acid derivative, since vinylbenzoate grafted butyl rubber has exhibited superior reactivity with DCP at 160°C.[42,43]

2.5 Conclusions.

H-atom abstraction from isoprene mers with IIR improves the isobutylene-rich polymer's H-atom transfer reactivity toward cumyoxyl, yielding an allyl radical population that significantly affects polymer modification outcomes. A preference of allyl radicals for termination by combination offsets molecular weight losses to primary alkyl radical scission, thereby reducing the copolymer's tendency to undergo radical degradation. However, the low reactivity of allylic radicals toward vinyltrialkoxysilane addition makes high isoprene grades of IIR less responsive to VTEOS grafting than a saturated PIB homopolymer. The higher peroxide AE performance can be used to support AOTEMPO-mediated cross-linking, where *in situ* macromonomer preparation is dependent on H-atom transfer yields.

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Chapter 3

Peroxide-initiated Modification of Polyolefins:
In search of a Latent Antioxidant

Manuscript prepared for the Journal of Macromolecular Rapid Communications

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3.1 Abstract.

Thermoset polyolefins require the addition of long term stabilizers before crosslinking is initiated. In this study, the effects of different stabilizers on peroxide mediated radical modification of molten LLDPE are discussed and quantified. Stabilizers selected to represent several antioxidant classes are evaluated as potential latent antioxidants. Additives are tested at high loadings while examining changes in elastic storage modulus of LLDPE cures initiated by cumyloxy and tert-butoxy radical intermediates. Each stabilizer was added to the cumyloxy mediated grafting reaction of vinyltriethoxysilane to cyclohexane at high temperature in the absence of oxygen and graft yields were determined by ^{1}H NMR. Stabilizers were analyzed at lower concentrations in LLDPE cures to evaluate the concentration at which each stabilizer begins to affect crosslinking. 2,2,6,6-tetramethylpiperidine (TEMPH) was selected as an ideal latent antioxidant owing to the requirement of oxidative activation to form a reactive nitroxyl radical. A survivability study was performed by analyzing amine concentration before and after reaction using gas chromatography and ^{1}H NMR. TEMPH was found to survive both grafting and crosslinking, while 1,2,2,6,6-pentamethylpiperidine (TEMPMe) did not. For confirmation, an oxidation study was used to verify the antioxidant properties of TEMPH and results are summarized and discussed by

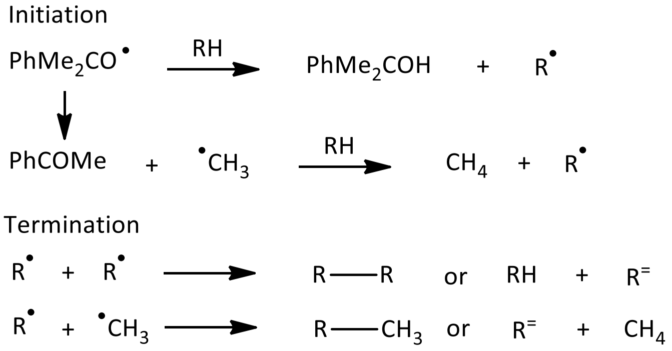
reviewing possible activation mechanisms for hindered amines to form nitroxyls that act as stabilizers.

3.2 Introduction.

The chemical modification of commodity polymers is a versatile synthetic approach for preparing materials that cannot be manufactured economically using conventional polymerization techniques. Although saturated polyolefins such as linear low density polyethylene (LLDPE) are not amenable to most catalytic and ionic functionalization chemistry, their architecture and chemical functionality can be changed efficiently using peroxide-initiated radical reactions.[1] Key examples include radical-mediated cross-linking to generate thermoset products,[2,3] and graft modification with maleic anhydride and vinyltrialkoxysilanes to yield reactive derivatives for use in adhesive, blend, and composite formulations.[1,4,5,6,7] These widely commercialized processes are conducted solvent-free in the melt state using conventional polymer processing equipment.[8,9]

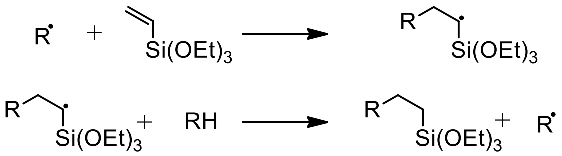
All polyolefin modifications proceed through reactions of the macroradicals generated by H-atom donation to initiator-derived intermediates.[10,11] For example, LLDPE crosslinking by dicumyl peroxide (DCP) involves H-atom abstraction by cumyloxy and methyl radicals, with ensuing macro-radical combination producing the desired change in molecular weight distribution (Scheme 23).[12,13] Cross-link yields are proportional to the peroxide concentration, with exact values being sensitive to the abstraction efficiency of the initiator as well as the ratio of macroradical combination to disproportionation.[14,15] As a result, additives that reduce macroradical yields generally compromise the crosslink density that the formulation could achieve in its absence.

Scheme 23. Peroxide-initiated crosslinking of polyethylene



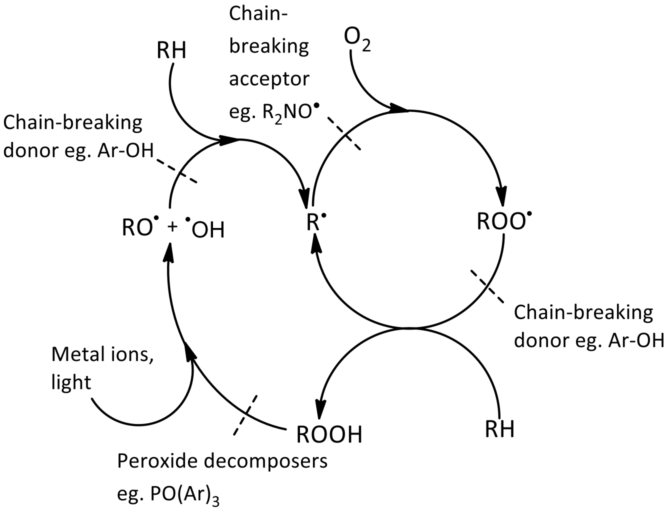
Graft modification with reagents such as vinyltriethoxysilane (VTEOS) similarly requires macroradical generation, which is accompanied by a propagation involving monomer addition and H-atom donation to monomer-derived radical adducts (Scheme 24).[11,16] When this closed propagation sequence is competitive with radical termination, multiple single grafts are introduced to the polymer for each macroradical generated by the initiator, giving an alkoxysilane functionalized polymer capable of moisture-curing and/or bonding with siliceous fillers.[17,18,19] Note that the polyolefin melting point establishes the lower temperature limit for a modification process, but much higher temperatures are often preferred to reduce melt viscosities. As such, peroxide-initiated crosslinking and graft modifications are generally high temperature (170-210°C), short duration (0.5 – 5 min) reactions.[18]

Scheme 24. Graft propagation sequence for VTEOS addition to a polyolefin



The temperatures used in polymer processing and modification are the most severe experienced by a polyolefin during its lifecycle. In general, the short duration minimizes opportunity for oxidative degradation, but unstabilized materials will incur extensive oxidation under typical service conditions, leading to an eventual mechanical failure.[20,21] Scheme 25 illustrates the generally accepted mechanism for radical oxidation, as well as three modes of antioxidant action. Sacrificial H-atom donors such as phenolics and diarylamines intervene by quenching alkyl, alkoxyl, peroxy and hydroxyl radicals, while nitroxyls such as TEMPO serve as alkyl radical traps through combination, and nucleophilic phosphites reduce hydroperoxides to their corresponding alcohols.[22,23] Virtually all consumer goods employ one or more of these stabilizing agents to meet polymer lifetime requirements.

Scheme 25. Radical oxidation with potential antioxidant interactions.



A longstanding challenge in the polyolefin modification field is to prepare thermoset articles that contain the necessary stabilizing agents.[24] Peroxide-initiated reaction yields are dependent on the uninhibited reactivity of alkoxyl and alkyl radical populations, while the long term service life of the article is contingent on the quenching of alkoxyl, alkyl and peroxy radical activity. Note that once a material is rendered thermoset, it is no longer possible to incorporate stabilizing agents. Therefore, these chemical modifications must be conducted in the presence of antagonistic antioxidants. In most cases, this dichotomy is resolved, albeit imperfectly, by using excessive amounts of initiator and stabilizers, exploiting the fact that some macroradicals can escape quenching to provide the required crosslink density, and residual antioxidant and/or its byproducts can provide the necessary stabilization.

Therefore, there is a need for compounds that do not compromise peroxide-initiated modification yields but provide antioxidant activity in thermosets and/or graft-modified polyolefins. The objective of this work is to develop a latent antioxidant that is inactive during the high temperature, short duration of radical modification processes, but is active under the long term oxidizing conditions experienced in standard service. Clearly, phenolic H-atom donors, nitroxyls and phophites are poor candidates for this application, as they are reactive in their native state.[25,26] However, within a broad class of stabilization agents, commonly referred to as hindered amine light stabilizers (HALS), are compounds that are generally believed to require chemical transformation before quenching radical oxidation activity.[27] These include 2,2,6,6-tetramethylpiperidine (TEMPH), 1,2,2,6,6-pentamethylpiperidine (TEMPMe) and 1-alkoxy-2,2,6,6-tetramethyl-4-piperidine (TEMPOR). Although this class of stabilizing agents is widely used in consumer goods, commercial development has outpaced studies of fundamental chemistry, and the mechanisms through which these compounds are activated under oxidation conditions remain unresolved. Nevertheless, the simple fact that transformation is needed offers the potential for latency, as defined in the present context.

This study begins with an experimental survey of the influence of common stabilizers on DCP-initiated LLDPE crosslinking and VTEOS graft conversion, before focusing on uniquely effective compounds bearing 2,2,6,6-tetramethylpiperidine (TEMPH) functionality. The performance of the most promising reagent in mitigating the extent of LLDPE oxidation is assessed using accelerated aging tests and the data is discussed in the context of established theories of TEMPH activation and antioxidant function.

3.3 Experimental Section.

3.3.1 Materials.

The following materials were used as received from Sigma-Aldrich (Oakville, Ontario): Dicumyl peroxide (DCP, 99%), 1,1-Bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane (L231, 92%), 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO, purified by sublimation, 99%), 2,2,6,6-tetramethylpiperidine (TEMPH, 99%), 1,2,2,6,6-pentamethylpiperidine (TEMPMe, 97%), bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (TEMPHS), bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate (OTEMPOS), 3,5-di-tert-4-butylhydroxytoluene (≥99%), (±)-α-tocopherol (96%), DL- α-tocopherol acetate (Vitamin E acetate, 96%), tris(2,4-di-tert-butylphenyl)phosphite (Irgaphos 168, 98%), vinyltriethoxysilane (VTEOS, 97%), cyclohexane (≥99.9%), Sodium chloride round crystal windows (diam. X thickness - 25 mm x 4 mm). Toluene (≥ 99.5%) and acetone (≥ 99.5%) were used as received from Fisher Scientific (Ottawa, Ontario). 4-acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl (AOTEMPO) was prepared as previously described.[28]

3.3.2 Instrumentation and Analysis.

Analysis of additive concentration and VTEOS conversion for vinylsilane grafting to cyclohexane was conducted with a Varian CP-3800 gas chromatograph equipped with a Chrompack CP 8771 silica column (30m x 0.25 mm x 8CB 1 μm) using 3.2 mL/min of helium as carrier gas. Injector and detector temperatures were held at 250°C and the oven temperature started at 50 °C for 2 min, ramping to 100°C at 2°C/min, holding for 1 min, ramping to 105 °C at 1 °C/min, holding for 1 min, ramping to 150 at 25°C/min, holding for 1 min, ramping to 155 °C at 1 °C/min, holding for 1 min, and ramping to 250°C at 25°C/min and holding for 1 min. ^{1}H-

NMR spectra were recorded in $CDCl_3$ using a Bruker AC-400 spectrometer, with chemical shifts reported in ppm relative to chloroform (δ 7.24). Oxidative degradation of LLDPE films was performed in a high pressure Parr 4540 reactor with the stirring mechanism disassembled and a separating disk platform. Infrared absorbance measurements were recorded from 4000cm^{-1} to 400cm^{-1} with a resolution of 4cm^{-1} and 16 scans using a Nicolet Avatar 360 FT-IR spectrometer with attenuated total reflectance and diffuse reflectance. Rheological tests for the change in dynamic storage moduli were recorded in a controlled strain rheometer (Advanced Polymer Analyzer 2000, Alpha Technologies) equipped with biconical disks and operating at 1 Hz and 3° arc.

3.3.3 Cure Rheology.

LLDPE (5.00 g) was ground and coated with an acetone solution containing DCP (0.025 g, 92.5 µmoles) or L231 (0.025 g, 83 µmoles) and the required amount of additive (none, 23, 46, 185, or 500 µmoles) and allowed to air dry. The ground LLDPE was cured between two nylon films within the cavity of the controlled strain rheometer. DCP initiated systems were cured for 60 min at 160°C and L231 initiated systems were cured for 60 min at 136°C.

3.3.4 Vinyltriethoxysilane grafting.

Cyclohexane (5g, 59 mmoles), DCP (0.0050g, 18.5 µmoles), VTEOS (0.25g, 1.3 mmoles), and one of the additives (185 µmoles or 500 µmoles) were charged to a 10 mL stainless steel vessel, which was degassed twice and pressurized to 1380 kPa with N_2. The vessel was stirred internally by magnetic stir bar at 100 rpm in an oil bath at 160°C for 60 min. A portion (100uL) of each reacted solution was removed and diluted with 500 µL of $CDCl_3$ to determine VTEOS conversion by ^{1}H-NMR spectrum integration using vinyl group resonances (5.8–6.2 ppm, m, 3H) relative to the $–CH_2-$ resonance of the ethoxy substituents (3.8 ppm, q, 6H).

3.3.5 Hindered Amine Conversion Study.

To determine whether TEMPH is consumed during peroxide-initiated VTEOS grafting, cyclohexane (5g, 59 mmoles), DCP (none or 0.0050 g, 18.5 µmoles), VTEOS (none or 0.25 g, 1.3 mmoles), and TEMPH (none or 0.0261 g,185 µmoles) were mixed in a 10 mL stainless steel reaction vessel, degassed twice and pressurized to 1380 kPa with N_2. The contents were stirred by magnetic stir bar at 100rpm in an oil bath at 160°C for 60 min. 2 mL of each reacted solution were extracted and undiluted, 10x, 100x and 1000x diluted samples were taken for GC analysis.

3.3.6 Polymer Oxidation.

LLDPE (0.5 g), purified by dissolution and precipitation in toluene/acetone, and antioxidant (185 µmoles or 500 µmoles, TEMPHS, OTEMPOS, or BHT) were dissolved in toluene (20 mL) at 80°C. Thin films were solution cast on NaCl disks, dried at 110°C for 15 min, analyzed by FT-IR spectroscopy prior to oxidation. The disks were sealed in a 25 ml Paar autoclave, the atmosphere was purged twice with O_2 before pressurizing to 400kPa. Disks removed at 6 and 16 days were analyzed by FT-IR using the carbonyl region absorbance (1600 cm^{-1} and 1850 cm^{-1}) normalized for film thickness using CH_2 symmetric stretching resonances (2750 cm^{-1} to 2875 cm^{-1})[29,30] The value prior to oxidation was subtracted from values at 6 and 16 days. The carbonyl index ($A_{1725cm^{-1}}/A_{2812cm^{-1}}$) was used as the measure of LLDPE oxidation to ascertain the effect of stabilizing agents relative to the additive-free control.[31,32]

3.4 Results

3.4.1 Peroxide-initiated LLDPE Crosslinking.

Peroxide crosslinking of ethylene-rich polyolefins is not a chain reaction, but a stoichiometric process wherein radicals are generated in pairs by slow initiator decomposition, and terminated in pairs by rapid combination/disproportionation. As a result, cure extents are proportional to peroxide loading, and crosslinking rates are dictated by the first-order decomposition kinetics of the initiator. With a half-life of 5.4 min for DCP at 160°C,[33] LLDPE crosslinking is essentially complete within 60 min. This is demonstrated by the cure rheometry data plotted in Figure 8, in which the dynamic storage modulus (G') of polymer formulations is monitored as a function of time at a constant temperature, frequency, and shear strain amplitude.[34] In the absence of additives, a DCP concentration of 18.5 µmole/g increased G' from 4 kPa to a final modulus of 189 kPa, giving a cure yield ($\Delta G' = G'_{max} - G'_{min}$) of 185 kPa.

Given that LLDPE cure extents, quantified by ΔG', vary linearly with the population of initiator-derived radicals, additives that quench RO·, $CH_3\cdot$, and alkyl macroradicals should be antagonistic toward crosslink density. The results plotted in Figure 8, along with the more expansive data set listed in

Table 3, confirm this expectation for the majority of antioxidants examined in this study. Carbon-centred radical traps TEMPO and its acrylated analogue AOTEMPO quenched the cure entirely, while phenolic H-atom donors (BHT, vitamin E) and the peroxidolytic additive, tris(2,4-di-tert-butylphenyl)phosphite, also demonstrated strong cure suppression.

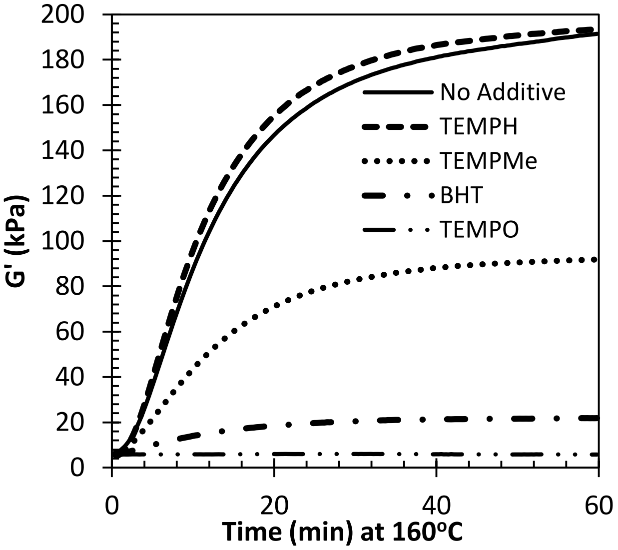


Figure 8. Cure dynamics for DCP-initiated LLDPE crosslinking with different additives ([DCP] = 18.5 µmole/g, [additive] = 100 µmole/g)

The most promising additives were the piperidene-based compounds (TEMPH/TEMPHS, TEMPMe, and OTEMPOS), with the tetramethylpiperidine functionality being the most compatible with DCP-initiated crosslinking (Figure 9). ΔG' observed for a LLDPE formulation containing 100 µmole/g of TEMPH was indistinguishable from that of the peroxide-only formulation. Similarly, LLDPE crosslinking at 136°C using 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane as a peroxide was unaffected by TEMPH, proving its compatibility with a *t*-butoxyl initiator system functioning at lower temperature.

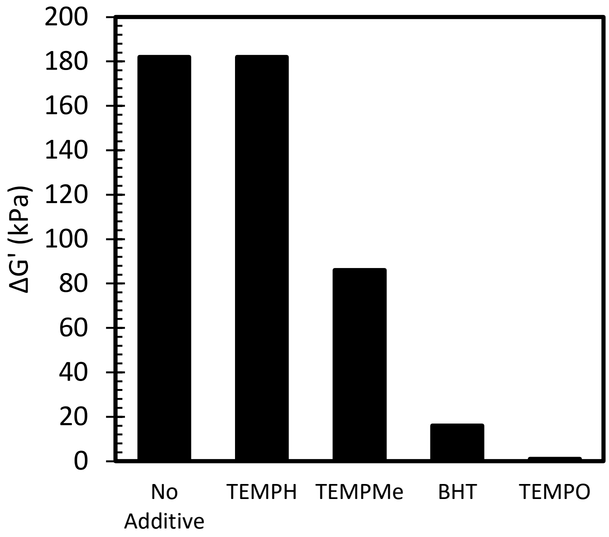
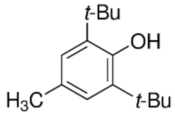
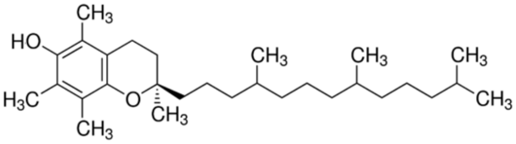
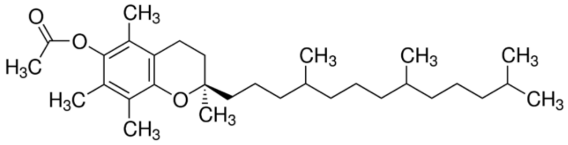
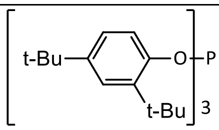
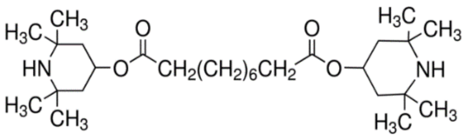
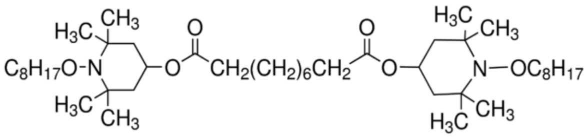
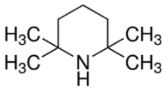
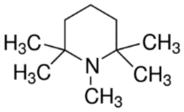
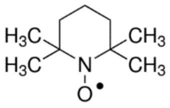
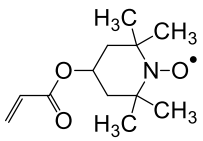


Figure 9. DCP-initiated LLDPE crosslinking yields ([DCP] = 18.5 µmole/g, [additive] = 100 µmole/g, 160ºC)

Table 3. Additive structures with additive effects on: a. modulus changes for peroxide-initiated melt-crosslinking of LLDPE, and b. conversion of VTEOS grafted to cyclohexane

Additive	Structure	ΔG' (kPa)[a]	VTEOS Conv.[b]	ΔG' (kPa)[c]	VTEOS Conv.[d]
3,5-di-tert-4-butylhydroxytoluene (BHT)		16	trace	27	trace
(±)-α-tocopherol (vitamin E)		trace	trace	trace	trace
DL-α-tocopherol acetate (vitamin E acetate)		33	0.59	66	0.71
tris(2,4-di-tert-butylphenyl)phosphite (Irgaphos 168)		17	N/A	64	N/A
bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (TEMPHS)		118	0.89	150	0.89
bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate (OTEMPOS)		61	0.16	122	0.52
2,2,6,6-tetramethylpiperidine (TEMPH)		184	0.85	185	0.89
1,2,2,6,6-pentamethylpiperidine (TEMPMe)		86	0.84	128	0.87
(2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO)		trace	trace	trace	trace
4-acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl (AOTEMPO)		trace	trace	trace	trace

a. Rheology at 160°C for 60 min with [DCP] = 18.5 µmole/g and [Additive] = 100 µmole/g in 5g LLDPE
b. Graft reaction at 160°C for 60 min with [DCP] = 3.7 µmole/g and [Additive] = 100 µmole/g in 5g cyclohexane
c. Rheology at 160°C for 60 min with [DCP] = 18.5 µmole/g and [Additive] = 37µmole/g in 5g LLDPE
d. Graft reaction at 160°C for 60 min with [DCP] = 3.7 µmole/g and [Additive] = 37 µmole/g in 5g cyclohexane

3.4.2 Effective Concentration of Latent AO's.

Many of the antioxidants considered are not latent at higher concentrations, but they still have a limit below which there is negligible effect on peroxide crosslinking. Table 4 is a summary of antioxidant effects on ΔG' at lower concentrations. All reactions in each column were performed in the presence of the same molar quantity of reactive additive at 160°C for 60 min (concentration of bi-functionalized additives halved for comparison).

Table 4. ΔG' for DCP crosslinking of LLDPE with additives

Additive	ΔG' (kPa)[a]	ΔG' (kPa)[b]
None	185	
TEMPO	135	86
AOTEMPO	194	124
OTEMPOS	185[c]	172[c]
TEMPHS	185[c]	184[c]
TEMPH	187	185
TEMPMe	185	170
Irgaphos168	116	80
Vitamn E acetate	133	98
Vitamin E	12	Trace
BHT	88	48

a. [DCP] = 18.5 µmole/g, [Additive] = 9.3 µmole/g.
b. [DCP] = 18.5 µmole/g, [Additive] = 18.5 µmole/g.
c. [DCP] = 18.5 µmole/g, [Additive] = ½ that of other additives in the same column.

At a molar concentration of 9.3 µmole/g all hindered amines and the alkoxyamine were found to have negligible impact on crosslinking. The cure containing AOTEMPO had noticeably larger gains in modulus than the DCP only cure suggesting the acrylate functionality reacted to make up for trapped alkyl radicals. The aryl phosphite significantly reduced ΔG', along with the acetate protected vitamin E.

3.4.3 Peroxide-initiated Grafting of VTEOS.

The radical-mediated addition of VTEOS to hydrocarbons involves the same radical intermediates as those that underlie peroxide crosslinking, but also includes monomer-derived alkyl radicals that support graft propagation (Scheme 2). The influence of additives on the DCP-initiated conversion of VTEOS was studied using a liquid hydrocarbon as opposed to LLDPE to improve the precision of analytical measurements. Heating a cyclohexane solution containing 3.7 µmole/g of DCP and 263 µmole/g of VTEOS to 160^{o}C for 60 min resulted in a monomer conversion of 90% (Figure 10). This corresponds to a peroxide yield of 32 mole/mole, meaning that 32 moles of VTEOS were consumed per mole of cumyloxy radicals derived from DCP thermolysis. This demonstrates the chain reaction character of the closed graft propagation sequence.

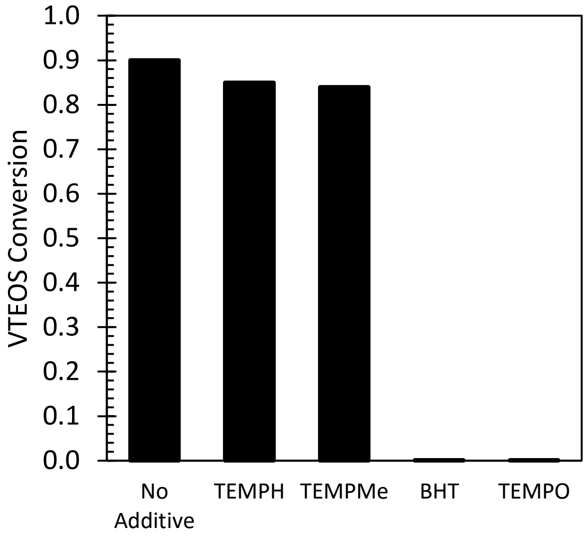


Figure 10. VTEOS conversion in cyclohexane ([DCP] = 3.7 µmole/g, [VTEOS] = 263 µmole/g, [Additive] = 100 µmole/g)

The response of VTEOS conversion to stabilizing additives was consistent with that observed for LLDPE crosslinking yields, with all but TEMPH and TEMPMe having a significant negative effect on reaction extent (**Table 3**). This result is also consistent with a polyolefin modification study conducted by Al-Malaika and coworkers, who were able to graft bis-(2,2,6,6-tetramethylpiperidin-4-yl) maleate to polypropylene at 180°C using DCP as a radical initiator, giving a derivative that was more photooxidatively stable than its parent material.[32] The question as to whether TEMPH is transformed during VTEOS modification, albeit without affecting the grafting process, was addressed by analysis of the reacted cyclohexane+VTEOS+DCP+TEMPH and cyclohexane+ DCP+TEMPH solutions. Gas chromatography measurements showed no significant TEMPH conversion, confirming that the radical populations and non-radical byproducts involved in polyolefin modifications do not activate TEMPH – it is indeed a latent stabilizing agent.

3.4.4 LLDPE oxidation.

While TEMPH is a well-documented antioxidant, for the sake of completeness, its potency for LLDPE stabilization was tested relative to other additives. In this study, the sebacate ester (TEMPHS) was used to avoid complications derived from the volatility of TEMPH. Figure 11 is a summary of the performance of TEMPHS, the alkoxyamine OTEMPOS and BHT in stabilizing LLDPE toward oxidation after 6 and 16 days exposure to 200kPa of O_2 at 110°C. Not surprisingly, the TEMPH-functionalized compound proved to be a capable oxidative stabilization agent.

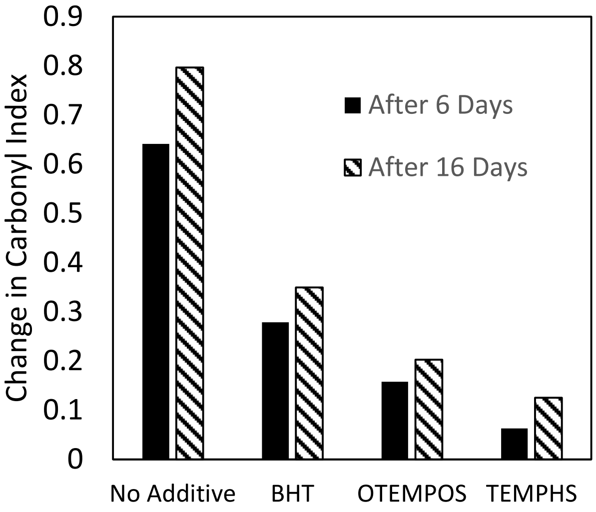


Figure 11. Oxidation of LLDPE films (110 °C, 400 kPa O_2, [Additive] = 100 µmole/g)

A study was also conducted with LLDPE containing 37 µmole/g of each additive and examined over the same time intervals. It was confirmed that OTEMPOS and TEMPHS are active antioxidants at lower concentrations as well.

3.5 Discussion.

The phenolic antioxidant BHT performed as expected in grafting and crosslinking reactions, echoing an earlier study done by Yamazaki & Seguchi detailing effects of BHT on a peroxide initiated cure in LDPE.[35] However, even at a high concentration of 100 µmol/g, it did not completely stop the formation of crosslinks, possibly owing to rapid alkyl radical termination (rate constants on the order of 10^8-10^9 $M^{-1}s^{-1}$).[36]

The other phenolic antioxidant tested was α-tocopherol, a potent sacrificial antioxidant that quenched all radicals produced even at a lower concentration of 18.5 µmole/g. This may be due to fast H-atom donation to peroxide derived radical intermediates (rate constant on the order of 10^9 $M^{-1}s^{-1}$).[37] Tocopherol has a well-established mechanism of AO activity, and it is capable of quenching more than twice its molar quantity in radicals generated in the system.[38] It has been shown to be more potent that BHT and it can be considered to have no detrimental effects to biological systems if leached from the polymer, giving it superior qualities.[39]

While it may be an excellent AO, vitamin E is not ideal for thermoset and grafting applications because it will quench radical activity. If the alcohol of tocopherol is protected with an acetate group, as is often done for the modification and synthesis of tocopherol, it has a significantly smaller effect on G’ gains and grafting yields, being found to allow 56% conversion of VTEOS at a concentration of 100 µmol/g. It may still be a reactive AO, however not nearly as effective as unprotected tocopherol. At lower concentrations (9.3 µmole/g), protected tocopherol still noticeably decreases net G' gains.

Aryl phosphites are extensively used as stabilizers for melt processing of polyolefins,[40] so it comes as no surprise that Irgaphos168 readily quenches peroxide cures. Aryl phosphites function as AOs by decomposing hydroperoxides, as well as trapping peroxy radicals. They are also capable of reacting with alkoxy radicals to form alkyl aryl phosphites and stabilized phenoxy radicals.[41] Irgaphos168 was not used in the grafting study because it did not adequately dissolve in cyclohexane to the required concentrations. However it can be expected to have a similar quenching effect, as it did on LLDPE crosslinking. A previous study corroborates this, as it provides evidence for phosphite consumption of cumyloxy radicals produced during heating of LDPE to 160°C.[42]

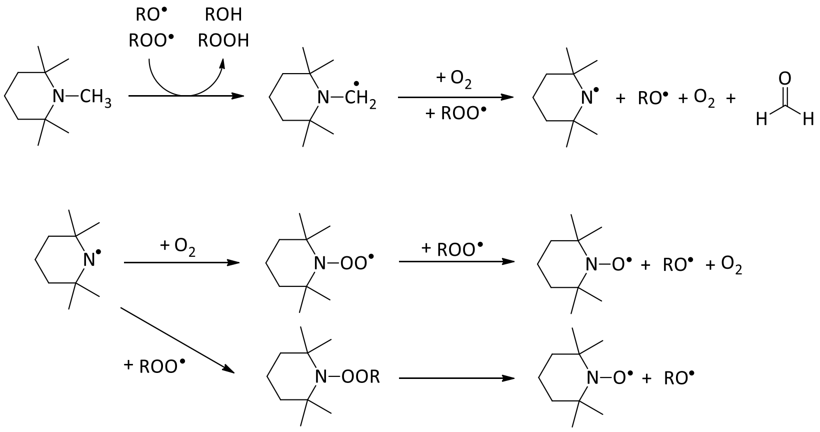
TEMPHS was found to perform well in a thermally oxidative environment, and not affect grafting or crosslinking over relatively short time intervals, indicating success in finding a latent AO. TEMPHS and its corresponding N-methylated hindered amine stabilizer (HAS) equivalent have similar stabilizing capacities in poly(propylene) tapes, as do their high molecular weight equivalents.[43,44] HAS of the type $R_2N\text{-}CH_3$ perform somewhat better than secondary hindered amines in pigmented coating applications, and alkoxyamine HAS were developed to provide stability where other HAS become deactivated.[45] In this study, TEMPHS is slightly better at preventing oxidation in the LLDPE films than its alkoxyamine equivalent. While this may be due to a mechanism of activation involving oxidation byproducts, it is not necessarily true that secondary amines will stabilize poly(ethylene) films better than their alkoxyamine counterparts.

It is generally accepted that hindered piperidines are oxidized to form nitroxy radicals, which are fast radical scavengers.[46,47] This study shows that the activation of TEMPH to nitroxyl does not proceed over the course of 60 minutes at 160°C or 136°C in the presence of cumyloxy radicals, *t*-butoxy radicals, methyl radicals, alkyl macroradicals, or vinyl monomer derived radicals. This is in contrast to results of a previous paper published by Yamazaki & Seguchi on the effect of hindered amine antioxidants on DCP-initiated cures in LDPE.[48] Electron spin resonance spectroscopy was used to observe radical concentrations in LDPE doped with DCP and hindered amine under vacuum when heated to 120°C, 155°C, and 180°C. A much higher concentration of DCP was used in the study, and nitroxyl concentrations were found to increase near the beginning of thermolysis. This was thought to be a sign of amine reacting with cumyloxy and methyl radicals, however our study discourages this possibility, at least under similar conditions and reactant concentrations.

In the present study, TEMPH survived radical activity without oxidizing to a nitroxyl species. While this does not rule out the possibility of H-atom donor reactivity of TEMPH in the presence of alkoxy radicals, it does put some constraints on the kinetics of such a reaction. In the case of oxidizing to form nitroxyls from R_2N-H and R_2N-CH_3, it is possible that oxidation proceeds by reaction with ground state molecular oxygen, ROO·, RC(O)OO·, ROOH, RC(O)OOH or O_3. As some confirmation of this theory, TEMPH was found to be an inefficient melt stabilizer for polypropylene. However, it was active in preventing photo-oxidation post-processing, which was hypothesized to be due to hydroperoxide oxidizing amine to form nitroxyl.[49] In order to gain a better understanding of why TEMPH was not activated under the conditions in our study, the mechanism of activation of hindered amines will be reviewed.

Gryn'ova and coworkers have published a paper in 2012 reviewing mechanisms of nitroxyl formation and regeneration.[50] In this paper, they used molecular orbital calculations to determine energy barriers to activation pathways. The most likely activation pathway for a secondary or tertiary hindered amine was determined to be H-atom abstraction by one of various polymeric radicals to form an aminyl (R_2N·) radical. Subsequently, the aminyl radical is oxidized to form a nitroxyl via the formation and decomposition of O-alkylperoxyamine or the addition of O_2 followed by radical coupling and decomposition (Scheme 26). In both this and a more recent paper, radical pathways involving H-atom abstraction by an alkyl and alkoxy radical were proposed, which was not observed in our study. [51]

Scheme 26. TEMPH aminyl radical activation, adapted from Gryn'ova and coworkers [50]



Evidence for the oxidation of TEMPMe ($R_2N\text{-}CH_3$), via a $R_2N\text{-}CH_2\cdot$ radical intermediate has been provided in this study by observing reactivity of TEMPMe with the cumyloxy radical. In other research, cumyloxy has been found to directly abstract an H-atom from TEMPMe, rather than forming a H-bonded amine/radical complex.[52] It was hypothesized that this would be followed by addition of oxygen and cleavage to yield $R_2N\text{-}CH_2O\cdot$, which undergoes β-scission to yield the aminyl radical. This mechanism is supported by Ingold and Pratt who published a paper detailing the same activation pathway.[53] TEMPMe nor TEMPH affected DCP decomposition over the period of the study. Surprisingly, TEMPMe did not significantly impact grafting yields when added in higher concentration. This occurrence might be explained by a difference in reactivity of the substrates. Geuskens & Kanda found that conversion of $R_2N\text{-}X$ proceeded with relative reactivity $R_2N\text{-}CH_3 < R_2N\text{-}H < R_2N\text{-}OR$.[54] This was in contrast with other findings, including those of our study for crosslinking LLDPE. Geuskens & Kanda noted that the reported trend may be strongly dependent on rate limiting steps governed by the nature of the hydrocarbon/polymer. Further investigation would be needed to determine if this was the case.

As a point of reference, significantly higher rate constants have been measured for TEMPMe α-C-H bond reactivity with cumyloxy radicals ($1.71 \times 10^8\ M^{-1}\ s^{-1}$) than for N-H bond H-atom abstraction from TEMPH ($3.13 \times 10^{6}\ M^{-1}\ s^{-1}$).[55] This difference in reactivity can be used to support the hypothesis that TEMPMe will donate an H-atnom and subsequently become oxidized to form a nitroxyl. However, the reactivity does not support an H-atom abstraction mechanism for TEMPH. Despite this difference in reactivity, the activation energy to form an aminyl radical from TEMPH ($\Delta G^{\ddagger}$ 14 kcal) is not much more than that of TEMPMe ($\Delta G^{\ddagger}$ 13 kcal).[53] Also, TEMPHS does oxidize over the period of several days to inhibit oxidative degradation of LLDPE. Thus, a major difference in time scales and oxidative conditions must play an important role in the mechanism of activation of secondary hindered amines. Peroxy radicals react much more slowly with amines than cumyloxy radicals.[55] Oxidation reactions start with auto-accelerated hydroperoxide formation, and the concentration of hydroperoxide proceeds to linearly increase.[56] Keeping this in mind, after an induction period, reaction with peroxyl radicals to form an aminyl radical becomes a much more likely pathway. It has also been suggested that instead of a direct abstraction, TEMPH might be more easily deprotonated by first undergoing single-electron oxidation.[57] In either case, it is very possible that the concentration of hydroperoxide has an effect on both the rate and mechanism of oxidation.

If reaction with hydroperoxides takes place, it might be possible to altogether avoid the formation of an aminyl radical through H-bonding with a hydroperoxide resulting in formation of a nitroxyl through a two-step mechanism (Scheme 27).[58]

Scheme 27. Simplified hydroperoxide 2 step reaction with secondary amine to produce nitroxyl

$$R_2N\text{-}H + ROOH \longrightarrow R_2N\text{-}O\text{-}R + H_2O$$

$$R_2N\text{-}O\text{-}R + ROOH \longrightarrow R_2N\text{-}O^{\bullet} + R\text{-}O^{\bullet} + R\text{-}OH$$

It was proposed that a complex of hindered amine with two or more hydroperoxide groups could be involved in the oxidation process, and with high concentrations of anime in the solid state, a stable bi-molecular reaction would be favored.[58] Impurities, including hindered amines, are expected to cluster in amorphous domains in the polymer where oxidation occurs quickly relative to crystalline areas.[59] In order to rationalize reactions with hydroperoxides it was mentioned that nitroxyls are better peroxide decomposers than hindered amines. It has been proposed that complexation between nitoxyls and hydroperoxides raises the local concentration of hydroperoxides in regions where alkyl radicals are generated, explaining – in part – the high stabilizing capacity.[60] This might lead to an auto catalyzing reaction for the activation of hindered amines in amorphous domains. However, even though oxidation is expected take place quickly in these domains, at higher temperatures and high partial pressures of oxygen (such as those used for our study), products are not as likely to amass in local amorphous domains.[61] Klemchuk and Gande have also mentioned that reactions between hindered piperidines and simple hydroperoxides would likely be too slow at lower temperatures to contribute in a significant way to hindered amine oxidation.[62]

Another possible mechanism detailed in literature involves reaction of an anime with an acylperoxy radical or peracid to form an association complex, followed by H-atom transfer.[60,63,64] It has been shown that addition of peracid to a polypropylene system will oxidize hindered amines in the absence of irradiation.[65] It may be more likely for a peracid to activate the secondary amine simply because the acidity of the conjugate acid of hindered amine increases from $R_2N\text{-}H < R_2N\text{-}CH_3 < R_2N\text{-}OR$, facilitating an acid-base interaction with secondary hindered amine.[45] This is analogous to the reactivity trend found for these compounds during peroxide-initiated modification.

There is no way to draw a conclusion on the mode of initiation at this point, however further investigation with respect to polymer structure and acidic activation may reveal multiple modes of activation in different conditions. Further work can be done by doping in different possible activators for crosslinking and grafting reactions to determine if nitroxyl is produced in significant quantities. The current state of HAS includes the use of several different types of HAS, each used preferentially in different applications, usually in concert with an ultra-violet (UV) absorber. New types of HAS have been created to maximize effectiveness of individual portions of a molecule containing functionality from HAS and UV-absorbers.[66,67] Instead of simply using multifunctional high molecular weight equivalents, several secondary and tertiary hindered amine compounds from a class of HAS containing vinyl functionality have been copolymerized with poly(propylene) and poly(ethylene) using metallocene catalysis.[68] The future of the polymer stabilization with HAS includes incorporation of these compounds directly into polymers and synergism with other stabilizers, however more work must be done to fully grasp activation requirements (compounds and kinetics) for nitroxyl formation.

3.6 Conclusions.

The effects of different stabilizers on peroxide mediated crosslinking and grafting reactions have been examined in the context of finding a latent antioxidant. Phenolic H-atom donors BHT and vitamin E, as well as aryl phosphite Irgaphose168 have been examined at a range of concentrations. Each of the stabilizers, including acetate protected vitamin E were found to be reactive H-atom donors at low concentrations.

Hindered amines and an alkoxyamine were added in high concentration to crosslinking reactions and to the grafting reaction involving closed sequence vinyltriethyoxysilane addition to cyclohexane at high temperature. TEMPH was selected as an ideal latent antioxidant because it does not undergo conversion or affect graft or crosslinking dynamics or yields at 160 °C or 136 °C in the presence of cumyloxy or *t*-butoxy radical intermediates over 60 min. TEMPMe, on the other hand, was found to be a relatively reactive H-atom donor. This was rationalized by a mechanism from literature involving oxidation of tertiary hindered amine to form a nitroxyl via H-atom abstraction from the N-CH_3.

Both the secondary hindered amine and the alkoxyamine were found to be effective at limiting polymer oxidation. A review of literature offered several possible mechanisms for the oxidation of secondary hindered amine to form a nitroxyl, including:

a) an aminyl radical intermediate derived from H-atom abstraction by peroxy or other polymer or peroxide derived radical,
b) H-atom bonding with hydroperoxides forming an alkoxyamine, or
c) reaction with acyl peroxy radical or peracid.

There still appears to be no way to conclude that a particular mechanism occurs based on the results to date. This study has shown that TEMPH activation does not readily occur under the melt-state crosslinking and grafting conditions experienced during reactive extrusion and processing, making it an ideal chemical additive for peroxide modifications of saturated polyolefins requiring long term stabilizers.

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Chapter 4: Conclusions and Future Work

4.1.1 H-atom Transfer Yields and Regioselectivity

The yield and regioselectivity of H-atom abstraction by cumyloxy radicals from IIR and PIB were quantified and examined in the context of crosslinking dynamics and VTEOS graft yields. Abstraction efficiencies and crosslinking extents of IIR materials with isoprene contents up to 5.8 mole% were measured in the presence of DCP. It was found that higher isoprene content increased the relative rate of crosslinking with respect to chain scission in IIR. Radical trapping experiments involving alkoxyamine formation showed that enhanced reactivity towards H-atom abstraction of high isoprene materials was due to allylic functionality provided by isoprene mers. It was implicated that some of the alkoxyamines formed were thermally unstable with respect to disproportionation at 160°C, yielding conjugated diene unsaturation in the polymer backbone. This is not conclusive, however, as DCP reaction with IIR model compound 2,2,4,8,8-pentamethyl-4-nonene was also observed to yield similar multiplets in a smaller quantity downfield in the ^{1}H NMR spectra.

Resonance stability of the allylic macroradical intermediates, formed from the reaction of IIR-5.8 with DCP, coupled with a preference for termination by combination, makes IIR materials of high isoprene content less prone to peroxide-initiated chain scission. However, despite heightened reactivity of IIR with respect to hydrogen atom donation, VTEOS addition yields in cyclohexane solution declined sharply with increases in unsaturation (addition of cyclohexene). It was hypothesized that this is due to allylic degradative chain transfer and low reactivity of allylic radicals towards VTEOS addition. This makes high isoprene grades of IIR less likely to undergo VTEOS addition than a saturated PIB homopolymer. While higher isoprene content hinders graft addition, higher reactivity facilitates acrylated radical (AOTEMPO) trapping of polymer macroradicals and subsequent oligomerization. This occurs in appreciable quantities in high isoprene IIR, giving a crosslinked network that is less prone to stress relaxation, whereas in PIB no network is formed.

4.1.2 In Search of a Latent Antioxidant

The effects of several antioxidants on peroxide mediated radical modifications were discussed. Thermoset applications require the addition of long term stabilizers before crosslinking reactions begin, thus additives were added in high concentrations to LLDPE cures initiated by cumyloxy and tert-butoxy radical intermediates. Changes in elastic storage modulus of the polymer were assessed in the presence of each antioxidant at concentrations above and below that of the peroxide initiator to give an approximation of the concentration where the additive starts to affect final crosslink density. Effects of each antioxidant on radical mediated grafting of VTEOS to cyclohexane at elevated temperatures under nitrogen were also assessed.

An aryl phosphite peroxide decomposer was shown to be effective at quenching radical intermediates generated during the cure, but it did not completely suppress crosslinking. Its effect on crosslinking was found to be similar to that of hindered hydroxyl phenol BHT. BHT was found to completely suppress grafting at similar concentrations. Vitamin E completely suppressed grafting and crosslinking reactions at much smaller concentrations, and it was found to be a more reactive H-atom donor than BHT. Acetate protected vitamin E interfered with crosslinking at lower concentrations, however it did not affect graft yields to the same degree, allowing for a 59% conversion even at the highest concentration.

Alkoxyamine and hindered amine were found to have a very small effect on crosslinking and grafting, while still suppressing oxidative degradation in LLDPE films for 16 days. Oxidation was inhibited to the same degree as LLDPE films containing BHT (industry standard). Thus, hindered amine 2,2,6,6-tetramethylpiperidine (TEMPH) was selected as an ideal latent antioxidant, as it had no significant effect on crosslinking and grafting reactions. This was explained by the requirement of oxidative activation to form a reactive nitroxyl radical. A survivability study was performed by analyzing reactant concentrations before and after reaction using gas chromatography and ^{1}H NMR. TEMPH was found to survive both grafting and crosslinking, while 1,2,2,6,6-pentamethylpiperidine (TEMPMe) did not. This was attributed to reactivity of the methyl substituted piperidine with respect to hydrogen atom donation, leading to nitroxyl formation.

Mechanisms of hindered piperidine activation were reviewed, and the most thoroughly investigated mode of initiation was found to involve H-atom abstraction, yielding an aminyl radical which could be oxidized to form the corresponding nitroxyl. This has been contested, however, so it does not preclude other mechanisms.

4.2 Future Work.

Further investigation into the possible disproportionation of 2,2,4,8,8-pentamethyl-4-nonene alkoxyamines to conjugated dienes would be prohibitive. It has been suggested, however, that alkoxyamines dissociate readily at these temperatures. Given this information, it would be imperative to assess the effect of disproportionation on the induction time of saturated polyolefins, as well as the effect of hindered amine regeneration on nitroxyl trapping efficiency.

It is theoretically possible to generate thermosets at much lower temperatures if the peroxide is activated by irradiation. This may allow for much less fragmentation of alkoxy radicals, resulting in higher macroradical yields. While photolysis of DCP may result in higher macroradical yields, it may also result in the generation of macroradicals by photolysis, which could impact cures in ways we will still need to understand. Further studies should examine the use of photolysis of peroxides to achieve equivalent thermoset properties to those achieved through thermolysis.

Protection of the hydroxyl group on tocopherol resulted in the substantial decrease in reactivity with respect to hydrogen atom donation. The acetate group was not readily removed by hydrolysis under conditions that could be found in the polymer in application. However, it is imaginable that one could protect the hydroxyl group using more reactive groups. A much more applicable protected AO could involve protection of hindered phenols with UV labile groups such as toluene. This group can be protected by a substitution reaction with bromophenol and at room temperature, without damage to the tocopherol molecule. Ideally the protecting group with render the AO latent to cure conditions, and it can also be removed by irradiation that naturally occurs post-processing. Although it may be impossible to create a truly latent AO from the simple hydroxyl group protection of tocopherol, it may be easier to demonstrate this concept using 2,4,6-trimethylphenol.

More work will have to be done on oxidation of 2,2,6,6-tetramethylpiperidine to produce reactive nitroxyl. Grafting and crosslinking reactions should also be run in the presence of polar media as well as unsaturated media with this hindered amine. In addition to this, activation should be attempted by compounding catalytic amounts of peracids and carboxylic acids into the polymer before processing to see if the amine responds to activation in the presence of acid catalysts. It is very likely that reactivity of the hindered piperidine will change dramatically depending on the type of polymer.

2,2,6,6-tetramethylpiperidine-1-oxyl compounds with added vinyl functionality (eg. AOTEMPO) are designed to undergo a secondary oligomerization phase during crosslinking to regain lost crosslink density and may confer oxidative stability to the polymer, but not without the required cycling to reproduce active nitroxyl. With this in mind, study of the ability of such oligomers to confer oxidative stability to the polymer could add insight to a cycling mechanism, as well as the effect of nitroxyl mobility on stabilization.