

**FUNCTIONALIZED-NITROXYLS FOR USE IN PEROXIDE-INITIATED
MODIFICATIONS OF POLYMERS**

by

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Abstract

Delayed-onset crosslinking of commodity polymers is accomplished by peroxide-initiated reactions of 4-acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl (AOTEMPO) under solvent-free conditions. Consistent with previous studies of polyethylene cure formulations, AOTEMPO provides predictable induction periods for ethylene-rich copolymers, such as poly(ethylene-co-propylene) (EPR) and poly(ethylene-co-vinyl acetate) (EVA), without compromising ultimate crosslink densities. However, cure yields for AOTEMPO formulations of 1,2-polybutadiene (vinyl-BR) and 1,4-butadiene (cis-BR) fell well below those of nitroxyl-free formulations, due to lost backbone C=C group oligomerization during the induction period. Quenching a radical in these butadiene-rich materials eliminates multiple crosslinks, creating a deficit that acrylate oligomerization cannot overcome. As a result, AOTEMPO can only delay the onset of polybutadiene cures at the expense of crosslink yield.

A new extension of AOTEMPO chemistry offers a means of crosslinking polymers that cleave when treated with peroxides alone. The severe degradation incurred by poly(ethylene oxide) (PEO) and polypropylene (PP) when heated with dicumyl peroxide (DCP) is arrested by nitroxyl trapping during the induction phase of the cure. Upon complete conversion of nitroxyl, oligomerization of pendant acrylate groups dominates scission of the polymer backbone, yielding the desired thermoset. Residual peroxide initiator beyond that required to convert macromonomer groups serves only to degrade the polymer network, necessitating the optimization of peroxide and AOTEMPO concentrations. Experiments conducted on PEO, PP, polyisobutylene (PIB), and poly(isobutylene-co-isoprene) (IIR) are discussed in terms of known principles of H-atom abstraction efficiency, acrylate oligomerization, and macroradical scission.

The importance of H-atom transfer to AOTEMPO formulation efficacy has motivated the study of a technique for measuring the yield of macroradicals produced by peroxide thermolysis in a polymer melt. DCP decomposition in polymer compounds containing 4-(1-naphthoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl (NTEMPO) generates polymer-bound alkoxyamines whose concentrations can be measured by fluorescence spectroscopy. Measurements of alkoxyamine yields are comparable to gas chromatography measurements of cumyl alcohol, which is an initiator byproduct of H-atom abstraction from the polymer.

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List of Abbreviations

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

μmol – micromoles

BDE – Bond Dissociation Energy

BHT – butylated hydroxytoluene

CDCl_3 – deuterated chloroform

cis-BR – 1,4-polybutadiene

DCP – dicumyl peroxide

EPDM – ethylene propylene diene

EPR – poly(ethylene-co-propylene)

EVA – poly (ethylene-co-vinyl acetate)

g – grams

G' – storage modulus

h – hours

Hz – Hertz

IIR – poly(isobutylene-co-isoprene)

IP – isoprene

kPa – kilopascals

LLDPE – Linear Low Density Polyethylene

min – minutes

mmol - millimoles

mol – moles

NTEMPO - 4-(1-naphthoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl

PE -Polyethylene

PIP – 1,4-polyisoprene

PP - Polypropylene

ROOR - peroxide

rpm – revolutions per minute

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

TEMPOH – 4-hydroxy TEMPO

vinyl-BR – 1,2-polybutadiene

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Chapter 1

Introduction

1.1 Fundamentals of Peroxide-Initiated Polymer Crosslinking

Commodity elastomers and thermoplastics are commonly transformed through chemical modification to generate value-added polymer intermediates as well as consumer products. A leading example is crosslinking to generate a covalent network of polymer chain segments (Figure 1). In the absence of crosslinking, polymers above their glass transition temperature are susceptible to stress relaxation and/or creep, since large-scale mobility allows chains to snake through their entanglements. As a covalent network is generated through crosslinking, chains are anchored by crosslink nodes, preventing bulk flow when subjected to an applied stress. The resulting thermoset materials have better heat distortion temperatures, and improved mechanical properties [1, 2].

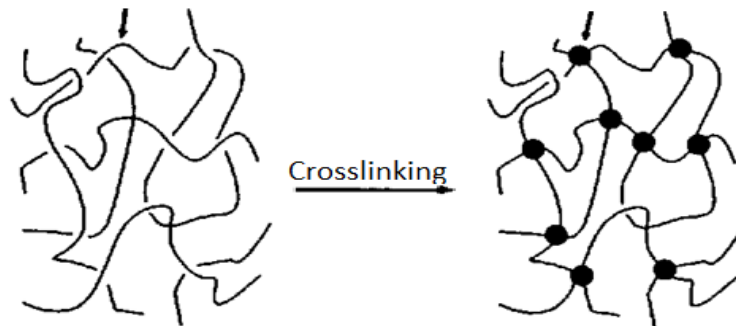


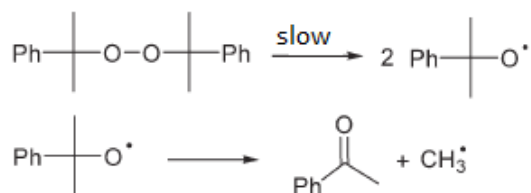
Figure 1: Covalent crosslinking of the amorphous phase within a polymeric material.

Crosslinking of commodity polymers is achieved using two main technologies, sulfur vulcanization and peroxide-initiated curing. Sulfur cures can provide exceptional dynamic mechanical properties, owing to the labile polysulfide bonds that comprise the covalent network.

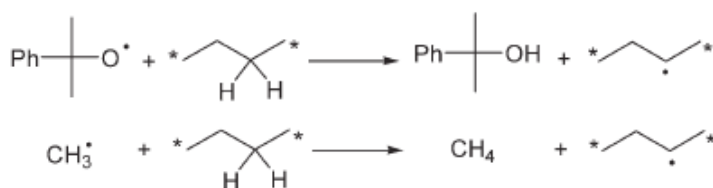
However, this chemistry only operates on polymers containing C=C unsaturation, and the resulting thermosets do not have the high temperature resistance provided by carbon-carbon crosslinks. Moreover, sulfur cure formulations require inorganic and organic additives to accelerate the cure and improve crosslinking yields [3].

Peroxide-initiated crosslinking forms C-C bonds that are much stronger than the bonds generated in sulfur cures, making their thermosets more useful for applications where stability to constant loads is paramount [4]. Furthermore, peroxide formulations function effectively on a wide range of saturated polymers and unsaturated materials [5, 6]. The mechanism for peroxide initiated crosslinking is relatively simple for ethylene-rich polymers, as illustrated in Scheme 1 for high density polyethylene. This process is stoichiometric, in that one initiator molecule gives rise to no more than one covalent crosslink, and cure yields generally scale linearly with peroxide concentration. As described below, inefficiencies exist due to limitations on H-atom abstraction from the polymer by initiator-derived radicals, as well as the potential for macroradicals to terminate by disproportionation as opposed to combination.

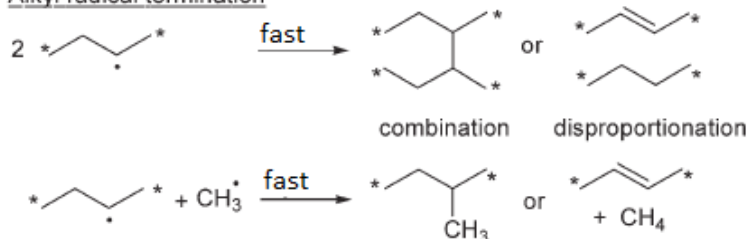
Peroxide thermolysis



Hydrogen atom abstraction



Alkyl radical termination



Scheme 1: Simplified mechanism for the crosslinking of polyethylene

The overall dynamics of peroxide cures are dictated by the rate of initiator thermolysis to give two alkoxy radical intermediates. This decomposition is a first-order kinetic process, meaning that the rate of radical generation in a curing compound is highest in the initial stages of the reaction, and falls as peroxide conversion increases. H-atom abstraction by cumyloxyl or the methyl radicals derived from cumyloxyl fragmentation gives the requisite alkyl macroradicals, whose combination gives the desired crosslinks. This radical-radical termination process has a very low activation energy, proceeding at the diffusion limit of reaction velocities in low viscosity solutions, with bimolecular rate constants on the order of 10^8 - $10^9 \text{M}^{-1}\text{s}^{-1}$ [7, 8]. The slow process of generating radicals, coupled with their rapid termination, results in radical lifetimes on

the order of milliseconds, and a low steady-state radical concentration at every moment during the cure process.

Figure 2 illustrates the dynamics of a DCP-initiated cure of LLDPE alongside the initiator conversion profile. The extent of polymer crosslinking at a given time is inferred from the dynamic storage modulus (G') of the compound, measured at a fixed temperature, frequency, and shear amplitude [9]. This standard method exploits the sensitivity of G' to restrictions in polymer chain segment mobility brought on by covalent network formation [10]. Note that the development of the polymer network mirrors the conversion of DCP, since initiator breakdown is the rate determining step of carbon-carbon crosslink production.

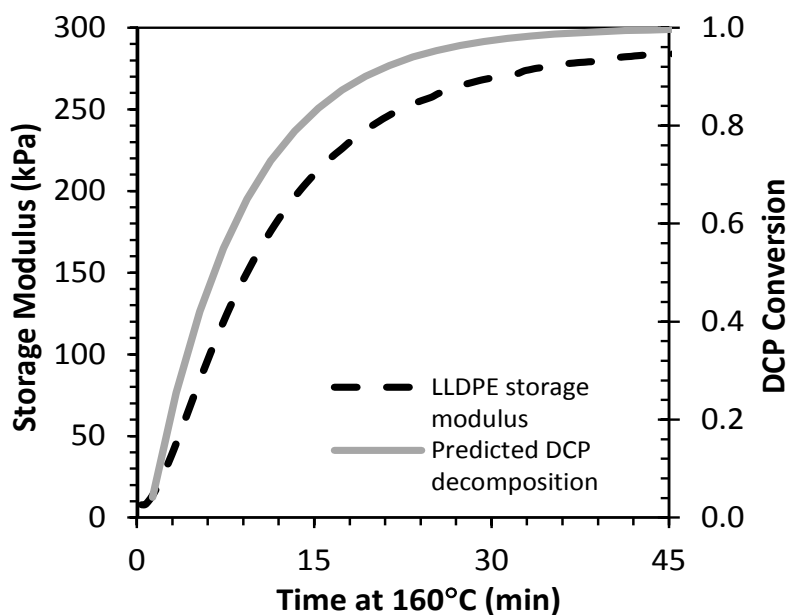
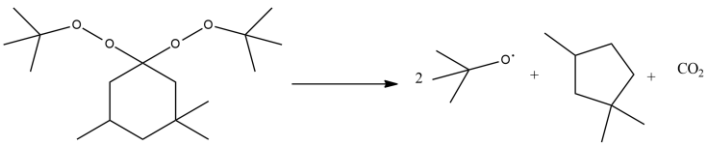
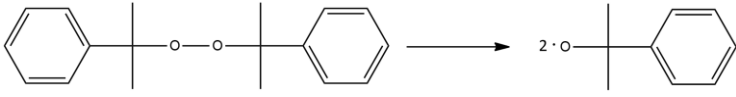


Figure 2: Dynamics of LLDPE crosslinking and DCP thermolysis [11]

A wide variety of peroxides are employed industrially, each yielding different radical intermediates at different rates. Table 1 summarizes the half-lives of two organic peroxides of

interest to this work, (1,1-bis(t-butylperoxy)-2,5,5-trimethylcyclohexane) (L-231) with a half-life of 3.5mins at 140°C, and DCP with a half-life of 45.1 mins at 140°C. These differences in peroxide reactivity provide chemists and engineers with the means to control the rate of a polymer modification at a given temperature. For example, where chain scission is problematic, a more reactive peroxide such as L-231 will decompose relatively quickly at the lower temperatures that discourage macroradical fragmentation [12] [13].

Table 1: Peroxides and decomposition products

Peroxide and Decomposition Products	Temperature (°C)	t _{1/2} (min)
1,1-bis(t-butylperoxy)-3,5,5-trimethylcyclohexane (L231)	140	3.85
	160	0.71
	180	0.16
	Dicumyl Peroxide	140
	160	5.67
	180	0.86

As noted above, inefficiencies in peroxide curing can be incurred during the H-atom transfer step of the process. Polymers that are poor H-atom donors provide lower macroradical yields, generating a proportionally lower crosslink density. The quality of a H-atom donor can often be gauged by quantifying initiator byproducts, since H-atom abstraction by cumyloxy yields cumyl alcohol in competition with β -scission, which gives acetophenone and a methyl radical (Scheme 1) [14, 15]. Polymers generating high abstraction efficiency (AE) values, defined by Equation 1, are relatively good H-atom donors, and are expected to provide high macroradical yields. Garret

et al. used this method to quantify the H-atom abstraction efficiency of DCP acting on a range of commercial polymers at temperatures relevant to industrial processing operations, and found that the reactivity of a polymer towards H-atom abstraction is entropy controlled if substituents on the polymer backbone present a steric barrier to H-atom transfer [16].

$$AE = \frac{\text{Ph}-\text{C}(\text{OH})-\text{H}}{\text{Ph}-\text{C}(\text{OH})-\text{H} + \text{Ph}-\text{C}(=\text{O})-\text{H}} \quad (1)$$

The regioselectivity of H-atom abstraction from unhindered C-H bonds is determined by the C-H bond dissociation energy (BDE) [17] with polyethylene(PE) providing an AE of 56% at 160°C, and poly(ethylene oxide) (PEO) giving an AE value of 69%, whose increased reactivity is presumably due to electron donating effects of the heteroatom [16]. Where significant steric hindrance is encountered, such as H-atom abstraction from groups adjacent to tertiary and quaternary carbons, entropic effects can be dominant. For example, despite the low BDE of tertiary C-H bonds, polypropylene provides an overall abstraction efficiency of just 37%, as a result of the steric hindrance imposed by the methyl substituent on the reactivity of secondary C-H bonds [18].

For macroradicals to generate a crosslink in a PE cure, termination must occur by combination as opposed to disproportionation (Scheme 1). The latter has no direct effect on polymer molecular weight, although it yields olefinic functionality that may be more reactive than secondary alkyl groups. In the case of polyethylene cures, as many as 30% of macroradicals can terminate through disproportionation [19], which presents a proportional loss in potential crosslink density.

Commercial examples of diene-containing polymers are widespread, and their allylic C-H bonds support a wide range of both ionic and radical chemistry. In the present context, unsaturated polymers are relatively good H-atom donors, due to resonance stabilization of allyl radicals [20,

21]. Furthermore, allyl radicals terminate exclusively by combination, so they are not just produced in high yield, they invariably produce the desired crosslink product. The potential also exists for unsaturated polymers to crosslink through C=C oligomerization, with the terminal vinyl functionality in 1,2-polybutadiene(vinyl-BR) reportedly providing multiple crosslinks per initiator molecule [22]. Steric inhibition is significant in more highly substituted systems such as 1,4-polybutadiene(cis-BR), for which lower crosslink densities are observed compared to its 1,2-analogue [23, 21]. As such, butadiene-rich polymers and polyisoprene (PIP) are crosslinked rapidly and to a high extent by peroxide formulations, and methods for regulating their cure dynamics and yields is of significant practical importance.

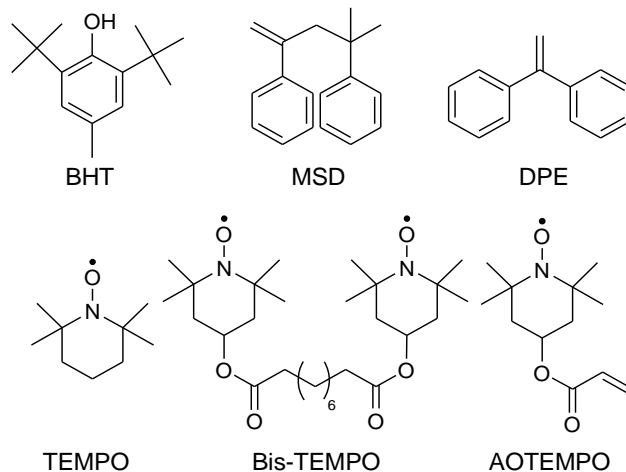
1.2 Scorch

Crosslinking reactions are typically performed industrially as non-isothermal batch reactions, where premixed polymer + curative compounds are formed into the desired shape and cured to give the desired thermoset. Rapid crosslinking maximizes process throughput, but can also render the compound thermoset before it assumes the shape of the mold cavity, a phenomenon known as scorch. For peroxide formulations whose cure kinetics are controlled by the first-order kinetics of initiator breakdown, scorch prevention requires a method of quenching radical concentrations in the initial stages of the process. This is usually accomplished by mixing antioxidants, known as scorch protectants, into peroxide formulations prior to the curing process.

1.2.1 Scorch Protectants

An ideal scorch protectant quenches all radicals for a finite and predictable time, while having no effect on the ultimate extent of cure. There are a number of additives in common use (Scheme 2), including 2,6-di-*t*-butyl-4-methylphenol (BHT), which is a chain breaking donor antioxidant that functions through H-atom donation to alkyl radicals, thereby quenching macroradical intermediates while generating benign aryloxy radical byproducts. This class of scorch protectant can suppress the rate of LLDPE crosslinking significantly, but at the expense of the cure extent

provided by a peroxide-only formulation [11]. An additional issue regarding common scorch protectants is the generation of volatile organic compounds in the form of radical quenching byproducts within the thermoset product.



Scheme 2: Structures of some common scorch protectants, as well as nitroxyls previously examined as scorch protectants

Nitroxyls such as TEMPO have several advantages over scorch protectants such as BHT. To achieve delayed-onset crosslinking, radical trapping must be faster than macroradical combination, and nitroxyls combine with alkyl radicals near the diffusion limit of reaction velocities [24, 25, 26]. Furthermore, they only trap carbon-centered radicals, as opposed to the alkoxy radicals produced by most peroxide initiators. Therefore, they do not interfere with macroradical formation, but selectively trap alkyl macroradicals and methyl radicals derived from peroxide initiation. Indeed, TEMPO has been shown to provide an induction period in DCP-initiated cures of LLDPE, during which crosslinking is completely suppressed at a variety of reaction temperatures [11, 27].

The induction time for LLDPE crosslinking, defined as the period between the heating of the compound and the onset of crosslinking, follows a simple relationship between peroxide and

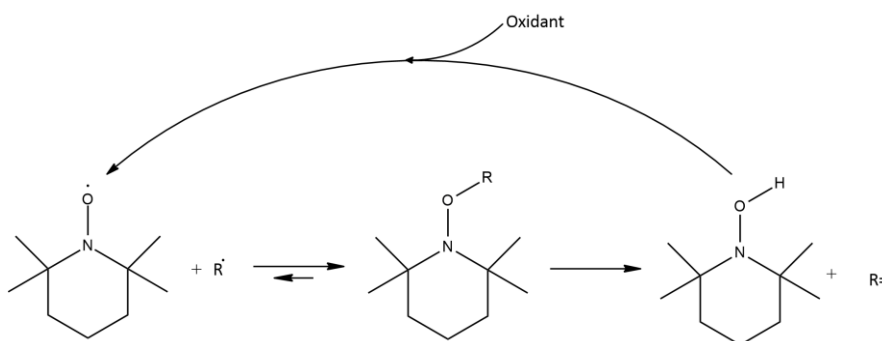
nitroxyl loading, described by Equation 2, where k_d is the first-order rate constant for DCP homolysis at the reaction temperature.

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

This expression contains the molar trapping ratio, defined in Equation 3, defined as the moles of nitroxyl divided by the moles of initiator-derived radicals, assuming that the peroxide yields two alkoxy radicals per molecule of initiator.

$$\text{Trapping Ratio} = \frac{[\text{nitroxyl}]}{2[\text{ROOR}]_o} \quad (3)$$

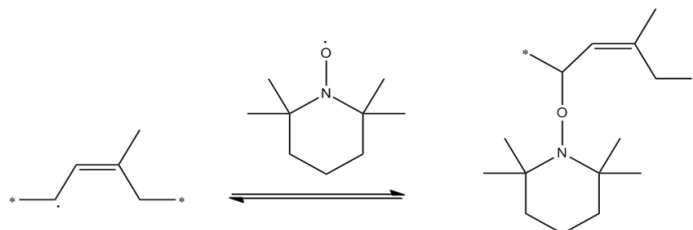
Using equations 2 and 3, formulations can be designed to provide the desired induction time, t_{ind} , for a given peroxide decomposition rate. This equation is derived on the assumption that nitroxyl trapping is rapid relative to other radical reactions, and that the resulting alkoxyamine is stable at the cure temperature. This condition holds for primary and secondary alkoxyamines [28], but must be validated in allylic systems as well as tertiary alkyl compounds such as those generated from polymers such as polypropylene. Scheme 3 illustrates two mechanisms of alkoxyamine breakdown that can affect the performance of nitroxyl-based scorch protectants.



Scheme 3: Radical trapping reactions of TEMPO

Alkoxyamine homolysis is fundamental to controlled radical polymerizations, as it generates nitroxyl and carbon-centered radicals in a dynamic equilibrium (Scheme 4). In the context of polymer crosslinking, this can support a small steady-state macroradical population that could

potentially terminate by combination to yield a small degree of crosslinking. Scott et al. showed that allylic alkoxyamines are susceptible to thermolysis at 160°C (Scheme 4), resulting in reversible trapping of allylic macroradicals by TEMPO [28]. While the allylic alkoxyamines derived from polyisoprene (PIP) are sufficiently stable to provide delayed-action performance, they cannot generate a period of absolute induction in DCP-initiated cures [11].



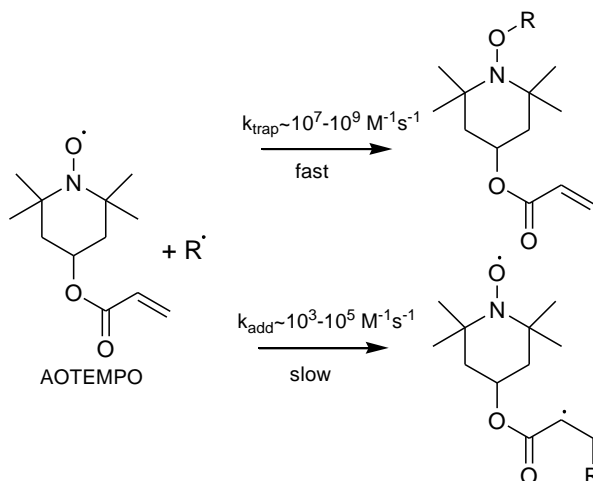
Scheme 4: Reversibility of allyl radical trapping by TEMPO

A second means of alkoxyamine decomposition is disproportionation to hydroxylamine and olefin. This reaction may occur through radical or non-radical pathways, but in any case, the resulting hydroxylamine is readily oxidized to TEMPO, which may trap another initiator-derived radical intermediate [29]. This nitroxyl regeneration sequence has been implicated in the extension of induction periods for macromonomer cures [30]. For instance, alkoxyamines formed through trapping of tertiary radicals generated during the thermal oxidation of polypropylene can regenerate the original nitroxyl species [31].

While TEMPO delays the onset of LLDPE cures, there is a proportional loss to crosslink density relative to a peroxide-only formulation. This is a result of the stoichiometric nature this system, where crosslinks are formed exclusively through macroradical combination. When macroradicals are trapped to form alkoxyamines, the yield of carbon-carbon cross-links declines proportionally. Functionalized derivatives of TEMPO, containing at least one polymerizable C=C group can delay polymer crosslinking without adversely affecting cure yields [32]. Hyslop and Parent

prepared nitroxyls bearing a range of acrylic functionality and tested their ability to provide scorch protection to DCP-initiated cures of LLDPE [27]. Irrespective of the structure of the acrylate group, these functional nitroxyls provided a predictable induction period, and a measure of post-induction cure recovery. However, only the most reactive acrylate functional group yielded the crosslink density of a DCP-only formulation, making AOTEMPO the primary target of this investigation. Note that AOTEMPO-mediated crosslinking also renders volatile methyl alkoxyamines polymer-bound into the thermoset, unlike standard antioxidants commonly used in scorch protectant applications [27, 33].

The efficacy of AOTEMPO is based on differences in kinetic reactivity of nitroxyls and the C=C functionality to carbon-centered radicals. As seen in Scheme 5, rate constants for nitroxyl combination with alkyl macroradicals are orders of magnitude higher than those for radical addition to the C=C in acrylates [25, 12]. AOTEMPO therefore traps macroradicals by combination, rather than radical addition, allowing for an induction period quenching all radical activity while transforming the polymer into a macromonomer containing pendant acrylate functionality.



Scheme 5: Radical Trapping by AOTEMPO

Figure 3 illustrates the dynamics of LLDPE cures initiated by DCP alone, and in combination with TEMPO and AOTEMPO, presented in a semi-log format to highlight the early stages of the reaction. A mechanism that accounts for the three phases of an AOTEMPO cure is provided in Scheme 6. In phase 1, an induction period is observed during which crosslinking is completely suppressed, as the nitroxyl concentration is greater than the concentration of alkyl radicals generated by H-atom abstraction. Under these conditions, trapping of methyl and polymer macroradicals by AOTEMPO is kinetically preferred to other combination reactions. Given that primary and secondary alkoxyamines are stable at the cure conditions, nitroxyl concentrations decrease as the reaction proceeds to the point where competing radical reactions become kinetically competitive. This point marks the end of the induction period of phase 1, and is marked by the induction time, t_{ind} .

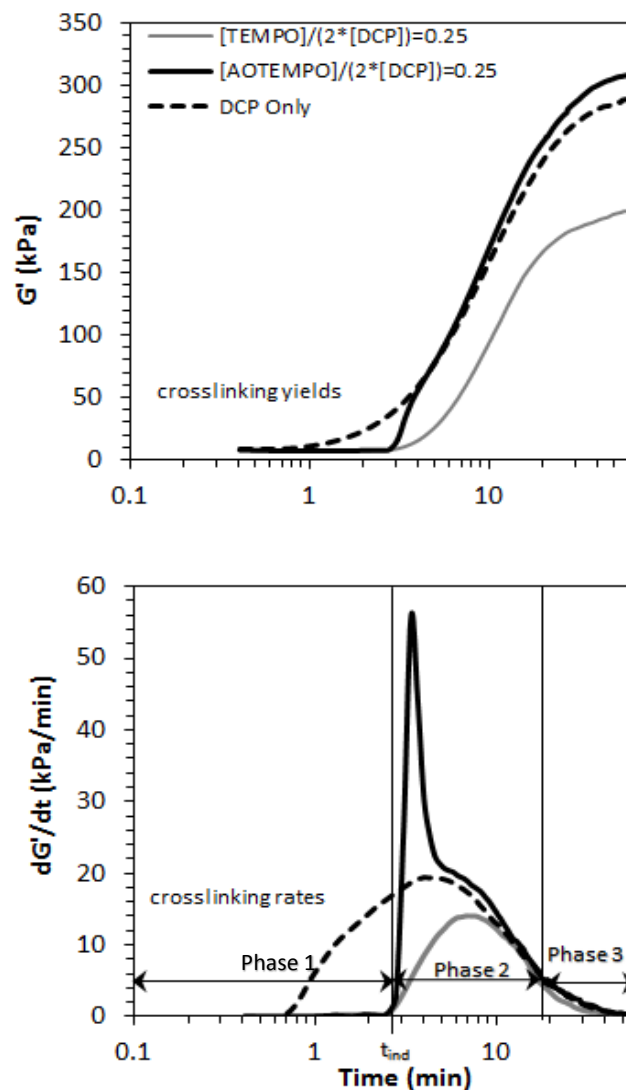
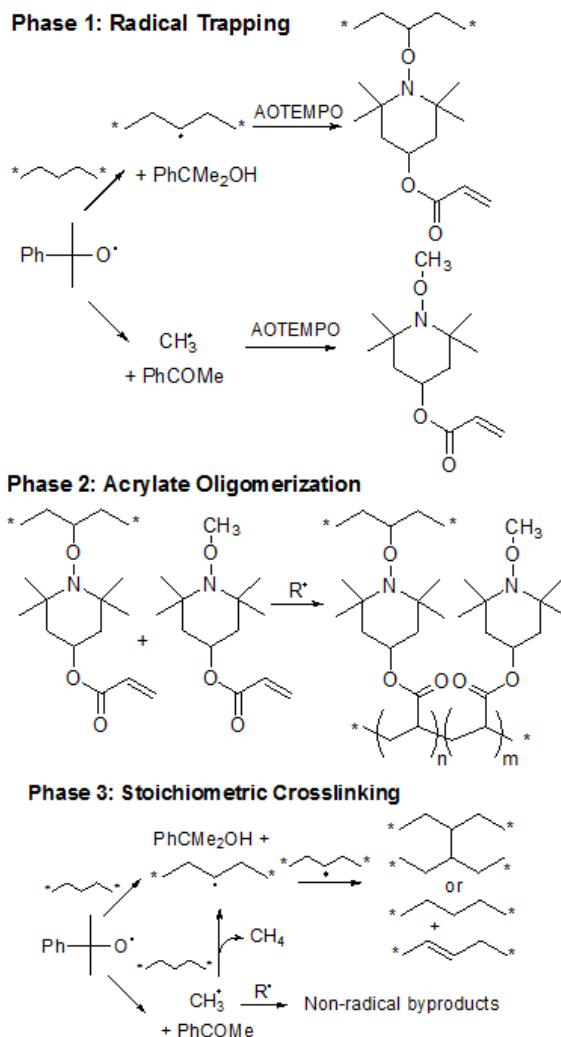


Figure 3: Crosslinking Yields and Rates of nitroxyl-mediated DCP crosslinking of LLDPE. [DCP]=18.5 μ mol/g; [TEMPO]=9.2 μ mol/g; [AOTEMPO]=9.2 μ mol/g

The beginning of phase 2 is marked by a rapid increase in storage modulus, often much greater than that produced by peroxide alone. This heightened cure reactivity is a result of oligomerization of polymer-bound acrylate groups, which proceeds through a kinetic chain reaction where multiple crosslinks are formed from a single initiating species. The complete conversion of this acrylate functionality marks the transition from phase 2 into phase 3, during

which crosslinking proceeds through standard peroxide-only dynamics. When applied to LLDPE, this three stage cure process is effective from 140°C to 180°C [11], and does not compromise crosslink densities when used to trapping ratios as high as 0.5 [33]. Moreover, the rheological and mechanical properties of LLDPE thermosets prepared from AOTEMPO did not differ from peroxide-only formulations [11].



Scheme 6: Idealized AOTEMPO-mediated crosslinking reaction mechanism

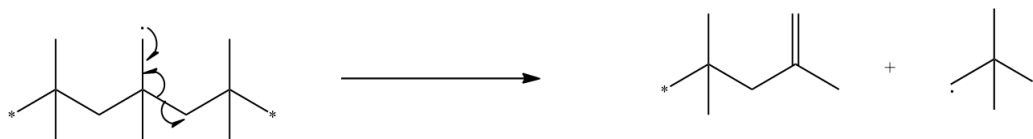
It must be noted that success in controlling the dynamics of LLDPE crosslinking may not translate directly to polymers with different architectures, H-atom abstraction efficiencies, and

molecular structures. The nature of the macroradicals generated by peroxide to be trapped by the nitroxyl is particularly important, as this has a direct effect on the stability of alkoxyamines formed through macroradical trapping [24]. For instance, the half-life of tertiary alkoxyamine decompositions is orders of magnitude shorter than their corresponding secondary alkoxyamines [24, 26]. Research into the efficacy of polymers containing different functionality, including C=C unsaturation, acetate, nitrile and ether functionality is required to broaden our understanding of the scope of AOTEMPO chemistry.

1.3 Scission-Prone Polymers

1.3.1 Isobutylene-Rich Elastomers

While peroxide-initiated crosslinking is ubiquitous in terms of its application to both saturated and unsaturated polymer systems, there are instances in which peroxides will cause degradation of the polymer backbone through chain scission. Consider the case of poly(isobutylene) (PIB). It is well documented that PIB will undergo chain scission in the presence of peroxides [34]. H-atom abstraction in PIB is limited to the methyl position forming primary radicals owing to steric hindrance imposed on secondary sites by quaternary carbons [16]. Although termination by combination occurs, these unstable primary radicals also undergo β -scission, as illustrated in Scheme 7.



Scheme 7: β -Scission of primary alkyl radicals in PIB

This chain scission leads to a reduction in polymer molecular weight. The dynamics of this degradation can be monitored in the same fashion as crosslinking reactions, however in the case of degradation a decrease in the storage modulus is observed, as seen in Figure 4.

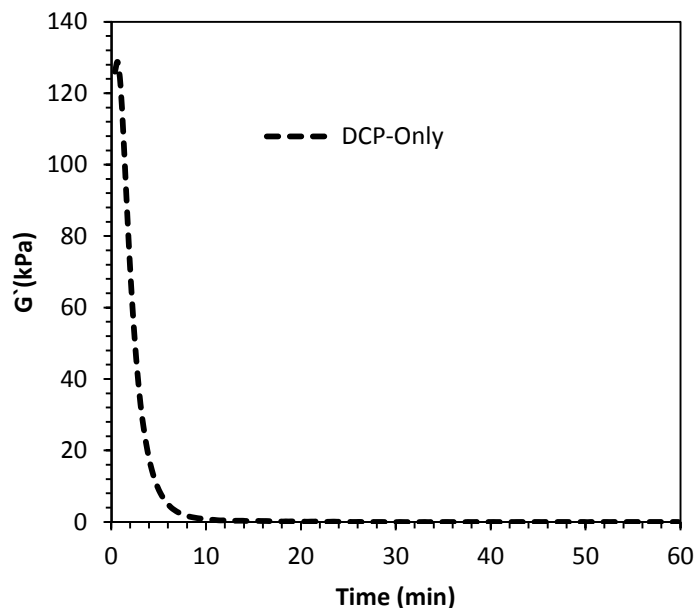
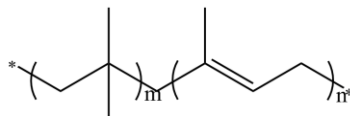


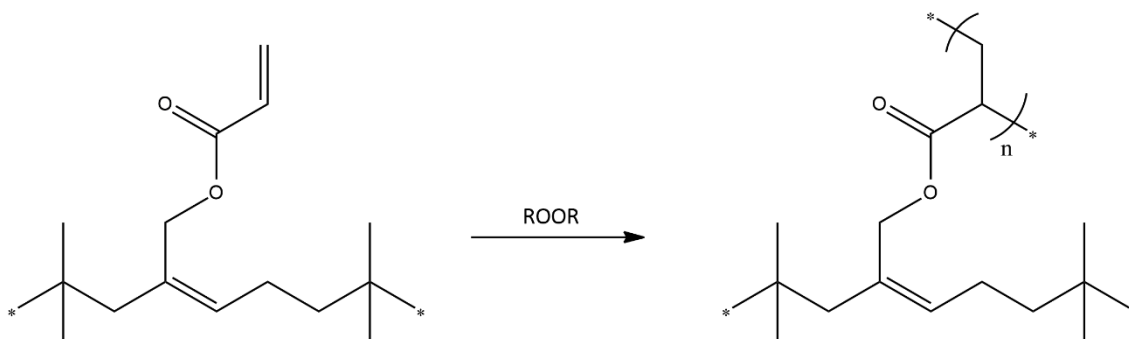
Figure 4: Dynamics of PIB degradation by DCP-initiated chain scission at 160°C, 1Hz, and 3°arc in the presence of varying AOTEMPO concentrations; [DCP]=37 μmol/g.

PIB can be made more amenable to chemical modification through copolymerization with 1-2mol% of isoprene (IP). The unsaturation in this random copolymer poly(isobutylene-co-isoprene), IIR, or butyl rubber, seen in Scheme 8 provides a site for sulfur crosslinking. The allylic sites provided by this C=C unsaturation also makes butyl rubber more reactive towards H-atom abstraction, and subsequently peroxide-cures. However, steric hindrance prevents significant oligomerization of the C=C of the isoprene mer, limiting the crosslinking efficiency of peroxides. The 1-2mol% of isoprene is insufficient to counteract degradation, with a minimum of 3mol% IP, what is known as high IP butyl rubber, required to generate a material that does not degrade in the presence of peroxides.



Scheme 8: poly(isobutylene-co-isoprene), otherwise known as butyl rubber or IIR

Further post-reactor modification of the polymer backbone of IIR to form terpolymers with pendant polymerizable functionality, known as macromonomers, results in materials with significantly improved peroxide cure performance. For instance, consider the acrylate-grafted butyl rubber macromonomer prepared by Xiao et al. (Scheme 9) [35]. In this two-step approach, polymer backbone radical intermediates are not required to generate crosslinks, instead relying upon free radical oligomerization of pendant C=C functionality to produce a covalent network.



Scheme 9: Peroxide-initiated crosslinking of acrylate functionalized butyl rubber

The peroxide yield of radical addition processes can be defined as the number of polymerizable groups consumed for each radical generated by the initiator. Acrylate-functionalized butyl rubber has been shown to achieve peroxide yields as high as 25 at 170°C. In contrast to stoichiometric peroxide cures, in which the crosslink density is limited by initiator loading, the high peroxide yield of a macromonomer cure provides a distinct advantage. This is offset somewhat by the need for post-reactor modification of butyl rubber prior to peroxide treatment, and the propensity for these macromonomers to suffer from scorch problems.

1.3.2 Poly(ethylene oxide) (PEO)

As a polyether with unhindered α -hydrogens, the $-\text{CH}_2-$ groups in PEO have very low C-H BDEs making it a good H-atom donating polymer. This makes PEO reactive towards peroxide modifications, with abstraction efficiencies of 69% for DCP acting at 160°C [18]. Macroradical fragmentation dominates other reaction pathways, and it is well documented that PEO suffers from severe molecular weight losses when heated with peroxide initiators [36, 37, 38]. There are other avenues to generate crosslinked networks from PEO however, including radiation, end group modification, and coagent-assisted peroxide crosslinking.

1.3.2.1 Radiation-induced crosslinking of PEO

γ -Induced radiation crosslinking of aqueous PEO solutions at room temperature was first developed in 1966 by Union Carbide [39]. Radiation generates hydroxy radicals from the aqueous medium that randomly abstract hydrogen from the polymer backbone to generate carbon-centered macroradicals, which can then combine to yield a covalent crosslink [40]. This method of radiation-induced crosslinking is particularly convenient for the crosslinking of PEO for medical applications such as surgical wound dressings as it allows for crosslinking and sterilization in a single step [41].

However, due to competition with chain scission, this method of crosslinking is limited to aqueous solutions [42], with the solid polymer in the presence of oxygen being much more prone to degradation than crosslinking [43]. Radiation of the solid polymer is in fact used to reduce the high molecular weight grades of PEO [44].

Sloop et al. studied the UV-initiated crosslinking of PEO, both with and without a photoinitiator [45]. It was found that the initial storage modulus of PEO decreased with short irradiation times, indicating that there was degradation of the sample. However, with very long irradiation times, an

increase in the storage modulus was observed from the uncrosslinked polymer. An optimum irradiation time to achieve maximum crosslink density in the sample was recognized, but crosslinking was determined to be non-homogenous [46].

Doytcheva et al. determined that, although commercial PEO does undergo crosslinking through UV irradiation, purified PEO does not, indicating both that PEO requires a photoinitiator for UV crosslinking, and that the additives present in commercial grades of PEO have some photoinitiating capabilities [46]. The susceptibility of PEO to UV-initiated crosslinking may also require UV-stabilizing agents, such as Hindered Amine Light Stabilizers (HALS) to prevent degradation over the lifetime of the product.

1.3.2.2 Chemical Crosslinking of PEO

Gnanou et al. crosslinked hydroxyl-terminated PEO, where the PEO parent material was modified to carry hydroxyl groups at both chain ends, by step growth polymerization involving multifunctional reagents such as pluriisocyanates [47]. The networks formed were homogeneous, with few structural defects, however long reaction times were required. Elevated reaction temperatures provided reduced reaction times at the expense of structural defects in the network [47]. The mechanical properties of these networks were far inferior to predicted values [48].

While chain scission is the predominant pathway for PEO treated with peroxide concentrations below 1wt%, initiator loadings above 3wt% can lead to gelation, as macroradical lifetimes decline to point where chain scission is suppressed relative to macroradical combination [49, 50, 51]. Indeed, Wu et al. found that at low DCP concentrations (0.5wt%) at 160°C, the molecular weight decreased from 132kg/mol to 38kg/mol, while doubling the peroxide concentration at the same reaction conditions led to a small amount of insoluble gel [37].

The performance of peroxide initiated crosslinking of PEO can be improved dramatically through the use of coagents such as N,N'-m-phenylenedimaleimide [38] or through the grafting of alkyne monomers onto PEO [37]. For instance, incorporating 0.51mmol/g of ethyl propiolate increased the insoluble gel content of PEO to 37% in a 1wt% DCP cure at 160°C compared to the 2% gel generated in the DCP-only formulation [37].

1.3.3 Polypropylene

As observed for PIB and PEO, polypropylene (PP) mainly undergoes degradation through chain scission in the presence of peroxides, [52, 13, 53] with branching and crosslinking occurring simultaneously. Degradation can be attributed to β -scission of tertiary radicals, while crosslinking and branching is achieved through macroradical combination [54, 55]. However, H-atom abstraction has been found to occur predominately at the tertiary position (64%) owing to steric hindrance imposed on the secondary positions [16]. Additionally, the high melting point of PP (165°C) requires elevated reaction temperatures, further favouring chain scission over crosslinking [56].

Peroxide-initiated crosslinking of PP can be improved through the use of polyfunctional monomers as coagents [57, 58, 59, 60]. For instance, at 170°C, a cure of PP initiated by 2wt% tertbutyl perbenzoate along with 1 wt% p-benzoquinone generated a gel content of 84% [57]. The kinetic reactivity and crosslinking efficiency of a coagent-peroxide pair can also be used to generate different branching structures in the polymer, which affects the material's rheological properties [61].

An alternative approach to generating crosslinked networks in PP is through grafting of functional groups such as vinyltrimethoxysilane (VTMS), which can then be moisture cured to generate a crosslinked network. However, to prepare PP derivatives that moisture cure effectively

requires the use of additional strategies such as triallyl trimellitate(TATM)-assisted thiol-ene addition to overcome extensive degradation that VTMS-modified PP is not capable of overcoming alone [62, 63]. The process of grafting and then moisture curing requires multiple processing steps, and therefore poses significant economic barriers towards commercial implementation.

1.4 Determination of Macroradical Yields

Despite the importance of H-atom abstraction to peroxide-initiated polymer modifications, there is no direct quantitative measure of macroradical yields in polymer melts. The analysis of abstraction byproducts produces useful information in the form of an abstraction efficiency, and serves as an indirect measure of macroradical concentrations. However this method is restricted to peroxides with non-volatile decomposition by-products that can be quantified by gas chromatography.

1.4.1 Polymer Blends

Polymer blends are comprised of two or more polymers, and have many commercial applications. For example, although isotactic PP is valued for its low density, its brittle nature limits its utility in applications requiring an elastic response. To improve the elastic performance of PP, it is often blended with elastomeric polyolefins such as EPR to give thermoplastic olefin (TPO) blends that provide a diverse range of properties, depending on the PP/elastomer ratio.

As with their homopolymers, the thermal and mechanical properties of TPOs can be improved through crosslinking to generate what are referred to as thermoplastic vulcanizates (TPV). In peroxide-initiated crosslinking of these blends, the competition between crosslinking of the elastomeric component and degradation of PP has a significant effect on the rheological and physical properties of the blend [64]. The concentration of macroradicals in each polymer phase is therefore integral to the properties of the TPV. Analysis of abstraction byproducts cannot be

applied to polymer blends, as it is incapable of determining the concentration of macroradicals in the different phases.

Fluorophore - functionalized nitroxyl can be used in an alternative method for the quantification of macroradical yields. Consider the naphthoyloxy ester of hydroxyl-TEMPO (NTEMPO) prepared by Jones et al. [65], which has been used to determine the concentration of primary radicals formed during pulsed laser photolysis [66]. Fluorescent polyolefins have recently been prepared by Cicogna et al. through peroxide-mediated post reactor modification, but no effort was made to quantify the yield of polymer-bound alkoxyamines [67]. The high sensitivity of spectrofluorometry may therefore provide a method to quantify the yield of fluorescent alkoxyamines generated through the trapping of macroradicals by NTEMPO, providing a direct measurement of macroradical yields.

1.4.2 Radiation Dosimetry

An additional application of fluorescence spectroscopy for quantification of radical concentrations is radiation dosimetry. Radiation therapy is a frequently used cancer treatment method, in which radiation is targeted at the tumor [68]. Accurate radiation dosing is therefore required to affect the tumor while minimizing damage to surrounding, healthy tissue. Radiation calibration is accomplished through radiation dosimetry, in which free radicals generated by the radiolysis of water initiate acrylamide polymerization and crosslinking to form dense polymer gels [69, 70]. The polymer precipitates from the aqueous phase, while remaining in place in a gelatin-matrix, allowing for a variety of imaging techniques for analysis. Note that acrylamide, the monomer most widely used in the development of these dosimeters, is both a neurotoxin and carcinogen, making dosimeters based on this technology difficult to use in a clinical setting.

Polyurethane dosimeters such as PRESAGE™, are formulated with a free radical initiator and a leuco-dye, therefore functioning as a radiochromic dosimeter. Optical CT scanning is typically used in the analysis of PREASGE™ dosimeters, and while more economical than gel dosimeters that commonly require MRI for analysis, the use of the technology is not widely practiced [71].

The use of fluorescent nitroxyls presents an attractive alternative to the development of radiation dosimetry. By covalently binding the fluorophore to a solid polymer, the issue of image diffusion is resolved. In addition to fluorescence being the most attractive option economically, it is much more widely practiced, and therefore poses reduced barriers towards commercialization and widespread clinical use.

1.5 Research Objectives

The objective of this research is to expand the scope of studies on AOTEMPO to include a broader range of polymer structures, and to develop a direct method of measuring macroradical yields in polymer melts. Specific goals include:

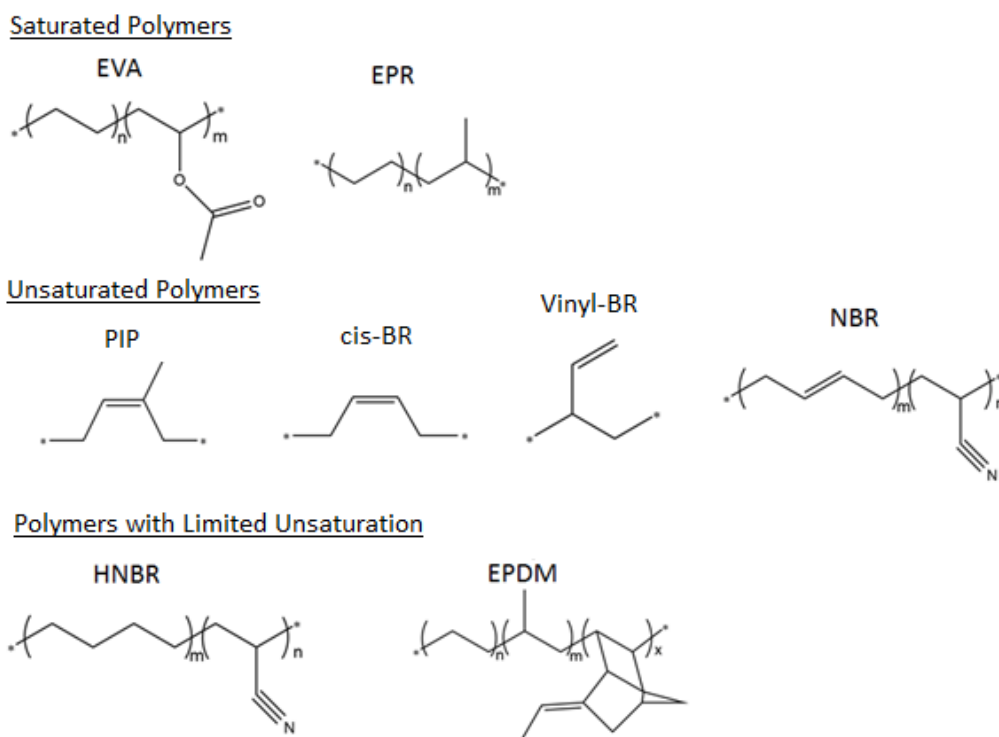
1. Determine the efficacy of AOTEMPO as a scorch protectant for crosslinking polymers bearing nitrile, acetate, and allylic functionality.
2. Assess whether AOTEMPO is capable of crosslinking polymers that degrade when treated with peroxides alone.
3. Validate a fluorescence technique for measuring alkoxyamine concentrations in polymers that are chemically modified using peroxide + nitroxyl formulations.

Chapter 2

AOTEMPO-Mediated Peroxide Crosslinking

2.1 Introduction

Research conducted on AOTEMPO-mediated cure chemistry has focused on peroxide-initiated crosslinking of LLDPE, where it is remarkably effective. However, good performance in a single saturated polyolefin does not necessarily translate to polymers with different chemical structures. The studies described in this chapter aimed to broaden the scope of our knowledge of AOTEMPO-mediated crosslinking by examining alternate saturated polymers, materials containing a high concentration of C=C bonds, and polymers that have a small amount of C=C unsaturation (Scheme 10).



Scheme 10: Polymers of Interest

The efficacy of AOTEMPO with respect to these polymer cures is judged on the basis of three criteria: the length of the induction period, the extent of crosslinking during the induction period, and the ultimate cure extent relative to a peroxide-only formulation. Ideally, AOTEMPO provides an induction time that is a simple function of the trapping ratio, a storage modulus that remains unchanged during the induction period, and a final storage modulus equal to that provided by DCP alone.

Recall equation 2, which describes the induction time (t_{ind}) for nitroxyl-mediated crosslinking of LLDPE. This function was derived on the assumption that the trapping of initiator-derived radicals is irreversible, meaning the resulting alkoxyamines are stable with respect to radical regeneration.

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

Deviations from this equation may be observed if polymer-bound alkoxyamines are prone to instability. Should the alkoxyamine decompose to an olefin and hydroxylamine, longer than predicted periods of induction may be observed, as the hydroxylamine is readily oxidized back to the original nitroxyl species which could then trap another initiator-derived macroradical [29].

Concerns over crosslinking during the induction period arise from the potential of alkoxyamines to undergo thermolysis to yield nitroxyl and a carbon-centred radical. Reversibility of macroradical trapping may support a steady-state concentration of alkyl radicals, whose combination would give rise to a “marching modulus” during the induction phase. This is of particular interest for allylic systems, whose alkoxyamines are prone to homolytic C-O cleavage.

The final evaluation criterion, ultimate cure extent, assesses whether the polymer-bound acrylate groups introduced by macroradical trapping can overcome losses in crosslink yield associated

with quenching a portion of the initiator. In saturated systems, macroradical trapping by nitroxyl results in a stoichiometric loss in cure yield. If an AOTEMPO-mediated formulation is to achieve the same crosslink density as peroxide-only cure, oligomerization of pendant acrylate functionality must compensate for the losses due to macroradical trapping. In unsaturated systems such as polybutadiene, the potential exists for peroxide-only formulations to benefit from C=C oligomerization, such that each initiator-derived radical can produce multiple crosslinks. Therefore, quenching a single macroradical with nitroxyl can eliminate multiple crosslinks making it more difficult for the macromonomer oligomerization phase of an AOTEMPO cure to recover the lost modulus.

This chapter describes the dynamics and yields of nitroxyl-mediated formulations applied to EVA, EPR, PIP, cis-BR, vinyl-BR, NBR, HNBR, and EPDM. A comprehensive study of cure rheology is presented for a range of reaction temperatures with resulting data discussed in the context of H-atom transfer efficiency, alkoxyamine stability, and the oligomerization of backbone C=C groups as well as polymer-bound acrylate functionality.

2.2 Experimental

2.2.1 Materials

PIP (97% cis, Mw~800,000, Scientific Polymer Products), 1,4 polybutadiene (98% cis, Sigma Aldrich), 1,2-polybutadiene (93% vinyl, Mw~100,000, Scientific Polymer Products), EPR(60wt% ethylene, Scientific Polymer Products), EPDM(60wt% Ethylene, 4% 5-ethylidene-2-norbornene, Scientific Polymer Products), poly(ethylene-co-vinyl acetate) (ELVAX 460, 18% Vinyl acetate, DuPont), HNBR(36% ACN, 96% Hydrogenated, Zeon Chemicals), NBR(35% ACN, Zeon Chemicals), were purified by dissolution/ precipitation and dried under vacuum prior to use. DCP (98%), hydroxy-TEMPO (4-hydroxy-2,2,6,6-tetramethylpiperidin-1-

oxyl, 97%), TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, 98%), triethylamine were used as received from Sigma Aldrich (Oakville, ON.). 4-Acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl (AOTEMPO) was prepared as described previously [9].

2.2.2 Rheological Analysis

Polymer (5g) was coated with an acetone solution containing the required amounts of peroxide initiator and scorch additive, hand-mixed and allowed to dry thoroughly. Rubbers were sheeted on a two-roll mill, treated with initiator solution and re-milled post drying. Excessive drying of solutions containing TEMPO was avoided. The polymer mixtures were then cured in a controlled strain rheometer (Advanced Polymer Analyzer 2000, Alpha Technologies) equipped with biconical plates and operating at 1Hz and 3° arc.

2.3 Results and Discussion

2.3.1 AOTEMPO-Mediated Crosslinking of Saturated Polymer Systems

Poly(ethylene-co-vinyl acetate), or EVA, is a random copolymer containing on the order of 10-20 mol% vinyl acetate that is produced on a commercial scale in support of a range of thermoset applications. For instance, the EVA used to encase photovoltaic modules is crosslinked to resist environmental degradation, and EVA foams are cured to provide improved melt strength. It has been shown that EVA is crosslinked effectively by DCP, providing a cure response that is better than LDPE [72]. This heightened crosslinking efficiency is attributed to acetate functionality, whose C-H bonds are more reactive towards H-atom abstraction due to resonance stabilization. As a result, H-atom abstraction from EVA by cumyloxyl is faster than in PE, leading to a greater macroradical yields and, by extension, crosslink extents.

Figure 5 illustrates the cure dynamics provided by EVA cure formulations comprised of DCP, DCP+TEMPO, and DCP+AOTEMPO when reacted at 140, 160, and 180°C. The results are entirely consistent with previous studies of LLDPE crosslinking, as both TEMPO and AOTEMPO retard crosslinking entirely for an induction period that corresponds with values calculated with Equation 2. Moreover, AOTEMPO provided this delayed onset character without compromising ultimate cure yields, indicating that vinyl acetate mers within EVA do not adversely affect AOTEMPO performance. This greatly simplifies cure formulation development for this class of ethylene-rich copolymer.

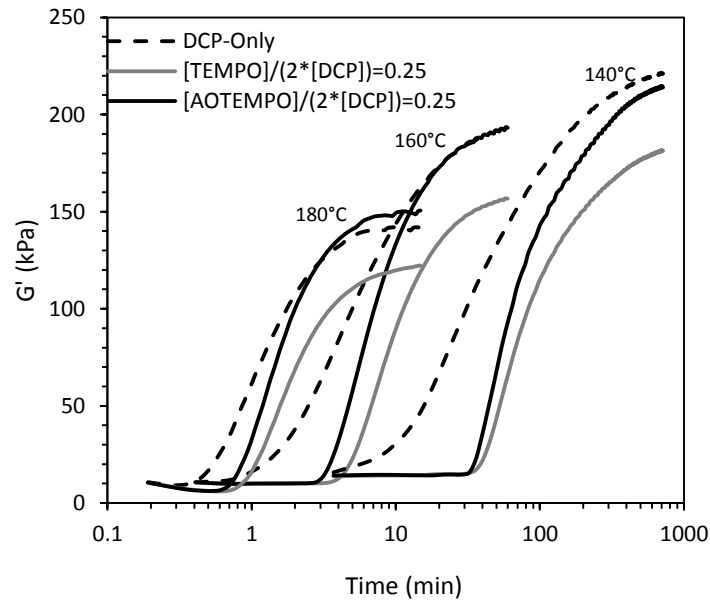


Figure 5: Dynamics of delayed-onset EVA cures at 1Hz, 3°arc ([DCP]=18.5 μ mol/g; [TEMPO]=9.2 μ mol/g; [AOTEMPO]=9.2 μ mol/g)

The other saturated material of interest to this study, poly(ethylene-co-propylene) (EPR), is a random copolymer that is peroxide-cured to give rubber thermosets with exceptional oxidative stability [73].

Figure 6 provides cure profiles for an EPR grade containing 60 mol% ethylene and 40 mol% propylene. As observed for the EVA and LLDPE systems, nitroxyl-mediated cures of EPR produced a period of complete crosslink suppression, with an induction period that is consistent with Equation 2. This is noteworthy, since the tertiary alkoxyamines derived from nitroxyl trapping of the corresponding PP macroradicals are known to be thermally unstable [24]. Indeed, in the thermal degradation of polypropylene, the alkoxyamines formed by the trapping of tertiary radicals by TEMPO can effectively regenerate nitroxyl [31, 74]. Although the regeneration of nitroxide could prolong the induction period, alkoxyamines generated from EPR support a stable, predictable induction period, followed by an acrylate oligomerization phase that recovers crosslink density losses incurred during the induction period.

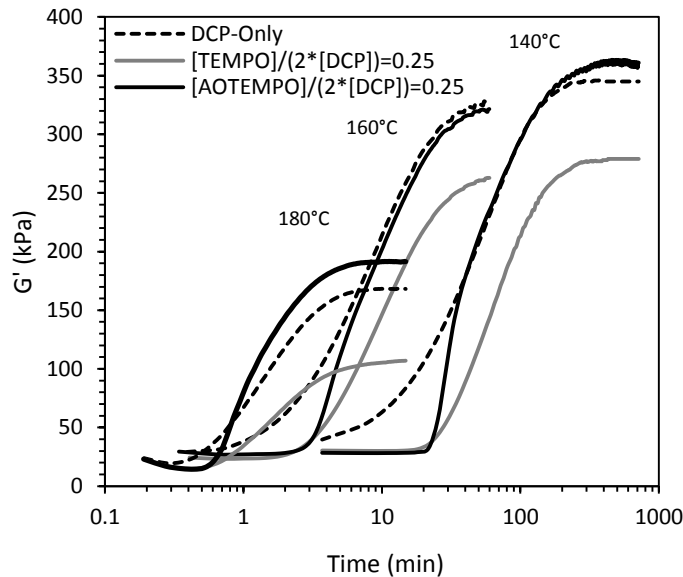
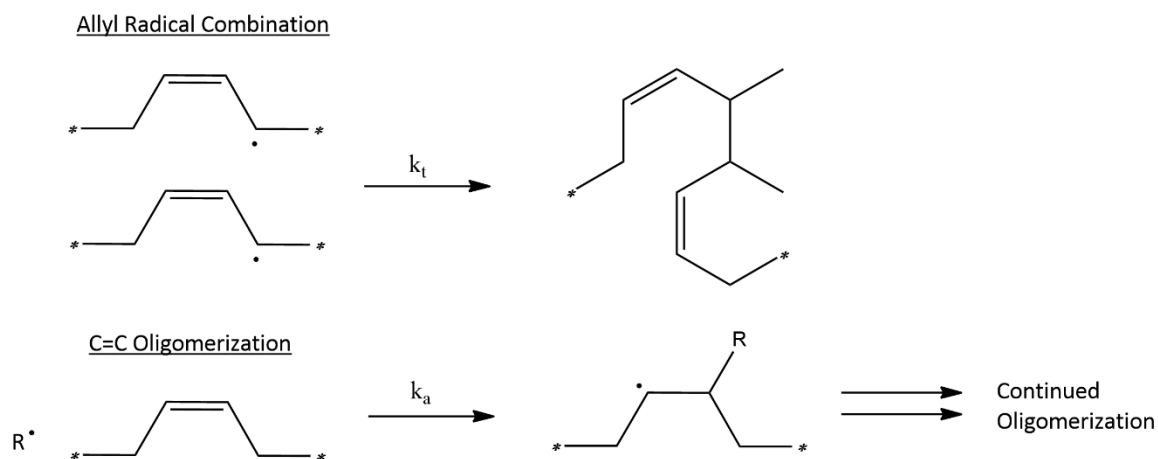


Figure 6: Dynamics of delayed-onset EPR cures at 1Hz, 3°arc; ([DCP]=18.5 μ mol/g; [TEMPO]=9.2 μ mol/g; [AOTEMPO]=9.2 μ mol/g)

2.3.2 Nitroxyl-Mediated Crosslinking of Allylic Polymer Systems

There are inherent differences between saturated and unsaturated polymers with respect towards peroxide-initiated crosslinking. Unsaturated polymer systems are better H-atom donors than their saturated counterparts due to the low BDE of allylic C-H bonds. This heightened reactivity results in increased macroradical yields, and correspondingly greater crosslink densities when compared to saturated materials like LLDPE [28]. Furthermore, disproportionation of allylic radicals is negligible and, as such, macroradical termination gives a higher proportion of crosslinks than systems involving alkyl radicals, for which disproportionation can be significant (Scheme 13). The potential also exists for unsaturated polymers to crosslink through the oligomerization of olefinic functionality, the extent of which is dependent upon the substituents about the C=C bond.



Scheme 11: Crosslinking pathways for polymers with C=C unsaturation on the polymer backbone

Consider Figure 7, where DCP-initiated crosslinking dynamics are presented for all the unsaturated polymers of interest. The cure extent, as measured by the change in storage modulus, declined in the order: 1,2-polybutadiene(vinyl-BR) \gg 1,4-polybutadiene(cis-BR) > EPDM > PIP \approx NBR \gg HNBR. The exceptional response of vinyl-BR to DCP is consistent with other

reports [23, 21], and results from R-CH=CH₂ oligomerization [75] to generate crosslinks without consuming macroradicals [22]. In contrast, the more highly substituted olefinic groups in cis-BR and PIP are less reactive toward radical addition, resulting in a cure process with reduced kinetic chain length. Although no quantitative data is available for vinyl-BR cures, Loan has estimated that cis-BR can produce up to 10 crosslinks per initiator radical, while PIP can generate just 1 crosslink per initiator fragment, due to reduced oligomerization activity of its trisubstituted olefin [21].

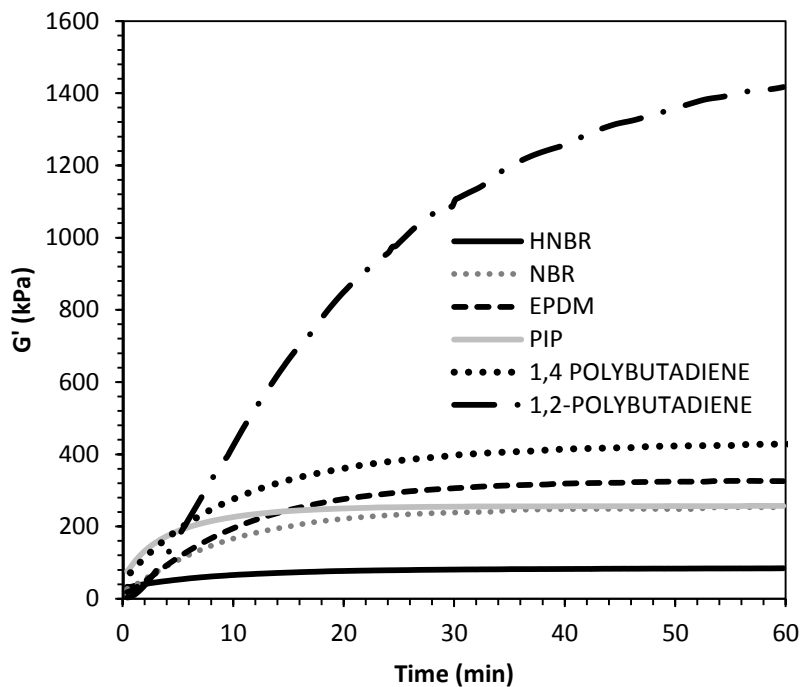
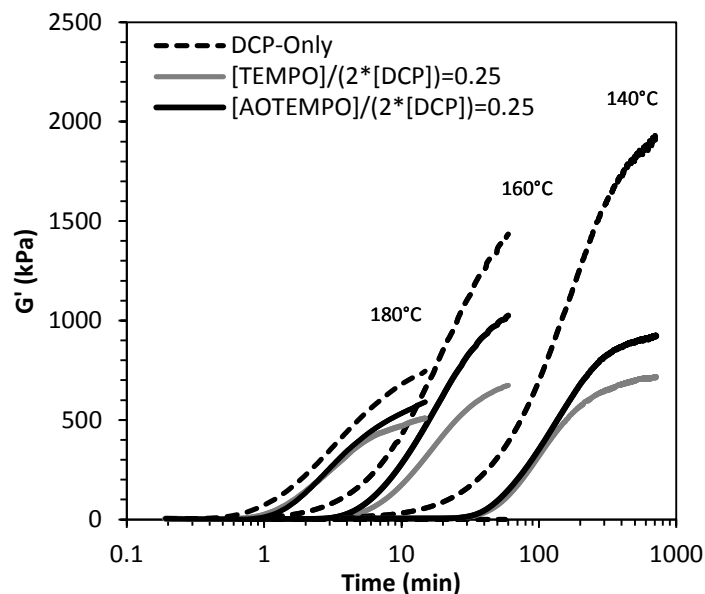


Figure 7: Crosslinking Dynamics of unsaturated polymers at 160°C, 1Hz, 3°arc; [DCP]=18.5µmol/g

The sample of NBR used in this study contained 34% acrylonitrile, with the balance being a mixture of 1,4-BR isomers. This nitrile functionality had a clear effect on cure yield, presumably because of a dilution of the H-atom abstraction reactivity provided by allylic groups [21]. Indeed,

DCP-initiated cure performance is improved for NBR grades of lower acrylonitrile content [76]. Not surprisingly, the highly saturated composition of HNBR, with just 4 mol% 1,4-butadiene functionality resulted in severe depression of its peroxide-curing reactivity.

Figure 8 provides cure profiles for peroxide-only and nitroxyl-mediated formulations of vinyl-BR. The AOTEMPO and TEMPO data demonstrate significant delayed-onset action across all tested temperatures, with induction times in good agreement with Equation 2. The most remarkable feature of these plots is the severe depression of crosslinking yields in the scorch-protected systems. This is a byproduct of vinyl group oligomerization, whose kinetic chain character yields multiple crosslinks per initiator-derived radical. In the vinyl-BR system, radical quenching does not only reduce the yield of combination products, but also the crosslinks that would, in the absence of nitroxyl, be generated by olefin oligomerization. As a result, crosslink density losses do not scale with nitroxyl loadings on a 1:1 basis, but are much more sensitive to the radical trap. Clearly, the amount of acrylate functionality introduced during the induction phase of an AOTEMPO cure is insufficient to offset these losses to vinyl group oligomerization.



**Figure 8: Dynamics of delayed-onset 1,2-polybutadiene cures at 1Hz, 3°arc;
([DCP]=18.5 μ mol/g; [TEMPO]=9.2 μ mol/g; [AOTEMPO]=9.2 μ mol/g)**

The cure dynamics data for cis-BR (Figure 9) are consistent with those acquired for vinyl-BR (Figure 8), in that nitroxyl formulations provided much lower cure extents than DCP alone. This is attributed to the kinetic chain character of butadiene-rich polymer cures, as discussed above. The cis-BR results are noteworthy in one additional aspect, as virtually no difference is observed between the AOTEMPO and TEMPO crosslinking profiles, despite the fact that polymer-bound alkoxyamine yields should be relatively high.

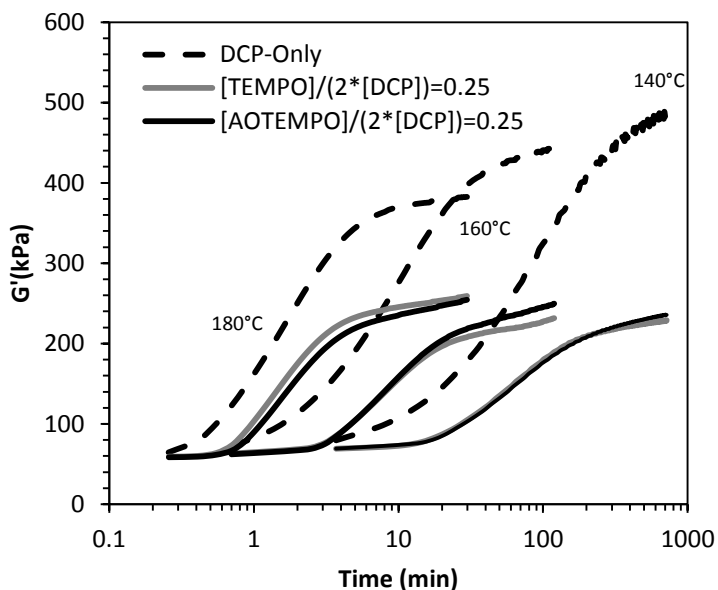
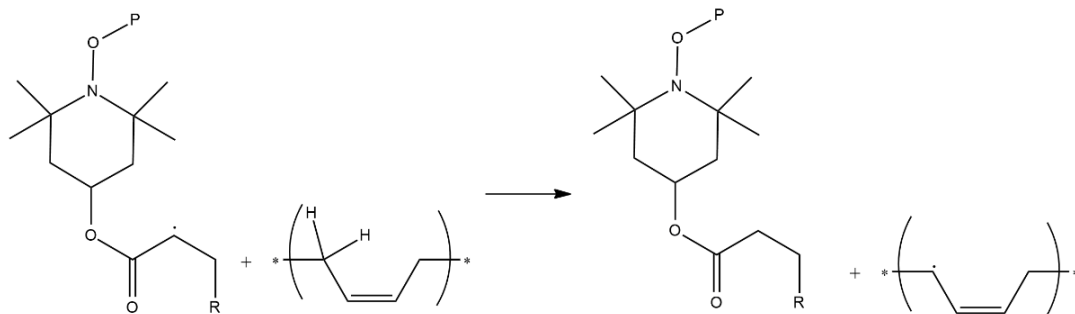


Figure 9: Dynamics of delayed-onset 1,4-polybutadiene cures at 1Hz, 3°arc;
 ([DCP]=18.5 μ mol/g; [TEMPO]=9.2 μ mol/g; [AOTEMPO]=9.2 μ mol/g)

The failure of acrylate functionality to produce significant amounts of crosslinking is likely the result of degradative chain transfer between propagating acrylate-derived radicals and allylic C-Hs (Scheme 12). This is closely related to monomer polymerizations that are plagued by chain transfer to solvent, as polymer molecular weight is reduced by H-atom donation by labile C-H bonds within abundant solvent molecules. It is also related to radical polymerization of allylic monomers such as propylene and allyl benzoate, in which low yields result from H-atom transfer in competition with radical addition to the C=C bond [77, 78]. In the present context, the population of allylic C-Hs in cis-BR appears to inhibit the polymerization of polymer-bound acrylate, thereby hindering the recovery of crosslink density.



Scheme 12: Degradative H-atom transfer from acrylate functionality in allylic polymer systems

Cis-1,4-polyisoprene (PIP) is a further extension of the diene-rich elastomer series. Each mer is comprised of a trisubstituted C=C bond that is less reactive toward oligomerization, owing to steric effects. The cure dynamics data plotted in Figure 10, shows that the early stages of TEMPO and AOTEMPO-mediated cures are nearly identical, retarding the rate of crosslinking significantly, but not completely. That is, a period of true induction in which G' is completely suppressed was not observed. Rather G' increased marginally in both formulations, which is consistent with reports of the thermal instability of allylic alkoxyamines [28]. As illustrated in Scheme 13, alkoxyamine thermolysis may establish a dynamic equilibrium between macroradical intermediates and their trapped state, providing a population of allylic macroradicals whose combination would yield crosslinks during the induction period. Fortunately, this equilibrium appears to favour the alkoxyamine, and nitroxyls are able to provide significant, if not perfect delayed-onset action.

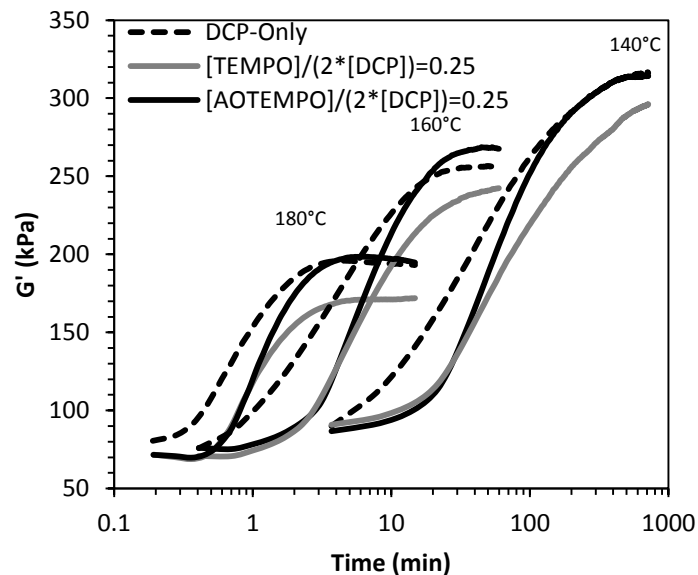
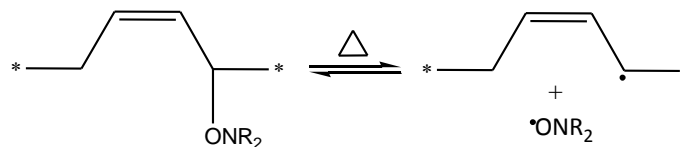


Figure 10: Dynamics of delayed-onset PIP cures at 1Hz, 3°arc; ([DCP]=18.5 μ mol/g; [TEMPO]=9.2 μ mol/g; [AOTEMPO]=9.2 μ mol/g)

Note that similar G' increases were observed during the induction periods of cis-BR crosslinking (Figure 9). However, the scale of the y-axis is such that the “marching modulus” is not as evident. Expansion of the induction period data (not shown) reveals evidence of this behaviour, suggesting that reversibility affects all systems that cure through allylic alkoxyamine intermediates.



Scheme 13: Reversible allyl radical trapping by nitroxyls

A comparison of two similar elastomers, poly(butadiene-co-acrylonitrile) (NBR) and its nearly saturated analogue hydrogenated poly(butadiene-co-acrylonitrile) (HNBR) is instructive (Figure 11). As observed for cis-BR, AOTEMPO and TEMPO produced nearly identical cure yields due to the inefficiency of macromonomer oligomerization. However, AOTEMPO-mediated DCP cures of HNBR provided a significant recovery of crosslink density, albeit incomplete. This may be the result of residual unsaturation within HNBR. Nevertheless, the data clearly demonstrates the inhibitory effect of residual unsaturation on AOTEMPO performance.

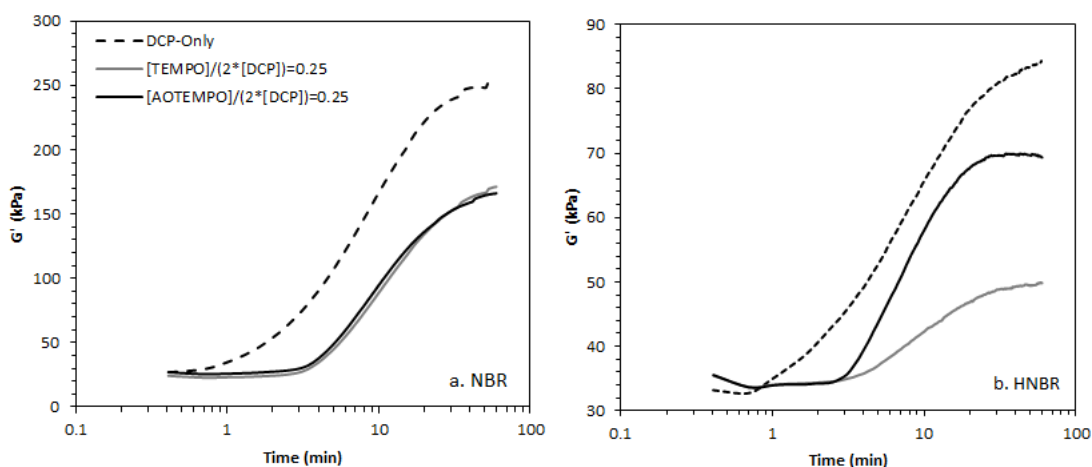


Figure 11: Dynamics of delayed-onset cures at 160°C, 1Hz, 3°arc; a. NBR; b. HNBR; ([DCP]=18.5 μ mol/g,[TEMPO]=9.2 μ mol/g; [AOTEMPO]=9.2 μ mol/g)

The study of unsaturated polymer cures concluded with an examination of terpolymer EPDM containing a small amount of pendant olefin functionality. The data presented in Figure 12 shows that AOTEMPO performs well on this substrate, generating good delayed onset character and cure recovery throughout the temperature range studied. It appears that degradative chain transfer is not significant in the EPDM system, as the acrylate oligomerization phase of the cure proved capable of providing crosslink yields of the same order of DCP alone.

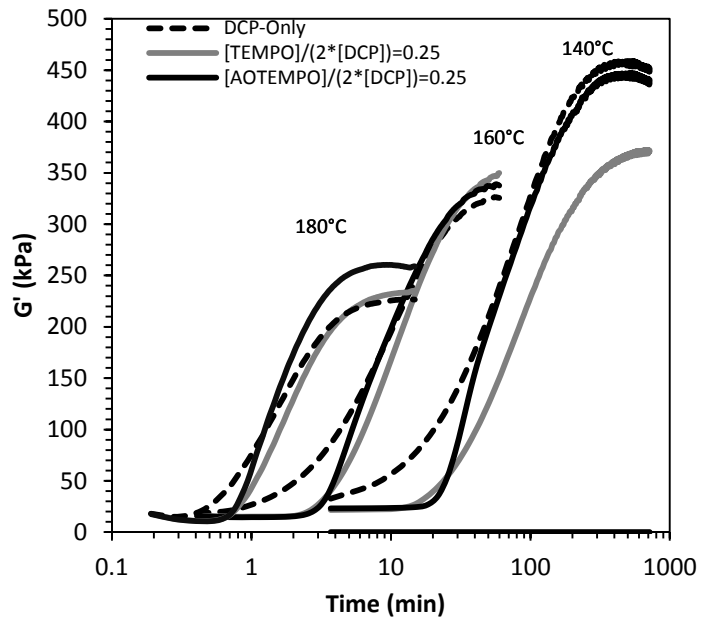


Figure 12: Dynamics of delayed-onset EPDM cures at 1Hz, 3°arc; ([DCP]=18.5 μ mol/g; [TEMPO]=9.2 μ mol/g; [AOTEMPO]=9.2 μ mol/g)

2.4 Conclusions

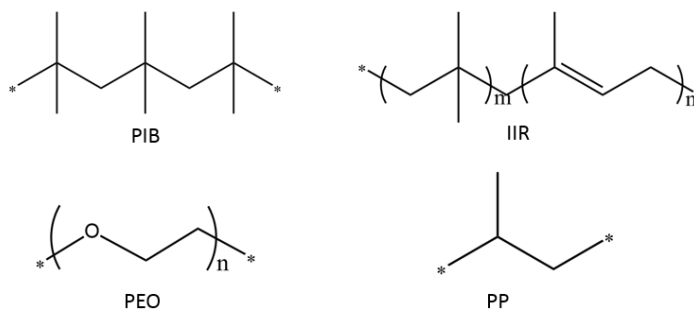
The scorch protection performance of AOTEMPO is greatest for ethylene-rich materials, whose 1:1 reaction stoichiometry and stable alkoxyamine trapping products provide ideal induction behaviour and no net losses in crosslink density. Polymers containing large amounts of allylic functionality are more problematic, as macroradical trapping prevents olefin oligomerization during the trapping phase of a nitroxyl-mediated cure, causing crosslink yield losses that are not easily recovered during the macromonomer oligomerization phase. Materials with a high concentration of allylic C-H bonds, such as cis-BR, present further complications as degradative chain transfer to propagating acrylate-derived radicals stunts the progress of macromonomer oligomerization, thereby suppressing the extent of modulus recovery during this phase of the cure.

Chapter 3

AOTEMPO-mediated crosslinking of scission-prone polymers

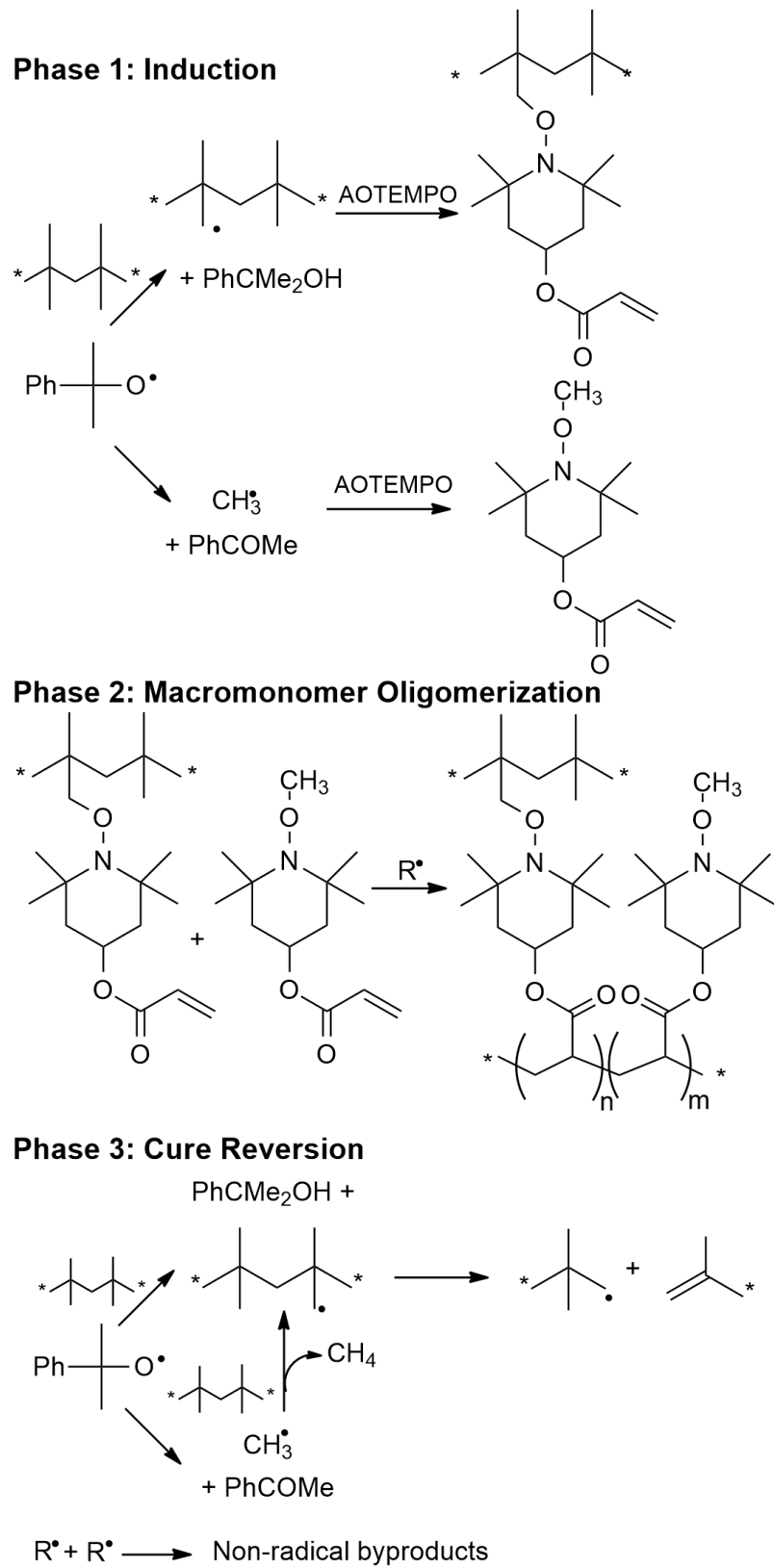
3.1 Introduction

Research conducted on AOTEMPO-mediated polymer modifications has focused on scorch protection for materials that crosslink under the action of peroxides. However, several materials degrade when subjected to radical initiators, owing to the predominance of macroradical β -scission over combination. This includes commercial polymers such as poly(isobutylene) (PIB), poly(isobutylene-co-isoprene) (IIR), poly(ethylene oxide) (PEO), and poly(propylene) (PP), the structures of which are shown in Scheme 14.



Scheme 14: Scission-prone polymers examined in this study

This chapter presents original research on the potential of AOTEMPO to effect the crosslinking of these materials. The strategy is to trap alkyl macroradicals to give pendant alkoxyamine groups bearing acrylate functionality, whose subsequent oligomerization provides the desired crosslinking. As such, this process should involve three distinct phases: induction, macromonomer oligomerization, and cure reversion (Scheme 15).



Scheme 15: Idealized reaction mechanism for AOTEMPO-mediated crosslinking of PIB.

Chain scission during the induction phase is expected to be marginal, since macroradical lifetimes are shortened by rapid quenching with free nitroxyl. Upon complete AOTEMPO consumption, oligomerization of polymer-bound acrylate groups is expected to crosslink the polymer at a rate that exceeds backbone macroradical scission, leading to large-scale crosslinking. Cure reversion is expected if all acrylate macromonomer functionality is consumed prior to the complete thermolysis of dicumyl peroxide (DCP), leaving backbone degradation to proceed unabated. Since cure reversion is undesirable, an important objective of this work is to determine the trapping ratio ($[AOTEMPO]/2*[DCP]$) that provides a high storage modulus (G') that does not decline significantly from its maximum value.

This chapter describes the dynamics and yields of AOTEMPO-based formulations applied to PIB, IIR, PEO, and PP. Comprehensive studies of changes in storage modulus (G') with time are presented for a range of temperatures, trapping ratios, initiator loadings, and peroxide structures. The data are discussed in the context of established principles of H-atom transfer reactivity, nitroxyl trapping chemistry, and monomer polymerization reactions.

3.2 Experimental

3.2.1 Materials

PIB (Scientific Polymer Products, M_w 4,700,000), IIR (6mol%IP, LANXESS), and IIR (3mol%IP, LANXESS) were purified by dissolution/precipitation in toluene/acetone and dried *in vacuo*. PP (Isotactic, MFR=0.5g/10min, M_n ~ 166,000, M_w ~580,000, Sigma Aldrich), PP (MFR=1.5g/10min, Total, Film Extrusion Grade), PEO (M_w ~5,000,000, Scientific Polymer Products), DCP (98%, Sigma Aldrich) were used as received. Luperox 231 (1,1-bis(*t*-

butylperoxy)-3,5,5-trimethylcyclohexane, L-231, 92%, Sigma Aldrich) 4-Acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl (AOTEMPO) was prepared as described previously [27].

3.2.2 Rheology

5g of each polymer was coated with an acetone solution containing the required amounts of peroxide initiator and AOTEMPO, hand-mixed and allowed to dry thoroughly. Rubbers were sheeted on a two-roll mill, treated with initiator solution and re-milled post drying. The polymer mixtures were then cured in a controlled strain rheometer (Advanced Polymer Analyzer 2000, Alpha Technologies) equipped with biconical disks and operating at 1Hz and 3arc.

3.2.3 Gel Contents

Gel contents were determined through extraction of cured products with refluxing xylenes stabilized with 100ppm BHT from 120-mesh sieve cloth for 2 hours. Unextracted material was dried *in vacuo* to a constant weight, with the gel content reported as the weight percent of insoluble polymer.

3.3 Results and Discussion

3.3.1 Isobutylene-rich Elastomers

PIB is an elastomeric polymer whose exceptional chemical stability [34] is attributed to its resistance to the H-atom abstraction reactions that support auto-oxidation as well as the peroxide-initiated modifications of present interest. Recent studies have shown that the secondary positions of PIB are sterically hindered by adjacent quaternary carbons, leaving only methyl groups as potential H-atom donors [79]. The yield of primary alkyl macroradicals generated by DCP at high temperatures is relatively small, owing to the high C-H bond dissociation energy at this position [16]. Nevertheless, fragmentation of these primary macroradical intermediates is sufficiently quick to overwhelm crosslinking by radical combination, resulting in polymer backbone degradation. This illustrated in Figure 14, which provides a plot of G' versus time for

PIB mixed with 37 μmol DCP/g and heated to 160°C. Within just 8 min of reaction time, the storage modulus declined from 126 kPa to a value that was lower than what can be measured accurately with the rheometer.

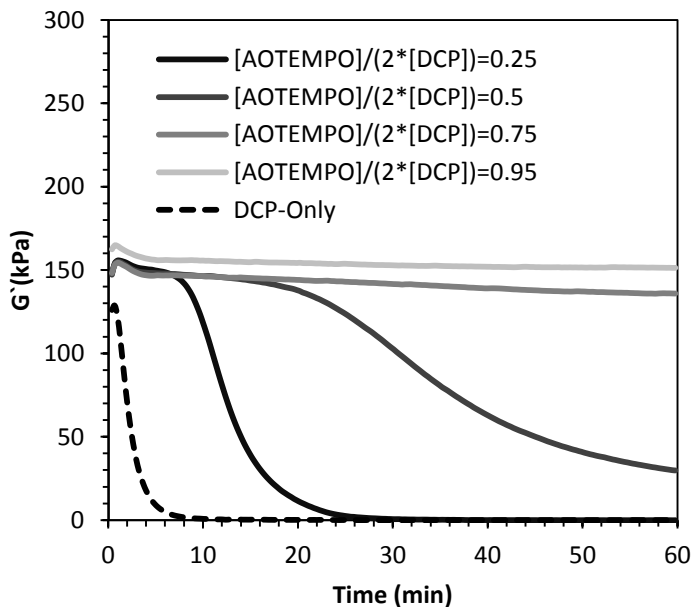


Figure 13: Dynamics of PIB degradation by DPC-initiated chain scission at 160°C, 1Hz, and 3°arc in the presence of varying AOTEMPO concentrations; [DCP]=37 μmol /g

Figure 13 also contains plots of DCP+AOTEMPO formulations prepared with different trapping ratios. These data show clear evidence of an induction phase, as G' remained constant for a time that is consistent with predictions based on peroxide half-life and nitroxyl trapping ratios.

However, no evidence of an oligomerization crosslinking phase is seen, as degradation followed immediately after the induction period, regardless of the AOTEMPO concentration.

The failure of AOTEMPO to produce a cross-linked PIB thermoset is likely the result of the stability of PIB toward H-atom abstraction. Note that the induction phase of the process must introduce enough macromonomer functionality to the polymer, such that acrylate polymerization

can dominate radical scission during the subsequent oligomerization phase. Garrett et al. have shown that of the DCP that undergoes thermolysis in PIB at 160°C, only 17% of the resulting cumyloxy radicals abstract a H-atom from the polymer, with the 83% of cumyloxy radical cleaving to acetophenone + methyl radical (CH₃·) [18]. This is in sharp contrast to more reactive polymers such as polyethylene, which provides a DCP abstraction efficiency of 56%. As a result of PIB's unreactive nature, just 17% of AOTEMPO charged to the formulation will produce the desired macromonomer functionality, while 83% will be consumed as the corresponding methyl alkoxyamine. At these low macromonomer yields, the oligomerization of polymer-bound acrylate groups is uncompetitive with backbone scission, the net result being polymer degradation as opposed to thermoset production.

Shifting to an alternate peroxide initiator is a simple means of affecting abstraction efficiencies as well as the competitive balance between macromonomer oligomerization and chain scission. (1,1-Bis(*t*-butylperoxy)-3,5,5-trimethylcyclohexane (L-231) is a peroxyketal that yields *tert*-butoxy radicals at temperatures that are significantly lower than those supported by DCP. The fragmentation of *t*-butoxyl to ketone + CH₃· remains significant at melt state processing temperatures [14, 80, 81, 82], but it is less susceptible than cumyloxyl [83]. Furthermore, L-231 provides a 5.1 min half-life at 136°C, as opposed to DCP which requires 160°C to decompose at this rate. Since high reaction temperatures favour β-scission of macro-radicals, operating at 136°C improves the likelihood that acrylate oligomerization can compete with backbone degradation.

The data provided in Figure 14 show that PIB degrades slowly when heated with L-231 alone at 136°C, but ultimately produces a near zero storage modulus. Formulations containing AOTEMPO showed improvement relative to the DCP trials described above, with a trapping ratio of 0.25 increasing G' from 145kPa to 164kPa at approximately 5 min, with subsequent reversion

eliminating these gains by the end of the process. It seems, therefore, that AOTEMPO is incapable of generating thermoset derivatives of PIB, owing to inefficiencies in macroradical production/trapping, and subsequent macromonomer oligomerization.

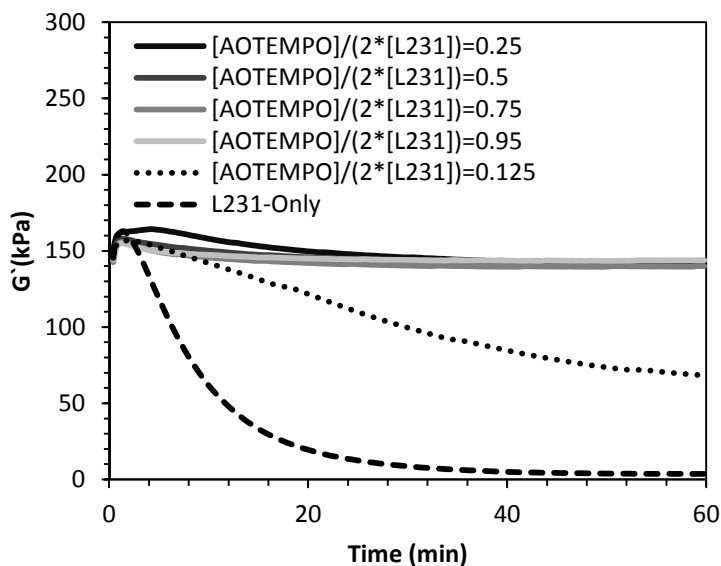


Figure 14: Dynamics of PIB degradation by L231-initiated chain scission at 136°C, 1Hz, and 3°arc in the presence of varying AOTEMPO concentrations; [L231]=74μmol/g

The random copolymer poly(isobutylene-co-isoprene) (IIR) is a better H-atom donor than PIB, owing to the reactivity of allylic C-H bonds provided by isoprene mers. Commercial grades of IIR containing about 2 mol% isoprene are crosslinked by conventional sulfur cure formulations, [79] since these materials remain susceptible to peroxide-initiated degradation [6, 84]. However, experimental grades of IIR containing higher isoprene (IP) contents are more amenable to peroxide crosslinking [21]. Figure 15 presents storage modulus data for a material that contains 6 mol% IP (IIR-6), which was mixed with L-231 alone, and in combination with varying amounts of AOTEMPO. At 136°C, the peroxide-only compound shows a modest gain in G' , in contrast to the severe G' loss observed for PIB under identical reaction conditions (Figure 15).

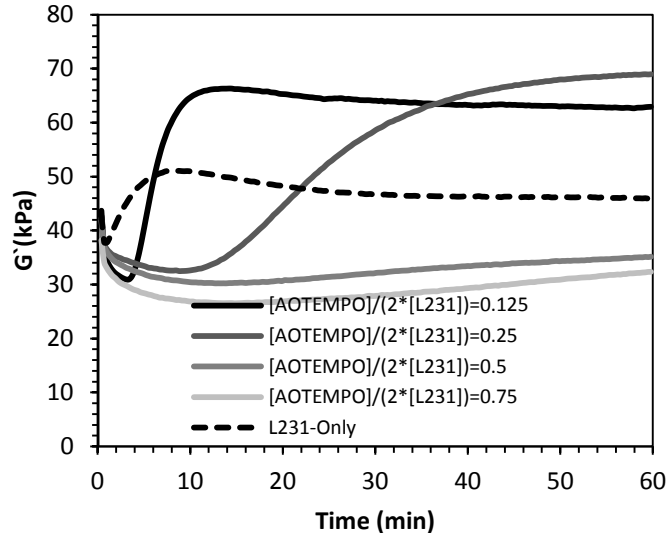


Figure 15: Dynamics of AOTEMPO mediated crosslinking of IIR-6%IP 136°C, 1Hz, and 3°; [L231]=74 μ mol/g.

When AOTEMPO was used at a trapping ratio of 0.125, a brief induction period was followed by a distinct macromonomer oligomerization phase, which brought the compound from a modulus of 30 kPa to a maximum of 66 kPa at the 11 min mark of the process. Slight reversion was observed beyond this point, as crosslinking generated through acrylate conversion became uncompetitive with chain scission, likely due to complete consumption of polymer-bound acrylate functionality [85]. Increasing the trapping ratio to 0.25 extended the induction period and prolonged the oligomerization phase, such that cure reversion was not observed within the 60 min timeframe of the experiment. Extending beyond this trapping ratio quenched the cure entirely, confirming that an optimal trapping ratio exists, which provides enough acrylate functionality to generate a crosslinked network, and enough peroxide to convert polymer-bound acrylate functionality without causing subsequent degradation of the backbone.

As described above, 6mol% IP is much greater than what is contained in typical industrial grades of butyl rubber. To determine whether AOTEMPO can generate thermosets from lower IP materials, a copolymer containing 3mol% IP (IIR-3) was studied. The data plotted in Figure 16 show that the lower IP elastomer is prone to degradation by L-231, and while AOTEMPO formulations could produce a net gain in G' , the ultimate cure extent did not match that provided by IIR-6.

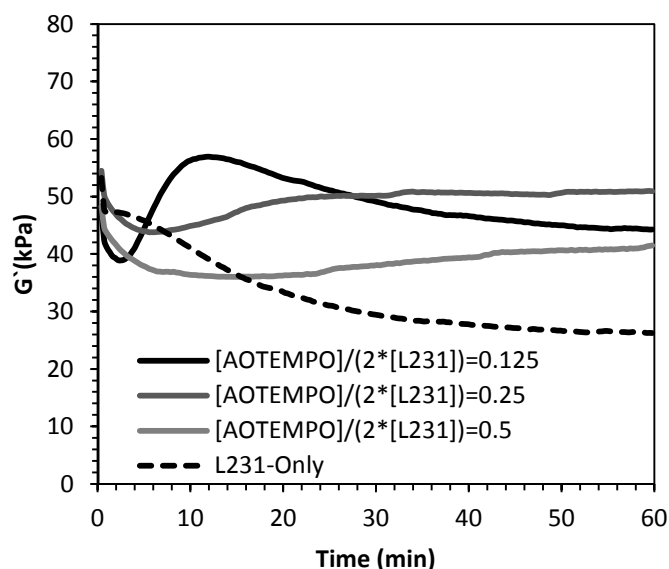


Figure 16: Dynamics of AOTEMPO mediated crosslinking of IIR-3%IP 136°C, 1Hz, and 3°; [L231]=74 μ mol/g.

3.3.2 Poly(ethylene oxide)

Poly(ethylene oxide) is a semi-crystalline homopolymer with a melting temperature of approx. 65°C and a glass transition temperature of about -67°C. It is highly susceptible to chain scission when mixed with peroxide loadings of less than 1wt% and heated to conventional cure temperatures [36, 37, 38]. However, peroxide formulations containing relatively small amounts of maleimide coagent such as N,N'-m-phenylenedimaleimide provide a remarkably efficient cure, owing to the efficiency of radical-mediated grafting of maleimide functionality to the polyether

backbone [38]. The downside of this coagent approach is rather poor scorch safety, and alternate PEO cure technology remains of considerable interest.

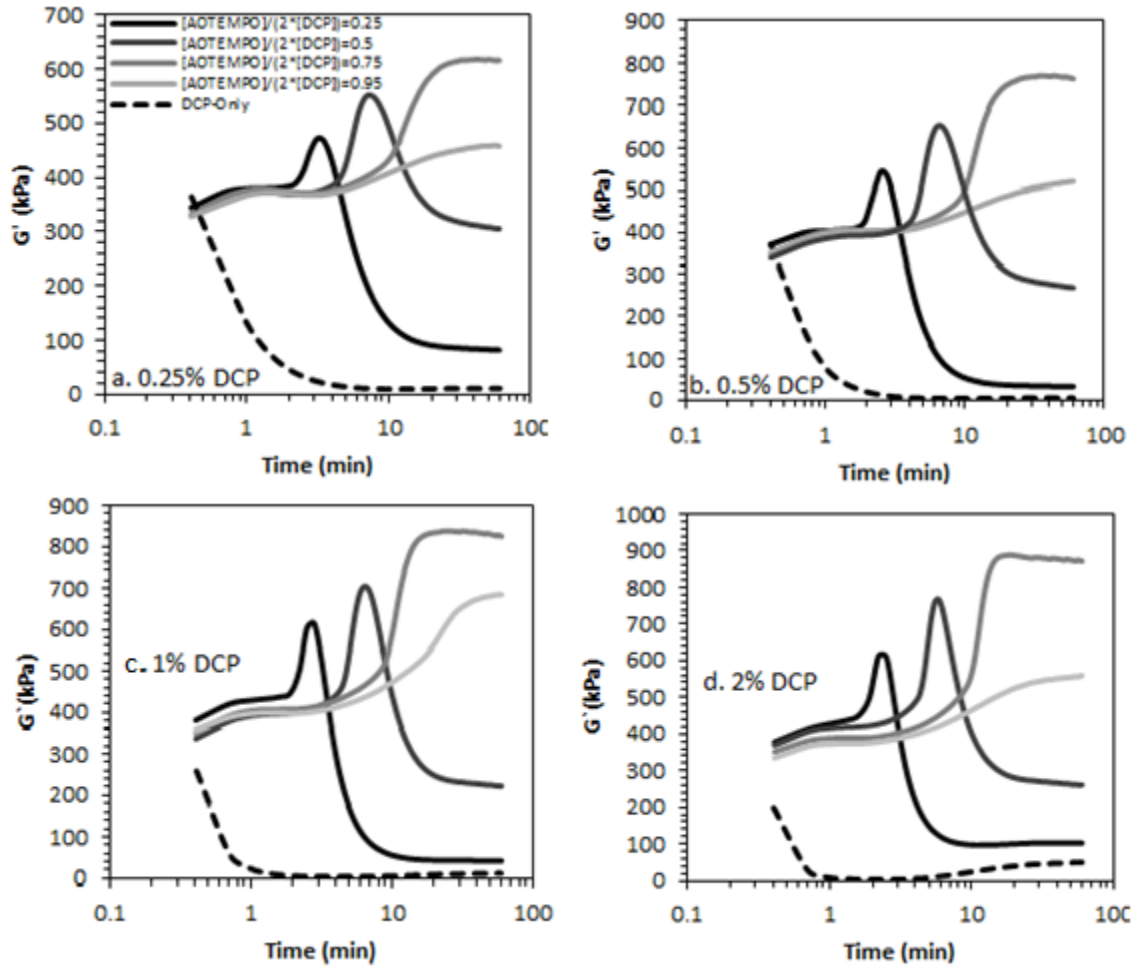


Figure 17: Dynamics of AOTEMPO mediated crosslinking of PEO at varying DCP and AOTEMPO loadings at 160°C, 1Hz, and 3°arc; a. [DCP]=9.75μmol/g ; b. [DCP]=18.5μmol/g, c. [DCP]=37μmol/g; d.[DCP]= 74μmol/g

Figure 17 provides storage modulus data that illustrate the extent of PEO degradation when the material is compounded with different amounts of DCP alone, and the complex cure dynamics that result when the polymer is mixed with DCP+AOTEMPO over a range of concentrations. As

expected, the DCP-only formulations degraded the polymer extensively. The AOTEMPO formulations demonstrate the three distinct phases described above: induction, macromonomer oligomerization, and cure reversion. The intensity and duration of these phases is strongly dependent on the trapping ratio and, to a lesser extent, the total peroxide loading.

Unlike other saturated polymers studied to date, the induction phase for PEO modifications does not demonstrate an unchanging modulus, but rather a slow increase. The origin of this effect is difficult to explain, given the propensity of PEO to undergo degradation. Macroradicals that escape nitroxyl quenching, either through slow radical-nitroxyl combination or by reversible alkoxyamine thermolysis, would be expected to cleave under these reaction conditions. Nonetheless, the observed induction times abide with predictions based on peroxide half-life and trapping ratios, and the extent of curing during this phase of the process is tolerable from a polymer processing perspective.

In contrast to isobutylene-rich elastomers that are relatively poor H-atom donors, PEO is highly reactive toward cumyloxyl, with a DCP abstraction efficiency of 69% at 160°C [18]. This suggests that 69% of AOTEMPO charged to a PEO formulation will produce the desired macromonomer functionality, with the remaining lost to methyl alkoxyamine. The higher yield of polymer bound acrylate groups supports an oligomerization process that is competitive with backbone scission, thereby resulting in an effective cure. This continues until macromonomer functionality is depleted to the point where crosslinking is no longer dominant, marking the transition to cure reversion [85].

The data plotted in Figure 17 clearly demonstrate the influence of trapping ratio on the transition between phase 2 and 3. At low AOTEMPO loadings, thermolysis of residual DCP after complete

conversion of acrylate groups results in rather severe thermoset degradation. This condition persists up to a trapping ratio of 0.50, but is not observed at 0.75, which provided a stable ultimate cure modulus irrespective of the peroxide loading employed. Note that the highly branched architectures generated through crosslinking reactions are much less prone to degradation than their parent materials, since events on a crosslinked material do not lower molecular weight, but only serve to cleave fragments from the network [86]. As such the thermoset produced at a trapping ratio of 0.75 should be more robust to chain scission than the material generated by a 0.5 trapping ratio. As expected, higher AOTEMPO loadings consumed too much initiator during the induction phase, leaving an insufficient amount of DCP to support the macromonomer oligomerization phase. The result is a stunted crosslinking process that does not suffer from cure reversion, but cannot access the high cross-link density provided by a 0.75 trapping ratio.

Simple stoichiometric cure formulations such as polyethylene + DCP provide a linear relationship between ultimate cross-link density and peroxide concentration. The PEO+AOTEMPO cure yield data plotted in Figure 18, do not follow this simple relationship, as the maximum G' observed for a 0.75 trapping ratio is clearly non-linear. This is not surprising, given the chemistry of AOTEMPO-mediated crosslinking of PEO is much more complex than a standard stoichiometric cure, with the effect of peroxide on PEO itself being complex in its own right [50].

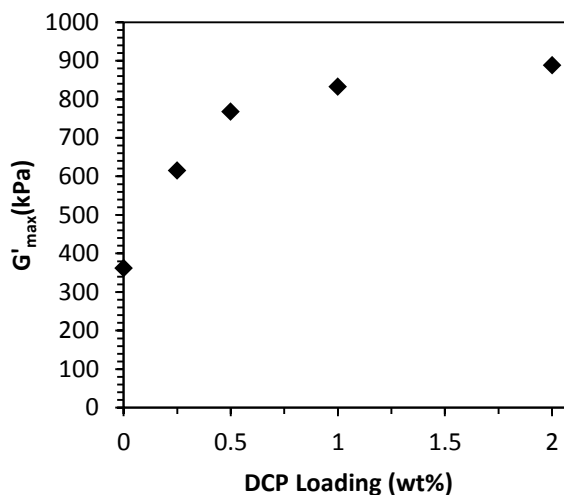


Figure 18: Effect of DCP loading on final modulus achieved of AOTEMPO-mediated cures of PEO at 160°C, 1Hz, and 3°arc.; [AOTEMPO]/(2*[DCP])=0.75

Further insight into the nature of an AOTEMPO-mediated PEO cure was gained by studying the effect of an unbound monomer, butyl acrylate, on the outcome of a nitroxyl-free polymer modification. Figure 19 is a summary of the effect of butyl acrylate had on PEO degradation when charged to a DCP formulation at a concentration equal to the acrylate loadings used in AOTEMPO experiments, what would amount to an equimolar acrylate functionality to the previously examined AOTEMPO cures. The data show that unbound monomer can mitigate PEO degradation when present in relatively high concentration, suggesting that butyl acrylate engages a fraction of the radical population that would otherwise affect the PEO backbone.

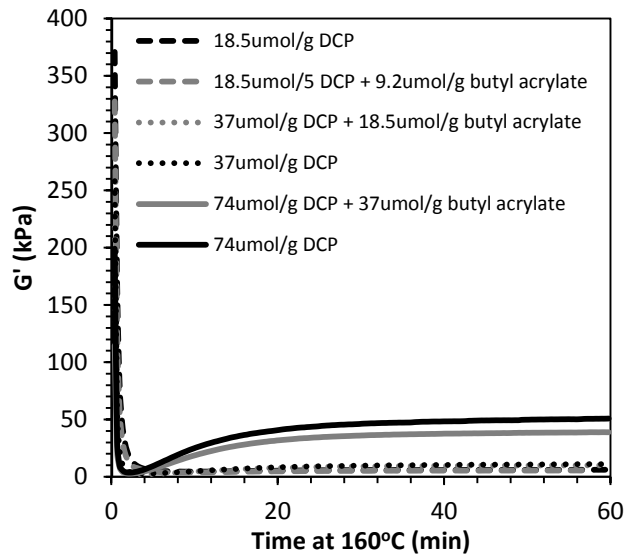


Figure 19: Dynamics of unbound butyl-acrylate monomer on DCP-initiated degradation of PEO at 160°C, 1Hz, and 3°arc

Secondly, the storage modulus increase beyond the 4 min mark indicates that crosslinking occurs immediately following a period of polymer degradation. This may arise from crosslinking reactions of scission byproducts. Emami et al. attempted to discern the mechanistic pathway of peroxide-initiated crosslinking of PEO, but were unable to account for all radical pathways owing to the heightened reactivity of the byproducts generated in the reaction [50]. Discerning the mechanism of this small degree of crosslinking is beyond the scope of this work, especially considering that 74umol/g DCP formulation increased G' to a final value of 50kPa, compared to the final modulus of ~900 kPa achieved using AOTEMPO.

3.3.3 Poly(propylene)

Perhaps the most interesting scission-prone polymer from a commercial standpoint is isotactic polypropylene (PP), which provides a melting temperature on the order of 160°C and a glass transition temperature of about -23°C. The structure of PP gives rise to primary, secondary, and

tertiary macroradicals whose generation by H-atom abstraction is subject to strong entropic effects as well as enthalpic effects. For example, while 64% of H-atom abstraction occurs from the low BDE tertiary position, 28% of successful abstractions are found to occur at primary positions, and just 8% occurring at the secondary position [18]. The tertiary macroradicals formed are far more likely to undergo β -scission than terminate through combination, and therefore PP degrades under the action of peroxides [52, 13, 53].

The relatively high melting temperature leads polymer processing operations to run above 160°C, often as high as 220°C over short periods. This encourages polymer degradation, making the synthesis of PP thermosets by simple radical chemistry particularly challenging. Small amounts of PP gel (<10%) have been achieved with peroxide formulations containing significant concentrations of triallyl or triacrylate coagents [63]. However, more efficient crosslinking processes are needed to provide the improved thermal and mechanical properties commonly associated with polymer crosslinking.

The efficacy of AOTEMPO formulations acting on PP grades of different molecular weight is illustrated in Figure 20. As observed for the PEO system, trapping ratios of 0.25 and 0.50 suffered from substantial cure reversion, owing to excess residual peroxide at the end of the macromonomer oligomerization phase. A trapping ratio of 0.75 was the best of the tested formulations, yielding a stable final modulus that was substantially greater than that of the starting material.

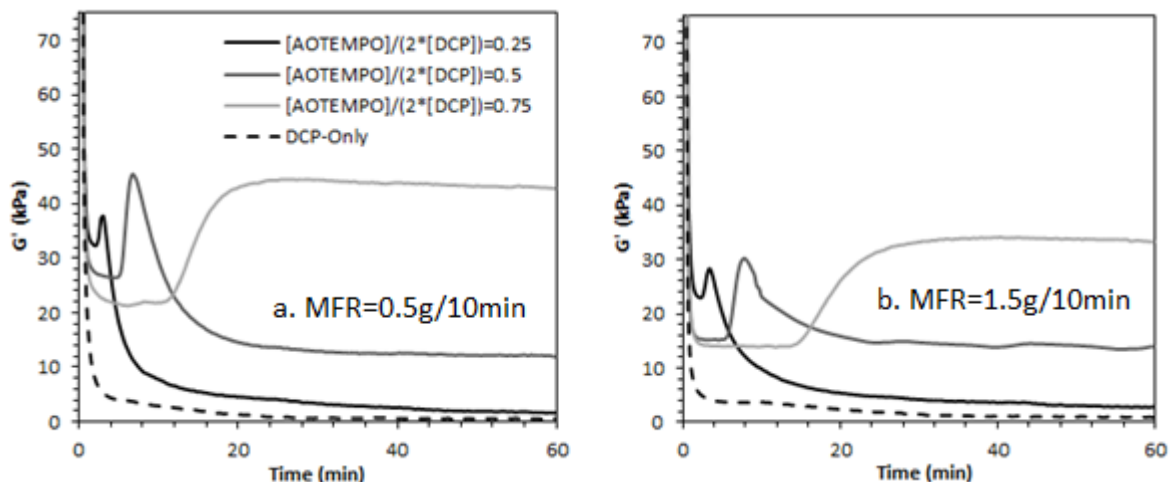


Figure 20: Dynamics of AOTEMPO mediated crosslinking of PP with varying AOTEMPO loadings in two different molecular weights at 165°C, 1Hz, and 3°arc, [DCP]=74 $\mu\text{mol/g}$; a. MFR=0.5g/10min, b. MFR=1.5g/10min.

Note that these reactions were carried out at 165°C, just above the polymer melting point. This is not industrially relevant, since higher temperatures are needed to decrease the melt viscosity and improve process productivity. As noted above, higher temperatures promote β -scission of tertiary alkyl macroradicals. At temperatures required to process isotactic polypropylene, fragmentation of tertiary alkyl radicals is much more prevalent. It also presents challenges in terms of alkoxyamine instability, since the disproportionation of tertiary alkoxyamines to give olefin + hydroxyl amine is significant at the temperatures of interest [24, 26]. The potential therefore exists that AOTEMPO may not trap all PP-derived macroradicals effectively, thereby affecting both the induction and macromonomer oligomerization phases of the process.

Figure 21 contains data acquired at 180°C that demonstrates the effectiveness of AOTEMPO under more severe reaction conditions. A pronounced induction period is followed by a moderate extent of PP crosslinking, with a 0.75 trapping ratio providing the requisite balance of

macromonomer production and conversion to crosslinks. Under these conditions, the higher molecular weight material yielded a higher cure extent than its lower molecular weight (MFI = 1.5 g/10 min) counterpart.

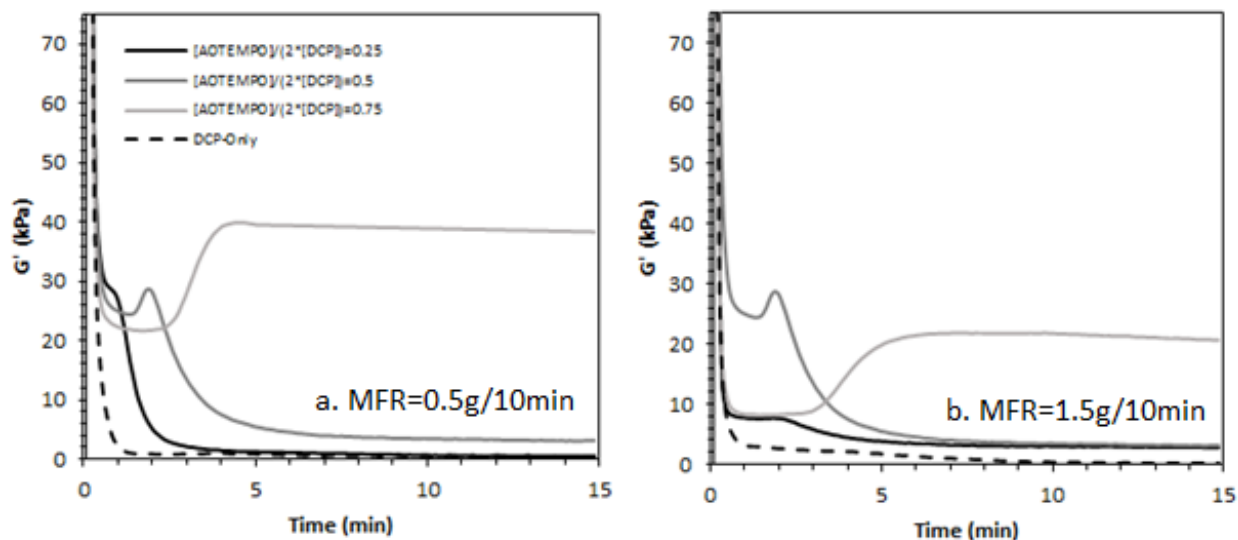


Figure 21: Dynamics of AOTEMPO mediated crosslinking of PP with varying AOTEMPO loadings in two different molecular weights at 180°C, 1Hz, and 3°arc, [DCP]=74 μ mol/g ; a. MFR=0.5g/10min, b. MFR=1.5g/10min.

A closer examination of the data reveals induction times far longer than that predicted by equation 2. Recall that this relationship holds well for nitroxyl-mediated cures of a wide range of saturated polymers as well as diene-based elastomers. Key assumptions underlying its derivation include the rapid, irreversible trapping of alkyl radicals by nitroxyl to give stable alkoxyamine products.

$$t_{ind} = -\frac{1}{k_d} \ln \left[1 - \frac{[AOTEMPO]}{2[DCP]_o} \right] \quad (2)$$

Figure 22 contains plots of observed induction times at 165°C and 180°C along with predictions based on equation 2, which clearly illustrate the extended induction periods incurred for the PP system.

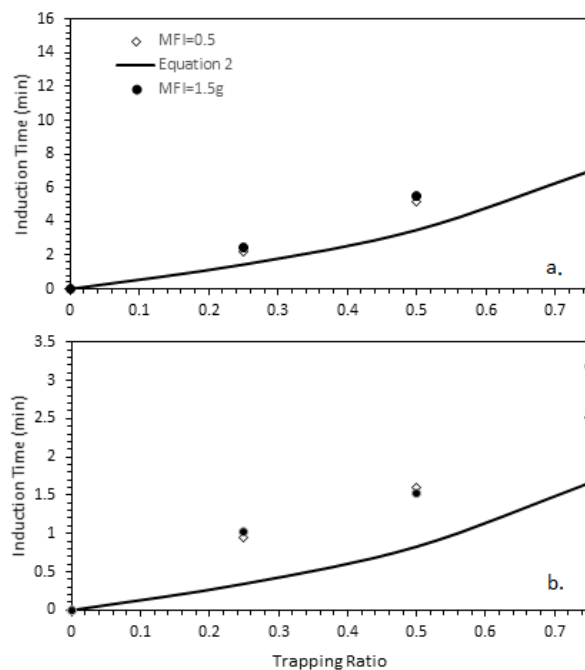
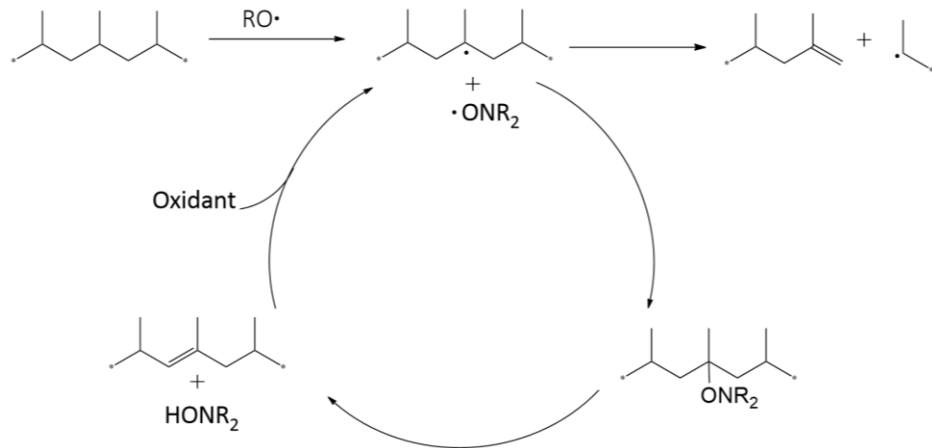


Figure 22: Influence of AOTEMPO on DCP-initiated PP cure dynamics [DCP]=74 μ mol/g; a. 165°C, b. 180°C

This departure from Equation 2 is likely the result of tertiary alkoxyamine instability, as noted above [31]. A potential mechanism is illustrated in Scheme 16, which involves disproportionation to alkene + hydroxylamine, followed by oxidation of the latter to regenerate AOTEMPO. The result of this sequence is the conversion of tertiary macroradicals to olefin, with no net change in the nitroxyl concentration. Hence, the induction period is extended beyond that predicated on the basis of a pathway involving alkoxyamines that are stable with respect to disproportionation [87].



Scheme 16: Proposed mechanism for the extended induction period of nitroxyl-mediated PP reactions.

Figure 23 shows the behaviour of AOTEMPO acting upon PP with a trapping ratio of 0.9. Unlike the PEO system where the oligomerization phase was observed beyond a trapping ratio of 0.95, the PP system showed no change in storage modulus, due to the extended induction phase created through tertiary alkoxyamine instability.

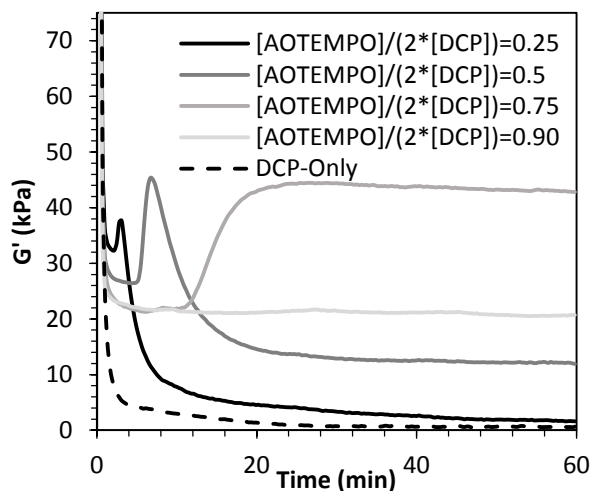


Figure 23: Dynamics of AOTEMPO mediated crosslinking of PP (MFR=0.5g/10min) with varying AOTEMPO loadings at 165°C, 1Hz, and 3°arc

Despite complications associated with radical trapping, AOTEMPO shows remarkable potential to crosslink PP. The gel content measurements listed in Table 2 show that the technology can produce substantial covalent networks, even at 180°C. This single-step process is much more efficient than coagent-based strategies and may also be a cost-effective means of producing long-chain branched PP derivatives for use in polymer processing operations that involve extensional deformations.

Table 2: Gel Content Measurements

Polymer	Reaction Temperature	Gel Content (%)			
		TR = 0	TR = 0.25	TR = 0.50	TR = 0.75
MFR = 0.5	165 °C	0	12	36	89
	180 °C	0	2	15	24
MFR = 1.5	165 °C	0	16	53	74
	180 °C	0	3	12	46

3.4 Conclusions

AOTEMPO-mediated crosslinking of scission-prone polymers is influenced greatly by the H-atom abstraction efficiency of the polymer, as well as the stability of the resulting alkoxyamine. In those systems whose abstraction efficiencies provide an adequate yield of alkoxyamines bearing pendant acrylate functionality, there exists a competitive balance between acrylate oligomerization and polymer degradation. In 6% IP-IIR, AOTEMPO produces a covalent network resistant to chain scission at a trapping ratio of 0.25, however in lower IP grades of IIR, and in PIB, AOTEMPO is incapable of generating significant crosslink density, regardless of trapping ratio or peroxide concentration employed. AOTEMPO-mediated crosslinking of PEO and PP is effective at a trapping ratio of 0.75, generating a stable cure across a variety of peroxide loadings.

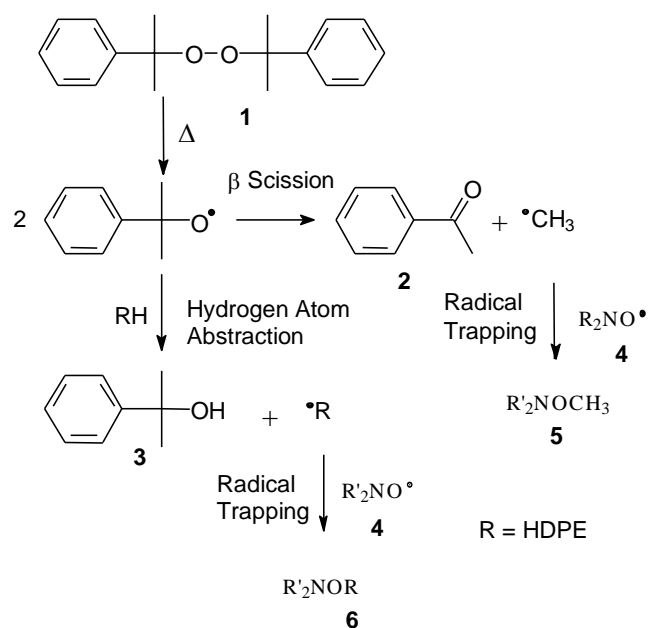
Chapter 4

Spectrofluorometry for the determination of macroradical yields in peroxide-initiated polymer modifications.

4.1 Introduction

To this point there has been significant discussion regarding the importance of H-atom abstraction and radical concentrations in peroxide-initiated polymer modifications. Despite the importance of a polymer's amenability towards H-atom transfer reactions, knowledge surrounding the fundamental chemistry of these free-radical processes has been far outpaced by commercial development. For instance, there is no established method to provide a direct quantitative measure of macroradical concentrations.

Garrett et al. [16] recently examined H-atom abstraction by cumyloxyl from a range of commercial polymers, generating insight into the enthalpic and entropic effects that govern reactivity and regioselectivity. These studies quantified H-atom transfer yields using the abstraction efficiency (AE), which is the yield of cumyl alcohol divided by the total concentration of dicumyl peroxide (DCP). This is illustrated in Scheme 17, which shows that cumyl alcohol (3) is generated by H-atom abstraction from the polymer backbone, in competition with the production of acetophenone (2) through cumyloxyl β -scission. Since these high boiling compounds are easily quantified by gas chromatography (GC), quantifying the amount of each initiator byproduct is a simple means of determining a polymer's H-atom donation reactivity.



Scheme 17: Nitroxyl trapping in DCP-initiated H-atom abstraction from HDPE

While relatively straightforward, the GC method is not applicable to initiators that produce volatile byproducts, such as where t-butoxyl is generated by peroxide thermolysis. A general method is needed to further our understanding of the initiation stage of polymer modification chemistry. Moreover, a need exists for a direct measure of macroradical concentrations in the various phases within polymer blends, as well as the dosage applied by 3D radiation therapy equipment used in cancer treatment.

This chapter presents the validation of a method to quantify initiator-derived macroradical concentrations in a variety of polymer substrates. Fluorescence excitation and emission spectra are presented for NTEMPO-modified HDPE. The synthesis of a model compound for HDPE-NTEMPO is described, and a calibration is developed to determine the abstraction efficiency from different polymers using their fluorescence emission spectra. The report concludes with a comparison of fluorescence results to AE values observed by Garret et al [16].

4.2 Experimental

4.2.1 Materials

DCP (98%), hydroxy-TEMPO (4-hydroxyl-2,2,6,6-tetramethylpiperidin-1-oxyl, 97%), 1-naphthoyl chloride, 1-cyclohexanol, and triethylamine were used as received from Sigma Aldrich(Oakville, ON.)

Atactic –polypropylene (PP, Mw=10000) from Scientific Polymer Products was hydrogenated prior to use by treatment of the polymer dissolved in hexane with platinum supported on carbon at 20bar of H₂, 100°C, for 50h, after which the polymer was recovered by precipitation from acetone and dried under vacuum. PEO (Mw~5,000,000, Scientific Polymer Products) was purified by dissolution/precipitation in DCM/hexanes and dried under vacuum. PIB (Mw~7,700,000, Scientific Polymer Products) was purified by dissolution/precipitation from toluene/acetone and dried under vacuum. Polyethylene (HDPE, SCLAIR 2907, Nova Chemicals), was dissolved in toluene at 90°C and precipitated from acetone before drying under vacuum.

4.2.2 Preparation of alkoxyamine grafts

For semicrystalline materials (PEO and HDPE), 3g of the material was coated with an acetone solution containing 18.5 μ mol/g DCP and a 3X molar excess of NTEMPO, hand mixed and allowed to dry thoroughly. The resulting compound was charged to a DSM micro-compounder, equipped with twin co-rotating screws operating at 100 rpm for 5 initiator half-lives. HDPE products were purified by dissolution in toluene at 90°C and precipitation from acetone, while PEO products were purified by dissolution/precipitation in DCM/hexanes.

For amorphous PIB, 0.5g of the polymer was coated with the DCP + NTEMPO acetone solution and allowed to dry. Samples were then passed through a 2-roll mill to ensure homogeneity. The

polymer was then charged to an Atlas laboratory mixer for 5 initiator half-lives. The product was dissolved in toluene and precipitated from acetone and dried *in vacuo*.

For atactic PP, the polymer was frozen with liquid nitrogen and was weighed into a round bottom flask. The flask was then brought to 100°C in an oil bath to allow for stirring. DCP + NTEMPO were added and the flask transferred to a second oil bath at the required reaction temperature for 5 initiator half-lives. The product was then purified by dissolution in toluene/acetone and dried *in vacuo*.

4.2.3 Synthesis

NTEMPO was prepared as described by Jones et al. [65]

Cyclohexyl-1-naphthoate

Naphthoyl chloride (6.98mmol, 1.33g) in toluene was added dropwise to a solution of 1-cyclohexanol (5.81mmol, 0.58g) and triethylamine (6.98mmol, 0.70g) in toluene at room temperature. The mixture was left to react for 48 hours. The precipitate was removed via vacuum filtration, and the solvent was removed *in vacuo* to yield a yellow oil. The crude product was then dissolved in ethyl acetate (100mL) and washed with HCL (1M) (2x50mL), saturated NaHCO₃(2x50mL), and saturated NaCl (2x50mL). The organic phase was dried with Na₂SO₄, and residual solvent was removed to yield a clear yellow oil which partially crystallized on standing. The crude products was dissolved in dichloromethane and applied to a silica column. The column was eluted with 99% hexanes 1% ethyl acetate to give cyclohexyl naphthoate (0.44g, 43% yield). ¹H NMR (CDCl₃) 8.90(d, 1H), 8.19(dd, 1H), 8.05(d, 1H), 7.89(dd, H), 7.65-7.49(m, 3H), 5.17(tt, 1H), 2.06(m, 2H), 1.85(m, 2H), 1.74-1.36(m, 6H). HRMS (EI): calculated for C₁₇H₁₈O₂ calculated m/z 254.1307 found m/z 254.1298

4.2.4 Instrumentation

^1H NMR spectra were recorded in CDCl_3 at 300 MHz on a Bruker AM-300 spectrometer with chemical shifts reported in ppm relative to TMS. Mass spectra were obtained on an Applied Biosystems QStar XL QqTOF mass 29 spectrometer.

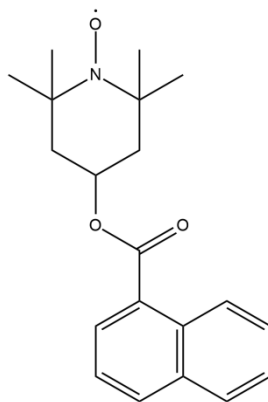
Fluorescence spectra were recorded with a Photon Technology International instrument equipped with a Xenon arc lamp and an excitation monochromator. Detection was done using a photomultiplier tube and digital emission monochromator. Polymer samples were dissolved with the aid of a high temperature oil bath and a heated cuvette holder. The temperature of the sample was confirmed with a thermocouple. Fluorescence measurements were made using tetradecane (~2.5mL) and either a small amount of polymer (0.001g) or a comparable molar amount of a model compound in a stirred cuvette at 130°C. The excitation wavelength was chosen as 280nm, with emission scanned from 290-350nm with peak area taken from 315-400nm.

4.3 Results and Discussion

Fluorescence occurs when a molecule that has been excited into a singlet state relaxes to its ground state through the release of light. Molecules that undergo fluorescence, known as fluorophores, are generally polyaromatic species owing to the low π - π^* energy gap in molecules with highly delocalized electrons. The high sensitivity and low detection limit of fluorescence spectroscopy provides an opportunity to measure the small concentration of alkoxyamines produced by radical trapping of typical polymer modification formulations.

The functionalization of nitroxyls with suitable fluorophores was demonstrated by Blough et al. [88, 89]. These fluorophore-functionalized nitroxyls such as NTEMPO (Scheme 18) prepared by Jones et al. [65] provide an interesting alternative to provide a more direct measure of macroradical concentrations in polymer modifications. The rapid trapping kinetics of nitroxyls

provides a means to trap macroradicals prior to other termination events, generating fluorescent alkoxyamines. This approach was employed by Moad et al. to measure the concentration of primary radicals formed during pulsed laser photolysis of azobisisobutyronitrile [66]. Fluorescent polyolefins have also recently been prepared through free radical modifications of polyolefins, however no attempt was made to determine the macroradical concentrations in the reaction [67].



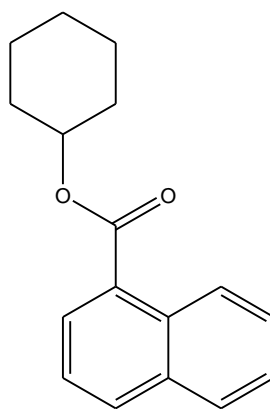
Scheme 18: NTEMPO (4-(1-naphthoxy)-2,2,6,6-tetramethylpiperidine-1-oxyl

Nitroxyls also quench excited electronic states through an electron exchange mechanism, resulting in reduced quantum yields and fluorescence lifetimes. Indeed, even strong fluorophores suffer depressed fluorescence emissions in the presence of a nitroxyl [89, 90]. The combination of the nitroxyl with a carbon centered radical to form an alkoxyamine reduces this quenching mechanism, with alkoxyamines exhibiting quantum yields up to 60 times higher than the parent nitroxyl [89, 88]. For this reason, all polymers were purified by dissolution/precipitation to remove any residual nitroxyl from the functionalized polymer to prevent errors due to nitroxyl quenching.

Furthermore, purification of the polymer following modification also removed Me-NTEMPO from the polymer, which would also make a contribution to the fluorescence emission. This

allowed for the intensity of the fluorescent polymer to be a direct measure of the number of initiator-derived macroradicals generated during the reaction.

For the purposes of calibrating the fluorescence spectrometer, a non-nitroxyl model compound bearing the same fluorophore functionality as NTEMPO was prepared as shown in Scheme 19 . This compound was chosen in place of a nitroxyl to prevent the quenching of excited electronic states.



Scheme 19: Cyclohexyl-1-naphthoate

As seen in Figure 24, the excitation and emission spectra of this compound was nearly identical to that of the polymeric system, allowing for this compound to be used as a calibration standard for fluorescence emission intensity.

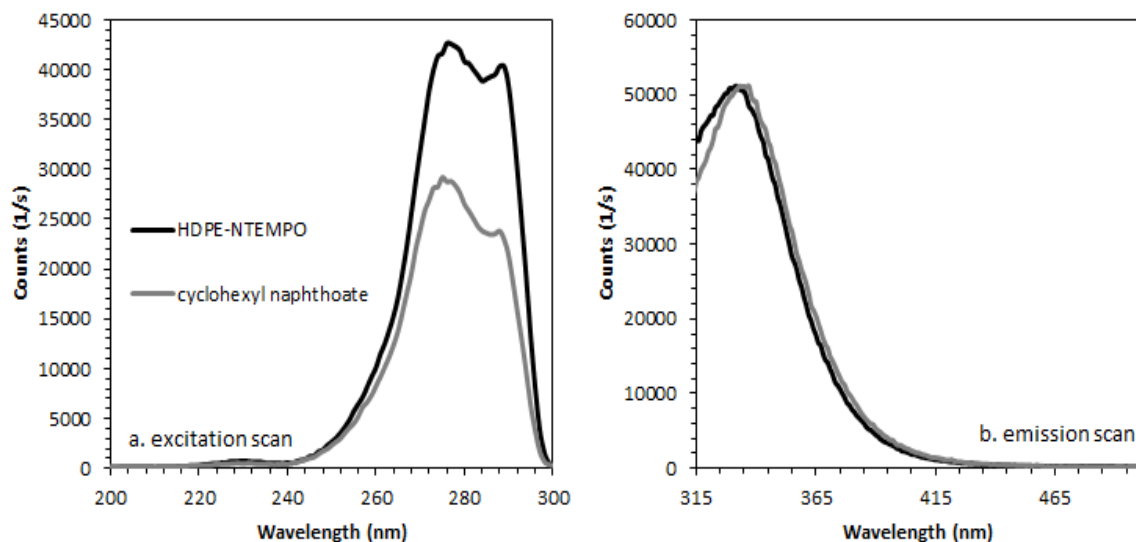


Figure 24: Excitation and Emission Spectra of HDPE-NTEMPO and model fluorophore at 130°C. Excitation scans were made from 150-300nm with emission at 290nm. Emission scans were taken from 300-550nm with excitation at 280nm, with peak areas taken from 315-400nm.

Inaccuracies in emission intensity can occur as a result of photochemical destruction of the fluorophore, known as photobleaching. Consider Figure 25, which displays emission spectra of a sample subjected to repeated excitations. Clear evidence of photobleaching is observed, with a decrease in the fluorescence intensity with an increasing number of scans. Complications associated with this issue were mitigated by storing samples under dark conditions, and using only the first scan to measure peak areas.

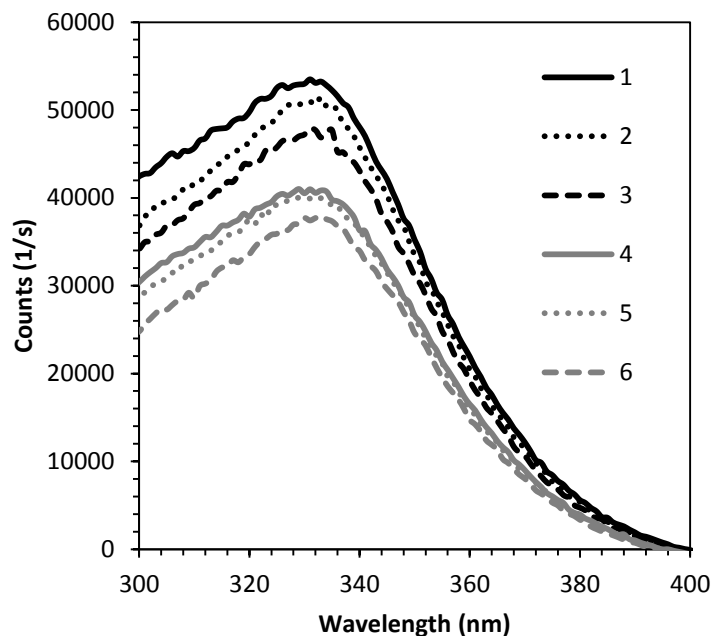


Figure 25: Emission Spectra of HDPE-NTEMPO at 130°C after repeated scans

Note that elevated temperatures are required to dissolve polymer samples in tetradecane. As seen in Figure 26, the emission intensity for a given alkoxyamine is highly temperature dependent. The calibration was therefore performed at 130°C, the same temperature used for analysis of polymer samples. Consider the calibration curve developed for the peak area as a function of concentration of calibration solution displayed in Figure 27.

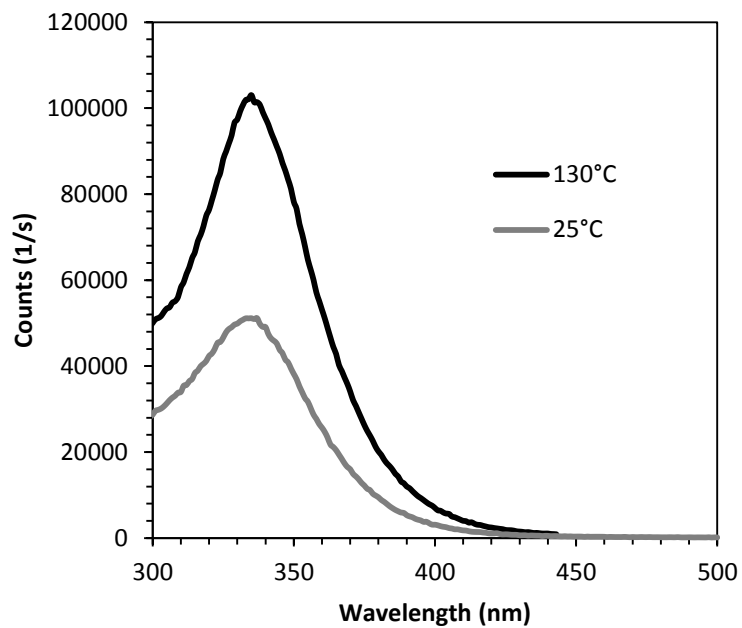


Figure 26: Temperature dependence on the emission intensity of cyclohexyl-1-naphthoate

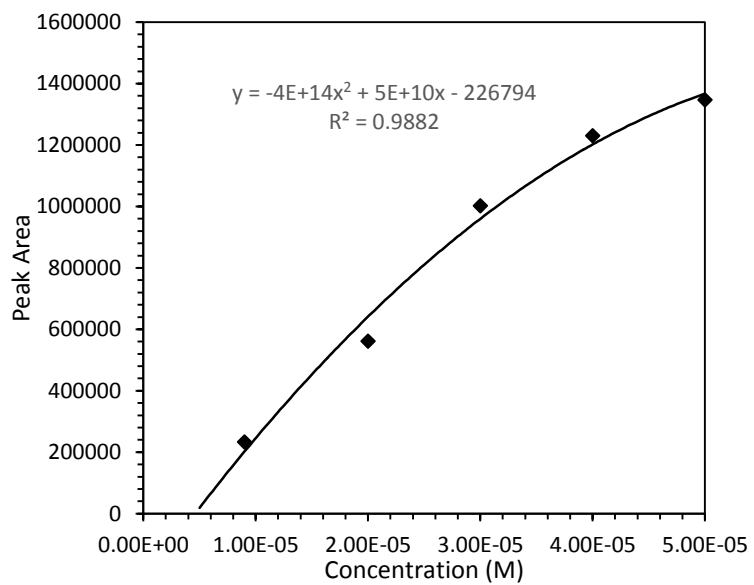


Figure 27: Calibration Curve of cyclohexyl-1-naphthoate in tetradecane at 130°C

Note that this curve is non-linear. Indeed, at high fluorophore concentrations, a phenomenon known as concentration quenching is often observed, in which a significant portion of the fluorescence emission is reabsorbed by fluorophores near the emission site [91]. It is therefore important to remain in a dilute solution regime to prevent this concentration quenching phenomenon from affecting concentration measurements. As seen in this figure, the curve provided an excellent fit to the data, and was therefore used to determine concentration of fluorophore grafted to the polymer. The concentration of fluorophore along with the initial peroxide concentration charged to the formulation was then used to determine the AE through Equation 4.

$$AE = \frac{[RONR_2]}{2 * [DCP]_0} \quad (4)$$

Table 3 lists the abstraction efficiencies from HDPE for a variety of temperatures, as well as a comparison to data generated from GC analysis of abstraction byproducts. As can be seen from this Table, the results of this study compare favourably with the results of the GC fragmentation analysis, with the abstraction efficiency remaining constant over the range of temperatures examined. Very good agreement was also observed in the AE of PIB at all three tested temperatures between the two methods. This suggests that spectrofluorometry can be used effectively to determine macroradical concentrations in polymers which lead to the formation of thermally stable alkoxyamines. Furthermore, the use of fluorescence allows for determination of abstraction efficiencies of different peroxides with volatile decomposition products which are not easily quantified by GC. An additional benefit of this method would be its application to polymer blends, as this method may allow for the determination of abstraction efficiency from the different phases of a blend, which is not possible through simple analysis of abstraction byproducts.

Table 3: Abstraction efficiency from saturated polymers determined through direct measurement of alkoxyamines by spectrofluorometry in comparison to indirect measurement of abstraction by-products by GC [18].

	Temperature (°C)	HDPE	PEO	PP	PIB
GC	140	0.63	0.74	0.37	0.18
	150	0.63	0.70	0.37	0.16
	160	0.56	0.69	0.37	0.17
Fluorescence	140	0.67	0.89	0.50	0.18
	150	0.67	0.68	0.27	0.20
	160	0.66	0.94	0.57	0.17

Inconsistencies do appear however in PEO and PP, where AE values were significantly higher than those recorded in the GC analysis. Alkoxyamines resulting from macroradical trapping in these polymers may be prone to alkoxyamine instabilities. For instance, previous chapters have demonstrated that PP-derived alkoxyamines are prone to thermal decomposition. It is difficult to discern if these inconsistencies are a result of alkoxyamine instabilities, or inherent limitations of the experimental method. For instance, atactic PP is a very viscous waxy solid, and errors observed in the AE measurements of this material may be due to errors in material handling. For instance, if PP remained on the walls of the flask and was not engaged in the reaction, the concentration of peroxide in the PP would be higher than predicted, and could lead to artificially inflated AE values. However as the technology is in its infancy, the results are very encouraging, and with further refinement this method can be expected to provide a sensitive and cost-effective method for the determination of macroradical concentrations generated in peroxide-initiated modifications.

4.3.1 Conclusions

Fluorescent nitroxyls can be used effectively in conjunction with peroxides to generate polymer-bound fluorescent alkoxyamines. Spectrofluorometry provides a method to obtain direct quantitative measures of these polymer-bound alkoxyamines, and thus a direct measure of initiator-derived macroradicals. This method produced results comparable to those obtained from analysis of abstraction by-products through GC for polymer systems that could be expected to form thermally stable alkoxyamines. Polymers that may be expected to form thermally unstable alkoxyamines, PP and PEO, exhibit variations in AE with temperature, and deviate significantly from the AE values obtained through GC-analysis. Data surrounding thermal stability of alkoxyamines at elevated temperatures is limited, and it is unclear if these deviations arise due to alkoxyamine instabilities or due to measurement error. Fundamental studies on the effect of macroradical structure on alkoxyamine stability at temperatures relevant to polymer processing would provide significant insight into the applicability of this analytical method to different polymer systems.

Chapter 5

Conclusions and Future Work

5.1 AOTEMPO-mediated crosslinking

The effect of AOTEMPO on the rate and yields of peroxide cure formulations for a variety of polymer systems has been studied. It was found that AOTEMPO functioned remarkably well in saturated polymer systems, producing predictable periods of complete suppression of crosslinking, as well as complete recovery of crosslink density.

The ability of AOTEMPO to delay the onset of crosslinking was found to be limited by the thermal stability of alkoxyamines generated in macroradical trapping reactions. In those polymer systems where macroradical derived alkoxyamines are susceptible to thermolysis, although significant delayed-onset action was achieved, complete crosslinking suppression was not observed.

The ability of acrylate oligomerization of ATOEMPO to recover crosslink density was found to be limited in systems that present labile H-atoms to undergo chain transfer reactions, with no improvement observed in AOTEMPO cures in comparison to TEMPO formulations.

Furthermore, in unsaturated polymers where oligomerization of C=C on the backbone plays a significant role in crosslink density, the use of nitroxyls leads to losses in crosslink density much greater than a result of stoichiometric radical trapping. These increased losses to cure yields are attributed to kinetic chain leveraging by nitroxyls.

5.2 AOTEMPO-mediated crosslinking of scission-prone materials

Polymers that degrade in the presence of peroxide can be made to cure to high extent by post reactor modification to form macromonomers bearing pendant oligomerizable functionality prior to peroxide treatment. These macromonomer cures progress through very high rates of cure making them prone to scorch. In this work an alternative approach to generating peroxide curable derivatives of scission prone materials was examined, in which AOTEMPO was used to generate macromonomers in-situ. It was found that the ability of AOTEMPO to generate a cure in these materials is determined by the reactivity of the polymer towards H-atom transfer reactions. Materials with poor reactivity such as isobutylene-rich elastomers show limited potential to generate thermosets in AOTEMPO-mediated peroxide cure formulations. AOTEMPO-mediated crosslinking of PEO and PP was found to be effective, curing articles to a high extent. AOTEMPO produced induction times much longer than expected from simple irreversible macroradical coupling in PP, likely a result of catalytic regeneration of the nitroxyl when alkoxyamine is thermally unstable.

5.3 Spectrofluorescence for quantification of macroradical concentrations

A method has been developed for the quantification of macroradical concentrations in peroxide modifications through the use of high temperature spectrofluorometry. It was found that through the use of a suitable alkoxyamine analog a calibration can be performed to provide a direct measure of initiator derived macroradicals in peroxide modifications in a variety of polymer systems. The application of this method was found to be most applicable to polymer systems that lead to thermally stable alkoxyamines.

5.4 Future Work

5.4.1 Alkoxyamine stabilities at temperatures relevant to polymer processing operations

The importance of alkoxyamine stability has been highlighted in this study. While significant data exists for alkoxyamine stability at lower temperatures for long-term use applications, little data exists for stability of alkoxyamines at the temperatures required for processing operations.

While many previous studies have attempted to determine the mechanism of alkoxyamine instabilities, insight into the alkoxyamine stability at elevated temperatures is required to further advance this technology.

The stability imparted upon the thermoset by generating a HALS-like alkoxyamine in-situ should also be examined, as these AOTEMPO-mediated thermosets may provide increased thermal and oxidative stability than their peroxide-only analogs. Should these AOTEMPO-mediated thermosets provide long term stability, significant economic and environmental savings could be achieved in industrial processes, as AOTEMPO could function both as a short term and long term antioxidant.

5.4.2 AOTEMPO-mediated crosslinking of TPV blends

The ability of AOTEMPO to generate thermosets from polymers that typically degrade in the presence of peroxides like PP leads to very interesting possibilities in the context of TPV blends.

In many blends, one phase is continuously crosslinking while a second phase suffers degradation, with poor interfacial interactions between the different phases. Interfacial adhesion however is essential in developing a blend with consistent physical and mechanical properties. The use of AOTEMPO in peroxide crosslinking of these blends could therefore lead to crosslinking in both phases, providing superior blend compatibilization and improved processing characteristics. For

instance, the crosslinking of both phases would result in consistent viscosities between the two phases which could significantly simplify mixing to achieve consistent phase distribution.

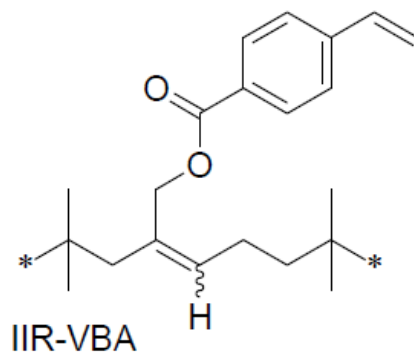
Knowledge of macroradical concentrations in the different polymer phases of these blends would provide significant insight into the resulting chemical and physical properties obtained in AOTEMPO-mediated crosslinking of these blends.

5.4.3 AOTEMPO mediated production of LCB-PP Derivatives

Long chain branched PP provides improved melt strength for applications involving extensional deformations. LCB-PP derivatives are typically produced through the use of coagents, leading to bimodal molecular weight distributions consisting of degraded and slightly branched chains, as well as a minor population of hyper-branched chains. Melt elasticity and extensional properties are enhanced when the molecular weight of these hyper branched chains exceeds the gel point. The use of AOTEMPO provides an interesting alternative for the production of these LCB-PP derivatives, and may in fact lead to the production of unimodal hyperbranched LCB-PP.

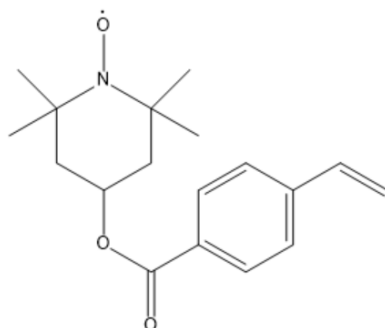
5.4.4 Alternate functional groups for nitroxyl-mediated crosslinking of scission prone polymers

Although AOTEMPO has been shown to be very effective in crosslinking PEO and PP, it has shown limited utility in generating thermosets from isobutylene-rich elastomers. The performance of functionalized nitroxyls in isobutylene-rich elastomers may be vastly improved through the use of a more reactive functional group, enabling for higher cure yields to be achieved with decreased peroxide concentrations. For example, although an acrylate grafted butyl rubber macromonomer was found to generate a significant crosslink density, the vinylbenzoate grafted butyl rubber macromonomer (Scheme 20) exhibited far superior reactivity to DCP at 160°C [30].



Scheme 20: IIR-VBA macromonomer shown to have increased reactivity in comparison to IIR-AA.

As few radical species are required to cure IIR-BVA to a high extent, it is assumed that the performance of VBA-TEMPO would be less dependent upon yield of polymer bound alkoxyamines to generate crosslinked thermosets than AOTEMPO. The use of a VBA-TEMPO (Scheme 21) may therefore provide the increased reactivity required to overcome degradation of isobutylene and generate substantial cures in PIB and commercial grades of IIR.



Scheme 21: VBA-TEMPO

5.4.5 Extension of Fluorescence technique to polymer blends and radiation dosimetry

The fluorescence method developed in this report poses significant potential towards gaining additional understanding of the role of peroxides in the generation of TPV blends. Recall that the

phase segregation of peroxides is essential in determining the properties of the blend. The use of this method may then provide additional insight into the concentration of macroradicals in the different polymer phases, allowing for improved knowledge with regards to the origins of TPV properties.

The use of fluorescence for radiation dosimetry poses significant potential for commercial opportunity. Current methods of radiation dosimetry require the use of toxic reagents and cost-prohibitive analytical equipment. Spectrofluorescence allows for the use of a cost-effective analytical technique that does not require the use of highly toxic reagents.

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Appendix

^1H NMR for cyclohexyl-1-naphthoate

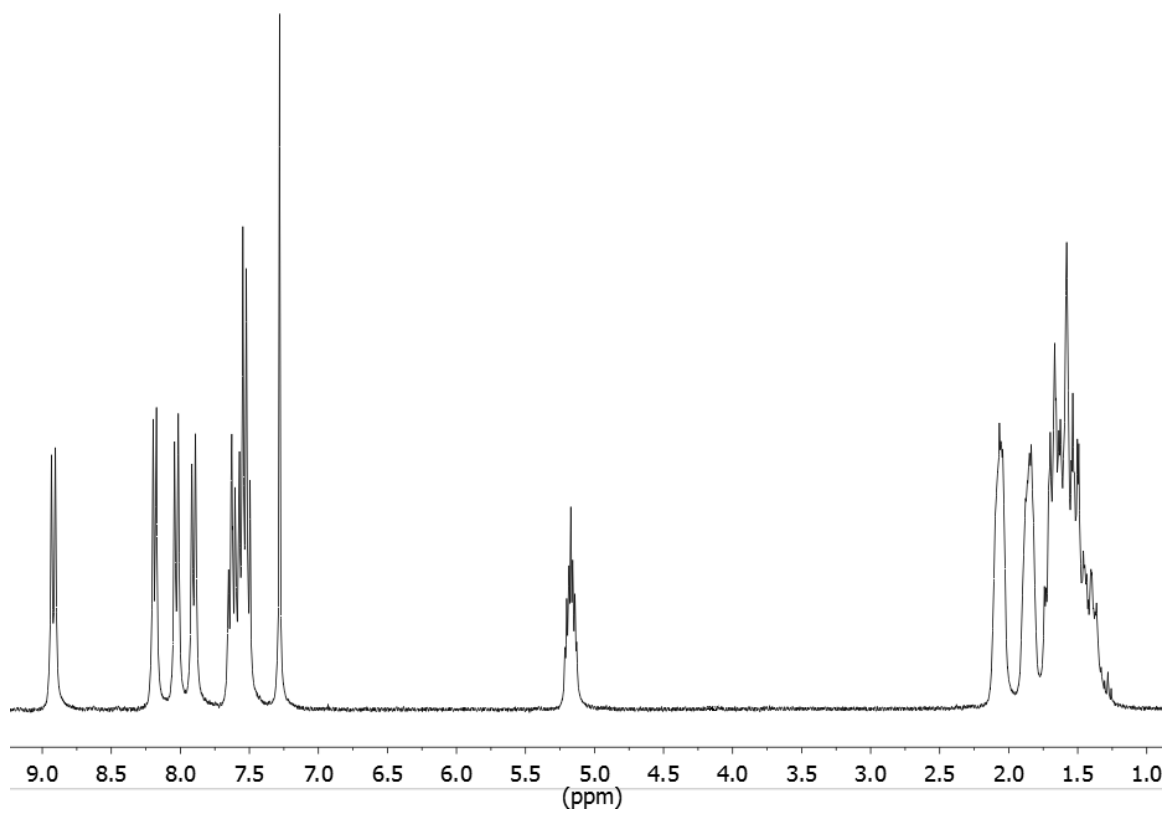


Figure 28: ^1H NMR of cyclohexyl naphthoate