Delayed-onset Polymer Cross-linking using Functional Nitroxyls

by

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Abstract

New polymer cure chemistry is described, wherein the onset of free radical cross-linking is delayed without compromising cure yields. The addition of an acrylate-functionalized nitroxyl, 4-acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl (AOTEMPO), to a peroxide-cure formulation quenches free radical activity during the initial stages of the cross-linking process, trapping alkyl radicals as alkoxyamines that bear acrylate functionality. Polymer cross-linking by macro-radical combination is suppressed until all nitroxyl is consumed, at which point radical oligomerization of polymer-bound acrylate groups generates the desired covalent network. As a result, cross-link density losses incurred during radical trapping are recovered during the oligomerization phase of the process. The effectiveness of this approach is demonstrated for a range of polymers, peroxide initiators, reaction temperatures and reagent loadings. Furthermore, AOTEMPO formulations are compared directly to other delayed-onset additives that are used in commercial practice.

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To my parents, John and Jayne, your love and encouragement have helped me to make the most of my youthful years. Thank you for instilling a desire for learning and value for education into my life. One could not possibly receive more devotion and selfless love than that which I have received from you.

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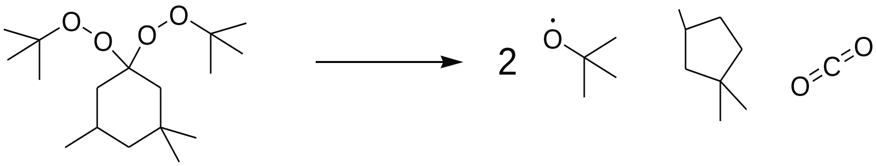
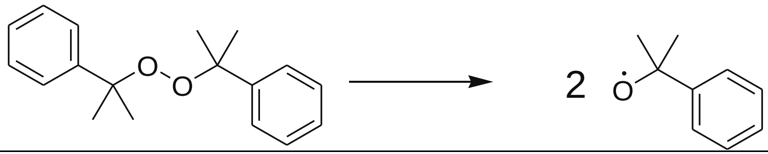
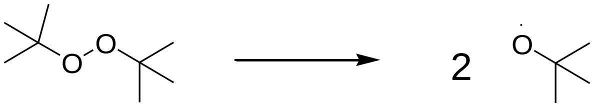
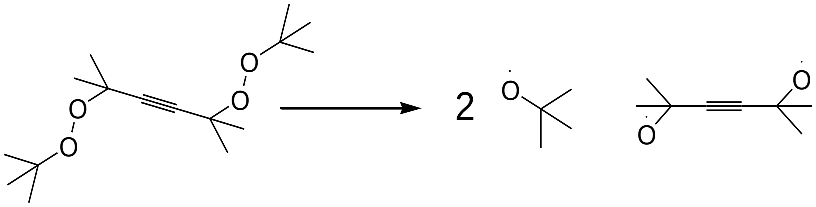
1.1. Fundamentals of Peroxide-initiated Polyolefin Cures

1.1.1. Polymer macro-radical generation by dialkyl peroxides

Organic peroxides are commonly used to initiate radical-mediated processes for curing or grafting purposes. Thermosensitive O-O bonds undergo homolysis at elevated temperatures to yield two oxygen-centred radical species. These radicals are capable of abstracting hydrogen from hydrocarbon sources to generate reactive carbon-centred radicals. This is particularly valuable, since polyolefins that are not amenable to ionic chemistry may instead be activated by radical reactions.

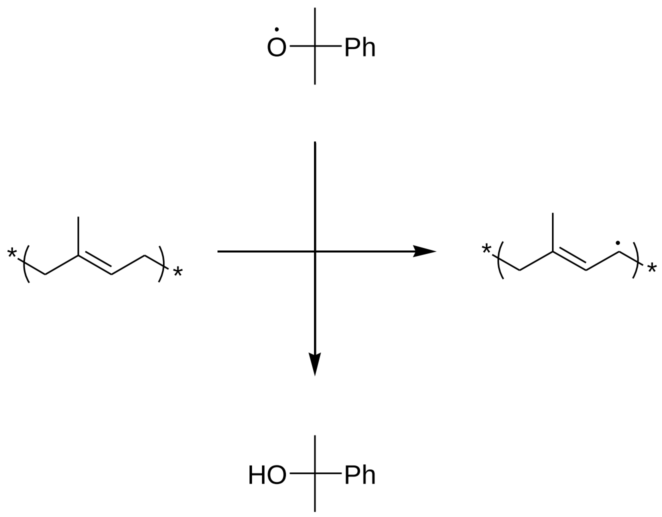
Peroxides are chosen based on thermal stability and decomposition products. Various peroxides exhibit decomposition over a wide range of temperatures, making organic peroxides versatile and applicable to many polymeric systems. Peroxides that degrade rapidly (more reactive at lower temperatures) typically have decomposition radical products with greater stability. Consider the half-lives of some well-known organic peroxides listed in Table 1.1.

Table 1.1. Stability of some various commonly used organic peroxides

	Temp. (°C)	Half-life (min)
1,1-Bis(*t*-butylperoxy)-3,5,5-trimethylcyclohexane 	130	9.36
	160	0.713
	180	0.155
Dicumyl peroxide 	130	137
	160	5.67
	180	0.86
Di-*t*-butyl peroxide 	130	581
	160	19.2
	180	2.54
2,5-Dimethyl-2,5-di-(*t*-butylperoxy)hexyne-3 	130	718
	160	26.5
	180	3.74

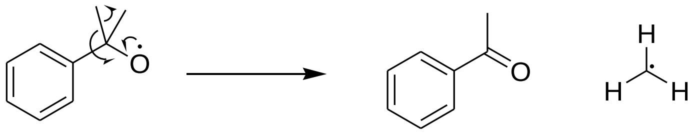
Dicumyl peroxide (DCP) is the initiating species of choice for this work, due to its moderate rate of decomposition at polyolefin modification temperatures, and its easily identifiable, stable decomposition byproducts. The cumyloxy radicals generated by DCP decomposition can abstract hydrogen from saturated hydrocarbons to form carbon-centred radicals of varying thermodynamic stability (Scheme 1.1). Rates of hydrogen abstraction by oxygen-centred radicals are quite high; *t*-butoxy radical abstraction rate constants in solution are reported to be on the magnitude of 10^6 - 10^7 $M^{-1}s^{-1}$ at 160°C

[1]. Successful abstraction and regioselectivity is determined by steric hindrance and resulting alkyl radical stability.



Scheme 1.1. Oxygen-centred radical abstracting hydrogen from polyisoprene

The fragmentation of cumyloxyl to acetophenone + methyl radical is more prevalent when the polymer is a poor hydrogen atom donor [2], and when temperatures are increased [1] [3]. At 40°C, *t*-butoxyl fragmentation/abstraction rate constants in cyclohexane are 1.5 x 10^5 s^{-1} [4] and 5 x 10^6 s^{-1} respectively, while at 160°C, the fragmentation rate constant is 5 x 10^6 s^{-1} [1] and that of abstraction is 1.5 x 10^7 s^{-1} [1].



Scheme 1.2. Cumyloxy radical fragmentation to yield carbon-centred methyl radical and acetophenone

Although methyl radicals are of comparable thermodynamic stability to alkoxy radicals, they are less reactive in hydrogen atom abstraction from electron rich alkanes. At temperatures in the range of

160°C - 200°C, some authors believe the species to be of high enough energy to abstract hydrogen from polyethylene [5] while others state addition to unsaturated sites is nearly exclusive [1][6]. The latter conclusion is supported by the rate constant for methyl radical addition to methyl acrylate at 160°C, reported to be 2-3 x 10^6 M^{-1} s^{-1} [1] while the rate constant for abstraction from isooctane is of the order of 1.2 x 10^4 M^{-1} s^{-1} [6]. The presence of methyl radicals in polyolefin modifications can generate a variety of cross termination products with other radicals, and can complicate the cure chemistry of more complex cross-linking formulations that include radical traps and cure-boosting coagents.

1.1.2. Ease of hydrogen atom abstraction

The reactivity of a polymer as a hydrogen atom donor can be defined by an ‘abstraction efficiency’, which is the fraction of oxygen-centred radicals that successfully abstract hydrogen from the hydrocarbon backbone to generate a macro-radical species. For example, if 8 moles of peroxide decompose in a polyethylene melt to generate 16 moles of cumyloxy radicals, which in turn lead to the formation 10 moles of macro-radicals, the abstraction efficiency would be 62.5% (100 * 10 / 16 = 62.5%). FT-IR measurements of acetophenone and cumyl alcohol by-products estimate the abstraction efficiency from polyethylene to be near 65% [7].

The abstraction efficiencies of polymers can vary significantly, owing to differences in their reactivity toward hydrogen atom transfer. In general, abstraction from a polymer is rapid when it presents hydrogen atoms that are not sterically encumbered, and the resulting carbon-centred radical is more thermodynamically stable than the abstracting species. Stabilization of a macro-radical by hyperconjugation and π-resonance makes hydrogen atom transfer more exothermic, thereby accelerating the process. Consider the series of carbon-centred radicals illustrated in Figure 1.1. All of these radicals are transient species with very short lifetimes. However, they differ substantially in terms of the lability of their hydrogen atoms and, hence, their reactivity toward cumyloxy radicals. For the linear low density polyethylene (LLDPE) cure formulations of interest to this work, secondary alkyl radicals are expected to be most abundant, while tertiary radicals generated from a small concentration of branch points and allylic radicals produced from very small unsaturation contents may contribute to the macro-radical population.

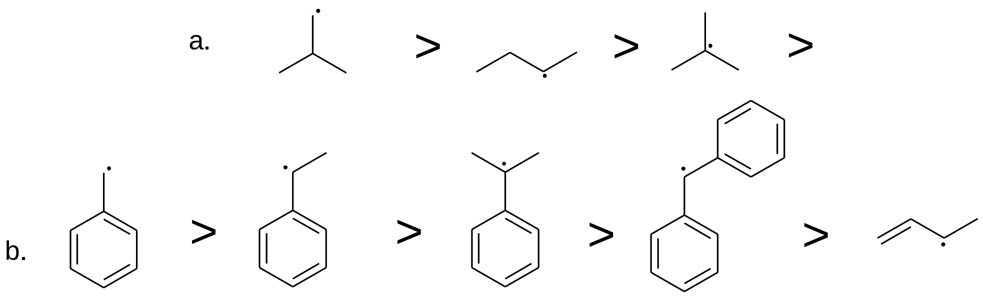
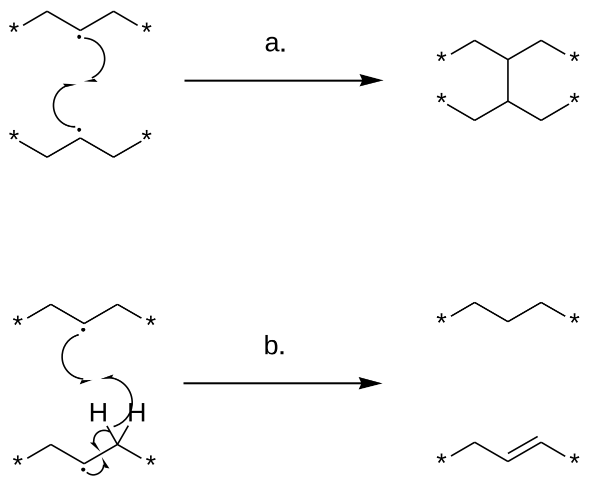


Figure 1.1. Hierarchy of alkyl radical reactivity defined as ability to abstract hydrogen arising from a) steric hindrance and b) steric hindrance & resonance stabilization [8]

1.1.3. Radical termination

The intermediates that support polyolefin cures are transient radicals with lifetimes on the order of milliseconds. This is a consequence of the extremely fast rate of radical termination to generate non-radical products through disproportionation and/or combination (Scheme 1.3). While combination yields a covalent cross-link between two polymer chains, disproportionation of two macro-radicals has no immediate effect on the polymer`s molecular weight.



Scheme 1.3. Alkyl macro-radical termination by a) combination and b) disproportionation

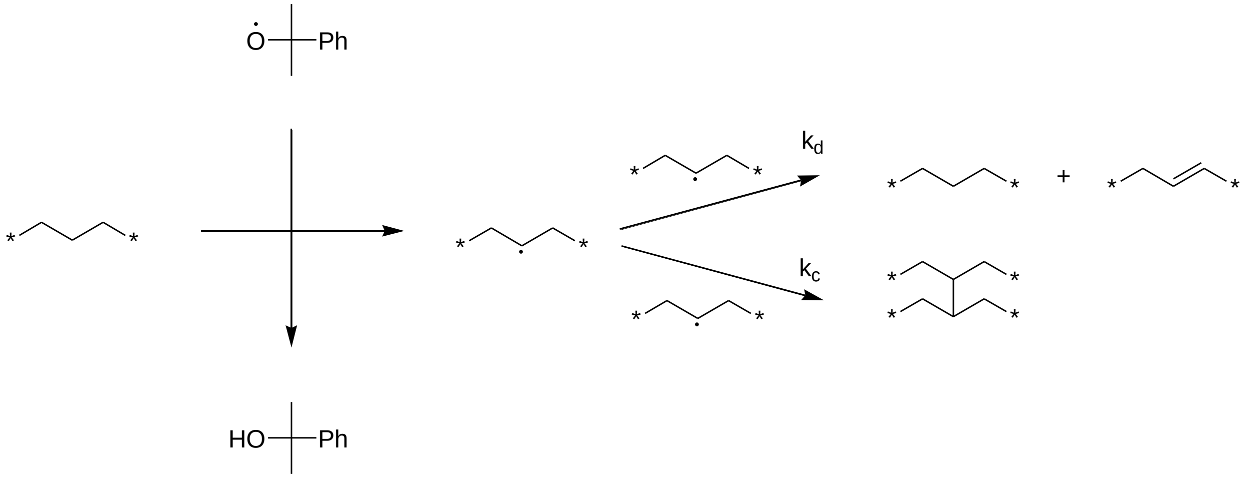
In low viscosity solution, alkyl radical termination proceeds at the diffusion limit of reaction velocities, with bimolecular rate constants order of 10^8 - 10^9 $M^{-1}s^{-1}$ [9][10][11][12][13][14][15]. The corresponding rate constants for high viscosity polymer melts are not as well understood [16], but evidence suggests that termination rates in these systems are considerably lower [17] [13].

Since radicals are generated in pairs and they terminate in pairs, the yield of peroxide-only cure formulations cannot exceed the initiator loading. Hence, polymer cures based on a macro-radical combination mechanism are referred to as a ‘stoichiometric cures’, a term that is based on the proportionality between the number of cross-links formed and the number of radicals introduced by initiator thermolysis. In practice, the yield of carbon-carbon cross-links can be considerably less than the peroxide concentration, given the limited abstraction efficiency of most initiators, and the propensity of alkyl radicals to undergo disproportionation in competition with combination.

1.2. Polyolefin Cross-linking Dynamics

1.2.1. Polyethylene cross-linking by dicumyl peroxide

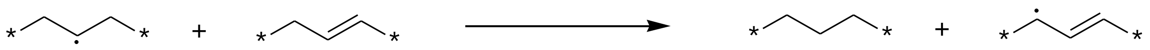
Cross-linking polyethylene improves dimensional stability as well as resistance to abrasion, impact and chemicals [2]. Polyethylene also has favourable dielectric properties, making it ideal for applications such as wire coating [2] [18].



Scheme 1.4. Polyethylene combination pathways leading to polymer unsaturation and cross-links in presence of dicumyl peroxide

Cumyloxy and methyl radicals formed from dicumyl peroxide thermolysis abstract hydrogen from polyethylene to generate macro-radicals that subsequently combine to yield cross-links, or disproportionate to yield unsaturation in the polymer backbone. About 50-60% of polyethylene macro-radicals are reported to terminate to yield cross-links while 30% disproportionate [3]. Representative secondary alkyl radical model compounds agree, reporting k_d/k_c of 1.0 – 1.2 [19]. Further studies with cyclohexane radicals report cyclohexene:bicyclohexyl product ratios of 1.1 [20].

Strong evidence using Electron Spin Resonance (ESR) spectroscopy supports the formation of resonance-stabilized allyl radicals by alkyl radical abstraction during the later stages of curing (Scheme 1.5) [21]. Allyl radicals terminate exclusively by combination to yield cross-links.



Scheme 1.5. Allylic abstraction in polyethylene to generate stable allyl radicals that terminate exclusively by combination

1.2.2. Scorch protection

Manufacturing processes aim to cure articles as fast as possible in order to maximize throughput. As a result, rapid cross-linking reactions are highly desired. For simple peroxide-initiated systems, DCP cross-linking of linear low-density polyethylene (LLDPE) included, the rate of cross-linking is dictated by the rate of peroxide decomposition and can, therefore, be managed quite easily by changing the organic peroxide, peroxide loading and reaction temperature. However, there are drawbacks associated with rapid cures, particularly when the thermoset article must be formed into intricate shapes prior to being cross-linked to the point where it can no longer be processed. Consider the data in Figure 1.2, which presents the storage modulus of a polyolefin that is undergoing cross-linking by peroxide. The rapid increase in the earliest stages of the cure can be problematic, since a low viscosity is required to allow the polymer to conform to the shape of a mold. Cross-linking that is too rapid to support material processing is commonly referred to as ‘scorch’, and additives that dampen this are often called ‘scorch inhibitors’, ‘scorch protectants’ or ‘scorch retarders’.

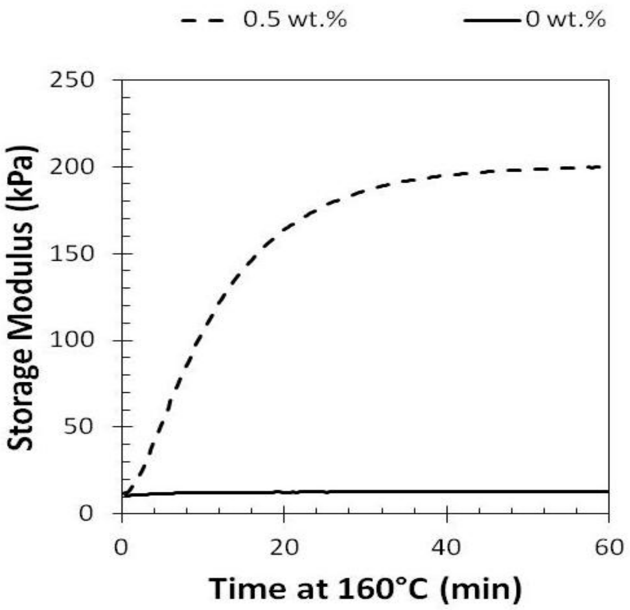


Figure 1.2. Linear low-density polyethylene cross-linking in the presence of dicumyl peroxide

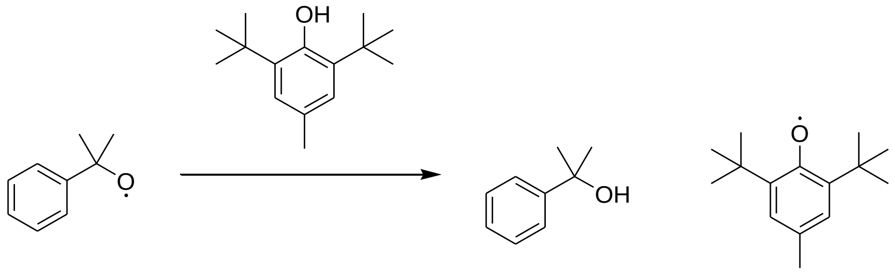
In some cases, scorch problems can be mitigated by processing the melt at a lower temperature, since this slows the rate of peroxide thermolysis. Once the melt has filled the mould, extruded to the desired profile, or otherwise formed into the required shape, it can then be heated further to decompose the peroxide more rapidly. This can be effective for polyolefins that have low melting points, but can present problems whenever high temperatures cannot be avoided for reasons of high melting temperatures or high melt viscosities [2].

1.2.3. Scorch protectants

Ideally, scorch additives prevent all polymer cross-linking until they are completely consumed. The effectiveness of a scorch inhibitor is dictated by the duration of scorch delay that it provides, and the effect it has on the cure extent of the thermoset properties. Additional consideration is also given to other material properties, such as adhesion and the presence of volatile organic compounds. A number of scorch retarders have been developed and applied commercially, each working on different principles to provide scorch protection.

1.2.4. 2,6-Di-*t*-butyl-4-methylphenol

2,6-Di-*t*-butyl-4-methylphenol (butylated hydroxyl-toluene, BHT) is a widely used antioxidant, whose rapid hydrogen atom donation to oxygen-centred and carbon-centred radicals quenches these intermediates, yielding relatively resonance-stabilized phenoxy radicals. Their inactivity in hydrogen atom transfer and radical additions makes termination the principal mode of phenoxy radical consumption. Indeed, electron spin resonance studies of peroxide-initiated polyethylene cross-linking have confirmed that BHT generates a population of phenoxyl intermediates whose concentration decays before evidence of macro-radials can be found [22].

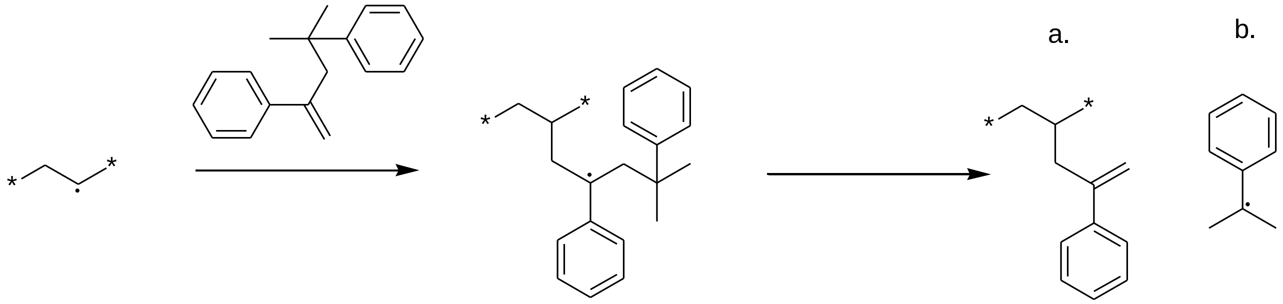


Scheme 1.6. Cumyloxyl H-abstraction from 2,6-di-*t*-butyl-4-methylphenol

The ability of phenolic antioxidants to quench initiator-derived alkoxy radicals as well as alkyl macro-radicals makes BHT applicable to a wide range of polymers and initiating systems. However, polyolefin cross-linking progresses only by macro-radical combination, meaning that the loss of macro-radical yields to BHT result in a proportional decline in cross-link density. Therefore, phenolic antioxidants provide scorch protection at the expense of cure yield.

1.2.5. 2,4-Diphenyl-4-methyl-1-pentene

2,4-Diphenyl-4-methyl-1-pentene (methyl styrene dimer, MSD) is a well-known chain-transfer agent for styrene polymerization [23] and has proven to be an effective additive in polyethylene cure formulations, providing scorch protection when applied at 145°C, and increasing cure extents when used at 180°C [24].



Scheme 1.7. Polyethylene macro-radical addition to 2,4-diphenyl-4-methyl-1-pentene and subsequent fragmentation

MSD is designed to quench radical intermediates by radical addition to the C=C bond, yielding a benzylic radical intermediate. Fragmentation to an α-substituted styrenic group + a cumyl radical transforms what was once an initiator-derived radical or a polymer macro-radical into a resonance-stabilized radical intermediate [24] [20] [25]. Cumyl radical termination by combination and disproportionation quenches radical concentrations, while the unsaturated end-group of the polymer may engage in further radical chemistry. From a curing perspective, if MSD is activated by a macro-radical to yield an unsaturated, MSD capped polymer chain, the resulting macromonomer may still contribute to the cross-link network at a later time by oligomerization of the styrenic functionality.

The mechanism of MSD action has received a considerable attention. DCP-initiated model compound studies (0.02 M) of concentrated MSD (2.0 M) in cyclohexane (4.7 M) at 140°C for 15h by Watanabe et al. generated two significant conclusions [20].

1) 47.5% of cumyloxy radicals had preference for addition to MSD over abstraction.

2) Radical abstraction occurred exclusively by cumyloxy radicals; nearly all methyl radicals added to MSD. This is confirmed by multiple sources reporting rate constants for methyl radical affinities for olefin monomers.

Suyama et. al examined the effect of MSD on peroxide-initiated reactions of polyethylene and model hydrocarbons [26]. Their model compound reactions involved 0.2 M di-*t*-butyl peroxide and 0.1 M MSD in *n*-undecane (4.7 M), which are much more concentrated than typical polymer reactions, but more considerably milder than those done by Watanabe et al. The reaction was only run until 19% of peroxide was decomposed at 140°C, limiting the study to be representative of only the initial stages of a polymer cure. Regardless, a few important conclusions were derived from this work.

1) 94% of the MSD ended up as the undecane addition product, 2-phenylallyl (analogous to a, Scheme 1.7), while 74% of MSD scission products ended up as biscumyl (dimer of b). Other studies have shown similar results regarding the formation of biscumyl [24], and the high rate of alkyl radical addition to styrenic groups. For example, the rate constant for 5-hexenyl radical addition to styrene is

reported to be on the order of 10^6 M^{-1} s^{-1} at 160°C [27].

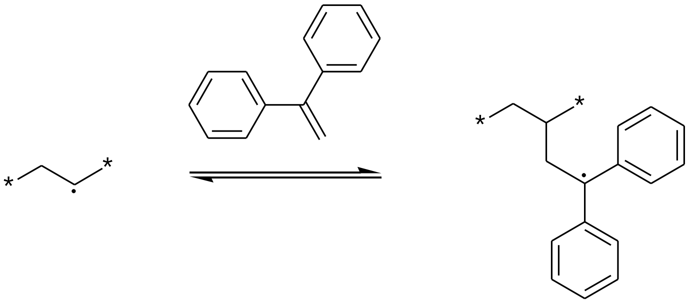
2) No undecanyl dimers representative of cross-links were observed during the model compound study. Conclusion 1 discounts the explanation of a lack of undecane radicals, since this population must have been substantial to form MSD adducts nearly exclusively. Thus, the preferential trapping over combination suggests good rates of addition, indicative of scorch potential, while MSD is present.

In a joint paper, Suyama et. al present data from DCP-initiated polyethylene cures containing MSD [24]. Good scorch inhibition is reported at 145°C, in agreement with [28] but making no reference to the effect on final yield, while cure boosting by as much as 50% at 180°C with no scorch inhibition. To explain the apparent temperature effects, the researchers hypothesized the addition of polymeric radicals to macromolecular unsaturated sites is more favourable at higher temperatures. Higher cross-linking efficiency is also explained as a result of 1) shifting the polyethylene macro-radical k_d/k_c ratio in favour of combination and 2) bonding three polymer chains at one location.

This work has indicated MSD has potential as a mild scorch protectant, limited by moderate rates of radical addition that struggle to compete with H-abstraction pathways. Furthermore, poor scorch recovery was observed. Possible explanations are likely due to MSD poisoning by cumyloxyl and methyl radical addition and low rates of addition to unsaturated macromolecules.

1.2.6. 1,1-Diphenylethylene

Macro-radical addition to 1,1-diphenylethylene (DPE) is studied most extensively in the context of controlled radical polymerizations [29] [30] [31]. Unlike MSD, little literature exists for its use as a scorch inhibitor. A mechanism is proposed by Wieland et. al whereby the usefulness of DPE in pseudo-living radical polymerizations is a result of reversible trapping of activated macromonomer chains at 80°C [29]. Possible para-combination with other DPE-terminated macro-radicals is also considered to be highly unstable [29] [30].



Scheme 1.8. Reversible macro-radical addition to 1,1-diphenylethylene

Patents exist for the use of DPE as a scorch inhibitor in polyethylene, claiming its capability in yielding a fully cured article [32]. The effectiveness of DPE depends on successful macro-radical addition and behaves much in the same way as MSD. Methyl radicals are believed to have a high affinity for vinyl addition in general and the stable addition for addition to diphenylethylene is believed to be a probable reaction in systems initiated by organic peroxides [33]. Methyl radicals are accredited to have H-abstraction tendency from hydrocarbon polymers and this addition pathway will compete, indicating potential grounds for scorch retardation in polymeric systems.

Alkyl macro-radical addition is apparently favourable and reversible, making this pathway integral to living radical polymerization techniques. Addition essentially temporarily terminates the radical precursor by forming highly resonance stabilized tertiary radicals that have very limited reactivity. Hypothetically, low instantaneous macro-radical populations will suppress termination by combination and slow the cure altogether.

1.2.7. (2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl

(2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl (TEMPO) is a stable free radical at room temperature. It is most commonly used as a reversible radical trap for growing alkyl macro-radicals in controlled/living radical polymerization processes [34]. As mentioned, nitroxyl combination with alkyl radicals in solution is reported to be near the diffusion limit of the polymer with rate constants on the order of 10^7–10^9 $M^{-1}s^{-1}$ [14] [15]. The basis for nitroxyl mediated radical polymerization (NMRP) is maintenance of low instantaneous alkyl radical concentrations, thereby suppressing alkyl-alkyl termination. This shifts the system in favour of polymerization since radical additions follow first-order kinetics with respect to radical concentration, whereas termination abides by a second-order dependence.

The potential exists for excellent scorch inhibition during polyolefin cures, since nitroxyls are capable of quenching alkyl radical intermediates as spin-paired alkoxyamines [5]. At temperatures commonly used in commercial practice, the secondary alkoxyamines generated by trapping of secondary alkyl radicals by TEMPO are relatively stable [35]. Hence, the kinetic reactivity of nitroxy radical traps, combined with the stability of the resulting alkoxyamines, should result in excellent scorch protection, but cross-link yield losses that are proportional to the amount of nitroxyl used in the formulation [5].

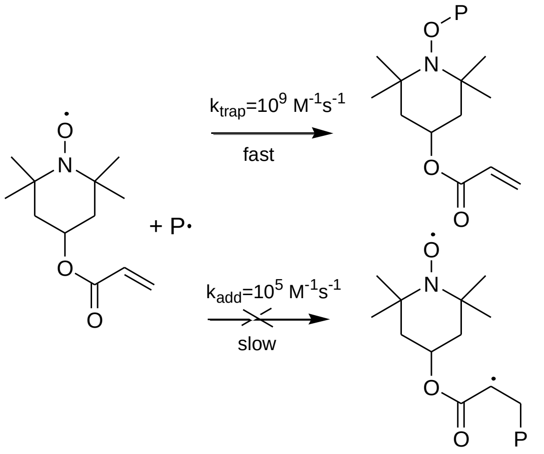
1.2.8. Bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate

Bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate (bis-TEMPO) is a variation on the nitroxyl chemistry presented above, in that the scorch protecting additive contains two nitroxyl moieties covalently attached by a sebacate diester. The utility of this approach was studied by Chaudhary et. al through a series of model compound and polyethylene cure studies [5]. Low density polyethylene (LDPE) cure formulations containing 1.7 wt% DCP (5.79×10^{-2} M) and 0.25 – 1.0 wt% bis-TEMPO (4.5×10^{-3} M – 1.8×10^{-2} M) were tested at 140°C, resulting in evidence of scorch inhibition. At 180°C, no scorch was observed while the yield was boosted substantially.

1.2.9. 4-Acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl

Acrylate-functionalized TEMPO (AOTEMPO) is a known compound that was designed for use in controlled monomer polymerizations to yield block copolymer architectures. For example, anionic copolymerization of AOTEMPO copolymerization with styrene and other acrylates has been used to prepare copolymers bearing pendant nitroxyl functionality. Subsequent free radical polymerization of styrene in the presence of these copolymers yields polystyrene branches at specific points along the backbone, thereby providing comb-type block copolymers [36] [37] .

The idea to use AOTEMPO, or structural analogues, in delayed-onset cure chemistry is based on differences in the reactivity of nitroxyls and acrylates toward alkyl radicals (Scheme 12). Nitroxyls trap alkyl radicals at the diffusion limit (rate constant = 10^8-10^9 $M^{-1}s^{-1}$), while acrylate addition to alkyl radicals proceeds much slower (rate constant 10^4-10^5 $M^{-1}s^{-1}$). Therefore, the reaction of AOTEMPO with a polymer macro-radical should exhibit a dramatic preference for alkoxyamine formation, as opposed to activation of the acrylate group by radical addition.



Scheme 12. Potential polymer macro-radical trapping reactions of AOTEMPO

Assuming that selectivity for alkyl radical trapping by alkoxyamine formation is highly favoured, a polyolefin cure formulation that includes AOTEMPO should exhibit three phases – nitroxyl trapping, bound acrylate oligomerization, and unaffected peroxide cure. The rapid and quantitative trapping of macro-radicals should provide delayed-onset characteristics, as polymer radicals are converted to pendant alkoxyamine groups that bear acrylate functionality. Once most nitroxyl is consumed, radical attack on pendant acrylate groups will lead to their oligomerization, thereby restoring the cross-link density that was lost early in the cure. In doing so, this delayed-onset cure process does not suffer from losses in cross-link density in the manner of simple antioxidant-based chemistry. Once all nitroxyl and acrylate functionality is consumed, the peroxide cure should proceed as normal.

1.3. Research Objectives

The research presented henceforth aims to design, characterize, and evaluate the potential of functional nitroxyls as scorch protectants in peroxide-initiated polyethylene cure formulations. The technical goals of the project include the following.

- Characterize the relative reactivity of AOTEMPO toward radical combination versus radical addition by model compound experimentation, and demonstrate the utility of AOTEMPO and structural analogues in polyolefin cure formulations.
- Develop formulation design principles that allow users of AOTEMPO technology to meet scorch protection and cure yield targets using a minimum amount of trial-and-error experimentation.
- Evaluate AOTEMPO technology relative to other scorch protecting strategies.

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Chapter 2 Functionalized Nitroxyls as Scorch Protectants

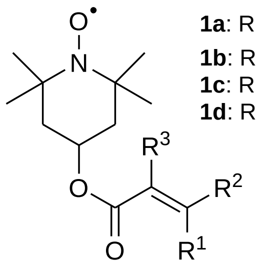
2.1. Introduction

The chemical modification of polyolefins using free radical chemistry is practiced widely to transform inexpensive commodity polymers into value-added materials. A leading example is the cross-linking of ethylene-rich thermoplastics to yield thermoset derivatives that demonstrate improved mechanical properties and high temperature stability. In their simplest form, these solvent-free processes operate on a polymer melt, using the thermolysis of dialkyl peroxides to generate alkoxy radical intermediates. Hydrogen atom abstraction from the polymer by initiator-derived radicals provides macro-radical intermediates, whose combination gives the desired network of carbon-carbon cross-links. While several factors govern the effectiveness of these cross-linking processes, the efficiency of hydrogen atom abstraction by alkoxy radicals from the polymer, and the relative rates of macro-radical combination and disproportionation are particularly influential.

Since cross-linking transforms a thermoplastic into a thermoset product, the polymer must be formed into its final shape before cross-linking renders the material unprocessable. A wide range of “scorch protection” strategies are reported in the literature, all of which are designed to quench radical activity in the early stages of the cross-linking process. Standard chain breaking donor antioxidants such as hydroquinones and hindered phenols are applied, as well as chain breaking acceptors such as nitroxyls. The latter are particularly effective, since their trapping of alkyl radicals by combination occurs at the diffusion limit of radical-radical encounters.

The primary deficiency of a standard antioxidant approach is the accompanying loss in cross-link density that is incurred as a direct result of radical quenching. Since simple peroxide cures are essentially stoichiometric processes that yield at most one cross-link per molecule of initiator, losses in macro-radical yield have a proportional effect on attainable cross-link density. Alternate strategies based on the chain transfer chemistry of 2,4-diphenyl-4-methyl-1-pentene, and the reversible alkyl radical trapping by 1,1-diphenylethylene have also been proposed. While these methods have the potential to retard cross-linking without compromising cure yields, their radical trapping kinetics are much slower than those of more reactive traps such as nitroxyls. As such, their ability to quench radical activity in the earliest stages of polyolefin cross-linking is less favourable.

This report describes a fundamentally different approach to controlling the dynamics and yields of polyolefin cross-linking processes. This strategy exploits differences in the rate of alkyl radical trapping by nitroxyl and acrylate functionalities to delay polymer cross-linking without sacrificing cure yields. Consider that the rate constants for alkyl radical addition to acrylates are of the order of 10^{3}-10^{5} $M^{-1}s^{1}$ [1], while the rate constants for alkyl radical combination with nitroxyls are generally of the order of 10^{8}-10^{9} $M^{-1}s^{1}$ [2]. As a result, the nitroxyls illustrated in Scheme 2.1 are expected to trap the macro-radical intermediates of a polyolefin cure by combination, as opposed to acrylate addition. In so doing, the polyolefin would be transformed into a macromonomer bearing pendant acrylate functional groups.

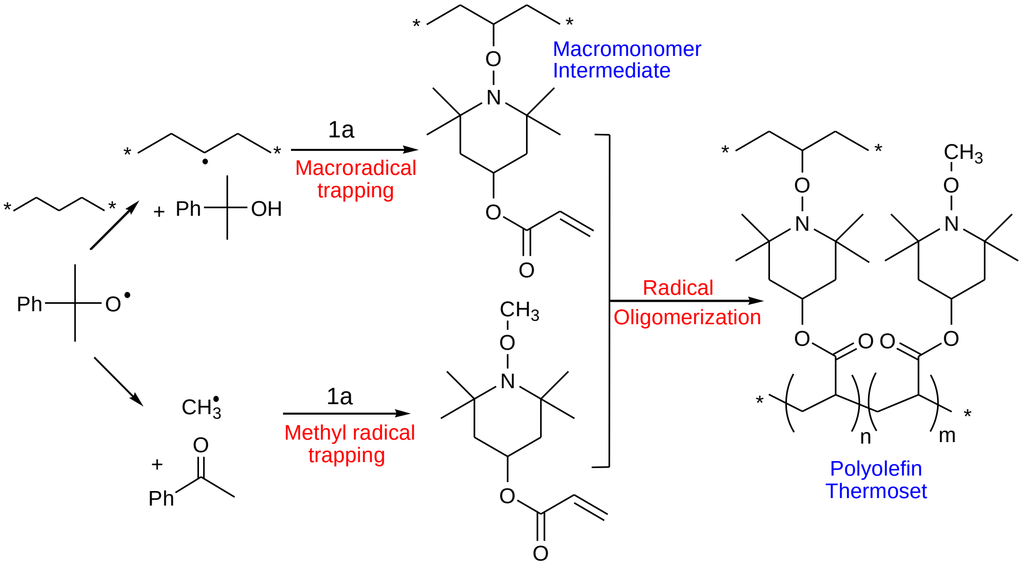


1a: $R^1=R^2=R^3=H$
1b: $R^1=R^2=H$; $R^3=Me$
1c: $R^1=Ph$; $R^2=R^3=H$
1d: $R^1=Me$; $R^2=R^3=H$

Scheme 2.1. Functional nitroxyls of interest

Under ideal circumstances, macro-radical trapping by nitroxyl dominates during the early stages of peroxide decomposition such that polyolefin cross-linking is suppressed until all nitroxyl is consumed (Scheme 2.2). This induction period is, in turn, followed by oligomerization of polymer-bound acrylate functionality to provide the desired cross-linked thermoset. We note that the kinetic chain length of acrylate oligomerization is important, since an efficient process requires small amounts of initiator to convert acrylate functionality into cross-links. As such, the stoichiometric loss of cross-link density incurred during the macro-radical trapping phase of the process can be recovered by the chain reaction that supports acrylate oligomerization.

This controlled cross-linking chemistry is a creative adaptation of the controlled radical polymerization (CRP) chemistry used to produce block copolymers. In CRP applications, radical trapping by the nitroxyl is designed to be reversible, thereby supporting quasi-living polymerization conditions. In the present context, trapping of the secondary alkyl radicals generated in linear low density polyethylene (LLDPE) cross-linking is designed to be irreversible, yielding alkoxyamines that are stable at the reaction temperatures commonly employed in polyolefin modifications. We have previously demonstrated the stability of 1-(1-ethylpentyloxy)-2,2,6,6-tetramethylpiperidine (TEMPO-heptane) to disproportionation and nitroxyl exchange at 160°C over the course of several hours [3].



Scheme 2.2. Idealized delayed-onset cross-linking process based on acrylated hydroxyl-TEMPO

This report presents model compound data and linear low density polyethylene (LLDPE) cure rheometry measurements that illustrate the fundamentals of controlled radical cross-linking chemistry as well as its efficacy on polymeric systems. Characterization of products derived from dicumyl peroxide (DCP) initiated reactions of cyclohexane and AOTEMPO are used to characterize the relative reactivity of nitroxyl and acrylate functionalities toward alkyl radicals. This basic knowledge is used to develop, evaluate, and analyze LLDPE cure dynamics and yields.

2.2. Experimental

2.2.1. Materials

Linear low density polyethylene (LLDPE, 5% hexane copolymer) was used for this study. Dicumyl peroxide (DCP, 98%), hydroxyl-TEMPO (4-hydroxyl-2,2,6,6-tetramethylpiperidin-1-oxyl, 97%), acryloyl chloride (≥97%, 400 ppm phenothiazine), methacryloyl chloride (97%, 200 ppm MEHQ), crotonoyl chloride (90%, 1500 ppm hydroquinone), cinnamoyl chloride (98%), triethylamine (≥99.5%), cyclohexane (99%) were used as received from Sigma Aldrich (Oakville, ON).

2.2.2. Synthesis

1-Cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-ol, 1-Methoxy-2,2,6,6-tetramethylpiperidin-4-ol

A solution containing DCP (5 wt%, 212 mg, 0.783 mmol) and 4-hydroxyl-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOH, 270 mg, 1.57 mmol) in cyclohexane (4.23 g) was pressurized to 200 psi and heated to 160°C under nitrogen for 1 hour. Upon cooling, vessel pressure was released and contents separated by elution through a packed silica column using a 1:1 hexanes:ethyl acetate mixture. Products were dried and both yielded a white crystalline solid. 1-Cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-ol: m.p. 77°C (lit. 67°C [4]). ^{1}H-NMR: ($CDCl_3$): δ (ppm) = 3.99 (1 H, m, HC-OH), 3.63 (1 H, m, CHON) 2.07 (2 H, s, cyclohexyl CH), 1.84 (2 H, d, cyclohexyl CH), 1.49 (2 H, t, piperidinyl CH), 1.23 (6 H, s, CH_3), 1.18 (6 H, s, CH_3), 1.10 – 1.30 (8 H, cyclohexyl H), OH not observed. High-res. M.S. $C_{15}H_{29}NO_2$ calculated m/z $[M+H]^+$ 256.2270; found m/z 256.2277. 1-Methoxy-2,2,6,6-tetramethylpiperidin-4-ol: m.p. 83°C. ^{1}H-NMR: ($CDCl_3$): δ (ppm) = 3.98 (1 H, m, HC-OH), 3.64 (3 H, s, NO-CH_3), 1.83 (2 H, d, piperidinyl CH), 1.49 (2 H, t, piperidinyl CH), 1.25 (6 H, s, CH_3), 1.17 (6 H, s, CH_3), OH not observed. High-res. M.S. $C_{10}H_{21}NO_2$ calculated m/z 187.1572; found m/z 186.1568.

1-Cyclohexyloxy-2,2,6,6-tetramethyl piperidin-4-yl acrylate

An acryloyl chloride (0.391 mmol, 35 mg, 0.032 mL) in toluene solution was added dropwise to a 1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-ol (0.326 mmol) and triethylamine (39 mg, 0.053 mL, 0.391 mmol) toluene solution. This mixture was left to react for 16 hours at room temperature. The precipitate was collected using a centrifuge and the clear liquid was decanted. The decanted liquid was reduced under vacuum to yield a pale yellow, crystalline solid. m.p. 50°C. ^{1}H-NMR: ($CDCl_3$): δ (ppm) = 6.40 (1 H, dd, HC=C), 6.11 (1 H, dd, C=CH-C), 5.82 (1 H, dd, HC=C), 5.13 (1 H, tt, HC-O-C), 3.63 (1 H, m, CHON), 2.06 (2 H, m, cyclohexyl CH), 1.89 (2 H, dd, piperidinyl CH), 1.78 (2 H, m, cyclohexyl CH), 1.67 (1 H, s, cyclohexyl CH), 1.626 (2 H, t, piperidinyl CH), 1.56 (1 H, d, cyclohexyl CH), 1.24 (12 H, s, CH_3) 1.0 – 1.4 (4 H, cyclohexyl CH). High-res. M.S. $C_{18}H_{31}NO_3$ calculated m/z 309.2304; found m/z 309.2296.

1-Methoxy-2,2,6,6-tetramethylpiperidin-4-yl acrylate

A 1-methoxy-2,2,6,6-tetramethylpiperidin-4-ol (148 mg, 0.792 mmol) and triethylamine (80 mg, 0.11 mL, 0.950 mmol) solution in toluene was made. A second solution containing acryloyl chloride (86 mg, 0.077 mL, 0.950 mmol) in toluene was added and left to react at room temperature for 24 hours. The liquid was decanted and reduced under reduced pressure to yield a viscous, tan liquid. ^{1}H-NMR: ($CDCl_3$): δ (ppm) = 6.21 (1 H, dd, HC=C), 5.98 (1 H, dd, C=CH-C), 5.66 (1 H, dd, HC=C), 5.104 (1 H, tt, HC-O-C), 3.633 (3 H, s, O-CH_3), 1.778 (2 H, dd, piperidinyl CH), 1.605 (2 H, t, piperidinyl CH), 1.20 - 1.25 (12 H, m, CH_3). High-res. M.S. $C_{13}H_{23}NO_3$ calculated m/z 241.1678; found m/z 241.1673.

Attempts were made to identify the following paramagnetic radical species by NMR. In some cases, characteristic peaks were observed; however, this was not possible for all species.

4-Acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl

A solution of TEMPOH (1 g, 5.81 mmol) and triethylamine (706 mg, 0.97 mL, 6.98 mmol) was reacted with acryloyl chloride (0.632 g, 0.57 mL, 6.98 mmol) in toluene at room temperature for 16 hours. The solids were removed by filtration and washed multiple times with toluene. The solution was dried under vacuum to yield orange crystals. Crystals were recrystallized from cyclohexane and dried under air flow. m.p. 92°C (lit. 93°C [5]). ^{1}H-NMR: ($CDCl_3$): δ (ppm) = 6.49 (1 H, dd, HC=C), 6.19 (1 H, dd, C=CH-C), 5.96 (1 H, dd, HC=C), 1.0 – 2.0 (17 H). High-res. M.S. $C_{12}H_{20}NO_3$ calculated m/z $[M+2H]^+$ 228.1596; found m/z 228.1599.

4-Methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl

Methacryloyl chloride (188 mg, 0.176 mL, 1.79 mmol) in toluene was reacted with a TEMPOH (0.25g, 1.45 mmol) and triethylamine (182 mg, 0.251 mL, 1.79 mmol) solution at room temperature for 18 hours and then further reacted at 70°C for 2 hours. The precipitate was filtered off to yield a dark orange liquid. Under vacuum, this liquid was reduced to yield orange crystals that were then recrystallized from cyclohexane. (m.p. 79°C (lit. 88°C -89°C [6]), ^{1}H-NMR: ($CDCl_3$): δ (ppm) = 6.27 (1 H, s, HC=C cis to O), 5.76 (1 H, s, HC=C trans to O). High-res. M.S. $C_{13}H_{22}NO_3$ calculated m/z 240.1600; found m/z 240.1597.

4-Cinnamoyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl

Cinnamoyl chloride (300 mg, 1.80 mmol) in toluene was reacted with a solution containing TEMPOH (250 mg, 1.50 mmol) and triethylamine (177 mg, 1.80 mmol, 0.244 mL) in toluene for 3 hours at 70°C.

The solids were allowed to settle and the liquid decanted. Reduction of the decanted liquid under reduced pressure produced orange crystals. m.p. 79°C. ^{1}H-NMR: ($CDCl_3$): δ (ppm) = 7.77 (1 H, m, HC=C), 7.58 (2 H, m, meta aromatic), 7.44 (2 H, m, ortho aromatic), 7.47 (1 H, m, para aromatic), 6.50 (1 H, m, HC=C), 3.14 (1 H, s, HC-O), 1.00 – 3.00 (16 H). High-res. M.S. $C_{18}H_{24}NO_3$ calculated m/z 302.1756; found m/z 302.1765.

4-Crotonoyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl

A toluene solution of crotonoyl chloride (188 mg, 1.80 mmol, 0.127 mL) was reacted with a second toluene solution containing TEMPOH (250 mg, 1.50 mmol) and triethylamine (177 mg, 1.80 mmol, 0.244 mL) for 3 hours at 70°C. White solids were allowed to settle and the orange liquid was decanted. The orange liquid was dried under vacuum. (^{1}H-NMR: ($CDCl_3$): δ (ppm) = 1.94 (3 H, dd, crotonate CH_3), High-res. M.S. $C_{13}H_{22}NO_3$ calculated m/z 240.1600; found m/z 240.1611.

2.2.3. Instrumentation and analysis

Rheometry measurements on treated LLDPE were performed using an Advanced Polymer Analyzer 2000 (Alpha Technologies) with a 3° arc and a frequency of 1 Hz. Gas chromatography measurements were measured using a Varian CP-3800 gas chromatograph equipped with a Chrompack Capillary Column (30m x 0.25mm, CP Sil 8 coating): 50°C for 2 minutes, increase to 89°C at 15°C/min for 1 minute, increase to 95 at 1°C /min for 1 minute, to 150°C at 15°C /min for 1 minute, to 155°C at 1°C /min for 1 minute, to 250°C at 15°C/min for 10 min.

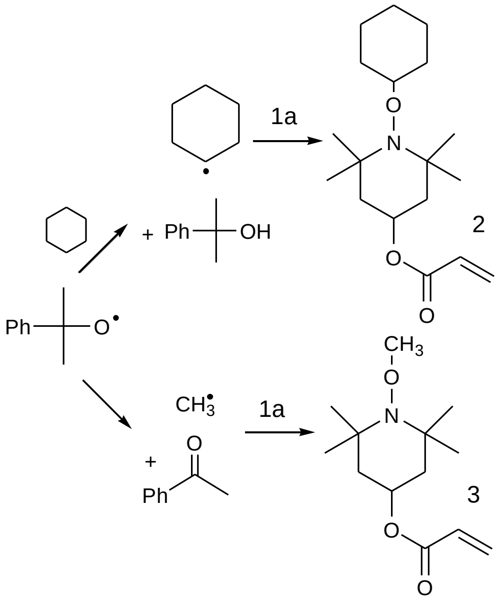
2.2.4. Polymer solution coating process

LLDPE pellets (5 g) were finely ground and coated with an acetone solution containing DCP initiator, desired nitroxyl species and any additional additives. The ground pellets were hand mixed and allowed to dry thoroughly. Rubbers were milled until flat, treated with solution and re-milled post-drying. Excessive drying of solutions containing sublimable nitroxyls (ie. TEMPO) was avoided. The treated polymer was then cured in an oscillating disk rheometer (Advanced Polymer Analyzer, Alpha Technologies) at the aforementioned strain rate.

2.3. Results and Discussion

2.3.1. Model compound studies

If a reagent such as AOTEMPO is to provide scorch protection without compromising cross-link densities, then it must trap alkyl radicals by combination with nitroxyl, as opposed to addition to acrylate functionality. Ideally, selectivity for AOTEMPO conversion to polymer-bound alkoxyamine would be absolute, with acrylate functionality only being activated once all nitroxyl is consumed. To test the trapping selectivity of **1a**, a model compound approach was adopted, wherein cyclohexane was used in place of LLDPE. This strategy is widely used to generate unambiguous information regarding the structure of reaction products when the low concentration of polymer-bound functionality and the insolubility of polymer thermosets make it impossible to accomplish for macromolecule systems. Our studies involved the thermolysis of known amounts of DCP in a standard solution of **1a** + cyclohexane. A cyclic hydrocarbon was used to eliminate regioisomers from the reaction products. The methyl and cyclohexyl alkoxyamines (**2** and **3**, Scheme 2.3), as well as the initiator byproducts acetophenone and cumyl alcohol, were quantified by GC analysis using authentic standards.



Scheme 2.3. Cumyloxy radical abstraction and fragmentation pathways in presence of cyclohexane and AOTEMPO

The β-scission of cumyloxy radicals to yield methyl radicals and acetophenone is competitive with hydrogen atom abstraction from a hydrocarbon. The extent of radical fragmentation increases with temperature and the C-H bond dissociation energy of potential hydrogen atom donors. Independent studies of cumyloxyl abstraction from cyclohexane have recorded abstraction efficiencies on the order of 55% at 140°C, with cumyl alcohol:acetophenone ratios of about 1.2 [7]. In the present context, this means that the alkoxyamines **2** and **3** would be produced in these proportions. The data illustrated in Figure 2.1 show that the cyclohexyl alkoxyamine was, in fact, produced in higher yields than the methyl alkoxyamine, irrespective of the amount of DCP charged to the reaction mixture.

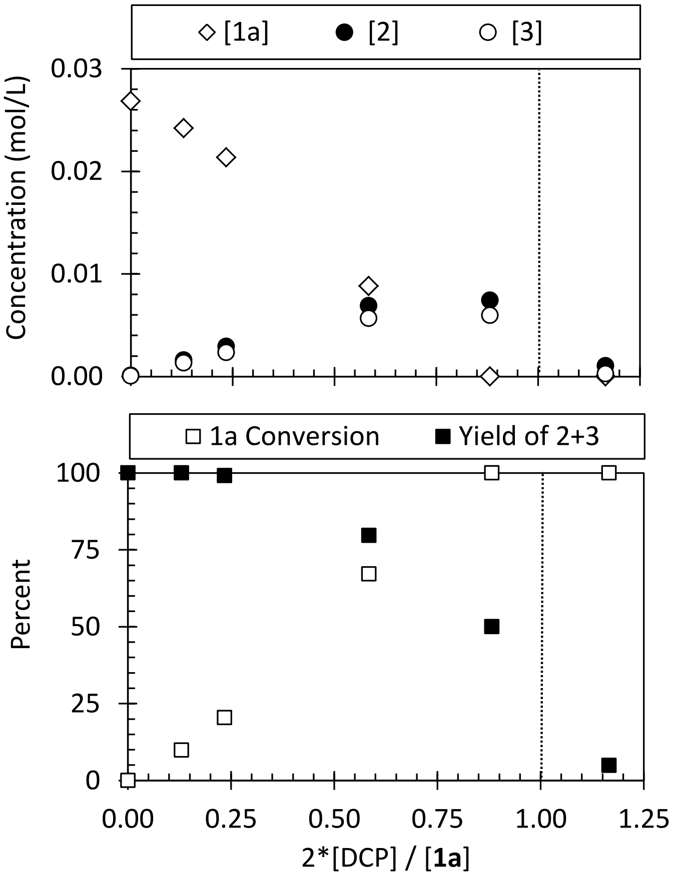


Figure 2.1. Model compound reaction products as a function of DCP loading; top. reagent and product concentrations; bottom. **1a** conversion and alkoxyamine yields ($[\mathbf{1a}]_o$ = 0.027 mol/l; 160°C)

Of greater interest is the relationship between DCP loading and AOTEMPO conversion, and the evolution of alkoxyamine yields with increasing initiator concentration. Figure 2.1 presents this data as a function of the total cumyloxy radical concentration (2*[DCP]) divided by the functional nitroxyl concentration ([**1a**]). Although nitroxyls do not trap oxygen centred radicals, they trap the alkyl radicals derived from cyclohexane activation and cumyloxyl fragmentation. As such, there should be a linear relationship between AOTEMPO conversion and 2*[DCP]/[**1a**], and conversion should approach 100% when the ratio approaches a value of 1.00. The **1a** conversion data demonstrate this linear relationship, with complete reagent consumption observed at 2*[DCP]/[**1a**] = 0.88, slightly less than the expected result.

Alkoxyamine yields at low DCP loadings are particularly important, as they reflect the intrinsic reactivity of **1a** in the absence of reaction products. The data show that up to 25% **1a** conversion, the alkoxyamine yield, ([**2**] + [**3**])/([**1a**]$_o$ - [**1a**]), was nearly 100%. This indicates that alkyl radical trapping by **1a** is, in fact, selective for alkoxyamine formation, as opposed to addition to acrylate functionality. However, higher initiator levels caused alkoxyamine concentrations to peak at a 2*[DCP]/[**1a**] value of 0.58 before declining continuously toward zero. Note that alkoxyamine consumption by alkyl radical addition to acrylate will occur when all nitroxyl functionality is consumed. Therefore, loss of **2** and **3** to acrylate oligomerization is expected when 2*[DCP]/[**1a**] = 0.88, according to the results plotted in Figure 2.1. That alkoxyamine yields declined before this ratio suggests that **2** and **3** engage in radical addition when their concentrations are high, and AOTEMPO concentrations are low. The resulting acrylate-derived radicals may, in fact, be trapped by AOTEMPO to produce a mixture of other alkoxyamines, whose characterization is beyond the scope of this work.

The synthesis of an intermediate alkoxyamine, 1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-ol, provided the opportunity to study the thermal stability of this secondary alkoxyamine. Heating a cyclohexane solution under N_2 to 160°C for prolonged periods showed no losses over the course of 2 hours, thereby confirming that alkoxyamine disproportionation was not significant under our reaction conditions, and providing confidence that the macromolecular analogues generated in the following polyethylene studies are similarly robust.

2.3.2. LLDPE cross-linking

Time-resolved measurements of the dynamic storage modulus (G’) recorded at fixed temperature, frequency, and shear strain amplitude, are the standard means of monitoring the dynamics and yields of all polymer cross-linking processes [8]. Because uncross-linked polymers efficiently dissipate energy in response to stress in their melt state, their response to an oscillating shear deformation is relatively inelastic. Peroxide-initiated chain coupling yields a covalent network that restricts polymer segment mobility, thereby raising a material’s storage modulus continuously as network densities increase. Figure 2.2 presents storage modulus data for an LLDPE sample containing 18.5 μmols DCP per gram of polymer. Heating this mixture to 160°C started to cross-link the polymer almost immediately, as the storage modulus increased from 9 kPa to 214 kPa over the course of 60 minutes. Of particular concern to this work are the onset of cross-linking, and the maximum storage modulus (G'_{max}) provided by the formulation.

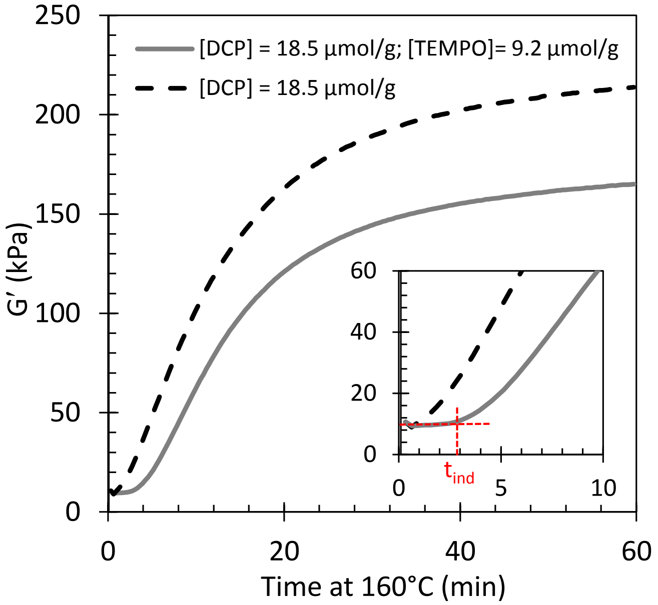


Figure 2.2. Dynamics of DCP-initiated LLDPE cross-linking; inset: expansion illustrating reaction induction time

Also presented in Figure 2.2 are data recorded for an LLDPE sample containing [DCP] = 18.5 µmol/g and [TEMPO] = 9.2 µmol/g. As expected, this unfunctionalized nitroxyl delayed the onset of cross-linking significantly, yielding an induction time, t_{ind}, of 2.7 minutes. We define t_{ind} as the point where the storage modulus increased from its minimum value. Note that the DCP-only cure formulation also shows some delayed onset character, owing to the approximately 1 minute needed to bring the sample from room temperature to 160°C. The increased induction time provided by TEMPO was gained at the expense of cross-link density, as the storage modulus of the product was 165 kPa, just 77% of that generated by DCP alone. Note that the ratio of radical trap to cumyloxy radicals, [TEMPO]/(2*[DCP]) was 0.25, meaning that the nitroxyl charged to the formulation could trap just 25% of the radicals generated by peroxide decomposition.

The TEMPO formulation data presented in Figure 2.3 are plotted in a semi-log format to better illustrate the early stages of the cross-linking process. The DCP-only and [TEMPO]/(2*[DCP])=0.25 data from

Figure 2.2 are replotted in this graph, along with cross-linking profiles generated at higher nitroxyl loadings. The full data set follows expected trends, with increasing TEMPO concentrations decreasing cross-linking yields while increasing induction times. The use of a stoichiometric amount of TEMPO relative to cumyloxy radicals, [TEMPO]/(2*[DCP])=1.00, quenched all macro-radical activity, as evidenced by the stable storage modulus observed throughout the 60 minute experiment.

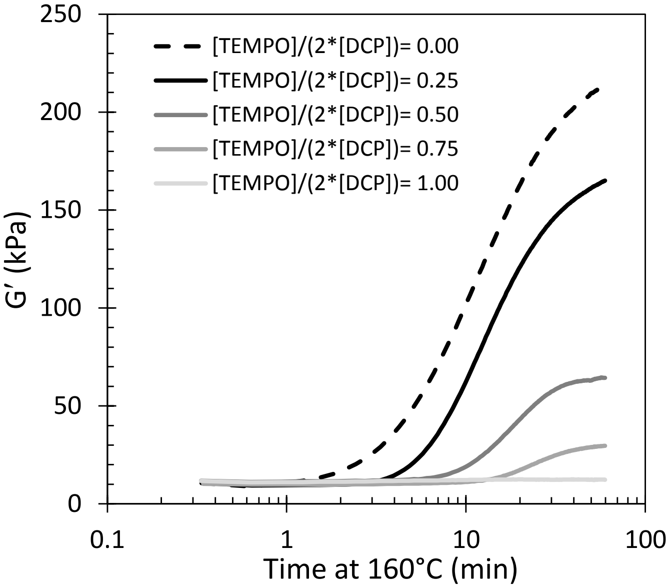


Figure 2.3. Influence of TEMPO on DCP-initiated LLDPE cure dynamics and yields ([DCP]=18.5 µmol/g)

The relationship between induction time, t_{ind}, and TEMPO loading can be derived from first principles, given that initiator thermolysis is a first-order decomposition reaction whose rate is not affected by the presence of nitroxyl. As such, the conversion of peroxide, X, with time can be expressed as,

$$X = \frac{[\mathrm{ROOR}]_o - [\mathrm{ROOR}]}{[\mathrm{ROOR}]_o} = 1 - e^{-k_d t} \tag{1}$$

where $[ROOR]_o$ is the initial peroxide loading, [ROOR] is the peroxide concentration remaining at time t, and k_d is the first-order rate constant for initiator homolysis at the reaction temperature. Given the fast rate of alkyl radical trapping by nitroxyls, we assume that all initiator-derived radicals produced in the presence of nitroxyl will be quenched. Under this assumption, the fraction of DCP-derived radicals trapped by nitroxyl will be $[nitroxyl]/(2*[ROOR]_o)$, during which time initiator will be converted without generating cross-linking activitiy. Therefore, the induction time can be expressed in terms of a simple ratio of nitroxyl and initiator concentrations,

$$\frac{[\mathrm{nitroxyl}]}{2[\mathrm{ROOR}]_o} = 1 - e^{-k_d t_{ind}} \tag{2}$$

which can be rearranged to give the induction time explicitly,

$$t_{ind} = -\frac{1}{k_d} \ln\left[1 - \frac{[\mathrm{nitroxyl}]}{2[\mathrm{ROOR}]_o}\right] \tag{3}$$

Equation 3 is plotted in Figure 2.4a for DCP thermolysis at 160°C (k_d=0.127 min^{-1}), along with the t_{ind} values extracted from DCP + TEMPO cure data. The agreement is quite good, with observed TEMPO induction times being slightly greater due to the time required to bring samples to the reaction temperature.

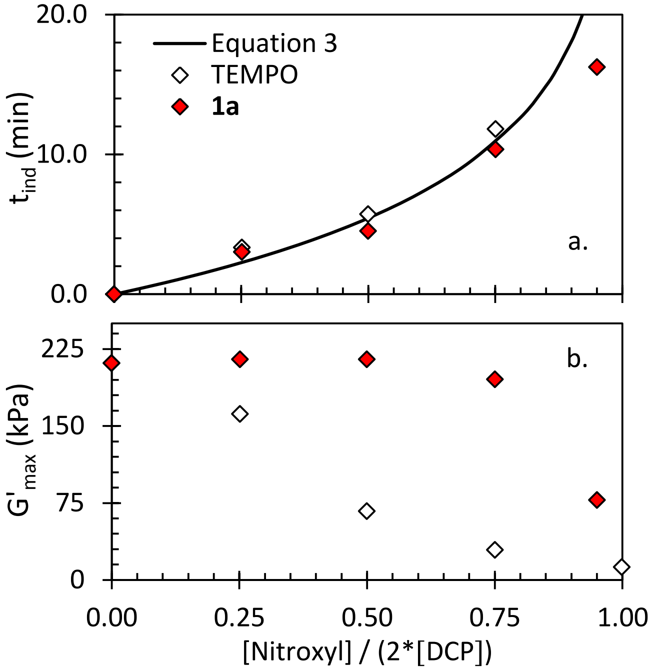


Figure 2.4. Influence of TEMPO and 1a on DCP-initiated LLDPE cure dynamics and yields ([DCP]=18.5 µmol/g, 160°C)

It is intuitive that the induction phase provided by TEMPO should be accompanied by a loss of cross-link density. We use the term "stoichiometric" to describe peroxide-only cross-linking formulations, since radicals are formed in pairs by peroxide breakdown, and leading to cross-link formation through pair-wise combination of macro-radicals. As such, cross-link yields cannot exceed initiator concentrations, and any radical trap that quenches macro-radicals should cause a proportional decline in cross-link density. We noted above that 0.25 molar equivalents of TEMPO relative to cumyloxy radicals suppressed the extent of cross-linking by 23%. The data provided in Figure 2.4b show that the maximum storage modulus (G'$_{max}$) declined continuously with TEMPO loading until [TEMPO]/(2*[DCP]) = 1.00, whereupon all cross-linking was suppressed (G'$_{max}$=G'$_{initial}$= 9 kPa).

The functionalized nitroxyls are designed to provide delayed-action cures that do not incur loss of cross-link yields. The objective is to trap all alkyl macro-radicals as functional alkoxyamines, effectively transforming the polymer into a macro-monomer. As a result, the mechanism of action is different from peroxide-only cures and delayed-onset formulations employing TEMPO, in that cross-links are produced not only by macro-radical combination, but also through radical oligomerization of polymer-bound C=C functionality. Since the latter can have considerable kinetic chain length, the potential exists to generate numerous cross-links from each initiator-derived radical. Curing is no longer a stoichiometric process with respect to peroxide loadings, and losses in cross-link density suffered during the trapping phase of the functional nitroxyl process can be regained by the conversion of pendant monomer groups.

The cure dynamics data plotted in Figure 2.5 show that an acrylate-functionalized nitroxyl (**1a**) can, in fact, provide exceptional delayed-onset performance while maintaining cross-link yields. Each nitroxyl cure formulation displayed three distinct phases; an induction period during which time the storage modulus was unchanged, a subsequent period of rapid cross-linking, and a final period wherein cross-linking proceeded at the same rate as that produced by DCP alone. Figure 2.4 summarizes the induction time, t_{ind}, and cross-link yields (G'_{max}) generated by DCP + **1a** mixtures. The induction times provided by the acrylated nitroxyl were predicted reasonably well by equation 3, but were less than those generated by TEMPO, and the discrepancy grew with increasing **1a** concentration. This is likely the result of acrylate oligomerization in the latter part of the induction phase, when nitroxyl concentrations have fallen to the point where macro-radical trapping rates are less competitive with attack on polymer-bound C=C functionality.

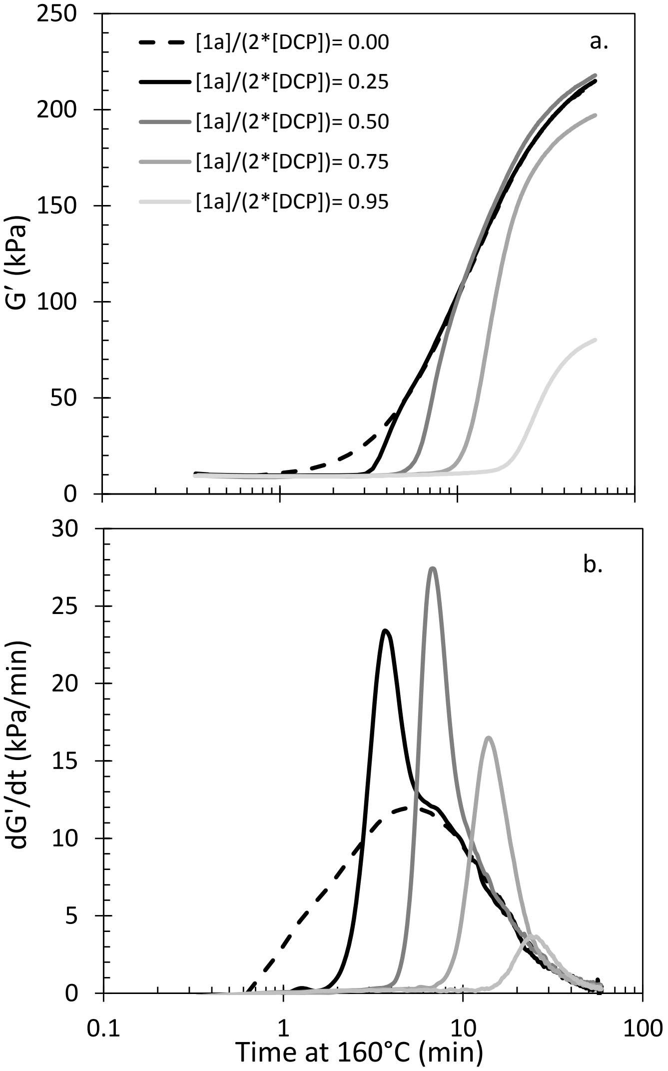


Figure 2.5. Influence of **1a** on DCP-initiated LLDPE cure dynamics and yields (a. G'; b. dG'/dt; [DCP]=18.5 µmol/g)

A slight shortening of t_{ind} brought on by acrylate oligomerization is offset by the maintenance of cross-link density. Figure 2.4b shows that up to one-half of initiator-derived radicals can be trapped by **1a** without affecting G'_{max}. Cross-link yields were only slightly compromised before severe losses were suffered at a ratio of 0.95. It is important to realize that nitroxyl concentrations in this high range are impractical, since it makes little sense to quench more than half the initiator in order to achieve a longer

t_{ind} target. If longer induction times are required, a peroxide providing a lower k_d at 160 °C (longer half-life) will extend t_{ind} at a given nitroxyl ratio, as governed by equation 3. Therefore, the performance of **1a** summarized in Figure 2.4 is adequate for practical applications.

The ability of **1a** to restore exactly the cross-link density lost to macro-radical trapping is somewhat surprising, since there is little fundamental basis for such a coincidence. Consider that cross-link densities generated by DCP-alone are dictated by the initiation efficiency for macro-radical generation, and the relative rate of macro-radical disproportionation versus combination, the latter giving a network comprised of “H-type” carbon-carbon cross-links. In contrast, the cross-link network provided by **1a** is expected to have a star-branched structure comprised of oligomers derived from polymer-bound acrylate functionality. The yield of this macro-monomer functionality is unknown, as is the relationship between converted acrylate groups and the resulting storage modulus. Therefore, the nearly exact matching of G'_{max} values observed for DCP-only and **1a**-mediated cure formulations is coincidental, and must reflect a balanced trade-off of reaction yields and polymer network structure effects.

In fact, one could argue that **1a** should be capable of providing **higher** cross-link densities than DCP alone. The ratio of cyclohexyl radical combination to disproportionation is 52:48 at 30°C [9], meaning that about one half the population of macro-radical intermediates of a DCP-only cure may not contribute directly to polymer cross-linking. On the other hand, nitroxyl trapping of these macro-radicals by nitroxyl occurs exclusively by combination to yield the corresponding alkoxyamine, thereby converting each macro-radical into a pendant acrylate group. Subsequent oligomerization of this polymer-bound functionality could, therefore, provide superior cross-link yields if this functionality is converted efficiently.

Insight into the dynamics of the **1a** cure system was gained from the derivative graphs shown in Figure 2.5b. These plots of the rate of change of storage modulus (dG'/dt) delineate the induction, acrylate oligomerization, and stoichiometric phases of a functional nitroxyl cure. The DCP-only formulation data provides the cross-linking rate for a standard peroxide cure involving macro-radical combination and, as such, is a useful reference. The induction phase is defined as the period over which dG'/dt = 0. Beyond t_{ind} is a stage of rapid modulus growth, owing to conversion of macro-monomer functionality into a cross-link network. Upon complete conversion of acrylate functionality, cross-linking returns to the stoichiometric cure rate provided by peroxide alone. For the **1a** formulations to generate the same G'_{max} as the DCP-only reaction, the area under the dG'/dt curves must be equal. This condition is held for [**1a**]/(2*[DCP]) ratios of 0.25 and 0.50, but to a lesser extent for 0.75, and not at all for 0.95.

There are two possibilities for the failure of high **1a** formulations to provide adequate cure recovery. The first is non-productive alkoxyamine consumption, as indicated by our model compound experiments. Recall that high **1a** conversions were accompanied by reduced yields of the corresponding cyclohexyl alkoxyamine (Figure 2.1). As the concentration of acrylated alkoxyamines increase at the expense of **1a**, so does the likelihood of radical addition to **2** and **3** as opposed to combination with nitroxyl. If the resulting acrylate-derived radical is trapped, this C=C moiety is consumed in a non-productive manner. That is, polymer bound acrylate groups that are activated during the induction period will not contribute to LLDPE cross-linking.

A second possibility for reduced yields involves inadequate initiator during the acrylate activation. Operating with [**1a**]/(2*[DCP]) = 0.95 provides relatively little residual peroxide to convert acrylate functionality to a covalent network. Therefore, at very high trapping ratios, incomplete acrylate conversion may stunt network growth. Fortunately these nitroxyl loadings are impractical, and such complications from unproductive/incomplete acrylate conversion are easily avoided.

The sensitivity of peroxide thermolysis rates to temperature provides a potent means of affecting cross-linking dynamics. Consider that the half-life of DCP is 43 min at 140°C (k_d= 0.016 min^{-1}), but just 0.83 min at 180°C (k_d= 0.837min^{-1}). Given that most peroxide cures are carried out for 5 initiator half-lives, the effect of temperature on overall reaction times is clear. From the perspective of delayed-onset cure chemistry, an induction time target is more difficult to meet at higher temperatures. According to equation 2, a one minute induction time requires a ratio of [nitroxyl]/(2*[DCP]) = 0.02 at 140°C, but [nitroxyl]/(2*[DCP]) = 0.56 at 180°C. The question of whether a functionalized nitroxyl can support these induction times without losing cure yield is addressed by Figure 2.6, which presents t_{ind} and G'_{max} data as a function of temperature for a fixed nitroxyl loading of [nitroxyl]/(2*[DCP]) = 0.25.

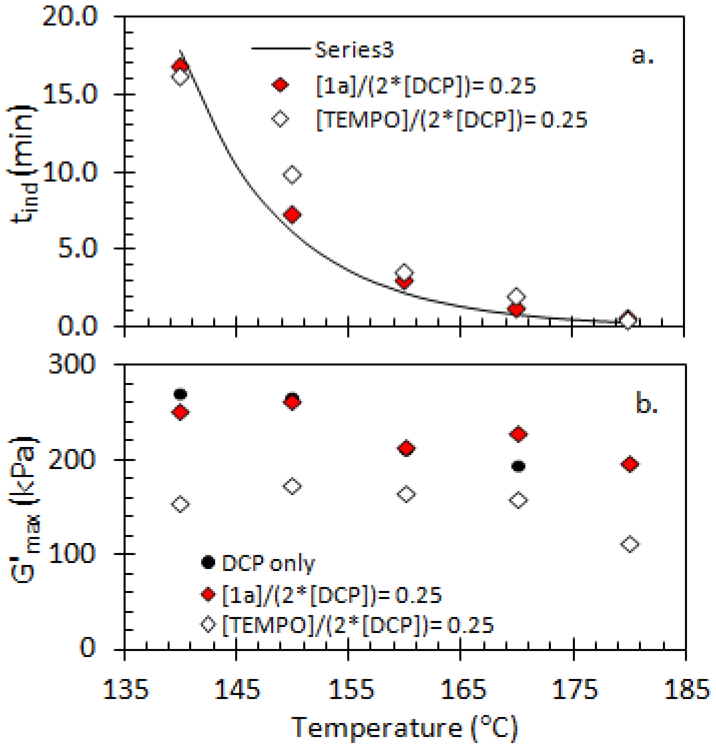


Figure 2.6. Influence of TEMPO and **1a** on DCP-initiated LLDPE cure dynamics and yields ([DCP]=18.5 µmol/g)

The induction time data plotted in Figure 2.6a show that experimental observations are in good agreement with predicted values derived from equation 3. Therefore, nitroxyl concentrations can be prescribed with confidence to satisfy induction time standards for a given peroxide loading and composition. In the present case, it is clear that controlling DCP-initiated processes becomes increasingly difficult at and above 180°C, requiring high concentrations of **1a** to quench a surge of radical activity in the early stages of the cure. Shifting to an alternate initiator such as 2,5-dimethyl-2,5-di-(*t*-butylperoxy)hexyne-3, whose half-life is 3.6 min at 180°C, would lower nitroxyl requirements by a factor of four.

The maximum cross-link densities provided by DCP-only, DCP+TEMPO, and DCP+**1a** at different temperatures are provided in Figure 2.6b. As observed throughout this study, **1a** proved capable of matching DCP-only cure performance, matching G'_{max} values throughout our 140-180°C temperature range. TEMPO, on the other hand, quenched radical activity without restoring the storage modulus to DCP-only values.

We conclude with a brief examination of alternate functionalized nitroxyls bearing methacrylate (**1b**), cinnamate (**1c**) and crotonate (**1d**) groups (Scheme 2.1). Based on published data on the homopolymerization of acrylate (**a**) and methacrylate (**b**) monomers at 30°C are 1.8 x 10^4 [10] and 1-4 x 10^2 M^{-1} s^{-1} [11] [12], respectively. Minimal data on the crotonate monomer (**c**) revealed propagation rate constants on the order of 10^0 M^{-1} s^{-1} at 60°C [13] while no data was found for cinnamate (**d**), presumably due to highly unfavourable homopolymerization kinetics. It is believed the reactivity of these monomers follow the order **a**:**b**:**c**:**d**. The data presented in Figure 2.7 show that this wide range in monomer reactivity is borne out in terms of cure reactivity, as the monomer oligomerization phase of the process is slower and less productive for the substituted monomers than observed for the simple acrylate system.

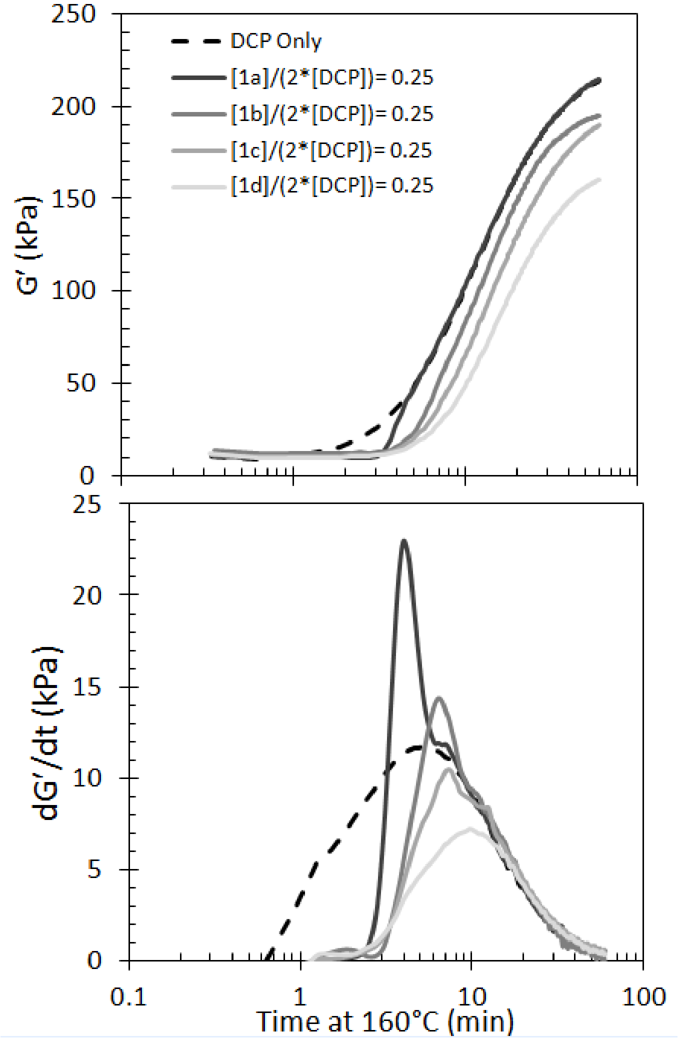


Figure 2.7. Storage modulus DCP-initiated LLDPE cures containing various functionalized nitroxyls ([DCP]=18.5 µmol/g; [nitroxyl]=9.3 µmol/g)

The less reactive monomers exhibit longer scorch periods, more reflective of non-functionalized TEMPO. Aggressive homo-oligomerization implies macromonomer addition is preferred over other addition pathways, leading to a longer kinetic chain length and tethering of a greater sum of macromolecules. It may be hypothesized that less reactive macromonomers have greater tendency to coexist alongside the formation of alkyl macro-radicals, resulting increased likelihood to terminate by combination. Furthermore, analogues bearing allylic hydrogens (**1b** and **1d**) may suffer further inefficient due to allylic abstraction. Cross-links still arise from stoichiometric pairing but to a lesser extent than oligomerization.

2.4. Conclusions

In conclusion, nitroxyls provide superb scorch protection during which time no rise is seen in polyethylene melts at a range of temperatures (140°C – 180°C). Non-functionalized nitroxyls such as TEMPO ultimately lead to a loss in cure that is proportional to the initial reagent loading. Functionalized nitroxyls such as AOTEMPO are able to provide scorch protection of equal quality and recover modulus by oligomerization of pendant groups. Modulus recovery is observed to be proportional to the reactivity of the functional group. The mechanism by which AOTEMPO operates is confirmed as rapid alkyl macro-radical trapping followed by subsequent oligomerization of pendant acrylate groups.

2.5. References

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Chapter 3 Nitroxyl Versatility and Coagent Compatibility

3.1. Introduction

The development of a polymer formulation involves a series of engineering decisions regarding the compositions and amounts of polymers, fillers, stabilizers, colourants and other additives, as well as the processes by which the compound will be mixed, formed, and stabilized in the desired shape. The focus of this work is on thermoset derivatives of ethylene-rich polyolefins, whose saturated polymer backbones are only amenable to free radical cross-linking. In applications such as wire coating, foaming, and reaction injection molding, control of cross-linking dynamics is critical, since viscosity increases during compounding and forming have a negative impact on material processing characteristics and thermoset properties.

In the previous chapter, a new approach to delaying the onset of cross-linking without compromising cure extent was described. This strategy exploits differences in the reactivity of nitroxyl functionality and acrylate functionality toward alkyl radicals. Of the various scorch-protecting additives prepared and tested, the acrylated nitroxyl, AOTEMPO, proved most capable of quenching macro-radicals in the earliest stages of the cure process, and restoring cross-link extents to additive-free levels by subsequent oligomerization of polymer-bound acrylate groups.

This chapter is concerned with the practical application of AOTEMPO chemistry, seeking a set of formulation design principles to help users meet cross-link density and induction time targets. Most formulation development exercises are trial-and error processes wherein peroxide loadings, scorch protector concentrations and other additive levels are tested, and then revised to meet specifications.

The current study examines the dynamics and yields of LLDPE cures over a wider range of peroxide, AOTEMPO, temperature, and initiator structure than was explored in Chapter 2. After mapping out the behaviour of DCP-initiated cures over a range of reagent loadings, alternate peroxides and reaction temperatures are explored. This is followed by a detailed analysis of the compatibility of AOTEMPO with cure-boosting coagents that are widely used in commercial practice.

3.2. Experimental

3.2.1. Materials

Linear low density polyethylene (LLDPE, 5% hexane copolymer) was used for this study. Dicumyl peroxide (DCP, 98%), hydroxyl-TEMPO (4-hydroxyl-2,2,6,6-tetramethylpiperidin-1-oxyl, 97%), acryloyl chloride (≥97%, 400 ppm phenothiazine), triethylamine (≥99.5%), neopentyl glycol diacrylate (225 ppm monomethyl ether hydroquinone) were used as received from Sigma Aldrich (Oakville, ON). Additional alkyl peroxides include Luperox® 130 (2,5-dimethyl-2,5-di-(*t*-butylperoxy)hexyne-3, L-130) and Luperox® 231 (1,1-bis(*t*-butylperoxy)-3,5,5-trimethylcyclohexane, L-231).

3.2.2. Synthesis

4-Acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl

A solution of TEMPOH (1 g, 5.81 mmol) and triethylamine (706 mg, 0.97 mL, 6.98 mmol) was reacted with acryloyl chloride (0.632 g, 0.57 mL, 6.98 mmol) in toluene at room temperature for 16 hours. The solids were removed by filtration and washed multiple times with toluene. The solution was dried under vacuum to yield orange crystals. Crystals were recrystallized from cyclohexane and dried under air flow. m.p. 92°C (lit. 93°C [1]). ^{1}H-NMR: ($CDCl_3$): δ (ppm) = 6.49 (1 H, dd, HC=C), 6.19 (1 H, dd, C=CH-C), 5.96 (1 H, dd, HC=C), 1.0 – 2.0 (17 H). High-res. M.S. $C_{12}H_{20}NO_3$ calculated m/z $[M+2H]^+$ 228.1596; found m/z 228.1599.

3.2.3. Instrumentation and analysis

Rheometry measurements on treated LLDPE were performed using an Advanced Polymer Analyzer 2000 (Alpha Technologies) with a 3° arc and a frequency of 1 Hz.

3.2.4. Polymer solution coating process

LLDPE pellets (5 g) were finely ground and coated with an acetone solution containing DCP initiator, AOTEMPO nitroxyl species and any additional diacrylate additive. The ground pellets were hand mixed and allowed to dry thoroughly. The treated polymer was then cured in an oscillating disk rheometer (Advanced Polymer Analyzer, Alpha Technologies) at the aforementioned strain rate.

3.3. Results and Discussion

3.3.1. Peroxide and AOTEMPO loadings

As discussed previously, peroxide-only cross-linking is a stoichiometric process wherein free radicals are generated in pairs, and terminate in pairs. As a result, cure extents generally scale with peroxide loading, with the response being strongest when the polymer is a good hydrogen atom donor, since this provides high macro-radical yields. Given that radical termination is much faster than peroxide thermolysis, the rate of cross-linking by macro-radical combination is dictated largely by the first-order decomposition kinetics of the initiator. Cure rates are high early in the process when peroxide concentrations are greatest, and they diminish as the initiator concentration declines.

Consider the DCP-initiated cross-linking of LLDPE, whose progress was measured by monitoring the storage modulus (G', Figure 3.1a) a0nd cure rate (dG'/dt, Figure 3.1b) as a function of time. In the absence of nitroxyl, the storage modulus evolved in a manner consistent with first-order dynamics. The initial cure rate was low, owing to the time required to bring the sample to temperature, but it peaked early in the process before demonstrating a steady decline to zero (Figure 3.1b). The ultimate storage modulus approached 600 kPa, which far exceeded the values reported in Chapter 2, due to the higher initiator loading (55.6 μmole/g) used to generate Figure 3.1, versus that used in the preceding study (18.5 μmole/g).

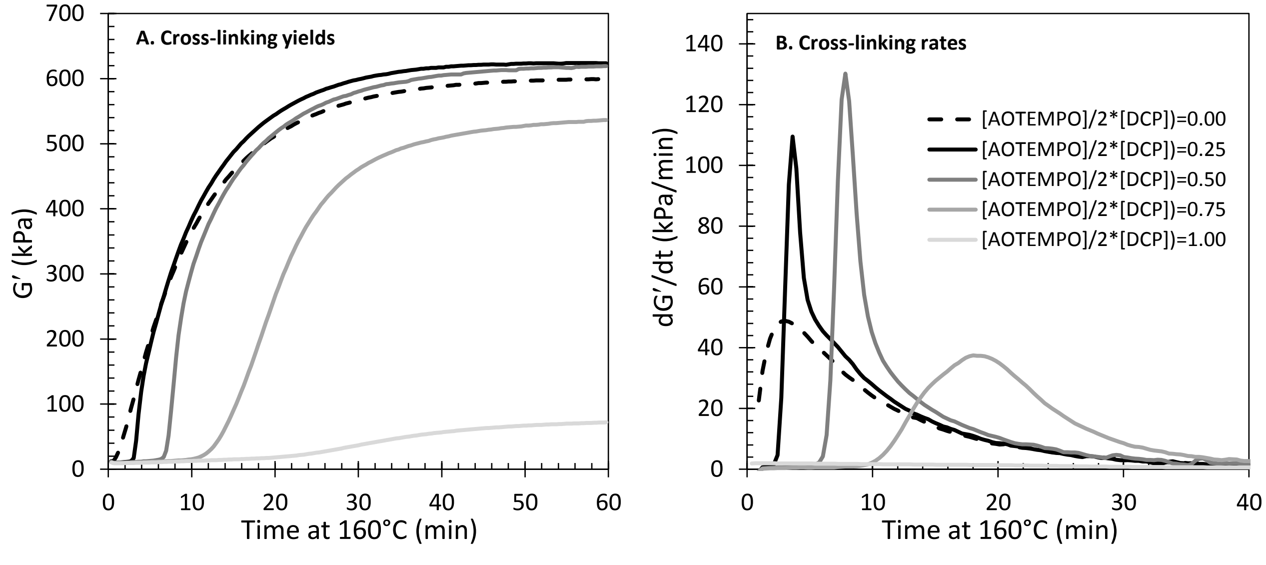

Figure 3.1. DCP-initiated LLDPE cure formulations containing different nitroxyl concentrations ([DCP]=55.6 μmole/g; a. Storage modulus, G'; b. Cure rate, dG'/dt)

The effect of AOTEMPO on these high-DCP loading formulations is consistent with the aforementioned low-initiator concentration data. Processes involving AOTEMPO are not simple stoichiometric cures, but more complex cross-linking reactions comprised of three distinct stages: a trapping phase in which carbon-centred radicals are quenched by combination with nitroxyl functionality; an oligomerization phase where cross-linking is achieved by activation of pendant acrylate functionality; and a stoichiometric phase wherein cross-linking occurs solely due to macro-radical coupling.

These stages are clearly illustrated by the dG′/dt data plotted in Figure 3.1b. The induction time, t_{ind}, marked the transition from the radical trapping phase, in which cross-linking was prevented by generating spin-paired alkoxyamines at the expense of alkyl radical + alkyl radical termination products. The accompanying loss of cure extent was recovered during the oligomerization phase as cross-links were generated by repeated acrylate addition to propagating macro-radicals, thereby producing multiple cross-links from relatively few initiator-derived radicals. Once all the acrylic macro-monomer functionality was consumed, the process entered the stoichiometric phase during which cross-linking rates were equal to those of DCP-only formulations.

The stated objective of this work is to establish principles of AOTEMPO formulation development to help users of the technology meet cross-link density and induction time targets. This requires knowledge of the relationship between formulation variables ([DCP], [AOTEMPO]) and process outcomes ($\Delta G'$, t_{ind}). Figure 3.2 presents this information in terms of the trapping ratio, [AOTEMPO]/(2*[DCP]), which represents the fraction of initiator-derived radicals that can be quenched by combination with nitroxyl. In theory, this ratio can be varied from zero to infinity, but cross-linking requires radical initiation. Therefore, trapping ratios cannot exceed one if the polymer is to be cured, and they should be considerably less than this limit if the peroxide is to be used with reasonable efficiency.

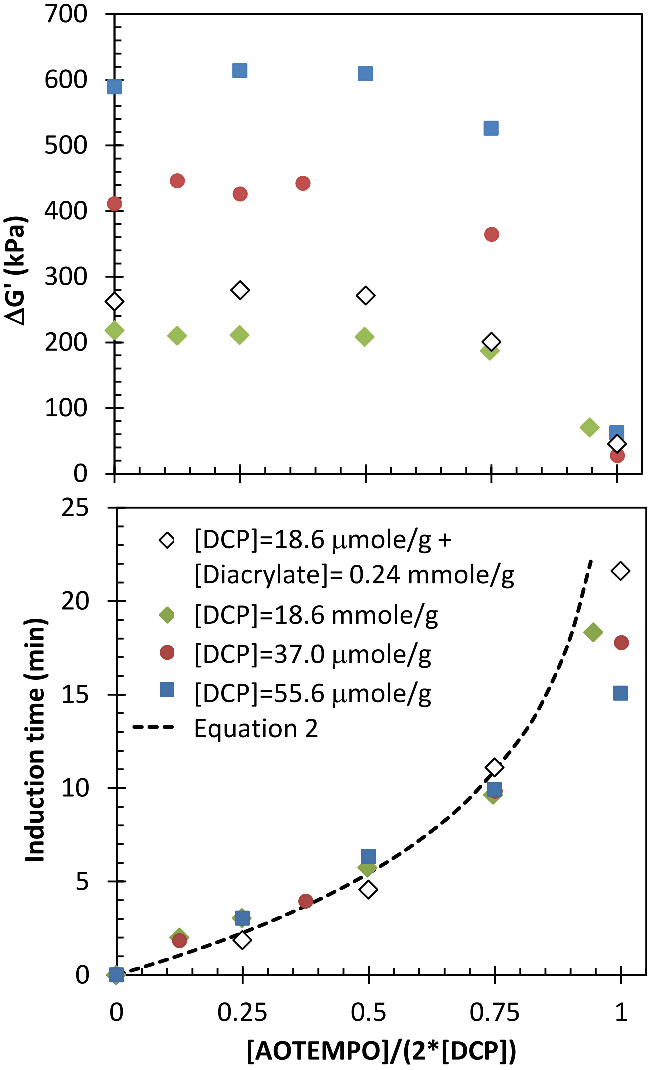

Figure 3.2. Cure yield (ΔG') and induction time (t_{ind}) as a function of radical trapping ratio (T=160°C)

Three series of experiments provided the data illustrated in Figure 3.2, each performed with a different initiator concentration. In the absence of AOTEMPO, the onset of DCP-initiated cross-linking was immediate, resulting in $t_{ind} \approx 0$ min. The cure yield (ΔG´) produced by peroxide alone scaled linearly with peroxide concentration, as expected of a stoichiometric curing reaction. This linearity simplifies the process of establishing the initiator loading needed to meet a cure yield target for a given polymer at a specific temperature. Of course, peroxide-only formulations cannot provide scorch protection, necessitating the use of an appropriate additive.

Most anti-oxidants provide scorch safety at the expense of cure extent, since they quench macro-radical activity without providing a mechanism to recover cross-link density. Since the concentration of such additives affects both the scorch time and the cure yield, only trial and error experimentation of peroxide and additive loading will provide an acceptable formulation. The application of AOTEMPO, on the other hand, is considerably simpler, since cure yields are insensitive to the concentration of acrylated nitroxyl. That is, at a given peroxide concentration, the cure yield remains constant up to a trapping ratio of 0.5, whereupon it declines continuously as it approaches 1.0. Therefore, as long as no more than one half of initiator-derived radicals must be trapped to satisfy a t_{ind} target, an AOTEMPO formulation will require the same DCP loading as an additive-free formulation.

The relationship between induction time, t_{ind}, and nitroxyl concentration was derived in Chapter 2. Recognizing that initiator-derived radicals generated in the presence of nitroxyl are quenched rapidly, the fraction of trapped DCP-derived radicals is $[AOTEMPO]/(2*[ROOR]_o)$. During this phase of the process, initiator is converted without generating cross-linking activitiy. Since DCP thermolysis is a first-order decomposition reaction that is not affected by the presence of nitroxyl, the induction time can be expressed by equation 1,

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

where k_d is the first-order rate constant for DCP homolysis at the reaction temperature. Industrial practitioners of curing technology generally prefer initiator half-lives to decomposition rate constants. Given the definition of initiator half-life, $t_{1/2} = -\ln(1/2)/k_d$, the induction time can be expressed in the form of equation 2.

$$t_{ind} = \frac{t_{1/2}}{\ln(1/2)} \ln\left[1 - \frac{[\text{AOTEMPO}]}{2[\text{ROOR}]_o}\right] \qquad (2)$$

Figure 3.2 presents observed induction times plotted as a function of trapping ratio for all three series of experiments. Irrespective of the DCP concentration employed, good agreement was observed between experimental t_{ind} values and those predicted by equation 2. As such, the equation can be used with confidence to calculate the trapping ratio needed to meet a t_{ind} specification. Armed with knowledge of the initiator loading required to satisfy a ΔG' target, the necessary AOTEMPO concentration is easily determined.

According to equation 2, induction times can range from a small fraction of $t_{1/2}$ to nearly 50 times the peroxide half-life, depending on the trapping ratio employed. However, practical limitations confine this range considerably, since the oligomerization phase of an AOTEMPO-based cure requires sufficient radical initiation to convert pendant acrylate functionality into cross-links. A failure in this regard will stunt cure yields, as illustrated in Figure 3.2 where trapping ratios of 0.75 and greater were used. If a limit of [AOTEMPO]/(2*[DCP]) = 0.5 is adopted, then the maximum induction available from a given formulation is equal to one initiator half-life. For the LLDPE cures of current interest, DCP thermolysis limits t_{ind} to 5.5 min at 160°C.

3.3.2. Reaction temperature

Peroxide half-life is a concern for all polyolefin modifications, not just the delayed-onset process of present interest. Complete initiator consumption is generally desired to maximize reaction yields, thereby establishing 5 half-lives (97% peroxide conversion) as a minimum overall time for most cross-linking processes. The half-lives of DCP at 140°C, 160°C and 180°C are 43 min, 5.5 min and 0.83 min, respectively. The cure rheology data plotted in Figure 3.3 confirm that on the order of $5*t_{1/2}$ is required to complete DCP-initiated processes operated at each of these temperatures. More significant is the performance of AOTEMPO throughout this temperature range. Not only did AOTEMPO provide the predicted induction time for a trapping ratio of 0.25, these delayed-onset formulations gave the same yield as their peroxide-only counterparts.

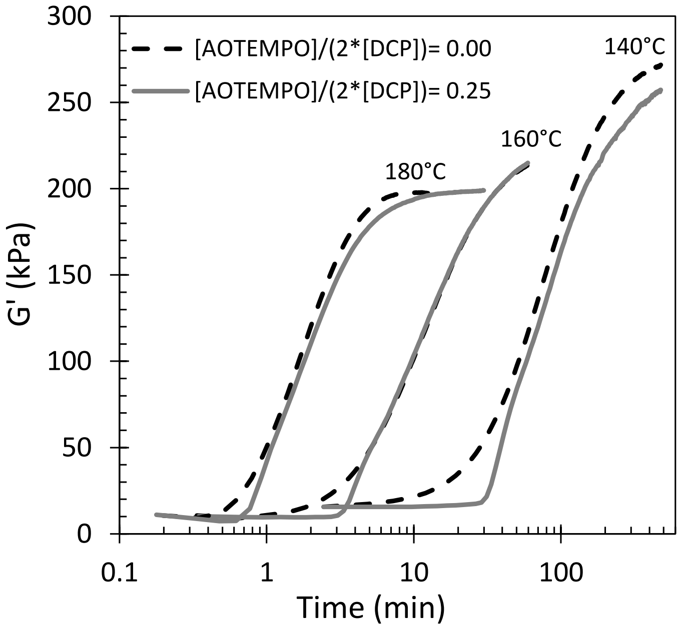

Figure 3.3. Dynamics of DCP-initiated LLDPE cure formulations operating at different temperatures ([DCP]=18.5 μmole/g; [AOTEMPO]=9.2μmole/g)

Initiator half-life restrictions and, by extension, t_{ind} limits, can be avoided through judicious choice of peroxide. Whereas a DCP-initiated process is too slow for practical application at 136°C, the half-life of 1,1-di(*t*-butylperoxy)-3,3,5-trimethylcyclohexane (L-231) is 5.5 min at this temperature. Conversely, the rapid decomposition of DCP at 176°C can be avoided by using 2,5-di(*t*-butylperoxy)-2,5-dimethyl-3-hexyne (L-130), whose half-life at this temperature is also 5.5 min. Figure 3.4 presents cross-linking data for these three peroxides, each operating at the temperature that provides a 5.5 min half-life. The dynamics of each process are very similar, as expected from their consistent initiator decomposition rates.

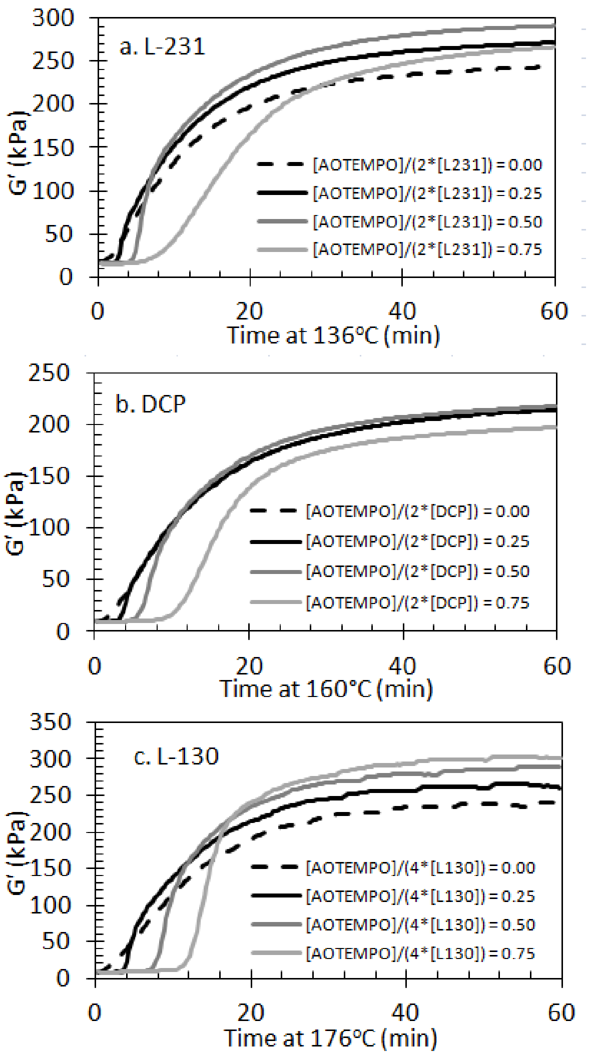

Figure 3.4. Dynamics of LLDPE cures initiated by different peroxides (a. L-231 at 136°C; b. DCP at 160°C; c. L-130 at 176°C)

The L-231 initiated process is remarkable in that the delayed onset formulations provided better cross-link density yields than the peroxide-alone process, whereas DCP-initiated cures showed little evidence of this effect. One potential explanation involves differences in the susceptibility of *t*-butoxyl and cumyloxy radicals toward β-scission. One of the drawbacks of peroxide cures is the fragmentation of peroxide-derived radicals to ketones + methyl radicals, since trapping of the latter by nitroxyl yields alkoxyamine that is not bound to the polymer. In the case of AOTEMPO cures, it is highly desirable to produce macro-radicals at the expense of methyl radicals, since high macro-radical yields gives rise to large amounts of pendant acrylate functionality in the macro-monomer intermediate. The L-231 formulation operating at 136°C has two advantages over DCP operating at 160°C, in that lower temperatures disfavour alkoxy radical fragmentation, and *t*-butoxyl is less susceptible to scission than cumyloxyl. This may account for the observed improvement in LLDPE cure yields.

3.3.3. Cross-linking coagent compatibility

This study of AOTEMPO formulation design concluded with an examination of the compatibility of delayed onset chemistry with reagents that are widely used to boost cross-link densities. These additives, commonly called coagents, are small molecules containing multiple allylic, acrylic, or maleimide groups. Activation of the C=C functionality within these coagents can produce cross-links through closed propagation sequences that do not consume radical intermediates. In the case of coagents such as neopentyl glycol diacrylate (NDA), polyolefin cross-linking is generally believed to occur by repeated C-H bond addition from the polymer to acrylate functionality. Grafting of polymer chains to multiple ends of the coagent and/or coagent oligomers gives a covalent polymer network without terminating radicals. Therefore, higher cross-link yields can often be achieved at a given peroxide initiator loading.

Coagents have been classified into two groups, so called Type I coagents that are kinetically very reactive, and Type II coagents that raise cross-link densities without affecting initial cross-linking rates substantially. Type I coagents include acrylate, styrenic and maleimide-based additives, whose activation by free radical addition can create severe scorch problems. As such, NDA-based formulations could benefit greatly from an effective delayed action strategy. Given that NDA and AOTEMPO both bear acrylate functionality, the potential exists for co-oligomerization between coagent and scorch protectant. This could prove to be beneficial, since the coagent would no longer have to graft to LLDPE by C-H bond addition, but could contribute to cross-linking by copolymerizing with polymer-bound macro-monomer groups.

Figure 3.5 presents a series of LLDPE cures that demonstrate the compatibility of NDA and AOTEMPO. As expected, when nitroxyl additive was omitted from the formulation, the diacrylate coagent increased the initial rate of LLDPE cross-linking as well as the final cross-link density. This is an inherent trade-off between scorch safety and cure yield imposed by acrylate-based coagents. However, an outstanding induction delay and cross-link density was accomplished using AOTEMPO at a trapping ratio of 0.5. The cure rate data shown in Figure 3.5b are instructive, as they show that NDA did not compromise the ability of AOTEMPO to provide the requisite induction time, but served only to accelerate the oligomerization phase of the cross-linking process. After about two initiator half-lives, cure rates diminished to the levels generated by a standard stoichiometric cure, indicating that both NDA and AOTEMPO-derived acrylate groups were consumed within the same time period.

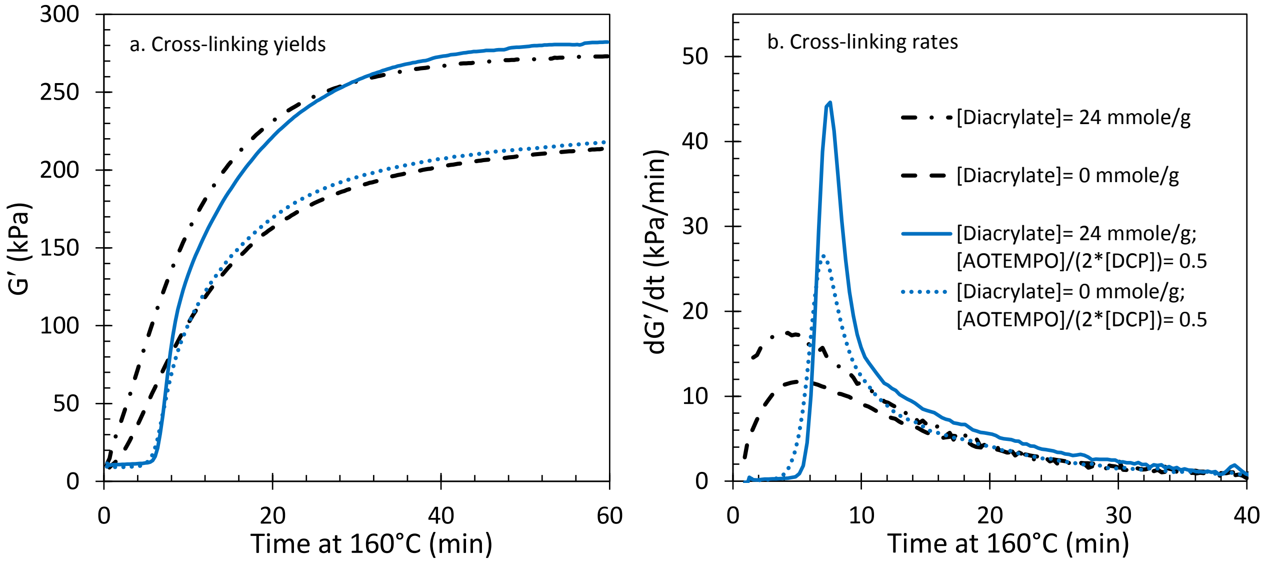

Figure 3.5. Coagent assisted LLDPE cures ([DCP] = 18.5 μmole/g; T=160°C)

3.4. Conclusions

AOTEMPO strategy effective over wide range of initiator structures, concentrations and decomposition temperatures. Cure rate data yields strong evidence of three distinct phases: alkyl radical trapping by AOTEMPO, pendant acrylate oligomerization and stoichiometric macro-radical combination. AOTEMPO loadings up to a trapping ratio of 0.5 result in modulus values equivalent to additive-free formulations. As such, G' targets are independent of AOTEMPO loading and nitroxyl concentrations are chosen solely to achieve induction targets. Different peroxides may be employed to achieve induction times that would otherwise require greater trapping ratios. In the presence of a cure boosting diacrylate coagent, the observed modulus increase was equal to the additive-free formulation. Complete induction was maintained and coagent oligomerization rates overlap with pendant acrylate functionality, exhibiting remarkable compatibility with diacrylate coagents.

3.5. References

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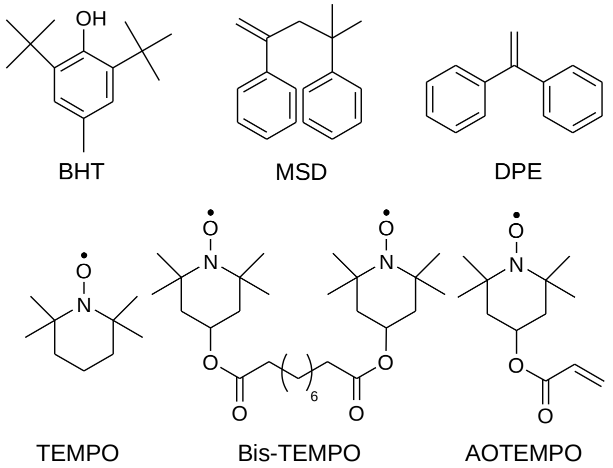
[1] M. Appelt and G. Schmidt-Naake, "Nitroxide-Controlled Grafting by an Insertion Mechanism using a Polymerizable N-Oxyl," *Macromolecules,* vol. 289, pp. 245-253, 2004.

Chapter 4 Comparative Analysis of Delayed-onset Peroxide Cure Formulations

4.1. Introduction

Previous chapters have described delayed-onset cure formulations based on nitroxy radical traps, whose kinetic reactivity and selectivity for carbon-centred radicals makes them well suited to the suppression of polyolefin cross-linking in the earliest stages of the curing process. The development of acrylated nitrxoxyls such as AOTEMPO (Scheme 4.1) is a significant advance in the state of art, since scorch delays can be predicted precisely, and induction times can be gained without compromising cross-link densities. However, there are a wide range of scorch-protecting additives that are described in the open and patent literature, some of which claim to provide both induction delays and improvements to cross-link densities. This chapter examines six additives, butylated hydroxyl toluene (BHT), α-methylstyrene dimer (MSD), 1,1-diphenylethylene (DPE), TEMPO, bis(1-oxyl-2,2,6,6-tetramethylpiperidine-4-yl)sebacate (bis-TEMPO), and AOTEMPO, with the objective of comparing their performance under standardized conditions.



Scheme 4.1. Scorch additives of interest

4.2. Experimental

4.2.1. Materials

Linear low density polyethylene (LLDPE, 5% hexane copolymer) and *cis*-1,4-polyisoprene (PIP, 97%) was used for this study. Dicumyl peroxide (DCP, 98%), hydroxyl-TEMPO (4-hydroxyl-2,2,6,6-tetramethylpiperidin-1-oxyl, 97%), acryloyl chloride (≥97%, 400 ppm phenothiazine), triethylamine (≥99.5%), sebacoyl chloride (95%), 1,1-diphenylethylene (DPE, 97%), 2,4-diphenyl-4-methyl pentene (MSD, 97%) were used as received from Sigma Aldrich (Oakville, ON).

4.2.2. Synthesis

4-Acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl

A solution of TEMPOH (1 g, 5.81 mmol) and triethylamine (706 mg, 0.97 mL, 6.98 mmol) was reacted with acryloyl chloride (0.632 g, 0.57 mL, 6.98 mmol) in toluene at room temperature for 16 hours. The solids were removed by filtration and washed multiple times with toluene. The solution was dried under vacuum to yield orange crystals. Crystals were recrystallized from cyclohexane and dried under air flow. m.p. 92°C (lit. 93°C [1]). ^{1}H-NMR: ($CDCl_3$): δ (ppm) = 6.49 (1 H, dd, HC=C), 6.19 (1 H, dd, C=CH-C), 5.96 (1 H, dd, HC=C), 1.0 – 2.0 (17 H). High-res. M.S. $C_{12}H_{20}NO_3$ calculated m/z $[M+2H]^+$ 228.1596; found m/z 228.1599.

Bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate

A solution containing excess TEMPOH (2.0 g, 12.8 mmol) and triethylamine (1.042 g, 1.436 mL, 10.6 mmol) was reacted with sebacoyl chloride (2.534 g, 2.230 mL, 10.6 mmol) in toluene at room temperature for 12 hours. A white precipitate reaction product was removed by centrifuging until compact and decanting the orange liquid. The orange liquid was dried under reduced pressure to yield a highly viscous, tan liquid. ^{1}H-NMR: ($CDCl_3$): δ (ppm) = 5.049 (2 H, tt, HC-O-C), 4.007 (4 H, tt, COOC-H), 1.753 (4 H, dd, piperidinyl CH), 1.604 (4 H, t, piperidinyl CH), 1.215 (3 H, s, piperidinyl CH_3), 1.170 (3 H, s, piperidinyl CH_3). High-res. M.S. $C_{28}H_{50}N_2O_6$ calculated m/z 510.3669; found m/z 510.3665.

4.2.3. Instrumentation and analysis

Rheology measurements were performed using an Advanced Polymer Analyzer 2000 (Alpha Technologies) with a 3° arc and a frequency of 1 Hz.

4.2.4. Polymer solution coating process

LLDPE pellets (5 g) were finely ground and coated with an acetone solution containing DCP initiator, desired nitroxyl species and any additional additives. The ground pellets were hand mixed and allowed to dry thoroughly. PIP and HNBR rubbers were milled until flat, treated with solution and re-milled post-drying. Excessive drying of solutions containing sublimable nitroxyls (ie. TEMPO) was avoided. The treated polymer was then cured in an oscillating disk rheometer (Advanced Polymer Analyzer, Alpha Technologies) at the aforementioned strain rate.

4.3. Results and Discussion

The additives illustrated in Scheme 4.1 were assessed by monitoring the storage modulus of LLDPE cure formulations operating at 140°C, 160°C and 180°C. Dicumyl peroxide (DCP) was used as initiator in each experiment, and the molar ratio of scorch additive to cumyloxy radicals was maintained at 0.25. If an additive is an effective scorch-protectant, this loading should be sufficient to quench cross-linking activity in the reaction's early stages. Moreover, if the additive affects the final cure yield (either positively or negatively), this concentration is sufficient to produce a measureable response.

Figure 4.1a shows the effect of BHT on the dynamics and yields of an LLDPE cure. The response to this additive is typical of a relatively efficient anti-oxidant, in that the initial cure rate is retarded but not quenched entirely. This indicates that the rate of hydrogen atom donation to cumyloxyl, methyl and macro-radical intermediates is not sufficient to eliminate all macro-radical termination events, resulting in a small degree of cross-linking from the onset of peroxide decomposition. Whereas a nitroxyl-based system such as TEMPO (Figure 4.1b) provides an induction period during which time the modulus is completely unchanged, kinetically less reactive traps such as BHT only slow the initial rate. As such, these additives are usually characterized by a scorch time, $t_{10\%}$, defined as the time needed for a cure formulation to rise by 10% of its initial melt modulus. For example, the BHT formulation run at 180°C has an initial melt modulus of 9.3 kPa and reached a 10% increase of this value (10.2 kPa) in 0.42 minutes, giving $t_{10\%}$=0.42 min.

A closer examination of the data in Figure 4.1a shows that the efficacy of BHT as a radical trap is highest at 140°C, both in terms of delaying cross-linking and affecting the final storage modulus. That only 0.25 equivalents of BHT relative to DCP-derived initiator radicals can have such a great effect on ultimate cross-link density is attributed to the multiple quenching reactions provided by this antioxidant. It is well known that hydrogen atom donation by BHT yields a resonance stabilized phenoxy radical whose relative stability precludes any potential activation of the polymer. Therefore, termination pathways are preferred, yielding non-radical products through typical combination or disproportionation reactions (Scheme 4.2). This trapping sequence can quench two radicals per molecule of BHT, but the actual trapping efficiency can be much greater, given that termination products are capable of further radical reactivity that mitigates the extent of macro-radical formation.

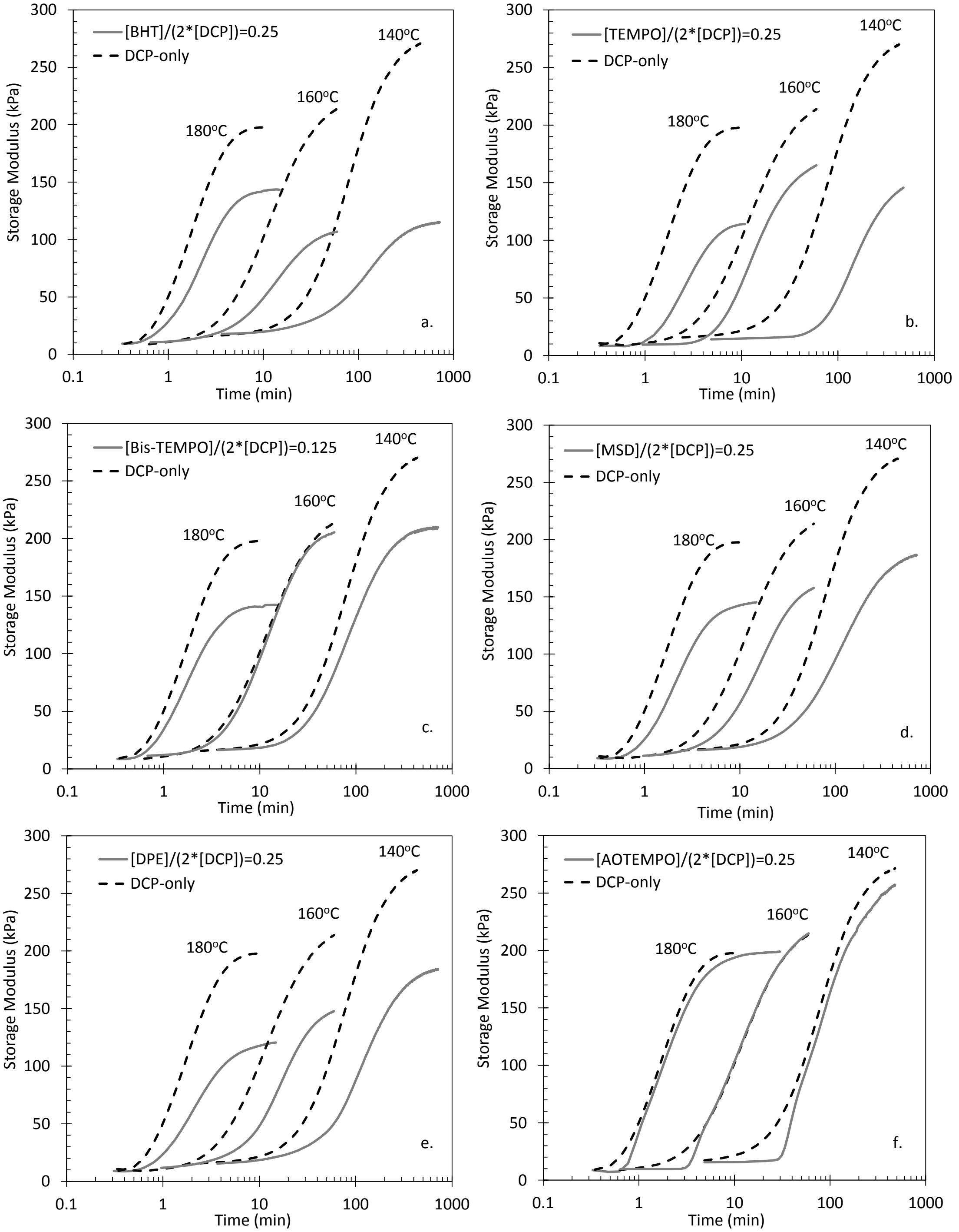
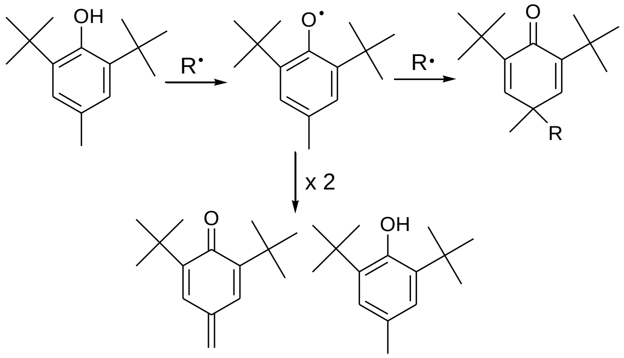


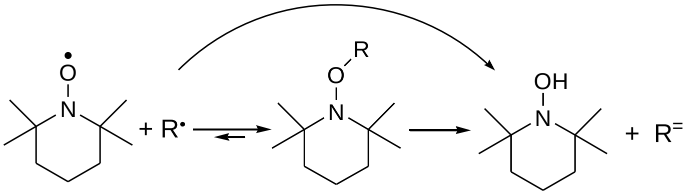
Figure 4.1. Dynamics of delayed-onset LLDPE cures at different temperatures ([DCP]=18.5 μmol/g; a. [BHT]=9.2 μmol/g; b. [TEMPO]=9.2 μmol/g; c.[Bis-TEMPO]= 4.6 μmol/g; d. [MSD]=9.2 μmol/g; e. [AOTEMPO]=9.2 μmol/g



Scheme 4.2. Initial trapping reactions of BHT (R· = alkyl, alkoxyl, radicals)

The macro-radical trapping efficiency of BHT, as indicated by the delayed onset character of its LLDPE cure formulations, is sufficient at 180°C to establish it as a scorch protecting additive. However, the depression of ultimate cross-link density is problematic. In order to reach a given modulus target, a BHT formulation will require more initiator than a BHT-free formulation. More initiator increases initial cure rates, thereby necessitating the use of more scorch protectant. Continued increasing of peroxide and anti-oxidant is not only undesirable from a cost perspective; it leads to higher reaction by-product concentrations in the thermoset. Because these by-products are not polymer-bound they may be extracted or leached from the article.

Nitroxyl-based additives such as TEMPO are superior in a number of ways. In the first place, they combine with alkyl radicals near the diffusion limit of reaction velocities [2] [3]. As demonstrated by Figure 4.1b, TEMPO provides induction times during which no cross-linking activity whatsoever is observed. This condition holds as well at 140°C as it does at 180°C, thereby providing a robust method of scorch protection. Alkyl radical quenching yields alkoxyamines whose stability to thermolysis and disproportionation depends on the alkyl substituent (Scheme 4.3). Reversibility is valued by those practicing controlled radical polymerization of acrylic and styrenic monomers, but not in scorch retardant applications. Since an ideal delayed-onset formulation does not generate unbound by-products, the polymeric alkoxyamines derived from macro-radical trapping by a nitroxyl should be thermally stable.

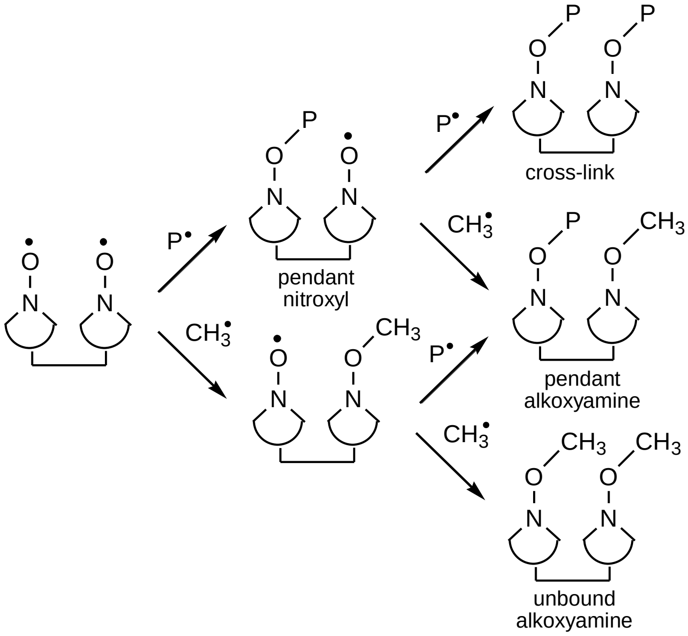


Scheme 4.3. Radical trapping and disproportionation reactions of TEMPO (R· = alkyl radicals, $R^{=}$ = unsaturated alkene)

The limited data available on alkoxyamine stability indicates that secondary alkoxyamines do not undergo nitroxyl exchange readily at 160°C, meaning that their formation under the present reaction conditions is effectively irreversible. Moreover, disproportionation to olefin and hydroxylamine requires on the order of hours to reach measurable conversion [4], indicating that alkoxyamine stability is sufficient for the purposes of polyolefin cross-linking. Note that the disproportionation mechanism is not well understood and the reaction may occur through radical or non-radical pathways. In either case, the resulting hydroxylamine would be readily oxidized back to TEMPO, thereby trapping another initiator-derived radical intermediate.

One of the potential benefits of a nitroxyl-based cure formulation is the binding of the scorch protecting reagent to the polymer, thereby rendering it unextractable from the cured product. Unlike phenolic anti-oxidants, DPE and MSD, nitroxyls do not trap oxygen-centred radicals, and cannot, therefore, quench cumyloxyl intermediates derived from DCP. Rather, they trap only polymer macro-radicals and the methyl radicals originating from cumyloxyl fragmentation. The latter are particularly troublesome from the perspective of by-product leaching, since 1-methoxy-2,2,6,6-tetramethyl-1-piperidine (methyl-TEMPO) is a volatile organic compound that is not covalently bonded to the polyolefin. The potential of the AOTEMPO system to convert methyl alkoxyamine to polymer-bound functionality will be considered, following an examination of the bis-TEMPO, MSD and DPE systems.

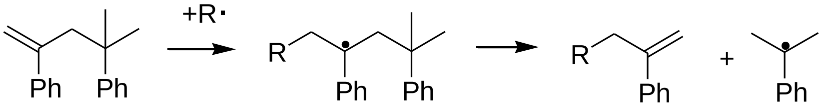
Figure 4.1c illustrates the effect of bis-TEMPO on peroxide-initiated LLDPE cures. This approach was advocated by Chaudhary et al.[5], who suggest that a bi-functional nitroxyl can retard initial cure rates at 140°C, and increase cure extents at 180°C, making this the first of the so called "cure-boosting" scorch retardants examined in this study. Their non-isothermal treatment of scorch protection is commonly practiced, given that most commercial thermoset processes activate the peroxide while heating continuously to a temperature that provides the appropriate melt viscosity. The data presented in Figure 4.1c show that bis-TEMPO had virtually no effect on our LLDPE cure system at 160°C, as the DCP-only and additive formulations were nearly indistinguishable. Several replicates of both data sets confirmed this coincidence. At temperatures above and below this point, some scorch delay was observed, albeit at the expense of cross-link density.



Scheme 4.4. Potential trapping products of bis-TEMPO (P· = alkyl macro-radical)

A comparison of the bis-TEMPO and TEMPO formulations is instructive. Whereas TEMPO provided an induction period during which the storage modulus was unchanged, bis-TEMPO only retarded the initial stages of the curing process slightly (Figure 4.1b, Figure 4.1c). Scheme 4.4 provides some insight into the inferior scorch protection performance of the bis-TEMPO system. Given that the nitroxyl functionality will trap methyl radicals and polymer macro-radicals at a rate that is limited only by molecular diffusion, the rate of alkoxyamine formation is controlled strictly by the rate of peroxide thermolysis. This is true of peroxide-only formulations as well, in which macro-radical termination rates are limited to the rate of peroxide breakdown. Note that initial trapping by bis-TEMPO does not quench a macro-radical, but merely converts it to a pendant nitroxyl intermediate. This new macro-radical can combine with another macro-radical to yield a cross-link, or with a methyl radical to give a pendant alkoxyamine. As such, bis-TEMPO cannot prevent polyolefin cross-linking in the manner of a mono-functional nitroxyl such as TEMPO.

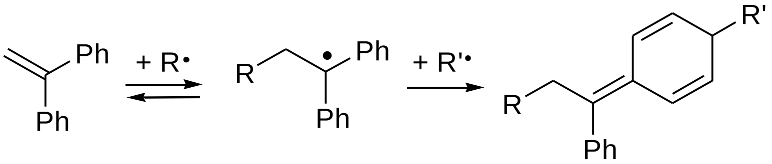
The α-methyl styrene dimer (MSD, Scheme 4.1) system is a rational approach to controlling cross-linking rates and yields. It is based on the trapping of macro-radicals by addition to give a benzylic radical that is susceptible to fragmentation (Scheme 4.5). The resulting cumyl radical is resonance-stabilized, and has a limited capacity to abstract hydrogen from the polyolefin. Hence, when R· is cumyloxyl, methyl or a macro-radical, addition to MSD quenches its reactivity, leading to cure-retardation. Because the rate of radical addition to a styrenic monomer is much slower than the rate of trapping by nitroxyl, MSD cannot provide the induction behaviour generated by a TEMPO (Figure 4.1d). However, macro-radical trapping by MSD can yield terminal styrenic functionality, thereby converting the polyolefin into a macro-monomer. If this functionality is oligomerized later in the cure process, the potential exists for recovering lost cross-link density. Unlike the stoichiometric macro-radical formation + macro-radical termination sequence that comprises a peroxide-only cure, a macro-monomer oligomerization process can have kinetic chain length, producing many cross-links from a single initiator-derived radical.



Scheme 4.5. Addition-fragmentation reactions of MSD (R· = alkyl macro-radical, methyl, alkoxy radicals)

While some reports indicate that MSD can boost cure yields, the data presented in Figure 4.1d show no such improvements for a LLDPE+DCP formulation. Clear evidence of scorch protection was observed, but irrespective of the temperature employed, significant losses in cross-link density were incurred. This may be due to excessive trapping of cumyloxyl by MSD, which could suppress cross-linking while producing the corresponding vinyl ether [6]. Ideally, MSD would intervene in the cross-linking process by trapping macro-radicals to give pendant styrenic groups in high yield. If the yield of macro-monomer groups is too low, then the potential for generating cross-links by oligomerization will be stunted, as observed in the present study.

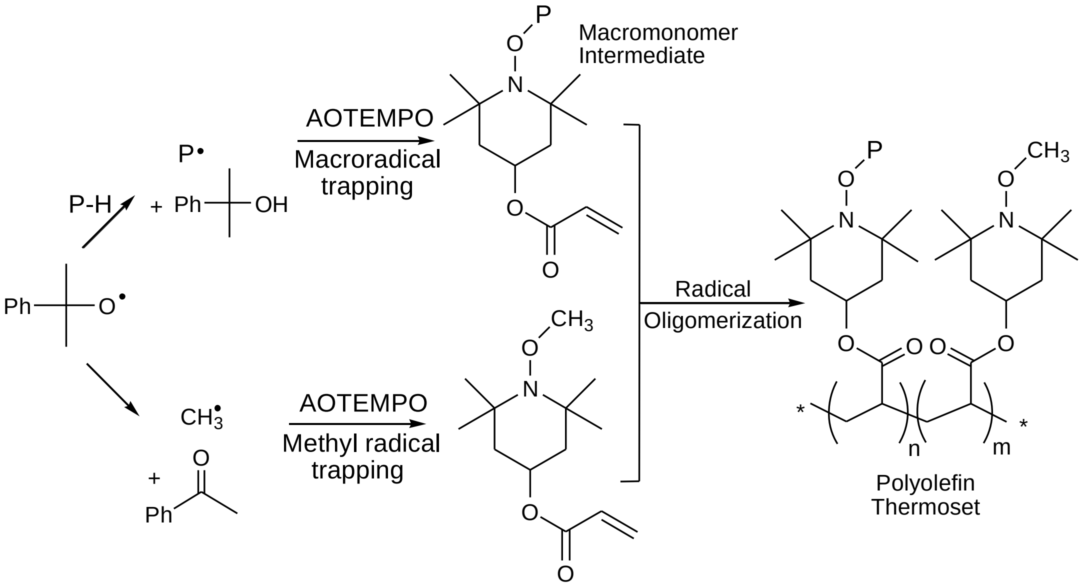
Based upon what little is known of the chemistry of DPE, the cure data plotted in Figure 4.1e is not surprising. At each reaction temperature, 0.25 equivalents of DPE relative to cumyloxyl served to depress both the rate and the extent of polyolefin cross-linking. The mechanism of action is likely to be similar to that of MSD, in that radical trapping by C=C addition yields a highly resonance-stabilized benzylic radical (Scheme 4.6). In this case, radical fragmentation is not favourable, and the likely outcome for the persistent radical intermediate is termination. Without a mechanism for regaining cross-link density, the use of DPE provides scorch protection at the expense of cure yield.



Scheme 4.6. Potential trapping reactions of DPE (R·, R’· = alkyl macro-radicals, methyl, alkoxy radicals)

AOTEMPO technology is a novel hybrid of the TEMPO and MSD scorch protection strategies. It is based upon differences in the kinetic reactivity of nitroxyl and C=C functionality toward radical trapping. Recall that the rate constants for alkyl radical combination with nitroxyls are generally of the order of 10^8-10^9 $M^{-1} s^1$ [2], while those for alkyl radical addition to acrylates are of the order of 10^3-10^5 $M^{-1} s^1$ [7]. Therefore, AOTEMPO can trap macro-radicals by combination, as opposed to acrylate addition, thereby quenching radical activity while transforming the polyolefin into a macromonomer bearing pendant acrylate functional groups. This approach is analogous to MSD, which has the potential to introduce styrenic functionality to the polymer (Scheme 4.5). However, the kinetic reactivity of AOTEMPO is far superior to that of MSD, as is its selectivity for carbon-centred radicals over oxygen-centred radicals. The latter is particularly important, since AOTEMPO allows cumyloxyl to abstract hydrogen from the polymer to produce the requisite macro-radical intermediates. The result is a superior yield of polymerizable functionality in the macromonomer.

The cure rheology data presented in Figure 4.1f demonstrate the three phases of an AOTEMPO cure, an induction period, an accelerated cross-linking phase, and continuing cross-linking phase involving peroxide-only chemistry. An idealized reaction mechanism is illustrated in Scheme 4.7. During the induction phase, macro-radicals and methyl radicals are trapped by combination with AOTEMPO, quenching radical activity to produce alkoxyamine intermediates. This eliminates cross-linking, until nitroxyl concentrations fall to the point where radical addition to acrylate functionality is kinetically competitive. Once all AOTEMPO is consumed, oligomerization of pendant acrylate groups generates cross-links by a kinetic chain process that requires relatively few initiating radical species, owing to the efficiency of acrylate polymerizations. Once all macromonomer functionality is converted, curing proceeds by the simple peroxide-only chemistry that supports conventional polyolefin cross-linking.



Scheme 4.7. Trapping and oligomerization reactions of AOTEMPO (P· = alkyl macro-radicals)

The performance of the AOTEMPO is remarkable, in that it provides an induction period of absolutely no cross-linking, followed by a complete recovery of cross-link density during the acrylate oligomerization phase of the process. This unique combination is not provided by any other additive, as can be seen from the scorch time and cure yield data summarized in Table 4.1. This chemistry is also remarkable in terms of its potential use of methyl radical byproducts. In all of the systems examined to date, scorch protection was achieved at the expense of volatile organic compound production. This has consequences in terms of thermoset properties such as colour, odor and potential toxicity. The AOTEMPO quenches methyl radicals to yield the corresponding acrylate, whose oligomerization is expected to render it polymer-bound, or as a high molecular weight acrylate oligomer. As such, this technology has the potential to be more environmentally friendly than other scorch protection strategies.

Table 4.1. Summary of scorch protecting reagent performance

Additive	Temp (°C)	$t_{10\%}$ (min)	ΔG' (kPa)	$\Delta G'_{DCP}$ - $\Delta G'_{Additive}$ (kPa)
None	140	4.9	256	---
BHT	140	9.6	97	159
DPE	140	7.4	169	87
MSD	140	7.8	171	85
Bis-TEMPO	140	9.2	194	62
AOTEMPO	**140**	**24.8**	**242**	**14**
TEMPO	140	26.8	148	108
None	160	0.80	205	---
BHT	160	1.15	95	110
DPE	160	1.15	137	68
MSD	160	1.31	147	58
Bis-TEMPO	160	1.16	196	9
AOTEMPO	**160**	**3.04**	**20**	**0**
TEMPO	160	3.08	162	43
None	180	0.39	188	---
BHT	180	0.42	134	54
DPE	180	0.51	112	77
MSD	180	0.51	137	52
Bis-TEMPO	180	0.48	134	71
AOTEMPO	**180**	**0.63**	**192**	**-3**
TEMPO	180	0.72	106	82

([DCP]=18.5 μmol/g; [BHT] = [TEMPO]= [MSD]= [AOTEMPO]=9.2 μmol/g; [Bis-TEMPO]=4.6 μmol/g

Up to this point in the study, the efficacy of scorch retardants was examined only on LLDPE; a saturated polyolefin that requires quenching of secondary and tertiary alkyl macro-radicals. However, good performance on these materials does not necessarily translate to unsaturated polymers such as cis-polyisoprene (PIP). These unsaturated materials are better hydrogen atom donors, owing to the low bond dissociation energy of allylic C-H bonds. As a result, hydrogen atom abstraction from these materials by cumyloxyl is faster, giving a greater proportion of allylic macro-radicals than methyl radicals, when compared with a polymer such as LLDPE. Moreover, the stability of quenched intermediates can differ substantially between alkyl and allylic radical systems. For example, cleavage of the benzylic radicals illustrated in Scheme 4.5 and Scheme 4.6 back to their starting materials may be more important for PIP cures than for a polyolefin system.

Figure 4.2 provides storage modulus data for DCP-initiated cure formulations of PIP operating at 160°C. Note that the PIP used in this work had a higher initial modulus than LLDPE, starting at 105 kPa compared to just 8 kPa for LLDPE. Nonetheless, 18.5 μmol DCP per gram of polymer cured the diene-based elastomer efficiently, yielding an ultimate modulus of 286 kPa after 60 min reaction time. The inability of MSD or DPE to affect the cure process is noteworthy, since both these additives retarded cure rates and yields in LLDPE formulations. In the case of PIP, 0.25 equivalents of these reagents relative to cumyloxyl had no measurable effect, implying that neither compound affected macro-radical concentrations at any point in the curing process.

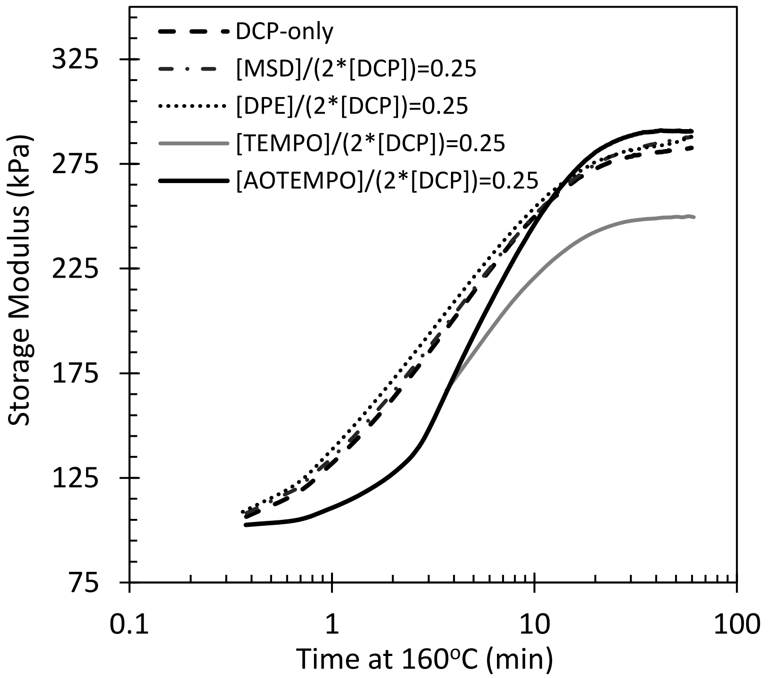
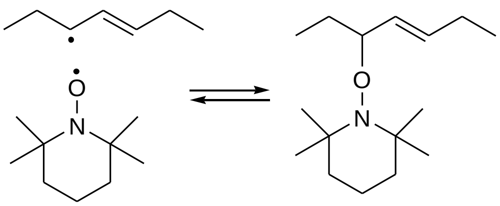


Figure 4.2. Dynamics of delayed-onset polyisoprene cures for various scorch retardants ([DCP]=18.5 µmol/g; [BHT]=[TEMPO]=[MSD]=[AOTEMPO]=9.2 µmol/g)

The nitroxyl-based reagents provided ample scorch protection by retarding cross-linking rates substantially, but not completely. The early stages of the TEMPO and AOTEMPO cures were indistinguishable, with the storage modulus increasing slowly but continuously, as opposed to the induction behaviour observed for LLDPE. Previous work by the Parent group on the stability of 1-(1-ethylpent-2-enyloxy)-2,2,6,6-tetramethylpiperidine (TEMPO-heptene) to nitroxyl exchange and disproportionation showed these allylic alkoxyamines to be susceptible to thermolysis at 160°C [3]. That is, the trapping of allylic radicals by TEMPO at these temperatures is reversible, with a dynamic equilibrium established between the radical reagents and the spin-paired alkoxyamine (Scheme 4.8). In the present context, this instability would support a small population of allylic macro-radicals, whose termination by combination gives rise to the observed storage modulus increases. Fortunately, the allylic alkoxyamines derived from PIP appear to be sufficiently stable to provide delayed-action cure behaviour.



Scheme 4.8. Reversibility of allyl radical trapping by TEMPO

Whereas the TEMPO formulation provided scorch protection at the expense of cross-link density, AOTEMPO proved capable of restoring the cross-link density lost to allyl radical quenching. The final modulus of the AOTEMPO formulation was slightly higher than that provided by DCP alone, and the thermoset showed no evidence of cure reversion. This is particularly important to engineering applications, where a stable ultimate modulus is required for end use performance.

4.4. Conclusions

H-donating additives like BHT provide only moderate scorch protection due to competition with H-donation from the polymer. Similarly, alkyl radical addition-reliant additives (MSD, DPE) are limited by the rate of addition and as such, only moderate scorch protection is observed. Evidence supporting this was provided by exploring alkyl radical stability on induction times through the use of PIP. Both classes of inhibitors lead to a loss in the final state of cure. As already observed, molecules bearing nitroxy radicals provide exemplary scorch protection; TEMPO lead to a decrease in final cure while AOTEMPO recovered entirely. Difunctional nitroxyls however, are unable to provide any scorch protection and this is believed to be due to the formation of nitroxyl linkages. These observations proved true regardless of temperature (140°C – 180°C).

4.5. References

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Chapter 5 Conclusions and Recommendations

AOTEMPO provided remarkable cure suppression and was capable of restoring the cross-linking extent to the additive-free equivalence. Less reactive functional groups exhibited varying degrees of recovery proportional to their tendency to homopolymerize.

In contrast, nitroxy radical-bearing TEMPO provided complete suppression of cross-linking for peroxide-initiated polyethylene cures over a range of temperatures (140°C – 180°C). Alkyl radical addition-reliant and H-donating additives also provided cure suppression but to a lesser extent. These additives, with TEMPO included, lowered the degree of cross-linking in the final article significantly.

Model compound work demonstrated AOTEMPO first traps alkyl radicals and subsequently oligomerizes macromonomer *in-situ*. Changes in polyethylene melt viscosity confirmed these results; curing rates indicated three distinct phases of trapping, oligomerization and alkyl macro-radical combination.

The AOTEMPO trapping / oligomerization strategy proved effective for a range of initiators, concentrations and decomposition temperatures. Complete compatibility was observed with cure boosting diacrylate coagents with no loss in induction time, cure suppression or cure recovery.

For future work, we recommend applying AOTEMPO to polymers that have tendency to otherwise degrade in the presence of free radicals (ie. polypropylene, poly(ethylene oxide), poly(isobutylene)). It is hypothesized that AOTEMPO may be able to trap alkyl radicals at rates greater than fragmentation and latently oligomerize acrylate groups to build a polymer network. Alkoxyamine stability will likely be a critical issue and experimentation with various nitroxyl bearing radicals may be required.