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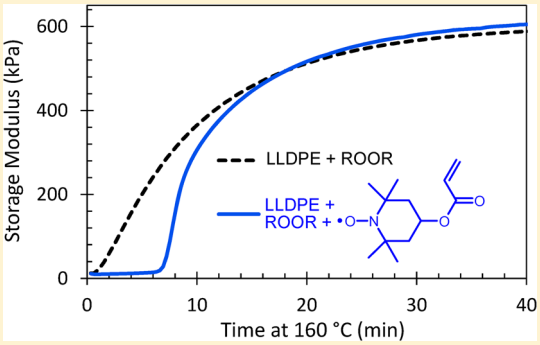
Functional Nitroxyls for Use in Delayed-Onset Polyolefin Cross-Linking

David K. Hyslop and J. Scott Parent*

Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada K7L 3N6

ABSTRACT: A new approach to controlling the dynamics and yields of polyolefin radical cross-linking is described, wherein 4-acryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (AOTEMPO) is used to quench macroradicals in the early stages of the process and to subsequently generate a covalent network through the oligomerization of polymer-bound acrylate functionality. Selectivity of alkyl radical trapping by AOTEMPO to give alkoxyamine intermediates in preference to acrylate addition products is discovered using model compound studies and through rheological measurements of linear low density polyethylene cross-linking. The latter demonstrate the ability of AOTEMPO to delay the onset of cross-linking while not compromising the cross-link density of the resulting thermoset. The influences of reagent loadings, peroxide decomposition rates, and the structure of polymerizable functionality are quantified and discussed.



INTRODUCTION

The chemical modification of polyolefins using radical chemistry is used widely to transform inexpensive commodity polymers into value-added materials.[1] A leading example is the cross-linking of ethylene-rich thermoplastics to yield thermoset derivatives that demonstrate improved mechanical properties and high temperature stability.[2] In their simplest form, these solvent-free processes operate on a polymer melt, using the thermolysis of dialkyl peroxides to generate alkoxy radicals as initiating species. Their hydrogen atom abstraction from the polymer provides macroradical intermediates, whose combination gives the desired network of carbon−carbon cross-links.[3] While several factors govern the effectiveness of these cross-linking processes, the efficiency of hydrogen atom abstraction from the polymer by alkoxyl radicals and the relative rates of macroradical combination and disproportionation are particularly influential.[4]

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. This can be difficult to achieve in radical cure systems, since peroxide decomposition is fastest in the initial phase of these batch reactions.[5] The need for chemistry that delays the onset of polymer cross-linking has led to a range of "scorch protection" strategies to quench radical activity in the early stages of the cross-linking process. Standard chain breaking donor antioxidants such as hindered phenols have been used[6] as well as chain breaking acceptors such as nitroxyls.[7] The latter can be highly effective since their trapping of alkyl radicals by combination occurs at the diffusion limit of radical−radical encounters.[8,9]

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.[10] Since simple peroxide cures are essentially stoichiometric processes that yield at most one cross-link per molecule of initiator, losses in macroradical yield have a proportional effect on attainable cross-link density. An alternate strategy that has the potential to retard initial cross-linking rates without adversely affecting ultimate cross-link densities has been developed based on the chain transfer chemistry of 2,4-diphenyl-4-methyl-1-pentene (α-MSD).[11] Macroradical trapping by α-MSD is proposed to suppress cross-linking while simultaneously introducing styrenic functionality to the polymer.[12] Oligomerization of these pendant vinyl groups could, in theory, generate cross-links that are lost to macroradical quenching.

This report describes an alternate 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.[13] Consider that the rate constants for alkyl radical addition to acrylates are of the order of 10^3−10^5 M^{-1} s^{-1},[14] while the rate constants for alkyl radical combination with nitroxyls are generally of the order of 10^8−10^9 M^{-1} s^{-1}.[15] As a result, the nitroxyls illustrated in Scheme 1 are expected to trap the macroradical 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.[16]

Under ideal circumstances, macroradical trapping by nitroxyl would dominate during the early stages of peroxide

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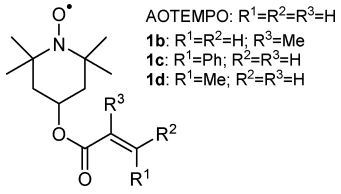
Scheme 1. Functional Nitroxyls of Interest



decomposition such that polyolefin cross-linking is suppressed until all nitroxyl is consumed (Scheme 2).[17,18] This induction period would, in turn, be 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 expected to be 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 macroradical trapping phase of the process has the potential to be recovered by the chain reaction that supports acrylate oligomerization.

This cross-linking chemistry is a creative use of reagents that have been developed for the controlled radical polymerization (CRP) of block copolymers.[19,20] 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 during polyethylene cross-linking should 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.[21] While the stability of secondary alkyoxyamines precludes their use in CRP, it should facilitate the delayed-onset cross-linking chemistry illustrated in Scheme 2.

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 4-acryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (AOTEMPO) are used to characterize the relative reactivity of nitroxyl and acrylate functionalities toward alkyl radicals. This fundamental knowledge is used to develop, evaluate, and analyze LLDPE cure dynamics and yields.

EXPERIMENTAL SECTION

Materials. Linear low density polyethylene (LLDPE, 5% hexane copolymer) was used as received from Dow Chemical. Dicumyl peroxide (DCP, 98%), 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOH, 97%), acryloyl chloride (≥97%), methacryloyl chloride (97%), crotonoyl chloride (90%), cinnamoyl chloride (98%), iron(II) sulfate (99%), hydrogen peroxide (30 wt % in H_2O), triethylamine (≥99.5%), and cyclohexane (99%) were used as received from Sigma-Aldrich.

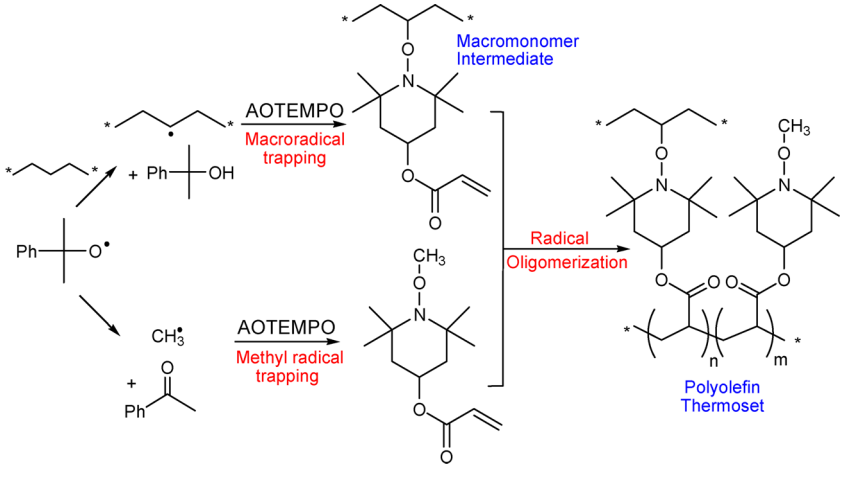
Instrumentation and Analysis. ^{1}H NMR spectra were recorded with Bruker AVANCE-400, -500, and -600 spectrometers in $CDCl_3$ solution. Characterization of paramagnetic species was attempted, yielding characteristic peaks for some, but not all resonances. High-resolution mass spectroscopy was conducted using a Waters/Micromass GCT- TOF mass spectrometer operating under electron impact mode. Gas chromatography was conducted using a Varian CP-3800 instrument equipped with a Chrompack capillary column (30 m × 0.25 mm, CP Sil 8 coating): Injector temperature: 200 °C; column temperature: 50 °C for 2 min, increase to 89 °C at 15 °C/min for 1 min, increase to 95 °C at 1 °C/min for 1 min, to 150 °C at 15 °C/min for 1 min, to 155 °C at 1 °C/min for 1 min, to 250 °C at 15 °C/min for 10 min.

LLDPE compounds were prepared by coating finely ground polymer LLDPE (5 g) with an acetone solution of the required DCP and nitroxyl, mixed by hand and allowed to dry. Samples were charged to an Advanced Polymer Analyzer 2000 (Alpha Technologies) equipped with biconical plates and operated with a 3° arc at a frequency of 1 Hz.

4-Acryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (AOTEMPO). Acryloyl chloride (632 mg, 0.57 mL, 6.98 mmol) in toluene (2.03 mL) was added dropwise to a solution of TEMPOH (1 g, 5.81 mmol) and triethylamine (706 mg, 0.97 mL, 6.98 mmol) in toluene (14.4 mL), and the mixture was stirred at room temperature for 16 h. The resulting solution was filtered before removing solvent under vacuum, yielding orange crystals that were recrystallized from cyclohexane. Yield: 59%; mp 92 °C; lit. 93 °C.[19] ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 6.50 (1 H, d, J_1 = 15.1 Hz), 6.19 (1 H, dd, J_1 = 12.0 Hz, J_2 = 7.9 Hz), 5.96 (1 H, d, J_1 = 7.93 Hz), 1.00–2.00 (17 H). IR (NaCl, thin film, cm^{-1}): 1722 (C═O), 1632 (C═C). HRMS (*m*/*z*): calcd for $C_{12}H_{22}NO_3$, 228.1596; found 228.1599 [M + 2H]$^+$.

4-Methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (1b). Methacryloyl chloride (188 mg, 0.176 mL, 1.79 mmol) in toluene (0.629 mL) was added dropwise to a solution of TEMPOH

Scheme 2. Idealized Delayed-Onset Cross-Linking Process Based on AOTEMPO



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(250 mg, 1.45 mmol) and triethylamine (182 mg, 0.251 mL, 1.79 mmol) in toluene (3.45 mL) at room temperature and left for 18 h before heating to 70 °C for 2 h. Filtration from a precipitate yielded orange liquid, which was reduced under vacuum to yield orange crystals that were then recrystallized from cyclohexane. Yield: 49%; mp 79 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.15 (1 H, s), 5.64 (1 H, s). IR (NaCl, thin film, cm^{-1}): 1715 (C═O), 1620 (C═C). HRMS (m/z): calcd for $C_{13}H_{22}NO_3$ 240.1600; found 240.1597.

4-Cinnamoyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (1c). Cinnamoyl chloride (300 mg, 1.80 mmol) in toluene (1.00 mL) added dropwise to a solution of TEMPOH (250 mg, 1.50 mmol) and triethylamine (177 mg, 1.80 mmol, 0.244 mL) in toluene (3.45 mL) and stirred for 3 h at 70 °C. The solids were allowed to settle, and the liquid decanted. The reduced liquid produced orange crystals under vacuum. Yield: 38%; mp 79 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.77 (1 H, m), 7.58 (2 H, m), 7.44 (2 H, m), 7.47 (1 H, m), 6.50 (1 H, m), 3.14 (1 H, s), 1.00−3.00 (16 H). IR (NaCl, thin film, cm^{-1}): 1709 (C═O), 1638 (C═C). HRMS (m/z): calcd for $C_{18}H_{24}NO_3$ 302.1756; found m/z 302.1765.

4-Crotonoyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (1d). A solution of crotonoyl chloride (188 mg, 1.80 mmol, 0.127 mL) in toluene (1.00 mL) was added dropwise to a solution of TEMPOH (250 mg, 1.50 mmol) and triethylamine (177 mg, 1.80 mmol, 0.244 mL) in toluene (3.45 mL), and the mixture was heated to 70 °C for 3 h. An orange liquid was decanted from white solids and reduced under vacuum to yield orange oil. Yield: 60%. IR (NaCl, thin film, cm^{-1}): 1735 (C═O), 1649 (C═C). HRMS (m/z): calcd for $C_{13}H_{22}NO_3$ 240.1600; found 240.1611.

1-Cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-ol, 1-Methoxy-2,2,6,6-tetramethylpiperidin-4-ol. DCP (5 wt %, 212 mg, 0.783 mmol) and TEMPOH (270 mg, 1.57 mmol) in cyclohexane (4.23 g) were charged to a stainless steel vessel and pressurized with N_2 to 14 bar prior to heating to 160 °C for 1 h. The vessel was cooled to room temperature and depressurized to give a crude reaction product, which was subjected to flash chromatography using a silica column (1:1 hexanes:ethyl acetate) to isolate the desired alkoxyamines as white crystalline solids. 1-Cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-ol: mp 77 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 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, J_1 = 9.54 Hz, piperidinyl CH), 1.77 (2 H, m, cyclohexyl CH), 1.49 (2 H, t, J_1 = 11.2 Hz, piperidinyl CH), 1.23 (6 H, s, CH_3), 1.18 (6 H, s, CH_3), 1.10−1.30 (6 H, cyclohexyl H), OH absent. HRMS (m/z): calcd for $C_{15}H_{29}NO_2$ $[M + H]^+$ 256.2270; found 256.2277. 1-Methoxy-2,2,6,6-tetramethylpiperidin-4-ol: mp 83 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 3.98 (1 H, m), 3.64 (3 H, s), 1.83 (2 H, d, J_1 = 9.40 Hz), 1.49 (2 H, t, J_1 = 11.9 Hz), 1.25 (6 H, s), 1.17 (6 H, s), OH absent. HRMS (m/z): calcd for $C_{10}H_{21}NO_2$ 187.1572; found 186.1568.

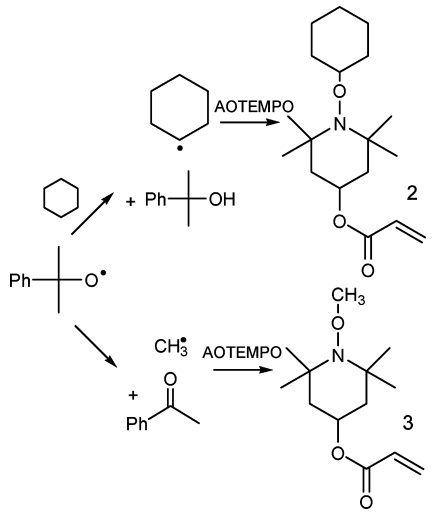
1-Cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl Acrylate (2). Acryloyl chloride (110 mg, 0.098 mL, 1.22 mmol) in toluene (0.349 mL) was added dropwise to a solution of 1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-ol (260 mg, 1.02 mmol) and triethylamine (123 mg, 0.169 mL, 1.22 mmol) in toluene (2.53 mL), and the mixture was stirred for 16 h at room temperature. A precipitate was compacted by centrifugation and a clear liquid decanted prior to evaporating residual solvent under high vacuum, yielding a pale yellow, crystalline solid; mp 50 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.40 (1 H, dd, J_1 = 17.3 Hz, J_2 = 1.10 Hz), 6.11 (1 H, dd, J_1 = 17.0 Hz, J_2 = 10.3 Hz), 5.82 (1 H, dd, J_1 = 10.5 Hz, J_2 = 0.92 Hz), 5.13 (1 H, tt, J_1 = 11.5 Hz, J_2 = 4.22 Hz, HC−O−C), 3.63 (1 H, m), 2.06 (2 H, m), 1.89 (2 H, dd, J_1 = 12.3 Hz, J_2 = 2.20 Hz), 1.78 (2 H, m), 1.67 (1 H, s), 1.63 (2 H, t, J_1 = 11.5 Hz), 1.56 (1 H, d, J_1 = 12.1 Hz), 1.24 (12 H, s), 1.0−1.4 (4 H). HRMS (m/z): calcd for $C_{18}H_{31}NO_3$ 309.2304; found 309.2296.

1-Methoxy-2,2,6,6-tetramethylpiperidin-4-yl Acrylate (3). Acryloyl chloride (86 mg, 0.077 mL, 0.950 mmol) in toluene (0.274 mL) was added to a solution of 1-methoxy-2,2,6,6-tetramethylpiperidin-4-ol (148 mg, 0.792 mmol) and triethylamine (80 mg, 0.11 mL, 0.950 mmol) in toluene (1.64 mL), and the mixture was stirred at room temperature for 24 h. The liquid was decanted and solvent removed under vacuum to yield a viscous, tan liquid. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.38 (1 H, dd, J_1 = 17.3 Hz, J_2 = 1.26 Hz), 6.10 (1 H, dd, J_1 = 17.5 Hz, J_2 = 10.4 Hz), 5.81 (1 H, dd, J_1 = 10.4 Hz, J_2 = 1.10 Hz), 5.10 (1 H, tt, J_1 = 11.3 Hz, J_2 = 4.41 Hz), 3.63 (3 H, s), 1.88 (2 H, dd, J_1 = 11.2 Hz, J_2 = 2.68 Hz), 1.60 (2 H, t, J_1 = 11.8 Hz), 1.20−1.25 (12 H, m). HRMS (m/z): calcd for $C_{13}H_{23}NO_3$ 241.1678; found 241.1673.

RESULTS AND DISCUSSION

Model Compound Studies. If a reagent such as AOTEMPO is to delay the onset of cross-linking 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 alkoxamine would be absolute, with acrylate functionality only being activated once all nitroxyl is consumed. To test the trapping selectivity of AOTEMPO, 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.[22] Our studies involved the thermolysis of known amounts of DCP in a standard solution of AOTEMPO + cyclohexane. A cyclic hydrocarbon was used to eliminate regioisomers from the reaction products. The cyclohexyl and methyl alkoxyamines (**2** and **3**, Scheme 3), as well as the initiator byproducts acetophenone and cumyl alcohol, were quantified by GC analysis using authentic standards.

Scheme 3. Analyzed Products of AOTEMPO Model Compound Reactions



At the temperatures used in polyolefin modifications, β-scission of cumyloxyl to yield methyl radicals + aceteophenone is competitive with hydrogen atom abstraction from a hydrocarbon.[23] The extent of radical fragmentation increases with temperature and the C−H bond dissociation energy of potential hydrogen atom donors.[24,25] Independent studies of hydrogen abstraction by cumyloxyl from cyclohexane have recorded abstraction efficiencies on the order of 53% at 160 °C, with cumyl alcohol:aceteophenone ratios of about 1:1.14.[26] In the present context, alkoxamines **2** and **3** should be produced in approximately these proportions. The data plotted in Figure 1

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show that the cyclohexyl alkoxamine **2** was, in fact, produced in higher yields than the methyl alkoxyamine, irrespective of the amount of DCP charged to the reaction mixture.

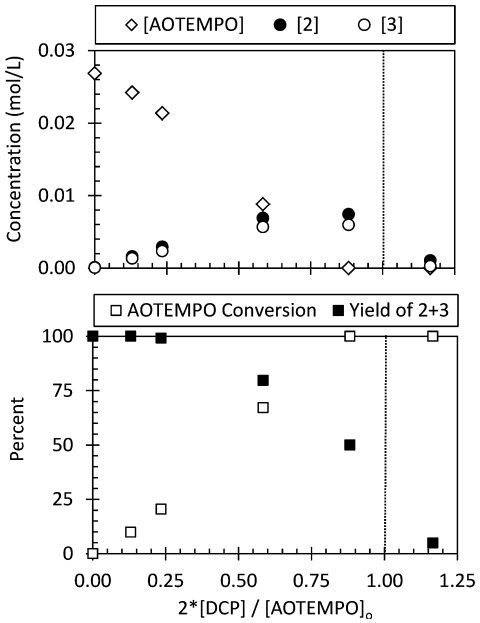

Figure 1. Model compound reaction products as a function of DCP loading: (top) reagent and product concentrations; (bottom) AOTEMPO conversion and alkoxyamine yields ($[AOTEMPO]_0$ = 0.027 mol/L; 160 °C).

Of greater interest is the relationship between DCP loading and the conversion of AOTEMPO to alkoxyamines **2** and **3** (Scheme 3). Figure 1 presents this data as a function of the total cumyloxy radical concentration (2[DCP]) divided by the initial nitroxyl concentration ($[AOTEMPO]_0$). Although nitroxyls do not trap oxygen-centered 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 $2[DCP]/[AOTEMPO]_0$, and conversion should approach 100% when the ratio approaches a value of 1.00. The conversion data demonstrate this linear relationship, with complete reagent consumption observed at $2[DCP]/[AOTEMPO]_0$ = 0.88, slightly less than a stoichiometric result.

Alkoxyamine yields at low DCP loadings are particularly important, as they reflect the intrinsic reactivity of AOTEMPO in the absence of reaction products. The data show that up to a AOTEMPO conversion of 25%, the alkoxyamine yield, $([\mathbf{2}] + [\mathbf{3}])/([AOTEMPO]_0 - [AOTEMPO])$, was nearly 100%. This indicates that alkyl radical trapping by AOTEMPO is, in fact, selective for alkoxyamine formation, as opposed to addition to acrylate functionality. However, higher initiator levels caused the concentrations of **2** and **3** to peak at a $2[DCP]/[AOTEMPO]_0$ 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 $2[DCP]/[AOTEMPO]_0$ = 0.88, according to the results plotted in Figure 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 nitroxyl to produce a mixture of other alkoxyamines, whose isolation and characterization are beyond the scope of this work.

1-Cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-ol was an intermediate in the synthesis of the model compound **2**, whose isolation provided an opportunity to study the thermal stability of this secondary alkoxyamine. Heating a cyclohexane solution of this compound under N_2 to 160 °C for prolonged periods showed no losses over the course of 2 h, confirming that alkoxyamine disproportionation was not significant under our reaction conditions and providing confidence that the macromolecular analogues generated in the following polyethylene studies may be similarly robust. This is in good agreement with our previous studies of nitroxyl exchange reactions of secondary alkoxyamines, which showed that 1-(1-ethylpentyloxy)-2,2,6,6-tetramethylpiperidine does not readily dissociate to TEMPO + alkyl radical and that disproportionation to olefin + hydroxylamine is very slow at 160 °C.[21]

Polymer Cross-Linking Studies. Time-resolved measurement of the dynamic storage modulus (G') recorded at fixed temperature, frequency, and shear strain amplitude is the standard means of monitoring the dynamics and yields of all polymer cross-linking processes.[27] Because un-cross-linked polymers undergo relatively efficient stress relaxation 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.[7] Figure 2 presents storage modulus

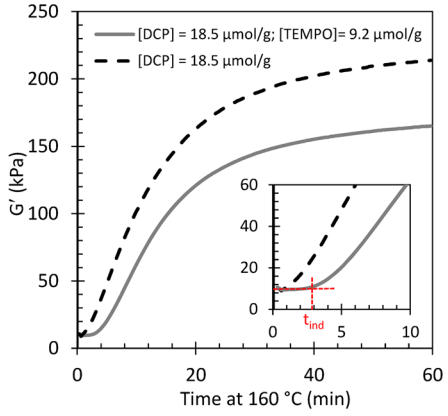

Figure 2. Dynamics of DCP-initiated LLDPE cross-linking. Inset: expansion illustrating reaction induction time.

data for an LLDPE sample containing 18.5 μmol of 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 to 214 kPa over the course of 60 min. Of particular concern to this work are the onset of cross-linking and the maximum storage modulus (G'_{max}) provided by the formulation.

Also presented in Figure 2 are data recorded for an LLDPE sample containing [DCP] = 18.5 μmol/g and [TEMPO] = 9.2 μmol/g. This unfunctionalized nitroxyl delayed the onset of cross-linking significantly, yielding an induction time, t_{ind}, of 2.7 min. We define t_{ind} as the point where the storage modulus increased from its minimum value. Note that the DCP-only cure formulation also showed some delayed onset character, owing to the ~1 min needed to bring the sample from room

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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 cumyloxyl radicals, [TEMPO]/(2[DCP]) was 0.25, meaning that the nitroxyl charged to the formulation could trap only 25% of the radicals generated by peroxide decomposition. Hereafter we call this quantity the trapping ratio, [nitroxyl]/(2[DCP]), and we will demonstrate its importance in determining induction times and cross-linking yields.

The TEMPO data presented in Figure 3 are plotted in a semilog 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 are replotted in this graph, along with cross-linking profiles generated at higher trapping ratios. The full data set follows expected trends, with increasing TEMPO concentrations lowering cross-linking yields while increasing induction times. The use of a stoichiometric amount of TEMPO relative to cumyloxyl radicals (trapping ratio = 1.00) quenched all macroradical activity, as evidenced by the stable storage modulus observed throughout the 60 min experiment.

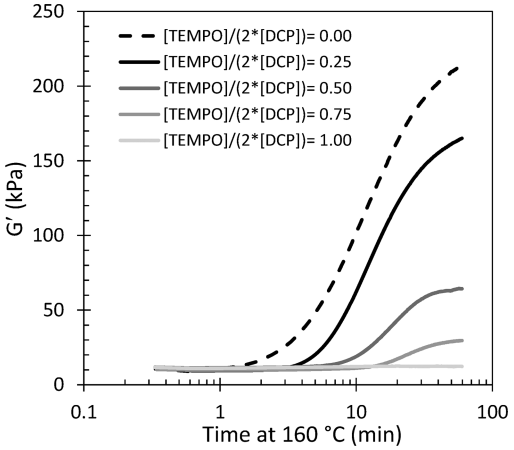

Figure 3. Influence of TEMPO on DCP-initiated LLDPE cure dynamics and yields ([DCP] = 18.5 μmol/g).

The relationship between induction time, t_{ind}, and TEMPO loading can be derived from first principles in a manner consistent with the work of Mani et al. on the radical cross-linking of vinyl-functionalized silicone rubber.[28] Since peroxide thermolysis is a first-order decomposition whose rate is not affected by the presence of nitroxyl, the initiator conversion, X, as a function of time can be expressed as

$$X = \frac{[\mathrm{ROOR}]_0 - [\mathrm{ROOR}]}{[\mathrm{ROOR}]_0} = 1 - e^{-k_d t} \quad (1)$$

where $[\mathrm{ROOR}]_0$ 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.[5] Given the fast rate of alkyl radical trapping by nitroxyls, we can assume that initiator-derived radicals produced in the presence of nitroxyl will be quenched. Under this assumption, t_{ind} marks the time where all nitroxyl functionality is consumed, at which point the DCP conversion will equal the trapping ratio, $[\mathrm{nitroxyl}]/(2[\mathrm{ROOR}]_0)$. Therefore, the induction time can be expressed in terms of a simple ratio of nitroxyl and initiator concentrations

$$\frac{[\mathrm{nitroxyl}]}{2[\mathrm{ROOR}]_0} = 1 - e^{-k_d t_{ind}} \quad (2)$$

which can be rearranged to give the induction time explicitly

$$t_{ind} = -\frac{1}{k_d} \ln\left[1 - \frac{[\mathrm{nitroxyl}]}{2[\mathrm{ROOR}]_0}\right] \quad (3)$$

Equation 3 is plotted in Figure 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 needed for samples to reach 160 °C.

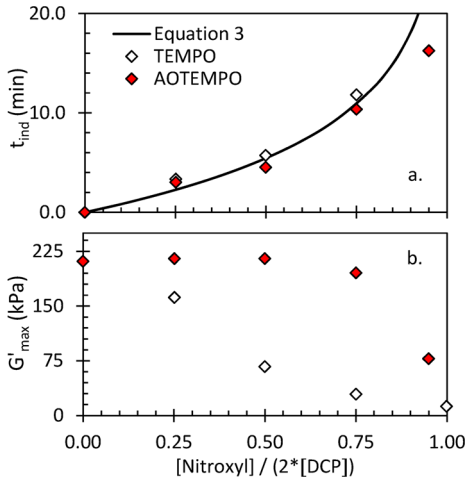

Figure 4. Influence of TEMPO and AOTEMPO on DCP-initiated LLDPE cure dynamics and yields ([DCP] = 18.5 μmol/g, 160 °C).

It is intuitively obvious 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 they generate cross-links through pairwise combination of macroradicals. As such, cross-link yields cannot exceed initiator concentrations, and any radical trap that quenches macroradicals should cause a proportional decline in cross-link density. We noted above that a trapping ratio of 0.25 suppressed the extent of cross-linking by 23%. The data provided in Figure 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 illustrated in Scheme 1 are designed to provide delayed-action cures that do not incur loss of cross-link yields. The objective is to trap all alkyl macroradicals as functional alkoxyamines, effectively transforming the polymer into a macromonomer. As a result, the mechanism of action is different from peroxide-only cures as well as delayed-onset formulations employing TEMPO, in that cross-links are produced through radical oligomerization of polymer-bound C=C functionality as well as macro-radical combination. Since acrylate oligomerizations can have considerable kinetic chain length, the potential exists to generate numerous cross-links from each initiator radical generated after t_{ind}. Curing is no longer a stoichiometric process with respect to peroxide loadings, and losses in cross-link density suffered

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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 5 show that AOTEMPO can, in fact, provide exceptional delayed-onset

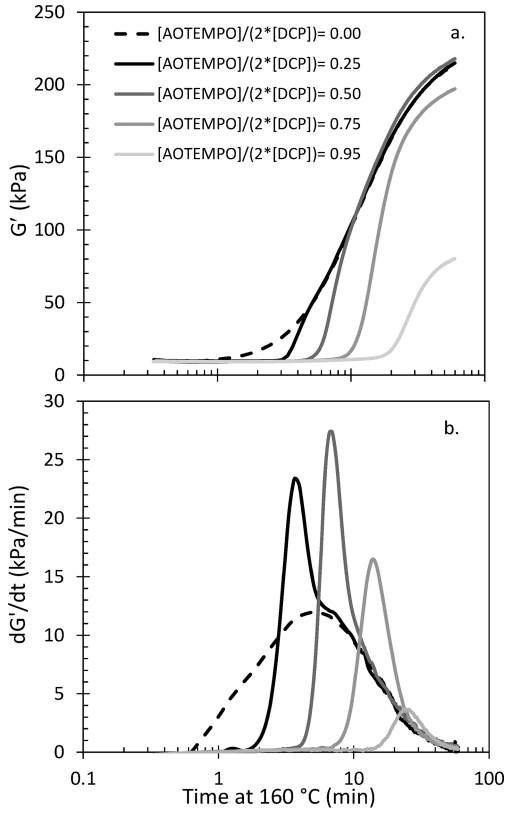

Figure 5. Influence of AOTEMPO on DCP-initiated LLDPE cure dynamics and yields (a: G'; b: dG'/dt; [DCP] = 18.5 μmol/g).

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 4 summarizes the induction time, t_{ind}, and cross-link yields (G'_{max}) generated by DCP + AOTEMPO mixtures. The induction times provided by the acrylated nitroxyl were predicted reasonably well by eq 3 but were less than those generated by TEMPO, and the discrepancy grew with increasing AOTEMPO 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 macroradical trapping rates are less competitive with attack on polymer-bound C═C functionality.

The slight reduction of t_{ind} brought on by acrylate oligomerization is offset by the maintenance of cross-link density. Figure 4b shows that up to one-half of initiator-derived radicals can be trapped by AOTEMPO without affecting G'_{max}. Cross-link yields were only slightly compromised at a trapping ratio of 0.75, before severe loses were suffered at a ratio of 0.95. Note 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) may extend t_{ind} at a given nitroxyl ratio, as governed by eq 3. Therefore, the performance of AOTEMPO summarized in Figure 4 should be adequate for most practical applications.

The ability of AOTEMPO to restore exactly the cross-link density lost to macroradical trapping is remarkable, 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 macroradical generation and the relative rate of macroradical disproportionation versus combination, the latter giving a network comprised of "H-type" carbon−carbon cross-links. In contrast, the cross-link network provided by AOTEMPO is expected to have a star-branched structure comprised of oligomers derived from polymer-bound acrylate functionality. The yield of this macromonomer 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 AOTEMPO-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 AOTEMPO 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,[29] meaning that about one-half the population of macroradical intermediates in a DCP-only cure may not contribute directly to polymer cross-linking. On the other hand, trapping of these macroradicals by nitroxyl occurs exclusively by combination to yield the corresponding alkoxyamine, thereby converting each macroradical into a pendant acrylate group. Subsequent oligomerization of this polymer-bound functionality could, therefore, provide superior cross-link yields if converted efficiently.

Further insight into the dynamics of the AOTEMPO cure system was gained from the derivative graphs shown in Figure 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 macroradical 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 macromonomer 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 AOTEMPO 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 [AOTEMPO]/(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 AOTEMPO formulations to provide adequate cure recovery. The first is nonproductive alkoxyamine consumption, as indicated by our model compound experiments. Recall that high AOTEMPO conversions were accompanied by reduced yields of the corresponding cyclohexyl alkoxyamine (Figure 1). As the concentration of acrylated alkoxyamines increase at the expense of AOTEMPO, 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 nonproductive manner. A second possibility for reduced yields involves inadequate initiator during the acrylate activation. Operating with [AOTEMPO]/(2[DCP]) = 0.95 provides relatively little residual peroxide to convert

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acrylate functionality to a covalent network. Therefore, at very high trapping ratios, incomplete acrylate conversion may stunt network growth.

The sensitivity of peroxide thermolysis 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 = 0.83 min^{-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 eq 2, a 1 min induction time requires a small trapping ratio of 0.02 at 140 °C, but a reaction conducted at 180 °C would require a trapping ratio of 0.56. The question of whether a functionalized nitroxyl can support these induction times without losing cure yield is addressed by Figure 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.

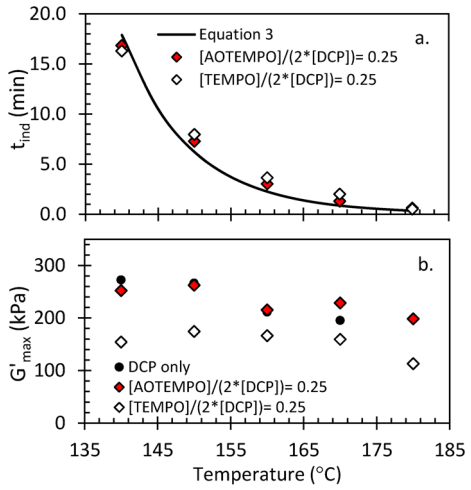

Figure 6. Influence of TEMPO and AOTEMPO on DCP-initiated LLDPE cross-linking induction times and yields ([DCP] = 18.5 μmol/g).

The induction time data plotted in Figure 6a show that experimental observations are in good agreement with values predicted by eq 3. Therefore, nitroxyl concentrations can be prescribed with confidence to satisfy induction time standards for a given peroxide loading and decomposition temperature. However, controlling DCP-initiated processes becomes increasingly difficult at and above 180 °C, requiring high concentrations of AOTEMPO to quench the surge of radical activity in the early stages of the cure. Shifting to an alternate initiator such as 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexyne-3, whose half-life is 3.6 min at 180 °C, could lower nitroxyl requirements by a factor of 4. The extension of functional nitroxyl chemistry to other initiating systems and polymer substrates is the subject of ongoing research.

The maximum cross-link densities provided by DCP-only, DCP + TEMPO, and DCP + AOTEMPO at different temperatures are provided in Figure 6b. As observed throughout this study, AOTEMPO proved capable of meeting 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 nitroxyls bearing methacrylate (**1b**), cinnamate (**1c**), and crotonate (**1d**) functionality (Scheme 1). It is difficult to quantify precisely the differences in homopolymerization rates for these functional groups, especially at the temperatures used in polyolefin cross-linking. In general, rate constants for aliphatic acrylates are of the order of 1.8 × 10^4 M^{-1} s^{-1} at 30 °C,[30] while methacrylate analogues fall in the range of (1−4) × 10^2 M^{-1} s^{-1}.[31,32] The homopolymerization of crotonates is considerably slower, with propagation rate constants on the order of 1 M^{-1} s^{-1} at 60 °C,[33] while cinnamate homopolymerization has not, to our knowledge, been subjected to detailed kinetic analysis. Nevertheless, the available data suggest the following order of functional group reactivity, AOTEMPO > **1b** > **1c** > **1d**.

The data presented in Figure 7 show that the cure reactivity generated by these functional nitroxyls is consistent with this

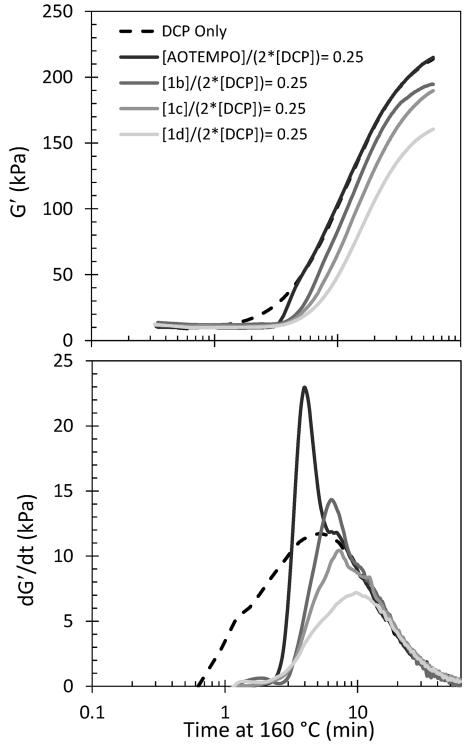

Figure 7. Storage modulus DCP-initiated LLDPE cures containing various functionalized nitroxyls ([DCP] = 18.5 μmol/g; [nitroxyl] = 9.3 μmol/g).

pattern. Recall that TEMPO suppressed cross-linking yield by 23% when applied at a trapping ratio of 0.25 (Figure 3). Using TEMPO as a reference, it is clear that the cinnamate ester **1d** could not restore losses in cross-link density incurred during the induction period, as the final G' recorded for this formulation was 26% less than that observed for DCP alone. The methacrylate and crotonate esters were more effective, but the oligomerization phase provided by these substituted monomers could not match that generated by the acrylate system. This suggests that the most effective functional nitroxyls for LLDPE cross-linking are those bearing the kinetically most reactive homopolymerizable groups.

■ CONCLUSIONS

AOTEMPO has been shown to delay the onset of LLDPE curing without compromising the thermoset's ultimate cross-

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link density. Quenching of alkyl radical intermediates as their corresponding alkoxyamines provides an induction period that abides by a simple function of the rate constant for initiator decomposition and the trapping ratio. Nitroxyl group consumption is followed by oligomerization of polymer-bound acrylate functionality to generate the desired covalent network, with no loss of cross-link density below trapping ratios of 0.5. This delayed onset chemistry is effective between 140 and 180 °C, providing consistent ultimate moduli as well as induction times that are inversely proportional to the peroxide thermolysis rate.

AUTHOR INFORMATION

Corresponding Author

*Phone 613-533-6266; e-mail parent@chee.queensu.ca.

Notes

The authors declare no competing financial interest.

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