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Functional group tolerance of AOTEMPO-mediated peroxide cure chemistry

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ABSTRACT

Delayed onset formulations for the peroxide-initiated crosslinking of a range of commodity polymers are described. 4-Acryloyloxy-2,2,6,6,-tetramethylpiperidin-*N*-oxyl (AOTEMPO) is effective for controlling the crosslinking dynamics and yields of linear low density polyethylene (LLDPE), poly(ethylene-*co*-vinyl acetate) (EVA), poly(ethylene-*co*-propylene) (EPR), and poly(ethylene-*co*-propylene-*co*-ethylidenenorbornadiene) (EPDM). However, the cure additive is inefficient for butadiene-based materials such as 1,2-polybutadiene (vinyl-BR) and *cis*-1,4-poly(butadiene) (*cis*-BR), since macroradical trapping by AOTEMPO stunts diene-monomer oligomerization, thereby eliminating multiple crosslinks that cannot be restored by a single polymer-bound acrylate group. Additional crosslink yield losses arise from allylic alkoxyamine instability, the details of which are revealed by independent ^{1}H NMR and rheology studies.

1. Introduction

Peroxide-initiated crosslinking is used widely to improve the physical properties of commodity thermoplastics and elastomers [1]. It provides several advantages over activated sulfur-based vulcanization, including applicability on both unsaturated and saturated polymers, a relatively straightforward relationship between crosslink extent and reagent concentrations, and reaction dynamics that are closely tied to the first-order rate of peroxide thermolysis [2,3]. Where a delay in the onset of crosslinking is required, the rate-controlling influence of initiator breakdown can be problematic, since rapid crosslinking in the earliest stages of the curing process can prevent the formulation from assuming the desired shape before it is rendered thermoset. In these situations, "scorch protection" is gained by charging a reagent that quenches radicals in the initial stages, thereby suppressing macroradical reactions that produce covalent crosslinks [4,5]. Unfortunately, this protection is often achieved at the expense of crosslink density.

We have recently described the fundamentals [6] and general utility [7] of acrylated nitroxyls for controlling the dynamics and yields of linear low density polyethylene (LLDPE) crosslinking. This approach exploits the preference of 4-acryloyloxy-2,2,6,6,-tetramethylpiperidin-*N*-oxyl (AOTEMPO) to combine with carbon-centred radicals, as opposed to undergoing addition to its C=C bond. As a result of this regioselectivity, LLDPE formulations comprised of dicumyl peroxide (DCP) as a radical initiator and AOTEMPO as a cure mediator progress through three phases; induction, macromonomer oligomerization, and stoichiometric crosslinking, the details of which are illustrated in our previous report [7]. During Phase 1, carbon-centred radicals derived from the initiator, including alkyl macroradicals and methyl radicals, are trapped as alkoxyamines by combination with nitroxyl [6,8]. This suppresses macroradical combination for as long as nitroxyl functionality is available, marking the beginning of Phase 2, whereupon the radical oligomerization of polymer-bound acrylate functionality rapidly increases the crosslink extent. This chain reaction recovers crosslink density lost during the induction period, and continues until all acrylate groups are consumed. Phase 3 follows, with residual peroxide initiating a conventional stoichiometric cure process involving macroradical generation by H-atom abstraction from the polymer, followed by termination by combination.

Although the aforementioned studies have demonstrated the principles of AOTEMPO-mediated chemistry, it remains to be seen whether it is effective for commodity polymers that contain one or more functional groups (Scheme 1). For example, differences in the efficiency of H-atom transfer from a polymer to initiator-derived alkoxyl radicals [9] have been shown to impact AOTEMPO performance by affecting the yield of polymer-bound alkoxyamine [10]. Of particular interest in this work is the potential for acetate, nitrile and olefin functionality to generate radical populations whose

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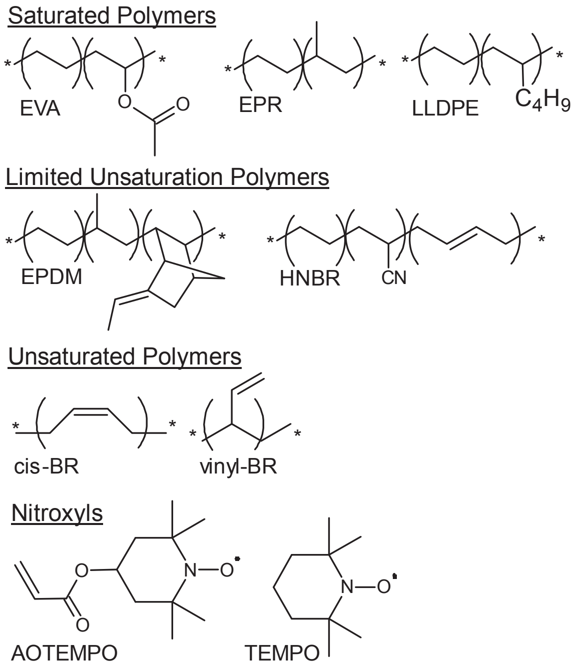

Scheme 1. Materials of Interest.

reactivity differs from the secondary alkyl radicals that dominate LLDPE chemistry, with consequences for radical trapping outcomes as well as acrylate oligomerization yields. The present work is concerned with the ability of AOTEMPO to control cures of poly(ethylene-*co*-vinyl acetate) (EVA), poly(ethylene-*co*-propylene) (EPR), 1,2-polybutadiene (vinyl-BR), *cis*-1,4-poly(butadiene) (*cis*-BR), hydrogenated poly(butadiene-*co*-acrylonitrile) (HNBR), and poly(ethylene-*co*-propylene-*co*-ethylidenenorbornadiene) (EPDM). In this report, comprehensive cure rheology data are provided for a range of reaction temperatures and discussed in the context of competitive H-atom transfer pathways, alkoxyamine stability, and C=C oligomerization reactivity.

2. Experimental

2.1. Materials

Linear low density polyethylene pellets (LLDPE, 5 mol % hexene, MFI = 3 g/10 min at 190 °C) were used as received from Dow Chemical, since purification by dissolution/precipitation (benzene/acetone) and drying was found to have no effect on peroxide-only and peroxide + AOTEMPO reaction outcomes. 1,4-Polybutadiene (98% cis, Sigma Aldrich), 1,2-polybutadiene (93% vinyl, Mw~100,000, Scientific Polymer Products), low MW 1,4-polybutadiene (75% cis, Sigma Aldrich, MW ~3000), EPR (60 wt% ethylene, Scientific Polymer Products), EPDM (60 wt% Ethylene, 4% 5-ethylidene-2-norbornene, Scientific Polymer Products), poly(ethylene-*co*-vinyl acetate) (ELVAX 460, 18 wt% vinyl acetate, DuPont), HNBR (36% ACN, 96% Hydrogenated, Zeon Chemicals) were purified by dissolution/precipitation and dried under vacuum prior to use. 4-Benzoyloxy-2,2,6,6,-tetramethylpiperidine-*N*-oxyl (Bz-TEMPO), DCP (98%), hydroxy-TEMPO (4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl, 97%), 1,1-bis(tert-butylperoxy)-3,5,5-trimethylcycohexane (L-231, 92%), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 98%) and triethylamine were used as received from Sigma Aldrich (Oakville, ON.). 4-Acryloyloxy-2,2,6,6,-tetramethylpiperidine-*N*-oxyl (AOTEMPO) was prepared as described previously [6].

2.2. Rheological analysis

Semi-crystalline polymers (5 g) were coated with an acetone solution containing the required amounts of peroxide and nitroxyl additive, hand-mixed, and allowed to dry. Note that excessive drying of polymer compounds containing a nitroxyl was avoided to limit sublimation losses. Elastomeric polymers were sheeted on a two-roll mill, treated with initiator solution and re-milled after drying. The polymer mixtures were cured in a controlled strain rheometer (Advanced Polymer Analyzer 2000, Alpha Technologies) equipped with biconical plates and operating at 1 Hz and 3° arc.

2.3. Polybutadiene-derived alkoxyamine synthesis and stability

Low MW polybutadiene (1.5 g) was heated to 70 °C in a Wheaton vial before adding Bz-TEMPO (0.15 g) and L-231 (0.075 g). The temperature was raised to 115 °C for 3.75 h, after which a second aliquot of nitroxyl and initiator was added and heating continued for 3.75 h. The product was cooled to room temperature, washed with acetone (10 × 2 ml) to remove initiator byproducts and residual Bz-TEMPO, and dried under a vacuum. ^{1}H NMR analysis of the purified product determined the polymer-bound nitroxyl content of 0.58 mmol/g•polymer (See Supplemental Data).

The thermal stability of this alkoxyamine was assessed by heating under N_2 to 180 °C for 20 min, and washing the product with acetone (10 × 1 ml). ^{1}H NMR analysis of the polymer provided a bound nitroxyl content of 0.33 mmol/g, 0.25 mmol/g less than in the starting material (See Supplemental Data). Gas chromatography analysis of the acetone extraction solution confirmed the presence of Bz-TEMPO as an oxidized byproduct of alkoxyamine decomposition.

3. Results and discussion

The efficacy of AOTEMPO was judged using three criteria: the length of the induction period, the extent of crosslinking incurred during the induction period, and the ultimate cure extent achieved relative to a peroxide-only formulation. Ideally, AOTEMPO provides an induction time that is a simple function of the trapping ratio, a storage modulus that remains unchanged during the induction period, and a final storage modulus approximately equal to that provided by DCP alone.

The induction time (t_{ind}) observed for LLDPE formulations is dictated by the peroxide decomposition rate constant (k_d), and the trapping ratio ($[\text{nitroxyl}]_o/2[\text{DCP}]_o$), which represents the fraction of initiator-derived radicals that can be quenched by the amount of nitroxyl charged to the mixture [4,7].

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

For example, a LLDPE + DCP + AOTEMPO compound with a trapping ratio of 0.25 will produce an induction time of 2.2 min at 160 °C. This simple equation is founded upon three key assumptions; that peroxide thermolysis is unaffected by the presence of nitroxyl, that alkyl radical trapping by nitroxyl is rapid relative to alternate radical reactions [11], and the resulting alkoxyamines are stable over the course of the curing process. Shifting from LLDPE to the polymers of interest has little bearing on the first two assumptions, but the potential exists for alkoxyamine instability to affect induction times as well as the constancy of the formulation's storage modulus during the induction period.

One mode of alkoxyamine instability is irreversible disproportionation to give olefin and hydroxylamine, the latter being readily oxidized to regenerate the starting nitroxyl (Scheme 2). Its influence depends on the disproportionation rate relative to the time