# Reactivity of Polyolefins toward Cumyloxy Radical: Yields and Regioselectivity of Hydrogen Atom Transfer

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**ABSTRACT:** Hydrogen atom abstraction from a series of homopolymers by cumyloxy radicals is examined under solvent-free conditions at temperatures that are relevant to radical-mediated polymer modifications. Abstraction efficiency data acquired for the thermolysis of dicumyl peroxide (DCP) within pure polymer samples establish an order of reactivity: poly(butadiene) (PBD) > poly(ethylene oxide) (PEO) > poly(ethylene) (PE) > poly(propylene) (PP) > poly(isobutylene) (PIB). The regioselectivity of hydrogen transfer from PE, PP, and PIB is assessed by model hydrocarbon experiments involving nitroxyl trapping of the alkyl radicals generated from pentane, 2,4-dimethylpentane, and 2,2,4,4-tetramethylpentane, respectively. Taken together, abstraction efficiency and regioselectivity data are discussed in terms of enthalpic and entropic contributions to H atom transfer rates, with particular emphasis on steric hindrance imposed by methyl substituents on secondary positions within PP and PIB. The utility of polymer oxidizability as a predictive measure of the reactivity of a polymer toward cumyloxyl and vinyltriethoxysilane graft modification is evaluated and discussed.

$$AE = \frac{k_a[RH]}{k_a[RH] + k_d}$$

$$= \frac{[PhCMe_2OH]}{[PhCMe_2OH] + [PhCOMe]}$$
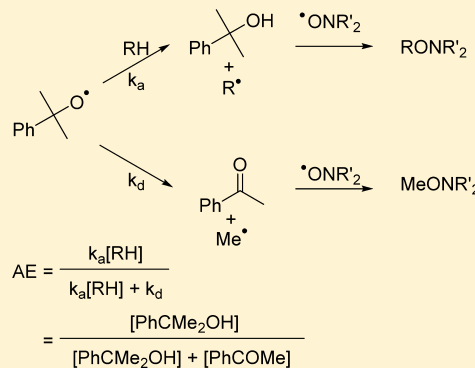
## INTRODUCTION

Solvent-free, peroxide-initiated polymer modifications are used widely to improve the physical and/or chemical properties of commodity plastics and elastomers.[1] Important examples include the cross-linking of ethylene-rich polymers into thermoset products,[2,3] the controlled degradation of propylene-rich polymers to improve their processing characteristics,[4,5] and the graft modification of polyolefins with maleic anhydride[6] and vinyltrialkoxysilanes[7] to produce functional derivatives that are suitable for a range of adhesive, blend, and composite formulations.[8] The introduction of long chain branches to propylene homopolymers has also attracted recent interest, owing to the improved extensional viscosity provided by branched architectures.[9,10] As is common in the polymer industry, commercial developments have outpaced studies of fundamental chemistry, and an improved understanding of high-temperature radical addition and atom transfer processes is needed to support further advances in the field.

To a great extent, the amenability of a polymer with respect to these technologies is dictated by its reactivity with respect to H atom transfer. Cross-linking[11] and controlled degradation[12] processes are initiated by H atom transfer from the polymer to peroxide-derived radical intermediates, with ensuing macroradical combination and/or fragmentation producing the intended changes to molecular weight distributions. Monomer grafting processes similarly require polymer macroradical generation but also involve H atom transfer between the polymer and monomer-derived radical adducts to support a chain propagation sequence.[13,14]

Much of what is known about the radical reactivity of polymers is derived from ambient temperature studies of their autoxidation. This process involves a chain reaction sequence of alkyl radical combination with oxygen, and H atom abstraction by the resulting peroxyl radical from the polymer, as shown below.[15]

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$$
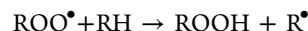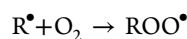
Since the latter reaction is rate determining at ambient temperatures, the susceptibility of a hydrocarbon to oxidation is influenced greatly by its reactivity as a H atom donor to peroxyl intermediates. This is reflected in measurements of substrate oxidizability, defined as the propagation rate constant for H atom transfer divided by the square root of the peroxyl radical termination rate constant. Tabulated values have demonstrated the importance of reaction enthalpy to the kinetics of this process, with compounds having low C—H bond dissociation energies (BDEs) (i.e., allylic groups, benzylic functionalities, and ethers bearing α-hydrogens) being particularly susceptible.[16] Limited amounts of oxidizability data on polymeric systems are consistent with small molecule results, with oxidizability values for *cis*-1,4-poly(isoprene) being greater than those recorded for polyolefins and acrylate-derived

polymers, owing to the low BDE of the allylic functionality,[17] and poly(propylene) is more easily oxidized than poly-(ethylene),[18,19] due to the reactivity of its tertiary H atom toward ROO•.[20,21]

For oxidizability to be a useful proxy for the polymer modifications described above, H atom transfer to peroxyl radicals must correlate with H atom transfer to alkoxy and alkyl radical intermediates. However, significant differences in the reactivity of peroxyl and alkoxyl radicals are widely recognized.[22,23] Indeed, H atom transfer to *t*-BuO• can be dominated by entropic effects, with transition states possessing relatively small enthalpies of activation.[24] Factors affecting the entropy of activation, including steric effects, can be controlling in these systems, making simple assumptions concerning the reactivity of polymeric C−H donors unreliable. Therefore, oxidizability may be a poor indicator of polymer reactivity, and a different measure may be required.

A complete understanding of the H atom transfers involved in polyolefin graft modification requires knowledge of abstraction by alkoxyl-, methyl-, and monomer-derived radicals from every distinguishable H atom donor presented by a polymer. This is a formidable challenge. However, considerable insight can be gained by examining the byproducts of dicumyl peroxide (DCP) thermolysis (Scheme 1). Since the rate of

**Scheme 1**



$$AE = \frac{k_a[RH]}{k_a[RH] + k_d}$$

$$= \frac{[PhCMe_2OH]}{[PhCMe_2OH] + [PhCOMe]}$$
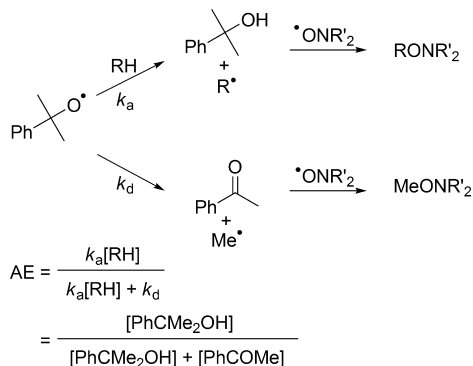
cumyloxyl radical fragmentation in nonpolar media is solely a function of temperature,[25,26] the relative amounts of cumyl alcohol and acetophenone generated within a hydrocarbon substrate provide a simple measure of the latter's intrinsic reactivity toward H atom donation.[27] This approach has been applied to H atom abstraction by cumyloxyl from a range of saturated hydrocarbons and alkylated aromatics[28,29] as well as H atom donation to *tert*-butoxyl by a limited range of polymers.[30]

In spite of the central role of H atom transfer in polymer modification chemistry, comprehensive data for the solvent-free activation of polymers are unavailable. The primary aim of this work was to quantify and rationalize the H atom abstraction efficiency (AE = [cumyl alcohol]/([cumyl alcohol] + [acetophenone])) of DCP acting on a range of commercial homopolymers at temperatures that are relevant to industrial practice. The resulting data, acquired for purified samples of *cis*-1,4-poly(butadiene) (PBD), poly(ethylene oxide) (PEO), high-density poly(ethylene) (PE), poly(propylene) (PP), and poly(isobutylene) (PIB), provide a consistent reference set for gauging the responsiveness of these materials toward chemical modification.

Where a polymer presents multiple H atom donors (e.g., polypropylene and polyisobutylene), knowledge of the relative reactivity of primary, secondary, and tertiary positions toward H atom transfer is required. These regioselectivity studies are usually performed on model hydrocarbons, owing to the difficulty of characterizing polymer reaction products unambiguously.[31,32] Electron spin resonance analysis of alkyl radicals or their spin-trapped derivatives has been used,[33,34] as has the quantification of alkoxyamine products generated by nitroxyl trapping.[35] Solomon and co-workers used the latter technique to gain insight into PP activation by studying the products derived from H atom transfer from 2,4-dimethylpentane to *tert*-butoxyl at 60 °C.[36] We have extended their approach to include model compounds for PE and PIB, using cumyloxyl at temperatures that are relevant to industrial practice.

A secondary objective of this work was to explore the relationship between AE measurements of H atom donation and the efficiency of polymer grafting modifications. The functionalization of a polymer with single grafts of maleic anhydride and vinyltrimethoxysilane (VTMS) is formally a C−H addition from the polymer to a C=C bond. Initiation occurs by H atom abstraction from the polymer to peroxide-derived alkoxyl radicals to produce a macroradical, whose propagation involves addition to an alkene as well as H atom abstraction. Therefore, polymers that are poor H atom donors are expected to be more difficult to functionalize by radical chemistry, providing lower graft yields and a smaller proportion of single graft adducts. Insight into the relationship between H atom abstraction efficiency and graft modification efficiency is provided through comparisons of AE data with independent measurements of VTMS addition yields for a range of saturated polymer substrates.

## ■ EXPERIMENTAL SECTION

**Instrumentation and Analysis.** NMR spectra were recorded on a Bruker spectrometer in CDCl$_3$ at 400 and 100 MHz for $^1$H and $^{13}$C measurements, respectively. High-resolution mass spectra were acquired with a QStar XL QqTOF instrument. Reverse-phase HPLC was conducted using a Waters 600E system controller employing a model 600 pump, a model 2487 UV detector, and an XBridgeTM semipreparative C18 column (10 by 150 mm) with 5 $\mu$m particle size. GC-MS analysis was conducted using an Agilent Technologies 6850 Network GC system coupled with a 5975C VL MS detector. The instrument was configured with an Agilent Technologies 19091S-433e HP-5MS column with an inlet temperature of 250 °C, pressure of 78 kPa, and flow rate of 52 mL/min. The initial temperature was 70 °C and was increased at a rate of 6 °C/min to 280 °C, where it was held for 5 min. Abstraction efficiency measurements derived from cumyl alcohol and acetophenone yields were determined using a Hewlett-Packard 5890 series II gas chromatograph equipped with a Supelco SPB-1 microbore column using 2 mL/min of helium as carrier gas. Injector and detector temperatures were held at 225 and 300 °C, respectively, with the oven temperature starting at 40 °C for 6 min, ramping to 150 °C at 10 °C/min, ramping to 280 °C at 12 °C/min, and holding for 15 min. FID calibration was accomplished using authentic samples.

**Materials.** Dicumyl peroxide (DCP, 98%), 2,4-dimethylpentane (DMP, 99%), hexadecane (97%), pentane (99%), and vinyltrimethoxysilane (VTMS, 95%) from Sigma-Aldrich and 2,2,4,4-tetramethyl-pentane (TMP, 98%) from Alfa Aesar were used as received. Di-*tert*-butyl hyponitrite was prepared by the esterification of sodium hyponitrite by *tert*-butyl bromide in the presence of ZnBr$_2$ according to the method of Mendenhall.[37] Polyisobutylene (PIB, $M_w$ = 85 000) and atactic-polypropylene (PP, $M_w$ = 10 000) from Scientific Polymer Products were hydrogenated prior to use by treatment of polymer dissolved in hexane with platinum supported on carbon at 20 bar of H$_2$

gas, 100 °C for 50 h, after which the polymer was recovered by precipitation from acetone and dried under vacuum. Polybutadiene (PBD, $M_n$ = 5000, Scientific Polymer Products) was purified by dissolution/precipitation (hexanes/methanol) and dried under vacuum. Poly(ethylene glycol) monomethyl ether (PEO, $M_n$ = 5000, Alfa Aesar) purified by dissolution/precipitation (THF/hexane) and dried under vacuum. Polyethylene (HDPE, $M_n$ = 1800, Scientific Polymer Products) (13.23 g) was dissolved toluene at 90 °C and precipitated from acetone before drying under vacuum.

*1,1,3,3-Tetramethylisoindolin-2-oxyl (TMIO).* 10% Pd/C (0.38 g) was placed in a 100 mL round-bottom flask, evacuated, and filled with argon. 2-Benzyl-1,1,3,3-tetramethylisoindoline[38] (3.56 g, 13.4 mmol) was dissolved in methanol (45 mL) and added dropwise prior to the addition of ammonium formate (5.23 g, 82.9 mmol). The mixture was heated to reflux for 12 h, cooled, and filtered through Celite prior to concentrating under vacuum to yield crude product (4.26 g), which was oxidized directly and recrystallized as described by Griffiths et al. to give TMIO (1.85 g, 9.7 mmol).[38]

**Preparation of Pentane-Derived Alkoxamines 1p, 1s, and 1s′.** Di-*tert*-butyl hyponitrite (1.0 mmol) and 1,1,3,3-tetramethylisoindolin-2-oxyl (2.2 mmol) in *n*-pentane (60 mmol) were deoxygenated by freeze−thaw degassing and heated under argon to 30 °C for 11 days (4 initiator half-lives).[39] The resulting mixture was concentrated using a rotary evaporator, diluted in methanol to a concentration of 5 mg/100 μL, and separated by HPLC (85/15 MeOH/H$_2$O, flow rate = 4 mL/min, UV = 270 nm). Fractions were combined and concentrated under reduced pressure until a white precipitate began to form, *but not until dryness*. Concentrated solutions were extracted with dichloromethane, dried (MgSO$_4$), and filtered. The organic layer was concentrated, diluted with methanol, and extracted once with an equal volume of hexanes. The hexanes were removed under reduced pressure, leaving alkoxamines 1p and a mixture of 1s and 1s′ as clear viscous oils.

*1,1,3,3-Tetramethyl-2-(pentyloxy)isoindoline (1p).* ^{1}H NMR (CDCl$_3$, 400 MHz): δ ppm = 7.22 (dd, 2H, J = 5.5, 3.2 Hz); 7.09 (dd, 2H, J = 5.5, 3.2 Hz); 3.91 (t, 2H, 6.6 Hz); 1.64 (m, 2H); 1.42 (br s, 12H); 1.26 (m, 4H); 0.98−0.92 (m, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ ppm = 127.08; 121.44; 99.97; 34.65; 29.05; 28.68; 25.27; 20.68; 11.41. HRMS (EI) *m/z* calcd for C$_{17}$H$_{27}$NO: 261.2093; found 261.2088. HPLC: $t_R$ = 20.7 min.

*1,1,3,3-Tetramethyl-2-(pentan-2-yloxy)isoindoline and 1,1,3,3-Tetramethyl-2-(pentan-3-yloxy)isoindoline (1s and 1s′).* Although these structural isomers were inseparable by HPLC, the isomers were separated from the primary abstraction products and characterized partially by NMR. The CH protons adjacent to the alkoxyamines of the two isomers were identified by their splitting patterns based on the symmetry of 1s′ versus 1s (3.91 and 3.70 ppm, respectively). These protons integrated at a 1:3.15 ratio of 1s′:1s. To determine if this ratio was artificially caused by the HPLC product separation, the mixture of secondary products, as well as the isolated 1p, was analyzed by GC/MS, revealing a 1:2.96 ratio of 1s′:1s, agreeing well with the NMR results. By comparison, a sample of the crude reaction mixture gave a ratio of secondary products (1s′:1s) of 1:2.39. ^{1}H NMR (CDCl$_3$, 400 MHz): δ ppm = 7.22 (m, 8.25H) 7.09 (m, 8.30H); 3.91 (h, 3.15H, J = 5.9 Hz); 3.70 (p, 1H, 5.7 Hz); 1.79−1.59 (m, 8.08H); 1.51−1.49 (s, 24.24H); 1.45−1.42 (m, 10.34H); 1.37 and 1.32 (brs, 25.56H); 1.23 (d, 9.45H); 0.96 (m, 15.66H).

**Preparation of 2,4-Dimethylpentane-Derived Alkoxamines 2p, 2s, and 2t.** The reaction and product isolation were carried out using 2,4-dimethylpentane using the procedure described above for pentane, except for a reaction temperature of 55 °C for 20 h (11 initiator half-lives).

*2-(2,4-Dimethylpentyloxy)-1,1,3,3-tetramethylisoindoline (2p).* ^{1}H NMR (CDCl$_3$, 400 MHz): δ ppm = 7.22 (dd, 2H, J = 5.5, 3.2 Hz); 7.09 (dd, 2H, J = 5.5, 3.2 Hz); 3.81 (dd, 1H, J = 8.7, 5.1 Hz); 3.69 (dd, 1H, 8.7, 6.9 Hz); 1.88 (m, 1H); 1.71 (m, 1H), 1.43 (br s, 12H); 1.33−1.05 (m, 2H); 1.01 (dd, 3H, J = 6.7 Hz); 0.92 (d, 3H, J = 6.6 Hz); 0.89 (d, 3H, J = 6.6 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz): δ ppm = 127.06; 121.42; 83.08; 31.03; 25.31; 17.94; 23.34; 23.36;

145.42; 67.18. HRMS (EI) *m/z* calcd for C$_{19}$H$_{31}$NO: 289.2406; found 289.2412. HPLC: $t_R$ = 35.3 min.

*2-(2,4-Dimethylpentan-3-yloxy)-1,1,3,3-tetramethylisoindoline (2s).* ^{1}H NMR (CDCl$_3$, 400 MHz): δ ppm = 7.22 (dd, 2H, J = 5.5, 3.2 Hz); 7.09 (dd, 2H, J = 5.5, 3.2 Hz); 3.47 (s, 1H); 2.26 (m, 2H); 1.51 (br s, 6H); 1.40 (br s, 6H); 1.04 (d, 6H, J = 7.0 Hz); 1.00 (d, 6H, J = 7.0 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz): δ ppm = 127.04; 121.37; 90.21; 28.13; 30.24; 25.62; 20.00; 19.67; 139.39; 67.18. HRMS (EI) *m/z* calcd for C$_{19}$H$_{31}$NO: 289.2406; found 289.2416. HPLC: $t_R$ = 38.8 min.

*2-(2,4-Dimethylpentan-2-yloxy)-1,1,3,3-tetramethylisoindoline (2t).* ^{1}H NMR (CDCl$_3$, 400 MHz): δ ppm = 7.22 (dd, 2H, 5.6, 3.2 Hz); 7.08 (dd, 2H, 5.6, 3.2 Hz) 1.85 (m, 1H); 1.52 (d, 2H, J = 5.6 Hz); 1.48 (s, 6H); 1.32 (s, 6H); 1.29 (s, 6H); 0.98 (d, 6H, J = 6.7). ^{13}C NMR (CDCl$_3$, 100 MHz): δ ppm =121.69; 126.99; 24.57; 30.70; 52.09; 27.51; 25.95; 30.70; 25.15; 145.68; 68.09; 79.13;. HRMS (EI) *m/z* calcd for C$_{19}$H$_{31}$NO: 289.2406; found 289.2417. HPLC: $t_R$ = 43.4 min.

**Preparation of 2,2,4,4-Tetramethylpentane-Derived Alkoxyamines 3p and 3s.** The reaction and product isolation were carried out using 2,2,4,4-tetramethylpentane according to the procedure described above for 2,4-dimethylpentane, except for the use of a 90/10 MeOH/H$_2$O HPLC eluent mixture.

*1,1,3,3-Tetramethyl-2-(2,2,4,4-tetramethylpentan-3-yloxy)-isoindoline (3p).* ^{1}H NMR (CDCl$_3$, 400 MHz): δ ppm = 7.23 (dd, 2H, J = 5.5, 3.2 Hz); 7.10 (dd, 2H, J = 5.5, 3.2); 3.67 (s, 2H); 1.45 (br s, 12H); 1.42 (s, 2H); 1.12 (s, 6H); 1.03 (s, 9H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ ppm = 121.54; 127.22; 88.21; 52.27; 32.24; 26.78; 145.65; 67.51; 36.99; 29.86. HRMS (EI) *m/z* calcd for C$_{19}$H$_{31}$NO: 317.2719; found 317.2731. HPLC: $t_R$ = 20.7 min.

*1,1,3,3-Tetramethyl-2-(2,2,4,4-tetramethylpentyloxy)isoindoline (3s).* ^{1}H NMR (CDCl$_3$, 400 MHz): δ ppm = 7.22 (dd, 2H, J = 5.6, 3.2 Hz); 7.07 (dd, 2H, J = 5.6, 3.2 Hz); 3.71 (s, 1H); 1.64 (br s, 6H); 1.54 (br s, 6H); 1.22 (s, 18H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ ppm = 127.21; 121.24; 93.04; 31.54; 146.07; 69.48; 38.83. HRMS (EI) *m/z* calcd for C$_{19}$H$_{31}$NO: 317.2719; found 317.2727. HPLC: $t_R$ = 25.7 min.

**Regioselectivity Measurements.** A 10 mL stainless steel vessel was charged with dicumyl peroxide (0.05 mmol), 1,1,3,3-tetramethylisoindolin-2-oxyl (0.1 mmol), and pentane (6 mmol) and degassed by pressurizing and releasing 24 bar of argon. The vessel was then sealed under 24 bar of argon and heated to 160 °C for 5 min (1 initiator half-life). Residual pentane was removed by rotary evaporation, and the products were diluted with MeOH to a concentration of 5 mg/100 μL prior to GC-MS analysis of relative amounts of 1s and 1s′. Reverse phase HPLC (85:15 methanol/water; 4 mL/min) fractionation of the sample followed by UV−vis peak integration provided the relative yields of 1p and 1s + 1s′ under the assumption that the extinction coefficient of each alkoxyamine at 270 nm is identical.[40] The overall yield of 1p:1s:1s′ was 12:56:31.

Alkoxyamines derived from 2,4-dimethylpentane were produced as described for pentane using reaction times of 5, 8, and 10 min. Product concentrations at each reaction time were quantified by integration of fully resolved HPLC UV−vis signals. The observed distributions of 2p:2s:2t were 31:7:63 at 5 min, 32:6:62 at 8 min, and 33:5:61 at 10 min, indicating that tertiary alkoxyamine instability was not problematic under the reaction conditions. Extrapolation of these yields to time zero provided a 2t:2p:2s distribution of 28:8:64.

Radical trapping products of 2,2,4,4-tetramethylpentane were generated as described for pentane, with HPLC UV−vis peak integration providing a 3p:3s distribution of 99:1.

**Abstraction Efficiency Studies.** H atom abstraction yields from small molecules (pentane, 2,4-dimethylpentane, 2,2,4,4-tetramethylpentane, hexadecane) were determined by charging a 10 mL stainless steel vessel with hydrocarbon (1.0 g) and DCP (0.02 g) and deoxygenating the solution by three cycles of pressurizing with N$_2$ to 14 bar, mixing, and releasing. The vessels were then pressured to 14 bar of N$_2$ and placed in an oil bath at 160 °C under constant magnetic stirring for 38 min. The contents were cooled to room temperature before injecting directly into the GC instrument to determine cumyl alcohol and acetophenone concentrations. Abstraction efficiencies

were calculated as [cumy alcohol]/([cumyl alcohol] + [acetophenone]). Note that cumyl alcohol dehydration to $\alpha$-methylstyrene was not observed under the conditions used.

Abstraction efficiencies for polymeric substrates (PBD, PEO, HDPE, PP, PIB) were measured by coating the material (0.5 g) with a small volume of DCP in acetone (~0.2 mL) to produce a peroxide concentration of 2 wt %. For ground samples of semicrystalline polymers (PEO, PE), the solvent was allowed to dry, and the resulting powder was tumble-mixed. For amorphous materials (PP, PBD, PIB), samples were dried and passed through a 2-roll mill to ensure homogeneity. Each mixture was then charged to an Atlas Laboratory Mixer at 140, 150, 160, 170, and 180 °C for seven initiator half-lives (302, 105, 39, 14, and 6 min, respectively). The product was dissolved in toluene (3 mL) and precipitated from acetone (25 mL). The resulting solution was further diluted and the contents analyzed by GC for acetophenone and cumyl alcohol. Note that the pooled standard deviation of AE data was 0.02.

**VTMS Grafting.** Small molecule grafting experiments involved charging a 10 mL stainless steel vessel with hydrocarbon (1 g), VTMS (0.05 g), and DCP (0.002g), deoxygenating, and pressurizing as described above. Samples were maintained under continuous stirring at 160 °C for 38 min before cooling and sampling for $^1$H NMR analysis. VTMS conversion was measured by integration of resonances derived from residual vinyl functionality ($\delta$ 5.8−6.2 ppm, 3H, −CH=CH$_2$) relative to those generated by methoxy substituents ($\delta$ 3.6 ppm, s, 9H, −SiOCH$_3$).

Samples for polymer grafting were prepared as described above for abstraction efficiency measurements, resulting in mixtures containing polymer (0.5 g), VTMS (0.025 g), and DCP (0.001 g), which were heated to 160 °C for 25 min. The graft-modified samples were purified by dissolution/precipitation and dried prior to analysis by $^1$H NMR. $^1$H NMR spectra of polyethylene were recorded in deuterated toluene at 70 °C using a Bruker AC-400 spectrometer.

## ■ RESULTS

**Abstraction Efficiency.** The fragmentation of cumyloxyl radical is a commonly used radical clock[41] method for measuring the kinetics of the reaction of cumyloxyl radicals and small-molecule H atom donors. The approach involves the determination of the ratio of cumyl alcohol and acetophenone products observed when DCP is decomposed in the presence of varying concentrations of an H atom donor. Since the product ratio depends on the ratio of rate constants ($k_a/k_d$) and the H atom donor concentration in solution (Scheme 1), with a known fragmentation rate constant, the rate constant for the H atom transfer reaction can be readily determined from a plot of the product ratios as a function of H atom donor concentration. Since molar concentrations in neat polymer systems are ambiguous, we present our data in terms of abstraction efficiency (AE), defined as the fraction of cumyloxyl radicals that abstract from the hydrocarbon as opposed to fragmentation to acetophenone and methyl radicals. AE values measured for DCP thermolysis in PBD, PEO, PE, PP, and PIB are plotted as a function of temperature in Figure 1.

The limited amount of literature pertaining to the polymers of interest compares favorably with the results of this work. Rowe and Thomas analyzed the byproducts of DCP thermolysis in poly(ethylene glycol), generating an AE value of 0.72 at 140 °C, which corresponds to our PEO result of 0.74.[42] Chodak and Bakos report AE values for cyclohexane of 0.62 at 145 °C, 0.53 at 160 °C, and 0.49 at 170 °C,[28] while Dannenberg et al. recorded AE values for mineral oil of 0.69 at 135 °C and 0.55 at 180 °C. These data are comparable to the PE measurements presented in Figure 1, showing a decline with increasing temperature that results from a higher activation energy for cumyloxyl fragmentation (14.6 kcal/mol for *tert*-
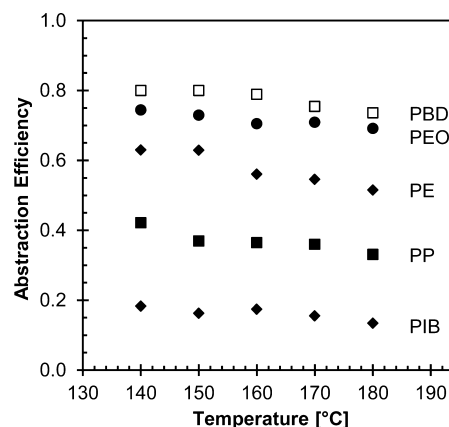


**Figure 1.** DCP abstraction efficiency as a function of reaction temperature.

butoxyl)[43] compared to that for H atom atom transfer (3.9 kcal/mol for methoxyl abstraction from isobutane).[44] This insensitivity has practical implications for a wide range of polymer modifications, as it indicates that the fate of DCP-derived radicals is not strongly temperature dependent.

Moad has discussed the importance of alkoxy radical fragmentation in polyolefin modification chemistry, reviewing differences in the reactivity of methyl and alkoxy radicals in both H atom transfer and monomer addition.[6] While cumyloxyl is relatively electrophilic and demonstrates a preference for H atom abstraction,[45] the opposite is true for methyl radicals, in that they are weakly nucleophilic and prefer monomer addition.[46,47] Our data show that reaction temperature does not strongly affect the proportions of methyl and polymer macroradicals generated by DCP. As such, the initiation efficiency of processes such as PE cross-linking and PP degradation is expected to be relatively constant over a wide temperature range. This has been demonstrated in small molecule systems, with van Drumpt and Oosterwijk showing that temperature has little effect on the efficiency of pentadecane cross-linking by *tert*-butyl perbenzoate between 130 and 165 °C.[48] Similarly, ESR studies of DCP-initiated macroradical generation from isotactic-PP found no influence of temperature on initiation efficiency.[49] This consistency in macroradical yield may, in part, explain why vinyltriethoxysilane addition to PE is insensitive to reaction temperature.[50]

The data plotted in Figure 1 reveal significant differences in H atom atom donation activity, with AE values declining in the order PBD > PEO > PE > PP > PIB. The drop observed for the first three homopolymers parallels the thermodynamic stability of the resulting secondary radicals. Consider the reported BDE values for H-3-but-1-enyl (345 kJ/mol) versus H-2-tetrahydrofuranyl (385 kJ/mol) versus H-cyclohexyl (400 kJ/mol).[51] Given the BDE of tertiary alcohols (444.9 ± 2.8 kJ/mol for *t*-BuOH),[52] it is clear that abstraction from all three polymers is exothermic. Moreover, quantum chemical calculations have shown that H atom abstraction from simple alkanes by alkoxy radicals is entropically favorable,[34,53] and as such, H atom transfer is exergonic.

Since H atom transfer reactions between alkoxyl radicals and hydrocarbons are highly exergonic, a conventional Evans−Polanyi correlation of the relevant kinetic and thermodynamic data ($\log(k_a) = \alpha\Delta H° + \text{constant}$; $\Delta H° = \text{BDE(C−H)} − \text{BDE(O−H)}$) is expected to produce a small proportionality constant $\alpha$, consistent with an early transition state. Data

published by Finn et al. have demonstrated that, even though the kinetic reactivity of *tert*-butoxyl can be dominated by entropy effects, H atom abstraction from hydrocarbons obeys a linear Evans−Polanyi relationship with $\alpha = 0.13$. This correlation appears to apply to the cumyloxyl system of present interest, with resonance stabilization of PBD- and PEO-derived radicals contributing to a heightened kinetic reactivity. With PBD, PEO, and PE presenting little difference in terms of steric effects, AE values mirror trends in bond dissociation energy.

As described above, the higher oxidizability of PP, coupled with the presence of tertiary sites of low BDE, suggests that this material could be more reactive toward cumyloxyl than PE. However, our data show the opposite, with AE values for PE proving to be 1.5 times those of PP between 140 and 180 °C. This result is consistent with low-temperature model compound studies. Dokolas et al. extended product distribution data for reactions of *tert*-butoxyl with 2,4-dimethylpentane and 3-methylpentane at 60 °C to estimate the reactivity of PP and linear low-density polyethylene (LLDPE), respectively.[54] Their extrapolations suggest that LLDPE containing 5% comonomer can provide AE values 1.3 times those of PP. Furthermore, Camara et al. conducted electron paramagnetic resonance experiments of H atom atom abstraction by *tert*-butoxyl at 25 °C from a series of model hydrocarbons, generating bimolecular rate constants of $7.1 \times 10^{-3}$ L/(mol s) for decane and $1.7 \times 10^{-3}$ L/(mol s) for 2,4-dimethylpentane.[34]

PIB is similar to PP, in that it undergoes chain scission when treated with low concentrations of dialkyl peroxides at standard polymer processing temperatures.[55,56] However, relatively large amounts of peroxide are required to bring about significant molecular weight reductions, and the oxidative stability of PIB is well established. This lack of radical reactivity is consistent with the low AE values recorded in this study and is likely the result of the steric crowding of secondary positions by adjacent quaternary centers. Unfortunately, the presence of multiple H atom donors in PIB complicates attempts to interpret AE data. Our analysis of the regioselectivity of H atom abstraction from PE, PP, and PIB follows a brief exploration of the relationship between cumyloxyl radical abstraction efficiencies and polymer graft modification yields.

**Graft Modification.** The chemical modification of saturated polymers by grafting to select monomers is widely practiced, with an ideal process operating with high kinetic chain length such that a small amount of peroxide can convert all monomer into polymer-bound functionality. This requires efficient macroradical generation by initiator-derived radicals as well as a fast sequence of monomer addition ($k_{add}$) and H atom atom transfer ($k_{tr}$) to the resulting monomer-derived radical (Scheme 2).[6,13] To assess the amenability of saturated polymers toward graft modification, we have measured grafting yields for a series of batch reactions. Vinyltrialkoxysilanes are particularly well suited to fundamental study, since they do not homopolymerize readily,[57,58] preferring H atom atom abstraction to yield single graft units versus repeated monomer addition to produce oligomeric side chains.[59,60] Furthermore, they are soluble in nonpolar hydrocarbons and polyolefins, thereby avoiding complications associated with phase-partitioning of monomer and initiator.

In Table 1 is a list of DCP abstraction efficiency and VTMS conversion data recorded for a range of polymers and small molecules. AE values are defined as above, while VTMS conversions are the fraction of monomer consumed as a result
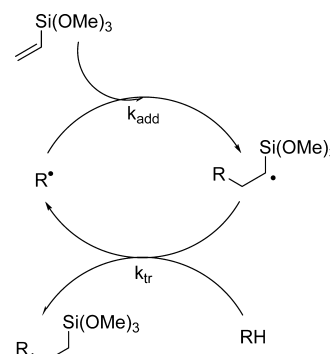
**Scheme 2**



**Table 1. Abstraction Efficiency and Vinyltrimethoxysilane (VTMS) Graft Conversions for Saturated Polymers and Model Hydrocarbons**

| R−H | abstraction efficiency[a] | VTMS graft conversion[b] | peroxide yield[c] (mol/mol) |
|---|---|---|---|
| poly(ethylene oxide) (PEO) | 0.69 | 1.00 | 21.6 |
| polyethylene (HDPE) | 0.56 | 0.78 | 16.9 |
| polypropylene (PP) | 0.37 | 0.23 | 5.0 |
| polyisobutylene (PIB) | 0.17 | 0.10 | 2.2 |
| hexadecane | 0.55 | 0.73 | 15.8 |
| pentane | 0.45 | 0.62 | 13.4 |
| 2,4-dimethylpentane (DMP) | 0.39 | 0.22 | 4.8 |
| 2,2,4-tetramethylpentane (TMP) | 0.18 | 0.12 | 2.6 |

[a]7.2 µmol DCP/g; 160 °C; 30 min. [b]7.2 µmol DCP/g; 320 µmol VTMS/g; 160 °C; 30 min. [c]Peroxide yield = mol VTMS converted/mol cumyloxyl.

of DCP initiation, and peroxide yields are the moles of VTMS consumed per mole of radicals (cumyloxyl and $CH_3^{\bullet}$) derived from DCP thermolysis. Peroxide yields are crude indicators of the kinetic chain length of VTMS addition, since the initiation efficiency of graft modification is unknown, and the concentration of VTMS dropped substantially over the course of several of these batch reactions. Note that the complete conversion of 320 µmol VTMS/g using 7.4 µmol DCP/g corresponds to a peroxide yield of 21.6 mol/mol. VTMS addition to PEO afforded this maximum value, meaning that most monomer was consumed through the chain propagation sequence illustrated in Scheme 2. The relatively low reactivity of PIB with respect to VTMS addition is reflected by a peroxide yield of 2.2.

The correlation between peroxide yield and abstraction efficiency for saturated hydrocarbons is particularly interesting (Figure 2). Abstraction efficiency is a specific measurement of H atom atom donation to cumyloxyl radicals, whereas peroxide yield relates, in part, to the propagation and termination of resulting alkyl macroradicals. It is reasonable to assume that initiation efficiency—the fraction of peroxide-derived radicals that initiate hydrocarbon addition to VTMS—will improve with increasing AE. However, the functional dependence between vinylsilane conversion and initiation efficiency is not consistent with the observed dependence of conversion on AE. We have previously demonstrated that vinylsilane conversion scales with the square root of the product of initiation efficiency and peroxide concentration,[50,61] whereas the data presented in
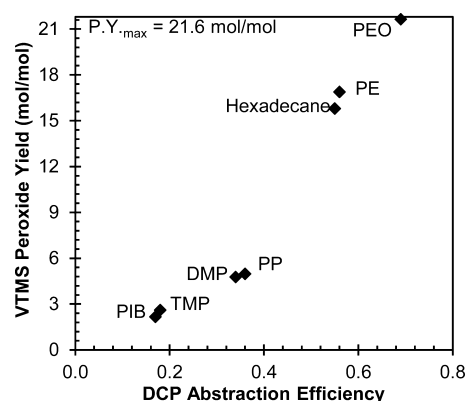
**Figure 2.** Peroxide yield of VTMS grafting versus AE ([DCP] = 0.2 wt %, [VTMS] = 5 wt %, 160 °C, 38 min).

Table 1 show VTMS conversions increasing monotonically with AE.

It is reasonable to assume that AE values reflect not only the efficiency of H atom donation by R—H to cumyloxyl ($k_a$, Scheme 1) but also the efficiency of H atom atom transfer to adduct radical intermediates ($k_{tr}$, Scheme 2). Additionally, steric effects on macroradical addition to monomer ($k_{add}$, Scheme 2) may influence the graft modification reactivity of the polymers of interest. Since steric effects act on H atom atom transfer and monomer addition in a parallel manner, a high AE measurement may be indicative of an efficient graft propagation sequence. Given sufficient monomer, these benefits will improve kinetic chain lengths and VTMS conversions. As such, AE may serve as a proxy measure of polymer reactivity that is superior to oxidizability. In the present case, both AE and VTMS conversion follow the same order: PEO > PE > PP > PIB. As noted above, PP is oxidized much faster than PE, making oxidizability unsuitable as an indicator of the amenability of a polymer toward graft modification chemistry.

**Regioselectivity of H Atom Atom Transfer.** The goal of our model compound study was to improve our understanding of the disparity in H atom atom donation reactivity of PE, PP, and PIB at industrial reaction temperatures. Pentane, 2,4-dimethylpentane (DMP), and 2,2,4,4-tetramethylpentane (TMP) contain the key structural elements of PE, PP, and PIB, respectively. AE and VTMS conversion data were in good agreement for the DMP-PP and TMP-PIB pairings, while tetradecane reflected the reactivity of PE better than pentane (Table 1). van Drumpt and Oosterwijk report similar findings for *tert*-butoxyl acting upon a homologous series of alkanes, with AE increasing with chain length owing to higher proportions of methylene versus methyl groups.[48] Nevertheless, pentane was chosen for further study, since it generates a limited number of positional isomers whose yields can, in turn, be compared directly with those produced by DMP and TMP.

First used in the polymer context to examine the initiation of methyl acrylate polymerization by *tert*-butoxyl,[62] the trapping of carbon-centered radicals with nitroxyls such as 1,1,3,3-tetramethylisoindolin-2-oxyl (TMIO) has been adapted for the purposes of H atom atom abstraction from alkanes, generating important insight into H atom donation by substrates such as DMP and 3-methylpentane.[36,63] Provided that the resulting alkoxyamines are sufficiently stable with respect to disproportionation, their relative yields reflect the radical population established by initial H atom transfer events (Scheme 1). The primary and secondary alkoxyamines isolated

in this work are quite robust,[64] while the stability of the tertiary alkoxyamine derived from DMP was examined carrying out the trapping reaction at different peroxide half-lives and verifying that that the alkoxyamine distribution remained constant.

A comparative analysis of PE, PP, and PIB requires an account of overall reactivity of the model alkane AE coupled with knowledge of regioselectivity. Taken together, these measurements reflect the absolute reactivity of the primary, secondary and tertiary sites in each substrate (Scheme 3). Of

**Scheme 3. Alkyl Radical Trapping Yields (160 °C; 27 mmol DCP/g; 54 mmol TMIO/g)**



| Pentane (1) | | | |
|---|---|---|---|
| | Yield | AE*Yield | AE*Yield / Group |
| **(1p)** | 12% | 6% | 3 |
| **(1s)** | 56% | 25% | 13 |
| **(1s')** | 32% | 14% | 14 |

| 2,4-Dimethylpentane (3) | | | |
|---|---|---|---|
| | Yield | AE*Yield | AE*Yield / Group |
| **(2p)** | 28% | 10% | 3 |
| **(2s)** | 8% | 3% | 3 |
| **(2t)** | 64% | 22% | 11 |

| 2,2,4,4-Tetramethylpentane (3) | | | |
|---|---|---|---|
| | Yield | AE*Yield | AE*Yield / Group |
| **(3p)** | 99% | 18% | 3 |
| **(3s)** | 1% | 0% | 0 |

the three hydrocarbons, pentane afforded the highest abstraction efficiency of 0.45, meaning that 45% of cumyloxyl radicals engaged in H atom atom abstraction from the alkane as opposed to fragmenting to $^\bullet CH_3$ + acetophenone. The product of AE and the isomer yield gives the percent of cumyloxyl radicals that abstract from a given position. Whereas just 6% of cumyloxyl radicals reacted at a methyl group, 25% and 14% abstracted from the methylene groups at the 2-position and 3-position, respectively. These positional abstraction efficiencies can be normalized with respect to the number of functional groups to account for statistical differences. Abstraction from a methyl group can be characterized with an AE*yield/group ratio of 3, whereas abstraction from methylene functionality is defined by a ratio in the range of 13–14.

For DMP, an AE of 0.34 was determined, with the greatest positional abstraction efficiency observed for the tertiary position. 22% of cumyloxyl radicals reacted at this site, producing a normalized AE*yield/group value of 11. It is known that, on a per H atom basis, the tertiary position of

DMP is most reactive.[36,34] We note, however, that on a per functional group basis, the tertiary position is no more reactive than the secondary position of pentane. Moreover, the normalized abstraction efficiency from the 3-position of DMP was 3, compared to 14 for pentane. This 4-fold loss in reactivity of the methylene group accounts for most of the difference in the AE values of DMP and pentane. We suggest that this is the underlying cause of the disparity in PE and PP reactivity toward cumyloxyl.

TMP presents an even more extreme example of the inhibitory effects imposed by methyl substituents. An overall AE of 0.18 is provided entirely by primary H atom abstraction, whose yield per group of 3 is consistent with that observed for the methyl substituents of pentane and DMP. Reaction at the 3-position is suppressed to such an extent that a secondary alkoxyamine is produced only in trace quantities. This result confirms speculation in an early report by Loan, in which the primary sites within poly(isobutylene-*co*-isoprene), or IIR, were suggested to be more reactive than secondary positions.[56] The regioselectivity of H atom transfer from the allylic positions within IIR is unknown but is the subject of ongoing studies.

### ■ DISCUSSION

Abstraction efficiency results, combined with regioselectivity data, have provided insight into H atom atom abstractions from a range of polymers under conditions that are relevant to industrial practice. On the basis of low-temperature model compound studies, Camera et al. concluded that H atom atom abstraction from *unhindered* C−H bonds mirrors their BDE's, allylic > tertiary > secondary > methyl, whereas the reactivity of *hindered* C−H bonds follows the order tertiary > methyl > secondary.[34] Our results are consistent with this view. Where steric effects were equivalent, abstraction efficiencies for −CH$_2$− groups reflected differences in reaction enthalpy (PBD > PEO > PE). However, entropic effects controlled the reactivity of −CH$_2$− groups bearing adjacent tertiary (PP) and quaternary carbons (PIB), with steric inhibition of these H atom donors accounting for differences in overall abstraction efficiencies (PE > PP > PIB).

As noted above, H atom atom abstraction by cumyloxyl from hydrocarbons is exergonic, with early transition states whose structures and energetics are relatively insensitive to the overall thermodynamics of possible reaction pathways. This results in a weak correlation between BDE's and cumyloxyl abstraction efficiencies that can only be observed where reagents present similar entropic barriers. In contrast, H atom abstraction by alkylperoxyl radicals is endergonic, which is attributable to the lower alkyl hydroperoxide OH bond strength (*tert*-butyl hydroperoxide 352.3 ± 8.8 kJ/mol)[52] compared to that of the corresponding alcohol (444.9 ± 2.8 kJ/mol),[52] with correspondingly later transition states.[65] Therefore, differences in the overall reaction enthalpy, as measured through BDE's, are expressed more strongly in the transition state free energies, the result being greater regioselectivity for tertiary over secondary and primary C−H bonds. This is not to say that entropic effects do not contribute to oxidizability,[66] as steric hindrance is often invoked to account for the relative stability of polymers such as polystyrene and poly(vinylcyclohexane) toward oxidation.[67] However, the presence of an extra oxygen atom in alkylperoxyl radicals increases the distance between the abstraction site and the steric bulk on the radical, reducing entropic effects compared to alkoxyl radicals.[68] Given the foregoing, it would appear that the balance between enthalpic

and entropic effects differs significantly between alkoxyl and alkylperoxyl radicals, making oxidizability a poor predictor of a polymer's response to peroxide activation as well as vinyltrialkoxysilane grafting. We suggest that abstraction efficiency is a more reliable indicator of the amenability of a polymer to graft modification.

The H atom atom transfer reactions of present interest are, in principle, amenable to gas-phase quantum chemical calculations, and several attempts to determine the structures and free energies of relevant transition states have been reported. An early attempt to calculate the overall thermodynamic and thermokinetic parameters for *t*-BuO$^{\bullet}$ reactivity confirmed that H atom abstraction from unhindered C−H bonds is under enthalpic control.[69] However, calculated activation enthalpies were significantly different from accepted experimental values. Similar difficulties are described by Bertin et al., who used density functional theory (DFT) to characterize the reaction of *t*-BuO$^{\bullet}$ with a polypropylene model compound.[53] This level of theory provided qualitative information regarding transition state energies, predicting that H atom abstraction from tertiary positions faces entropic barriers that are greater than enthalpic contributions to free energies. That is, activation of the secondary positions within PP by *t*-BuO$^{\bullet}$ is made difficult by the steric demands of the adjacent tertiary positions.

Interestingly, subsequent DFT calculations on PP degradation confirmed that the reactivity of alkylperoxyl radicals with respect to this hydrocarbon differs from that of alkoxy radicals, in that enthalpic barriers are greater than entropic contributions to transition state energies, leading to a kinetic preference for reaction that follows the thermodynamics of the reaction; that is, tertiary C−H abstraction is favored over secondary C−H abstraction, which is favored over abstraction from the primary position.[68] This is consistent with our assertion that oxidizability is not a reliable indicator of polypropylene's reactivity toward the high-energy alkoxyl and alkyl radical intermediates that underlie typical nonoxidative cross-linking, degradation and chemical modification processes.

### ■ CONCLUSIONS

The reactivity of cumyloxyl radicals at temperatures relevant to industrial practice is entropy-controlled where substituents present a steric barrier to H atom atom transfer. Therefore, PP is a less reactive H atom donor than is PE, despite the low BDE of its tertiary positions, owing to steric hindrance of abstraction from the secondary C−H bonds. The reactivity if PIB is limited almost exclusively to methyl group activation, with secondary macroradical generation inhibited almost entirely by adjacent quaternary carbons. Differences in the reactivity of ROO$^{\bullet}$ and RO$^{\bullet}$ in H atom transfer are significant enough to render oxidizability a poor measure of the amenability of a polyolefin toward radical-mediated chemical modification.

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**Notes**

The authors declare no competing financial interest.

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