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Selective and Mild Oxyfunctionalization of Model Polyolefins

Nicole K. Boaen and Marc A. Hillmyer*

Department of Chemistry, University of Minnesota, 207 Pleasant St. SE,
Minneapolis, Minnesota 55455

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ABSTRACT: The direct oxyfunctionalization of a model polyolefin, polyethylene-*alt*-propylene (PEP), was achieved utilizing a straightforward, mild process. In the presence of a manganese complex, manganese *meso*-tetra-2,6-dichlorophenylporphyrin acetate (Mn(TDCPP)OAc), imidazole, a phase transfer agent, and potassium peroxymonosulfate (Oxone), PEP was functionalized under ambient conditions without chain degradation. The primary oxidation products contained tertiary alcohols and ketones based on IR, ^{1}H NMR, ^{13}C NMR, and DEPT ^{13}C NMR spectroscopy of the oxyfunctionalized products. The oxyfunctionalization of squalane, a small molecule, structural analogue of PEP, was also demonstrated. Spectroscopic analyses of the main products from the squalane oxidation were nearly identical with the functional groups identified in the PEP oxidation products. The degree of functionalization was modulated by changing the relative concentration of the oxidant, Oxone. The degree of functionalization and the thermal properties are reported for these new polymeric materials.

Introduction

The chemical modification of polymers is a valuable method for the preparation of new materials with tailored properties and useful functionality. A widespread example is the postpolymerization modification of polydienes, utilizing reactions such as hydrogenation, epoxidation, chlorosilation, hydroboration, and carbene addition.[1−3] These reactions apply established transformations of carbon−carbon double bonds to add functionality within and along a polymer backbone. In the case of polyolefins (macromolecular alkanes), postpolymerization modification is challenging due to the absence of any suitably reactive functional groups. Still, the search to develop routes to functionalized specialty materials from inexpensive, commercial polyolefins is unwavering due to their intrinsic value-added properties, including improved compatibility with pigments and other macromolecules, in addition to potentially useful adhesion, thermal, and barrier properties.[4,5] Even the introduction of a small amount of polar functionality into polyolefins would open new possibilities for macromolecular grafting and reactive compatibilization.[6,7]

In search of a convenient method for the functionalization of polyolefins, we considered previous work aimed at the functionalization of alkanes.[8−16] Historically, functionalization of alkanes has been achieved via free radical reactions, where highly reactive species can effectively functionalize these inert substrates. Unfortunately, these free radical reactions also typically result in side reactions, such as β-scission, chain transfer, and coupling reactions, that reduce the efficiency of this synthetic approach.[17] These chain-coupling and chain-breaking reactions can be especially detrimental to polymer modification systems, since they disrupt the molecular weight distribution of the polymer sample, possibly compromising the desirable mechanical and processing properties of the starting material.[18,19] Alternatively, an ideal functionalization system would utilize an environmentally benign oxygen donor, such as molecular oxygen, and a readily available catalyst active under mild conditions. Previous work has demonstrated that organometallic complexes can induce the activation of alkane C−H bonds.[8] However, to the best of our knowledge, the only other system reported for the selective and mild oxyfunctionalization of polyolefins was only recently published.[20]

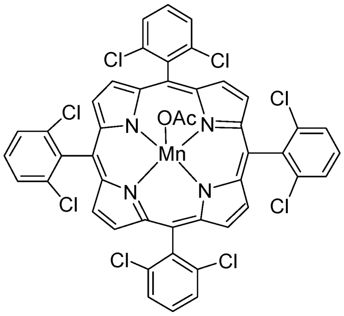

Figure 1. An effective alkane oxidation catalyst: manganese *meso*-tetra-2,6-dichlorophenylporphyrin acetate (Mn(TDCPP)-OAc).

One promising class of compounds for polyolefin oxidations are those designed to mimic the activity of biological systems, such as methane monooxygenase[21−31] and cytochrome P-450,[8,32−34] which catalyze the hydroxylation of toxic, inert substances in the body to facilitate their excretion. These model systems provided novel synthetic approaches for adding polar functionality to alkanes under ambient conditions.[33,35−38] Particularly, manganese *meso*-tetra-2,6-dichlorophenylporphyrin, Mn(TDCPP)X, where X is a counterion (e.g., acetate or chloride), has been recognized as an effective catalyst for the hydroxylation of alkanes and the epoxidation of alkenes in the presence of various oxygen donors, including hypochlorite, hydrogen peroxide, peroxyacids, sodium periodate, and potassium hydrogen persulfate from Oxone and a nitrogen base cocatalyst, such as imidazole or substituted pyridines (Figure 1). In the presence of one of these oxygen donors and a nitrogen base,[39] an active oxygenating species is formed that can transfer an oxygen atom to alkanes or olefins.[40−43] Furthermore, these synthetic halogenated

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* To whom correspondence should be addressed: e-mail hillmyer@chem.umn.edu.

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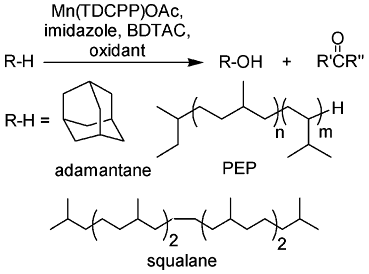

Figure 2. Oxyfunctionalization of alkanes.

metalloporphyrin models of cytochrome P-450 are robust catalysts resistant to oxidative destruction.[34,40]

Given the desirable features of this system, we explored Mn(TDCPP)OAc as an oxygenation catalyst for polyolefins. To effectively probe this reaction, the reactivity of a Mn(TDCPP)OAc/imidazole system was examined for both a model polymer, poly(ethylene-*alt*-propylene) (PEP), and squalane, a small molecule structurally similar to PEP (Figure 2). The model polymer was synthesized with controlled molecular weight and a narrow molecular weight distribution using anionic polymerization followed by hydrogenation.[44,45] Size exclusion chromatography (SEC) of reaction products from this model material allowed for the ready identification of any active chain-coupling or chain-cleavage side reactions. Utilizing this manganese oxidation system, we were able to effectively incorporate oxygen functionality into model polyolefins. In this report, we show that spectral evidence, mass spectrometry, and elemental analyses of oxyfunctionalized products corroborate the successful, direct, mild oxyfunctionalization of model polyolefins under ambient conditions.

Results and Discussion

Synthesis of Mn(TDCPP)OAc. We prepared the manganese catalyst shown in Figure 1 using a modified Lindsey procedure for the synthesis of the sterically hindered porphyrin ligand, *meso*-tetra-2,6-dichlorophenylporphyrin (H_2TDCPP), followed by metal insertion.[42,46−48] The yield for the large-scale synthesis of the porphyrin ligand was typical (25%). The ^{1}H NMR spectrum, the Soret band at 418 nm in the UV/vis spectra, and the low-resolution fast atom bombardment mass spectrometric (FAB-MS) analysis were consistent with that previously reported.[42,46] The metalation reaction with manganese(II) acetate to give Mn(III)(TDCPP)OAc was monitored by UV/vis spectroscopy (shift in the Soret band to 478 nm). The ^{1}H NMR spectrum of Mn(TDCPP)OAc consisted of very broad peaks with chemical shifts significantly outside of the normal range for organic compounds, presumably due to the paramagnetic manganese(III) center.[42,46,49] The oxidation of Mn(II) to Mn(III) typically occurs in this type of system when oxygen is present.[50] Mn(TDCPP)OAc can be purified by Soxhlet extraction with hexanes, followed by extraction of the desired product with methylene chloride and subsequent column chromatography (54% yield). The crude product could also be directly purified by column chromatography, followed by recrystallization in a methylene chloride/hexane mixture, with a substantial decrease in isolation yield. High-resolution FAB-MS of the catalyst confirmed the presence of the molecular ion $[C_{44}H_{20}N_4Cl_8Mn]^+$.

Oxyfunctionalization of Adamantane. Oxidation reactions of adamantane were performed to verify the activity of the previously published Mn(TDCPP)/imidazole system.[41] A typical two-phase reaction consisted of Mn(TDCPP)OAc, adamantane, and imidazole in methylene chloride and an aqueous solution of sodium periodate ($NaIO_4$) (Figure 2). A phase transfer catalyst, benzyldimethyltetradecylammonium chloride (BDTAC), was employed to facilitate the transfer of the oxidant to the organic phase.[41] The biphasic reaction was vigorously stirred at room temperature for 24 h, after which the organic phase was washed with distilled water, concentrated, and analyzed by gas chromatography−mass spectrometry (GC−MS) and ^{1}H NMR spectroscopy. The effects of the $NaIO_4$, imidazole, and BDTAC concentrations on the oxidation efficiency were independently investigated to determine the optimal reaction conditions. While we only examined adamantane reactions using $NaIO_4$, other oxidants including magnesium monoperoxyphthalate hexahydrate, H_2O_2, sodium hypochlorite (NaOCl), and potassium hydrogen persulfate from Oxone (potassium peroxymonosulfate) have previously been reported as active oxygen donors in the oxyfunctionalization of adamantane with manganese porphyrin complexes.[42,43,51,52] We found the optimal mole ratios for the oxidation reactions were $[NaIO_4]_0/[Mn(TDCPP)OAc]_0 = 400$, $[adamantane]_0/[Mn(TDCPP)OAc]_0 = 82$, $[imidazole]_0/[Mn(TDCPP)OAc]_0 = 10$, and $[BDTAC]_0/[Mn(TDCPP)OAc]_0 = 40$, similar to those mole ratios previously reported.[41] These conditions typically led to high conversion of adamantane (84%).

The two major products were 1-adamantanol and 2-adamantanone, typically present in a one-to-one mole ratio. Previous work employing different oxidants and shorter reactions times reported similar conversions for the adamantane oxidation but reported 1- and 2-adamantanol as the principal products.[53] Perhaps the ketone product in our longer experiments could be explained by the subsequent oxidation of 2-adamantanol to 2-adamantanone.[54] GC−MS also revealed there were no coupled products, suggesting the reaction does not involve long-lived free radical intermediates.[54] In a separate control experiment, we found that no oxyfunctionalized products were formed in the absence of Mn(TDCPP)OAc. Having effectively generated an active oxyfunctionalization system, we examined a model substrate for the targeted polyolefin reaction.

Oxyfunctionalization of Squalane. Squalane is a structurally similar, small molecule analogue of PEP; thus, application of the manganese oxidation system to squalane was the next step to explore the potential of this system toward the oxyfunctionalization of polyolefins (Figure 2). The optimized conditions for the adamantane reactions were applied to the squalane oxyfunctionalization. Additional experiments using $NaIO_4$, NaOCl, or Oxone as the oxidant revealed that similar products were produced for all of the reactions. A typical oxyfunctionalization using Oxone was monitored by ^{13}C NMR spectroscopy for new chemical shifts in the range for carbons in close proximity to oxygen-containing functional groups. After a reaction time of 48 h, the intensity of the new signals appeared virtually unchanged, and the reaction was stopped. The organic layer was washed with distilled water, concentrated, and analyzed by thin-layer chromatography (TLC). Column chromatography was used to crudely fractionate the complex mixture. The fractions collected were divided into groups based on R_f values (Table 1). On

Table 1. Summary of Functionalized Squalane Product Mixtures[a]

group[b]	elution solvent[c]	R_f[d]	mass (g)
S1	10:1	0.58–0.74	0.026
S2	10:1	0.29–0.45	0.058
S3	5:1	0.18	0.047
S4	CH_2Cl_2[e]	0.02	0.014

[a] Isolated from a reaction of Mn(TDCPP)OAc (31.2 mg, 30.9 μmol), imidazole (22.1 mg, 0.320 mmol), benzyldimethyltetradecylammonium chloride (BDTAC) (0.5083 g, 1.26 mmol), squalane (0.5263 g, 1.24 mmol), and 5 mL of CH_2Cl_2. The oxidant, Oxone (1.59 g, 2.59 mmol), was added to the reaction as a solution in 50 mL of 0.25 M phosphate buffer, pH = 7. The biphasic mixture was stirred vigorously for 2 days. [b] Groups identified in the Supporting Information. [c] Pentane:Et_2O. [d] TLC solvent development solution 5:1 pentane/Et_2O. [e] Pure methylene chloride was used as the eluent.

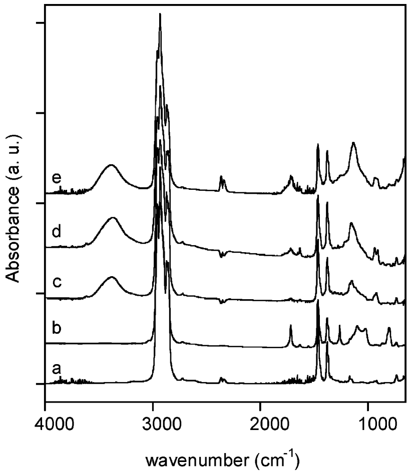

Figure 3. IR spectra of squalane and functionalized derivatives [thin film/NaCl plate]: (a) squalane, (b) group S1, (c) group S2, (d) group S3, (e) group S4 from Table 1.

the basis of the mass of recovered squalane, approximately 70% of the starting material was functionalized (see Supporting Information). Characterization of the four isolated product mixtures was accomplished using elemental analysis, ^{1}H NMR, ^{13}C NMR, distortionless enhancement by polarization transfer (DEPT) ^{13}C NMR, and IR spectroscopy.

IR spectra of squalane and oxyfunctionalized products (groups S1–S4) are given in Figure 3. The absorbance at 1716 cm^{-1} in the spectrum of group S1 is characteristic for a C=O stretch, indicating the presence of carbonyl-containing functional groups. The absorbances at 3376 cm^{-1}, near 1100 cm^{-1}, and at 1716 cm^{-1} in the spectra for groups S2–S4 were respectively assigned for an O–H stretch and a C–O stretch in an alcohol and a C=O stretch of a carbonyl-containing functional group. Therefore, we conclude that groups S1–S4 are oxyfunctionalized, and the more polar fractions contain both hydroxyl and carbonyl functionalities.

^{1}H NMR spectra of the oxyfunctionalized products were largely unchanged from the spectrum of squalane. However, new chemical shifts were observed near 2.6 ppm in the spectra of groups S1, S3, and S4, which are consistent with resonances for methylene or methine protons on a carbon α to a carbonyl group in a ketone. Furthermore, no additional resonances in the normal range for carboxylic acids or aldehydes were observed, providing further support that the carbonyl functional groups in the isolated products are ketones. The absence of a resonance at 2.6 ppm in the proton spectrum of group S2 indicates the concentration of any carbonyl-containing functional group was small, consistent with the IR analysis. Moreover, the absence of new chemical shifts for methylene or methine protons α to a hydroxyl group suggests that the alcohol products identified in the IR analysis are tertiary alcohols.

Although carbonyl-containing functional groups were identified in IR and ^{1}H NMR spectroscopic analyses, no characteristic resonances were observed in the ^{13}C NMR spectra (Figure 4), presumably due to the poor sensitivity of these quaternary carbons. The following analysis of the ^{13}C NMR spectra will serve to highlight the salient features, identifying the predominant functional groups of the oxidation products. Using a DEPT ^{13}C NMR experiment, all resonances were assigned as quaternary, methine, methylene, or methyl carbons. The ^{13}C NMR spectrum of group S1 exhibited two new chemical shifts at 54.0 and 46.4 ppm that were very low in intensity, indicating low concentrations of these carbons. These new signals were assigned to methylene and methine carbons α to a carbonyl group, respectively, based on group additivity calculations using squalane as a base molecule. Thus, one type of ketone product is proposed for group S1, having a carbonyl group adjacent to a tertiary carbon. The ^{13}C NMR spectrum of group S2 revealed new chemical shifts at 73 and 42 ppm. These two carbons were identified as a quaternary carbon and a secondary carbon, respectively. Since there are no quaternary carbons in squalane and the chemical shift is in the characteristic region for carbons α to a hydroxyl group, we propose that the products contain tertiary alcohols. Using group additivity, the additional new chemical shift at 42 ppm was assigned to methylene carbon(s) β to the hydroxyl functional group, which is expected as all tertiary alcohol products would be adjacent to at least one methylene group in squalane. The ^{13}C NMR spectrum of group S3 had carbons resonating in the same range as those identified for group S2. Similarly, the chemical shifts for a quaternary carbon at 71 ppm and a methylene carbon at 44 ppm were ascribed to a tertiary alcohol product. The slightly shifted values for the signals can be attributed to different isomers of the tertiary alcohol squalane product. For example, the tertiary carbons could be hydroxylated on the end of the chain or within the molecule. The ^{13}C NMR spectrum of group S4 contained resonances present in both group S2 and group S3. Since group S4 is more polar than groups S2 or S3 (see R_f values in Table 1), it is most likely that group S4 contains both types of hydroxyl groups, as opposed to being a mixture of products from groups S2 and S3.

Elemental analysis (C, H, O) of the four groups (Table 1) allowed the average number of oxygen atoms per squalane molecule to be determined. Elemental analysis of group S1 gave an average of 1.4 oxygen atoms per squalane molecule (5.0% by mass), suggesting there is a mixture of molecules containing one and two oxygen atoms. Elemental analysis of groups S2, S3, and S4 revealed there were 1.2, 1.1, and 2.4 oxygen atoms per squalane molecule, respectively. Importantly, the C, H, O data did not always equal 100%, indicating there were some non-C, H, O impurities present. These impurities could be trace fragments of oxidized catalyst, as suggested by the colored products[55] and by liquid chromatography–mass spectrometric (LC–MS) analysis. High-resolution FAB–MS analyses of two products obtained from separate reactions confirmed the presence of the

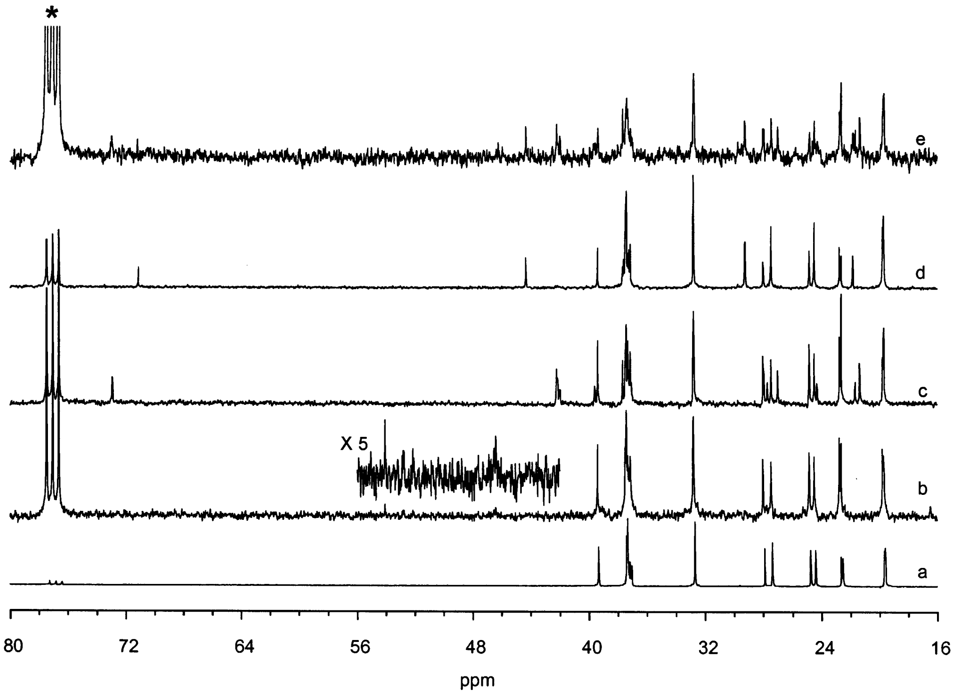

Figure 4. ^{13}C NMR spectra of oxyfunctionalized products and squalane [ca. 14−50 mg/mL $CDCl_3$; $d_1 = 5$ s, $n_t = 450$]: (a) squalane, (b) group S1, (c) group S2, (d) group S3, (e) group S4 from Table 1. [*] denotes solvent peaks.

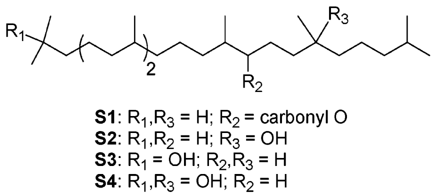

Figure 5. Functionalized squalane candidates based on ^{13}C chemical shifts and IR absorption bands.

Table 2. Summary of Functionalized PEP Products[a]

group[b]	elution solvent[c]	R_f[d]	no. of OH/chain[e]	no. of OH/100 carbons[e]	mass (g)
P1	10:1	0.71−0.84	0.7	0.3	0.397
P2	10:1	0.42−0.52	1.7	0.6	0.133
P3	5:2	0.09−0.15	1.5	0.5	0.108
P4	5:2, 2:1	0.03−0.05	3.1	1.1	0.073
P5	2:1	0.02	2.5	0.9	0.089

[a] Isolated from reaction of Mn(TDCPP)OAc (43.6 mg, 43.5 μmol), imidazole (29.4 mg, 0.435 mmol), benzyldimethyltetradecylammonium chloride (BDTAC) (0.7072 g, 1.75 mmol), PEP (M_n = 5 kg/mol) (1.0815 g, 0.235 mmol, 15.45 mmol monomer), and 10 mL of CH_2Cl_2. The oxidant, Oxone (1.79 g, 2.91 mmol), was added to the reaction as a solution in 60 mL of 0.25 M phosphate buffer, pH = 7. The biphasic mixture was stirred vigorously for 5 days. [b] Corresponds to product identification in the Supporting Information. [c] Pentane:Et_2O. [d] TLC solvent development solution 5:1 pentane/Et_2O. [e] Average value determined from ^{1}H NMR analysis of acetylated products; ca. 70 repeat units (280 backbone carbons) per chain.[58]

molecular ions, $[C_{30}H_{62}O + Na]^+$ and $[C_{30}H_{62}O_2 + Na]^+$, consistent with the mono- and dihydroxylated products, respectively (see Supporting Information).

All of the characterization data substantiate the successful incorporation of oxygen into squalane. Spectroscopic evidence suggests the oxygen-containing functional groups are tertiary alcohols and ketones. Some possible products are presented in Figure 5. Mass spectrometry and elemental analysis of the products quantified the degree of functionalization of the products as containing exclusively one oxygen atom per squalane up to an average close to two oxygen atoms per molecule. This trend was consistent with decreasing R_f values for more highly substituted products.

Oxyfunctionalization of a Low-Molecular-Weight Model PEP. Given the success with the oxidation of squalane, we examined the oxidation of a model polyolefin. Specifically, the gram scale postpolymerization oxyfunctionalization reactions of a low-molecular-weight (5 kg/mol) model PEP was performed utilizing the manganese system with Mn(TDCPP)OAc, imidazole, BDTAC, and Oxone (Figure 2). After 5 days,[56] the reaction was stopped, washed with distilled water, dried, and concentrated. The complex product mixture was crudely purified using column chromatography, and the fractions collected were combined into groups based on R_f values (Table 2). The conversion of PEP to functionalized derivatives was estimated to be 80% based on recovered PEP. The isolated product mixtures were characterized by IR and NMR spectroscopy.[57] IR spectra of PEP and two representative fractions are presented in Figure 6. The absorbance near 3500 cm^{-1}, characteristic of an O−H stretch in an alcohol, was observed in the IR spectrum of group P1. The IR spectra for groups P2−P5 were virtually identical, having a broad absorbance near 3400 cm^{-1}, which was assigned for an O−H stretch, in addition to a peak near 1710 cm^{-1}, which is typical for a C=O stretch.

^{1}H NMR spectra of the oxyfunctionalized products were similar. New chemical shifts were observed near 2.6 ppm, consistent with methylene or methine protons of a carbon α to a carbonyl group of a ketone. These signals are similar to those observed in the ^{1}H NMR spectra of squalane oxidation products. No other resonances were observed in the normal range for other oxyfunctionalized derivatives. Furthermore, the absence of methylene or methine protons α to a hydroxyl group strongly supports the alcohol functionality identified by IR spectroscopic analysis is a tertiary alcohol.

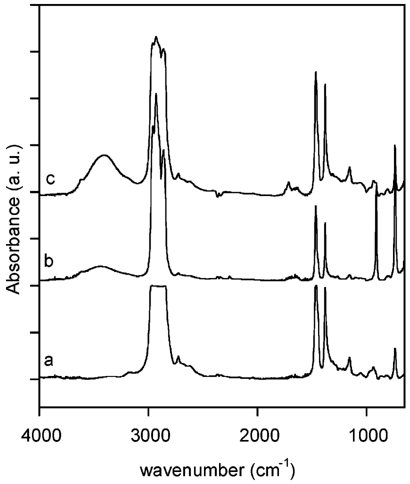

Figure 6. IR spectra of 5 kg/mol PEP starting material and functionalized derivatives [thin film/NaCl plates]: (a) 5 kg/mol PEP starting material, (b) group P1, (c) group P3 from Table 2.

The ^{13}C NMR spectra of groups P1–P5 all exhibited the same resonances, suggesting all of the products contain similar functional groups. A representative spectrum is presented in Figure 7. Two new signals were seen at 73 and 42 ppm for quaternary and methylene carbons, respectively. All other chemical shifts were consistent with the PEP starting material. (The resonance at 44 ppm is due to the methine carbon of the minor 4,3-repeat unit (<5%) in the PI precursor to PEP.) The resonance at 73 ppm is in the typical range for a carbon α to a hydroxyl group,[19] and the peak at 42 ppm was assigned to a methylene carbons β to a hydroxyl group. These chemical shifts were similar to those reported for group S2 of the oxyfunctionalized squalane products, consistent with our prediction that the selectivity of the reaction for PEP would be similar to that exhibited for squalane, based on the structural similarity of the molecules. Spectral evidence suggests the types of functional groups proposed in Figure 8 are present in the products. Again, the absence of ^{13}C resonances expected from IR analysis for carbonyl carbons is explained by the poor sensitivity of these quaternary carbons.[59]

Derivatization of the hydroxyl groups of the oxyfunctionalized products was performed with acetyl chloride and pyridine in methylene chloride, providing further evidence that hydroxyl groups are present in the oxyfunctionalized PEP products and accessible for further functionalization.[60] Assuming all of the hydroxyl groups reacted, an average number of hydroxyl groups per chain could be determined from integration values of the ^{1}H NMR spectra. Specifically, the methyl protons of the acetyl group near 2.0 ppm were integrated relative to the protons of the polymer chain to determine the degree of hydroxylation of the functionalized product. ^{1}H NMR analysis of the acetylated products was consistent with the functionalized products having one to three hydroxyl functional groups per chain or 0.4–1.1 hydroxyl groups per 100 backbone carbons.[58] From IR analysis, we also know that carbonyl groups are present in groups P2–P5 as well.

SEC analyses of the crude reaction and isolated product mixtures indicated that the reaction conditions did not significantly alter the number-average molecular weight (M_n) or the molecular weight distribution (PDI) of the PEP starting material (Figure 9). Only a very small amount of coupled product was identified from the SEC trace, but perhaps most importantly, virtually no chain degradation was observed. Previous efforts in this field of research have been characterized by severe chain degradation and loss of mechanical properties.[61,62]

We investigated the effects of increasing reaction temperature (50 °C) and varying the oxidant concentration on the reaction. The effect of temperature was investigated by performing two parallel experiments in sealed, high-pressure glass vessels; one was heated to 50 °C, while the second was performed at room temperature. Each reaction was sampled daily, and the samples were characterized by NMR and IR spectroscopy as well as SEC. In both cases, hydroxylated product was observed after 1 day by ^{13}C NMR spectroscopy.[56] IR spectroscopy of the two reactions revealed that both product mixtures contained hydroxylated products, but the reaction at 50 °C had a reasonable amount of carbonyl-containing product as well. The characteristic peak near 1700 cm^{-1} was not observed for the room temperature reaction until after 2 days. The sample aliquots were crudely fractionated to separate the unfunctionalized PEP from the functionalized product. Heating does not appear to disrupt the molecular weight distribution, or PDI, of the crude polymer products, and relative conversions based on recovered unfunctionalized PEP were both 90% or greater after 2 days (see Supporting Information). Using the aforementioned acetylation, the average number of hydroxyl groups did not appear to increase with longer reaction times, with most products containing between two and four hydroxyl groups per polymer chain (ca. 70 repeat units)

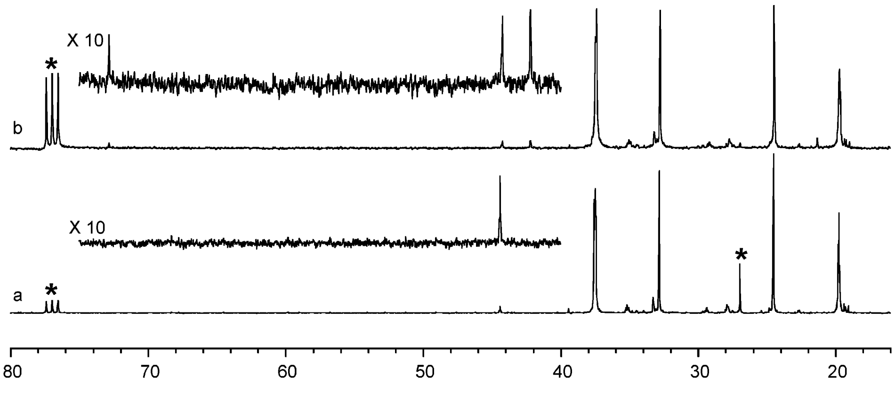

Figure 7. ^{13}C NMR spectra of 5 kg/mol PEP and functionalized PEP [ca. 50 mg/mL CDCl$_3$; $d_1 = 5$ s, $n_t = 450$]: (a) 5 kg/mol PEP starting material, (b) group P3 from Table 2. [*] designates solvent peaks.

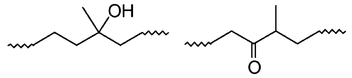

Figure 8. Possible functional groups present in PEP products.

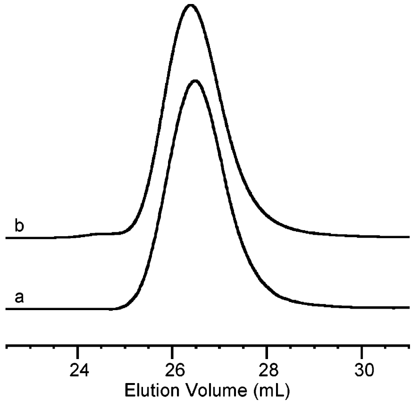

Figure 9. Size exclusion chromatogram [10 mg/mL in THF] for (a) 5 kg/mol PEP [M_n = 8.9 kg/mol, PDI = 1.1] and the (b) crude functionalized product [M_n = 8.8 kg/mol, PDI = 1.1]. M_n values relative to polystyrene standards.

or 0.7–1.4 hydroxyl groups per 100 backbone carbons.[58] While the values were similar in both cases, the products isolated from a few aliquots of the reaction at 50 °C contained slightly higher degree of functionalization relative to those obtained from the room temperature reaction.

The effect of changing the concentration of Oxone relative to the concentration of monomer repeat units was examined at 50 °C. Five parallel reactions were conducted for approximately 2 days and worked up in the usual way. Conversions, based on recovered unfunctionalized PEP, increased with higher concentrations of Oxone. The PDI of the isolated functionalized products remained narrow, except for the reaction employing the highest concentration of Oxone ($[\text{Oxone}]_0/[\text{monomer}]_0 = 0.91$). This particular reaction was the first example in our studies using this system where chain scission has been identified by the broad PDI and the large decrease in the number-average molecular weight (see Table S2 in Supporting Information for details). Subsequent acetylation of the functionalized products revealed a general trend for the degree of oxyfunctionalization increasing with higher concentrations of Oxone (see Figure 10 and Supporting Information).

Thermal Characterization. Introduction of polar functionality, such as hydroxyl groups, into a nonpolar polymer can increase the glass transition temperature (T_g) of the polymer.[5,20] We measured the T_g of the PEP starting material and several functionalized products using differential scanning calorimetry (DSC). The results are presented in Figure 11 as a function of hydroxyl groups per chain to demonstrate the effect the degree of oxyfunctionalization on the T_g. The general trend is consistent with previously reported examples whereby the T_g increased with higher levels of functionalization. A near linear trend is observed for the products from reactions performed at room temperature. However, T_g's for the samples obtained from reactions performed at 50 °C deviate somewhat from this linear relationship. In the previous section, the formation of ketone functionality was pronounced in the products obtained from reactions at 50 °C. Therefore, the variability in T_g for the samples between 1.5 and 2.5 hydroxyl groups per chain may be explained by the presence of a variable level of other polar functional groups (i.e., ketones). These functional groups would be inert to the acetylation reaction and would therefore remain unaccounted.

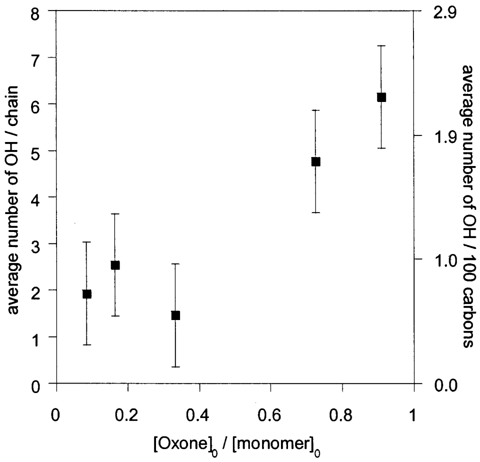

Figure 10. Effect of Oxone concentration on the resultant degree of hydroxylation of 5 kg/mol PEP. Hydroxyl values determined by ^{1}H NMR analysis of the acetylated products.[58]

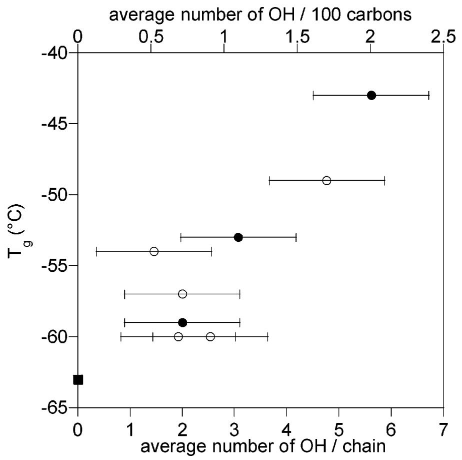

Figure 11. Relationship between the degree of hydroxylation and the glass transition temperature (T_g) of a series of functionalized 5 kg/mol PEP products. Filled circles: the oxyfunctionalized products obtained from reactions performed at room temperature. Open circles: the oxyfunctionalized products obtained from reactions performed at 50 °C. Filled square: unfunctionalized PEP starting material. The degree of hydroxylation of PEP was determined from ^{1}H NMR analysis of acetylated products.[58] T_g of the functionalized products was determined using DSC.

Oxyfunctionalization of a High-Molecular-Weight Model PEP. Successful application of this system to a high-molecular-weight model PEP (50 kg/mol) exemplifies the practical significance of this approach. The optimal conditions for oxyfunctionalization were obtained when the $[\text{Oxone}]_0/[\text{monomer}]_0$ was less than 0.25 and reaction was performed at room temperature. Chloroform was used as the solvent due to the poor solubility of the high-molecular-weight substrate in methylene chloride. The reaction was worked up in the usual way, and the functionalized material was isolated using column chromatography. Characterization of the functionalized product by NMR and IR spectroscopy, in addition to SEC, was consistent with the incorporation of tertiary alcohol and ketone products, similar to those identified in the low-molecular-weight example, without chain degradation (Figure 12).[63] While a small amount of coupling was identified by SEC, it is impressive that

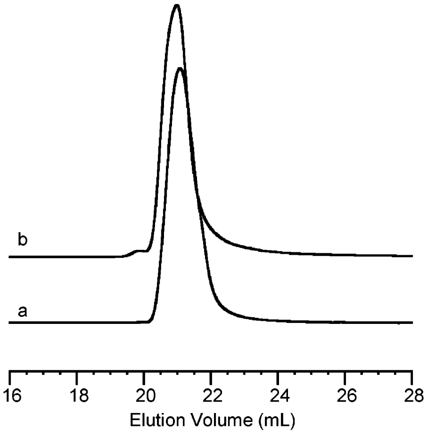

Figure 12. Size exclusion chromatogram [10 mg/mL in THF] for (a) 50 kg/mol PEP [$M_n = 62.0$ kg/mol, PDI = 1.1] and the (b) crude functionalized product [$M_n = 63.7$ kg/mol, PDI = 1.1]. M_n values relative to polystyrene standards.

the narrow PDI of the model material (1.1) was retained through the functionalization. Acetylation of the isolated product mixture further demonstrated the presence of hydroxyl groups in the products, and integration values from the ^{1}H NMR spectrum provided an average of 12 hydroxyl groups per chain (730 repeat units). Thermal analysis of the functionalized material showed a 4 °C increase in the T_g as compared to the high-molecular-weight PEP starting material.

While the oxyfunctionalization of squalane, low-molecular-weight PEP, and high-molecular-weight PEP were selective for the formation of tertiary alcohols, the degree of hydroxylation per 100 backbone carbons generally decreased on going from squalane to the polymeric cases. For sterically hindered manganese porphyrins such as Mn(TDCPP)OAc, regioselectivity in the oxyfunctionalization of low-molecular-weight *n*-alkanes is influenced by the degree of steric bulk around the metal and the length of the *n*-alkane.[43,64] The internal carbons are less accessible in the longer alkanes. Therefore, the observed decrease in the degree of hydroxylation with increasing molecular weight of our substrates could be a result of the increased portion of the alkane substrate that cannot readily access the sterically hindered active site.

Conclusions

The direct oxyfunctionalization of PEP, a model polyolefin, and squalane, a small molecule, structural analogue of PEP, has been demonstrated utilizing a Mn(TDCPP)OAc/imidazole system in the presence of a phase transfer agent and an oxygen donor, such as Oxone. Reasonable yields of functionalized products were obtained and completely characterized. Both the low-molecular-weight and high-molecular-weight functionalized polymers exhibit essentially no degradation by SEC under the reaction conditions. Furthermore, the reaction products suggest that the oxyfunctionalization reaction is selective for the hydroxylation of tertiary carbons. There is also the possibility that secondary alcohols are formed and then rapidly oxidized to ketone products. The versatility of this system to employ a variety of oxygen donors, in conjunction with the possibility of using a supported Mn(TDCPP) catalyst under mild reaction conditions,[65] makes this system an attractive polyolefin functionalization methodology.

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Supporting Information Available: Experimental section and tabular data summarizing the reaction conditions for the reactions performed at 50 °C and different Oxone concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(57) Reactions were also performed in the absence of PEP to prove the new chemical shifts were not due to byproducts formed in the reaction.
(58) The error in average number of OH/chain was estimated by performing three parallel acetylation reactions of the same functionalized product, working up the reactions in the same manner described in the Supporting Information, and integrating the resultant ^{1}H NMR spectra. The standard deviation was calculated from these values and used as an estimate of the error for each sample.
(59) A high-sensitivity spectrum of a functionalized low-molecular-weight PEP was obtained on a 300 MHz instrument equipped with a broadband C{H} probe over 12 h using ca. 10 wt % in $CDCl_3$ and a longer relaxation delay time of 20 s; however, the carbonyl carbons could still not be distinguished.
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