



Oxyfunctionalization of polystyrene by hydrogen peroxide using non-heme iron catalysts

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ABSTRACT

The non-polar nature of polystyrene (PS) permits this material to be used in a variety of industrial and household applications. This same property also limits its interactions with polar materials while its stability renders it slow to undergo biological degradation, making polystyrene an environmental concern. That said, the introduction of polar groups along the backbone could increase its compatibility with polar materials as well as possibly render PS biodegradable. This paper presents an investigation into the oxyfunctionalization of PS utilizing two iron based coordination complexes which catalyze the C–H activation and hydrogen peroxide oxidation of small molecule alkanes to ketones and alcohols. In principle, the chemistry applicable to small molecules should also be applicable to macromolecules, and the iron-based catalysts, [Fe(TPA)(MeCN)₂][OTf]₂ (**I**, TPA = tris(2-pyridylmethyl)amine) and [Fe(BPMEN)][OTf]₂ (**II**, BPMEN = N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)ethane-1,2-diamine) are used to induce oxyfunctionalization of PS by H₂O₂ to give polymeric products containing keto and hydroxyl groups. The polymeric products are characterized by IR and ¹H NMR spectroscopy and by DSC and by GPC measurements.

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1. Introduction

Atactic polystyrene (PS) is a material that is ubiquitous in everyday life, in large part because of its chemical inertness [1–3]. However, the inert nature of PS poses a challenge for disposal of the consumer material since, although recycling programs exist, material which does end up as waste and litter does not readily undergo biodegradation. As well, the non-polar nature of PS which contributes to its inertness also limits its ability to interact with polar substances, limiting potential applications [4]. Thus methods have been developed to introduce polar functionality such as hydroxyl and carbonyl groups into non-polar polymers, either during the polymerization

process itself or afterward as a post polymerization modification. Low levels of functionality are desired to slightly alter the surface properties without changing the bulk mechanical properties [5].

There is an extensive literature describing the copolymerization of simple olefinic monomers with polar monomers [6], but polar monomer incorporation is usually very low and few useful materials have resulted. There is also considerable interest in post polymerization modification processes; flames [7] and plasmas [8] can also be used to incorporate oxygen functionality onto the surface of a solid polymer, but the procedures are generally difficult to control.

Post polymerization modification may also be potentially enabled utilizing catalysts which effect C–H activation of small molecule alkanes, although this avenue has not been widely pursued [5,9]. However in seminal

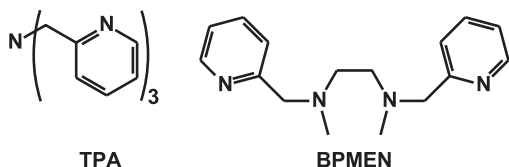
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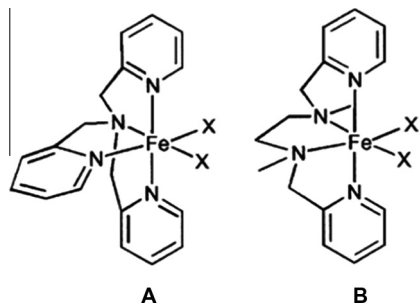
research Hillmyer et al. have successfully hydroxylated the methyl groups of branched polyethylethylene via borylation utilizing a $[\text{Cp}^*\text{RhCl}_2]_2/\text{bis-pinacoldiboron}$ catalyst system followed by treatment with hydrogen peroxide [10], hydroxylation being confirmed in part by a broad OH band in the IR spectrum at 3300 cm^{-1} . Hydroxylation was also suggested by an increased T_g for the materials, possibly suggesting significant hydrogen bonding involving hydroxyl groups. In subsequent work, a manganese porphyrin complex was found to catalyze the introduction of hydroxyl and keto functionalities into squalane and polyethylene-*alt*-propylene using KHSO_5 as oxidant [11]. Functionalization was confirmed by observation of IR peaks for OH and ketone functionalities at 3400 and 1710 cm^{-1} respectively; the T_g of the material also increased.

Transition metal catalyzed hydrocarbon oxyfunctionalization by hydrogen peroxide has a long history [12–15] and oxyfunctionalization of alkanes using metalloporphyrins was first reported 1979 [16]. Since then substituted porphyrins of iron, copper and ruthenium have also been successfully used as oxyfunctionalization catalysts [17,18], showing high selectivity for tertiary or activated C–H bonds, but only moderate chemo- and regio-selectivity [18].

In comparison to heme systems, non-heme catalysts offer greater degrees of variability when constructing ligands and attempting to tune electronic and steric effects [18]. Of these, complexes of tris(2-pyridylmethyl)amine (TPA) [19] and N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)ethane-1,2-diamine (BPMEN) [19c,d,20] and their derivatives are most relevant here.



TPA is a nitrogen-based, tetradentate tripodal ligand which forms cis-octahedral coordination complexes of type **A** ($X = \text{anionic, neutral ligands}$).



Numerous variations on the ligand structure and functionality are known, [19c] and iron(II) complexes such as $[\text{Fe}(\text{TPA})(\text{MeCN})_2][\text{OTf}]_2$ (**I**) [19a,e] have been prepared with various counter ions; all give $[\text{Fe}(\text{TPA})(\text{MeCN})_2]^{2+}$, the species present at the beginning of catalytic reactions in acetonitrile [19a]. BPMEN is a linear, nitrogen based tetradentate ligand which forms analogous tripodal iron complexes, of type **B** ($X = \text{anionic, neutral ligands}$) and $[\text{Fe}(\text{BPMEN})(\text{MeCN})_2][\text{OTf}]_2$ (**II**) [19d] exhibits characteristics and activity similar to that of **I** [19c]. Complexes of TPA and BPMEN have been used in many investigations of the ligand effects on iron-catalyzed oxyfunctionalization of hydrocarbons such as cyclohexane and adamantane [19d,20b–d], standard reactions throughout the literature with the oxidant generally being hydrogen peroxide or *tert*-butyl hydroperoxide. Many reports look at a broader substrate scope [20c,d], but the use of these two catalysts has permitted basic comparisons of the catalytic activities and selectivities of potential catalysts.

Many investigations of general catalytic conditions involve acetonitrile as solvent and hydrogen peroxide as oxidant, with combined alcohol and ketone yields and alcohol:ketone ratios being of interest. In research of great relevance here, Britovsek et al. compared iron complexes of TPA, BPMEN and rigid tridentate ligands [20c] and found that oxyfunctionalization of cyclohexane with tetradentate iron complexes resulted in an approximately ten-fold greater combined yield and a two-fold better alcohol:ketone ratio than with tridentate ligands. Britovsek et al. also investigated the effects of pyridine donors versus amine donors by taking TPA and systematically changing the pyridyl groups for amine groups [19d]. The results showed that both the yield of oxyfunctionalized cyclohexane and the alcohol:ketone ratio decreased significantly for ligands with three or more amine groups, and that BPMEN and TPA gave the highest yields and the highest alcohol:ketone ratio.

As mentioned above, if catalytic oxyfunctionalization is possible with small molecules, then it should in principle also be possible with structurally analogous polymers. Indeed, problems involving poor selectivity and low levels of conversion, which provide major challenges to the use of oxyfunctionalization catalysis for C–H activation of small molecules [21], would not be an issue with polyolefins in which there are very few types of sites to be attacked. In addition, a low degree of oxyfunctionalization of a polyolefin would be desirable if biodegradability without significant alteration of bulk polymer properties is desired.

This paper describes research into the utilization of **I** and **II** to oxyfunctionalize polystyrene with hydrogen peroxide as oxidant. It was anticipated that both hydroxyl and ketone groups could result, as in **C–E**, and therefore infrared spectroscopy was used for initial characterization of all products.

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