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Selective Functionalization of Poly(4-methylstyrene)

Quan Sheng and Harald D. H. Stöver*

Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

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ABSTRACT: The oxidation of poly(4-methylstyrene) with cerium(IV) and cobalt(III) complexes in glacial acetic acid introduces functional groups selectively into the 4-methyl position. The polymer backbone methine groups are almost completely protected from oxidation due to stereo-electronic effects. The reaction proceeds by double electron transfer to give intermediate polymeric benzyl cations. These combine with nucleophiles present in the reaction mixture, such as acetic acid, trichloroacetic acid, or nitrate, to give polymeric benzyl acetates, benzyl trichloroacetates, and benzyl nitrates. These substituents can be exchanged for each other, leading to poly(4-methylstyrenes) containing between 10 and 45% of a single reactive leaving group. The effects of reaction conditions on oxidation yields and selectivity are described.

Introduction

The chemical modification of styrene type polymers to introduce a range of functional groups, as well as their subsequent reactions and uses, is academically and industrially interesting.[1] Significant advances have recently been made in functionalizing poly(4-methylstyrene) and 4-methylstyrene copolymers, especially with regards to avoiding sidereactions on the aromatic ring or the backbone methine. Several approaches involve radical chlorination[2,3] and bromination[4,5] at the 4-methyl site. Recently, superbases have been successfully used to introduce electrophiles selectively into the 4-methyl positions of poly(4-methylstyrene).[6,7] We have reported the cobalt-catalyzed air oxidation of poly(4-methylstyrene), converting up to 95% of the 4-methyl groups to aldehyde and carboxylic acid.[8,9,10] This reaction is related to the industrially important cobalt-catalyzed air oxidations of alkylbenzenes.[11−13]

In all these modifications, the steric hindrance provided by the polymer backbone reduces the reactivity of the backbone methine and shifts the selectivities strongly toward the 4-methyl group. It appears that the transition state leading toward cleavage of a primary benzylic (methyl) carbon−hydrogen bond is more efficiently stabilized by the aromatic ring than the corresponding transition state leading to cleavage of a tertiary benzylic (methine) carbon−hydrogen bond.

In the present paper we report the direct introduction of several functional groups into poly(4-methylstyrene), by stoichiometric oxidation with cerium(IV) diammonium hexanitrate (CAN) and cobalt(III) triacetate, in the absence of molecular oxygen. Cerium(IV) and cobalt(III) metal complexes are known to oxidize methylbenzenes to the corresponding benzyl acetates and related products.[14−18] Applied to poly(4-methylstyrene), we found these reactions to yield novel functional copolymers containing vinylbenzyl acteate and related groups. As in the previously reported air oxidations of poly(4-methylstyrene),[10] the backbone benzylic methine groups are largely protected from oxidation through steric interference of the polymer backbone. The selectivities for methyl oxidation over backbone methine oxidation in poly(4-methylstyrene) are in fact significantly larger than those reported for competitive oxidations of toluene and isopropylbenzene (cumene)[18] or the corresponding intramolecular selectivities in the oxidation of *p*-cymene.[19,20] This fact is particularly pronounced in the case of CAN-mediated oxidations, and reflects the steric effect of the polymeric backbone.

Experimental Section

Materials. 2,2′-Azobis(2-methylpropionitrile) was purchased from Kodak and was used as received. Cerium(IV) ammonium nitrate (CAN) was purchased from Sigma Chemical Co. Cobalt(II) acetate, glacial acetic acid, trichloroacetic acid, benzene, *n*-heptane, methyl ethyl ketone, and diethylene glycol dimethylether were purchased from Aldrich. CAN was dried at 85 °C for 1 h and stored in a desiccator, while the other reagents and solvents were used as received. 4-Methylstyrene was purchased from Deltech Corp. and passed neat through a short alumina column prior to polymerization to remove inhibitors.

Poly(4-methylstyrene) was prepared by free-radical solution polymerization as described earlier.[10] One 30 g batch of poly(4-methylstyrene) having a number average molecular weight (M_n) of 17 800 and a polydispersity index (M_w/M_n) of 1.75 was used for all CAN oxidations reported here. Another 30 g batch having a number average molecular weight (M_n) of 19 800 and a polydispersity index of 1.74 was used for all cobalt(III) acetate oxidations. Cobalt(III) acetate was prepared by ozonation of cobalt(II) acetate in a mixture of glacial acetic acid and acetic anhydride according to the procedure reported by Lande et al.[21]

General Oxidation Procedure using Cerium(IV) Ammonium Nitrate (CAN). A 0.296 g (2.5 mmol) sample of poly(4-methylstyrene) was dissolved in a mixture of 30 mL of glacial acetic acid and 30 mL of benzene (or other organic cosolvent) in a 100 mL three-neck flask fitted with a condenser, a nitrogen inlet, and a thermometer reaching below the liquid level. The temperature was raised to 80 °C, and 1.37 g (2.5 mmol) of CAN was added to the flask at once.[22]

After 1 h of reaction, the mixture was cooled and filtered, and the benzene component was removed on a rotary evaporator. The remaining acetic acid solution, containing oxidized polymer and cerium salts, was precipitated into 200 mL of a mixture of methanol and water (4:1 v/v). After the mixture was allowed to stand overnight, the white polymer precipitate was filtered, washed with a 4:1 methanol/water mixture, and dried under vacuum at 60 °C overnight. Isolated polymer yields were typically around 90%.

Displacement of the Nitrate Groups by Acetoxy Groups. A 0.29 g sample of CAN-oxidized polymer was dissolved in 35 mL of glacial acetic acid and heated to reflux under nitrogen. Aliquots were removed at 3.5 and 10 h and precipitated into methanol/water (4:1 v/v) mixtures as described above. After 10 h of reflux, all benzyl nitrate groups were converted into benzyl acetate groups. There was no evidence of cross-linking during this displacement reaction, and the modifed polymer was isolated quantitatively.

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General Oxidation Procedure using Cobalt(III) Acetate. The procedure used was similar to the one described above for the oxidation with CAN. Poly(4-methylstyrene) (2.5 mmol, 0.296 g) and cobalt(III) acetate (5.0 mmol, 1.18 g), were dissolved in a mixture of trichloroacetic acid (37.5 mmol, 6.13 g), acetic acid (30 mL), and benzene (30 mL). The reaction was carried out under nitrogen at 50 °C for 3 h, during which time the color of the mixture changed from black to dark red. The oxidized polymers were isolated in quantitative yield as described above.

Displacement of Trichloroacetate Groups with Acetate Groups. The oxidized polymer (0.3 g) was dissolved in the mixture of 30 mL of glacial acetic acid and 10 mL of *p*-xylene. Two drops of concentrated sulfuric acid were added, and the mixture was heated to reflux for 12 h under nitrogen. The resulting polymer showed no signs of cross-linking and was isolated quantitatively by precipitation into methanol. ^{1}H-NMR was used to confirm that all trichloroacetate groups had been replaced by acetate groups.

Displacement of Acetate Groups with Trichloroacetate Groups. Another sample of the oxidized polymer (0.3 g) was dissolved in an excess of warm trichloroacetic acid and kept under vacuum (10^{-2} Torr) at 60 °C for 10 min. The resulting polymer was isolated quantitatively by dilution with benzene and precipitation into methanol. ^{1}H-NMR was used to confirm quantitative displacement of the acetate groups by trichloroacetate groups.

Characterization. Polymer molecular weights were measured on a Waters size exclusion chromatograph using three Waters Ultramicrostyragel columns in series. ^{1}H NMR spectra were measured on Bruker AC200 and AC300 NMR instruments, in chloroform-*d* solution, with chemical shifts reported in ppm relative to TMS. Elemental analyses were carried out by Guelph Analytical Laboratories, Guelph, Canada.

Results and Discussion

Oxidations of low molecular weight alkyl aromatics such as methylbenzenes, isopropylbenzene, and isopropyltoluene (*p*-cymene), have long been studied by fundamental and applied organic chemists. Reaction may occur at benzylic positions, on ring carbons, or on nonactivated aliphatic carbons, depending on substrate structure and oxidant used. Polystyrene and, in particular, poly(methylstyrenes), on the other hand, are the polymeric analogs of isopropylbenzene and isopropyltoluene. Oxidations of such polymers are usually discussed under the topic of side reactions or polymer decomposition, reflecting the often undesirable mechanical deterioration that accompanies backbone oxidation and backbone cleavage.[23,24]

This paper describes potentially useful polymer modifications that are based on selective oxidation of the methyl groups in polymeric alkylbenzenes. At the same time, it may contribute to the ongoing discussion of the mechanisms of such oxidation reactions. Accordingly, it may be appropriate to review some of the relevant background.

Cerium(IV) Ammonium Nitrate (CAN) Oxidations of Alkylbenzenes. In 1966, Trahanovsky and Young reported the oxidation of toluene with a 2−8-fold molar excess of CAN in absence of oxygen. When carried out in glacial acetic acid as solvent, this reaction resulted in a 90% yield of benzyl acetate.[16] Dust and Gill report the formation of corresponding benzyl nitrates from the oxidation of toluene with CAN in 3.5 N nitric acid/acetic acid mixtures.[25] Baciocchi et al. extensively studied the CAN oxidation of alkylbenzenes in acetic acid under nitrogen, finding benzyl acetates and benzyl nitrates as major products.[26,27] The mechanism for these reactions, as originally proposed by Wiberg[28] and Andrulis et al.,[15] involves double electron transfer as described in the scheme below:

$$\mathrm{ArCH_3 + Ce(IV) \rightarrow ArCH_3^{+\bullet} + Ce(III)} \tag{1}$$

$$\mathrm{ArCH_3^{+\bullet} \rightarrow ArCH_2^{\bullet} + H^+} \tag{2}$$

$$\mathrm{ArCH_2^{\bullet} + Ce(IV) \rightarrow [ArCH_2{\cdot}Ce(IV)]} \tag{3}$$

$$\mathrm{[ArCH_2{\cdot}Ce(IV)] + AcO^- \rightarrow ArCH_2OAc + Ce(III)} \tag{4a}$$

$$\mathrm{[ArCH_2{\cdot}Ce(IV)] + NO_3^- \rightarrow ArCH_2NO_3 + Ce(III)} \tag{4b}$$

First, the substrate transfers an electron to the Ce(IV) complex to form a benzylic cation radical (eq 1). This loses a proton to form the key benzylic radical (eq 2). In the absence of oxygen, this radical transfers another electron to CAN to form the benzyl cation. This last step may proceed through an intermediate benzyl−Ce(IV) complex (eq 3) that subsequently undergoes both oxidative solvolysis (eq 4a) and oxidative displacement (eq 4b), leading to benzyl acetate and benzyl nitrate, respectively. As some of the nitrate ligands of CAN are likely replaced by acetate,[29] direct ligand transfer from the mixed cerium complex to the forming benzyl cation could also explain the formation of the mixed polymeric benzyl acetate and nitrate.[30]

Large hydrogen isotope effects[31] and model reactions[32] point to deprotonation as the rate-determining step in the CAN oxidation of alkylbenzenes. As well, the products and rates observed in CAN oxidations closely resembled those found in electrochemical oxidations, which are known to proceed through radical cation intermediates.[33−35]

The selectivity in CAN oxidation of unsymmetrical dialkylbenzenes is still the focus of active research. Baciocchi et al. reported an intramolecular isopropyl: methyl reactivity ratio (statistically corrected for number of benzylic hydrogens) of 3.0, from CAN oxidations of *p*-cymene.[36] This agrees with earlier results of the anodic oxidation of *p*-cymene, giving a reactivity of the isopropyl over methyl of 2:1.[37] More recently, Baciocchi et al. studied the effect of α-substituents on the deprotonation of α-substituted *p*-xylene radical cations. They found that while replacing a benzylic hydrogen with a methyl substituent (as in 1-ethyl-4-methylbenzene) increases the (rate-limiting) deprotonation by a factor of 5.2 (for CAN oxidation) or 14.1 (anodic oxidation), replacing it with a *tert*-butyl substituent will slow the deprotonation of the corresponding radical cation by a factor of at least 100, for both CAN and anodic oxidation.[35] It appears that the bulky *tert*-butyl group prevents overlap between the breaking benzylic C−H bond and the aromatic π system.

Combining these results suggests that the relative ratios for CAN oxidation of such alkyl benzenes follows the order of (alkyl=) methyl:ethyl:isopropyl:*tert*-butylmethyl (neopentyl) = 1:5.2:3:0.01. On this scale, the backbone of poly(4-methylstyrene) would fall somewhere to the right of the isopropyl group, and it was hence of substantial interest to us to study the actual ratio of methyl:backbone oxidation of poly(4-methylstyrene), using CAN.

Cobalt(III) Acetate Oxidations of Alkylbenzenes. Cobalt(III) acetate mediated oxidations have also remained in the focus of active research for many years. In 1969, Sakota et al. reported a study of the oxidation of toluene and other alkylbenzenes by cobalt(III) acetate in acetic acid under argon.[17] The relative side chain reactivities at 40 °C (per benzylic hydrogen) were 1:1.2:0.2 for toluene:ethylbenzene:cumene. In the same year, Heiba et al. reported relative overall rates of cobalt(III) acetate oxidation of the same compounds of 1:1.3:0.3[18] and Onopchenko et al. in 1972 reported a 1:0.1 ratio of cobalt(III) oxidation rates for the methyl and isopropyl groups of *p*-cymene.[20] As well, their Co(III) acetate oxidation of *p*-cymene gave predominantly *p*-isopropylbenzoic acid (oxygen atmosphere) and *p*-isopropylbenzyl acetate (nitrogen atmosphere).[19]

These regio selectivities differ from those seen in the case of CAN and are in fact opposite to those observed in radical reactions[38] and oxidations.[39] Onopchenko et al. suggested that these low reactivities of the isopropyl groups in Co(III) oxidations result from insufficient overlap of the C−H bond with the aromatic π-system during the transition state.[19] An oxidation mechanism similar to the one described above for CAN was postulated. It would involve a reversible and rate-determining electron transfer from the aromatic substrate to Co(III), followed by proton loss to give the benzylic radical.[17,40,41] In absence of oxygen, this radical would transfer another electron to form the benzyl cation, which would finally capture acetic acid to yield the corresponding benzyl acetate.

Subsequent research confirmed the presence of a radical cation intermediate in the case of CAN, but not in the case of Co(III).[33,42−44] Baciocchi and Ruzziconi[32] compared the CAN and Co(III) oxidations of 1,2-diphenylethane and 1,1,2,2-tetramethyl-1,2-diphenylethane, finding evidence for a direct hydrogen abstraction by the Co(III) complex, leading to the benzylic radical (eq 5).

$$\mathrm{ArCH_3 + Co(III) \rightarrow ArCH_2^{\bullet} + H^+ + Co(II)} \quad (5)$$

In summary, oxidation of alkylbenzenes under anaerobic conditions by both Ce(IV) and Co(III) leads to intermediate alkylbenzyl radicals, arguably through an initial radical cation. The Co(III) oxidations show a strong selectivity for the methyl group (compared to the isopropyl group), due to more efficient aromatic stabilization during the transition state of electron or hydrogen atom loss from benzylic methyl groups. The CAN oxidations show a small selectivity for isopropyl over methyl substituents, though there are indications that larger substituents would shift this selectivity further toward the methyl group as well.

Poly(4-methylstyrene) appears to be a very interesting substrate for both CAN and Co(III) oxidations. First, the polymer backbone mimics a very large methine substituent, and should shift the selectivity of oxidation firmly toward the methyl group. Second, the resulting functional polymers may be useful for a number of potential applications.[8,45]

CAN Oxidation of Poly(4-methylstyrene). We found cerium ammonium nitrate (CAN) to cleanly oxidize poly(4-methylstyrene) dissolved in a glacial acetic acid/benzene mixture. The initial product of the reaction is a polymer carrying both acetoxymethyl and nitrate groups. The proposed mechanism for this reaction, based on the above discussion, is shown in Figure 1. Initial electron transfer leads to a cation radical (**1**) that loses a proton to give an intermediate benzyl radical (**2**). In the absence of oxygen, this radical transfers a second electron to another CAN to form a polymeric benzyl cation (**3**). Reaction with nitrate or acetate leads to the multifunctional polymer (**4**). We found that heating with glacial acetic acid quantitatively replaces the nitrate groups with acetate groups to give the final, monofunctional polymer (**5**).

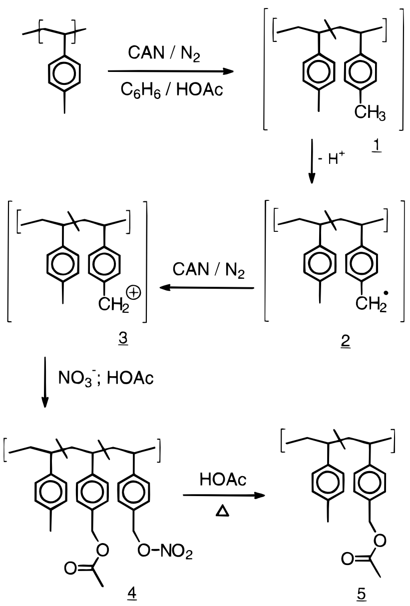

Figure 1. Mechanism of CAN oxidation of poly(4-methylstyrene) in acetic acid/benzene.

Representative ^{1}H NMR spectra of poly(4-methylstyrene) and of the oxidized polymer are shown in parts A and B of Figure 2. The oxidized polymer shows two benzylic methylene signals. The singlet at 5.00 ppm corresponds to the benzyl acetate methylenes, and the singlet at 5.29 ppm corresponds to the benzyl nitrate methylenes. The nitrate/acetate ratio was found to be constant at 1.7 ± 0.15, for all reactions. Furthermore, this ratio did not drift during individual reactions, indicating that acetolysis of the benzyl nitrate is not noticeable under our oxidation conditions, though it had been observed in the corresponding CAN oxidations of tri- and tetramethylbenzenes.[26] Apparently, (polymeric) dialkylbenzenes are not sufficiently activated to exchange substituents under the oxidation conditions. Refluxing the initial multifunctional polymer (**4**) in glacial acetic acid for 10 h did however replace the nitrate groups with acetate groups, without any evidence of cross-linking. The corresponding ^{1}H NMR spectrum (Figure 2c) shows complete replacement of nitrate by acetate groups. Below we report on the effects of several reaction parameters.

Solvent Effects. The need to react polar CAN with the nonpolar polymer prompted us to use mixed solvents consisting of equal volume fractions of glacial acetic acid (a polar solvent commonly used in such oxidations) and an organic cosolvent (benzene, *n*-heptane, methyl ethyl ketone (MEK), and diethylene glycol dimethylether). Reactions were carried out at low polymer concentrations in order to avoid cross-linking through radical coupling or electrophilic aromatic substitution. The results of cosolvent composition are summarized in Table 1.[46]

The four cosolvents are all good solvents for poly(4-methylstyrene), and cover a wide range of polarity. The benzene/acetic acid and the *n*-heptane/acetic acid mixtures are the least polar mixtures systems studied but gave the highest yield. Diethylene glycol dimethylether resulted in a low degree of oxidation, while no oxidation of the polymer was observed in the methyl ethyl ketone system. This is surprising as methyl ethyl ketone may be used as cosolvent in the oxidation of poly(4-methylstyrene) using cobalt/bromide and air. It is possible that

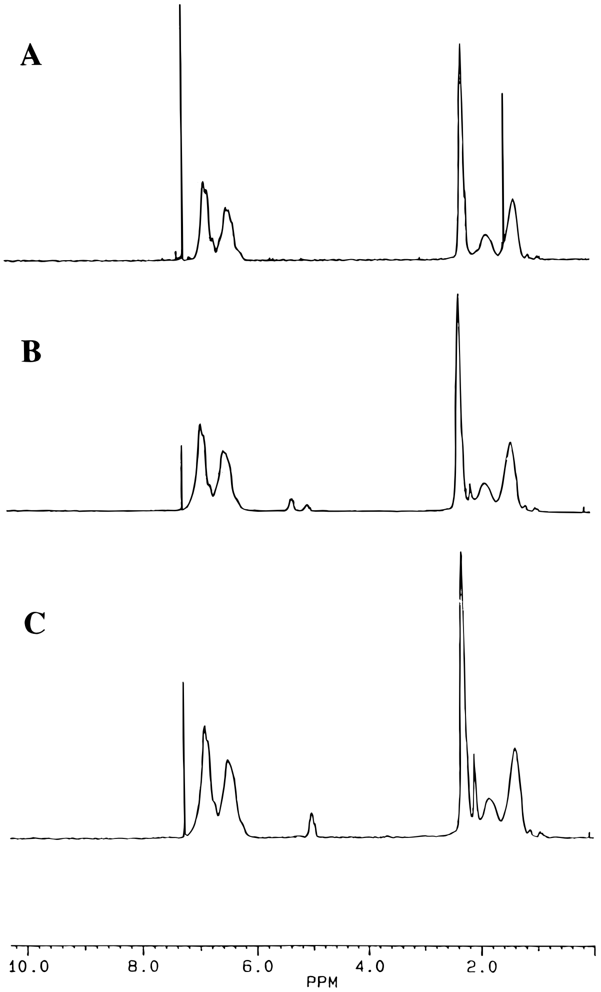

Figure 2. ^1H NMR: (A) poly(4-methylstyrene); (B) poly(4-methylstyrene) after oxidation with CAN (P4MS 2.5 mmol; CAN 2.5 mmol; HOAc 30 mL; benzene 30 mL; 1 h; N_2; 60 °C); (C) polymer B after heating with glacial acetic acid. The sharp peaks at 7.24 and 1.8 ppm are due to solvent impurities ($CHCl_3$, H_2O).

Table 1. Effect of Cosolvents on Oxidation[a]

cosolvent	% acetate	% nitrate	% tot. oxidn	M_n	M_w/M_n
benzene	12.3	21.7	34	8100	1.82
n-heptane	9.4	15.1	24.5	9500	1.94
diethylene glycol dimethyl ether	1.2	5.7	6.9	14500	2.24
MEK				18200	1.85

[a] Reaction conditions: P4MS, 2.5 mmol; CAN, 2.5 mmol; HOAc, 30 mL; cosolvent, 30 mL; 80 °C; 1 h; N_2.

these two polar solvents were oxidized faster than the polymer under our conditions, although no attempt was made to analyze solvent oxidation products.

Effect of the Molar Ratio of CAN/P4MS. The oxidation of alkyl aromatic compounds to benzyl acetates by CAN in absence of oxygen requires two moles of CAN per mol of hydrocarbon, according to the mechanism shown in Figure 1. Table 2 shows that the oxidation yield increased with increasing molar ratio of CAN/P4MS, to a point. In the second entry, 34% of the methyl groups on the polymer have been oxidized, corresponding to a 68% yield based on CAN.

Table 2. Effect of CAN/P4MS Ratio on Oxidation[a]

P4MS (mmol)	CAN (mmol)	% acetate	% nitrate	% tot. oxidn	M_n[b]
2.5	5.0	14.2	23.9	38.1	8400
2.5	2.5	12.3	21.7	34	8100
2.5	1.25	6.6	10.2	16.8	11800
2.5	1.0	5.3	9.0	14.3	13200

[a] Reaction conditions: P4MS, 2.5 mmol; HOAc, 30 mL; benzene, 30 mL; 80 °C; 1 h; N_2. [b] M_w/M_n values are 1.82 ± 0.03.

Table 3. Effects of Reaction Time[a]

reaction time (h)	% acetate	% nitrate	% tot. oxidn	M_n[b]
3.0	12.9	23.8	36.7	7400
2.0	14.6	23.9	38.5	7600
1.5	13.6	25.8	39.4	7600
1.0	12.3	21.7	34.0	8100
0.5	10.1	14.1	24.2	10600

[a] Reaction conditions: P4MS, 2.5 mmol; CAN, 2.5 mmol; HOAc, 30 mL; benzene, 30 mL; 80 °C; N_2. [b] M_w/M_n values are 1.80 ± 0.05.

Table 4. Effect of Reaction Temperature[a]

reaction temp (°C)	% acetate	% nitrate	% tot. oxidn	M_n[b]
80	12.3	21.7	34.0	8100
70	9.3	14.3	23.6	11300
60	5.3	7.4	12.7	14900
50	1.5	2.5	4.0	17000
30				17300

[a] Reaction conditions: P4MS, 2.5 mmol; CAN, 2.5 mmol; HOAc, 30 mL; benzene, 30 mL; 1 h; N_2. [b] M_w/M_n values are 1.80 ± 0.04.

Table 5. Effect of Sodium Acetate Addition[a]

CAN (mmol)	NaOAc (mmol)	P4MS (mmol)	% acetate	% nitrate	% tot. oxidn	M_n[b]
5		2.5	14.2	23.9	38.1	8400
5	5	2.5	16.9	28.3	45.2	6500

[a] Reaction conditions: top, HOAc and benzene, 30 mL each; bottom, HOAc and benzene, 60 mL each. [b] M_w/M_n values are 1.72 ± 0.07.

Effect of Reaction Time. The effect of reaction time on oxidation is shown in Table 3. The oxidation yield increases with reaction time up to approximately 1.5 h, to give a 39.4% degree of oxidation.[47] This corresponds to a 78.8% chemical yield based on CAN. Visually, some undissolved CAN turned from orange to white around this time.

Reaction Temperature. Table 4 shows the effect of reaction temperature on oxidation of poly(4-methylstyrene) in benzene/acetic acid mixtures. No oxidation was observed at 30 °C, above which the degree of oxidation increased with temperature, presumably in part due to the higher solubility of the CAN. Most subsequent reactions were therefore carried out at 80 °C.

Effect of Presence of Sodium Acetate. The oxidized polymers resulting from our process are thought to contain acetate and nitrate groups randomly distributed along the backbone. The ratio of nitrate to acetate group observed in all reactions is 1.7 (± 0.15) under our conditions, with no significant variation. This product ratio likely reflects the relative rates of acetoxy and nitrate anion transfer from the cerium(IV) complex to the benzyl cation.[27] Increasing the acetic acid/CAN ratio (Table 2) had no effect of the resulting acetate/nitrate ratio, presumably because the limiting ligand shell distribution of acetate and nitrate anions does not vary over the range covered. Similarly, addition of moderate amounts of sodium acetate did not shift the acetate/nitrate ratio noticeably (Table 5). This matches Baciocchi's observation that addition of ammonium nitrate did not affect the acetate/nitrate ratio in the CAN oxidation of tri- and tetramethylbenzene.[26]

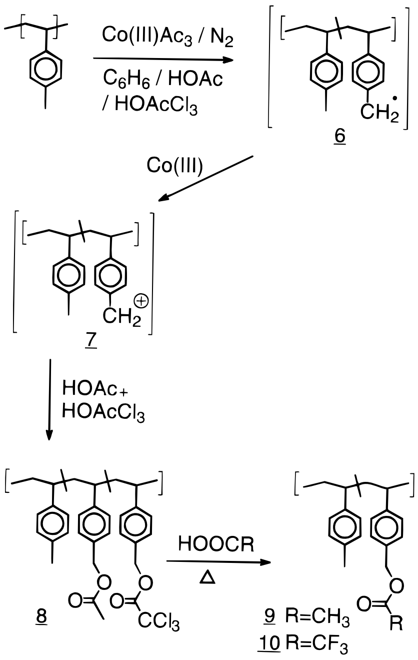

Figure 3. Mechanism of cobalt(III) acetate oxidation of poly(4-methylstyrene).

The polymer described in the second entry in Table 5 was submitted for elemental analysis and the results compared to the NMR data. According to the ^{1}H NMR data (shown in Table 5), the expected percentage compositions for carbon, hydrogen, nitrogen and oxyen were 77.24, 6.93, 2.73, and 13.10. Elemental analysis returned the percentage amounts of 76.61, 7.08, 2.81, and (by difference) 13.50, respectively, which are in close agreement with the NMR data.

CAN Oxidation of poly(4-methylstyrene) is accompanied by significant polymer backbone cleavage, due to competing oxidation of the backbone methine groups. This is discussed below as part of a comparison of the selectivities of CAN and Co(III) oxidations. The polymer segments after cleavage still contain on average about 70 or more monomer units, such that the end groups do not show in the NMR spectra.

Cobalt(III) Acetate Oxidations of Poly(4-methylstyrene). Cobalt(III) acetate was prepared by ozonation of cobalt(II) acetate following the procedure by Lande et al.[21] The oxidations of poly(4-methylstyrene) with cobalt(III) acetate were carried out in benzene/glacial acetic acid or cyclohexane/glacial acetic acid cosolvent mixtures, containing trichloroacetic acid as activator.

The reaction mechanism is shown in Figure 3. Similar to the case of CAN discussed above, the Co(III) oxidation proceeds first to the benzylic radical and then further to the intermediate benzylic cation, which is finally captured by the most reactive nucleophiles present. In our system, trichloroacetic acid is required to activate the Co(III) oxidant. Hence, both acetic acid and trichloroacetic acid (or their corresponding anions) compete for the benzyl cations, resulting in polymers carrying both functional groups as shown below. Again, posttreatment with either of the neat acids produces the corresponding single-functional polymer. As in the case of CAN oxidation, below we describe the effects of several reaction parameters.

Table 6. Effect of Trichloroacetic Acid on Oxidation[a]

trichloroacetic acid (mmol)	% acetoxymethyl	% (trichloroacetoxy)methyl	% tot.	M_n	M_w/M_n
37.5	19	6.0	25	18 500	1.89
25.0	7.4	1.0	8.4	20 800	1.87
12.5	3.5		3.5	18 200	2.22
0.0				19 900	1.80

[a] Reaction conditions: P4MS, 2.5 mmol; $Co(OAc)_3$, 5.0 mmol; HOAc, 30 mL; benzene, 30 mL; 50 °C; 3 h; N_2.

Table 7. Effect of Molar Ratio of Cobaltic Acetate on Oxidation[a]

P4MS (mmol)	Co(III) (mmol)	% acetoxymethyl	% (trichloroacetoxy)methyl	% tot.	M_n[b]
2.5	5.0	19	6.0	25	18 500
2.5	2.5	9.8	2.5	12.3	17 400
2.5	1.25	2.7	<0.3	<3.0	19 000
2.5	1.00	2.3	<0.3	<2.6	18 000
2.5	0.5	<0.5		<0.5	18 900

[a] Reaction conditions: P4MS, 2.5 mmol; CCl_3COOH, 37.5 mmol; HOAc, 30 mL; benzene, 30 mL; 50 °C; 3 h; N_2. [b] M_w/M_n values are 1.89 ± 0.07.

Table 8. Effect of Reaction Time on Oxidation[a]

reaction time (h)	% acetoxymethyl	% (trichloroacetoxy)methyl	% tot.	M_n[b]
3.0	19	6.0	25	18 500
2.5	15.6	4.8	20.4	18 600
2.0	14.8	4.0	18.8	18 500
1.0	12.6	3.4	16.0	19 000
0.5	10.7	3.4	14.1	18 700

[a] Reaction conditions: P4MS, 2.5 mmol; $Co(OAc)_3$, 5.0 mmol; CCl_3COOH, 37.5 mmol; HOAc, 30 mL; benzene, 30 mL; 50 °C; N_2. [b] M_w/M_n values are 1.91 ± 0.1.

Trichloroacetic Acid Mole Fraction. The effect of trichloroacetic acid on the oxidation of poly(4-methylstyrene) was remarkable (Table 6). No reaction took place in absence of trichloroacetic acid. Trichloroacetic acid is a strong acid known to facilitate oxidations of alkylarenes by cobaltic acetate in acetic acid, plausibly by dissociating less reactive Co(III) dimers thought to be dominant in concentrated systems.[48]

With increasing amounts of trichloroacetic acid, the oxidation yield increased, with a maximum degree of oxidation of 25% obtained for a 15:1 molar excess of trichloroacetic acid (37.5 mmol) over P4MS (2.5 mmol). Accordingly, subsequent reactions were usually carried out using 37.5 mmol of trichloroacetic acid. The ratio of (trichloroacetoxy)methyl to acetoxymethyl groups on the final polymers also increases with trichloroacetic acid fraction, suggesting the participation of the trichloroacetate anion in the cobalt(III) complex.

Cobalt(III) Acetate/P4MS Ratio. In addition to trichloroacetic acid, the reaction required a molar ratio of cobalt(III) acetate/P4MS of at least 1, below which no oxidation was observed (Table 7). At higher oxidant/polymer ratios the degree of oxidation increased to a maximum of 25%.[49]

Table 8 shows that the ratio of trichloroacetate to acetate does not change during the reaction, indicating that no solvolysis occurs under the (relatively mild) oxidation conditions.

The effects of cosolvents on oxidation of poly(4-methylstyrene) are similar to those seen in the CAN system: benzene and *n*-heptane as cosolvents result in substantial conversion, while no reaction was observed when using methyl ethyl ketone or diethylene glycol dimethylether as cosolvents. Additional experiments

Table 9. Effect of Acetic Acid on Oxidation[a]

n-heptane (mL)	C_6H_6 (mL)	HOAc (mL)	% acetoxy-methyl	% (trichloro-acetoxy)-methyl	% tot.	M_n	M_w/M_n
	30	30	19	6	25	18500	1.89
	30	2.5[b]	11	11.2	22.2	8000	2.3
	30	0.0	5.4	16.2	21.6	8100	1.62
30		30	15.8	4.5	20.3	18900	1.79
30		0.0		13.3	13.3	7900	8.6

[a] Reaction conditions: P4MS, 2.5 mmol; $Co(OAc)_3$, 5.0 mmol; CCl_3COOH, 37.5 mmol; 50 °C; 3 h (except last entry: 2 h); N_2. [b] 37.5 mmol.

indicated that the reaction temperature has little effect on oxidation yields, in fact oxidations could be efficiently carried out at 30 °C. At temperatures above 50 °C the reaction yield does not change, but the selectivity for the methyl group decreases and backbone cleavage becomes comparable to that seen in CAN oxidations above.

Acetic Acid Volume Fraction. Table 9 summarizes our efforts to increase the trichloroacetate/acetate ratio during the reaction.

Typically, reactions were carried out in equal volumes of benzene (or heptane) and acetic acid. When the acetic acid fraction was reduced to a 1:1 molar ratio relative to trichloroacetic acid, the resulting oxidized polymer contained a 1:1 molar ratio of acetoxy to trichloroacetate units, but with significantly reduced molecular weight (enhanced backbone cleavage). In the complete absence of acetic acid, trichloroacetate groups (16.2%) were predominantly introduced into the polymer side chains, with only a few percent of acetate groups (5.4%), derived from the cobalt(III) acetate. Again, backbone cleavage was significant.

At low acetic acid concentrations, a small peak appears at 3.7−3.8 ppm in the ^1H NMR spectra. It was assigned to the diphenylmethylene units formed by the electrophilic aromatic substitution reaction between intermediate polymeric benzyl cations and the cosolvent benzene. In principle, this side reaction should increase the aromatic/aliphatic proton ratio in the ^1H NMR. This was not observed, presumably due to the small amount (less than 5% of initial 4-methylstyrene) of diphenylmethane units formed.

Using other solvents such as *n*-heptane gave similar results. In the presence of acetic acid, acetate groups were introduced predominantly, with little backbone cleavage. In the absence of acetic acid, trichloroacetate groups were introduced predominantly, with significant backbone cleavage. No ^1H NMR signals were found at 3.7−3.8 ppm in these oxidations, as heptane is inert toward benzyl cations.

Figure 4 shows the ^1H NMR spectrum of a cobalt(III) acetate oxidized poly(4-methylstyrene). The two benzylic methylene signals correspond to trichloroacetate groups (5.25 ppm) and acetate groups (5.00 ppm), respectively. In addition, the sharp peak at 2.05 ppm corresponds to the methyl group of the benzylic acetate. If a functional poly(4-methylstyrene), containing only trichloroacetate as functional groups, is desired, the residual acetate groups can be quantitatively displaced by heating the polymer in presence of trichloroacetic acid under vacuum at 60 °C for 10 min. The resulting polymer presents only one (trichloroacetate) benzylic proton signal at 5.25 ppm (not shown). Conversely, if a polymer containing only acetate groups is desired, the residual trichloroacetate groups can be replaced by refluxing the oxidized polymer[50] in a 3:1 mixture of acetic acid and *p*-xylene in presence of two drops of concentrated sulfuric acid for 12 h under nitrogen. The resulting acetoxymethylated polymer is obtained in quantitative yield, with no evidence of cross-linking.

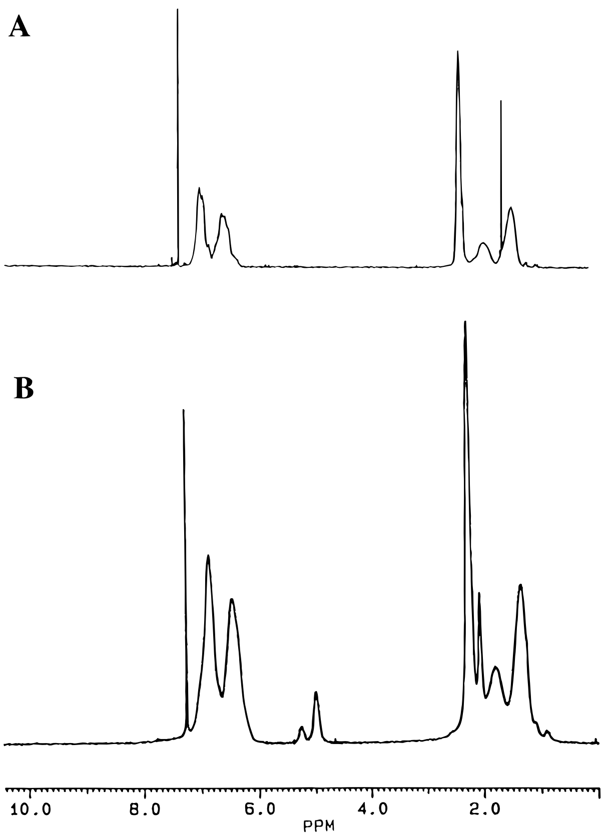

Figure 4. ^1H NMR spectrum of poly(4-methylstyrene) oxidized with cobalt(III) acetate (P4MS 2.5 mmol; $Co(OAc)_3$ 5.0 mmol; trichloroacetic acid 37.5 mmol; HOAc 30 mL; benzene 30 mL; 50 °C; 3 h; N_2). The sharp peaks at 7.24 and 1.8 ppm are due to solvent ($CHCl_3$, H_2O).

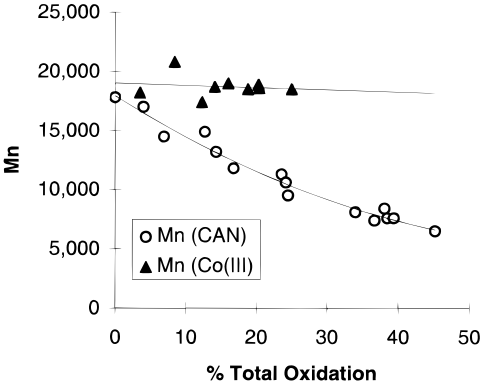

Figure 5. Comparison of M_n/% Total Oxidation for CAN (at 80 °C) and Co(III) (at 50 °C).

In Co(III) oxidations carried out at 50 °C in presence of acetic acid, no molecular weight change is observed, in contrast with the CAN oxidations carried out at 80 °C described above. Figure 5 shows the plot of molecular weight vs total oxidation percentage for all CAN and Ce(III) reactions reported in this paper (with the exception of entries 2, 3, and 5 from Table 9). Much of the difference in selectivity (slope) is likely due to the different reaction temperatures: the Co(III) reactions were carried out at 50 °C, while the CAN reactions (which did not proceed at all below 60 °C) were carried out at 80 °C.

The lines in Figure 5 were fitted using a second-order polynomial, which was considered to best reflect the second order relation between backbone cleavage events and residual chain length. The methyl/backbone methine selectivity for the CAN oxidations at 80°C can be estimated from Figure 5 to be approximately 40:1 in favor of methyl oxidation. It would appear that the extended polymer backbone quite efficiently suppresses backbone (methine) oxidation, likely through steric hindrance to aromatic stabilization of forming benzylic radicals or radical cations. This effect becomes even larger in the case of Co(III) oxidations at 50 °C. Here, no molecular weight reduction is observed, indicating an almost complete suppression of methine oxidation.[51]

Conclusion

It is clear that the polymer backbone provides substantial steric protection against backbone oxidation, comparable to that provided by a *tert*-butyl substituent. The increased selectivity in case of cobalt(III) compared to CAN seems to corresponds to the results described above for small substrates such as *p*-cymene. However, the effect of reaction temperature needs to be examined further.

The cerium(IV) and cobalt(III) oxidations of poly(4-methylstyrene) offer new, and almost direct, access to vinylbenzyl acetate-type copolymers. The procedures are facile and lead to interesting functional polymers in one or two steps. In particular, the cobalt(III) oxidation in presence of acetic acid is very selective and shows no competing backbone cleavage. The degree of functionalization can be controlled through the reaction parameters. The resulting functional polymers may be useful as acid-curable resins or may provide access to other functionalized poly(4-methylstyrene). We will continue to study similar oxidations of copolymers and small model compounds.

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(46) In cobalt-catalyzed air oxidations reported earlier [Shaver et al.,[2]] the rate of oxidation increased approximately linearly with acetic acid volume fraction. No attempt was made to study the effects of the cosolvent ratio in this work.

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(49) This corresponds to a yield based on cobalt(III) acetate of only 25%, well below the 70−80% yield based on CAN described above. However, it is possible that longer reaction times (Table 8) might increase conversion and yield.

(50) Third entry, Table 8.

(51) It is unlikely that backbone cleavage and polymer−polymer coupling (through radical combination or Friedel−Crafts alkylation) just balance to give constant MW, as the molecular weights were not sensitive to Co(III) concentration or to reaction time. At least the radical combination route would be sensitive to such changes of conditions.

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