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Notes

Cobalt-Catalyzed Oxidation of Poly(4-methylstyrene)

LORENZO P. FERRARI AND HARALD D. H. STÖVER*

Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4M1, Canada

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The oxidation of alkylbenzenes to carboxylic acids by cobalt salts and molecular oxygen in acetic acid solution has been widely studied. Indeed, terephthalic acid is produced industrially on a scale of about 8.3 million tons/year by cobalt-catalyzed oxidation of *p*-xylene.[1,2] In the case of asymmetrically substituted aromatic compounds, this reaction can exhibit unusual selectivities. The cobalt-catalyzed oxidation of *p*-cymene for example has been shown to yield 90% *p*-isopropylbenzoic acid and 10% *p*-acetylbenzoic acid (Figure 1).[3] Voronenkov and Kokorev have attempted to rationalize this selectivity using calculated values for the stabilities of the intermediate primary and tertiary radical cations of *p*-cymene.[4]

Poly(4-methylstyrene) can be viewed as a high molecular weight analogue of *p*-cymene, and its selective oxidation could provide a new access to functional polymers. We report here the facile cobalt-catalyzed oxidation of poly(4-methylstyrene) to the terpolymer containing 4-vinylbenzaldehyde and 4-vinylbenzoic acid units besides unreacted 4-methylstyrene units. In addition, we describe the subsequent reduction of the terpolymer to the polyalcohols, followed by acetylation with acetic anhydride (Figure 2).

The reaction mechanism appears to involve initial hydrogen abstraction from the primary benzylic positions and has been described in some detail for *p*-xylene and *p*-cymene in acetic acid solution.[5-8] The presence of bromide anion was reported to increase the oxidation rate by a factor of between 10 and 100, through formation of a very reactive, blue cobalt(III) acetate bromide (CAB) complex.[5]

The starting polymer, poly(4-methylstyrene) (M_n, 10 700; M_w/M_n, 1.44), was prepared by a standard solution polymerization of 4-methylstyrene in toluene using AIBN as the radical initiator. As poly(4-methylstyrene) is not soluble in acetic acid, we used a mixture of dimethoxyethane with acetic acid in the ratio of 3.5:1 as solvent in all oxidation reactions. A typical reaction mixture contained 1.0 g of poly(4-methylstyrene) in 55 mL of solvent mixture together with 0.2 g of cobalt(II) acetate tetrahydrate and 0.3 g of sodium bromide. The mixture was heated to 60 °C and oxygen bubbled through at a rate of about 0.5 L/min for 24 h. Precipitation of the reaction mixture into methanol yielded 38% of a lightly oxidized, nonpolar polymer 1. The filtrate solution was reduced in vacuum and precipitated into distilled water to give a polar, highly oxidized polymer fraction in the form of a light yellow solid, in 60% yield (2).

Alternatively, the reaction mixture was precipitated directly into water, following a reaction time of only 3 h. This procedure gave a quantitative yield of lightly oxidized polymer 3 and avoided the fractionation experienced above.

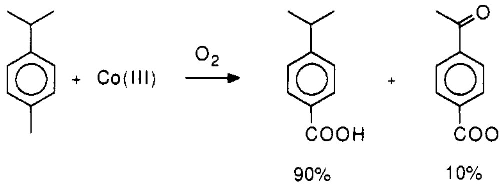

Figure 1. Cobalt-catalyzed oxidation of *p*-cymene.

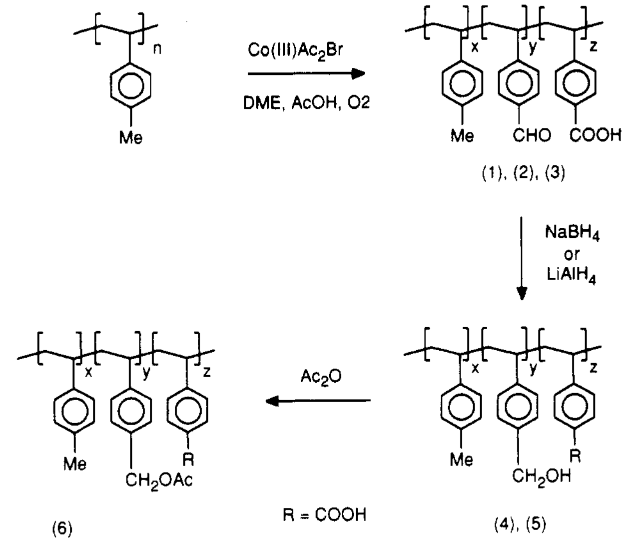

Figure 2. Oxidation and functionalization of poly(4-methylstyrene). Cobalt-catalyzed oxidation of poly(4-methylstyrene), followed by reduction and acetylation. R indicates residual carboxylic acid.

Table I
Summary of Oxidation Reactions

polymer	reaction time, h	aldehyde, %	carboxylic acid, %	yield, %	M_n (M_w/M_n)
poly(4-methyl styrene)				85	10 700 (1.44)
1	24[a]	14	14	38	11 800 (1.46)
2	24[b]	11	50	60	1 100 (1.78)
3	3[b]	7	5	95	7 800 (1.63)

[a] Precipitated into methanol. [b] Precipitated into distilled water.

The oxidized polymers differ in their total degree of oxidation, in their ratio of aldehyde to carboxylic acid groups, and in their molecular weight (see Table I). Their ^1H NMR spectra are shown in Figure 3, together with the spectrum for poly(4-methylstyrene) (Figure 3A). The proton spectrum of the lightly oxidized polymer fraction 1 reveals an aldehyde signal at 9.85 ppm (Figure 3B). As well, the aromatic region shows two signals corresponding to the aromatic protons in the ortho position to the aldehydes (7.5 ppm) and in the ortho position to the carboxylic acid (7.8 ppm), respectively. Gel permeation chromatography (GPC) of this fraction gives a molecular weight (M_n) of 11 800, almost unchanged from that of the starting polymer.

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Table II
Reductions and Acetylation

product	from	reagent	yield, %	hydroxymethyl, %	carboxylic acid, %	acetoxymethyl, %	M_n (M_w/M_n)
4	3	$LiAlH_4$	95	10	2		insoluble in THF
5	1	$NaBH_4$	95	14	14		insoluble in THF
6	5	$(Ac)_2O$	95		14	14	14 200 (1.45)

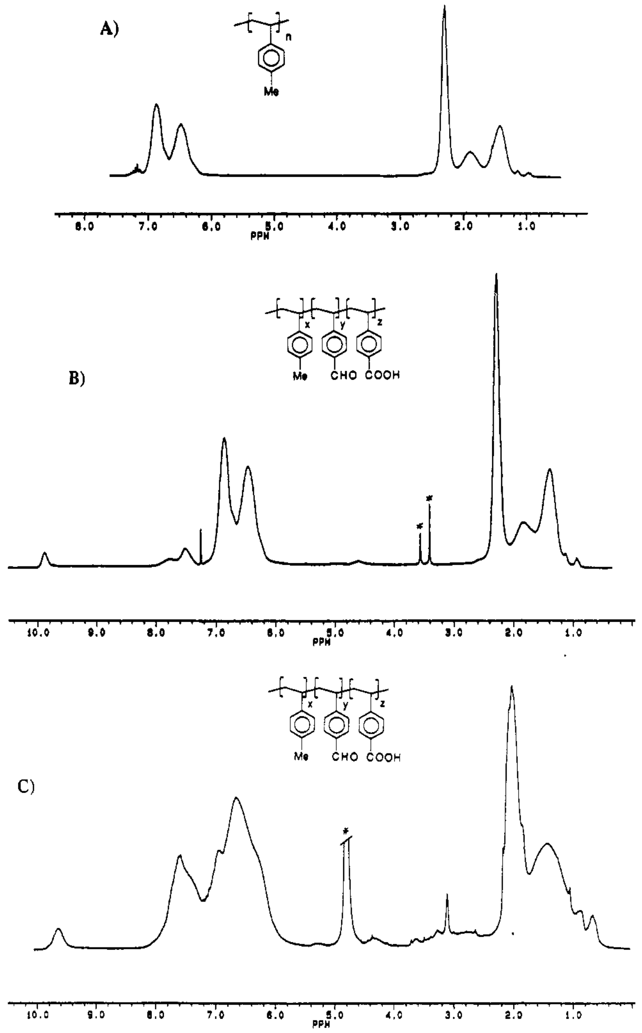

Figure 3. ^1H NMR spectra: (A) poly(4-methylstyrene); (B) lightly oxidized polymer fraction 1 in deuteriochloroform; (C) highly oxidized polymer fraction 2 in methanol-d_4. Solvent signals are marked with a asterisk.

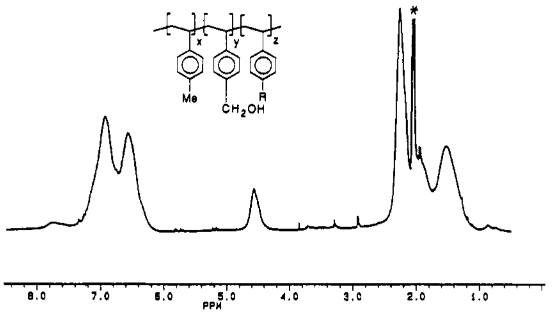

Figure 4. ^1H NMR spectrum of polyalcohol 4. R stands for some residual carboxylic acid. The asterisk marks the signal due to residual acetic acid.

The ^1H NMR spectrum of the highly oxidized fraction 2 is shown in Figure 3C. In addition to the aldehyde peak at 9.6 ppm there are now two strong signals at 7.6 and 7.0 ppm, corresponding to the aromatic protons in positions ortho and meta to the carboxylic acid. The carboxylic acid group appears at 170 ppm in the ^{13}C NMR spectrum.

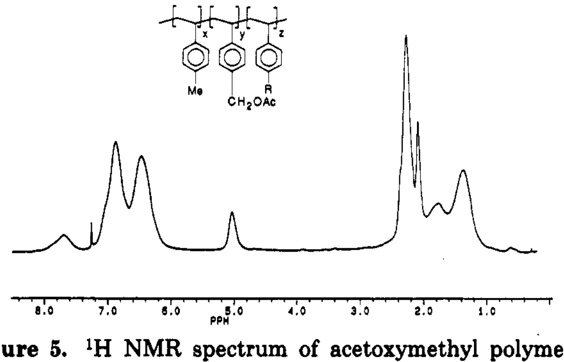

Figure 5. ^1H NMR spectrum of acetoxymethyl polymer 6. Polymer 6 after reduction of 1 with sodium borohydride and acetylation with acetic anhydride. R stands for carboxylic acid.

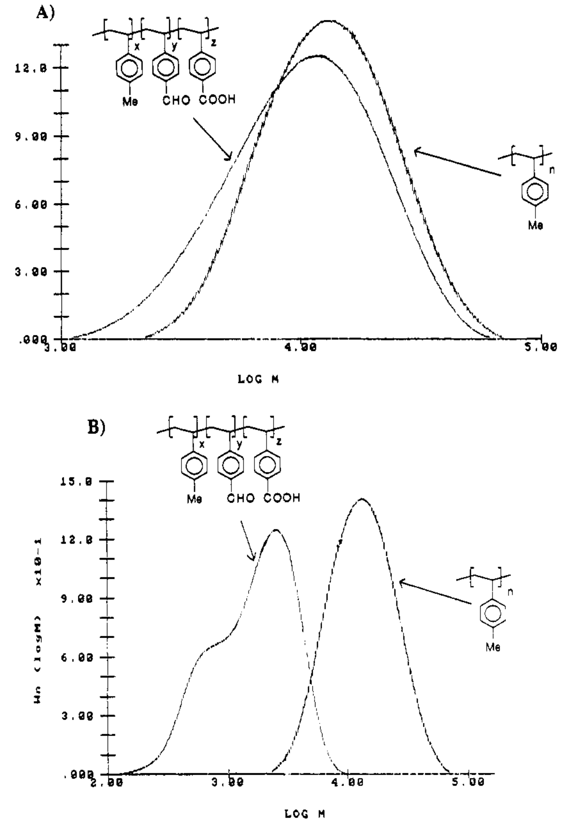

Figure 6. GPC of oxidized polymers. Overlay of GPC of poly(4-methylstyrene) with those of (A) the lightly oxidized polymer fraction 3 and (B) the highly oxidized polymer fraction 2. GPC were measured on a Waters system with three Ultrastyragel linear columns and a refractive index detector, calibrated with monodisperse polystyrene standards, and having a flow rate of 1 mL of tetrahydrofuran/min.

This polymer fraction shows substantial backbone cleavage by GPC (M_n, 1100; MWD, 1.78), indicating significant reaction at the methine carbon.

The polymer obtained from the 3-h oxidation (3) was subsequently reduced with lithium aluminum hydride in dimethoxyethane. Figure 4 shows the ^1H NMR spectrum of the resulting polymer 4, characterized by its strong methylene signal at 4.6 ppm. Some residual carboxylic acid is revealed by its ortho proton NMR signal at 7.7 ppm and may be due to the fact that the polymer precipitated during the course of the reduction.

Reduction of the lightly oxidized polymer 1 with sodium borohydride quantitatively converted the aldehyde groups into benzyl alcohol groups, while leaving the carboxylic acid groups untouched. Acetylation of the resulting polyol **5** with excess acetic anhydride (room temperature, 24 h) led to the copolymer **6** bearing acetoxymethyl groups besides the carboxylic acid units. In the ^{1}H NMR spectrum of this copolymer (**6**; Figure 5), the benzylic methylene protons appear at 5.0 ppm, characteristic of the benzyl acetate function. A sharp peak at 2.2 ppm further confirms the presence of the acetoxymethyl group.

Figure 6A shows the overlay of the GPC traces of the original poly(4-methylstyrene) and of the polymer obtained after 3 h of oxidation (**3**). The oxidized polymer shows partial backbone cleavage, indicated by a low molecular weight tail and a slightly reduced number-average molecular weight of 7800. Figure 6B shows the same overlay with the highly oxidized fraction obtained after 24 h of oxidation (**2**). Significant backbone cleavage is apparent from the low number-average molecular weight of 1100 and from the bimodal molecular weight distribution.

Properties and Reactions of the Functionalized Polymers. The highly oxidized polymer fraction **2** is soluble in dilute aqueous sodium hydroxide and precipitates out upon reacidification. Water-soluble polymers are used in many industrial applications. The polyols **4** and **5**, and especially the polymer containing acetoxymethyl groups (**6**), rapidly cross-link in the presence of acids through electrophilic aromatic substitution. Indeed, phenolic resins containing (acetoxymethyl)styrene units are known to be highly sensitive negative photoresists.[9,10]

Conclusions. The selective cobalt-catalyzed oxidation of the commodity polymer poly(4-methylstyrene) gives access to a potentially large class of functionalized polymers including poly(carboxylic acids) and polyols. These materials may find direct applications as water-soluble polymers and as reactive polymer films or photoresists. The oxidation reaction is characterized by the high selectivity of the catalyst for primary benzylic positions. We are currently working on extending the scope of this reaction to other polymer systems containing 4-methylstyrene. Our future research will also focus on further increasing the selectivity of the oxidation reaction in order to achieve high degrees of functionalization without excessive backbone cleavage.

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Registry No. $H_2C{=}CHC_6H_4$-*p*-CH_3 (homopolymer), 24936-41-2; NaBr, 7647-15-6; cobalt(II) acetate tetrahydrate, 71-48-7.