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A New Route to (Chloromethyl)styrene Polymers

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Functional polystyrenes such as poly(styrene-*co*-(chloromethyl)styrene) serve as versatile intermediates in polymer chemistry, as their chlorine groups are easily displaced by nucleophiles[1,2] to produce anion-exchange polymers,[3] solid state synthesis (Merrifield) resins,[4,5] and electron beam negative resists.[6−8] The two main preparative routes used today are chloromethylation of polystyrene[3] and copolymerization of vinylbenzyl chloride with styrene.[9] Chloromethylation is carried out using chloromethyl alkyl ethers[10] in the presence of Lewis acid catalysts and can suffer from poor control of the degree of chloromethylation and unwanted cross-linking. The copolymerization approach involves a specialty monomer (vinylbenzyl chloride), and is limited to radical copolymerization processes.

Several years ago, poly(4-methylstyrene) was discovered as a potential precurser polymer. 4-Methylstyrene is commercially available[11] and, much like styrene, may be polymerized by free radical, living anionic, and cationic processes to give polymers of controlled molecular weight. The 4-methyl groups offer a handle for post-polymerization modifications, and methods aiming at direct and selective halogenation at the 4-methyl site were developed. Ford[12] and Jones[13] described radical chlorinations using hypochlorite and phase transfer agents, indicating that the high reactivity of the chlorine radicals caused some backbone and aromatic chlorination. Wang and Powers at Exxon developed a method for the free radical bromination of poly(isobutylene-*co*-4-methylstyrene)s.[14,15] Due to the lower reactivity of the bromine radicals, aromatic and backbone methylene sites are not affected, and the backbone benzylic methine is effectively protected by the neighboring isobutylene sites. This method is especially elegant, with multiple bromination at the 4-methyl sites being only observed at quite high degrees of bromination. More recently, direct metalation of poly(isobutylene-*co*-4-methylstyrene)s with superbases was used to selectively incorporate electrophiles into the 4-methyl site.[16,17]

Recently, we reported the cobalt-catalyzed air oxidation of the 4-methyl groups in poly(4-methylstyrene) to aldehyde and carboxylic acid,[18] as well as the stoichiometric oxidation of poly(4-methylstyrene) by cobalt(III) acetate and cerium(IV) ammonium nitrate.[19] The latter oxidation proceeds through intermediate polymeric benzyl cations that quench with the acetate and nitrate nucleophiles present in the system.

In this paper we report the related oxidation of poly(4-methylstyrene) with cobalt(III) acetate in presence of lithium chloride. Here, the polymeric benzyl cations are intercepted by chloride anions, to form in one step poly(4-methylstyrene-*co*-(chloromethyl)styrene)s of up to 21% (chloromethyl)styrene content.[20] No aromatic, aliphatic, or backbone chlorination is observed at this level of chlorination. Formation of dichloromethyl groups is not observed, which is likely due to the cationic mechanism of the reaction.

Figure 1 shows the proposed mechanism for this reaction, based on the similar chlorination of toluene reported by Heiba et *al*.[21]

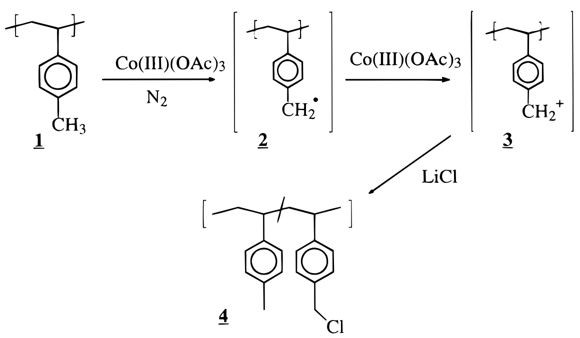

Figure 1. Mechanism of oxidative chlorination of poly(4-methylstyrene).

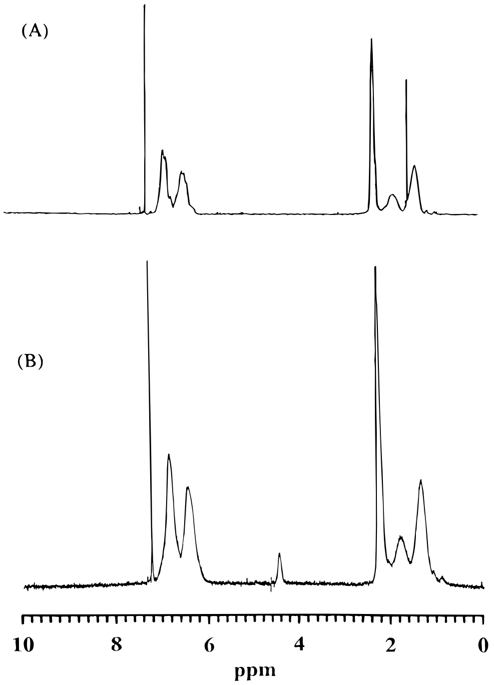

Figure 2. ^{1}H NMR spectra of poly(4-methylstyrene) (A) and 12.5% chlorinated poly(4-methylstyrene) (B).

The first step involves either sequential electron transfer to the Co(III) chloride complex followed by proton loss, or direct abstraction of a hydrogen atom from poly(4-methylstyrene) (**1**), to form the intermediate polymeric benzyl radical (**2**).[19] This radical subsequently transfers an electron to a second Co(III) complex to form the intermediate benzylic cation (**3**). This cation finally quenches with chloride ions to form the final chloromethyl copolymer (**4**). In this reaction, lithium chloride serves both as a chloride source and as an activator for the cobalt(III) acetate.

Comparison of the ^{1}H NMR spectra for poly(4-methylstyrene) (Figure 2a) and for the 12.5% oxidized product (Figure 2b) shows the appearance of the 4-chloromethyl group at 4.48 ppm. The ^{13}C NMR spectra of poly(4-methylstyrene) (Figure 3a) and a 21% oxidized polymer (Figure 3b) show the appearance of both the chloromethyl carbon at 46.29 ppm and the *ipso* quaternary carbon at 145.78 ppm. FT-IR shows characteristic chloromethyl absorptions at 1266, 816, and 676 cm^{-1}.

Table 1 shows a comparison of the degrees of chlorination as measured by elemental analysis (EA),[22] neutron activation analysis (NAA),[23] and ^{1}H NMR (chloromethyl signal). The values obtained by these three independent methods are in close agreement,

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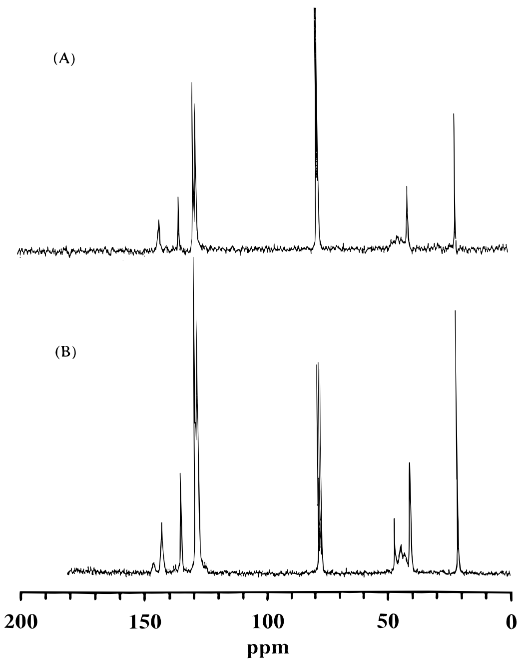

Figure 3. ^{13}C NMR spectra of poly(4-methylstyrene) (A) and 21% chlorinated poly(4-methylstyrene) (B).

Table 1. Chlorine Analyses

	% C	% H	% Cl	mol % $-CH_2Cl$
EA[a]	85.59	7.90	6.07	21.5[c]
NAA[b]			6.0	20.6[c]
^1H NMR			6.04	21.0[d]

[a] EA (elemental analysis) sums to 99.56%. [b] Neutron activation analysis. [c] Expressed as CH_2Cl. [d] Based on integration of the CH_2Cl signal.

Table 2. Effect of Lithium Chloride on Degree of Chlorination[a]

LiCl [mmol]	M_n	M_w/M_n	mol % of $-CH_2Cl$
7.0	16 500	2.05	1.3
15	16 900	1.79	12.5
20	17 000	1.92	15.1
30	14 200	1.93	21.2

[a] Conditions: 2.5 mmol of P4MS; 5 mmol of $Co(Ac)_3$; 15 mL each of benzene and glacial acetic acid; 50 °C; N_2; 2 h.

Table 3. Effect of Cobalt(III) Acetate on Oxidation[a]

$[Co(OAc)_3]$ (mmol)	M_n	M_w/M_n	mol % of $-CH_2Cl$
0.5	17 400	1.85	0.7
1.0	16 200	1.89	1.9
2.5	15 600	1.89	8.0
5.0	17 000	1.92	15.1
10	17 000	1.89	13.8

[a] Conditions: 2.5 mmol of P4MS; 20 mmol of LiCl; 15 mL each of benzene and glacial acetic acid; 50 °C; N_2; 2 h.

Table 4. Effect of Reaction Time on Oxidation[a]

reaction time (hours)	M_n	M_w/M_n	mol % of $-CH_2Cl$
1.0	16 400	1.81	6.4
2.0	17 000	1.92	15.1
3.0	13 600	1.94	14.7
5.0	11 900	2.12	16.5

[a] Conditions: 2.5 mmol of P4MS; 5 mmol of $Co(Ac)_3$; 20 mmol of LiCl; 15 mL each of benzene and glacial acetic acid; 50 °C; N_2.

supporting the absence of aromatic or backbone chlorination, and of dichloromethyl groups. In Tables 2−5, the values shown for CH_2Cl were determined by ^1H NMR.

Table 5. Effect of Reaction Temperature on Oxidation[a]

reaction temp (°C)	M_n	M_w/M_n	mol % of $-CH_2Cl$
35	16,700	1.91	15.8
50	17,000	1.92	15.1
60	12,400	2.06	14.7
70	9,600	2.45	20.1
80	9,600	2.26	18.5

[a] Conditions: 2.5 mmol of P4MS; 5 mmol of $Co(Ac)_3$; 20 mmol of LiCl; 15 mL each of benzene and glacial acetic acid; N_2; 2 h.

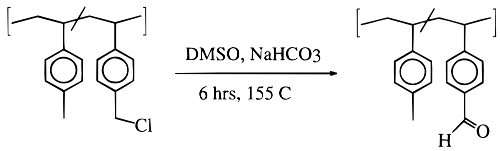

Figure 4. Reaction of 21% chlorinated poly(4-methylstyrene) with DMSO.

The chloride ions appears to serve a dual role in this reaction:

(1) No reaction was observed between cobalt(III) acetate and poly(4-methylstyrene) in acetic acid/benzene in the absence of lithium chloride. Plausibly the chloride ion forms an activated Co(III) complex.

(2) The intermediate polymeric benzyl cation is quenched by chloride anions present in the system to form exclusively chloromethyl groups. No acetoxymethyl or nonselective chlorination products were observed. This suggests ligand transfer of chloride from the cobalt complex to the benzyl cation.

The degree of chlorination increased with increasing lithium chloride concentration (Table 2). This is in contrast to the findings by Heiba et *al.* for the analogous chlorination of toluene, where lithium chloride concentrations from 0.24 molar to 1.2 M gave similar degrees of chlorination (70−76%).[21]

As the solutions became turbid at the highest lithium chloride concentrations (1 M) due to undissolved salt, subsequent reactions were run at 665 mM in lithium chloride (20 mmol of LiCl/30 mL). This fairly low lithium chloride concentration, as well as steric hindrance in the backbone (out-of-plane conformation of the competing methine cation[19]), is likely responsible for suppressing both the ring chlorination reported by Heiba[21] and the backbone chlorination.

The degree of chlorination increased with cobalt(III) acetate concentration (Table 3), showing a maximum at a molar ratio of Co(III):P4MS of 2:1.

Oxidation beyond 2 h did not increase the degree of chlorination, indicating essentially complete conversion of cobalt(III) at that time (Table 4).

While the degree of chlorination increased slightly with temperature, this came at the expense of significant backbone cleavage. This backbone cleavage likely proceeds through formation of a tertiary backbone cation followed by β-scission and becomes significant only at temperatures above 50 °C.[19]

Methyl ethyl ketone and *n*-heptane were tested as cosolvents instead of benzene. No reaction or molecular weight change was observed in these cases, likely due to the reduced solubility of lithium chloride.

To illustrate the versatility of chloromethylated polystyrenes, we converted[24] the chloromethyl groups into aldehyde by oxidation in dimethyl sulfoxide as shown in Figure 4 below.[25−27] The ^1H NMR spectrum of the product polymer showed quantitative conversion of chloromethyl to benzaldehyde groups (aldehyde, 9.9 ppm; aromatic hydrogens *ortho* to the aldehyde, 7.48

ppm; no chloromethyl signals). There was no evidence of functional groups other than aldehyde.[28]

In conclusion, we report a process to chlorinate up to 21% of the methyl groups in poly(4-methylstyrene), without detectable side reactions. The process uses cobalt(III) acetate as an oxidant in the presence of lithium chloride. Functional polymers with number average molecular weights between 13 000 and 17 000 were obtained, indicating slight backbone cleavage from the starting molecular weight of 18 900. This backbone cleavage was minimized by limiting the reaction temperature to 50 °C. The resulting chloromethyl copolymers can be further modified, thus giving access to a wide range of functional polymers.

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References and Notes

(1) Akelah, A.; Sherrington, D. C. *Polymer* **1983**, *24*, 1369−1386.

(2) Montheard, J.-P.; Chatzopoulos, M.; Camps, M. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *128*, 503.

(3) Pepper, K. W.; Paisley, H. M.; Young, M. A. *J. Chem. Soc.* **1953**, 4097−4105.

(4) Sherrington, D. C.; Hodge, P. *Synthesis and Separations using Functional Polymers*; John Wiley & Sons: New. York, 1988.

(5) (a) Merrifield, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2149−2154. (b) Merrifield, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 304−305.

(6) Griffiths, L. G.; Johns, R. G. *Makromol. Chem., Makromol. Symp.* **1989**, *24*, 201−207.

(7) Griffiths, L. G.; Johns, R. G; Brambley, D. R. *Polym. Commun.* **1988**, *29*, 173−174.

(8) Imamura, S.; Tamamura, T.; Harada, K.; Sugawara, S. *J. Appl. Polym. Sci.* **1982**, *27*, 937−949.

(9) Balakrishnan, T.; Ford, W. T. *J. Appl. Polym. Sci.* **1982**, *27*, 133−138.

(10) For a study of the carcinogenicity of such ethers, see: Weiss, W. J. *J. Occup. Med.* **1976**, *18*, 194.

(11) 4-Methylstyrene is commercially available from Deltech Inc., Baton Rouge, LA.

(12) Mohanraj, S.; Ford, W. T. *Macromolecules* **1986**, *19*, 2470−2472.

(13) Jones, R. G.; Matsubayashi, Y. *Polymer* **1990**, *31*, 1519−1525; **1992**, *33*, 1069−1072).

(14) Wang, H. C.; Powers, K. W. *Elastomerics* **1992**, *124* (1), 14−19.

(15) Powers, K. W.; Wang, H. C.; Chung, N.-J.; Diaz, A. J.; Olkusz, J. A. U.S. Patent 5,162,445, 1992.

(16) Steinke, J. H. G.; Haque, S. A.; Frechet, J. M. J.; Wang, H. C. *Macromolecules* **1996**, *29*, 6081−6089.

(17) Lochmann, L.; Janata, M.; Holler, P.; Tuzar, Z.; Kratchovil, P. *Macromolecules* **1996**, *29*, 8092−8095.

(18) Shaver, R. T.; Vlaovic, D.; Whittaker, R.; Reviakine, I.; Ferrari, L. P.; Stöver, H. D. H. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 957−965. See also: Ferrari, L. P.; Stöver, H. D. H. *Macromolecules* **1991**, *24*, 6340−6343.

(19) Sheng, Q.; Stöver, H. D. H. *Macromolecules*, in press.

(20) Poly(4-methylstyrene) (M_n = 18 900; MWD = 1.73) was prepared by solution polymerization in toluene as reported before.[12] Cobalt(III) acetate was prepared by ozonation of cobalt(II) according to: Lande, S. S.; Falk, C. D.; Kochi, J. K. *J. Inorg. Nucl. Chem.* **1971**, *33*, 4101−4109. General oxidation procedure: 0.30 g (2.5 mmol) of poly(4-methylstyrene) and 0.85 g (20 mmol) of lithium chloride were dissolved in a mixture of 15 mL of glacial acetic acid and 15 mL of benzene under nitrogen. The temperature was raised to 50 °C, and 1.18 g (5.0 mmol) of cobalt(III) acetate was added to form a dark green solution. After 2 h, the reaction mixture was cooled and filtered and the benzene component removed on a rotary evaporator. The remaining solution of oxidized polymer and cobalt salts was precipitated into 200 mL of 4:1 methanol/water. The white precipitate was collected by filtration, washed, and dried under vacuum at 60 °C overnight to yield typically around 90% of polymeric product.

(21) Heiba, E. I.; Dessau, R. M.; Koehl, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 6830−6837.

(22) Elemental analyses were carried out at Guelph Chemical Laboatories, Guelph, Ontario, Canada.

(23) NAA was carried out at the McMaster Neutron Activation Facility attached to the McMaster Nuclear Reactor.

(24) A 0.20 g sample of 20% poly(4-methylstyrene-*co*-4-(chloromethyl)styrene) and 0.30 g sodium hydrogen carbonate were stirred in 18 mL of dimethyl sulfoxide for 6 h at 155 °C. The product was filtered, washed with dimethyl sulfoxide and hot water, and dried at 60 °C under vacuum overnight.

(25) Ayres, J. T.; Mann, C. K. *Polym. Lett.* **1965**, *3*, 505.

(26) Engler, E. M.; Kaufman, F. B. *U.S. Patent* 4,142,783, **1978**.

(27) Bhatti, A.; Davies, J. A.; Dollimore, D.; Sood, A. *Thermochim. Acta* **1985**, *87*, 211−2118.

(28) Gibson, H. W. Bailey, F. C. *J. Polym. Sci., Polym. Chem.* **1975**, *13*, 1951.

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