554 *Macromolecules* **1993,** *26,* 554–556

A Novel and Convenient Method for Synthesis of Formylated Polystyrene via Oxidative Scission from Poly[(methoxymethyl)styrene] Mediated by a Nitroxyl Radical

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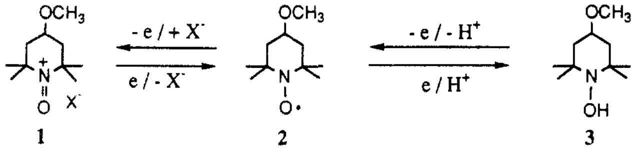
Received June 24, 1992
Revised Manuscript Received October 9, 1992

Introduction

Formylated polystyrenes are quite important as one of the reactive polymers, and attention has been paid to their photo- and electrochemical properties in recent years. However, few preparative methods for formylated polystyrene have been reported. Preparation from cross-linked polystyrene via several steps involving bromination[1] or oxidation of chloromethylated polystyrene with dimethyl sulfoxide has been applied to the synthesis of formylated polystyrenes.[2] The formylation for linear polymers having aromatic groups has recently been reported, but the degree of formylation, especially in the case of polystyrene, is low.[3] Furthermore, the polymerization of formylstyrene has been reported to lead to formation of gelled polymer and polymers with high polydispersity.[4] In the present paper, we describe a convenient preparative method for formylated polystyrene involving polymer modification via the oxidative scission of a benzyl ether moiety mediated by a nitroxyl radical.

4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (2), a nitroxyl radical which is well-known as a spin trapping or labeling agent, forms the following reversible redox system.



Oxoaminium halide (1) obtained by one-electron oxidation of 2 is a selective and efficient oxidant of alcohols[5–7] and can also oxidize smoothly benzyl alkyl ether. In particular, oxoaminium bromide (1, X = Br) quantitatively converts benzyl methyl ether to benzaldehyde.[8] However, it seems to be difficult to apply 1 to a polymer modification reaction because of the difficulty in preparation and instability of 1 (X = Br). So, oxoaminium chloride (1, X = Cl) is more stable for that reaction than the bromide (1, X = Br). This paper describes a convenient synthesis of formylated polystyrene via oxidative scission of the ether linkage of poly[*p*-(methoxymethyl)styrene] (PMMSt) with Cu(NO_3)$_2$ mediated by 2. Furthermore, this method will be extremely significant from the viewpoint of a one-pot synthesis of formylated polystyrene from PMMSt readily obtainable from chloromethylated styrene.[9]

Experimental Section

Measurements. IR spectra were recorded with a Jasco FT/IR-3 Fourier transform infrared spectrometer. ^{1}H-NMR spectra were obtained with a JEOL EX-90 NMR spectrometer. Gel permeation chromatography (GPC) was performed with a Toyo Soda CCP&8000 with a data processing system (eluent, THF; calibration, polystyrene standard).

Materials. 4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (2) was prepared by the previously reported method.[5] Benzyl methyl ether and (chloromethyl)styrene were obtained from Tokyo Kasei Kogyo and Mitsubishi Kasei Co., Ltd., respectively. Styrene and methyl methacrylate were washed with aqueous 5% NaOH and water, dried over anhydrous $MgSO_4$ for several hours, and then distilled over CaH_2 under reduced pressure before use. $Cu(NO_3)_2 \cdot 3H_2O$ and $Cu(OH)_2$ were dried for several hours in vacuo before use.

(Methoxymethyl)styrene. To a stirred solution of 3.03 g (56.1 mmol) of sodium methoxide in 150 mL of anhydrous DMF was added a mixture of 12.84 g (84.1 mmol) of *p*-(chloromethyl)styrene and 30 mL of DMF at 0 °C under N_2. After stirring for 24 h at room temperature the reaction mixture was extracted with ether in the presence of a small quantity of hexane. The ether layer was dried over anhydrous $MgSO_4$ and then evaporated to obtain the crude product. The product was chromatographed on silica gel using benzene to remove the *p*-(chloromethyl)styrene. The collected product was distilled under reduced pressure to obtain *p*-(methoxymethyl)styrene (MMSt). Yield: 4.59 g (55%).

Poly[(methoxymethyl)styrene]. A total of 917 mg (6.19 mmol) of MMSt and 10.2 mg (0.0621 mmol) of AIBN were placed in an ampule, immersed in a dry ice–acetone Dewar bottle, and degassed. Freeze degassing was repeated three times, argon gas was introduced, and the ampule was sealed. After the mixture was heated at 60 °C for 24 h, the ampule was cooled to room temperature. The product was dissolved in 10 mL of benzene and precipitated into methanol. The precipitate was collected and dried in vacuo at room temperature to obtain poly(MMSt) (white powder). Yield: 860 mg (94%). IR (KBr): 3050, 2982, 2924, 2849, 2820, 1512, 1451, 1422, 1381, 1190, 1099, 1020, 965, 916, 818 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.1–6.1 (m, Ar), 4.27 (s, CH_2O), 3.27 (s, OCH_3), 2.2–1.0 (m, CH_2CH).

Copoly(styrene–MMSt). A total of 478 mg (4.58 mmol) of styrene (St), 120 mg (0.809 mmol) of MMSt, and 8.7 mg (0.0536 mmol) of AIBN were placed in an ampule, immersed in a dry ice–acetone Dewar bottle, and degassed. Freeze degassing was repeated three times, argon gas was introduced, and the ampule was sealed. After the mixture was heated at 60 °C for 7 h, the ampule was cooled to room temperature. The polymer was dissolved in 10 mL of benzene and precipitated into methanol. The precipitate was collected and dried in vacuo at room temperature to obtain copoly(St–MMSt) (St:MMSt = 85:15 by ^{1}H-NMR) (white powder). Yield: 543 mg (91%). IR (KBr): 3059, 3026, 2922, 2849, 1601, 1493, 1453, 1379, 1184, 1100, 1028, 909, 818, 758, 698, 540 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 7.5–6.2 (m, Ar), 4.34 (s, CH_2O), 3.30 (s, OCH_3), 2.3–1.0 (m, CH_2CH).

Oxidation of Benzyl Methyl Ether. To a stirred solution of 56.0 mg (0.458 mmol) of benzyl methyl ether in 5 mL of acetonitrile were added 886 mg (3.67 mmol) of copper nitrate, 89.0 mg (0.912 mmol) of copper hydroxide, and 34.0 mg (0.183 mmol) of 2 at room temperature. The reaction progress was monitored by subjecting an aliquot of the reaction mixture to gas chromatography. In 2 days, benzaldehyde was obtained in 93% yield.

Oxidation of Copoly(St–MMSt). To a stirred solution of 100 mg (0.903 mmol of repeating unit) of poly(St–MMSt) (St: MMSt = 85:15) dissolved in 15 mL of dry benzene were added 88.0 mg (0.902 mmol) of copper hydroxide, a solution of 1.74 g (7.20 mmol) of copper nitrate, 32.5 μL (1.18 mmol) of distilled water, and 168 mg (0.903 mmol) of 2 at room temperature in that order. After stirring for 4 days at room temperature, the mixture was decanted to remove the white–green precipitate, and the precipitate-free solution was poured into 500 mL of methanol. After stirring for 3 h, a white polymer was collected by filtration (96.5 mg, 98%). IR (KBr): 3059, 3026, 2922, 2849, 1703, 1604, 1493, 1453, 1213, 1169, 1105, 1069, 1028, 907, 828, 758, 698, 542 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 9.89 (s, CHO), 7.8–6.1 (m, Ar), 5.30 (s, CH), 3.22 (s, $(OCH_3)_2$), 2.4–0.8 (m, CH_2CH).

Deacetalization of Copoly(St–FSt-DMAL). To a stirred solution of 40.0 mg (0.367 mmol of repeating unit) of copoly(St–FSt-DMAL) (St:FSt:DMAL = 85:14:1) in 5 mL of benzene were added 1.5 mL of acetic acid and 0.7 mL of distilled water at room temperature. The mixture was kept at 60 °C for 16 h and poured into 250 mL of methanol. The precipitate was collected to obtain the product copoly(St–FSt) quantiatively. IR (KBr): 3059, 3026, 2922, 2849, 1703, 1604, 1493, 1452, 1213, 1169, 1101, 1055, 1028, 909, 828, 758, 700, 542 cm^{-1}. ^{1}H-NMR (C_6D_6): δ 9.72 (s, CHO), 7.8–6.2 (m, Ar), 2.4–1.1 (m, CH_2CH).

0024-9297/93/2226-0554$04.00/0

Table I
Oxidative Scission of Copoly(St-MMSt)[a] to Copoly(St-FSt)

expt no.	H_2O, equiv	time, day	conv,[b] %	yield, %	unit,[c] mol % St	MMSt	FSt	DMAL	$\bar{M}_n$[d] before ox.	after ox.
1		2	93	100	85	1	8.5	5.5	32 000	29 000
2	2	2	93	100	85	1	14	0	32 000	32 000
3	2	4	100	98	85	0	14	1	32 000	29 000

[a] St:MMSt = 85:15. [b] Conversion of the MMSt unit. [c] Estimated by ^{1}H-NMR. [d] Estimated by GPC based on a PSt standard.

Scheme I

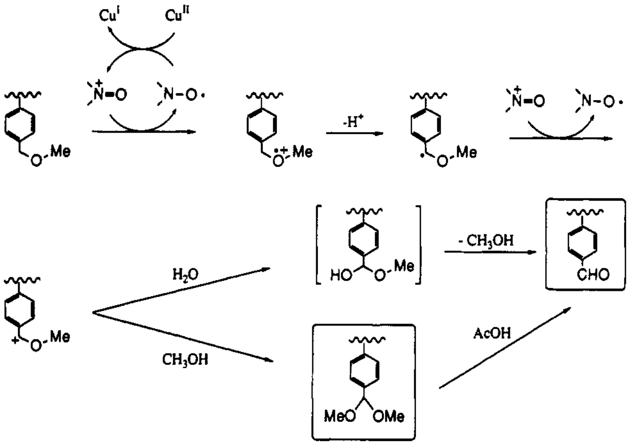


Table II
Oxidative Scission of Copoly(St-MMSt) to Copoly(St-FSt)

x,[a] mol %	y,[b] mol %	conv,[c] %	yield, %	unit,[d] mol % St	FSt	DMAL	$\bar{M}_n$[e] before ox.	after ox.
0	100		97[f]				7 700	
50	50	100	96	50	36	14	37 000	31 000
76	24	100	91	76	22	2	32 000	23 000
79	21	100	97	79	19	2	31 000	26 000
85	15	100	98	85	14	1	32 000	29 000
90	10	100	100	90	10	0	23 000	24 000

[a] The proportion of the St unit. [b] The proportion of the MMSt unit. [c] Conversion of the MMSt unit. [d] Estimated by ^{1}H-NMR. [e] Estimated by GPC based on a PSt standard. [f] Gel product.

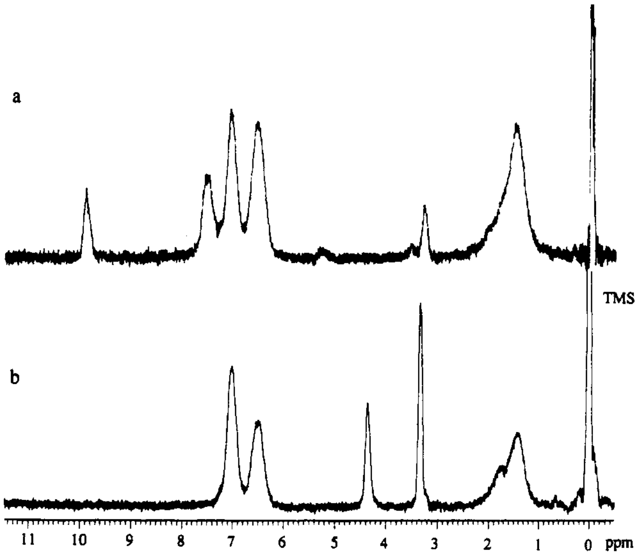


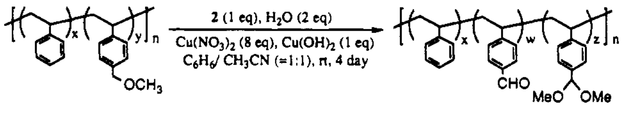
Figure 1. ^{1}H-NMR spectra of copoly(St-FSt-DMAL) (unit ratio 50:36:14) (a), obtained by the oxidation of copoly(St-MMSt) (unit ratio 50:50) (b). (Solvent: $CDCl_3$.)

Results and Discussion

As a model reaction, the oxidation of benzyl methyl ether was carried out with 8 equiv of $Cu(NO_3)_2$, 1 equiv of $Cu(OH)_2$, and 0.4 equiv of **2** as a catalyst in acetonitrile at room temperature for 2 days and benzaldehyde was obtained in 93% yield. In this reaction, **2** can act as an electron-transfer agent to catalyze the oxidation by $Cu(NO_3)_2$, and the actual oxidant, oxoaminium salt (**1**), is prepared in situ.[10] This system was applied to the oxidation of the copolymer of St with MMSt (=85:15) in a mixed solvent of benzene and acetonitrile (1:1). The results are shown in Table I. The addition of water suppressed acetalization to facilitate the conversion of the MMSt unit to the FSt unit. No change in the number-average molecular weight ($\bar{M}_n$) and the ratio of the St unit in its ^{1}H-NMR was observed between before and after the oxidation, indicating that this oxidation system does not harm the main chain and St unit. The reaction process is speculated in Scheme I. $Cu(OH)_2$ efficiently serves as scavenger for nitric acid formed during the oxidation to eventually convert to water.

When the product (Table I, expt no. 3) was treated with acetic acid in benzene at 60 °C for 16 h, no peaks based on methine and methylene protons of the dimethyl acetal unit were observed by the ^{1}H-NMR spectrum, whereas the integral intensity of the aldehyde proton increased. Further, IR absorption of the C–O bond (1069 cm^{-1}) completely disappeared, indicating that the dimethyl acetal unit was fully converted to the FSt unit (yield 100%, $\bar{M}_n$ = 35 000).

A similar reaction was applied to the homopolymer of MMSt as well as copolymers of MMSt with St. The results are shown in Table II.



Although the oxidation of the MMSt homopolymer proceeded as expected, the product obtained was gelled during the isolation. Although most MMSt units would be converted to FSt units because the gelled product showed a strong carbonyl absorption at 1703 cm^{-1} in its IR spectrum, the exact unit ratio of w and z could not be determined by ^{1}H-NMR due to the gelation. The gelation is likely to be caused by cross-linking between aldehyde groups. The conversion of the MMSt unit and the unit ratio were estimated from comparison of the integral intensities of the corresponding aldehyde or methine protons of the pendant groups to the methylene and methine protons of the polymer main chain. Figure 1 illustrates ^{1}H-NMR spectra before and after the oxidation of copoly(St-MMSt) (St:MMSt = 50:50). In the ^{1}H-NMR spectrum after oxidation, the aldehyde signal at 9.9 ppm was observed in addition to the proton signals originating from the methine and methyl protons of the dimethyl acetal unit, appearing at 5.2 and 3.2 ppm. These change are well consistent with the expected disappearance of two signals based on benzyl and methyl protons of the methoxymethyl group at 4.4 and 3.3 ppm. The broad singlet signal around the peak at 7.5 ppm would be due to aromatic protons at the 3- and 5-positions of the FSt and DMAL units formed.

Oxidation of the copolymer of MMA with MMSt (MMA: MMSt = 90:10, $\bar{M}_n$ = 11 000) was also carried out under the same conditions, and MMA–FSt–DMAL (MMA:FSt: DMAL = 90:8:2, $\bar{M}_n$ = 10 000) was obtained in 100% yield.

In conclusion, the 2–$Cu(NO_3)_2$ oxidation system could cause oxidative scission of the ether linkage of the MMSt unit in the polymers to efficiently give FSt and its dimethyl acetal units. Furthermore, the dimethyl acetal moieties could be easily converted to the FSt unit by treatment with acetic acid. Therefore, the present study demonstrated that this oxidation system is a useful method for the convenient synthesis of poly(FSt).

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