

# A Comparison of the Oxidizing Ability of Polystyrene-Supported Linear and Cyclic Polyoxyethylene Bound Permanganates

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**ABSTRACT:** The grafting of linear and cyclic polyoxyethylenes into DVB-crosslinked chloromethylpolystyrene was carried out by treating with polyethyleneglycol (PEG<sub>600</sub>). The complexations of crosslinked polystyrene-supported linear and cyclic polyoxyethylene with permanganate functions were carried out. With this reagent, primary alcohols and secondary alcohols were converted to aldehydes and ketones and aldehyde to acid. The polymer acts as a reservoir of permanganate functions and releases them slowly as the substrates are being used up. The effect of solvent, molar excess of reagent, time, and temperature on oxidation be-

havior were investigated by choosing benzoin to benzil conversion as the model reaction. The linear polymeric reagent has greater reactivity than the cyclic polymer due to the greater availability of the reactive sites in the linear polymer than the cyclic polymer. Polymeric reagent could be used in excess to get a good yield without causing any separation problems and over oxidation products. The reagents have advantages of easy separation, regeneration and reuse. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1897–1905, 2005

**Key words:** polystyrene; supports; matrix; crosslinking

## INTRODUCTION

The use of polymer-supported reagents, as an aid to organic synthesis is becoming an interesting common feature in both academic and industrial research.<sup>1–4</sup> A functional polymer can be considered as a macromolecule to which reactive functional groups are incorporated by ionic, covalent, coordination, or other less-specific interactions. Hence it shows the physical properties of the polymer support and chemical properties of the attached reactive function.<sup>5</sup> Attachment of a reactive group to a polymer generates a new reagent with different structure and reactivity.<sup>6</sup> The major thrust behind the widespread use of polymer-supported reagent is the simplification achieved in separation and purification of synthetic intermediates, products, and catalyst or decontamination from impurities, side products, and toxins.<sup>7</sup>

The complexed polyethers are held together by electrostatic attraction between the cations and the C–O dipoles of the polyethers.<sup>8,9</sup> The cation binding ability of crown ether is high in organic solvents and is very low in aqueous media because of the strong hydration of cations.<sup>10,11</sup> Potassium permanganate complex of crown ether in benzene provides a convenient and efficient oxidant for organic compounds. In the absence of crown ether potassium permanganate has no

detectable solubility in benzene and no reaction with organic substrate.<sup>12</sup>

The main objective of this article involves the development of a new class of polymeric oxidizing agent based on permanganate incorporated 2 mol % DVB-crosslinked polystyrene-supported linear and cyclic polyoxyethylenes.

## EXPERIMENTAL PROCEDURES

### Materials and methods

Macroporous chloromethyl polystyrene (Merrifield resin, 2 mol % DVB-crosslinked) was supplied by Fluka, Switzerland. Polyethylene glycol (PEG<sub>600</sub>) was the commercial product obtained from Merck, Germany. Commercially available low-molecular-weight compounds were purified by literature procedures. AR grade solvents were purified by distillation. Electronic spectra were recorded on a Shimadzu UV-160A spectrophotometer. NMR spectra were recorded on a Bruker 250 MHz instrument. CHN analysis was carried out using a Perkin–Elmer PE 2400 CHN analyzer. IR spectra were recorded on a Shimadzu IR-470 spectrophotometer. Melting points were obtained from a Buchi-530 melting point apparatus.

### Preparation of polystyrene-supported linear and cyclic polyoxyethylenes

Dry chloromethyl polystyrene (4.2 mmol Cl/g) was allowed to swell in THF for 1 h. Polyethylene glycol

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(PEG<sub>600</sub>) and metallic sodium were added and the temperature was maintained at 80°C. For the incorporation of linear polyoxyethylene, the chlorine to PEG ratio was 1 : 5. In the case of cyclic polyoxyethylene incorporation, the molar ratio of polystyrene to diol was 2 : 1 to ensure the coupling of both ends of diol with the polystyrene support. Heating and stirring were continued for 35 h in an oil bath. The resulting polymers were cooled, collected by filtration; washed with water, methanol, and acetone; and dried in vacuum.

### Estimation of hydroxyl capacity

To estimate the presence of free hydroxyl group after treatment with polyethylene glycol, 200 mg of the dry polystyrene-supported linear and cyclic polyoxyethylenes were heated with acetic anhydride (1 mL) in pyridine (9 mL) in two conical flasks. The flask was fitted with a reflux condenser and heated with occasional shaking in a water bath for 2 h. Dry benzene (10 mL) was added and the flask was shaken vigorously. Subsequently, water was added, shaken well, and titrated against 0.1N KOH with phenolphthalien as indicator.

### Estimation of residual chlorine by modified Volhard's method

The chlorometylated resin (100 mg) was fused with pyridine (4 mL) in a boiling tube at 100°C for 6 h. It was then extracted with 50% acetic acid (30 mL) conc. HNO<sub>3</sub> (5 mL) and AgNO<sub>3</sub> (0.5N, 5 mL) were added and titrated against standard ammonium thiocyanate using ferric alum as indicator. From the titer values the chlorine capacity in millimole per gram of the resin was calculated.

### Synthesis of polystyrene-supported permanganates

Incorporation of permanganate functions: General procedure

To polystyrene-supported linear and cyclic polyoxyethylene (5 g) in benzene (20 mL), excess KMnO<sub>4</sub> was added and stirred at room temperature for 10 h. The black colored resins were isolated and washed with distilled water until the filtrates were completely free from permanganate ion. The resins were washed with benzene, methanol, and acetone and dried in vacuum. These resins were used for the oxidation reactions.

Determination of the capacity of permanganate functions

A definite amount of the dry permanganate complexed linear and cyclic resins was accurately weighed and suspended in an excess known volume of 2N

**TABLE I**  
Swelling Studies of Various Polystyrene-Supported Systems

Solvent	Extent of swelling ( $\alpha$ )				
	PS	PSPOE (linear)	PSPOE (cyclic)	PSPOE-KMnO <sub>4</sub> (linear)	PSPOE-KMnO <sub>4</sub> (cyclic)
Cyclohexane	4.6	4.3	4.0	3.5	2.8
Benzene	4.4	4.2	3.8	3.3	2.7
Tetrahydrofuran	4.3	4.2	3.6	3.1	2.5
Chloroform	4.2	4.1	3.7	3.0	1.9
Dioxane	4.1	3.8	3.3	2.5	1.6

H<sub>2</sub>SO<sub>4</sub> for 1 h. A known excess of standard Mohr's salt solution was added and stirred until the complete disappearance of the dark color of the resins. The unreacted ferrous ammonium sulfate solution was titrated against standard KMnO<sub>4</sub> solutions.

### Swelling studies

In a dry previously weighed sintered crucible (G<sub>3</sub>), dry resin (2 g) was taken and equilibrated with solvents such as cyclohexane, dioxane, chloroform, tetrahydrofuran, and benzene for 24 h. The excess solvent was drained. The extent of swelling ( $\alpha$ ) was calculated from the dry and swollen weights and the results are summarized in Table I.

### Oxidation studies of the permanganate complexes of DVB-crosslinked polystyrene-supported linear and cyclic polyoxyethylenes

To about fivefold molar excess of DVB-crosslinked polystyrene-supported linear and cyclic polyoxyethylene bound permanganates, 20 mL cyclohexane and the substrate were added. The extent of conversion of the substrates to products were followed at different time intervals by TLC. After complete conversion, the insoluble spent polymers were filtered and washed with solvent. The solutions were concentrated to dryness. The products were purified by column chromatography and characterized.

### Monitoring the course of the oxidation reaction

The progress of oxidation reaction was followed spectrophotometrically. The conversion of benzoin to benzil was selected as the model reaction. A calibration curve with concentration of benzil versus absorbance at 387 nm was plotted. Aliquots from the reaction mixture were withdrawn and the absorbance was measured. From the absorbance, the percentage of benzil in the reaction mixture was calculated. Similar calibration curves were plotted for other solvents

such as tetrahydrofuran, chloroform, cyclohexane, benzene, and dioxane.

### Effect of reaction conditions on the course of oxidation reactions

#### Effect of solvent

To investigate the solvent dependence on the extent of oxidation with various crosslinked polystyrene supports, benzoin to benzil conversion was selected as a model reaction. The typical procedure is as follows: 100 mg of benzoin was dissolved in 10 mL solvent and the required amount of polymeric reagent was added and heated to below the refluxing temperature of the solvent. The reaction mixture (0.5 mL) was withdrawn using a micropipette at regular intervals of time. It was diluted to 5 mL and the absorbance at 387 nm was measured. From the absorbance the percentage of benzil formed was calculated using a calibration curve. The experiment was repeated using various solvents having different polarities, such as chloroform, benzene, cyclohexane, dioxane, and tetrahydrofuran.

#### Effect of temperature

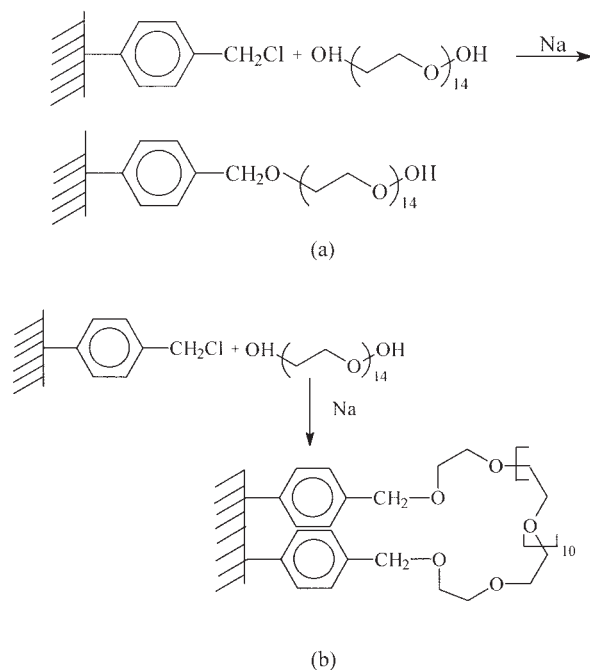
To study the effect of temperature on the extent of reaction, the above experiment was repeated in different temperatures ranging from room temperature to the refluxing temperature of the solvent used. The progress of the reaction was followed spectrophotometrically at 387 nm.

#### Effect of molar excess of the reagent

A calculated amount of the reagent (for appropriate molar excess based on oxidizing capacity) was added to benzoin (100 mg) dissolved in solvent (10 mL) and stirred below refluxing temperature. The progress of the reaction was followed as detailed above.

### Recycling and reuse

The spent polymers (5 g) were washed thoroughly with chloroform, dioxane, and methanol to remove any residual soluble organic substrate or product. The washed polymers were dried and stirred for 2 h with 2N (20 mL) solution of ferrous ammonium sulfate in the presence of 2N, H<sub>2</sub>SO<sub>4</sub> (10 mL), to remove all manganese oxides. The white beads were filtered, washed with distilled water, and dried. The polymer was swelled in benzene (20 mL); excess saturated potassium permanganate solution was added and stirred at room temperature for 10 h. The black colored resins were isolated and washed with distilled water until the filtrates were completely



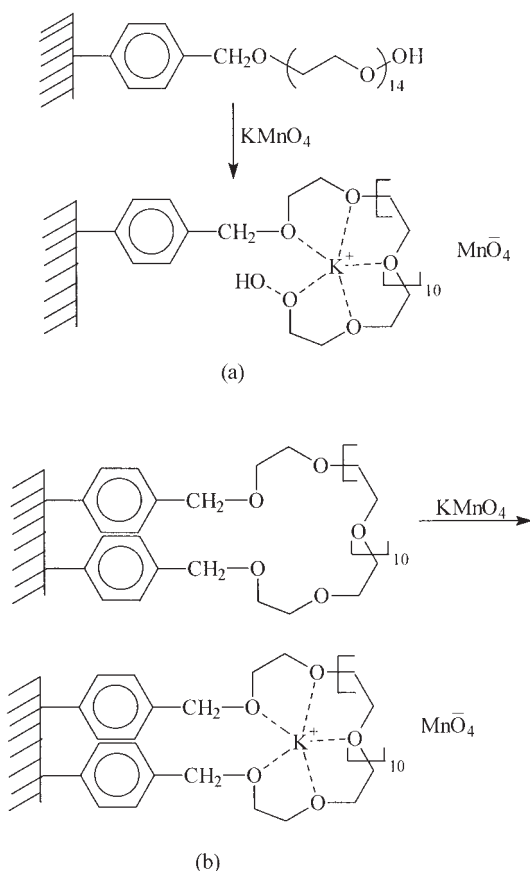
**Scheme 1** Preparation of 2 mol % DVB-crosslinked polystyrene-supported (a) linear and (b) cyclic polyoxyethylenes.

free from permanganate ion. The resins were washed with benzene, methanol, and acetone and dried in vacuum. These resins were used for the oxidation of benzoin in cyclohexane at 70°C in 5 : 1 reagent to substrate ratio as detailed earlier. The linear and crosslinked systems required 3 and 7 h, respectively.

## RESULTS AND DISCUSSION

### Preparation of 2 mol % DVB-crosslinked polystyrene-supported linear and cyclic polyoxyethylenes

For the synthesis of polystyrene-supported linear and cyclic polyoxyethylenes, 2 mol % DVB-crosslinked chloromethyl polystyrene was allowed to swell in tetrahydrofuran. The swelled resin was treated with polyethyleneglycol (PEG<sub>600</sub>) and metallic sodium at 80°C in an oil bath for 35 h (Scheme 1). For the incorporation of linear polyoxyethylene, excess polyethyleneglycol and corresponding metallic sodium were used. In the case of cyclic polyoxyethylene incorporation, the diol to chloromethyl ratio was 1 : 2 to ensure the coupling of both ends of polyoxyethylenglycol. The resultant polymer was washed with water, methanol, and acetone and dried in an oven at 50°C. The residual chlorine content of linear and cyclic polyoxyethylene-incorporated polystyrene was found to be 0.89 and 1.24 mmol/g, calculated by the modified Volhard's method.<sup>13</sup>



**Scheme 2** Complexation of polystyrene-supported (a) linear and (b) cyclic polyoxyethylene with potassium permanganate.

### Complexation of polystyrene-supported linear and cyclic polyoxyethylene with potassium permanganates

Macroporous 2 mol % DVB-crosslinked polystyrene-supported linear and cyclic polyoxyethylenes were allowed to swell in benzene in closed amber-colored reagent bottles. The swelled resins were equilibrated with excess potassium permanganate and stirred in a twist action shaker at room temperature for 10 h (Scheme 2). The black colored polymer beads were filtered and washed with distilled water to remove all the manganese dioxide. The product resins were dried in vacuum.

Both IR and UV spectral studies were used for the characterization of permanganate-bound polymer.<sup>14,15</sup> The IR spectrum of the resulting polymers showed a strong band at  $1100\text{ cm}^{-1}$  due to asymmetrical C–O–C stretching of the oxyethylene units. The values for the  ${}^1t_1 \rightarrow {}^3T_2(\text{cm}^{-1})$ ,  ${}^3t_2 \rightarrow {}^1T_1(\text{cm}^{-1})$ ,  ${}^1t_1 \rightarrow {}^1T_2(\text{cm}^{-1})$ ,  ${}^3t_2 \rightarrow {}^1T_1(\text{cm}^{-1})$  transitions are 18,552, 22,471, 33,333 and  $40,160\text{ cm}^{-1}$ , respectively.

To verify the presence of any free hydroxyl group, the resin was treated with excess acetic anhydride in pyridine and the unreacted acetic anhydride was de-

composed to acetic acid. It was titrated against alkali using phenolphthalein as indicator.<sup>16</sup> The hydroxyl group capacity of the linear polyoxyethylene incorporated system was found to be  $1.22\text{ mmol/g}$  while the cyclic polyoxyethylene incorporated system did not have any free hydroxyl capacity. The cyclic polyoxyethylene confirms the existence of the incorporated unit as polyoxyethylene.

For the estimation of potassium permanganate incorporation in linear and cyclic polyoxyethylenes supported on polystyrene, a definite amount of the functionalized polymer were suspended in excess known volumes of  $2N\text{ H}_2\text{SO}_4$ . A measured excess of standard ferrous ammonium sulfate solution or standard oxalic acid was added and stirred until the dark color of the resin completely disappeared and turned to white. The unreacted ferrous ammonium sulfate solutions were titrated against standard  $\text{KMnO}_4$  solution. The binding capacities for linear and cyclic systems were found to be  $2.01$  and  $1.86\text{ mmol/g}$ , respectively.

### Swelling studies

Swelling characteristics of chloromethylated polystyrene, polystyrene-supported linear and cyclic polyoxyethylenes, and  $\text{KMnO}_4$  complexed systems were carried out in solvents of varying polarity (Table I). Generally, swelling studies will give an idea about the suitable reaction medium for polymer-supported oxidations. The crosslink ratio and the polymer support used determine the swelling nature of the resin. In the present study, the extent of swelling ( $\alpha$ ) of the polymer in solvent is expressed as

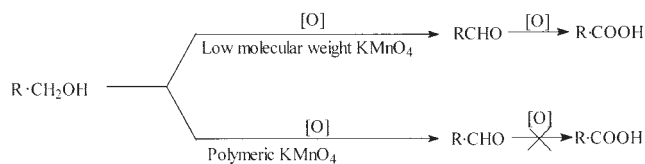
$$\alpha = \frac{\text{Weight of swollen resin} - \text{Weight of dry resin}}{\text{Weight of dry resin}}$$

All polymer systems were found to have maximum swelling in cyclohexane. The extent of swelling of a polymer depends on the compatibility of the polymer matrix with solvent. The swelling nature of the polymer varies on the functionalization. Thus, upon the incorporation of polyoxyethylene, the swelling decreased and it again decreased on complexation with potassium permanganate. The swelling characteristics of the cyclic polyoxyethylenes systems were lower than the linear system.

### Oxidation studies of polystyrene-supported linear and cyclic polyoxyethylene-based permanganates

The oxidation reactions were carried out using 2 mol % DVB-crosslinked polystyrene-supported linear and cyclic polyoxyethylene-bound polymers. These polymers have the ability to oxidize primary alcohols to aldehydes and secondary alcohols to ketones whereas





**Scheme 3** Oxidation reaction using various permanganates.

the oxidation of aldehydes results in acids. The oxidation of alcohol using low-molecular-weight potassium permanganate gave corresponding acid through the intermediate carbonyl compound. But it is observed that, for the oxidation of primary alcohol, by using crosslinked polystyrene-supported linear and cyclic polyoxyethylene-KMnO<sub>4</sub> resins, the product is only the aldehyde instead of acid (Scheme 3).

The observation is the same even with a large excess of the polymeric permanganate species and extended duration of the reaction. The termination of the oxidation of the primary alcohol as aldehyde is due to the nonavailability of the permanganate species in the polymer networks. This difference suggests the role of polymer matrix in controlling the oxidizing ability of the permanganate species.

The oxidation reactions using macroporous DVB-crosslinked polystyrene-supported linear and cyclic polyoxyethylene-bound permanganates were carried out using a fivefold molar excess of the reagent in cyclohexane at 70°C. The progress of the reaction was followed by TLC. Simple filtration was sufficient for the separation of the crude product from the reaction mixture. The column chromatography was used to separate the pure product from the unreacted substrate. Synthetic reactions conducted using permanganate resin are listed in Tables II and III.

In the linear system, the availability of permanganates is more and hence the oxidation reaction is more feasible. Also the yield of the product is greater with the linear polyoxyethylene system. In cyclic polymer, the polymeric reagents act as a reservoir of permanganate species, releasing them slowly to the reaction mixture as they are being consumed in the course of the reaction. The rigidity of the cyclic system and the lesser swelling of the hydrophobic and rigid resin are the reasons for the slow release of the permanganate species.

### Characterization of the oxidation products

The progress of the reactions was followed by thin layer chromatography. The crude products were purified by column chromatography (SiO<sub>2</sub>, hexane-ethylacetate 5 : 2). The physical, elemental analysis, and spectral data of the products are given below.

Benzyl alcohol → Benzaldehyde bp: 178°C; IR: 1700 cm<sup>-1</sup> (-CHO). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.5 (s, 1H), 7.75 (m, 2H), 7.5 (m, 3H). Anal. Calcd. for C<sub>7</sub>H<sub>6</sub>O: C, 79.22%; H, 5.70%; O, 15.08%. Found: C, 79.20%; H, 5.76%; O, 15.04%

4-Hydroxybenzyl alcohol → 4-Hydroxybenzaldehyde mp: 118°C; IR (KBr): 1660 cm<sup>-1</sup> (-CHO). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 9.8 (s, 1H), 7.8 (d, 2H), 6.9 (d, 2H). Anal. Calcd. for C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>: C, 68.85%; H, 4.95%; O, 26.20%. Found: C, 68.27%; H, 5.03%; O, 26.70%.

2-Nitrobenzyl alcohol → 2-Nitrobenzaldehyde mp: 43°C; IR (KBr): 1690 cm<sup>-1</sup> (-CHO). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 10.43 (s, 1H), 8.1 (t, 1H), 7.9 (t, 1H), 7.8 (m, 2H). Anal. Calcd. for C<sub>7</sub>H<sub>5</sub>NO<sub>3</sub>: C, 55.63%; H, 3.33%; N, 9.27%; O, 31.76%. Found: C, 55.52%; H, 3.36%; O, 31.82%; N, 9.30%.

4-Nitrobenzyl alcohol → 4-Nitrobenzaldehyde mp: 105°C; IR (KBr): 1720 cm<sup>-1</sup> (-CHO). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 11.2 (s, 1H), 8.4 (m, 4H). Anal. Calcd. for C<sub>7</sub>H<sub>5</sub>NO<sub>3</sub>: C, 55.63%; H, 3.33%; O, 31.76%; N, 9.27%. Found: C, 55.61%; H, 3.23%; O, 31.73%; N, 9.43%.

α-Phenyl ethanol → Acetophenone bp: 202°C; IR: 1700 cm<sup>-1</sup> (-CO). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.9 (dd, 2H), 7.5 (m, 3H), 2.6 (s, 3H). Anal. Calcd. for C<sub>8</sub>H<sub>8</sub>O: C, 79.97%; H, 6.71%; O, 13.32%. Found: C, 80.03%; H, 6.78%; O, 13.19%.

Benzhydrol → Benzophenone mp: 48°C; IR (KBr): 1670 cm<sup>-1</sup> (-CO). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.9 (d, 2H), 7.7 (d, 2H), 7.5 (m, 6H). Anal. Calcd. for C<sub>13</sub>H<sub>10</sub>O: C, 85.69%; H, 5.53%; O, 8.78%. Found: C, 85.66%; H, 5.58%; O, 8.76%.

Benzoin → Benzil mp: 94.5°C; IR (KBr): 1650 cm<sup>-1</sup> (-CO). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.9 (d, 2H), 7.8 (d, 2H), 7.5 (m, 3H). Anal. Calcd. for C<sub>14</sub>H<sub>10</sub>O<sub>2</sub>: C, 79.98%; H, 4.79%; O, 15.22%. Found: C, 79.89%; H, 4.88%; O, 15.23%.

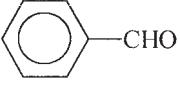
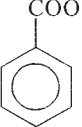
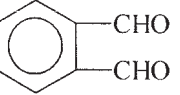
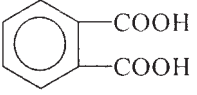
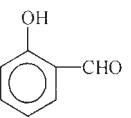
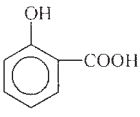
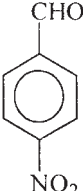
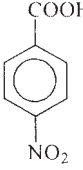
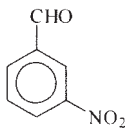
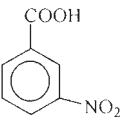
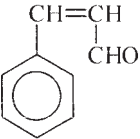
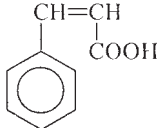
Benzaldehyde → Benzoic acid mp: 122°C; IR (KBr): 2800 cm<sup>-1</sup> (-COOH). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 8.1 (dd, 2H), 7.5 (m, 3H). Anal. Calcd. for C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>: C, 68.85%; H, 4.95%; O, 26.20%. Found: C, 68.84%; H, 4.98%; O, 26.18%.

3-Nitrobenzaldehyde → 3-Nitrobenzoic acid mp: 141°C; IR (KBr): 2810 cm<sup>-1</sup> (-COOH). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub> + CDCl<sub>3</sub>): δ 8.7 (t, 1H), 8.4 (q, 1H), 8.3 (t, 1H), 7.8 (t, 1H). Anal. Calcd. for C<sub>7</sub>H<sub>5</sub>NO<sub>4</sub>: C, 50.31%; H, 3.02%; O, 38.29%; N, 8.38%. Found: C, 50.27%; H, 3.03%; N, 8.31%; O, 38.39%.

4-Nitrobenzaldehyde → 4-Nitrobenzoic acid mp: 241°C; IR (KBr): 2850 cm<sup>-1</sup> (-COOH). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub> + CDCl<sub>3</sub>): δ 8.7 (s, 2H), 8.3 (s, 2H). Anal. Calcd. for C<sub>7</sub>H<sub>5</sub>NO<sub>4</sub>: C, 50.31%; H, 3.02%; O, 38.29%; N, 8.38%. Found: C, 50.19%; H, 3.03%; O, 38.37%; N, 8.41%.

Phthalaldehyde → Phthalic acid mp: 205°C; IR (KBr): 2900 cm<sup>-1</sup> (-COOH). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub> + CDCl<sub>3</sub>): δ 12 (s, 2H), 7.85 (m, 4H). Anal. Calcd. for C<sub>8</sub>H<sub>6</sub>O<sub>4</sub>: C, 57.84%; H, 3.64%; O, 38.52%. Found: C, 58.02%; H, 3.62%; O, 38.36%.

**TABLE II**  
**Oxidation of Aldehydes Using 2 mol % DVB-Crosslinked Polystyrene- Supported Linear and Cyclic Polyoxyethylene Permanganates**

Substrate	Time (h)	Product	Yield (%)	
			Linear	Cyclic
 Benzaldehyde	3 10	 Benzoic acid	70 97	45
 Phthalaldehyde	3 16	 Phthalic acid	55 95	25 84
 Salicylaldehyde	3 16	 Salicylic acid	60 95	27 86
 4-Nitrobenzaldehyde	3 16	 4-Nitrobenzoic acid	58 95	35 84
 3-Nitrobenzaldehyde	3 16	 3-Nitrobenzoic acid	60 95	33 85
 Cinnamaldehyde	3 16	 Cinnamic acid	58 95	34 82

Cinnamaldehyde  $\rightarrow$  Cinnamic acid mp: 133.6°C; IR (KBr): 2800  $\text{cm}^{-1}$  ( $-\text{COOH}$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.83 (d, 1H), 6.46 (d, 1H), 7.5 (m, 5H). Anal. Calcd. for  $\text{C}_9\text{H}_8\text{O}_2$ : C, 72.96%; H, 5.44%; O, 21.60%. Found: C, 72.98%; H, 5.38%; O, 21.64%.

Salicylaldehyde  $\rightarrow$  Salicylic acid mp: 159°C; IR (KBr): 2860  $\text{cm}^{-1}$  ( $-\text{COOH}$ ).  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6 + \text{CDdCl}_3$ ):  $\delta$  7.8 (d, 1H), 7.3 (t, 2H), 6.8 (m, 1H). Anal. Calcd. for  $\text{C}_7\text{H}_6\text{O}_3$ : C, 60.87%; H, 4.38%; O, 34.75%. Found: C, 60.88%; H, 4.32%; O, 34.80%.

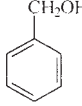
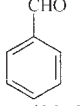
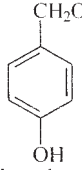
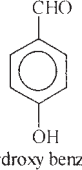
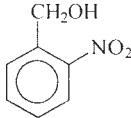
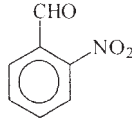
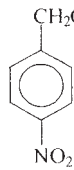
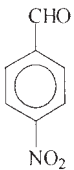
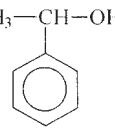
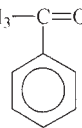
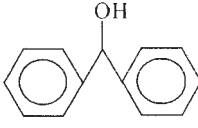
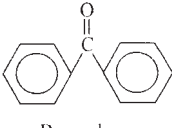
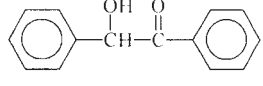
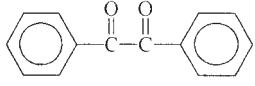
#### Effect of reaction conditions on the course of oxidation reactions

The effect of solvent, temperature, and molar excess of the reagent were investigated using benzoin to benzil oxidation as a model reaction.

#### Solvent effect

In the case of insoluble, crosslinked polymers, the accessibility of low-molecular-weight substrate into the polymer

**TABLE III**  
**Oxidation of Primary and Secondary Alcohols using 2 mol % DVB- Crosslinked Linear and Cyclic PSPOE Permanganates**

Substrate	Product	Time (h)	Yield (%)	
			Linear	Cyclic
 Benzyl alcohol	 Benzaldehyde	7 24	55 95	42 91
 4-Hydroxy benzyl alcohol	 4-Hydroxy benzaldehyde	7 24	40 85	30 80
 2-Nitrobenzyl alcohol	 2-Nitrobenzaldehyde	7 24	45 90	37 85
 4-Nitrobenzyl alcohol	 4-Nitrobenzaldehyde	7 24	45 90	35 80
 $\alpha$ -Phenyl ethanol	 Aceto phenone	7 24	45 85	35 80
 Benzhydrol	 Benzophenone	7 24	35 80	25 75
 Benzoin	 Benzil	3	100	60

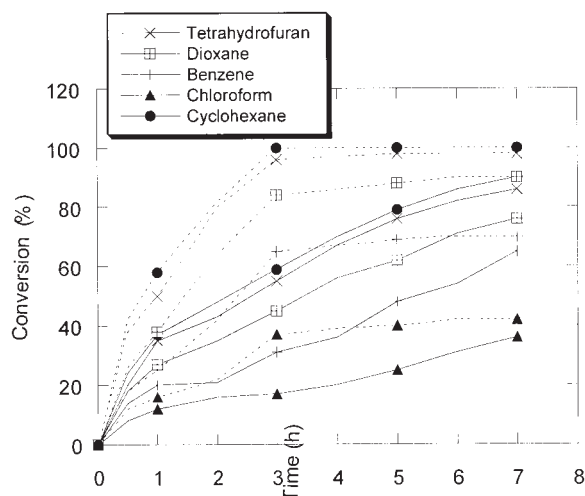
matrix facilitates the rate of reaction. Easy penetration of low-molecular-weight substrate occurs only in presence of good solvent. In good solvents the polymer network expands considerably and thus the functional groups are exposed. The hydrophilic-hydrophobic balance of the polymer matrix influences the swelling characteristics.

The oxidation reactions using polymer-supported permanganate derivatives were found to be affected by changing the reaction media. To study the effect of solvent on the extent of oxidation reactions, solvents of varying polarity, such as tetrahydrofuran, cyclohexane, benzene, chloroform, and dioxane, were used and

cyclohexane was found to be the best solvent (Fig. 1). In the linear system the flexible polyoxyethylene-bound permanganate is easily available for oxidation. The polymer network as well as the polyoxyethylene units expands easily and thus the functional groups are highly exposed in good solvents.

#### Effect of temperature

As the temperature increased the rate of reaction also increased. When the temperature is elevated easy penetration of the solvent and swelling of the polymer



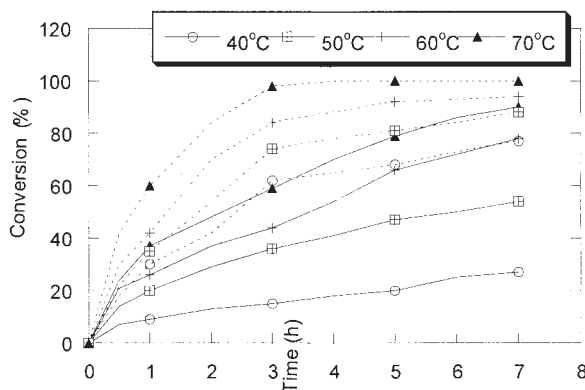
**Figure 1** Effect of solvent on the oxidation of benzoin by 2 mol % DVB-crosslinked polystyrene-supported linear (....) and cyclic (—) polyoxyethylene-bound permanganates (Chloroform, 50°C; Dioxane, 80°C; Benzene, 60°C; Cyclohexane, 70°C; Tetrahydrofuran, 60°C).

matrix takes place. Hence diffusion of soluble substrate into the polymeric reagent was enhanced, resulting in a high oxidation rate.

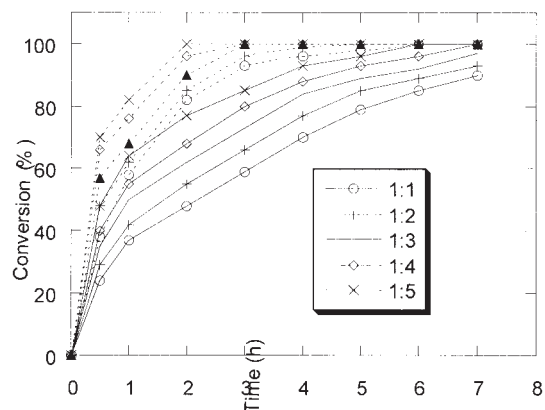
The effect of temperature was carried out at different temperatures ranging from room temperature to refluxing temperature (Fig. 2). At room temperature there was no reaction. As the temperature increased, the percentage conversion also increased. In the linear system, 80% conversion take place after 3 h, but, in the cyclic system, 90% is formed after 7 h at 70°C. This arises from the increased swelling of the DVB-crosslinked linear resin at high temperatures.

#### Effect of molar excess of the reagent

To investigate the effect of molar excess of the reagent on oxidizing ability, oxidation was carried out using



**Figure 2** Effect of temperature on the oxidation of benzoin by 2 mol % DVB-crosslinked polystyrene-supported linear (....) and cyclic (—) polyoxyethylene-bound permanganates in cyclohexane.



**Figure 3** Effect of molar excess of the reagent on the oxidation of benzoin by polystyrene-supported linear (....) and cyclic (—) polyoxyethylene-bound permanganates in cyclohexane at 70°C.

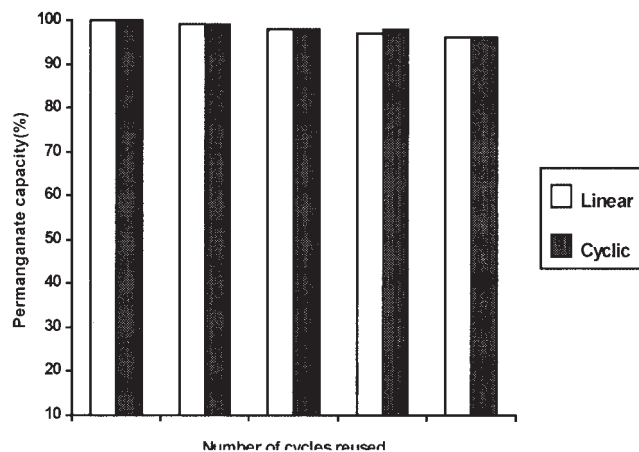
different reagent to substrate ratios. In all cases it was found that rate of reaction increases with increasing molar ratio of the reagent (Fig. 3). For 1 : 1 reagent to substrate ratio of the resin, percentage of conversion is very low and it increases with increasing reagent to substrate ratio.

#### Recycling and reuse of the reagents

One of the major advantages in the use of polymeric reagent over their low-molecular-weight counterparts is their recyclability. The used polymeric reagents can be regenerated in a single step without any appreciable loss in activity. The regeneration of the spent permanganate polymer was carried out by removing all the manganese oxides by treating with acidic ferrous ammonium sulfate solution or oxalic acid solution. The regenerated species was filtered, washed, and dried in an oven and permanganate capacity was determined.

In the present study, the polymeric reagents were recycled up to five times without any appreciable loss of activity. For this, benzoin to benzil oxidation was used as a model. There is no significant difference between the yield of oxidation reaction with a fresh sample of the polymeric reagent and with a regenerated sample. Even though a gradual decrease in the capacity of the resin on successive recycling was observed, the physical nature and filterability were found to be retained under these recycling conditions. The details of the regeneration of crosslinked polystyrene-supported linear and cyclic polyoxyethylene-bound permanganate are given in Figure 4. The complete conversion of benzoin to benzil was possible with the regenerated permanganate polymer in cyclohexane at 70°C in 5 : 1 reagent to substrate ratio.





**Figure 4** Regeneration of polystyrene-supported linear and cyclic polyoxyethylene-bound permanganates in the oxidation of benzoin in cyclohexane at 70°C in 5 : 1 reagent to substrate ratio.

### CONCLUSIONS

The work presented in this article is an attempt to study the nature of  $\text{KMnO}_4$  complexed polystyrene-supported linear and cyclic polyoxyethylene in oxidation reactions toward low-molecular-weight alcohols and aldehyde. In linear polyoxyethylene-bound permanganate polymer, the availability of permanganate is greater and hence the oxidation reaction is more feasible. Also the yield of the product is greater with the linear polyoxyethylene system. The effects of solvent, molar excess of reagent, time, and temperature on oxidation behavior were investigated by choosing benzoin to benzil conversion as the model reaction. The effect of solvent was studied using polar as well as nonpolar solvents and cyclohexane was found to be the suitable solvent. At low temperature the reaction

was very slow and the rate of reaction increased with temperature. Polymeric reagent could be used in excess to obtain a good yield without causing any separation or overoxidation products. The reagents have the advantages of easy separation, regeneration, and reuse.

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