

Polystyrene-Supported Polyoxyethylene Bound Potassium Permanganate as a Heterogeneous Oxidizing Agent

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ABSTRACT: Oxidation behavior of a 2 mol % divinylbenzene (DVB)-crosslinked polystyrene-supported permanganate function was investigated toward low molecular weight primary and secondary alcohols and aldehydes. The permanganate function was attached to a polystyrene support through cyclic polyoxyethylene (POE) units immobilized on the support. Contrary to the oxidations catalyzed by low molecular weight permanganate reagents, the oxidation of primary alcohol terminated in the aldehyde stage. The secondary alcohols were converted to the respective ketone and aldehyde to acid. The effect of the variable parameters

similar to solvent, temperature, and reagent to substrate ratio was followed. Nonpolar cyclohexane was found to be the best solvent for the present study. Also the reactivity increased with increasing temperature. The oxidizing reagent possesses a long shelf life and could be recycled several times without reduction of capacity and mechanical stability. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3708–3717, 2003

Key words: polymer supports; crosslinking; matrix; macroporous polymer; polystyrene

INTRODUCTION

The chemistry and technology of reactive functional polymers are areas which have achieved rapid progress in the recent past.^{1–4} The application of the functionalized polymers^{5–9} has achieved widespread acceptance in organic chemical transformations after the revolutionary invention of solid-phase peptide synthesis by Merrifield in 1963.^{10,11} A functional polymer can be considered as a macromolecule on which reactive functions are attached. The binding of a functional group to a polymer chain generally results in a new moiety with different structure, reactivity, and selectivity.¹² When polymers are used as supports for catalysts or organic reagents, the reactivity and selectivity of the supported catalyst or reagent may be changed by the so-called “polymer effect.”¹³ Functionalized polymers can be employed to promote organic chemical transformations and serve as an effective alternative to its low molecular weight counterpart. The polymer-supported reagent has a number of practical advantages in organic synthesis such as easy separation, reuse and recyclability, and selectivity or specificity toward chemical reactions. The attachment of a reactive function on an insoluble macromolecular matrix can also solve the problems of liability, toxicity, or odor, often experienced with low molecular weight reagents.¹⁴

Potassium permanganate is widely used as an oxidizing reagent for organic substrates.^{15–17} Ability to complex metal salts with crown ethers are of interest because of the possibility of increased salt solubility and increased anion reactivity in organic solvents.^{18,19} Sam *et al.*²⁰ found that potassium permanganate can be solubilized in benzene by complexing with dicyclohexyl-18-crown-6 to provide a convenient and efficient oxidant for organic compounds under mild conditions. In the absence of crown ether, potassium permanganate has no detectable solubility in benzene and is not reactive. Because of the high cost of crown ethers, we proposed a heterogeneous “pseudo-crown ether”-type heterogeneous permanganate oxidizing agent. For this, polyoxyethylene was attached to 2 mol % divinylbenzene (DVB)-crosslinked macroporous polystyrene by a polymer-analogous reaction. The main objective of this article involves the development of a new class of polymeric oxidizing agents based on the permanganate function attached to cyclic polyoxyethylene supported on 2 mol % DVB-crosslinked polystyrene.

EXPERIMENTAL

Materials and methods

Electronic spectra were recorded on a Shimadzu UV-160A spectrophotometer (Tokyo, Japan). IR spectra were recorded on Shimadzu IR-470 spectrophotometer. NMR spectra were recorded on a Bruker 250 MHz instrument. CHN analysis was carried out by using a Perkin-Elmer PE 2400 CHN analyzer. Melting points

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were obtained from a Buchi-530 melting point apparatus. Merrifield resin (2 mol % DVB-crosslinked, 3.84 mmol Cl/g) was supplied by Fluka, Switzerland. Polyethylene glycol (PEG₆₀₀) was a commercial product obtained from Merck, Germany. Commercially available low molecular weight compounds were purified by literature procedures. AR grade solvents were purified by distillation.

Preparation of polystyrene-supported polyoxyethylene (PSPOE)

Dry chloromethylpolystyrene (10 g, 38.4 mmol Cl) was allowed to swell in THF for 1 h. PEG₆₀₀ (23.05 mL, 38.4 mmol) was added and the temperature was maintained at 80°C. Small pieces of metallic sodium (0.8712 g, 38.4 mmol) were added slowly and heating and stirring were continued for 35 h. The resin was cooled and collected by filtration, washed with THF (2 × 20 mL), dioxane (3 × 20 mL), and hot water to remove free chloride ions and finally with methanol and dried at 50°C to constant weight.

Estimation of chlorine capacity by Volhard's method

The functionalized resin (100 mg) was fused with pyridine (4 mL) in a boiling tube for 6 h at 100°C. It was then extracted with 50% acetic acid (30 mL); conc. HNO₃ (5 mL) and AgNO₃ (0.5N, 5 mL) were added, diluted with water (20 mL), and stirred well. The unreacted AgNO₃ was titrated against standard ammonium thiocyanate with the use of ferric alum as indicator. From the titer values the chlorine capacity in millimole per gram of the resin was calculated. The chlorine capacities of the polyoxyethylene-incorporated polystyrene is 2.56 mmol/g.

Estimation of hydroxyl capacity

To estimate the presence of free hydroxyl groups after treatment with PEG, 200 mg of the dry polyoxyethylene incorporated polystyrene was heated with acetic anhydride (1 mL) in pyridine (9 mL) in a conical flask. 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 (10 mL) was added, shaken well, and titrated against 0.1N potassium hydroxide with phenolphthalein as indicator. No considerable hydroxyl value was obtained on titration.

Synthesis of polystyrene-supported potassium permanganate

To a suspension of polystyrene-supported polyoxyethylene (5 g) in benzene (20 mL), excess KMnO₄ was

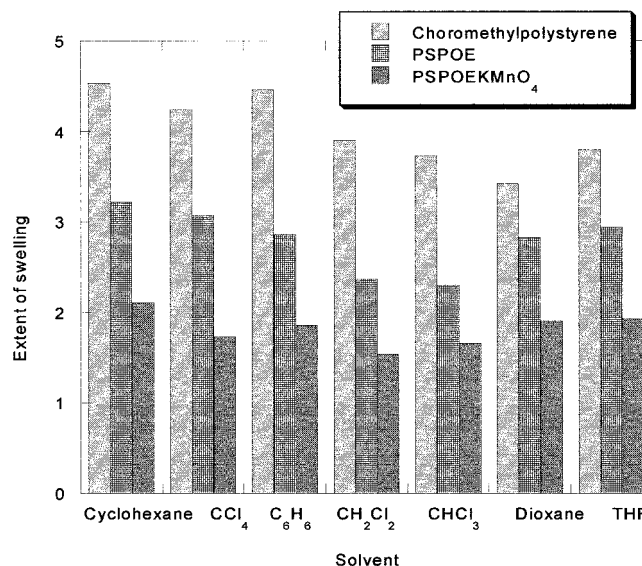


Figure 1 Swelling studies of 2 mol % DVB-crosslinked chloromethylpolystyrene, PSPOE, and PSPOE-KMnO₄.

added and stirred at room temperature for 10 h. The black-colored resin was isolated and washed with distilled water until the filtrate was completely free from permanganate ion. The resin was washed with benzene, methanol, and acetone and dried in vacuum. This resin was used for the oxidation reactions.

Determination of the extent of permanganate functions

A definite amount of the dry permanganate complexed resins was accurately weighed and suspended in excess known volume of 2N H₂SO₄ for 1 h. A known excess of standard ferrous ammonium sulfate solution was added and stirred until the dark color of the resin had completely disappeared. The unreacted ferrous ammonium sulfate solution was titrated against standard KMnO₄ solution. Permanganate content was 1.86 mmol/g.

Swelling studies

The extent of swelling was determined in the case of chloromethylpolystyrene, polymer-supported polyoxyethylene, and permanganate-complexed resins. In a dry previously weighed sintered crucible (G₃), dry resin (2 g) was taken and equilibrated with solvents such as cyclohexane, benzene, dioxane, carbon tetrachloride, chloroform, dichloromethane, and tetrahydrofuran for 24 h. The excess of solvent was drained. The weight of swollen resin was calculated from the difference in weights. For each case, the extent of swelling (α) was calculated from the dry and swollen weights; the results are summarized in Figure 1.

Oxidation studies using potassium permanganate complexes of DVB-crosslinked polystyrene-supported polyoxyethylene

Oxidation reactions

To fivefold molar excess of macroporous DVB-crosslinked polystyrene-supported polyoxyethylene bound permanganate resin, substrate in 20 mL cyclohexane was added. The reaction mixture was stirred at 70°C. The extent of the conversion of the substrate to product was followed at different time intervals by thin-layer chromatography. After complete conversion, the insoluble spent resin was filtered and washed with solvent. The solution was concentrated to dryness. The product was 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. Initially standard solutions of benzoin and benzil were prepared in dioxane having a concentration of 1 mg/mL. By using these two different solution mixtures, different concentrations of benzoin to benzil were prepared and their absorbances were measured at 387 nm using UV spectrophotometer and a calibration curve of concentration of benzil versus absorbance 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. Calibration curve was plotted by using other solvents such as tetrahydrofuran, dichloromethane, carbon tetrachloride, chloroform, cyclohexane, and benzene.

Effect of solvent on the extent of oxidation

To investigate the solvent dependence on the extent of oxidation with various polystyrene supports, benzoin to benzil conversion was selected as a model reaction. The typical procedure is as follows: 100 mg benzoin was dissolved in 10 mL solvent and the required amount of polymeric reagent was added and heated below the refluxing temperature of the solvent. By using a micropipette, 0.5 mL of the reaction mixture was withdrawn, at regular intervals of time. It was transferred into a 5 mL standard measuring flask and made up to 5 mL. The absorbance of this solution was measured at 387 nm. From the absorbance, the percentage of benzil formed was calculated by using the calibration curve. The experiment was repeated by using various solvents having different polarities. The solvents used were chloroform, carbon tetrachloride, dichloromethane, benzene, cyclohexane, dioxane, and tetrahydrofuran.

Effect of temperature

The experiment described above was repeated at different temperatures ranging from room temperature to below the refluxing temperature of the solvent used to study the effect of temperature on the extent of reaction. The progress of the reaction was followed spectrophotometrically at 387 nm. From the absorbance, the percentage of benzil formed at each temperature was calculated by using the calibration curve.

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. By using a micropipette, a definite volume (5 mL) of the reaction mixture was transferred to a 5-mL standard flask and made up to 5 mL. The absorbance of this solution was measured at 387 nm. From the absorbance, the percentage of benzil formed was calculated by using the calibration curve.

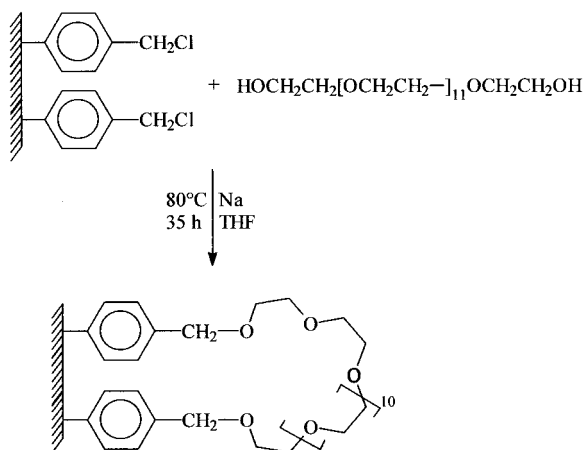
Recycling and reuse of the spent polymeric permanganate resin

The spent polymer was washed thoroughly with chloroform, dioxane, and methanol to remove any residual soluble organic substrate or product. The washed resin was dried and stirred for 2 h with 2N solution of ferrous ammonium sulfate in the presence of 2N H₂SO₄ (10 mL) to remove all oxides of manganese. The white beads were filtered, washed with distilled water, and dried. The regenerated polymer was functionalized with potassium permanganate. This regenerated polystyrene-supported polyoxyethylene-bound permanganate resin was used for the oxidation of alcohols and aldehydes.

RESULTS AND DISCUSSION

Preparation of polystyrene-supported polyoxyethylene

For the synthesis of polystyrene-supported polyoxyethylene, 2 mmol % DVB-crosslinked chloromethyl macroporous polystyrene was allowed to swell in THF. The swelled resin was treated with PEG₆₀₀ and metallic sodium. The reaction was carried out at 80°C in an oil bath for 35 h. The method of preparation is listed in Scheme 1. The molar ratio of diol to polystyrene was 1 : 2 to ensure the coupling of both ends of diol with the polystyrene support. The resultant polymer was washed with water, methanol, acetone, and Soxhlet extracted with THF and dried in an oven at 40°C.



Scheme 1 Preparation of polystyrene-supported polyoxyethylene (PSPOE).

The various crosslinked resins were characterized by IR (KBr) spectroscopy. It was found that in all cases a strong band was obtained at 1100 cm^{-1} because of asymmetrical C—O—C stretching of the oxyethylene units. This band indicates the presence of ether linkage in the polymer. 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 decomposed to acetic acid. This was titrated against alkali by using phenolphthalein as indicator.²² However, the estimation did not give the presence of any free hydroxyl groups. The residual chlorine in crosslinked polystyrene-supported polyoxyethylene (POE) was estimated by the pyridine fusion method.²³ The extent of grafting of POE into chloromethylated crosslinked polystyrene was calculated from the residual chlorine content, which corresponds to 67% of chlorine substitution by polyoxyethylene units.

Incorporation of potassium permanganate into DVB-crosslinked polystyrene-supported polyoxyethylene (PSPOE- K^+MnO_4^-)

The DVB-crosslinked polymeric polyoxyethylene was allowed to swell in benzene in a closed amber-colored reagent bottle. The swelled resin was equilibrated with excess potassium permanganate and stirred in a

twist action shaker at room temperature for 10 h (Scheme 2). The black-colored resin was filtered and washed with distilled water to remove all the manganese dioxide. The product resin was dried in vacuum. In all cases, the weight of the complexed resin was found to be twice the weight of the starting material.

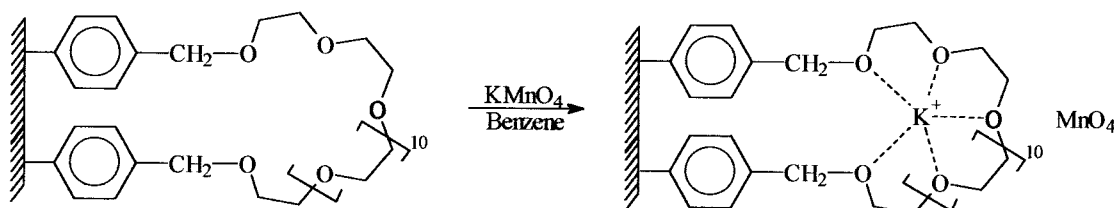
The IR spectrum (KBr) of the functionalized resins showed absorptions at 840 and 940 cm^{-1} because of ν_1 and ν_2 vibrations of MnO_4^- ion.²⁴ The UV spectroscopy is also used for the characterization of KMnO_4 -bound resins.²⁵ The observed transitions are $18,552$ (${}^1t_1 \rightarrow {}^3T_2$), $22,471$ (${}^3t_2 \rightarrow {}^1T_1$), $33,333$ (${}^1t_1 \rightarrow {}^1T_2$), and $40,160\text{ cm}^{-1}$ (${}^3t_2 \rightarrow {}^1T_1$).

For the estimation of potassium permanganate incorporation, a definite amount of the functionalized resin was suspended in excess known volume of $2\text{N H}_2\text{SO}_4$. A measured excess standard ferrous ammonium sulfate solution was added and stirred until the dark color of the resin completely disappeared and turned white. The unreacted ferrous ammonium sulfate solution was titrated against standard KMnO_4 solution. These estimations were also conducted by using oxalic acid titrations in the presence of dilute sulfuric acid. Permanganate capacity was 1.86 mmol/g .

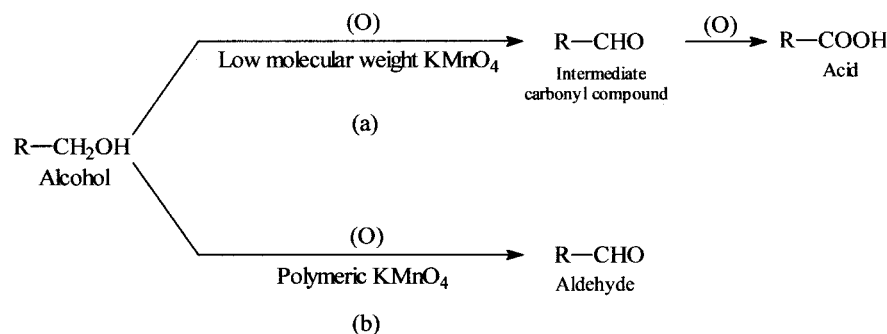
Swelling studies

Swelling characteristics of crosslinked chloromethylated polystyrene, polystyrene-supported polyoxyethylene, and KMnO_4 complexed resins were carried out in solvents of varying polarities (Fig. 1). The swelling studies are important for identifying the good solvent to select the suitable reaction medium for performing reaction on polymer supports.²⁶ The extent of swelling depends on the crosslink ratio and the chemical nature of the polymer support used. The crosslink ratio controls the behavior of a resin on contact with a solvent and is inversely proportional to the degree of swelling.²⁷ In the present study, the extent of swelling (α) of polymer in solvent is expressed as:

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



Scheme 2 Complexation of PSPOE with potassium permanganate.



Scheme 3 Oxidation of alcohols using (a) low molecular weight KMnO_4 , and (b) polymeric KMnO_4 .

From Figure 1 it is found that in all cases, nonpolar DVB-crosslinked system shows maximum swelling in nonpolar solvent. In all cases DVB-crosslinked polymer was found to have maximum swelling in cyclohexane. The swelling nature of the polymer varies on functionalization. Thus, on the incorporation of POE, the swelling decreased and it again decreased on complexation with potassium permanganate.

Oxidation reactions using DVB-crosslinked PSPOE- KMnO_4 resin

The oxidation reactions were carried out by using 2 mol % crosslinked PSPOE- KMnO_4 resin. These resins have the ability to oxidize primary and secondary alcohols to aldehydes and ketones, respectively. Oxidation of aldehyde resulted in acids. The oxidation reactions of alcohols using low molecular weight potassium permanganate give acid through the intermediate carbonyl compound but it is observed that by using crosslinked PSPOE- KMnO_4 resin, the product is only aldehyde instead of acid. This observation is same even with large excess of the polymeric permanganate species and is extended during the reaction. This termination of the oxidation of the primary alcohol as aldehyde may be due to the nonavailability of the permanganate species in the polymer networks. This difference suggests the role of the polymer matrix in controlling the oxidizing ability of the permanganate species. A general scheme of the oxidation of alcohol to acid through aldehyde by using low molecular weight KMnO_4 and the oxidation of alcohol by using polymeric KMnO_4 is given in Scheme 3.

Oxidation reactions using DVB-crosslinked PSPOE- KMnO_4 resin

The details of the oxidation reactions carried out by using DVB-crosslinked PSPOE- KMnO_4 resin are given in Tables I and II. The reaction was carried out by stirring a solution of low molecular weight substrate in cyclohexane with fivefold molar excess of the reagent at 70°C . The progress of the reaction was fol-

lowed by thin-layer chromatography. In this case, the time required for the completion of the reaction was found to be much higher because the polymeric reagent acts as a reservoir of permanganate species and releases them slowly to the reaction mixture as they are being consumed in the course of the reaction. The rigidity of the DVB crosslinking and the lower swelling of the macroporous resin are the reason for the slow release of the permanganate species. The crude product was separated by filtration and column chromatography is used to separate the product from the unreacted substrate.

Characterization of the products

The progress of the reactions was followed by thin-layer chromatography. Whenever required, the crude products were purified by column chromatography (SiO_2 , hexane-ethylacetate 5 : 2). The physical, elemental analysis, and spectral data of the products are given below.

Benzyl alcohol \rightarrow Benzaldehyde

mp: 178°C ; IR: 1700 cm^{-1} ($-\text{CHO}$); $^1\text{H-NMR}$ (CDCl_3): δ 7.5 (s, 1H), 7.75 (m, 2H), 7.5 (m, 3H). ANAL. calcd for $\text{C}_7\text{H}_6\text{O}$: C, 79.22%; H, 5.70%; O, 15.08%. Found: C, 79.20%; H, 5.76%; O, 15.04%.



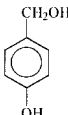
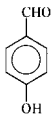


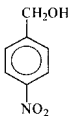
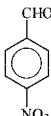
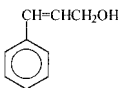



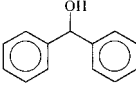
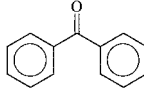
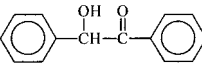
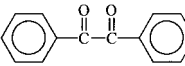
4-Hydroxybenzyl alcohol \rightarrow 4-Hydroxybenzaldehyde

mp: 118°C ; IR (KBr): 1660 cm^{-1} ($-\text{CHO}$); $^1\text{H-NMR}$ (CDCl_3): δ 9.8 (s, 1H), 7.8 (d, 2H), 6.9 (d, 2H). ANAL. calcd for $\text{C}_7\text{H}_6\text{O}_2$: C, 68.85%; H, 4.95%; O, 26.20%. Found: C, 68.27%; H, 5.03%; O, 26.70%.

2-Nitrobenzyl alcohol \rightarrow 2-Nitrobenzaldehyde

mp: 43°C ; IR (KBr): 1690 cm^{-1} ($-\text{CHO}$); $^1\text{H-NMR}$ (CDCl_3): δ 10.43 (s, 1H); 8.1 (t, 1H); 7.9 (t, 1H); 7.8 (m, 2H). ANAL. calcd for $\text{C}_7\text{H}_5\text{NO}_3$: C, 55.63%; H, 3.33%; O, 31.76%; N, 9.27%. Found: C, 55.52%; H, 3.36%; O, 31.82%; N, 9.30%.

TABLE I
Oxidation of Primary and Secondary Alcohols Using DVB-PSPOE-KMnO₄^a

Substrate	Time (h)	Product ^b	Yield ^c (%)
 Benzyl alcohol	7 24	 Benzaldehyde	42 90
 4-Hydroxybenzyl alcohol	7 24	 4-Hydroxybenzaldehyde	28 76
 2-Nitrobenzyl alcohol	7 24	 2-Nitrobenzaldehyde	35 83
 4-Nitrobenzyl alcohol	7 24	 4-Nitrobenzaldehyde	30 78
 Cinnamyl alcohol	7 24	 Cinnamaldehyde	37 80
 α -Phenyl ethanol	7 24	 Acetophenone	38 85
 Benzhydrol	7 24	 Benzophenone	35 80
 Benzoin	6	 Benzil	100

^a All the reactions were carried out in cyclohexane using fivefold molar excess of the reagent at 70°C.

^b Products were characterized by comparison with authentic samples.

^c Isolated yield.

4-Nitrobenzyl alcohol \rightarrow 4-Nitrobenzaldehyde

mp: 105°C; IR (KBr): 1720 cm⁻¹ (—CHO); ¹H-NMR (CDCl₃): δ 11.2 (s, 1H), 8.4 (m, 4H). ANAL. calcd for C₇H₅NO₃: 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%.

Cinnamyl alcohol \rightarrow Cinnamaldehyde

bp: 249°C; IR: 1670 cm⁻¹ (—CHO); ¹H-NMR (CDCl₃): δ 9.7 (d, 1H), 7.4 (m, 3H), 6.6 (q, 2H). ANAL. calcd for C₉H₈O: C, 81.79%; H, 6.10%; O, 12.11%. Found: C, 81.80%; H, 6.03%; O, 12.17%.





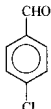
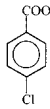


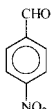
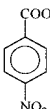

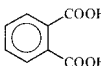

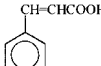


α -Phenyl ethanol \rightarrow Acetophenone

bp: 202°C; IR: 1700 cm⁻¹ (—CO); ¹H-NMR (CDCl₃): δ 7.9 (dd, 2H), 7.5 (m, 3H), 2.6 (s, 3H). ANAL. calcd for C₈H₈O: C, 79.97%; H, 6.71%; O, 13.32%. Found: C, 80.03%; H, 6.78%; O, 13.19%.

Benzhydrol \rightarrow Benzophenone

mp: 48°C; IR (KBr): 1670 cm⁻¹ (—CO); ¹H-NMR (CDCl₃): δ 7.9 (d, 2H), 7.7 (d, 2H), 7.5 (m, 6H); ANAL. calcd for C₁₃H₁₀O: C, 88.81%; H, 5.61%; O, 5.58%.

TABLE II
Oxidation of Aldehydes Using DVB-PSPOE-KMnO₄^a

Substrate	Time (h)	Product ^b	Yield ^c (%)
 Benzaldehyde	7 20	 Benzoic acid	58 20
 2-Chlorobenzaldehyde	7 24	 2-Chlorobenzoic acid	38 89
 4-Chlorobenzaldehyde	7 24	 4-Chlorobenzoic acid	32 81
 3-Nitrobenzaldehyde	7 24	 3-Nitrobenzoic acid	38 86
 4-Nitrobenzaldehyde	7 24	 4-Nitrobenzoic acid	40 90
 Phthalaldehyde	7 24	 Phthalic acid	25 69
 Cinnamaldehyde	7 24	 Cinnamic acid	40 93
 Salicylaldehyde	7 24	 Salicylic acid	36 88

^a All the reactions were carried out in cyclohexane using fivefold molar excess of the reagent at 70°C.

^b Products were characterized by comparison with authentic samples.

^c Isolated yield.

C, 85.69%; H, 5.53%; O, 8.78%. Found: C, 85.66%; H, 5.58%; O, 8.76%.

C₁₄H₁₀O₂: C, 79.98%; H, 4.79%; O, 15.22%. Found: C, 79.89%; H, 4.88%; O, 15.23%.

Benzoin → Benzil

mp: 94.5°C; IR (KBr): 1650 cm⁻¹ (—CO); ¹H-NMR (CDCl₃): δ 7.9 (d, 2H), 7.8 (d, 2H), 7.5 (m, 3H). ANAL. calcd for

Benzaldehyde → Benzoic acid

mp: 122°C; IR (KBr): 2800 cm⁻¹ (—COOH); ¹H-NMR (CDCl₃): δ 8.1 (dd, 2H), 7.5 (m, 3H). ANAL. calcd for C₇H₆O₂:

C, 68.85%; H, 4.95%; O, 26.20%. Found: C, 68.84%; H, 4.98%; O, 26.18%.

2-Chlorobenzaldehyde → 2-Chlorobenzoic acid

mp: 139°C; IR (KBr): 2900 cm^{-1} (—COOH); $^1\text{H-NMR}$ (DMSO- d_6 + CDCl_3): δ 9.0 (s, 1H), 7.8 (q, 1H), 7.4 (m, 2H). ANAL. calcd for $\text{C}_7\text{H}_5\text{ClO}_2$: C, 53.70%; H, 3.22%; O, 20.44%. Found: C, 53.78%; H, 3.28%.

4-Chlorobenzaldehyde → 4-Chlorobenzoic acid

mp: 240°C; IR (KBr): 2816 cm^{-1} (—COOH); $^1\text{H-NMR}$ (DMSO- d_6 + CDCl_3): δ 7.9 (d, 2H), 7.4 (d, 2H). ANAL. calcd for $\text{C}_7\text{H}_5\text{ClO}_2$: C, 53.70%; H, 3.22%; O, 20.44%. Found: C, 53.72%; H, 3.30%.

3-Nitrobenzaldehyde → 3-Nitrobenzoic acid

mp: 141°C; IR (KBr): 2810 cm^{-1} (—COOH); $^1\text{H-NMR}$ (DMSO- d_6 + CDCl_3): δ 8.7 (t, 1H), 8.4 (q, 1H), 8.3 (t, 1H), 7.8 (t, 1H). ANAL. calcd for $\text{C}_7\text{H}_5\text{NO}_4$: 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^{-1} (—COOH); $^1\text{H-NMR}$ (DMSO- d_6 + CDCl_3): δ 8.7 (s, 2H), 8.3 (s, 2H). ANAL. calcd for $\text{C}_7\text{H}_5\text{NO}_4$: 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^{-1} (—COOH); $^1\text{H-NMR}$ (DMSO- d_6 + CDCl_3): δ 12 (s, 2H), 7.85 (m, 4H). ANAL. calcd for $\text{C}_8\text{H}_6\text{O}_4$: C, 57.84%; H, 3.64%; O, 38.52%. Found: C, 58.02%; H, 3.62%; O, 38.36%.

Cinnamaldehyde → Cinnamic acid

mp: 133.6°C; IR (KBr): 2800 cm^{-1} (—COOH); $^1\text{H-NMR}$ (CDCl_3): δ 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 → Salicylic acid

mp: 159°C; IR (KBr): 2860 cm^{-1} (—COOH); $^1\text{H-NMR}$ (DMSO- d_6 + CDCl_3): δ 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, time, temperature, and molar excess of the polymeric reagent was investigated by using benzoin to benzil oxidation as a model reaction.

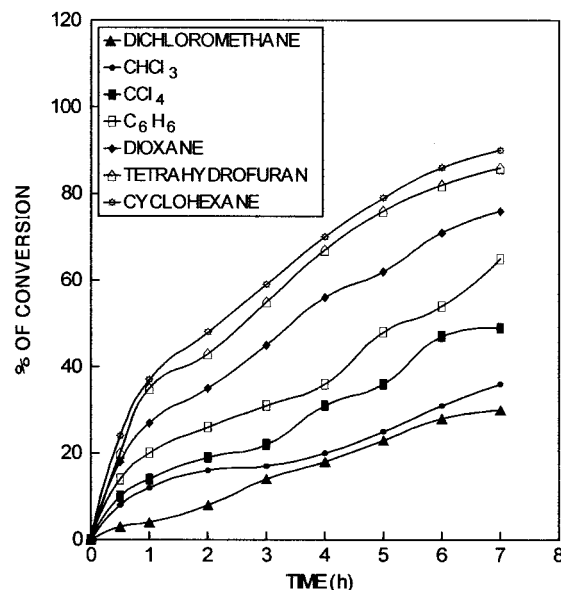


Figure 2 Effect of solvent on the extent of reaction of 2 mol % DVB-crosslinked PSPOE- KMnO_4 resin.

To follow the extent of reaction, 5 mL of the reaction mixture was pipetted out by using a micropipette without solid particles and transferred into a 5-mL standard flask and made up to definite volume. The progress of the reaction was followed spectrophotometrically at 387 nm at different time intervals.

Solvent effect

In the case of insoluble, crosslinked polymers, the accessibility of low molecular weight substrate into the polymer matrix facilitates the rate of reaction. Easy penetration of the low molecular weight substrate occurs only in presence of good solvent because in good solvents, polymer network expanded considerably and thus the functional groups are exposed to the continuous phase.

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, carbon tetrachloride, 1,4-dioxane, and dichloromethane were used. In the present system, cyclohexane was found to be the best solvent (Fig. 2). This is due to the compatibility between the polymer support and cyclohexane.

Temperature effect

As the temperature increases, the rate of conversion of benzoin to benzil also increased. At elevated temperature, easy penetration of the solvent and extensive swelling of the polymer matrices take place. Hence,

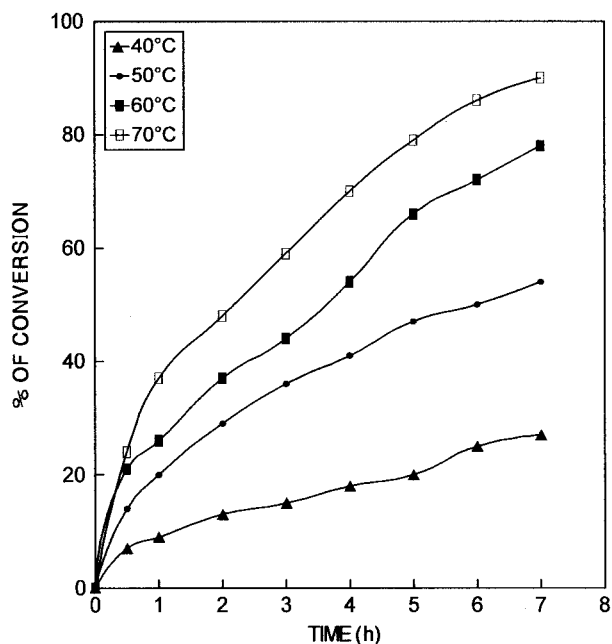


Figure 3 Effect of temperature on the extent of reaction of 2 mol % DVB-crosslinked PSPOE-KMnO₄ resin.

the diffusion of soluble substrate into the polymeric reagent was enhanced and hence greater conversion of the substrate took place.

The effect of temperature in the case of macroporous DVB-crosslinked PSPOE-KMnO₄ was carried out at different temperatures in cyclohexane (Fig. 3). At 30°C, benzoin was not oxidized by using this resin. This is due to high rigidity of the macroporous DVB-crosslinked system and hence the penetration of substrate through the pores was also restricted. As the temperature increases, the percentage of conversion also increases. It was found that 90% conversion occur at 70°C after 7 h.

Effect of molar excess of the reagent

To investigate the effect of reagent to substrate ratio on oxidizing ability, oxidations were carried out by using different reagent-to-substrate ratios. In all cases, it was found that rate of reaction increases with increasing the molar ratio of the reagent. Using 5 : 1 reagent-to-substrate ratio, 100% oxidation of benzoin occurs at 6 h by using macroporous DVB-crosslinked PSPOE-KMnO₄ in cyclohexane at 70°C (Fig. 4).

Stability and shelf life of the reagent

KMnO₄ complexed polystyrene-supported polyoxyethylene resin can be stored for a long time without appreciable loss in capacity. To study the shelf-life period of the polymeric reagents, the polymers were kept in sealed bottles in a dessicator for a period of 1

year and the capacities were determined again. It is observed that in the capacities of the permanganate resins no appreciable change was observed even after 1 year.

Recycling and reuse of the reagents

One of the major advantages in the use of the 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 resin was carried out after 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. The dried DVB-crosslinked polystyrene-supported polyoxyethylene resin was equilibrated with potassium permanganate in benzene medium.

In the present study, the polymeric reagents were recycled up to seven times without any appreciable loss of activity. These recycled polymers were used in oxidation studies. There is no significant difference between the yield of oxidation reactions 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 but the physical nature and filterability were found to be retained under these recycling conditions. The loss observed during the successive recycling was only mechanical. The details of the regeneration and

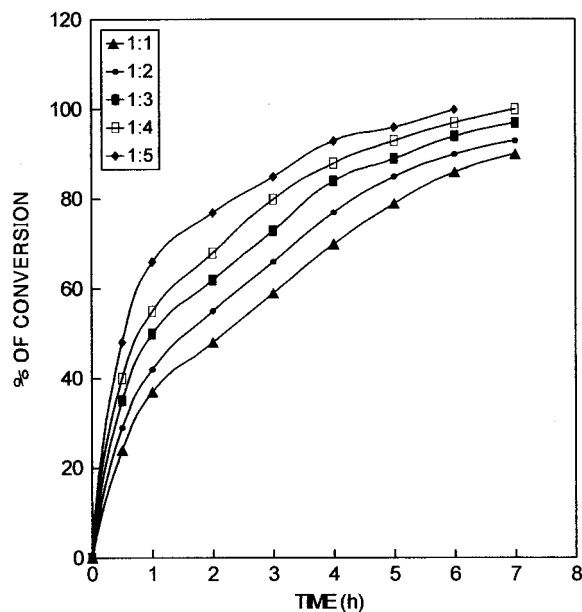


Figure 4 Effect of molar excess on the extent of reaction of 2 mol % DVB-crosslinked PSPOE-KMnO₄ resin.

TABLE 3
Recyclability of KMnO_4 Complexed Resin

No. of cycles/regeneration	Permanganate capacity (mmol/g)
1	1.86
2	1.86
3	1.85
4	1.85
5	1.85
6	1.83
7	1.80

recycling of crosslinked-PSPOE- K^+MnO_4^- are given in Table III.

CONCLUSION

The work presented in this article deals with the chemistry and synthetic application of a new class of solid-phase synthetic oxidizing reagent for the oxidation of primary and secondary alcohols, and aldehydes. From these results, it is clear that the permanganate-incorporated polystyrene-supported polyoxyethylenes is effective in carrying out the oxidation of primary and secondary alcohols to aldehydes and ketones, and aldehydes to acids. The termination of the oxidation of primary alcohol to aldehyde is contrary to the corresponding oxidation, using a low molecular oxidizing agent in which acid is the final oxidation product. This is due to the role of the three-dimensional polymer matrix. The effect of variables of the oxidation reactions such as solvent, temperature, and molar excess of the reagent were followed. The extent of oxidation was followed for the conversion of benzoin to benzil as a model reaction. Investigations reveal that the nonpolar DVB-crosslinked system was compatible with nonpolar solvent cyclohexane. When the temperature and molar excess were increased, the percentage of conversion also increased.

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