

Polystyrene-Supported Polyoxyethylene Bound Permanganate as Oxidising Agent: Effect of the Nature of Crosslinking on Oxidation Behaviour

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The effect of the nature of crosslinking agent on the oxidation of polystyrene supported polyoxyethylene bound permanganate is present in this paper. For this microporous rigid divinyl benzene (DVB)-crosslinked and flexible 1,6-hexanediol diarylate (HDODA)-crosslinked polystyrene were used as supports. Polyoxyethylene is incorporated by polymer-analogous reactions. Permanganate functions were incorporated by equilibration with potassium permanganate in benzene medium. The permanganate capacity is higher for the flexible HDODA-crosslinked system. The oxidizing abilities of these heterogeneous oxidizing agents were investigated towards primary and secondary alcohols to aldehydes and ketons. The effect of various reaction parameters on oxidation behaviour was also investigated. The oxidizing ability of flexible HDODA-crosslinked system is higher than the rigid DVB-crosslinked system. The spent polystyrene-supported polyoxyethylene bound permanganate resin could be recycled and reused without loss of activity.

Key Words: Microporous polymer, Matrix, Polystyrene, Supports, Crosslinking.

INTRODUCTION

A number of reactive functions attached to polymeric supports can be used in organic synthesis¹⁻⁴. The binding of a functional group into a polymer chain generally results in a new reagent with different structure, reactivity and selectivity⁵. Polymeric reagents are the reactive species bound to a polymeric backbone. They possess the physical properties of the polymer and the chemical properties of the attached reagent function⁶. A polymer-supported organic reagent can provide an effective alternative to its low molecular weight counterpart. Easy separation, reuse, and recyclability, selectivity/specificity towards chemical reactions are the advantages of the polymer-supported reagent. The polyethers form complexes with salts by electrostatic force of attraction between the cations and the C-O dipoles of the polyethers⁷. The cation binding ability of crown ether is high in organic media and is very slow in aqueous media because of the strong hydration of cations⁸. The synthesis of polymeric pseudocrown

ethers and their complexation with ions and acids are reported⁹. The crown ether bound permanganate is an efficient oxidant only in benzene medium¹⁰.

This literature includes the effect of nature of crosslinking agents on the oxidation of low molecular weight alcohols and aldehydes catalyzed by polystyrene-supported polyoxyethylene bound permanganate. The polymer supports used are polyoxyethylene (POE) incorporated low crosslinked microporous polystyrene with divinylbenzene (DVB) and 1,6-hexanediol diacrylate (HDODA) crosslinking. The permanganate functions were attached by the complexation of potassium permanganate with the ether oxygen of the polystyrene-supported polyoxyethylene.

EXPERIMENTAL

All the reagents were of certified ACS reagent grade. Styrene, divinylbenzene and 1,6-hexanediol diacrylate were purchased from Aldrich Chemical Company, USA. Polyvinyl alcohol (PV A 72,000) was purchased from Sigma Chemical Company, USA. Benzoyl peroxide (recrystallized before use) was from Sisco, Mumbai. Polyethyleneglycol (PEG₆₀₀) was obtained from Merck, Germany. Electronic spectra were recorded on Shimadzu UV 160A spectrophotometer. IR-spectra were recorded on Shimadzu IR-470 spectrophotometer and NMR on a Bruker 250 MHz instrument. CHN analysis was carried out using a Perkin Elmer PE 2400 CHN analyzer. Melting points were obtained from Buchi-530 melting point apparatus.

Preparation of 2 mol % DVB- and HDODA-crosslinked polystyrenes

Styrene and divinylbenzene were washed with 1 % sodium hydroxide solution (15 mL × 3) and distilled water and dried over anhydrous sodium sulfate. Polyvinyl alcohol, 1 % solution, (mol. wt. 72,000) in distilled water was kept at 80°C. A mixture of styrene, crosslinking agent, toluene (as diluent, 10 mL) and benzoyl peroxide (as initiator) were prepared and flushed with nitrogen gas. This mixture was added to the polyvinyl alcohol solution with stirring. After 6 h the beaded polymers were collected and washed with hot water, acetone, benzene, chloroform and finally with methanol and dried in the oven at 50°C.

Chloromethylation of crosslinked polystyrene¹¹

The dry polystyrene beads (10 g) were allowed to swell in dichloromethane (60 mL). Stannic chloride (1 mL, 99.9 %) was added to the swollen crosslinked polymer containing chloromethyl methyl ether (60 mL) for 10 h at 0°C with magnetic stirring. The functionalized resin was collected by filtration, washed with THF, THF-H₂O (1:1), THF in HCl (1:1), THF, hot water and finally with methanol. For further purification the resin was Soxhlet extracted with THF and dried.

The extent of chloromethylation was followed by modified Volhard's method¹². The chloromethyl polystyrene (200 mg) was fused with pyridine (4 mL) for 6 h at 100°C. It was then extracted with 50 % acetic acid (30 mL), conc. HNO₃ (5 mL) and AgNO₃ (0.5 N, 5 mL) and diluted with water (20 mL) and stirred well. The excess silver nitrate was back titrated against standard ammonium thiocyanate using ferric alum as indicator.

Synthesis of polystyrene-supported polyoxyethylene (PSPOE)

Chloromethylpolystyrene (10 g) was allowed to swell in THF and polyethyleneglycol (PEG₆₀₀) was added at 80°C. Small pieces of metallic sodium were added slowly and heating and stirring were continued for 35 h. The resin was collected by filtration, washed with THF (2 × 20 mL), dioxane (3 × 20 mL) and hot water and finely with methanol and dried in vacuum.

Estimation of hydroxyl group capacity¹³: 200 mg of the dry polystyrene-supported polyoxyethylene was heated with acetic anhydride (1 mL) in pyridine (9 mL) in a conical flask with occasional shaking 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 0.1 N potassium hydroxide with phenolphthalein as indicator. No detectable presence of hydroxyl group was observed.

Incorporation of permanganate functions to 2 mol % DVB- and HDODA-crosslinked polystyrenes

The polystyrene-supported polyoxyethylene (5 g) in benzene (20 mL), excess potassium permanganate was added and stirred at room temperature for 10 h. The black coloured resin was washed with distilled water, benzene, methanol and acetone and dried in vacuum. This resin is used in the oxidation reactions.

Determination of the extent of permanganate functions¹⁴: The permanganate complexed polymer (2 g) was suspended in 2 N H₂SO₄ (10 mL) for 1 h. A known excess of standard ferrous ammonium sulphate solution was added and stirred until the dark colour of the polymer had completely disappeared. The unreacted ferrous ammonium sulphate solution was titrated against standard potassium permanganate solution.

Swelling studies of 2 mol % DVB- and HDODA-crosslinked polystyrenes

The dry polymer (2 g) was taken in a previously weighed sintered crucible (G₃) and equilibrated with solvents such as cyclohexane, benzene, dioxane, CCl₄, CHCl₃, CH₂Cl₂ and THF for 24 h. The excess of solvent was drained. The weight of the swollen polymer was calculated from the difference in weights. The extent of swelling (α) was calculated from the dry and swollen weights and the results are summarized in Table-2.

Oxidation reactions of potassium permanganate complexes of cross-linked polystyrene-supported polyoxyethylene

The crosslinked polystyrene-supported polyoxyethylene bound permanganate resin (five fold molar excess) in suitable solvent (20 mL) was stirred with the substrate under reflux temperature. The extent of the conversion of the substrate to product was followed by thin layer chromatography. After complete conversion, the insoluble spent polymer was filtered and washed with solvent. The product was purified by column chromatography and characterized.

Monitoring the course of the oxidation reaction: The standard solutions of benzoin and benzil were prepared and their absorbances different concentrations were measured at 387 nm using UV spectrophotometer. From the absorbance, the percentage of benzil in the reaction mixture was calculated. Calibration curve was plotted using solvents such as cyclohexane, benzene, dioxane, CCl_4 , CHCl_3 , CH_2Cl_2 and THF.

Effect of solvent: Benzoin to benzil is selected as the model reaction to study the effect of various parameters like solvent, temperature and molar excess on the oxidation reactions. The percentage of benzil was calculated using the calibration curve.

Benzoin (100 mg) was dissolved in solvent (10 mL) and the required amount of polymeric reagent was added and heated below the refluxing temperature of the solvent. 0.5 mL of the reaction mixture was transferred into a 5 mL standard measuring flask and make up to 5 mL. The absorbance of the make up solution was measured at 387 nm. The percentage of benzil formed was calculated using calibration curve. The solvents used were cyclohexane, benzene, dioxane, CCl_4 , CHCl_3 , CH_2Cl_2 and THF.

Effect of temperature: The experiment was repeated at different temperatures ranging from room temperature to below the refluxing temperature of the solvent. 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.

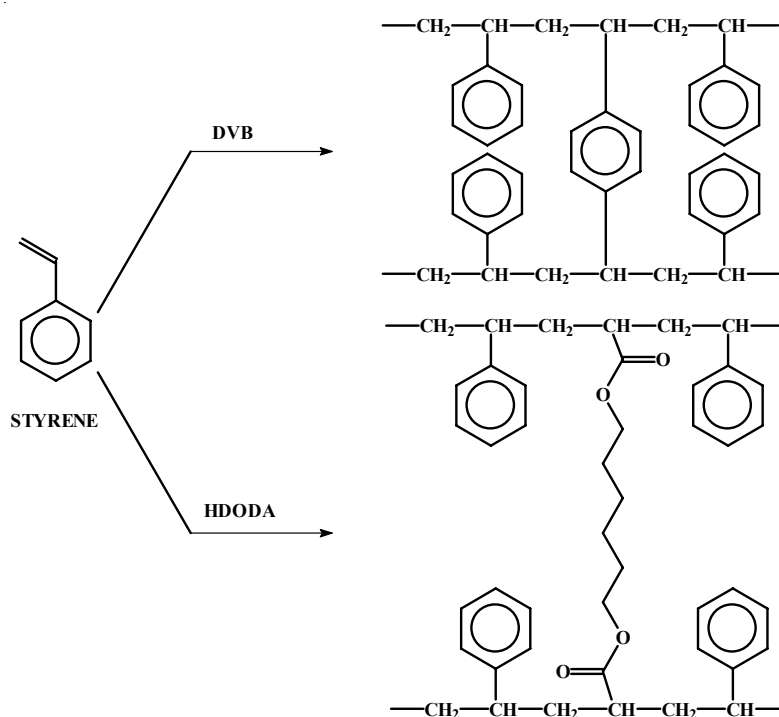
Recycling and reuse of the spent permanganate resin

The washed polymer was dried and stirred for 2 h with 2 N solution of ferrous ammonium sulphate in the presence of 2 N H_2SO_4 (10 mL) to remove all oxides of manganese. The regenerated white polymer was functionalized with potassium permanganate. Regenerated polystyrene-supported polyoxyethylene-bound permanganate polymer was used for the oxidation of aldehydes and alcohols.

RESULTS AND DISCUSSION

Preparation of 2 mol % DVB- and HDODA-crosslinked polystyrenes

Polystyrene with 2 mol % DVB- and HDODA-crosslinking were prepared by free radical suspension polymerization at 80°C using benzoyl peroxide as initiator and toluene as a diluent. Comparing the crosslinked systems, DVB is perfectly rigid and hydrophobic while HDODA is hydrophilic and flexible (**Scheme-I**).

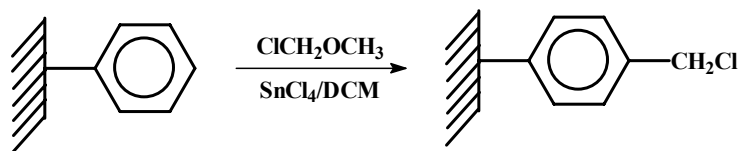


Scheme-I Synthesis of 2 mol % of DVB- and HDODA-crosslinked polystyrenes

IR (KBr) spectroscopy shows a sharp peak at 1720 cm^{-1} due to ester carbonyl group of HDODA- and for DVB-crosslinked polystyrenes shows characteristic bands of benzene ring was at 3010 cm^{-1} .

Chloromethylation of 2 mol % DVB- and HDODA-crosslinked polystyrenes

Introduction of chloromethyl groups on the crosslinked polymer was done using chloromethyl methyl ether and anhydrous stannic chloride as Lewis acid catalyst in dichloromethane¹² at 0°C (**Scheme-II**). The infrared spectra of the crosslinked polystyrenes showed the characteristics (C-Cl) stretch around 690, 1420 cm^{-1} and (H-C-Cl) vibration at 1250 cm^{-1} .



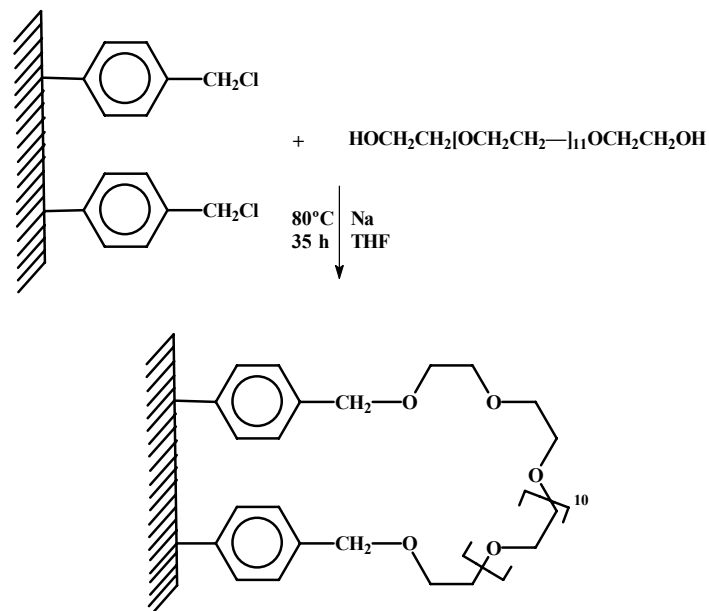
Scheme-II Chloromethylation of crosslinked polystyrene

The chlorine capacities of DVB- and HDODA-crosslinked polystyrenes were estimated by modified Volhard's method¹² and are: DVB - 4.1 and HDODA - 4.79 mmol/g. The degree of chloromethylation was found to be less in the case of rigid DVB-crosslinked resin, but in the case of HDODA-crosslinked resins, as the spacing between the crosslinking agent increases the chlorine capacity increases. This is due to the availability of the reactive sites in the interior of the networks favouring maximum incorporation of chloromethyl groups.

Synthesis of 2 mol % DVB- and HDODA-crosslinked polystyrene-supported polyoxyethylenes

The crosslinked chloromethylated polystyrene was allowed to swell in THF, treated with polyethylene glycol (m.w. 600) and metallic sodium for 35 h at 80°C (**Scheme-III**). The molar ratio of diol to polystyrene was 1:2 to ensure the coupling of both ends of diol with the polystyrene support resulting in the formation of cyclic polyether. The resultant polymer was washed with water, methanol, acetone and soxhlet extracted with THF and dried in an oven at 50°C.

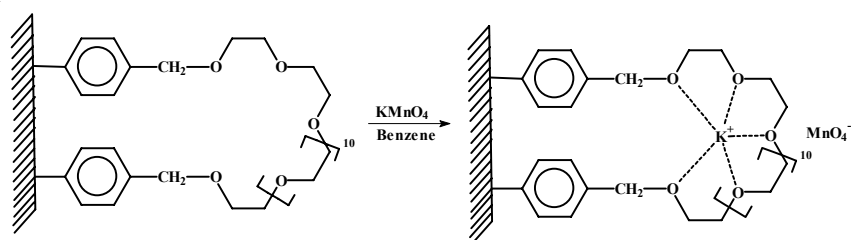
The crosslinked resins were characterized by IR (KBr) spectroscopy. It was found that in all cases a strong band was obtained at 1100 cm⁻¹ due to asymmetrical C-O-C stretching of the oxyethylene units. This band indicates the presence of ether linkage in the polystyrene incorporated polyoxyethylene. In order to verify the presence of any free hydroxyl group, the resin was treated with excess acetic anhydride in pyridine and the unreacted acetic anhydride decomposed to acetic acid was titrated against alkali using phenolphthalein as indicator¹³. But the estimation did not give the presence of any free hydroxyl group. The residual chlorine in crosslinked polystyrene-supported polyoxyethylene was estimated by pyridine fusion method¹² and are: DVB-3.24 and HDODA- 4.3 mmol/g. From the results, it is found that DVB-crosslinked polystyrene-supported polyoxyethylene has low grafting of polyoxyethylene due to its rigid and hydrophobic character. The grafting of polyoxyethylene to HDODA-crosslinked system is high due to its flexible character. This is because of its high flexibility and hydrophilicity permitting the permeation of the long polyethylene glycol molecule through the flexible networks.



Scheme-III Preparation of polystyrene-supported polyoxyethylene (PSPOE)

Incorporation of potassium permanganate into 2 mol % DVB- and HDODA-crosslinked polystyrene-supported polyoxyethylene (PSPOE)

The DYB- and HDODA-crosslinked polymeric polyoxyethylenes were allowed to swell in benzene in a closed amber coloured bottle. The swelled polymers were equilibrated with excess potassium permanganate and stirred in a twist action shaker at room temperature for 10 h (**Scheme-IV**). The black coloured polymers were filtered and washed with distilled water to remove all the manganese dioxide and the polymers were dried in vacuum. In all cases the weight of the complexed polymers were found to be twice the weight of the starting polymers.



Scheme-IV Complexation of PSPOE with potassium permanganate

The IR spectrum (KBr) of the functionalized polymers showed absorptions at 840 and 940 cm^{-1} due to ν_1 and ν_2 vibrations of MnO_4^- ion¹⁴. The UV spectroscopy is also used for the characterization of KMnO_4 bound polymers¹⁵ (Table-1).

TABLE-1
DETAILS OF THE UV SPECTRA OF KMnO₄ COMPLEXED PSPOE

Crosslinking agent	Electronic transitions (cm ⁻¹)			
	¹ t ₁ → ³ T ₂	³ t ₂ → ¹ T ₁	¹ t ₁ → ¹ T ₂	³ t ₂ → ¹ T ₁
DVB-	18518	29154	33670	40000
HDODA-	17793	19267	34602	41322

For the estimation of potassium permanganate incorporation, definite amount of the functionalized polymer was suspended in excess known volume of 2 N H₂SO₄. The dark colour of the polymer completely disappeared by treating with standard ferrous ammonium sulphate solution. The unreacted ferrous ammonium sulphate solution was titrated against standard KMnO₄ solution. From the titre values, the binding capacities of DVB and HDODA systems are 2.95 and 3.87 mmol/g, respectively.

As the flexibility of the crosslinking agent increased the binding capacity also increased. Highly flexible HDODA-crosslinked PSPOE has high binding capacity. Low binding capacity of the DVB-crosslinked system is due to its rigid and hydrophobic character.

Swelling studies

The crosslinked ratio controls the behaviour of a polymer on contact with a solvent and is inversely proportional to the degree of swelling¹⁶. Swelling characteristics of crosslinked chloromethylated polystyrene, polystyrene-supported polyoxyethylene and polystyrene supported polyoxyethylene bound permanganate resins were carried out in solvents of varying polarity (Table-2). The extent of swelling (α) of polymer in solvent is expressed as:

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

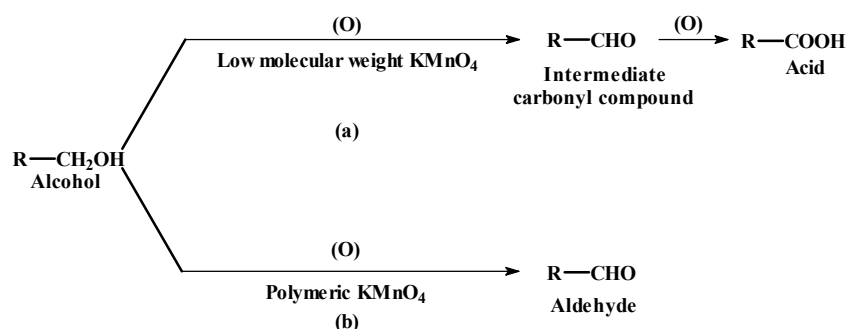
TABLE-2
SWELLING STUDIES OF CROSSLINKED CHLOROMETHYLATED POLYSTYRENE

Solvent	Extent of swelling (α)					
	DVB-			HDODA-		
	PS	PSPOE	PSPOE KMnO ₄	PS	PSPOE	PSPOE KMnO ₄
Cyclohexane	5.73	4.54	3.15	8.03	7.54	6.37
Carbon tetrachloride	5.60	4.32	2.57	8.45	7.90	7.03
Benzene	5.70	4.69	3.23	8.70	8.40	7.16
Dichloromethane	4.45	3.33	2.15	9.05	8.74	7.51
Chloroform	4.58	3.47	2.42	10.50	9.53	8.01
Dioxane	5.01	3.93	3.20	9.56	8.97	7.20
Tetrahydrofuran	4.83	3.84	2.80	9.02	8.12	6.34

In all cases, rigid and non-polar DVB-crosslinked polystyrene has maximum swelling in nonpolar solvents like benzene. Highly flexible and polar HDODA-crosslinked system has maximum swelling in chloroform. Hence the extent of swelling of a polymer depends on the hydrophobic/hydrophilic balance of the polymer matrix. Thus on the incorporation of polyoxyethylene the swelling decreased and it again decreased on complexation with potassium permanganate. This is due to the addition cross links formed by the attachment of the two ends of polyethyleneglycol as well the further complexation of the ether oxygens with potassium ions.

Oxidations by 2 mol % DVB- and HDODA-crosslinked polystyrene-supported polyoxyethylene bound permanganates

The oxidation reactions were carried out to investigate the nature of hydrophobic/hydrophilic nature of the polymer matrix using 2 mol % crosslinked microporous polystyrene-supported polyoxyethylene bound permanganate resins. These polymers have the ability to oxidise 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 polystyrene-supported polyoxyethylene bound permanganate resin, the product is only the aldehyde instead of acid. This observation is same even with large excess of the polymeric permanganate species and extended duration of the reaction. This termination of the oxidation of the primary alcohol as aldehyde may be due to the non availability of the permanganate species buried within the polymer networks. This difference suggests the role of the polymer matrix in controlling the oxidising ability of the permanganate species.



Scheme-V Oxidation of alcohols using (a) low molecular weight KMnO_4 and (b) polymeric KMnO_4

Oxidation reactions for DVB-crosslinked system benzene were used as solvent at 70°C. For HDODA-crosslinked system, chloroform at 50°C was used as the solvent. TLC was used to follow the progress of the reaction. Simple filtration was sufficient for the separation of the crude product from the reaction mixture. The column chromatography is used to separate the pure product from the reaction mixture. Synthetic reactions conducted using permanganate resin are listed in Tables 3 and 4.

TABLE-3
OXIDATION OF ALDEHYDES USING 2 mol % DVB AND
HDODA-PSPOE-KMnO₄

Substrate	Product	Yield (%)		
		Time (h)	DVB-	HDODA-
Benzaldehyde	Benzoic acid	5	60	96
2-Chloro benzaldehyde	2-Chloro benzoic acid	7	54	83
2-Chloro benzaldehyde	2-Chloro benzoic acid	10	63	96
4-Chloro benzaldehyde	4-Chloro benzoic acid	7	52	80
4-Chloro benzaldehyde	4-Chloro benzoic acid	11	70	94
3-Nitro benzaldehyde	3-Nitro benzoic acid	7	48	83
3-Nitro benzaldehyde	3-Nitro benzoic acid	14	50	92
4-Nitro benzaldehyde	4-Nitro benzoic acid	7	50	89
4-Nitro benzaldehyde	4-Nitro benzoic acid	12	69	94
Phthalaldehyde	Phthalic acid	7	40	75
Phthalaldehyde	Phthalic acid	17	87	90
Cinnamaldehyde	Cinnamic acid	7	58	90
Salicylaldehyde	Salicylic acid	7	55	84
Salicylaldehyde	Salicylic acid	10	66	92

Increase in the yield of the product for 1,6-hexanediol dimethacrylate-crosslinked PSPOE-KMnO₄ system is due to its flexible, polar and hydrophilic nature. Hence in good solvent the permanganate species are exposed to the continuous phase.

Characterization of the products

The progress of the oxidation reaction was followed by TLC. The crude products were purified by column chromatography (silica, hexane-ethyl acetate 5:2). The products have been characterized with NMR and elementary analysis. All result were in good agreement with the expected.

TABLE-4
 OXIDATION OF PRIMARY AND SECONDARY ALCOHOLS
 USING 2 mol % DVB AND HDODA-PSPOE-KMnO₄

Substrate	Product	Yield (%)		
		Time (h)	DVB-	HDODA-
Benzyl alcohol	Benzaldehyde	7	58	86
Benzyl alcohol	Benzaldehyde	10	73	98
4-Hydroxy benzyl alcohol	4-Hydroxy benzaldehyde	7	40	84
4-Hydroxy benzyl alcohol	4-Hydroxy benzaldehyde	13	61	94
2-Nitro benzyl alcohol	2-Nitro benzaldehyde	7	54	82
2-Nitro benzyl alcohol	2-Nitro benzaldehyde	11	75	97
4-Nitro benzyl alcohol	4-Nitro benzaldehyde	7	43	73
4-Nitro benzyl alcohol	4-Nitro benzaldehyde	14	67	95
Cinnamyl alcohol	Cinnamaldehyde	7	50	80
Cinnamyl alcohol	Cinnamaldehyde	11	78	94
α -Phenyl ethanol	Acetophenone	7	52	76
α -Phenyl ethanol	Acetophenone	12	77	98
Benzhydrol	Benzophenone	7	48	76
Benzhydrol	Benzophenone	11	72	94
Benzoin	Benzil	2	78	100

Effect of reaction conditions on the course of oxidation reactions

The effect of various parameters such as solvent, time, temperature and molar excess of the polymeric reagent was investigated by using benzoin to benzil oxidation as a model reaction.

Solvent effect: The oxidation reactions using polymer-supported permanganate derivatives were found to be affected by changing the reaction media. In order to study the effect of solvent on the extent of oxidation reactions, solvents or varying polarity like benzene, chloroform, carbon tetrachloride, tetrahydrofuran, cyclohexane, 1,4-dioxane and dichloromethane were used.

From these studies, it is clear that the polymer matrix has an influence on the reactivity of the attached function. The polarity of the polymer support depends on the nature of crosslinking agent. Divinylbenzene is rigid and hydrophobic and thus the polymer became more rigid and hydrophobic on crosslinking with DVB. It was found that non-polar crosslinking agent like DVB-crosslinked polymer found to be matched with non-polar solvent. In the case of DVB-crosslinked polystyrene-supported polyoxyethylene bound permanganate resin, benzene was found to be the best solvent. But in the highly flexible and polar crosslinking agent HDODA- gave maximum conversion of benzoin in polar solvent like chloroform (Fig. 1).

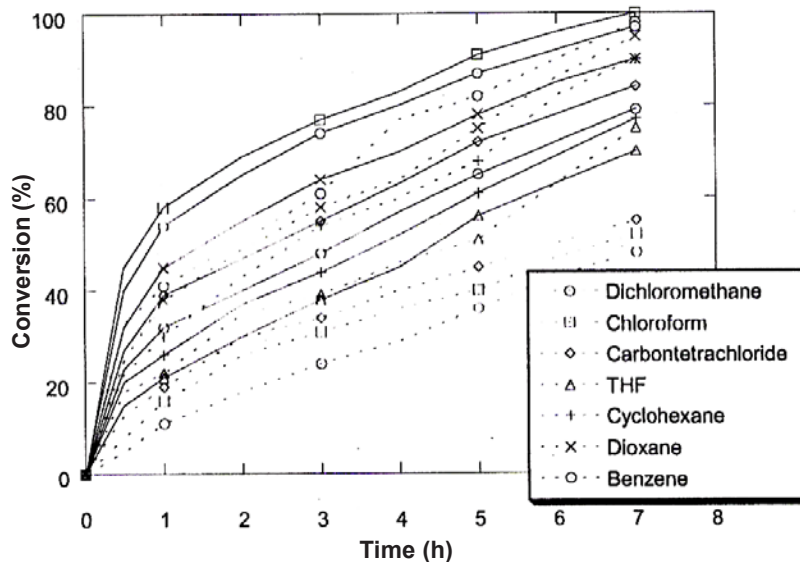


Fig. 1. Effect of solvent on the extent of reaction of 2 mol % DVB- (····) and HDODA- (—) crosslinked PSPOE-KMnO₄ systems

Temperature effect

At elevated temperature, easy penetration of the solvent and extensive swelling of the polymer matrices takes place. Hence the diffusion of soluble substrate into the polymeric reagent was enhanced and hence greater conversion of the substrate took place.

For rigid, non-polar and hydrophobic DVB-crosslinked polystyrene-supported polyoxyethylene bound permanganate systems, at 30°C, 15 % of benzil was obtained in 7 h, but at 70°C, 98 % of benzil was formed in 7 h. This arises from the increase in swelling of the DVB-crosslinked resin at high temperature (Fig. 2) In the highly flexible, polar and hydrophilic HDODA-crosslinked polystyrene-supported polyoxyethylene bound permanganate system, in chloroform at 30°C, benzoin to benzil conversion was 50 % and at 55°C, the conversion was 100 % at 7 h.

The rate of reaction increased with temperature because at high temperature, polymer networks could swell more and hence the easy penetration of the low molecular weight substrate into the interior of the crosslinked polymer matrix takes place.

Effect of molar excess of the reagent: The oxidation reactions were carried out using different reagent to substrate ratios to study the effect of molar excess. In all cases, it was found that rate of reaction increases with increasing the molar ratio of the reagent. DVB-crosslinked polystyrene-supported polyoxyethylene bound permanganate systems showed full conversion of benzoin at 5 h in benzene at 70°C (Fig. 3). In the case of

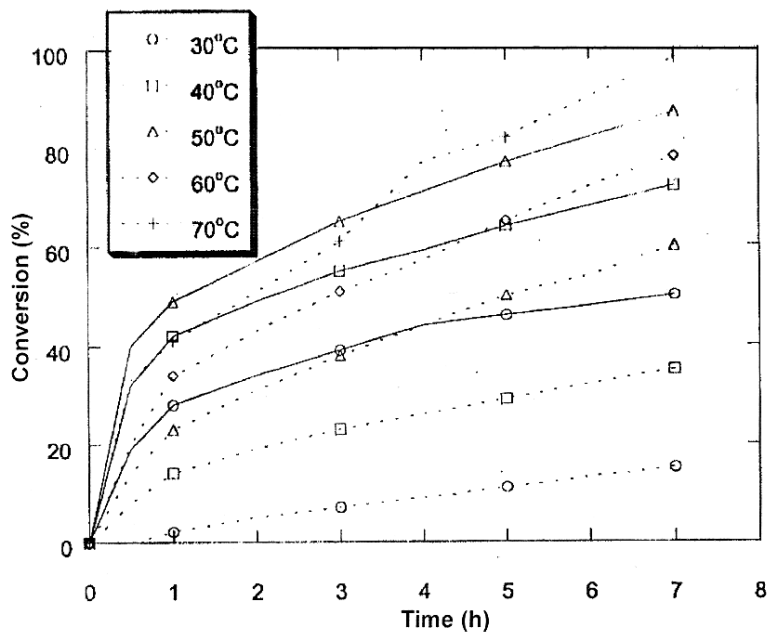


Fig. 2. Effect of temperature on the extent of reaction of 2 mol % DVB- (····) and HDODA- (—) crosslinked PSPOE-KMnO₄ systems

highly flexible HDODA-crosslinked polystyrene-supported polyoxyethylene bound permanganate systems, only 2 h needs for the full conversion of benzoin in chloroform at 55°C. This is due to high flexibility of the polymer matrix by the presence of HDODA as crosslinking agent.

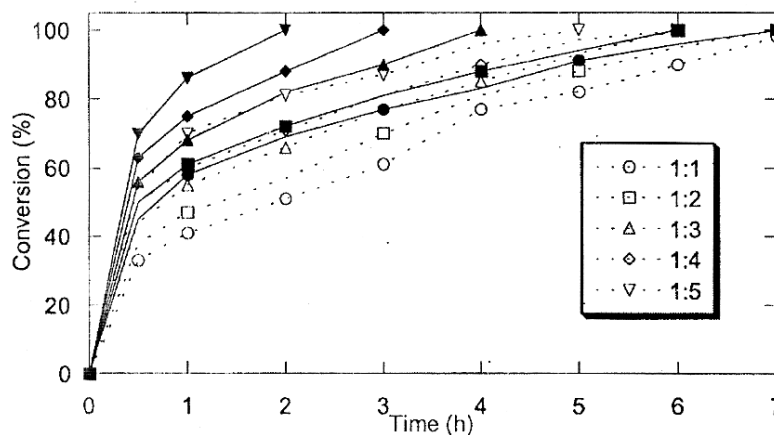


Fig. 3. Effect of molar excess on the extent of reaction of 2 mol % DVB- (—) and HDODA (····) crosslinked PSPOE-KMnO₄ systems

Stability and shelf life of the reagents

Polystyrene-supported polyoxyethylene bound permanganate polymer can be stored for long time without appreciable loss in capacity. For this, the polymers were kept in sealed bottles in desiccators for a period of one year and the capacities were determined again. The results are presented in Table-5. It is observed that in the capacities of the permanganate polymer no appreciable change was observed even after one year.

TABLE-5
STABILITY OF VARIOUS PSPOE-KMnO₄ SYSTEMS

Polymer	Initial capacity (mmol/g)	Capacity after 1 year (mmol/g)
DVB-PSPOE-KMnO ₄	2.95	2.92
HDODA-PSPOE- KMnO ₄	3.87	3.83

Recycling and reuse of the reagents

The used polymeric reagents can be regenerated in a single step without any appreciable loss in activity. The spent permanganate reagent was treated with acidic ferrous ammonium sulphate solution or oxalic acid solution for removing all the manganese oxides. The dried crosslinked polystyrene-supported polyoxyethylene reagent 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 in 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 polymer 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 recycling of crosslinked-PSPOE-KMnO₄ are given in Table-6.

TABLE-6
RECYCLABILITY OF KMnO₄ COMPLEXED SYSTEMS

No. of cycles	Permanganate capacity (mmol/g)	
	DVB-	HDODA-
1	2.95	3.87
2	2.94	3.84
3	2.94	3.83
4	2.92	3.80
5	2.90	3.80
6	2.88	3.76
7	2.85	3.73

Conclusion

The comparison of the oxidizing ability of the flexible and polar HDODA-crosslinked system with hydrophobic, non-polar and rigid DVB-crosslinked system is described in this paper. Chlorometylation is done by modified Volhard's methods followed by the introduction of polyoxyethylene group. The complexation of polyoxyethylene with potassium permanganate results in the filling of the polyoxyethylene cavity. The permanganate incorporated polyoxyethylene act as the oxidizing agents for alcohols and aldehydes. The effect of various reaction parameters such as solvent, temperature and molar excess of the reagent on the oxidizing agents were studied. For flexible and polar HDODA-crosslinked systems chloroform is the best solvent, hydrophobic, non-polar and rigid DVB-crosslinked systems benzene is the best solvent. The oxidizing ability of the polystyrene supported polyoxyethylene bound permanganate system increases with temperature and with molar excess of the reagent The reagents have the advantages of easy separation, regeneration and reuse.

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