Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Chacko, Asha and Mathew, Beena(2003) 'Influence of the Nature of Crosslinking Agent on the Oxidation Behavior of Crosslinked Polystyrene-Supported Polyoxyethylene Bound Permanganate', Journal of Macromolecular Science, Part A, 40: 10, 1035 — 1056

To link to this Article: DOI: 10.1081/MA-120024462

URL: http://dx.doi.org/10.1081/MA-120024462

JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. A40, No. 10, pp. 1035–1056, 2003

Influence of the Nature of Crosslinking Agent on the Oxidation Behavior of Crosslinked Polystyrene-Supported Polyoxyethylene Bound Permanganate

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ABSTRACT

Polystyrene-supported polyoxyethylene (PSPOE) bound permanganate with varying crosslinking agents have been prepared and used as a new class of recyclable oxidizing agents for low molecular weight alcohols and aldehydes. The effect of the nature of crosslinking agents on the oxidation reactions was studied in detail. The crosslinking agents used were ethyleneglycol dimethacrylate (EGDMA), 1,4-butanediol dimethacrylate (BDDMA), and 1,6-hexanediol diacrylate (HDODA). Polymer supports were synthesized by free radical suspension polymerization. Chloromethylation was done using the Friedel-Crafts reaction. A cyclic polyether type compound was developed by the reaction of functionlized resin with polyethylene glycol (PEG_{600}) and sodium. Polystyrene-supported polyoxyethylene was equilibrated with potassium permanganate in benzene to give the oxidizing agent. The results reveal that the reactivity of HDODA-crosslinked system shows higher reactivity than the BDDMA, and EGDMA-crosslinked systems. This is due to higher flexibility of the HDODA-crosslinked system compared to the BDDMA, and EGDMA-crosslinked systems. The effect of solvent, temperature, and molar concentration of the reagent on oxidation were carried out using benzoin to benzil as the model reaction. For a less flexibile EGDMA-crosslinked resin, tetrahydrofuran (THF) is the best solvent, for BDDMA-crosslinked system dioxane and for the highly flexible HDODA-crosslinked system $CHCl_3$ is found to be best. In all cases, the

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DOI: 10.1081/MA-120024462
1060-1325 (Print); 1520-5738 (Online)
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reactivity of the reagent increased with an increase in temperature and molar excess of the reagent.

Key Words: Poly-sytrene supported; Polyoxyethylene; Nature of crosslinking; Permanganate; Oxidation.

INTRODUCTION

The application of polymeric reagents in oxidation reactions has received much attention during the last few decades.[1–4] A polymeric reagent can be considered as a macromolecule on which reactive functions are attached. A polymeric reagent possess a combination of the physical properties of the polymer support and the chemical reactivities of the attached reagent function.[5] 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 study on macrocyclic ethers revealed that polyethers form complexes with salts, which are held together by electrostatic attraction between the cations and the C—O dipoles of the polyethers.[6,7] 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.[8,9] A 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 an organic substrate.[10]

The present work involves investigation of the dependence of the nature of the crosslinking agent on the oxidation of low molecular weight alcohols and aldehydes catalyzed by polymer-supported permanganate. The polymer supports used are polyoxyethylene (POE) incorporated low crosslinked microporous polystyrene with different types of crosslinking agents like ethyleneglycol dimethacrylate (EGDMA), 1,4-butanediol dimethacrylate (BDDMA), and 1,6-hexanediol diacrylate (HDODA). Permanganate functions were incorporated by the complexation of the potassium ion with the ether oxygens of the polystyrene-supported polyoxyethylene (PSPOE).

EXPERIMENTAL

Styrene, EGDMA, BDDMA, and HDODA were purchased from Aldrich Chemical Company, USA. The crosslinked polymers were prepared by suspension copolymerization. Polyvinyl alcohol (PVA, 72,000) was purchased from Sigma Chemical Company, USA. Benzoyl peroxide (recrystallized before use) was from Sisco, Mumbai. Polyethyleneglycol (PEG_{600}) was a commercial product obtained from Merck, Germany. Commercially available low molecular weight compounds and solvents were purified according to literature procedures. Electronic spectra were recorded on a Shimadzu UV-160A spectrophotometer. IR-spectra were recorded on a Shimadzu IR-470 spectrophotometer. NMR spectra were recorded using a Bruker 250-MHz instrument. CHN analysis was carried out using a Perkin-Elmer PE: 2400 CHN analyzer. Melting points were obtained from a Buchi-530 melting point apparatus.

Preparation of 2 mol% EGDMA-, BDDMA-, and HDODA-Crosslinked Polystyrenes: General Procedure

Styrene was destabilized by washing with 1% sodium hydroxide solution (15 mL × 3) and distilled water until all the sodium hydroxide was removed and dried over anhydrous calcium chloride. Polyvinyl alcohol (1.75 g), in distilled water (1% solution) was kept mechanically stirred at 600 rpm in a cylindrical polymerization vessel under nitrogen atmosphere in a water bath at 80°C. A mixture of styrene, crosslinking agent, toluene (10 mL) as inert diluent and benzoyl peroxide (500 mg) was prepared and flushed with nitrogen. The composition of styrene, the crosslinking agent used for each polymerization, and the yield obtained are listed in Table 1. This mixture was then added to a PVA solution with stirring. After 6 h, the beaded polymers were collected by filtration, and washed thoroughly with hot water to remove PVA, acetone, benzene, chloroform, and finally, with methanol to remove all low molecular weight impurities and linear polymers. The resin obtained was Soxhlet extracted with dichloromethane, followed by acetone and dried in an oven at 50°C.

Chloromethylation of EGDMA-, BDDMA-, and HDODA-Crosslinked Polystyrenes: General Procedure

Preparation of Chloromethyl Methyl Ether[11]

Dry HCl was allowed to pass through a mixture of formaldehyde (126 mL) and methanol (66 mL) at 0°C. Dry HCl was passed continuously till the ether was clearly separated from the aqueous phase. The appearance of an oily layer indicated the formation of chloromethyl methyl ether (CMME). The solvent mixture was transferred into a separating funnel and the oily layer was separated and dried over calcium chloride, obtaining a 95 mL product yield. Chloromethyl methyl ether is highly carcinogenic. This was used for chloromethylation without any further purification. Yield: 95 mL.

Chloromethylation of Crosslinked Polystyrenes[12]

Dry polystyrene resins (5 g, 200–400 mesh) were swelled in dry dichloromethane (50 mL). Chloromethyl methyl ether (30 mL) and 0.5 mL stannic chloride (99.9%) as catalyst were added to the swelled resin at 0°C. The temperature of the reaction mixture was allowed to increase slowly to room temperature and kept for 48 h with stirring. The functionalised resin was filtered, washed with THF, THF–H_2O (1 : 1, 6 times), THF–1 N HCl (1 : 1, 6 times), THF, hot water, until free from chloride ion and with methanol. For further purification, the resin was Soxhlet extracted with THF and dried in vacuum.

Estimation of Chlorine Capacity by Volhard's Method[13]

The chloromethylated 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. HNO_3 (5 mL) and $AgNO_3$ (0.5 N, 5 mL) were added and diluted with water (20 mL) and stirred well.

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The chlorine capacities of various resins were calculated by titrating against standard ammonium thiocyanate using ferric alum as indicator.

Preparation of 2 mol% EGDMA-, BDDMA-, and HDODA-Crosslinked PSPOE

Dry chloromethylpolystyrene was allowed to swell in THF for 1 h. Polyethylene glycol (PEG_{600}) was added and the temperature was maintained at 80°C. Small pieces of metallic sodium were added slowly and heating and stirring were continued for 35 h. The molar ratio of polystyrene to diol was 2 : 1 to ensure the coupling of both ends of diol with the polystyrene support resulting in the formation of cyclic polyether. 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 unreacted polyethylene glycol and finally, with methanol and dried in vacuum.

Estimation of Hydroxyl Group Capacity[14]

In order to estimate free hydroxyl groups after treatment with polyethylene glycol, 200 mg of the dry PSPOE 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 0.1 N potassium hydroxide with phenolphthalein as indicator. No detectable presence of hydroxyl group was observed.

Synthesis of 2 mol% EGDMA-, BDDMA-, and HDODA-Crosslinked Polystyrene-Supported Permanganates

Incorporation of Permanganate Functions

To a suspension of PSPOE (5 g) in benzene (20 mL) excess $KMnO_4$ was 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, with subsequent use in the oxidation reactions.

Determination of the Extent of Permanganate Incorporation

A definite amount of the dry permanganate complexed resin was accurately weighed and suspended in a excess known volume of 2 N H_2SO_4 for 1 h. A known excess of standard ferrous ammonium sulphate solution was added and stirred until the dark color of the resin completely disappeared. The unreacted ferrous ammonium sulphate solution was titrated against standard $KMnO_4$ solution.

Swelling Studies of EGDMA-, BDDMA-, and HDODA-Crosslinked Systems

The extent of swelling was determined in the case of crosslinked polystyrene, PSPOE and permanganate complexed resins. In a dry, previously weighed crucible (G_3), dry resin (2 g) was taken and equilibrated with solvents such as cyclohexane, benzene, dioxane, carbontetrachloride, chloroform, dichloromethane, and tetrahydrofuran for 24 h. The excess solvent was drained. The weight of the swollen resin was calculated from the difference in weights. The extent of swelling (α) of the various systems was calculated from the dry and swollen weights and the results are summarized in Table 3.

Oxidation Studies Using Potassium Permanganate Complexes of Various Crosslinked PSPOE: General Procedure

To five-fold molar excess of various crosslinked PSPOE bound permanganate resins, substrate in 20 mL suitable solvent was added. The reaction mixture was heated under reflux temperature with stirring. 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 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 of concentration of benzil vs. 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. A calibration curve was plotted using other solvents such as tetrahydrofuran, dichloromethane, carbontetrachloride, chloroform, cyclohexane, and benzene.

Effect of Solvent on the Extent of Oxidation

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. Then 0.5 mL of the reaction mixture was withdrawn using a micro-pipette at regular intervals of time. It was diluted to a 5 mL and the absorbance at 387 nm was measured. From the absorbance the percentage of benzil formed was calculated using the calibration curve. The experiment was repeated using various solvents having different polarity. The solvents used were chloroform, carbontetrachloride, dichloromethane, benzene, cyclohexane, dioxane, and tetrahydrofuran.

Effect of Temperature

The experiment described above was repeated in different temperatures ranging from room temperature to refluxing temperature of the solvent. The progress of the reaction was followed spectrophotometrically at 387 nm. From the absorbance, the percentage of benzil formed at each temperature was calculated 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. Using a micro-pipette, a definite volume (0.5 mL) of the reaction mixture was withdrawn and 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 using the calibration curve.

Recycling and Reuse of the Spent Polymeric Permanganate Resins

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 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 white beads were filtered, washed with distilled water, dried, and treated with potassium permanganate. The oxidizing properties of regenerated PSPOEs were investigated towards alcohols and aldehydes.

RESULTS AND DISCUSSION

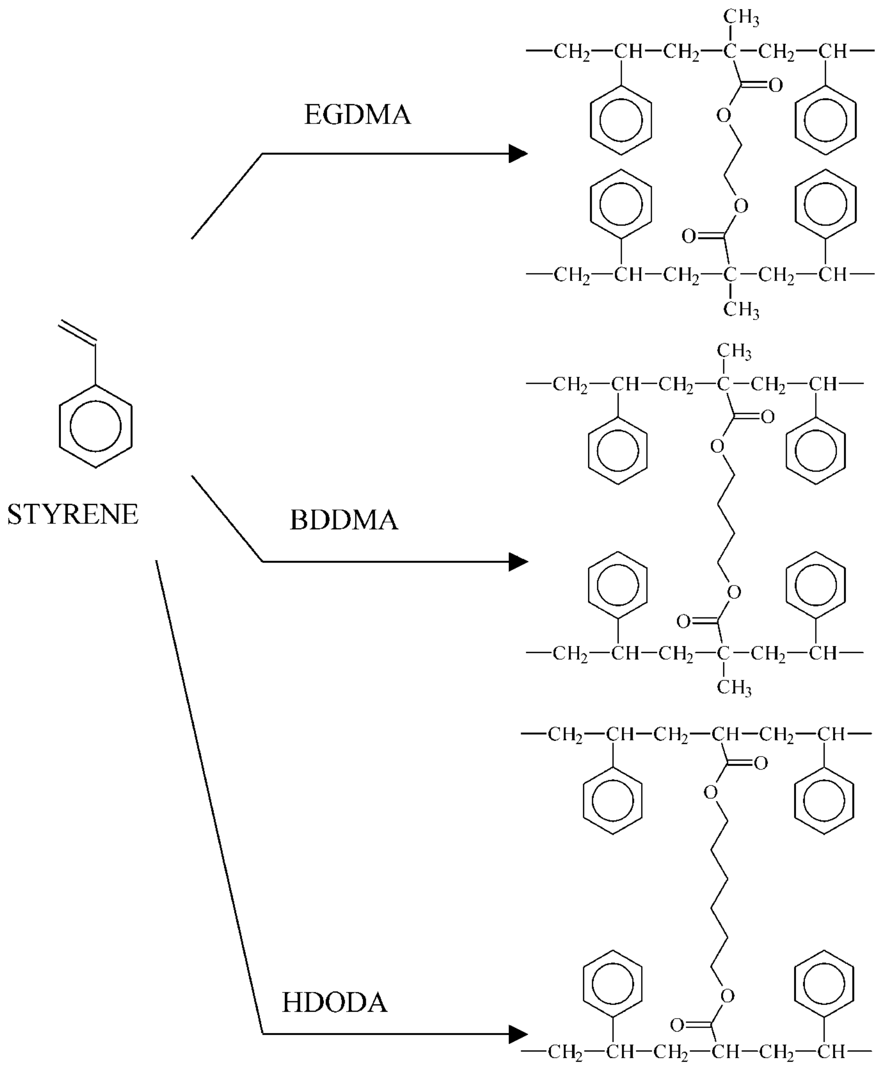
Preparation of 2 mol% of EGDMA-, BDDMA-, and HDODA-Crosslinked Polystyrenes

The 2 mol% EGDMA-, BDDMA-, and HDODA-crosslinked polystyrenes were prepared by free radical suspension polymerization using benzoyl peroxide as the initiator in water at 80°C (Sch. 1). The composition of styrene and crosslinking agent used for each polymerization, and the yield obtained are listed in Table 1.

IR spectra of the various crosslinked resins showed a sharp band at 1720 cm^{-1} corresponding to the ester carbonyl group of the crosslinking agent in addition to the characteristic bands of a benzene ring at 3010 cm^{-1}.

Chloromethylation of 2 mol% EGDMA-, BDDMA-, and HDODA-Crosslinked Polystyrenes[16]

The chloromethyl methyl ether was prepared from methanol and formaldehyde in presence of dry HCl.[11] Introduction of chloromethyl groups on the crosslinked polymer



Scheme 1. Synthesis of various crosslinked polystyrenes.

was done using chloromethyl methyl ether and anhydrous stannic chloride as Lewis acid catalyst in dichloromethane[12] at 0°C (Sch. 2).

The IR spectra of various crosslinked chloromethyl polystyrenes showed the characteristic C—Cl stretching around 690 cm^{-1} and 1420 cm^{-1}, and H—C—Cl vibration at 1250 cm^{-1}. The chlorine extent was estimated by modified Volhard's method.[13] The chlorine capacities of various crosslinked polystyrenes are: EGDMA—4.32, BDDMA—4.53, and HDODA—4.79 mmol/g.

As the spacing between the vinyl groups of the crosslinking agent increases, chlorine capacity increases. Thus chlorine capacity variation with crosslinking agent

Table 1. Preparation of 2 mol% EGDMA-, BDDMA- and HDODA-crosslinked polystyrenes.

Crosslinking agent	Styrene (mL)	Crosslinking agent (mL)	Yield (%)
EGDMA	11.23	0.38	80
BDDMA	11.23	0.44	83
HDODA	11.23	0.45	87

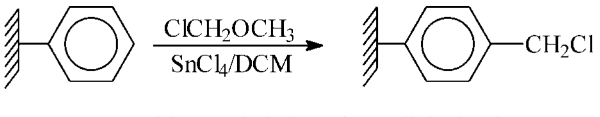
is: HDODA- > BDDMA- > EGDMA-crosslinked chloromethylpolystyrenes. This is due to the availability of the reactive sites in the interior of the networks favoring maximum incorporation of chloromethyl groups.

Synthesis of 2 mol% EGDMA-, BDDMA-, and HDODA-Crosslinked PSPOE

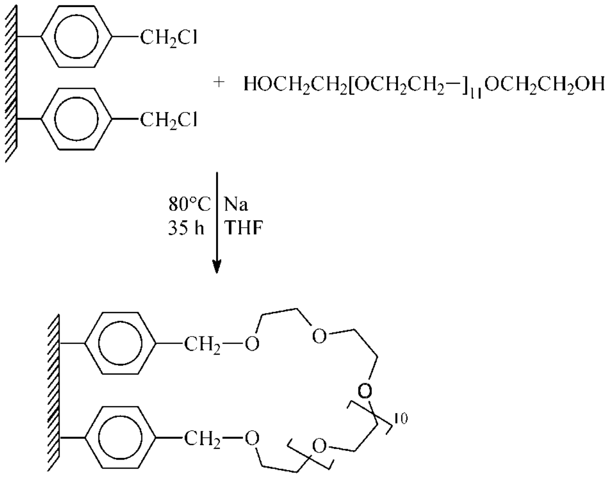
For the synthesis of PSPOE, the crosslinked chloromethylpolystyrene was allowed to swell in THF. The swelled resin was treated with polyethylene glycol (PEG_{600}) and metallic sodium. The reaction was carried out at 80°C in an oil bath for 35 h. The method of preparation is listed in Sch. 3. The molar ratio of diol to polystyrene was in 1 : 2 to ensure the coupling of both ends of diol with the polystyrene support resulting 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 various crosslinked resins were characterized by IR (KBr) spectroscopy. It was found that in all cases a strong band was obtained at $1100\,cm^{-1}$ due to asymmetrical C—O—C stretching of the oxyethylene units. This band indicates the presence of ether linkage in the POE incorporated polystyrenes. 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 indicator.[14] But the estimation did not give the presence of any free hydroxyl group. This confirms the existence of the incorporated unit as cyclic POE and not as polymer-supported polyethylene glycol. The residual chlorine in crosslinked PSPOE was estimated by a pyridine fusion method.[13] The extent of grafting of POE into chloromethylated crosslinked polystyrene was calculated from the residual chlorine content. The POE capacities of various crosslinked chloromethyl polystyrenes are: EGDMA—3.65, BDDMA—3.97, and HDODA—4.3 mmol/g.

As the flexibility and hydrophilicity increases the extent of grafting of POE also increased. Hence, maximum grafting of POE is in the more flexible HDODA-crosslinked system. This is because of its high flexibility and permitting the permeation of the long PEG molecule through the flexible networks.



Scheme 2. Chloromethylation of crosslinked polystyrens.



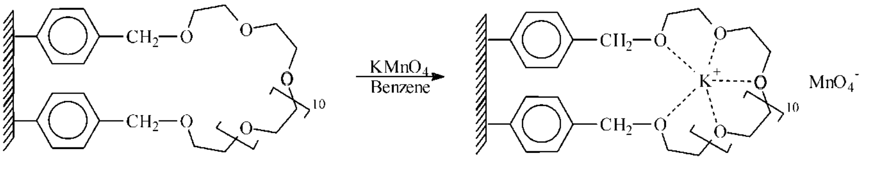
Scheme 3. Preparation of PSPOE.

Incorporation of Potassium Permanganate into EGDMA-, BDDMA-, and HDODA-Crosslinked PSPOE-$K^+MnO_4^-$

The EGDMA-, BDDMA-, and HDODA-crosslinked polymeric POEs were allowed to swell in benzene in an amber-colored closed reagent bottle. The swelled resin was equilibrated with excess potassium permanganate and stirred in a twist action shaker at room temperature for 10 h (Sch. 4). 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 spectra (KBr) of the functionalized resins showed absorptions at 840 and 940 cm^{-1} due to ν_1 and ν_2 vibrations of MnO_4^- ion.[15] The UV spectroscopy is also used for the characterization of $KMnO_4$ bound resins.[16] The observed transitions are given in Table 2.

For the estimation of potassium permanganate incorporation, definite amount of the functionalized resin was suspended in excess known volume of 2 N H_2SO_4. A measured excess standard ferrous ammonium sulphate solution was added and stirred until the dark color of the resin completely disappeared and turned to white. The unreacted ferrous ammonium sulphate solution was titrated against standard $KMnO_4$ solution. These estimations were also conducted using oxalic acid titration in the presence of dilute



Scheme 4. Complexation of PSPOE with potassium permanganate.

Table 2. Details of the UV spectra of $KMnO_4$ complexed PSPOE.

	Electronic transitions (cm^{-1})			
Polymer	${}^1t_1 \rightarrow {}^3T_2$	${}^3t_2 \rightarrow {}^1T_1$	${}^1t_1 \rightarrow {}^1T_2$	${}^3t_2 \rightarrow {}^1T_1$
EGDMA	18,484	21,929	33,783	41,152
BDDMA	18,484	21,052	29,154	33,557
HDODA	17,793	19,267	34,602	41,322

sulphuric acid. From EGDMA- to HDODA-crosslinked systems, the binding capacity increases with increase in the number of methylene units in the crosslinking agent. The binding capacities of potassium permanganate into EGDMA-, BDDMA-, and HDODA-crosslinked PSPOE are: EGDMA—3.23, BDDMA—3.65, and HDODA—3.87 mmol/g.

Swelling Studies

The swelling studies are important for identifying the best solvent use, i.e., to prepare the most suitable reaction medium for performing reactions on polymer supports. The extent of swelling depends on the crosslink ratio and the chemical nature of the polymer support used. Swelling characteristics of crosslinked chloromethylated polystyrene, PSPOE and $KMnO_4$ complexed resins were carried out in solvents of varying polarity (Table 3). In the present study, the extent of swelling (α) of polymer in solvent is expressed as:

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

EGDMA-crosslinked polymer has maximum swelling in THF, while BDDMA-crosslinked polystyrene in dioxane. Highly flexible 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. The swelling nature of the polymer varies on functionalization. Thus, on the incorporation of cyclic POE, the swelling decreased and it again decreased on complexation with potassium permanganate. The incorporation of cyclic POE hinders the passage of solvent molecules in to the interior of the polymer matrix. The cyclic POE units act as additional crosslinking. The complexation of polyoxyethylene with potassium ion results in the filling of the POE cavity, also the interaction of central potassium ion with ethylene oxide units contracts the POE moiety to a certain level resulting in a further decrease of swelling.

Oxidation Reactions Using 2 mol% EGDMA-, BDDMA-, and HDODA-Crosslinked PSPOE Bound Permanganates

In order to investigate the dependence of the nature of crosslinking agent on the oxidation behavior, the oxidation reactions of 2 mol% EGDMA-, BDDMA-, and HDODA-crosslinked PSPOE permanganate resins were carried out. These resins have the ability to

Table 3. Swelling studies of crosslinked chloromethylated polystyrene, crosslinked PSPOE, and crosslinked PSPOE-$KMnO_4$.

	Extent of swelling (α)								
	EGDMA-crosslinked system			BDDMA-crosslinked system			HDODA-crosslinked system		
Solvent	PS	PSPOE	MnO_4^-	PS	PSPOE	MnO_4^-	PS	PSPOE	MnO_4^-
Cyclohexane	7.1	5.9	4.3	7.6	6.8	6.0	8.0	7.54	6.4
Carbontetra-chloride	7.0	6.1	4.7	6.8	6.1	5.9	8.5	7.90	7.0
Benzene	7.6	6.8	5.5	7.5	6.7	6.0	8.7	8.40	7.2
Dichloromethane	7.8	6.7	4.9	7.9	7.1	6.3	9.0	8.74	7.5
Chloroform	8.2	7.1	5.2	8.1	7.4	5.9	10.5	9.53	8.0
Dioxane	8.5	7.3	5.8	8.6	7.6	6.5	9.6	8.97	7.2
Tetrahydrofuran	8.4	7.4	5.9	8.4	7.0	5.7	9.0	8.12	6.3

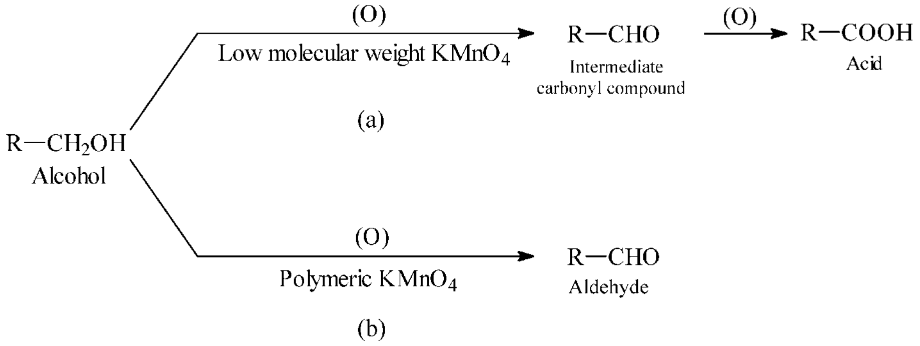
oxidize primary and secondary alcohols to aldehydes and ketones, respectively. Oxidation of aldehyde resulted in acids. The oxidation reactions of alcohols using low molecular weight potassium permanganate gave acid through the intermediate carbonyl compound. But, it is observed that by using crosslinked PSPOE permanganate resin, the product is only the aldehyde instead of acid (Sch. 5). This observation is the same even with a large excess of the polymeric permanganate reagent 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 oxidizing ability of the permanganate species.

The oxidation reactions using EGDMA-crosslinked resin were carried out using a five-fold molar excess of the reagent in THF at 60°C. For BDDMA-crosslinked resin dioxane was used as a solvent at 80°C and for HDODA-crosslinked system, chloroform at 55°C was used for oxidation reactions. TLC was used to follow the progress of the reactions. Simple filtration is sufficient for the separation of the crude product from the reaction mixture. The column chromatography is used to separate the pure product from the unreacted substrate. Synthetic reactions conducted using permanganate resin are listed in Tables 4 and 5.

Characterization of the Products

The progress of the oxidation reactions was followed by thin layer chromatography. The crude products were purified by column chromatography. The analytical and spectral data of the products are given below:

Benzyl alcohol → Benzaldehyde
mp: 178°C IR: 1700 cm^{-1} (—CHO)
^{1}H-NMR (CDCl$_3$): δ 7.5 (s, 1H), 7.75 (m, 2H), 7.5 (m, 3H)
Anal. Calcd. for C_7H_6O: C—79.22%, H—5.70%, O—15.08%
Found: C—79.20%, H—5.76%, O—15.04%



Scheme 5. Oxidation of alcohols using (a) low molecular weight $KMnO_4$ and (b) polymeric $KMnO_4$.

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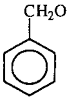
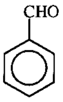
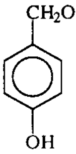
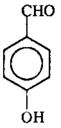
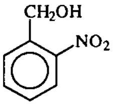
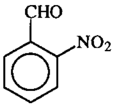
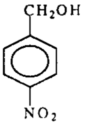
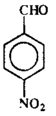
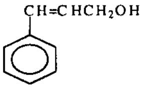
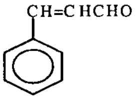
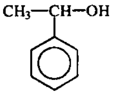
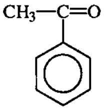
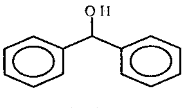
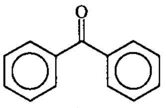
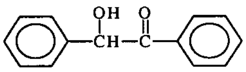
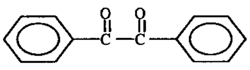
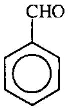
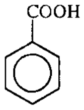
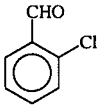
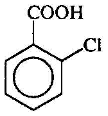
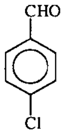
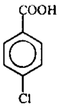
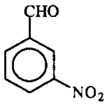
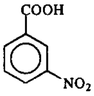
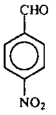
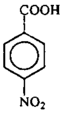
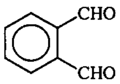
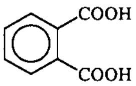
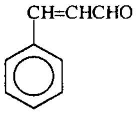
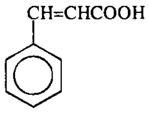
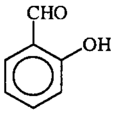
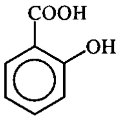
Table 4. Oxidation of primary and secondary alcohols using 2 mol% EGDMA-, BDDMA-, and HDODA-PSPOE-$KMnO_4$ resin.[a]

			Yield (%)[c]		
Substrate	Time (h)	Product[b]	EGDMA	BDDMA	HDODA
 Benzyl alcohol	7	 Benzaldehyde	73	82	86
	10		83	94	98
 4-Hydroxybenzyl alcohol	7	 4-Hydroxybenzaldehyde	65	72	84
	13		87	90	94
 2-Nitrobenzyl alcohol	7	 2-Nitrobenzaldehyde	68	80	82
	11		81	89	97
 4-Nitrobenzyl alcohol	7	 4-Nitrobenzaldehyde	62	71	73
	14		78	86	95
 Cinnamyl alcohol	7	 Cinnamaldehyde	68	79	80
	11		76	85	94
 α-Phenyl ethanol	7	 Acetophenone	67	70	76
	12		85	94	98
 Benzydrol	7	 Benzophenone	60	71	76
	11		83	86	94
 Benzoin	2	 Benzil	91	95	100

[a] All the reactions were carried out using five fold molar excess of the reagent.
[b] Products were characterized by comparison with authentic samples.
[c] Isolated yield.

Table 5. Oxidation of aldehydes using 2 mol% EGDMA-, BDDMA-, and HDODA-PSPOE-$KMnO_4$ resin.[a]

Substrate	Time (h)	Product[b]	Yield (%)[c]		
			EGDMA	BDDMA	HDODA
 Benzaldehyde	5	 Benzoic acid	75	83	96
 2-Chlorobenzaldehyde	7 10	 2-Chlorobenzoic acid	67 75	76 86	83 96
 4-Chlorobenzaldehyde	7 11	 4-Chlorobenzoic acid	64 88	74 90	80 94
 3-Nitobenzaldehyde	7 14	 3-Nitrobenzoic acid	62 74	70 86	83 92
 4-Nitrobenzaldehyde	7 12	 4-Nitrobenzoic acid	68 77	75 85	89 94
 Phthalaldehyde	7 17	 Phthalic acid	58 73	64 88	75 90
 Cinnamaldehyde	7	 Cinnamic acid	68	75	90
 Salicyladehyde	7 10	 Salycylic acid	68 76	77 88	84 92

[a] All the reactions were carried out using five fold molar excess of the reagent.
[b] Products were characterized by comparison with authentic samples.
[c] Isolated yield.

4-Hydroxybenzyl alcohol → 4-Hydroxybenzaldehyde
mp: 118°C IR (KBr): 1660 cm^{-1} (—CHO)
^{1}H-NMR ($CDCl_3$): δ 9.8 (s, 1H), 7.8 (d, 2H), 6.9 (d, 2H)
Anal. Calcd. for $C_7H_6O_2$: 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^{-1} (—CHO)
^{1}H-NMR ($CDCl_3$): δ 10.43 (s, 1H), 8.1 (t, 1H), 7.9 (t, 1H), 7.8 (m, 2H)
Anal. Calcd. for $C_7H_5NO_3$: N—9.27%, C—55.63%, H—3.33%, 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^{-1} (—CHO)
^{1}H-NMR ($CDCl_3$): δ 11.2 (s, 1H), 8.4 (m, 4H)
Anal. Calcd. for $C_7H_5NO_3$: 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 → Cinnamaldehyde
bp: 249°C IR: 1670 cm^{-1} (—CHO)
^{1}H-NMR ($CDCl_3$): δ 9.7 (d, 1H), 7.4 (m, 3H), 6.6 (q, 2H)
Anal. Calcd. for C_9H_8O: C—81.79%, H—6.10%, O—12.11%
Found: C—81.80%, H—6.03%, O—12.17%

α-Phenyl ethanol → Acetophenone
bp: 202°C IR: 1700 cm^{-1} (—CO)
^{1}H-NMR ($CDCl_3$): δ 7.9 (dd, 2H), 7.5 (m, 3H), 2.6(s, 3H)
Anal. Calcd. for C_8H_8O: 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^{-1} (—CO)
^{1}H-NMR ($CDCl_3$): δ 7.9 (d, 2H), 7.7 (d, 2H), 7.5 (m, 6H)
Anal. Calcd. for $C_{13}H_{10}O$: 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^{-1} (—CO)
^{1}H-NMR ($CDCl_3$): δ 7.9 (d, 2H), 7.8 (d, 2H), 7.5 (m, 3H)
Anal. Calcd. for $C_{14}H_{10}O_2$: 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^{-1} (—COOH)
^{1}H-NMR ($CDCl_3$): δ 8.1 (dd, 2H), 7.5 (m, 3H)
Anal. Calcd. for $C_7H_6O_2$: 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}H-NMR (DMSO-d_6 + $CDCl_3$): δ 9.0 (s, 1H), 7.8 (q, 1H), 7.4 (m, 2H)
Anal. Calcd. for $C_7H_5ClO_2$: C—53.70%, H—3.22%, O—20.44%
Found: C—53.78%, H—3.28%, O—42.94%

4-Chlorobenzaldehyde → 4-Chlorobenzoic acid
mp: 240°C IR (KBr): 2816 cm^{-1} (—COOH)
^{1}H-NMR (DMSO-d_6 + $CDCl_3$): δ 7.9 (d, 2H), 7.4 (d, 2H)
Anal. Calcd. for $C_7H_5ClO_2$: C—53.70%, H—3.22%, O—20.44%
Found: C—53.72%, H—3.30%, O—42.98%

3-Nitrobenzaldehyde → 3-Nitrobenzoic acid
mp: 141°C IR (KBr): 2810 cm^{-1} (—COOH)
^{1}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 $C_7H_5NO_4$: 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}H-NMR (DMSO-d_6 + $CDCl_3$): δ 8.7 (s, 2H), 8.3 (s, 2H)
Anal. Calcd. for $C_7H_5NO_4$: 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}H-NMR (DMSO-d_6 + $CDCl_3$): δ 12 (s, 2H), 7.85 (m, 4H)
Anal. Calcd. for $C_8H_6O_4$: 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}H-NMR ($CDCl_3$): δ 7.83 (d, 1H), 6.46 (d, 1H), 7.5 (m, 5H)
Anal. Calcd. for $C_9H_8O_2$: C—72.96%, H—5.44%, O—21.60%
Found: C—72.98%, H—5.38%, O—21.64%

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Salicylaldehyde → Salicylic acid
mp: 159°C IR (KBr): 2860 cm^{-1} (—COOH)
^{1}H-NMR (DMSO-d_6 + $CDCl_3$): δ 7.8 (d, 1H), 7.3 (t, 2H), 6.8 (m, 1H)
Anal. Calcd. for $C_7H_6O_3$: 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. To follow the extent of reaction, 0.5 mL of the reaction mixture was pipetted out using a micro-pipette and transferred into a 5 mL standard flask and made up to definite volume. The progress of the reaction was followed at different time intervals by spectrophotometry at 387 nm.

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 the presence of good solvent. In good solvents, the polymer network expands considerably and thus the functional groups are exposed to the continuous phase. The hydrophobic–hydrophilic balance of the polymer matrix influence the swelling characteristics. 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 of varying polarity such as tetrahydrofuran, cyclohexane, benzene, chloroform, carbontetrachloride, 1,4-dioxane, and dichloromethane were used.

For the EGDMA-crosslinked system, the reactivity in various solvents decreased in the order: THF > Dioxane > Benzene > $CHCl_3$ > CH_2Cl_2 > CCl_4 > Cyclohexane. Whereas in the BDDMA-crosslinked system the reactivity varies with solvent is: Dioxane > CH_2Cl_2 > $CHCl_3$ > Benzene > CCl_4 > Cyclohexene > THF. For the HDODA-crosslinked system the variation is: $CHCl_3$ > Benzene > Dioxane > CCl_4 > CH_2Cl_2 > Cyclohexene > THF (Fig. 1). This variation in the reactivity of different crosslinked system with various solvents arises from the compatibility between the polymer support and the solvent employed. Thus, THF is the best solvent for oxidation using EGDMA-crosslinked system, dioxane for the BDDMA-crosslinked system and, $CHCl_3$ for HDODA-crosslined system.

From these studies, it is clear that the polymer matrix has an influence on the reactivity of the attached function. The flexibility of the polymer support depends on the nature of crosslinking agent.

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 the diffusion of soluble substrate into the

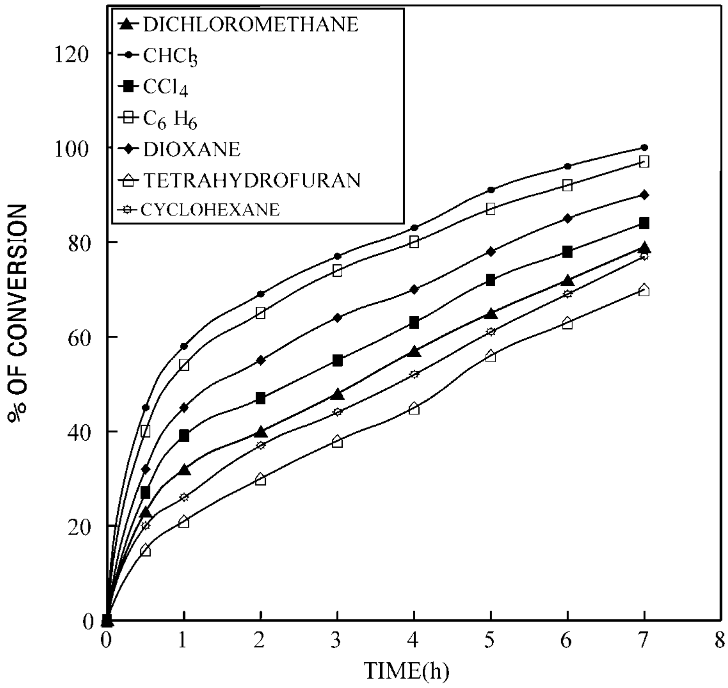

Figure 1. Effect of solvent on the extent of reaction of 2 mol% HDODA-crosslinked PSPOEK-MnO_4 resin.

polymeric reagent was enhanced and hence greater conversion of the substrate took place. It was observed that by changing the polarity of the polymer matrix, time required for the conversion of benzoin to benzil also changed.

By using EGDMA-crosslinked PSPOE-$KMnO_4$ resin, oxidation reactions were carried out at different temperatures. It was found that at 30°C, after 7 h, only 35% conversion of benzoin occurred, whereas at 60°C it is 100%. In flexible BDDMA-crosslinked PSPOE-$KMnO_4$, in dioxane at 80°C 100% benzil was obtained at 7 h. In the highly flexible HDODA-crosslinked PSPOE-$KMnO_4$ system in chloroform at 30°C, benzoin to benzil conversion was 50% and at 55°C, the conversion was 100% at 7 h (Fig. 2). For all crosslinked systems at room temperature the extent of conversion was 25–40%. On increasing temperature the oxidation also increased. Complete conversion was obtained below the refluxing temperature of each case. At high temperature, polymer networks could swell more and easy penetration of the low molecular weight substrate into the interior of the crosslinked polymer matrix takes place. This facilitates the high rate of reaction.

Effect of Molar Excess of the Reagent

In order to investigate the effect of reagent to substrate ratio on oxidizing ability, oxidations were carried out using different reagent to substrate ratios. In all cases, it was found that the rate of reaction increases with increasing molar ratio of the reagent. In the

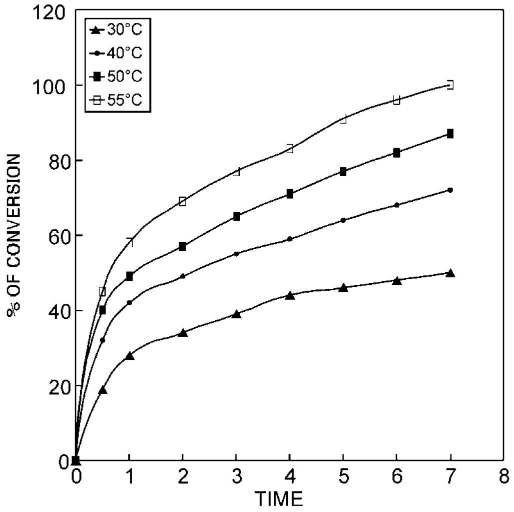

Figure 2. Effect of temperature on the extent of reaction of 2 mol% HDODA-crosslinked PSPOE-$KMnO_4$ resin.

case of EGDMA-crosslinked PSPOE-$KMnO_4$ resin, it was found that there is no further change beyond 1 : 4 molar ratio. It was observed that maximum yield of benzil was obtained at 4 h in THF at 60°C. In polar and flexible BDDMA-crosslinked PSPOE-$KMnO_4$, 100% conversion of benzoin at 3 h was observed in dioxane at 80°C. In the case of highly flexible HDODA-crosslinked PSPOE-$KMnO_4$ resin, only 2 h is needed for full conversion of benzoin in chloroform at 55°C (Fig. 3). This is due to high flexibility of the polymer matrix by the presence of HDODA as crosslinking agent.

Stability and Shelf Life of the Reagents

$KMnO_4$ complexed PSPOE resin can be stored for an extended time without appreciable loss in capacity. In order to study the shelf life period of the polymeric reagents, the polymers were kept in sealed bottles in a dessicator for a period of one year and the capacities were determined again. The results are presented in Table 6. It is seen that in the capacities of the permanganate resins no appreciable change was observed even after one 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 sulphate solution or oxalic acid solution. The regenerated species was filtered, washed and dried in an oven. The dried crosslinked PSPOE resin was equilibrated with potassium permanganate in benzene medium.

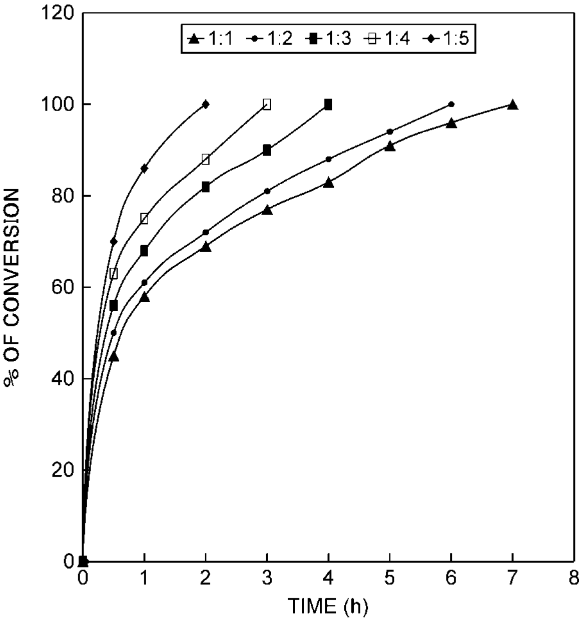

Figure 3. Effect of molar excess on the extent of reaction of 2 mol% HDODA-crosslinked PSPOE-$KMnO_4$ resin.

In the present study, the polymeric reagents were recycled up to seven times, with subsequent use in oxidation studies, with no appreciable loss of activity. 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 recycling of various crosslinked-PSPOE bound permanganate are given in Table 7.

CONCLUSION

This article describes the generation of a new polymeric reagent for oxidation reactions. It comprises a detailed study of the dependence of the nature of the crosslinking

Table 6. Stability of various PSPOE-$KMnO_4$ resins.

Reagent	Initial capacity (mmol/g)	Capacity after 1 year (mmol/g)
EGDMA-PSPOE-$KMnO_4$	3.23	3.00
BDDMA-PSPOE-$KMnO_4$	3.65	3.60
HDODA-PSPOE-$KMnO_4$	3.87	3.83

Table 7. Recyclability of $KMnO_4$ complexed resin.

No. of cycles/ regeneration	Permanganate capacity (mmol/g)		
	EGDMA	BDDMA	HDODA
1	3.23	3.65	3.87
2	3.23	3.60	3.84
3	3.21	3.60	3.83
4	3.20	3.59	3.80
5	3.20	3.59	3.80
6	3.17	3.55	3.76
7	3.14	3.52	3.73

agent on the oxidations of primary and secondary alcohols to aldehydes and ketones, and aldehydes to acids. Ethyleneglycol dimethacrylate-, BDDMA-, HDODA-crosslinked polystyrenes were prepared by suspension polymerization. The permanganate incorporated POEs was prepared by equilibrating PSPOEs with $KMnO_4$ in benzene medium. The effects of various reaction parameters such as solvent, temperature, and molar excess on the oxidising agents were studied. For the EGDMA-crosslinked reagent, THF is the best solvent for oxidations. Dioxane is the best for BDDMA-crosslinked system and $CHCl_3$ is for HDODA-crosslinked system. The reactivity of the reagents increased with increasing temperature and molar excess of the reagent. The oxidations of primary and secondary alcohols to aldehydes and ketones, and aldehydes to acids are effective in carrying out using permanganate bound PSOOE. The reactivity of the oxidizing reagents decreases in the order: HDODA- > BDDMA- > EGDMA-crosslinked system. This is due to increasing flexibility of the crosslinking agent from EGDMA to HDODA. The termination of the oxidation of primary alcohol to aldehyde is contrary to the corresponding oxidation using a low molecular oxidising agent in which acid is the final oxidation product. This is due to the role of the three-dimensional polymer matrix. This oxidizing reagent was found to posses the desired characteristics of the polymeric reagent including operational simplicity, filterability, recyclability, and reusability.

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Received March 2003
Revised May 2003