

## **POLYMER BOUND OXIDISING REAGENTS : PREPARATION, CHARACTERIZATION AND REACTIONS OF COPOLY (PYRROLIDONE-TETRAETHYLENEGLYCOL DIACRYLATE PERMANGANATE)**

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### **ABSTRACT**

A resin has been prepared, which consists of a crosslinked polyvinylpyrrolidone tetraethyleneglycol diacrylate matrix with varying extent of crosslinking. These insoluble polymers were functionalized with permanganate groups and the reactivity of the resulting polymeric permanganates were investigated under different conditions. The quantity of functional group can be determined titrimetrically using ferrous sulphate/oxalic acid solution. The capacities of the reagents varied from 1.85 to 5.15 meq/g. The resin oxidises alcohols to the carbonyl compounds. The extent of crosslinking, the reactivity and the hydrophilic-hydrophobic nature of the various systems used were investigated. The influence of solvent and duration of reaction of the reagent in oxidation reactions were investigated to find out the optimum conditions for effective reaction. These studies revealed that the optimum condition for a specific extent of reaction can be arrived at only by a judicious choice of the crosslink density, mechanical integrity of the particles, temperature and molar excess of the polymeric reagent. In these studies the polymeric reagent is found to be most effective with 15% crosslink density, at reflux temperature, with three fold molar excess of reagent and dichloromethane as the solvent.

**Key words :** Crosslinked polyvinyl pyrrolidone, Polymeric reagents, Ketones.

### **INTRODUCTION**

An increasing number of polymeric reagents have been developed for use in organic synthesis<sup>1-2</sup>. These have been developed for use in simple processes such as epoxidation,<sup>3</sup> oxidation,<sup>4-7</sup> acylation<sup>8</sup> or halogenation<sup>9</sup> In all these applications, advantage is taken of the insolubility of the polymeric reagent and of its by-product, which allows for the easy removal of any excess reagent or spent material from the desired product. In addition to being insoluble, polymeric reagents should be easy to prepare, have a capacity sufficient for use on a practical scale, and be designed in such a way that the spent reagent can be regenerated to its initial activity in an easy fashion<sup>10-12</sup>. Investigations with various polymeric reagents revealed that the nature of the polymeric backbone does influence the kinetics and extent of functional group conversions in polymer-aided reactions. The binding of an active species to a polymer chain results in a

new reagent with different structure, reactivity and selectivity. Apart from the effect of possible heterogenization, polymer attachment gives systems containing several active species per macromolecule, which can behave differently from the low-molecular weight analogues.

This paper describes the preparation of permanganate derivatives of poly (vinyl pyrrolidone-co-tetraethyleneglycol diacrylate)s and their application as oxidizing reagents. The application of permanganate species is well documented in organic chemistry<sup>13</sup>. Because of the several oxidation states to which the permanganate species can be reduced, which are being determined by reaction conditions, it can be used for different step reactions. The reactivity of the permanganate depends to a large extent on whether the reaction condition is acidic, basic or neutral. The problems associated with the oxidation of organic substrates with potassium permanganate are mainly about its solubility in organic solvents. They are usually insoluble or only partially soluble in organic solvents. Moreover, most organic solvents are readily oxidized by potassium permanganate. These factors reduce the effectiveness of potassium permanganate as an oxidizing agent and hence heterogeneous conditions are sometimes preferred. Here we report the preparation and characterization of copoly (pyrrolidone-tetraethyleneglycol diacrylate permanganate) and its use as oxidising reagent. The effects of the extent of crosslinking on the reactivity of the polymeric reagents under various conditions were investigated.

## EXPERIMENTAL

### Materials

1-vinyl-2-pyrrolidone was the commercial product obtained from Fluka, Switzerland and tetraethyleneglycoldiacrylate (TTEGDA) from Aldrich, U.S.A. Solvents were purified by standard procedures. All low-molecular weight substrates used were commercially available samples purified by distillation or crystallisation.

### Preparation of TTEGDA- crosslinked poly (1-vinyl 2-pyrrolidone)

A solution of 0.23 g of a 10% aqueous solution of sodium dibasic phosphate and 20 g of sodium sulphate in 120 mL of water, heated to 50-60°C, was added to a solution of 1-vinyl-2-pyrrolidone (21.76 g) and TTEGDA (0.61 g) and AIBN (0.12 g) with stirring under nitrogen atmosphere. The mixture was heated at 60-65°C for 4 h. A mixture of 0.04 g of AIBN, 0.4 g of AIBN, 10 g of ethanol and 10 mL of water was added and heating was continued for 2 h at 60-65°C. The mixture was then cooled to room temperature with stirring. The product was filtered, washed with water (30 mL x 5 times), methanol (25 mL x 5 times) and acetone (25 mL x 5 times) and dried at 70°C. After drying 19.31 g of white resin beads were obtained.

### Preparation of crosslinked poly [1-vinyl-(2-pyrrolidonium permanganate)]

To a suspension of crosslinked poly(1-vinyl-2-pyrrolidone) (10 g) in water (40 mL), 1N H<sub>2</sub>SO<sub>4</sub> (10 mL) was added and stirred for 1 h. A solution of KMnO<sub>4</sub> (10 g) in water (100mL) containing 1N H<sub>2</sub>SO<sub>4</sub> (10 ml) was added to the suspension with vigorous stirring at 0°C. The



mixture was stirred for 2 h at 0°C and for another 2 h at room temperature. The product resin was filtered and washed with water until the filtrate was completely free from permanganate. The resin was washed with acetone and dried at 70°C. Yield : 18.5 g.

#### Determination of the capacity of the permanganate resin

Approximately 300 mg of the functionalized resin was accurately weighed and suspended in excess of 2N H<sub>2</sub>SO<sub>4</sub> (20-25 mL) for 1 h. A known excess of the standard ferrous ammonium sulphate solution was added and stirred until the dark colour of the resin completely disappeared and turned to almost white. The unreacted ferrous ammonium sulphate solution was titrated against a standard KMnO<sub>4</sub> solution. From the titre values, the permanganate equivalent of the resin was calculated. Capacity : 5.15 meq g<sup>-1</sup>.

#### Oxidation reactions: General procedure

The organic substrate (100 mg) was dissolved in 20 mL of chloroform and a three-fold molar excess of the poly [1-vinyl-(2-pyrrolidonium permanganate)] was added to it. The reaction mixture was stirred for the indicated period at refluxing temperature. The reactions were followed by thin layer chromatography. After complete conversion, the insoluble spent resin was filtered, and washed with solvent. The filtrate was dried over anhydrous sodium sulphate. Removal of solvent from the combined filtrate and washings afforded the product. The details of the different oxidation reactions are given in Table 1.

**Table 1. Oxidation of alcohols using TTEGDA crosslinked poly[1-vinyl (2-pyrrolidonium permanganate)] resin**

Substrate*	Time (h)	Product**	Yield*** (%)
Benzoin	1	Benzil	98
Benzyl alcohol	4	Benzaldehyde	86
Menthol	5	Menthone	90
1-Acenaphthenol	8	1-Acenaphthenone	88
2-Nitro benzyl alcohol	6	2-Nitro benzaldehyde	90
1-Phenyl ethanol	7	Acetophenone	85
2-Adamentanol	4	2-Adamentanone	76
Benzhydrol	3	Benzophenone	88

\*All reactions were carried out in chloroform using 2% crosslinked reagent at reflux temperature.

\*\*Products were characterised by comparison (m.p, b.p, I.R, NMR or TLC) with authentic samples.

\*\*\* Isolated yield.

#### Effect of solvent on the oxidation reactions

A definite amount (3 molar excess) of the polymeric reagent was added to benzoin (100 mg) dissolved in CHCl<sub>3</sub> (10 mL) and stirred at 65°C. A definite volume (0.5 mL) of the reaction

mixture was withdrawn using a micropipette at specific time intervals (avoiding the solid reagent), transferred to a 5 mL standard flask and made up to the mark. The absorbance of the made up solution was measured using a UV-vis. spectrophotometer at 387 nm. From the optical density, the percentage of benzil formed was calculated using a calibration curve. The experiment was repeated by varying the solvent.

#### Recycling and reuse of the spent resin

The spent polymer (5 g) obtained from different oxidation reactions was combined and washed thoroughly with  $\text{CHCl}_3$  to remove any residual soluble organic substrate or product. It was stirred for 2 h with 2N solution (50 mL) of ferrous ammonium sulphate in presence of 2N  $\text{H}_2\text{SO}_4$  (20 mL) to remove all oxides of manganese. The resin was filtered, washed with water and dried. The regenerated polymer was functionalized with permanganate following the procedure described earlier. The oxidising capacities of the regenerated polymer in different regeneration cycles are given in the Fig. 1.

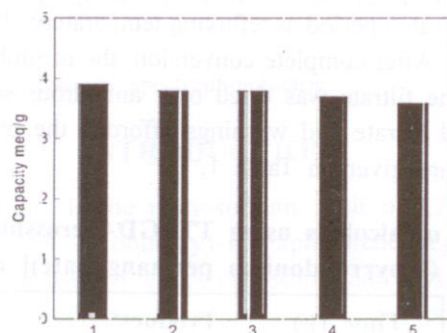
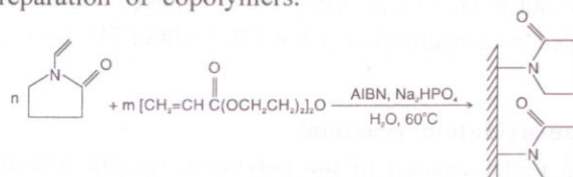


Figure 1. Effect of recycling on capacity of crosslinked poly[1-vinyl (2-pyrrolidonium permanganate)] resin.

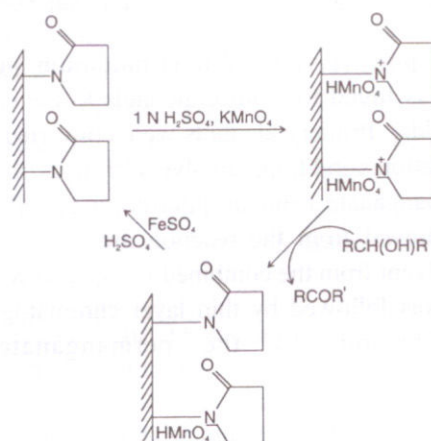
## RESULTS AND DISCUSSION

Tetraethyleneglycol diacrylate crosslinked poly(1-vinyl-2-pyrrolidone)s were prepared by free radical suspension copolymerization of 1-vinyl-2-pyrrolidone using azobisisobutyronitrile (AIBN) as the free radical initiator (Scheme 1). Under these conditions, the resin could be obtained in bead form. In the present study, 2, 10, 15 and 20 mol percentage of the bifunctional monomers were used for the preparation of copolymers.



Scheme 1. Preparation of TTEGDA-crosslinked poly(1-vinyl-2-pyrrolidone).

The crosslinked polymers were functionalized to the corresponding permanganate species by treatment with potassium permanganate in presence of dil.  $\text{H}_2\text{SO}_4$  (Scheme 2). The weight of the product resin after functionalization was found to be twice the weight of the starting material Table 2.



**Scheme 2. Functionalisation and reactions of TTEGDA-crosslinked poly[1-vinyl (2-pyrrolidonium permanganate)].**

**Table 2. Functionalization of poly(1-vinyl-2-pyrrolidone) resin with permanganate**

Percentage crosslinks	Weight of the starting polymer (g)	Weight of the functionalized resin (g)	Capacity (meq/g)
2	20	39.6	5.15
10	15	29.0	3.75
15	8	15.4	2.25
20	5	8.2	1.85

It can be seen that the capacity decreases with crosslinking. The resin retained the bead form characteristic of the polymer. On functionalization the colour of the resin beads changed to dark and it was stable towards light and heat upto  $225^\circ\text{C}$ . The proposed structure for the functionalized resin is in analogy with the poly [4-vinyl (pyridinium chlorochromate)] resin prepared by Frechet et al.<sup>13,14</sup>

#### Characterization of the functionalized resins

The oxidising capacity of the functionalized resin was determined by back titration with standard ferrous ammonium sulphate solution in the presence of dil.  $\text{H}_2\text{SO}_4$ . The infrared spectra of the permanganate functionalized species showed a remarkable shift of the carbonyl peak. Unfunctionalized resin shows a peak at  $1660\text{ cm}^{-1}$  due to the amide carbonyl, which shifted to  $1695\text{ cm}^{-1}$  on permanganate functionalization. From the T. G analysis, it is found that the functionalized resin



is stable upto 225°C. A two-stage decomposition of the polymer was observed from the thermogram. The first stage, which started from 70°C and finished at 150°C is due to the removal of absorbed water. In the second stage, decomposition of both permanganate function and the polymer takes place simultaneously at 225°C.

#### **Oxidation of alcohols using poly [1-vinyl (2-pyrrolidonium permanganate)] resin**

The permanganate resin was found to oxidise alcohols to the corresponding carbonyl compounds in near quantitative yields. Primary alcohols were converted to aldehydes and secondary alcohols to ketones. The oxidation conditions involve stirring of the alcohols with two to three fold molar excess of the permanganate resin in chloroform at reflux temperature for a period of 1-8 hrs. The resin was removed from the reaction mixture by filtration and washed with chloroform. Removal of the solvent from the combined filtrate and washings afforded the product. The progress of the reaction was followed by thin layer chromatography<sup>15</sup>. The details of the oxidation reactions carried out by the permanganate resin are given in Table 1.

One of the striking differences observed with the polyvinyl pyridinium permanganate compared to the polymeric pyrrolidone permanganate is the wetting of the resin with water. Wetting of the resin with water is found to be necessary for oxidation reactions using polyvinyl pyridinium permanganate,<sup>16</sup> whereas in the case of polymeric pyrrolidonium permanganate, no wetting of the resin is required. The time required for the conversion of alcohols to carbonyl compounds is low compared to polymeric chlorochromate<sup>12</sup> polymeric N-bromoacrylamide<sup>9</sup> and polymer-supported analogue of t-butyl hypohalites. The product isolation and purification steps were made easy by the fact that no products of overoxidation (acids in the case of primary alcohols) were found in the reaction mixture once the oxidation was complete.

Oxidation reactions using poly [1-vinyl(2-pyrrolidonium permanganate)] shows some distinct differences from the oxidations with potassium permanganate. Alcohols on oxidation using  $\text{KMnO}_4$  generally yield the corresponding acids through the intermediate carbonyl compounds. But on using the polymeric analogue under the same conditions the oxidation stops at carbonyl state even with large excess of the polymeric permanganate species and extended duration of the reaction. This distinction indicates the effect of the polymer matrix. The time required for the completion of reaction in this case was found to be much higher. This is because the polymeric reagent acts as a reservoir of permanganate species and release them slowly to the reaction mixtures as they are being consumed during the course of the reaction.

The slow release of active functions give selectivity to the reagent. It is incapable of oxidising substrates such as cholesterol, cholic acid and cyclohexanol under identical conditions. In contrast to the action of potassium permanganate on unsaturated compounds the poly[1-vinyl(2-pyrrolidonium permanganate)] is not having any action on stilbene and cinnamic acid. Moreover this polymeric permanganate species do not have any reactivity change in presence of dilute alkali or acid on action of unsaturated compounds and oxidation reactions of alcohols. But in the case of

N-bromo derivatives of poly (acrylamide) polymers show a rate enhancement effect by the addition of a trace of acid, in the oxidation and halogenation reactions.<sup>17,18</sup>

#### Stability, recycling and reuse of the spent resin

The resins recovered after the oxidation reactions were collected and washed thoroughly with different solvents. It can be regenerated in a single step without any appreciable loss in activity. The regeneration of the spent permanganate resin was carried out by removing all manganese states by treating with acidic ferrous ammonium sulphate solution. It was filtered, washed and treated with acidic permanganate solution to obtain the permanganate resin. The polymeric reagents were recycled upto five times without any appreciable loss of activity. Oxidation reactions were carried out using the recycled reagents. There is no significant difference between the yield in oxidation reactions with a fresh sample of the polymeric reagent and with a regenerated sample.

There was a gradual decrease in the capacity of the resin on successive recycling (Fig. 1). The physical nature and filterability were found to be retained under these recycling conditions. The loss observed during the successive recycling was only mechanical.

#### Effect of solvents on the oxidation reaction

The oxidation reactions using the crosslinked poly[1-vinyl (2-pyrrolidonium permanganate)] resins were found to be affected by a change in the reaction solvents. To investigate the effect of solvents on reactivity, the oxidation of benzoin was conducted in a variety of solvents (Fig. 2). The solvents used were chloroform, dichloromethane, cyclohexane, benzene and carbon tetrachloride. Dichloromethane is found to be the best solvent for the oxidation of benzoin. The effectiveness of a solvent in a particular reaction depends on the polarity of the solvent and that of the polymeric backbone. Even though the reagent appears to be a solid, insoluble in solvents, it virtually behaves as a true gel, which expands to a large extent in good solvents.

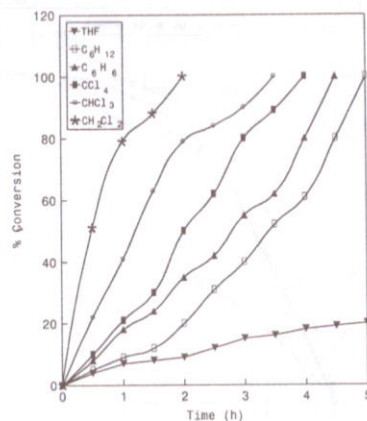


Figure 2. Effect of solvent on reactivity of TTEGDA-crosslinked poly [1-vinyl(2-pyrrolidonium permanganate)] resin.



### Dependence of the nature and extent of crosslinking on oxidation reactions

On comparing the reactivities of the differently crosslinked (2, 10, 15 and 20 percentage crosslinks) reagents, it was found that the reactivity first decreased for the 2% crosslinked reagent, then increased for the 10 and 15% crosslinked reagents and then decreased considerably in the case of 20% crosslinked reagents. These behavioural patterns can be explained on the basis of the hydrophobic-hydrophilic balance of the polymer matrix, the polarity of the polymeric reagent and the nature of the solvent and substrate. The degree of crosslinking of the polymer matrix is instrumental in deciding the net polarity of the polymeric reagent. As the crosslink density increases the hydrophilicity of the polymer matrix changes. Poly(1-vinyl-2-pyrrolidone) is somewhat hydrophilic and substrate used are hydrophobic. This affects the compatibility between the reagent and substrates. As the optimisation of the hydrophilic-hydrophobic balance of the substrate and polymer takes place, greater will be the extent of reaction.

With higher extents of crosslinking the polymer matrix becomes more rigid and the penetration of the solvent and substrate molecules to the active sites of the reagent is difficult. The access of the reactive groups on highly crosslinked networks are considerably diminished as they are flanked by a large frequency of crosslinks leading to a decreased reactivity. The mechanical stability of the polymer increased with the extent of crosslinking. The filtration and the product work-up become easier with the highly crosslinked reagents. With a good solvent, highly crosslinked resins are extremely fragile and even mechanical or magnetic stirring may cause considerable mechanical degradations and attrition of the support. Increased physical stability can be achieved with increased crosslinking but there always exists a balance between the required mechanical properties and reactivity. Highly crosslinked resins were mechanically stable and rigid, but lacked reactivity. From the analysis of the various reaction sequences carried out for the preparation of poly[1-vinyl (2-pyrrolidonium permanganate)] crosslinked with TTEGDA, the 15% crosslinked resin is found to be the best for oxidation reactions. (Fig. 3).

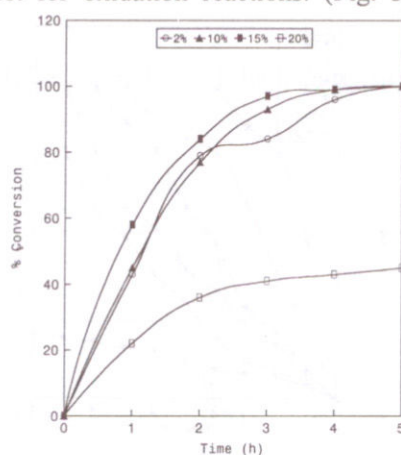


Figure 3. Effect of crosslink density on reactivity of TTEGDA-crosslinked poly [1-vinyl(2-pyrrolidonium permanganate)] resin.



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