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Functionalization of Poly[1-Vinyl (2-Pyrrolidone)] with Permanganate: Preparation and Application as a New Polymeric Oxidizing Reagent

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Poly [I-vinyl(2-pyrrolidonium permanganate)] was prepared from NN′-methylene-bis-acrylamide (NNMBA)-crosslinked poly-(1-vinyl 2-pyrrrolidone) resins by reaction with $KMnO_4$. The insoluble polymeric reagent with a capacity of 2.6–5 mequiv of permanaganate/g was used for the oxidation of alcohols to carbonyl compounds. It possesses the desired characteristics of the polymeric reagents including filterability, operational simplicity, possibility of automation and reusability. The effects of solvent, duration of reaction and molar excess on the oxidation reactions were investigated to optimize the conditions for effective oxidations. The reagent can be stored for months without any loss of activitv. The capacity and efficiency of the reagent were found to be practically unchanged even after several cycles of operation.

Key words: Functionalization, Poly[1-vinyl (2-pyrrolidone)], Polymeric oxidizing reagent.

INTRODUCTION

Polymeric reagents which are reactive species bound to a polymer support have the physical properties of the polymer and chemical properties of the bound reagent function. The main advantages of crosslinked polymer-supported solid phase organic regents over their monomeric counterparts in organic synthesis are the ease of separation of the excess reagents and byproducts from the desired reaction product and reusability[1–3]. In addition the polymer matrix can provide a specific microenvironment that might induce selectivity in a chemical reaction due to steric factors arising from the macromolecular structure, crosslink density and pore size or a dilute distribution of reactive functions on the polymer chain. The attachment to the insoluble macromolecular matrix can also solve the problems of volatility, toxicity, liability or odour often experienced with monopolymeric low molecular reagents. A number of polymer-supported reagents have been reported for oxidation reactions of organic substrates[4–7]. This paper

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describes the preparation of a new solid polymeric reagent poly[1-vinyl 2-pyrrolidonium permanganate)] and its application in organic oxidation.[8] The preparation of poly(N-vinylpyrrolidone) hydrotribromide and its application in organic synthesis has been recently reported from this laboratory[9].

EXPERIMENTAL

Preparation of crosslinked poly(1-vinyl-2-pyrrolidone) (PVP)

A solution of 0.46 g of a 10% aqueous solution of sodium dibasic phosphate (Na_2HPO_4) and 40 g of sodium sulphate in 240 mL of water heated to 50–65°C was added to a mixture of 40 g of 1-vinyl-2-pyrrolidone, 0.12 g of AIBN and 1.65 g of methylene bis-acrylamide with stirring under nitrogen atmosphere. The mixture was heated at 60–65°C for 4 h. A mixture of 0.4 g of AIBN, 0.4 g of NN′-methylenebis-acrylamide, 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 and dried under reduced pressure. Yield: 40.5 g.

Preparation of poly[1-vinyl(2-pyrrolidonium)] permanganate ($PVPMnO_4$)

To a suspension of crosslinked PVP (10 g) in water (40 mL), 1 N H_2SO_4 (10 mL) was added and stirred for 1 h. A solution of $KMnO_4$ (12 g) in water (100 mL) containing 1 N H_2SO_4 (10 mL) was added to the suspension with vigorous stirring at 0°C. The mixture was stirred for 1 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 in vacuum to afford a dark powder. Yield: 21 g.

Determination of the capacity of the permanganate resin

Approximately 300 mg of the functionalized resin was accurately weighed and suspended in excess of 2 N H_2SO_4 (20–25 mL) for 1 h. A known excess of 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 $KMnO_4$ solution. From the titre values the permanganate equivalent of $PVPMnO_4$ was calculated.

Oxidation reactions: General procedure

The organic substrate (100 mg) was dissolved in 20 mL of chloroform and a four-fold molar excess of the poly[1-vinyl(2-pyrrolidonium permanganate)] was added to it. The reaction mixture was stirred at 65°C for the indicated period (Table-1). The reactions were followed by thin layer chromatography. After complete conversion, the insoluble spent resin was filtered and washed with chloroform. 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 POLY[1-VINYl(2-PYRROLIDONIUM PERMANGANATE)] IN CHLOROFORM AT 65°C

Substrate	Time (h)	Yield (%)	Product[a]	m.p. (°C)
1-Acenaphthenol	33	90	1-Acenaphthenone	190
Borneol	22	85	Camphor	179
Benzoin	0.5	99	Benzil	92
Trans-1,2-cyclohexanediol	23	92	1,2-Cyclohexanedione	35
4-Nitrobenzyl alcohol	11	98	4-Nitrobenzaldehyde	105
Benzhydrol	18	98	Benzophenone	49
Dibenzosurberinol	14	95	Dibenzosuberinone	88
2-Adamantanol	30	92	2-Adamantanone	255

[a]Characterised by comparison (mp, bp, TLC, NMR or IR) with authentic samples.

Recycling and reuse of the spent polymeric reagent

The spent polymer (*ca.* 5 g) obtained from the different oxidation reactions was combined and washed thoroughly with chloroform to remove any residual soluble organic substrate or product. It was stirred for 2 h with 2 N solution (50 mL) of ferrous ammonium sulphate in the presence of 2 N H_2SO_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 above. The regenerated and functionalized $PVPMnO_4$ was used for oxidations of alcohols as described earlier. The samples were found to be as active as the original resins even after five successive oxidation-regeneration cycles.

Effect of solvent and molar excess on the oxidation reactions

Benzoin (100 mg, 0.48 mmol) was dissolved in $CHCl_3$ (20 mL). A calculated quantity of the polymeric reagent (for appropriate molar excess, based on oxidising capacity) was weighed and wetted with water, added to the benzoin solution and stirred at 65°C. The progress of the reaction was followed by TLC[9, 10]. The experiment described above was repeated using the various solvents given in Table-2.

RESULTS AND DISCUSSION

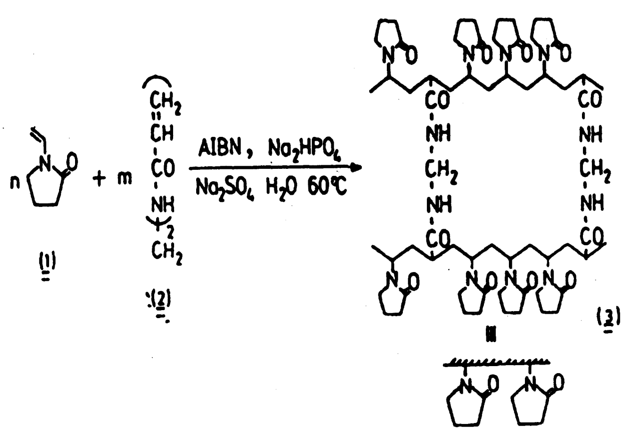
Crosslinked poly[1-vinyl (2-pyrrolidone)] (PVP) was prepared by free radical suspension polymerization of 1-vinyl-2-pyrrolidone (**1**) and NN′- methylenebisacrylamide (**2**) using AIBN as the radical initiator (**Scheme-1**). The functionalization with the permanganate is depicted in **Scheme-2.** Under these conditions the resin could be obtained in convenient bead form. In the present study 3% NNMBA crosslinked samples were used.

TABLE-2
EFFECT OF TEMPERATURE, SOLVENT AND MOLAR EXCESS OF THE REAGENT ON THE EXTENT OF CONVERSION OF BENZOIN

Molar excess of reagent	Temp. (°C)	Solvent	Time for complete[a] conversion, h
Molar equiv.	Reflux	Chloroform	b
2	"	"	c
3	"	"	0.5
4	"	"	0.5
5	"	"	0.5
5	28	"	no reaction
5	reflux	Carbon tetrachloride	0.75
5	"	Cyclohexane	1.25
5	"	Dichloromethane	1.0
5	"	Benzene	0.75
5	"	Tetrahydrofuran	d

[a]As determined by TLC,[b] 45% conversion after 14 h,[c] 55% conversion after 14 h, [d] 65% conversion after 12 h.

The product polymer poly [1-vinyl (2-pyrrolidonium permanganate)] (4) can be washed free of any unbound permanganate and acid, washed with water and dried to obtain a black powder. The weight of the product resin in this functionalization step was found to be double the weight of the starting material, which is in agreement with the theoretically expected value. The permanganate capacity of the functionalized resin was determined by excess back titration with standard ferrous ammonium sulphate solution in the presence of dilute H_2SO_4. The permanganate equivalent of 1 g of the resin from different preparations calculated by this method ranged from 2.6–5 mequiv/g. The IR spectrurm (KBr) of the unfunctionalized resin shows a peak at 1660 cm^{-1} due to the amide carbonyl, which shifted to 1695 cm^{-1}, on permanganate functionalization. From the TG analysis, it is found that the



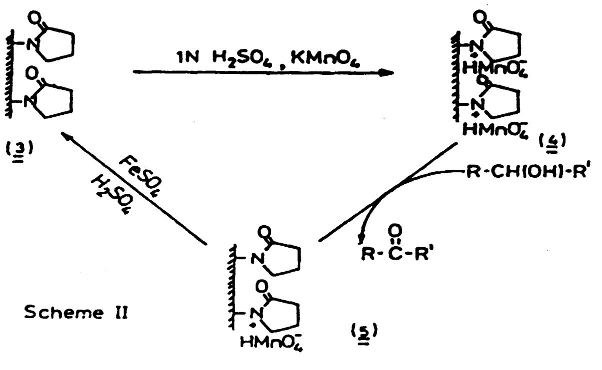
Scheme-1

functionalized resin is stable up to 225°C. A two-stage decomposition of the polymer was observed from the thermogram. The first stage, which started from 75°C and finished at 140°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 220°C.

The resin was investigated in detail for its ability to oxidise alcohols to carbonyl compounds. Primary alcohols were converted to aldehydes and secondary alcohols to ketones in 80–99% isolable yields (Table-1). The oxidation conditions involved refluxing the reaction mixture in chloroform. The progress of the reactions was followed in the case of benzoin to benzil conversion spectrophotometrically[11] at 390 nm and by TLC.

The oxidation with this polymeric reagent shows some distinct differences from the oxidation with $KMnO_4$. Oxidation of alcohols with $KMnO_4$ generally yields the corresponding acids through the intermediate carbonyl compound. But in the case of the polymer-supported permanganate, the oxidation stops at the carbonyl stage even with a large excess of the reagent and extended duration of the reaction. This can be assumed as the effect of the polymer matrix. The oxidation reactions were investigated in different solvents (Table-2). The systematic investigation of the effect of solvent on the oxidation of alcohols using this reagent reveals that $CHCl_3$ is the most effective solvent. This is due to the compatibility of the solvent with the polymeric support having an optimum hydrophilic-hydrophobic balance. The oxidation of benzoin was carried out by changing the molar excess of the resin keeping other experimental conditions the same. The results show that the increase in molar excess beyond 3 does not have any positive effect on the course of the reaction.

The spent resin from the oxidation reaction can be recycled for further use (**Scheme-2**). The regeneration of the partially spent resin (**5**) was achieved by removing all manganese oxidation states by treating with acidic ferrous ammonium sulphate solution and by suspending the resin in water and then treating with $KMnO_4$ as described under the original preparation of the reagent. It was observed that the capacity remained almost the same even after five cycles of regeneration and reuse.



Scheme-2

Conclusion

The foregoing investigations on the preparation of poly [1-vinyl(2-pyrrolidonium permanganate)] and its use as an oxidising agent clearly indicate that this new reagent fulfills the requirements of an effective, convenient and recyclable polymeric reagent. The fact that the capacity of the reagent remains practically unchanged even after successive oxidation, recycling and reuse points to the possibility of automation. The solvent studies indicate the role of the crosslinking agent in deciding the polarity and hence the solvent compatability of the agent.

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