

Polyvinyl Pyrrolidone-Supported Chromates As A Recyclable Heterogeneous Oxidising Agent

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Abstract: Selective oxidation of primary and secondary alcohols to carbonyl compounds can be easily accomplished by using polymer-supported chromium (VI) reagents under anhydrous conditions. Polyvinyl pyrrolidone-supported chromate is prepared easily from 1, 6-hexanedioldiacrylate as the crosslinking agent by reacting with chromic anhydride in water. The insoluble reagent is useful in the selective oxidation of primary and secondary alcohols to their corresponding carbonyl compounds in high yield. The spent reagent after oxidation can be easily removed by filtration and be regenerated several times by treating with CrO_3 without loss of capacity. The effect of reaction parameters like nature of solvent, temperature, reagent to substrate ratio and time was followed using the oxidation of benzoin to benzil as the model reaction. The oxidising reagent possesses a long shelf life and could be recycled several times without reduction of capacity and mechanical stability.

Keywords: polymer supports; crosslinking; chromate; polyvinyl pyrrolidone; heterogeneous; oxidising agents.

I. INTRODUCTION

The use of an insoluble crosslinked macromolecule had provided a facile method for isolating and purifying the product of each condensation step. Since then functionalised polymers have found widespread application in organic synthesis and related fields. It is increasingly recognised that, when polymers are used as supports for catalysts or organic reagents, the reactivity and selectivity of the supported catalysts or reagents may be seriously changed by polymer effects, the origin of which may be physical or chemical. Some of the important advantages of solid phase chemistry includes: the polymeric support has the advantage to provide a particular reaction environment capable of enhancing the nucleophilicity of the ion and reducing the working-up to a mere filtration; the polymer bound reagents may be used in excess to drive a reaction to completion, the byproducts remains support-bound, the reactions can be monitored by standard TLC and NMR methods and the work up involves only simple filtration and evaporation of the solvent and this eliminates the need for any time-consuming chromatographic

work-up. The reactivity of functional groups attached to the polymeric network were influenced by a number of characteristic features of the polymer matrix like the degree of crosslinking and the topographical nature of the gel network. The effect of crosslink density on the reactivity of polymer supported reagents has been the subject of a few investigations. Chromic acid is known to be a versatile oxidizing agent, reacting with almost all types of oxidisable groups. The oxidation of primary alcohols by chromic acid leads to extra problems, the aldehydes formed are fairly easily oxidised, to the corresponding carboxylic acids. With the help of polymer supported Cr(VI) based oxidants, alcohols can be selectively oxidised to carbonyl compounds. The present study describes the synthesis of HDODA-crosslinked polyvinyl pyrrolidone-chromate polymers with varying mole percentage of crosslinking. Oxidations of various primary and secondary alcohols were carried out. The effect of reaction conditions like temperature, solvent, molar ratio and crosslink density were also examined to find the optimum conditions for oxidation reactions.

II. EXPERIMENTAL

MATERIALS AND METHODS

Hexanediol diacrylate (HDODA) was a commercial product available from Aldrich Chemical Company, USA and N-vinylpyrrolidone was purchased from E Merck, Germany. All low molecular weight compounds were commercially available samples and were purified by literature procedures. AR grade solvents were purified by distillation. IR spectra were recorded on a Shimadzu FT-IR-8400 S spectrophotometer. UV spectra were recorded using Shimadzu UV-2450 spectrophotometer. ¹H NMR spectroscopy using BRUKER BZH 500MHz NMR spectrometer, melting points were measured using Buchi-530 melting point apparatus

PREPARATION OF HDODA-CROSSLINKED POLYVINYL PYRROLIDONES

Dissolve 40g of sodium sulphate in 240 ml of water. About 0.6 g of sodium dibasic phosphate was added and heated to 80-85°C. For preparing 2 mol% crosslinked polymer, a solution of NVP (21.76ml), HDODA (0.904 ml) and AIBN (0.12g) was added. Heating and stirring continued for 5h. It was cooled to room temperature with stirring. The product was filtered, washed with water (25mlx4 times) soxhletted using acetone, dried at 60°C. Using the same procedure 5, 10, 15 and 20 mol% HDODA-crosslinked polymers were prepared.

PREPARATION OF CROSSLINKED POLYVINYL PYRROLIDONE-CHROMATES

To a suspension of polyvinyl pyrrolidone (5g) in water, CrO₃ (5g) was added and stirred at 0°C for 2 h and at room temperature for 4h. The product was filtered and washed with water until the filtrate was completely free from CrO₃. The polymer was washed with methanol and acetone and dried in vacuum to afford orange coloured polymer.

DETERMINATION OF THE CAPACITY OF THE POLYVINYL PYRROLIDONE-CHROMATES

100mg of the complex was suspended in 10 ml 2N KOH overnight with occasional stirring. To the resulting solution 10% KI and 3ml conc HCl was added. Diluted to 50ml and titrated against standard sodium thiosulphate using starch as indicator.

OXIDATION REACTIONS USING CROSSLINKED PVP-CHROMATE: GENERAL PROCEDURE

To a five fold excess of the reagent moistened with water, 100mg of the substrate in chloroform (20ml) were added. The reaction mixture was refluxed for the indicated period (Table.III.5). The course of the reaction was followed by TLC. After the complete conversion, the spent polymer was filtered and washed with solvent. The filtrate was dried over

anhydrous sodium sulphate and the product was isolated by evaporating the solvent.

MONITORING THE COURSE OF OXIDATION REACTIONS

The oxidation reactions were followed using a UV spectrophotometer. The oxidation of benzoin to benzil was selected as the model reaction. Standard solutions of benzoin and benzil were prepared in chloroform, THF and cyclohexane with a concentration of 1mg/ml each. Mixtures of different concentrations were prepared from these two solutions and their absorbance was measured at 387nm using spectrophotometer. A calibration curve was constructed. Aliquots from the reaction mixture were withdrawn and the absorbance measured. From the absorbance the percentage of benzil in the reaction mixture was calculated.

INVESTIGATION OF THE EFFECT OF REACTION CONDITIONS ON THE EXTENT OF OXIDATION

To study the effect of various solvents on the rate of oxidation, the oxidation of benzoin to benzil was carried out in solvents of varying polarity. The various solvents used were chloroform, tetrahydrofuran, dioxane, cyclohexane, ethyl acetate and dichloromethane. The effect of molar excess of the reagent on reaction rate was studied using a calculated quantity of the reagent (for the appropriate molar excess based on capacity) by taking oxidation of benzoin to benzil as the model reaction. Benzoin (100mg) was dissolved in chloroform, THF or cyclohexane (10ml), refluxed and a definite (0.1ml) volume of the reaction mixture was withdrawn after specific time intervals. The solvent was evaporated, suitable solvent (5ml) was added to the residue and concentration of the benzil was measured on a UV spectrophotometer at 387nm.

A five fold molar excess of the reagent was added to benzoin (100mg) in chloroform, THF or cyclohexane at room temperature. After 20h of stirring, the reaction was stopped and the concentration of benzil was measured at 387 nm. The same experiment was repeated at temperatures 40, 50 and refluxing temperature of the selected solvents. To study the effect of time on the rate of oxidation aliquots from the reaction mixture was taken out at time intervals of 2, 5,10,15 and 20h. In all cases the extent of reaction was calculated

SWELLING STUDIES

The dry polymers were equilibrated with the solvents (chloroform, tetrahydrofuran, ethyl acetate, cyclohexane, dioxane and dichloromethane) in dry previously weighed sintered crucibles (G₃) for 24h. The excess solvent was drained. Adhering traces of solvents were removed by pressing with filter paper. The weight of the swollen polymer was noted. From the difference in weights the extent of swelling was calculated. Swelling studies were carried out for functionalised and non functionalised polymers.

$$\alpha = \frac{m - m_0}{m_0}$$

RECYCLING AND REUSE OF THE SPENT REAGENT

The spent samples of the polymer obtained from the different oxidation and reactions were washed thoroughly with chloroform to remove any residual soluble organic substrate or product. The washed polymer was treated with Dil HCl (2N, 4X30ml), NaOH (2N, 4X30ml), and washed with distilled water (2X100ml) and finally with acetone. The polymer was then treated with CrO₃ in H₂O at room temperature. Filtered, washed with water till the filtrate becomes colorless.

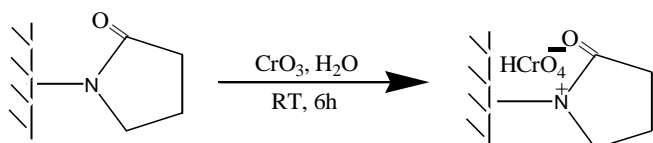
III. RESULTS AND DISCUSSION

SYNTHESIS OF 2-20 MOL% HDODA-CROSSLINKED POLYVINYL PYRROLIDONES

HDODA-crosslinked polymers of varying crosslink densities were prepared by suspension polymerization using AIBN as the radical initiator. The polymerisation of vinyl pyrrolidone was done in an aqueous medium in the presence of a slightly basic buffer. Polymerisation was completed after 5 h and the polymer was filtered, washed several times with water, methanol and Soxhlett extracted using acetone.

PREPARATION OF CHROMATE COMPLEXES OF CROSSLINKED POLYVINYL PYRROLIDONES

Crosslinked polyvinyl pyrrolidone-chromate complexes were prepared by shaking the crosslinked polymer with a saturated solution of CrO₃ in water at room temperature for about 6h. (Scheme 1). The dark brown coloured polymer was collected by suction filtration, washed with water till free from CrO₃ and finally with acetone. The polymer was vacuum dried and the yield was noted. The PVP-chromate complexes are highly stable and the hygroscopic nature of the polymer is reduced on complexation with chromate function.



Scheme III.6: Preparation of PVP-chromate complex

The chromate capacities of the polymers were determined by iodometric titrations and are represented graphically in Fig. 2. Due to the flexibility and hydrophilic nature of the HDODA-crosslinked polymers solvents and low molecular weight reagents can easily penetrate into the crosslinked polymer matrix. For all the crosslinked systems, the chromate capacity decreased with increasing crosslink density.

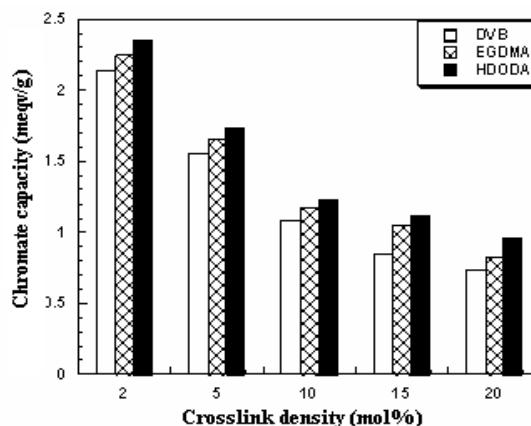


Figure 2: Chromate capacities of PVP-chromates

CHARACTERISATION OF CROSSLINKED POLYVINYL PYRROLIDONES AND CHROMATES

The crosslinked polyvinyl pyrrolidones and their chromate complexes were characterised by FT-IR and ¹³C CP-MAS NMR, thermal analysis and scanning electron microscopy. The FT-IR spectrum of crosslinked polyvinyl pyrrolidones showed characteristic absorptions of pyrrolidone ring at 1660 (amide carbonyl), 1295(C-N_{str}) and at 1425 cm⁻¹(C-H_{def}). There is a broad band at 3500 cm⁻¹, due to the bound or adsorbed water. Due to the hygroscopic nature of PVP polymers, the polymer can easily adsorb water. In addition to the absorptions corresponding to the pyrrolidone ring, the IR spectrum of HDODA-crosslinked polyvinyl pyrrolidone shows absorptions due to ester linkage at 1720 cm⁻¹. In the FT-IR spectrum of HDODA-crosslinked PVP-chromates the carbonyl absorption of the amide shows a red shift of 15cm⁻¹ in its position due to the interaction between PVP and chromate through the amide carbonyl of PVP. The spectrum showed absorptions at 941, 890, 860 and 755 cm⁻¹ which are characteristic of the chromate group.

All the characteristic peaks observed in the ¹³C CP-MAS NMR spectrum of starting polymer were found in the chromate incorporated polymer also, but all the peaks of the functionalised polymers appeared at a lower field compared to uncomplexed polymer. The change in the chemical shift values may be attributed to the complexation of chromate with the pyrrolidone unit and the interaction may be through the functionality attached to the carbonyl carbon. The highly flexible HDODA crosslinks makes the surface of the crosslinked polymer appear irregular and porous in the scanning electron micrograph. Introduction of the chromate function to the polymer matrix made the surface of the crosslinked polymers more rough. Thermogravimetric analysis of 5 mol% HDODA-crosslinked PVP and their chromate complexes were carried out under an inert atmosphere. The crosslinked polymers showed two stage decomposition whereas the chromate complexes had three stages of decomposition. In all the cases, the initial mass loss is due to the removal of adsorbed water.

SWELLING STUDIES

The swelling characteristics of the crosslinked polyvinyl pyrrolidones and chromate complexes with different crosslinking agents and with different crosslink densities were studied by determining the equilibrium swelling ratios of these polymers in different solvents. The solvents used for the swelling studies were cyclohexane, dichloromethane, tetrahydrofuran, chloroform, ethyl acetate and 1, 4 dioxane. The hydrophilic and flexible crosslinks impart more flexibility and chain mobility to HDODA-PVP polymers and hence allow easy penetration of the solvent molecules into the polymer matrix. The HDODA-crosslinked polymers are more polar and hence show maximum swelling in polar solvents. The incorporation of chromate group into crosslinked polyvinyl pyrrolidones reduces the extent of swelling but gave some polarity to the network and show maximum swelling in chloroform.

EFFECT OF DEGREE OF CROSSLINKING AND REACTION CONDITIONS ON THE EXTENT OF OXIDATION

2-20 mol% HDODA-crosslinked polyvinyl pyrrolidones were prepared and functionalised using CrO_3 . The oxidation was carried out in chloroform at refluxing temperature and in all cases a five fold molar excess of the reagent was used. The results are graphically represented in Fig.3. It is seen that in the case of HDODA-crosslinked chromates, the reactivity increases as the crosslink density increases upto 5% and then decreases. Similar variations of the extent of reactivity with increasing degree of crosslinking is reported. This is due to the variation in the hydrophilic-hydrophobic balance and development of microdomains with favourable reaction environment with certain crosslinking agents.

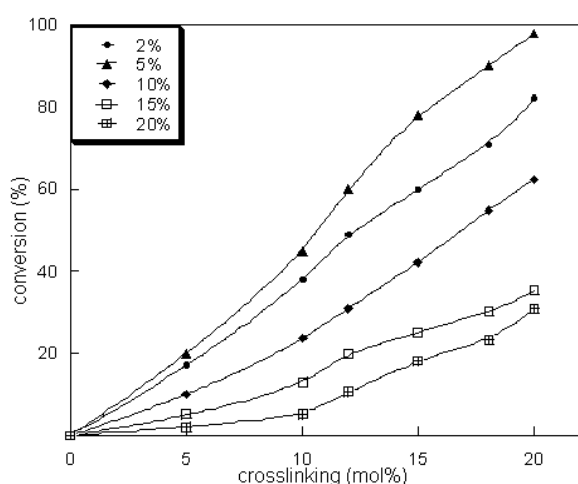


Figure 3: Effect of degree of crosslinking on the oxidation of benzoin using HDODA-crosslinked PVP-chromates

In order to investigate the effect of solvents on the reactivity, the oxidation reactions were carried out in cyclohexane, dichloromethane, tetrahydrofuran, chloroform, ethyl acetate and dioxane. HDODA-crosslinked systems are polar and hence polar solvents facilitate the reaction. Chloroform was found to be the best solvent and least reactivity was found in cyclohexane, which is a nonpolar

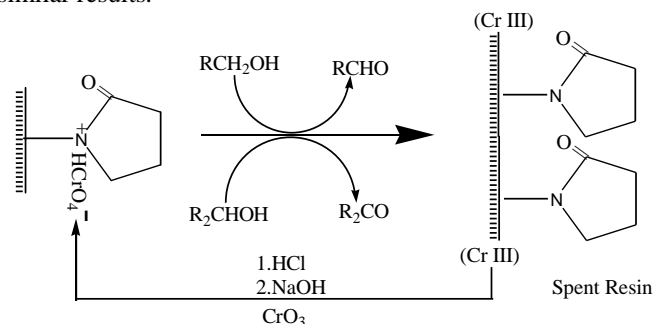
solvent. The enhanced reactivity in polar solvents is due to the effective swelling of the polymer backbone in these solvents. In nonpolar solvents, the swelling of the polymer matrix is not so effective and hence the transports of low molecular weight reagents become diffusion-controlled.

Reactions using polymer-supported reagents are found to be dependent on the concentration of the reagent function. The oxidation of benzoin to benzil was conducted at different reagent to substrate ratio such as 1:1, 1:3, and 1:5. With an increase in the polymer to substrate ratio, there was a corresponding increase in the percentage of benzil formed. Maximum conversion was observed when the molar ratio was 1:5 in all the three systems.

To study the effect of temperature on the reactivity of polyvinyl pyrrolidone-supported chromates, benzoin to benzil oxidation reaction was conducted at various temperatures ranging from 30°C- 60°C in chloroform. The extent of conversion increases as the temperature increases from room temperature to 60°C. The higher reactivity of the oxidising agent at higher temperature may be due to the attainment of the required activation energy by the molecules. At higher temperature penetration of the solvent becomes easier, extensive swelling is possible, thereby facilitating easy diffusion of the substrate into the macromolecular system, and hence high reaction rates were obtained.

OXIDATION REACTIONS USING POLYVINYL PYRROLIDONE-SUPPORTED CHROMATES

PVP-chromate complexes were found to oxidise primary and secondary alcohols to their corresponding carbonyl compounds. It can be seen that the time required for completion of the reaction in the case of HDODA-crosslinked PVP-supported chromates are higher in contrast to the comparatively much shorter time for low molecular weight oxidation. This may be a consequence of the crosslinked macromolecular matrix and the availability of the reactive function in low concentration. Substituents present on the substrates have no detrimental effect on the reaction time and yield. The presence of electron donating and electron withdrawing groups on the benzene ring produced almost similar results.



Scheme 2: Oxidation of primary and secondary alcohols using crosslinked PVP-chromates

The reactions were carried out by refluxing a solution of the low molecular weight substrate in chloroform with five fold molar excess of the reagent. In polymer-supported reactions, excess of the reagent is required since not all the active sites on the polymer are readily accessible. The best results were obtained by using the wet reagent and the reaction

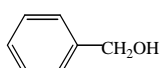
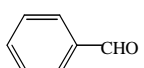
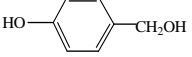

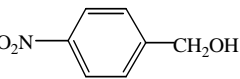
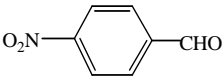
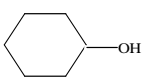
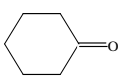
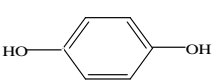
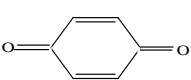
of alcohols afforded carbonyl compounds without the formation of side products. The progress of the reaction was monitored by thin layer chromatography. The time required for the completion of the reaction was found to be much higher compared to low molecular weight compounds.

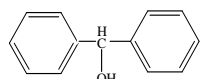
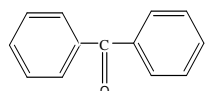
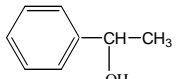
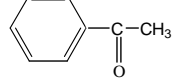
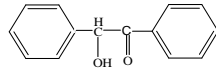
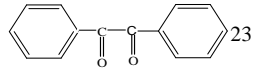
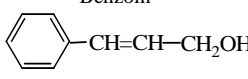
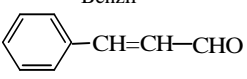
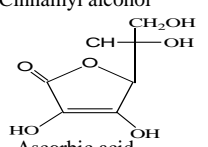
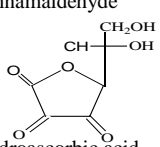
Hexanediol diacrylate is a flexible and hydrophilic crosslinking agent. From the time required for the completion of oxidations, it is clear that 5% HDODA-crosslinked chromate is an efficient and selective oxidising agent. Maximum swelling and compatibility of the HDODA-crosslinked polymer with the solvents facilitates the reactivity of the polymer.

The polymeric reagent acts as a reservoir of chromate species and releases them slowly to the reaction mixture as they are being consumed in the course of the reaction. Furthermore, in all polymer-supported reactions, the initial rate of the reaction is usually quite high but the reaction slows down as the reactive sites are consumed. It should be noted that, although the reaction times are sometimes quite long, no products of over oxidation were detected with any of the alcohols tested. After complete conversion, the product was separated by filtration, washed with solvent, concentrated to dryness and yield was noted. Recycling of the reagent can be accomplished by using a simple washing, reactivation procedure.

RECYCLING AND REUSE OF THE SPENT REAGENT

One of the main advantages of polymer-supported reagents over monomeric reagents is that the spent reagent can be recovered quantitatively at the end of the reaction to their initial activities. The polymeric byproduct obtained after the oxidation reaction was found to have Cr(III) along with some unreacted Cr(VI) species. All the chromium species was removed from the polymer as potassium salt. The regenerated polymer on reaction with CrO₃ in water resulted in the formation of PVP-supported chromate as in the original case. The capacity of the regenerated polymer remained almost the same even after five cycles of regeneration and reuse. The physical nature, filterability and swelling characteristics were found to be retained under these recycling conditions.

Substrate	Product ^b	Time(h)	Yield ^c (%)
		23	90
Benzyl alcohol	Benzaldehyde		
		21	90
4-Hydroxybenzyl alcohol	4-Hydroxybenzaldehyde		
		23	91
4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde		
		16	89
Cyclohexanol	Cyclohexanone		
		18	90

Substrate	Product	Time(h)	Yield (%)
		36	90
Benzhydrol	Benzophenone		
		32	91
α-Phenyl ethanol	Acetophenone		
		23	93
Benzoin	Benzil		
		24	93
Cinnamyl alcohol	Cinnamaldehyde		
		21	90
Ascorbic acid	Dehydroascorbic acid		

^aAll the reactions were carried out in chloroform using five fold molar excess at 60°C;

^bProducts were characterised by comparison with authentic specimens. ^cIsolated yield.

Table 1: Oxidations using 5%HDODA-crosslinked PVP chromates^a

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