

Poly(methyl methacrylate) supported Cr(VI) reagents: Preparation and applications

SHINEY ABRAHAM, P K RAJAN and K SREEKUMAR*

Department of Chemistry, University of Kerala, Kariavattom, Thiruvananthapuram 695 581, India

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Abstract. Divinyl benzene (DVB), ethyleneglycoldimethacrylate (EGDMA) and NN'-methylene bis-acrylamide (NN'-MBA) cross-linked poly(methyl methacrylate)(PMMA)-supported pyrazolinium chromate, chlorochromate and pyrazole-CrO₃ complex resins, were prepared and used as oxidising reagents for alcohols. These resins selectively oxidise primary alcohols to aldehydes and secondary alcohols to ketones. They possess the desired characteristics of polymeric reagents, including operational simplicity, filterability and regenerability. NN'-MBA cross-linked poly(methyl methacrylate)-supported pyrazolinium Cr(VI) reagents are more efficient in terms of functional group capacity, reaction time and product yield.

Keywords. Poly(methyl methacrylate)-supported Cr(VI) reagents; polymeric reagents; macromolecular matrix properties.

1. Introduction

Synthetic reagents bound to polymeric backbones have been widely used in organic chemistry in the past two decades (Rebek 1979; Hodge and Sherrington 1980; Mathur *et al* 1980; Pillai and Mutter 1982; Sreekumar and Pillai 1987; George and Pillai 1988; Devaky and Pillai 1990). These insoluble reagents possess the advantages of easy separation from the reaction mixture and of regenerability. In addition, the polymer matrix can provide selectivity in a reaction either due to the steric constraints imposed by the macromolecular matrix or due to microenvironmental effects (Leznoff 1978; Merrifield 1986; George and Pillai 1989; Sreekumar and Pillai 1989).

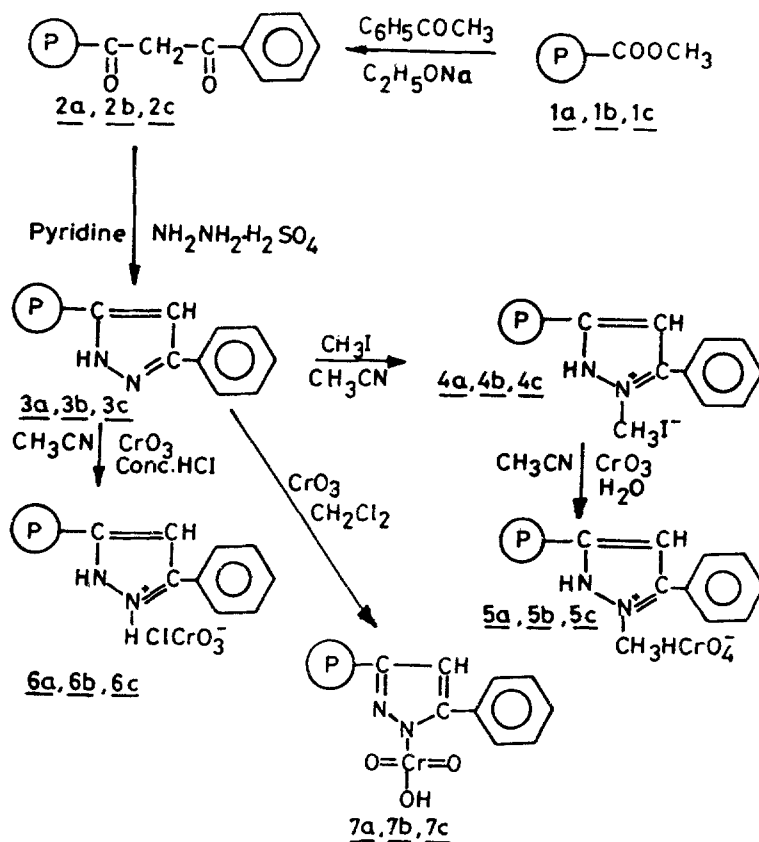
This paper describes the preparation and synthetic applications of poly(methyl methacrylate)-supported pyrazolinium chromate, chlorochromate and pyrazole-CrO₃ complex resins (scheme 1).

2. Experimental

2.1 General

Solvents used were reagent grade and were purified by the following literature procedures. Melting points were determined on a hot-stage melting point apparatus and are uncorrected. Microanalyses were performed at the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras. Infrared spectra were recorded on Perkin-Elmer 397 spectrometer with KBr pellets. MMA-DVB and

*For correspondence



Scheme 1. Preparation of poly(methyl methacrylate) supported Cr(VI) reagents

MMA-EGDMA copolymers were prepared by suspension polymerisation technique (Hart 1977), and MMA-NN'MBA copolymer by solution polymerisation technique.

2.2 Preparation of poly(methyl methacrylate) bound 1,3-diketones

The poly(methyl methacrylate) resin (10 g) preswollen in acetonitrile (20 ml) was heated with acetophenone (20 ml) and sodium ethoxide (5 g) at refluxing temperature for 12 h. Finally, the reaction mixture was cooled in an ice-bath and acidified with sulphuric acid (2N, 20 ml) solution. The product resin was collected by filtration, washed with water, ethanol, and acetone (20 ml \times 3 times each), and then dried in vacuum to constant weight. Yields 11.0, 11.2 and 11.4 g respectively for MMA-DVB, MMA-EGDMA and MMA-NN'MBA, cross-linked poly(methyl methacrylate) supported resins IR (KBr): 1670–1690 (C=O...H str), 2900(OH str), 1700–1740 C=O str), 3030(C–H arom str).

2.3 Preparation of poly(methyl methacrylate) bound pyrazole

Poly(methyl methacrylate) supported 1,3 diketones (10 g) preswollen in acetonitrile (20 ml) was stirred with hydrazine sulphate (10 g) in the presence of pyridine (10 ml) at room temperature for 12 h. The reaction mixture was cooled and the resin particles were collected

by filtration at the pump. The resin was washed successively with acetonitrile, dioxane-water (1:1), ethanol, methanol and dried in vacuum to constant weight. Yields 9.4, 9.3, 9.0 g respectively for DVB, EGDMA and NN'MBA cross-linked resins. IR(KBr): 1620 cm^{-1} (C=N str), 1300 cm^{-1} (C-N str), 3440 cm^{-1} (N-H str), 1650 cm^{-1} (C=C str)

2.4 Quaternisation of pyrazole resins with methyl iodide

Polymeric pyrazole resin (10 g), preswollen in acetonitrile (20 ml) was reacted with methyl iodide (10 ml) at refluxing temperature for 10 h. After the reaction, the mixture was filtered, washed with water, ethanol and acetone (20 ml \times 3 times each), then dried and weighed. Yield 10.2, 10.35 and 10.52 g respectively for DVB, EGDMA and NN'MBA crosslinked resins. IR(KBr): 2800 cm^{-1} (N-CH₃ str), 3440 cm^{-1} (N-H str), 1650 cm^{-1} (C-C str), 1620 cm^{-1} (C=N str).

2.5 Preparation of pyrazolinium chromate resin

Quaternised polymeric pyrazole resin (10 g) preswollen in acetonitrile (10 ml) was stirred at 30°C with CrO₃ (3 g) dissolved in water (10 ml) for a period of 10 h. The resin was filtered and washed with distilled water until the filtrate was clear. It was then washed with acetone, dried and weighed. Yields were of the order 10.11, 10.12 and 10.31 g respectively for DVB, EGDMA and NN'MBA cross-linked resins. IR(KBr): 2800 cm^{-1} (N-CH₃ str), 860, 755, 945, 890 cm^{-1} , (HCrO₄⁻ str), 1620 cm^{-1} (C=N str), 1650 cm^{-1} (C=C str).

2.6 Preparation of pyrazolinium chlorochromate resin

Polymeric pyrazole resin (10 g) preswollen in acetonitrile (20 ml) was suspended in acetonitrile-water mixture (1:1 v/v) (20 ml), then CrO₃ (4 g) and conc. HCl (10 ml) were added. The mixture was stirred at room temperature for 10 h and filtered. The resin was washed with distilled water until the filtrate was clear. Finally, it was washed with acetone (10 ml) and dried. Yields were of the order of 10.2, 10.28, 10.32 g respectively for DVB, EGDMA and NN'MBA cross-linked resins respectively. IR(KBr): 3030 cm^{-1} (N-H str), 950, 910, 835, 755 cm^{-1} (ClCrO₃⁻ str) 1620 cm^{-1} (C=N str), 1650 cm^{-1} (C=C str).

2.7 Preparation of pyrazole-CrO₃ complex resin

Polymeric pyrazole resin (10 g), preswollen in dichloromethane (20 ml), was added to a suspension of CrO₃ (3 g) in dichloromethane (20 ml) and the mixture was stirred at room temperature for 10 h. The resulting dark brown resin was filtered, washed with dichloromethane, chloroform, acetonitrile, water and acetone (20 ml \times 3 times each) and then dried. Yields were of the order of 10.4, 10.52, 10.6 g respectively for DVB, EGDMA and NN'MBA cross-linked resins.

2.8 Oxidation of alcohols

The alcohol (1 mmol) was dissolved in chloroform (10 ml). A two-fold molar excess of the polymeric reagent (1.66 g, 1.54 g and 1.8 g respectively for resins 4a, 5a and 6a) was added and the reaction mixture stirred. H₂SO₄ (10% 1 ml) was also added in the case of pyrazole-CrO₃ complex reagent. The reaction was followed by thin layer chromatography. After the completion of the reaction, the spent resin was filtered off and washed with chloroform. The combined filtrate and washings on evaporation of the solvent afforded the corresponding carbonyl compounds. The products were identified and characterised by comparison (m.p/b.p and IR) with authentic samples.

3. Results and discussion

3.1 Preparation and characterisation of PMMA-based Cr(VI) oxidising reagents

The ester group of the PMMA resin can be chemically modified under mild conditions. The ester group was converted to the β -diketo function by the Claisen condensation reaction with acetophenone and sodium ethoxide. The enol capacities, estimated by the acetylation method (Siggia 1954), were 60, 68 and 70% respectively for resins 2a, 2b and 2c. The β -diketo resin was then converted to the pyrazole resin by reaction with hydrazine sulphate in pyridine. The presence of nitrogen was estimated by Kjeldahl's method. The percentage of nitrogen estimated was 6.8, 7.0 and 7.5% respectively for resins, 3a, 3b and 3c. The pyrazole resin was then quaternised with CH_3I . The capacity of the I^- incorporated in the resin was determined by treatment of the resin with AgNO_3 followed by determination of the displaced iodide as silver iodide. The capacities were found to be 1.6, 2.0 and 2.1 meq/g respectively for resins 4a, 4b and 4c. The pyrazolinium iodide resin on treatment with CrO_3 in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ medium afforded pyrazolinium chromate reagent. The capacity estimated by iodometric method was found to be 1.2, 1.3 and 1.4 meq/g respectively for resins 5a, 5b and 5c. Treatment of pyrazole resin with CrO_3 and conc. HCl in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ mixture resulted in the formation of pyrazolinium chlorochromate resin. The capacities determined by the iodometric method were 1.3, 1.4 and 1.5 meq/g respectively for resins 6a, 6b and 6c.

Similarly pyrazole resin on treatment with CrO_3 in dichloromethane gave pyrazole- CrO_3 complex resin, the capacities of which, estimated by dichrometric method were 1.1, 1.2 and 1.3 respectively for the resins 7a, 7b and 7c.

In the case of DVB-crosslinked PMMA supported Cr(VI) reagents, even though the functional groups have slight polar character, the presence of hydrophobic DVB

Table 1. Oxidation reactions using DVB-cross-linked PMMA-supported pyrazolinium chromate, chlorochromate and pyrazole- CrO_3 complex resins.

Alcohol ^a	Time ^b (h)			Product ^c	Isolated yield (%)			m.p/ (b.p)
	<u>4a</u>	<u>5a</u>	<u>6a</u>		<u>4a</u>	<u>5a</u>	<u>6a</u>	
Benzoin	34	32	43	Benzil	82	84	80	95
Benzhydrol	39	37	40	Benzophenone	81	82	80	49
Benzyl alcohol	43	41	43	Benzaldehyde	79	78	78	(179)
<i>n</i> -Butanol	41	40	42	<i>n</i> -Butyraldehyde	79	80	78	(75)
Cholesterol	43	42	44	Δ^5 -Cholestenone	75	77	73	85
<i>p</i> -Nitro benzyl alcohol	45	44	46	<i>p</i> -Nitro benzaldehyde	72	73	70	58
α -Phenyl ethanol	41	39	42	Acetophenone	82	83	81	(202)
<i>p</i> -Methyl benzyl alcohol	40	39	41	<i>p</i> -Methyl benzaldehyde	78	79	75	(205)
<i>cis</i> -1,2-Cyclohexane diol	35	33	36	2-Hydroxy cyclohexanone	83	86	81	105
<i>p</i> -Methoxy α -phenyl ethanol	39	37	40	<i>p</i> -Methoxy acetophenone	82	84	80	39

^a Alcohol, 1 mmol, resin, 1.66 g (4a), 1.54 g (5a), 1.8 g (6a); solvent, chloroform; temperature, 30°C;

^b includes time for preswelling also; ^c characterised by comparison with authentic samples (IR and m.p/b.p)

Table 2. Oxidation reactions using EGDMA-cross-linked PMMA-supported pyrazolinium chromate, chlorochromate and pyrazole-CrO₃ complex resins.

Alcohol ^a	Time ^b (h)			Product ^c	Isolated yield(%)			m.p/ (b.p)
	4b	5b	6b		4b	5b	6b	
Benzoin	33	31	34	Benzil	85	86	82	95
Benzhydrol	38	36	39	Benzophenone	82	84	80	49
Benzyl alcohol	43	40	42	Benzaldehyde	80	81	79	(179)
<i>n</i> -Butanol	41	40	42	<i>n</i> -Butyraldehyde	80	82	80	(75)
Cholesterol	44	42	45	Δ ⁵ -Cholestenone	78	79	75	85
<i>p</i> -Nitro benzyl alcohol	46	43	46	<i>p</i> -Nitro benzaldehyde	75	76	73	58
α-Phenyl ethanol	42	39	42	Acetophenone	84	86	82	(202)
<i>p</i> -Methyl benzyl alcohol	40	39	41	<i>p</i> -Methyl benzaldehyde	82	84	80	(205)
<i>cis</i> -1,2-Cyclohexane diol	34	32	35	2-Hydroxy cyclohexanone	81	83	80	105
<i>p</i> -Methoxy α-phenyl ethanol	40	37	41	<i>p</i> -Methoxy acetophenone	86	87	83	39

^a Alcohol, 1 mmol, resin, 1.54 g (4b), 1.43 g (5b), 1.66 g (6b); solvent, chloroform; temperature, 30°C; ^b includes time for preswelling also; ^c characterised by comparison with authentic samples (IR and m.p/b.p).

Table 3. Oxidation reactions using NN'MBA-cross-linked PMMA-supported pyrazolinium chromate, chlorochromate and pyrazole-CrO₃ complex resins.

Alcohol ^a	Time ^b (h)			Product ^c	Isolated yield(%)			m.p/ (b.p)
	4c	5c	6c		4c	5c	6c	
Benzoin	32	30	33	Benzil	87	88	84	95
Benzhydrol	37	35	38	Benzophenone	84	85	82	49
Benzyl alcohol	41	40	42	Benzaldehyde	82	83	80	(179)
<i>n</i> -Butanol	39	38	40	<i>n</i> -Butyraldehyde	80	80	78	(75)
Cholesterol	41	41	43	Δ ⁵ -Cholestenone	80	81	75	85
<i>p</i> -Nitro benzyl alcohol	45	44	45	<i>p</i> -Nitro benzaldehyde	78	80	74	58
α-Phenyl ethanol	40	39	41	Acetophenone	86	85	83	(202)
<i>p</i> -Methyl benzyl alcohol	39	38	40	<i>p</i> -Methyl benzaldehyde	84	85	81	(205)
<i>cis</i> -1,2-Cyclohexane diol	33	31	34	2-Hydroxy cyclohexanone	82	85	80	105
<i>p</i> -Methoxy α-phenyl ethanol	38	37	40	<i>p</i> -Methoxy acetophenone	86	88	85	39

^a Alcohol, 1 mmol, resin, 1.43 g (4c), 1.33 g (5c), 1.54 g (6c); solvent, chloroform; temperature, 30°C; ^b includes time for preswelling also; ^c characterised by comparison with authentic samples (IR and m.p/b.p).

present in the polymer matrix reduces the polarity of the active function. This can be made clear by taking into account the capacities of DVB-cross-linked PMMA-supported Cr(VI) reagents EGDMA and NN'MBA cross-linked varieties. Though all of them were developed under the same conditions the latter two have higher values of

capacity. This could be attributed to the flexibility of the system due to the polar cross-linkers NN'MBA and EGDMA.

3.2 Oxidation of alcohols

Alcohols were converted to the corresponding carbonyl compounds in near quantitative yields by reaction with PMMA-based Cr(VI) reagents. The reaction involved stirring of the alcohol with the Cr(VI) reagents in 1:2 molar ratio (1 mmol alcohol and 1.66 and 1.54 and 1.8 g respectively of resins **4a**, **5a** and **6a**) in solvents like chloroform at room temperature. The reaction was monitored by TLC. After the completion of the reaction, it was filtered and the resin was washed repeatedly with solvent. Evaporation of the solvent from the combined filtrate and washings followed by recrystallisation of the residue afforded the carbonyl compounds. The products were characterised by comparison with authentic samples (IR and m.p./b.p.). Details are given in tables 1, 2 and 3.

It was observed that chlorochromate resin is more efficient in carrying out the oxidation reaction in terms of reaction time and product yield compared to chromate and pyrazole-CrO₃ complex resin. This may be due to the less basic nature of the anion bound to chromium in chlorochromate (Brunelet *et al* 1986).

3.3 Reaction conditions and extent of oxidation reaction

Oxidation reactions using poly(methyl methacrylate)-supported pyrazolinium chromate, chlorochromate and pyrazole-CrO₃ complex resins are affected by the nature of the solvent, temperature, catalyst and the effective concentration of the reagent function. It has been observed that favourable interaction between the solvent and the polymer facilitates synthetic reactions involving a polymeric reagent.

The influence of the nature of solvents on the reactivity of the pyrazolinium chromate reagents in the oxidation of benzoin was studied in solvents such as dichloromethane, tetrahydrofuran, chloroform, dioxane, benzene, acetonitrile and cyclohexane. The time for maximum conversion for these solvents was 37, 35, 34, 33, 35, 32, and 37 h, 36, 32, 33, 37, 36, 30 and 37 h, and 32, 30, 32, 32, 34, 29 and 35 h respectively, for DVB, EGDMA and NN'MBA cross-linked PMMA-supported reagents.

The reactivity was found to be maximum in acetonitrile as the solvent. The introduction of a polar chromatic group on to the polymer matrix increases its hydrophilic character and it therefore showed affinity towards more polar solvents like acetonitrile.

Temperature has a major influence on the rate of polymer-supported reactions, Oxidation of benzoin using PMMA-supported pyrazolinium chromate reagent was conducted at temperatures ranging from 20°–60°C. Time for maximum conversion was 39, 34, 29, 23 and 18 h, 38, 33, 28, 21 and 19 h and 36, 32, 27, 22 and 17 h respectively, for DVB, EGDMA and NN'MBA cross-linked PMMA-supported reagents at 20, 30, 40, 50 and 60°C.

The presence of small amounts of acids was also found to have a pronounced effect on the rate of the oxidation reaction. The oxidation of benzoin was carried out by varying the nature and concentration of the acid catalyst. The time for maximum conversion using 2N H₂SO₄, glacial acetic acid, H₂O, and no catalyst was 27, 28, 31 and 34, 26, 27, 30 and 33 h and 25, 27, 39 and 32 h respectively, for DVB, EGDMA and NN'MBA cross-linked PMMA-supported reagents.

To study the effect of molar ratio on the extent of oxidation reaction, oxidation of benzoin was conducted using various reagents to substrate ratios such as 1:1, 2:1, 3:1, 4:1 and 5:1 for about 10 hours. The conversion was 19, 30, 37, 40 and 48%; 22, 34, 42, 46 and 50%; and 25, 37, 45, 48 and 54%, respectively for DVB, EGDMA and NN'MBA cross-linked resins. Whenever a higher molar ratio was used, an increased rate of reaction was observed. Use of higher molar ratios did not cause any side reaction or difficulty in the separation of the product.

One of the major advantages of a polymeric reagent is its recyclability. The Cr(VI) reagents after oxidation was found to contain chromium in the + 3 oxidation state with some unreacted Cr(VI) species, which can be removed by washing with KOH solution. The regenerated resins obtained were refunctionalised using CrO₃ as in the original case. The regenerated resins were equally good in oxidising alcohols. The capacities were found to be 1.2, 1.1, 1, 1, and 0.9 meq/g; 1.3, 1.2, 1.1, 1, 1 and 1.0 meq/g; and 1.5, 1.4, 1.3, 1.2 and 1.2 meq/g respectively for DVB, EGDMA and NN'MBA cross-linked PMMA-supported pyrazolinium chromate resins after the 1st, 2nd, 3rd, 4th and 5th cycles of regeneration.

The foregoing observations indicate that the PMMA-based pyrazolinium chromate, chlorochromate and pyrazole-CrO₃ complex resins fulfill the requirements of an efficient polymeric oxidising reagent suitable for selective oxidation of alcohols. The reagent has the advantages of operational simplicity, possibility of regeneration and reuse.

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