

Quaternized Poly(vinylpyridine) Supported Periodate, Iodate, and Bromate As New Polymeric Oxidizing Agents

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Received 16 October 2002; accepted 1 March 2003

ABSTRACT

Cross-linked poly(n-butyl-4-vinylpyridinium)periodate, iodate, and bromate are easily synthesized and applied as new polymeric oxidizing reagents. These reagents are capable of oxidizing different organic compounds, such as primary and secondary benzylic alcohols to their corresponding aldehydes and ketones in an appropriate solvent. With these oxidants the oxidation of thiols to disulphides, hydroquinones to quinones, acyloins, oximes, allylic alcohols, and diols to their corresponding carbonyl compounds have also been investigated. These polymeric oxidizing agents are stable and can be easily regenerated and used.

Iranian Polymer Journal, **12** (4), 2003, 331-338

Key Words:

polymeric oxidizing agent;
quaternized poly(vinylpyridine);
polymer supported periodate;
iodate, and bromate oxidation.

INTRODUCTION

Functional polymers are macromolecules to which, chemically, functional groups are attached; they have the potential advantages of small molecules with the same functional groups [1].

Probably the most important

advantage in using a functionalized polymer as a reagent or a catalyst is the simplification of product work-up, separation, and isolation. Supported reagents may also be used more conveniently in excess to drive reactions to completion, without

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incurring a penalty in work-up procedures [1]. In addition, in most cases the used polymeric reagents can be regenerated.

The development of polymer supported oxidants has proceeded parallel to the development of polymeric reagents over the past decades [1,2]. One of the most interesting types of polymer supported oxidizing agents are polymer bound anionic oxidizing agents. These reagents can usually be prepared from commercial anion exchange resins or from polymers such as cross-linked poly(vinylpyridine) as supports. Among these, the polymer supported chromates [3], chlorochromate [4], dichromate [5], metal dichromates [6], permanganate species [7], and sodium ruthenate [8], have special places, and have been used for oxidation of a variety of organic compounds.

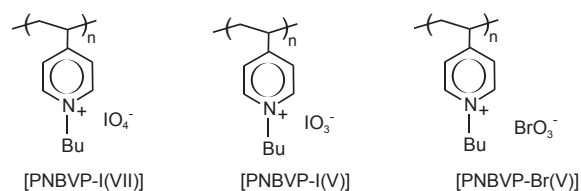
The periodate and iodate anions oxidize various functional groups but the solubility properties of sodium and potassium periodates are such that these salts can generally be used only in hydroxylic media [9]. Reactions can be carried out in aprotic solvents by using periodic acid [10], or by certain lipophilic quaternary ammonium periodate [11]. To overcome the solubility problem and also to make use of the advantages of polymeric reagents, iodate and periodate supported on commercial anionic resin Amberlyst A26 [12], and also on poly(vinylpyridine) [13], were synthesized and reported to oxidize different organic functional groups in a range of solvents including aprotic solvents.

Bromates have been used for oxidation of a variety of inorganic and a few organic compounds. Oxidation of alcohols by NaBrO_3 in the presence of cerium (IV) ammonium nitrate (CAN) [14], bromine [15], NaHCO_3 [16], HClO_4 [17], NH_4Cl [18], and oxidation of different organic compounds by NaBrO_3 and AgNO_3 in the presence of Lewis acids [19], are instances that have been reported. In addition, oxidation of different organic functional groups by bromate supported on commercial resin Amberlyst A26 and poly(vinylpyridine) [20], has been investigated. By using these polymeric oxidizing agents it is possible to overcome many problems associated with using metal bromates, such as the necessity of having a strong acidic solutions or the presence of Lewis acids.

It is generally known that the efficiency of active functional groups attached to a polymeric support, either covalently or ionically, is affected by the structural features of the polymeric support such as polarity,

swellability, nature and extent of cross-linking, etc. [1].

Considering this fact and as a part of a general programme to investigate the reaction of the polymer supported reagents, in this paper synthesis and applications of polymer supported periodate, iodate and bromate based on quaternized poly(vinylpyridine), as new polymer supported oxidizing agents are reported (Scheme I):



Scheme I

EXPERIMENTAL

General

Substrates were either prepared in our laboratory or were purchased from Fluka AG and Merck Companies. Cross-linked poly(4-vinylpyridine) (2% divinylbenzene as cross-linking agent) was a commercial product (Fluka). All products were known compounds, and they were identified by comparison of their spectra and physical data with those of the authentic samples. Melting points were determined in open capillaries on Buchi 510 apparatus. Progress of the reactions were followed by TLC or by GLC on a Shimadzu model-GC-8A instrument with a flame ionization detector and using a column of 15% carbowax 20 M on Chromosorb-w acid washed 60-80 mesh. IR Spectra were obtained using a Perkin-Elmer spectrometer 781. The ^1H NMR, and ^{13}C NMR spectra were obtained using a Bruker Advance DPX 250 spectrometer.

Preparation of Cross-linked Poly(n-butyl-4-vinylpyridinium) Iodide and Bromide, ([PNBVP-I] and [PNBVP-Br])

Cross-linked poly(4-vinylpyridine) (1.0 g) was suspended in sulpholane (7 mL) and allowed to swell for about 24 h at room temperature. To this suspension, freshly distilled n-butyl iodide or n-butyl bromide (4 mL) was slowly added and the reaction mixture was heated at 80-85°C for 48 h. An additional portion of n-butyl iodide or n-butyl bromide (2 mL) was added and the heating was continued for about 24 h. The reaction mixture was then filtered, washed with distilled water

(60 mL) and ether (15 mL). The yellow, [PNBVP-I] and cream-coloured solid, [PNBVP-Br] were dried in the presence of P_2O_5 under vacuum at $40^\circ C$ overnight to give products, 2.25 g and 1.81 g, respectively. The amounts of iodide and bromide were determined by gravimetric and potentiometric titration methods [21], and were 3.12 mmol I^- and 3.20 mmol Br^- per gram of polymers, respectively.

Preparation of Poly(n-butyl-4-vinylpyridinium) Periodate, Iodate, and Bromate, ([PNBVP-I(VII)], [PNBVP-I(V)] and [PNBVP-Br(V)])

For preparation of [PNBVP-I(VII)] and [PNBVP-I(V)], to solutions of sodium periodate (2.12 g) and sodium iodate (2.0 g) in water, [PNBVP-Br] (1.0 g) was added and for preparation of [PNBVP-Br(V)], to a solution of sodium bromate (4.0 g) in water [PNBVP-I] (1.0 g) was added and they were gently stirred for 48 h at room temperature. The reaction mixtures were filtered and the solid materials were washed with distilled water several times (5×20 mL) and dried in a vacuum desiccator in the presence of P_2O_5 at $50^\circ C$ overnight to obtain [PNBVP-I(VII)] (1.34 g), [PNBVP-I(V)] (1.05 g) and [PNBVP-Br(V)], (1.03 g). The capacity of [PNBVP-I(VII)] and [PNBVP-I(V)] were determined by gravimetric and iodometric titration methods and were 1.99 mmol IO_4^- and 1.23 mmol IO_3^- per gram of polymeric reagents, respectively. Also, the capacity of [PNBVP-Br(V)] was determined by gravimetric and potentiometric titration methods and it was found to be 1.25 mmol BrO_3^- per gram of the polymeric reagent.

General Procedure for Oxidation of Hydroxy and Other Organic Compounds with [PNBVP-I(VII)], [PNBVP-I(V)] and [PNBVP-Br(V)]

To a solution of the substrate (1 mmol) in an appropriate solvent (10 mL) in a round-bottomed flask (50 mL) equipped with a condenser and magnetic stirrer, each reagent (1-2 mmol, based on its capacity) was added and refluxed for 0.5-12 h. [PNBVP-Br(V)] could oxidize organic compounds only in the presence of a catalytic amount of a Lewis acid. Therefore, for oxidation reactions the same procedure as above was used by adding $SnCl_4$ (0.3 mmol) as a catalyst. The progress of the reaction was monitored by TLC (eluent: petroleum ether/ethyl acetate) or GLC. On completion of the reaction, the mixture was cooled to room temperature and filtered and washed with the reaction solvent

(2×5 mL). The combined filterates were evaporated and the pure product was obtained in moderate to excellent yield. In few cases in which when the reaction was not complete the crude product was purified on a silica gel with an appropriate eluent.

Regeneration of Cross-linked [PNBVP-I(VII)], [PNBVP-I(V)] and [PNBVP-Br(V)]

The utilized dark polymeric reagents (1.0 g) collected from different experiments were washed successively with hydrobromic acid (2N, 430 mL), $NaHCO_3$ (4N, 4×25 mL), distilled water (2×10 mL) and ether (2×10 mL). Then each polymer was stirred with its corresponding salt ($NaIO_4$, $NaIO_3$, and $NaBrO_3$) to provide the initial polymeric oxidizing reagents.

RESULTS AND DISCUSSION

Cross-linked poly(n-butyl-4-vinylpyridinium) periodate, iodate, and bromate are easily prepared by the exchange reaction of their corresponding quaternized form of the polymers with an aqueous solution of sodium periodate, iodate and bromate at room temperature, respectively. These polymeric reagents are stable and can be stored for months without losing their activities. These reagents were used to oxidize a variety of organic compounds. The representative results are shown in Table 1. [PNBVP-Br(V)] proved to be completely inactive in oxidation reactions, a fact which has also been reported for Amberlyst A26 supported BrO_3^- [20]. However, the reactions could be promoted by the use of catalytic amounts of Lewis acids such as $AlCl_3$, $SnCl_4$, $SnCl_2$ or $ZnCl_2$. $SnCl_4$ in 1:0.3 molar ratio (substrate/catalyst) proved to be the best catalyst. Optimization of the reaction conditions with different solvents showed that for oxidation reactions with [PNBVP-I(VII)], [PNBVP-I(V)] and [PNBVP-Br(V)] cyclohexane, methylene chloride and acetonitrile were the best, respectively. The existence of the n-butyl moiety on these polymeric reagents results in a better solubility i.e., swelling of these reagents in such organic solvents. Also, optimization of oxidant to substrate showed that for [PNBVP-I(V)] and [PNBVP-Br(V)] in all cases, 2:1, and for [PNBVP-I(VII)], 2:1, and in some cases, 1.5:1, and, 1:1, molar ratios were the best.

All the reactions were performed under reflux condition (except, hydroquinones that were oxidized with [PNBVP-I(VII)] at room temperature). These oxidizing

Table 1. Typical examples of oxidation of different types of organic compounds with [PNBVP-Br(V)]^a, [NBVP-I(V)]^b and [PNBVP-I(VII)]^c.

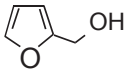
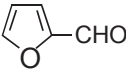


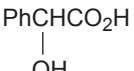
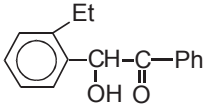
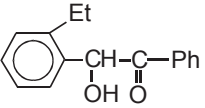


No.	Substrate	Product ^d	Molar ratio oxid: subs.	Time (h)	Isolated yield (%)
1	Benzyl alcohol	Benzaldehyde	2:1 ^a	1.45	90
			2:1 ^b	1.45	98
			2:1 ^c	0.83	98
2	<i>p</i> -Chlorobenzyl alcohol	<i>p</i> -Chlorobenzaldehyde	2:1 ^a	2.45	90
			2:1 ^b	4	90
			1.5:1 ^c	1	98
3			2:1 ^a	2.45	80
			2:1 ^b	3.20	85
			1.5:1 ^c	0.5	98
4	PhCH(OH)Ph		2:1 ^a	5.45	90
			2:1 ^b	5	80
			1.5:1 ^c	4	96
5	PhCH(OH)Et		2:1 ^a	3.20	85
			2:1 ^b	3.5	90
			1.5:1 ^c	3.5	98
6		PhCHO	2:1 ^a	7	65
			2:1 ^b	5.5	80
			1.5:1 ^c	2	98
7			2:1 ^a	5.5	90
			2:1 ^b	4.5	92
			1.5:1 ^c	1.5	90
8			2:1 ^a	4	Trace
			2:1 ^b	4	Trace
			1.5:1 ^c	5	10

Table 1 continued



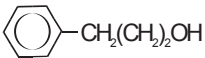
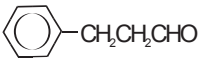

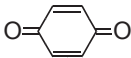
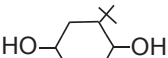
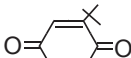
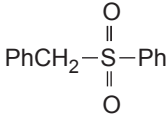
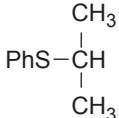
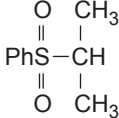
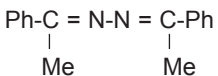

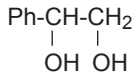
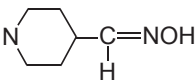
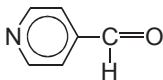
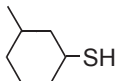
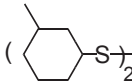
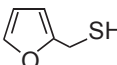
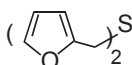
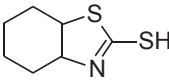
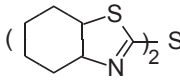
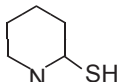
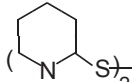
No.	Substrate	Product ^d	Molar ratio oxid: subs.	Time (h)	Isolated yield (%)
9	Ph-CH=CHCH ₂ CH	PhCH=CH-CHO	2:1 ^a	3.45	70
			2:1 ^b	5	90
			1.5:1 ^c	2	98
10			2:1 ^a	4	88
			2:1 ^b	4	7
			1.5:1 ^c	5	4
11			2:1 ^a	4	5
			2:1 ^b	5	12
			1.5:1 ^c	3	50
12			2:1 ^a	1.15	90
			2:1 ^b	0.5	98
			1.5:1 ^c	0.1	98
13			2:1 ^a	9	60
			2:1 ^b	10	90
			1.5:1 ^c	0.25	98
14	PhCH ₂ SPh		2:1 ^a	5	0
			2:1 ^b	5	0
			1.5:1 ^c	12	30
15			2:1 ^a	9	0
			2:1 ^b	9	0
			2:1 ^c	8.5	50
16			2:1 ^a	5	0
			2:1 ^b	5	0
			1.5:1 ^c	12	30
17		PhCHO+CH ₂ O	2:1 ^a	5	0
			2:1 ^b	5	0
			1.5:1 ^c	0.5	98

Table 1 continued

No.	Substrate	Product ^d	Molar ratio oxid: subs.	Time (h)	Isolated yield (%)
18	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}_3\text{CC}-\text{CCH}_3 \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	CH ₃ CHO	2:1 ^a	5	0
			2:1 ^b	5	0
			1.5:1 ^c	0.5	96
19	$\begin{array}{c} \text{Ph-C} = \text{N-OH} \\ \\ \text{H} \end{array}$	PhCHO	2:1 ^a	1.5	0
			2:1 ^b	1.45	0
			1.5:1 ^c	1	98
20	$\begin{array}{c} \text{NOH} \\ \\ \text{Ph-C-Ph} \end{array}$	PhCOPh	2:1 ^a	3.5	80
			2:1 ^b	3.5	80
			1.5:1 ^c	1	90
21			2:1 ^a	4.15	80
			2:1 ^b	4.5	80
			1.5:1 ^c	1.3	98
22			2:1 ^a	4.15	80
			2:1 ^b	4.5	80
			1.5:1 ^c	1.3	98
23			2:1 ^a	3.45	75
			2:1 ^b	3.15	80
			2:1 ^c	1.75	98
24			2:1 ^a	3.45	90
			2:1 ^b	3.5	91
			2:1 ^c	2.5	90
25			2:1 ^a	4.5	80
			2:1 ^b	3.5	80
			1.5:1 ^c	1	95

(a) Poly(n-butyl-4-vinylpyridinium) bromate as oxidant catalyzed by SnCl₄ in refluxing CH₃CN; (b) poly(n-butyl-4-vinylpyridinium)iodate as oxidant in refluxing CH₂Cl₂; (c) poly(n-butyl-4-vinylpyridinium) periodate as oxidant in refluxing C₆H₁₂; (d) products were identified by comparison of their IR, and NMR spectra and physical data with those of the authentic samples.

reagents were able to oxidize primary and secondary benzylic alcohols (entries 1-7), hydroquinones (entries 12-13), oximes (entries 19-21) to their corresponding carbonyl compounds. [PNBVP-I(VII)], also oxidizes sulphides and azines in moderate yield (entries 14-16) and diols to their corresponding carbonyl compounds in excellent yield (entries 17-18). All these oxidizing agents are able to oxidize thiols to their corresponding disulphides in good yields (entries 22-25).

The results in Table 1 proved that [PNBVP-I(VII)] is more efficient than the two other reagents. In addition, [PNBVP-I(VII)] is more efficient than Amberlyst A26 and poly(4-vinylpyridinium) supported periodate[12,13]. This is probably related to better solubility of this polymer in organic solvents (more swelling), due to n-butyl moiety. These polymeric reagents can be regenerated to their original form without any change in their capacity and can be used again for oxidation reactions.

CONCLUSION

Poly(n-butyl-4-vinylpyridinium)-supported periodate, iodate and bromate were easily synthesized, and used for the efficient and selective oxidation of different organic compounds to their corresponding oxidation products. Ease of product isolation, stability, safe handling, selectivity and mildness of these polymeric oxidizing agents make them a useful addition to other reported polymeric oxidizing reagents used in the organic synthesis.

ACKNOWLEDGEMENTS

We are thankful to Shiraz University Research Council for partial support of this work.

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