



Poly(vinylpyridine) Supported Reagents: A Review

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Received 15 June 2008; accepted 21 February 2009

ABSTRACT

Polymer supported reagents have become the subject of considerable and increasing interest as insoluble materials in the organic synthesis. The attachment of the reagents to the insoluble macromolecular matrix can solve the problems of tedious work-up, lability, toxicity, or unrecyclability often experienced with non-polymeric low-molecular weight reagents. A literature survey shows that a review on poly(vinylpyridine)-supported reagents is not available yet. This review will focus on the implementation of methodologies for polymer supported reagents based on poly(vinylpyridine) (PVPy), in the organic synthesis appeared in the literature until the year of 2009. The aim is to distill the literature into three categories and to present each as a short table listing the functionalized polymers involved, along with their relevant applications as reagents. In the text, discussions on the structural and transformation of some typical polymeric reagents are given, although there is not detailed procedure provided in the text about the synthesis of the polymers or their transformations. When appropriate, comparison between the behaviour of supported reagents versus non-supported reagents is attempted. This review does not include the patent literature.

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Key Words:

polymeric reagents;
poly(vinylpyridine) supported reagents;
polymeric oxidizing agents;
polymeric reducing agents;
polymeric halogenating agents.

INTRUDUCTION

Functional polymers are macromolecules to which chemically functional groups are attached; they have the potential advantages of small molecules with the same functional groups [1-13]. Their

usefulness is related both to the functional groups and to their polymeric nature whose characteristic properties depend mainly on the extraordinarily large size of the molecules. The attachment of a chemical functionality to a polymeric support has been realized by

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physical adsorption or by chemical bonding. The former technique is sometimes unsatisfactory; dissociation can occur too easily and hence this method is unsuitable for column or cyclic flow-reactor applications. The chemical attachment has been achieved through two different strategies [1]. In one strategy, functional groups can be fixed on the polymer via electrostatic force, which may be of a coordinative or ionic interaction. In the coordinative interactions (or chelation mode of attachment) a part of polymer support, for example, its pendant groups act as a ligand for the bound functional group. The ionic mode of attachment is mainly found in ion-exchange resins and is highly attractive. In the other strategy, the functional groups are covalently bonded to the polymer. In this case, functional groups are chemically bonded to the polymer backbone or its pendant groups either directly or via a spacer group. The main advantages of those polymer supported species as polymeric reagents over their monomeric counterparts are: (1) the ease of separation of the supported species from a reaction mixture, by filtration and subsequent washing, (2) the possibility to use an excess of the reagent to force the reaction to completion with no work-up problems, (3) reuse of the supported reagent after regeneration, (4) the ease of adoption to continuous-flow processes and hence use in automated synthesis, (5) the reduced toxicity and odour of supported species compared with low molecular weight unsupported analogues, and (6) in many cases, increase stability and selectivity compared to their low molecular weight analogues. A lot of published works on functionalized polymers can be found in two recent reviews [10,11].

One of the most frequently used polymer as support for numerous reagents and catalysts is cross-linked polystyrene [1-3]. Other polymer supports of different natures and polarities have also been used and their supported reagents and catalysts have proven to be useful in many organic reaction transformations. One of such polymers is cross-linked poly(vinylpyridine) (PVPy). Many organic synthetic methodologies based on PVPy-supported reagents and catalysts have shown great success. Cross-linked PVPy, as an insoluble polymer having remarkable properties, has attracted much attention because: (1) it undergoes facile functionalization, (2) it has a large

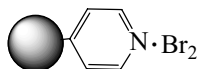
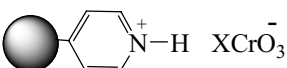
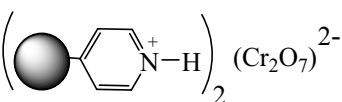
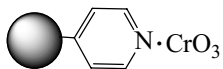
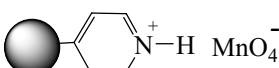
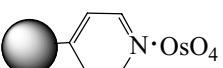
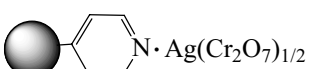
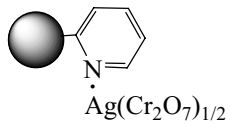
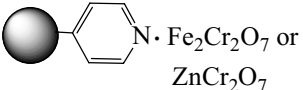
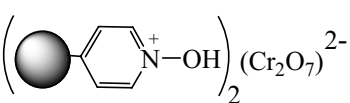
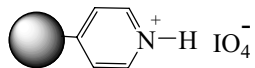
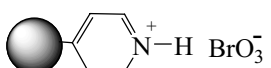
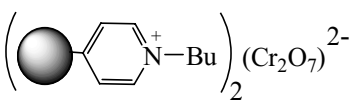
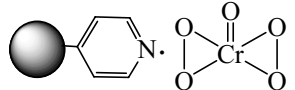
proportion of functional groups which show good accessibility, (3) it is non-hygroscopic, (4) it is prepared readily and is available commercially, (5) it is easy to filter, and (6) it swells in many organic solvents. The 2% cross-linked PVPy by divinylbenzene (DVB) is used most often because of its commercial availability, its stability, reasonable high loading capacity, good swelling characteristics, and good physicochemical structure. More highly cross-linked PVPy is more rigid and can be used as support, but the polymer chains are susceptible to degradative scission during physical handling. Usually, cross-linked PVPy is prepared by emulsion polymerization in the presence of azobisisobutyronitrile (AZBN) initiator and 1-5% divinylbenzene using various combinations of water-soluble polymers and surfactants to help in the formation of porous beads [14]. PVPy has two commercially available isomers namely poly(4-vinylpyridine) (P_4VPy), and poly(2-vinylpyridine) (P_2VPy). Differences in the behaviour and properties between some derivatives of P_4VPy and P_2VPy have been reported in the literature [15-19]. Only P_2VPy can be made with different tacticities which show interesting physical and chemical behaviours. A literature survey shows that the supported reagents made from P_4VPy are considerably more effective than those made from P_2VPy , and except for a few cases almost all of the polymeric reagents based on PVPy have been prepared from P_4VPy . The observed higher efficiencies of P_4VPy supported reagents with respect to those of P_2VPy are probably due to the higher local concentration and/or better availability of the reagent species on this polymer support (due to less steric crowding) for interacting with the substrates.

POLYMERIC REAGENTS

Polymeric Oxidizing Agents Based on PVPy

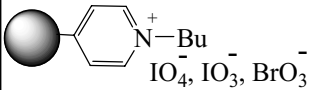
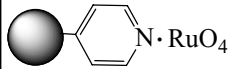
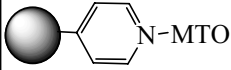
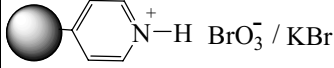
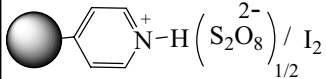
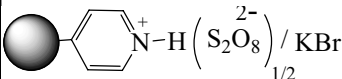
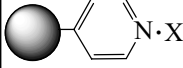
Although many useful procedures for oxidation of different organic compounds have been reported, the main disadvantage of these is the relative difficulty in the preparation of the reagents and in the working-up of the reaction mixture. Polymer bound oxidizing agents were one of the earliest examples of polymeric reagents which alleviate these difficulties [10,20].

Table 1. Polymeric oxidizing agents based on PVPy.

Entry	Reagent	Transformation	Ref.
1		Conversion of thiols to disulphides	21
2	 X = Cl X = Br, F	-Oxidation of alcohols -Oxidation of alcohols and oximes -Oxidation of alcohols	22 23 24-25
3		-Selective oxidation of allylic alcohols over alkyl alcohols	26
4		Oxidation of alcohols	27
5		Oxidation of alcohols	28
6		-Hydroxylation of olefins -Cleavage of olefins to their carbonyl compounds	29 30
7	 	-Oxidation of different hydroxy compounds, oximes, amines, thiols, and aromatic hydrocarbons	31-32
8		Oxidation of alcohols, acyloins, hydroquinones, naphthalene, anthracene, styrene and trans-stilbene	33
9		Oxidation of benzylic alcohols, allylic alcohols, oximes, amines, acyloines and thiols	34
10		-Oxidation of benzylic alcohols, hydroquinones, acyloines, diols, sulphides, thiols, oximes, azines, and decarboxylation of arylacetic acids -Oxidative C-C cleavage of oxiranes to their carbonyl compounds	35 36
11		Oxidation of alcohols, α -hydroxy acids, hydroquinones, diols, thiols, aldehydes, primary and secondary benzylic C-H bonds	37
12		Oxidation of alcohols, hydroquinones, acyloins, and allylic alcohols	38
13	 Chromium peroxide	Oxidation of benzylic and allylic alcohols	39

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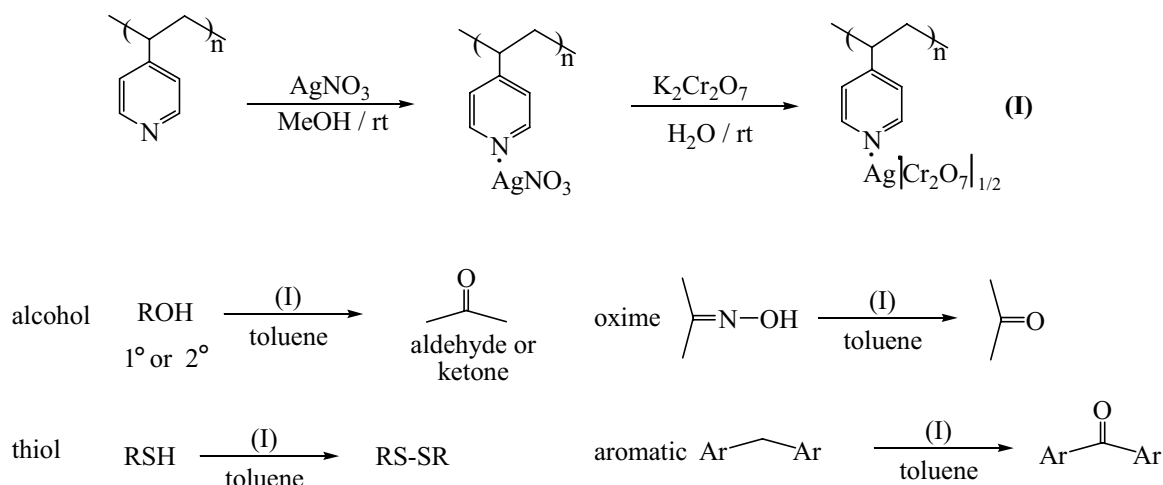
Table 1. Polymeric oxidizing agents based on PVPy.

Entry	Reagent	Transformation	Ref.
14		Oxidation of benzylic alcohols, thiols, oximes, diols, and hydroquinones	40
15	Poly(propylene)-grafted-PVPy-dichromate	Oxidation of alcohols	41
16		Oxidation of alcohols in the presence of co-oxidants such as H ₂ O ₂ , NaOCl	42
17	 MTO= methyltrioxorhenium	Selective oxidation of α -pinene	43
18		Bromination of aromatic compounds	44
19		<i>Para</i> -iodination of methoxyarenes, phenols, and anilines	45
20		<i>Para</i> -bromination of aromatic compounds	46
21	 X = HBr X = HCl, H ₂ SO ₄ (1:1 mix) X = HF, HCl, HBr, HI	As a catalytic electron carrier (mediator) -Electrochemical oxidation of alcohols to their carbonyl compounds -Electrochemical side-chain oxidation of alkylbenzenes -Electrochemical epoxidation of olefins -Electrochemical oxidation of sulphides to sulphoxide, where sulphone was also formed when a chloride-containing resin was used -Electrochemical oxidation of phenyl substituted alkenes as well as alcohols	47 48 49 50 51

PVPy has been used as a support for many oxidizing agents. Representative polymer supported oxidizing agents based on PVPy and their applications are summarized in Table 1.

Oxidizing agents can be fixed on PVPy via electrostatic force, which may be of an ion-exchange or chelation type. For example poly(4-vinylpyridinium chlorochromate) (P₄VPy-CC), and poly(4-vinylpyridinium dichromate) (P₄VPy-DC), have been reported

as ion-exchange types by Frechet et al. which are both commercially available (Table 1, entries 2-3). P₄VPy-CC is prepared by adding a slight excess of chromium trioxide and concentrated hydrochloric acid to the cross-linked PVPy, and P₄VPy-DC is prepared by adding a slight excess of chromium trioxide in water to the cross-linked PVPy. Both oxidizing reagents are efficient for oxidation of alcohols and compared to their corresponding alkali metal salts oxidation can be



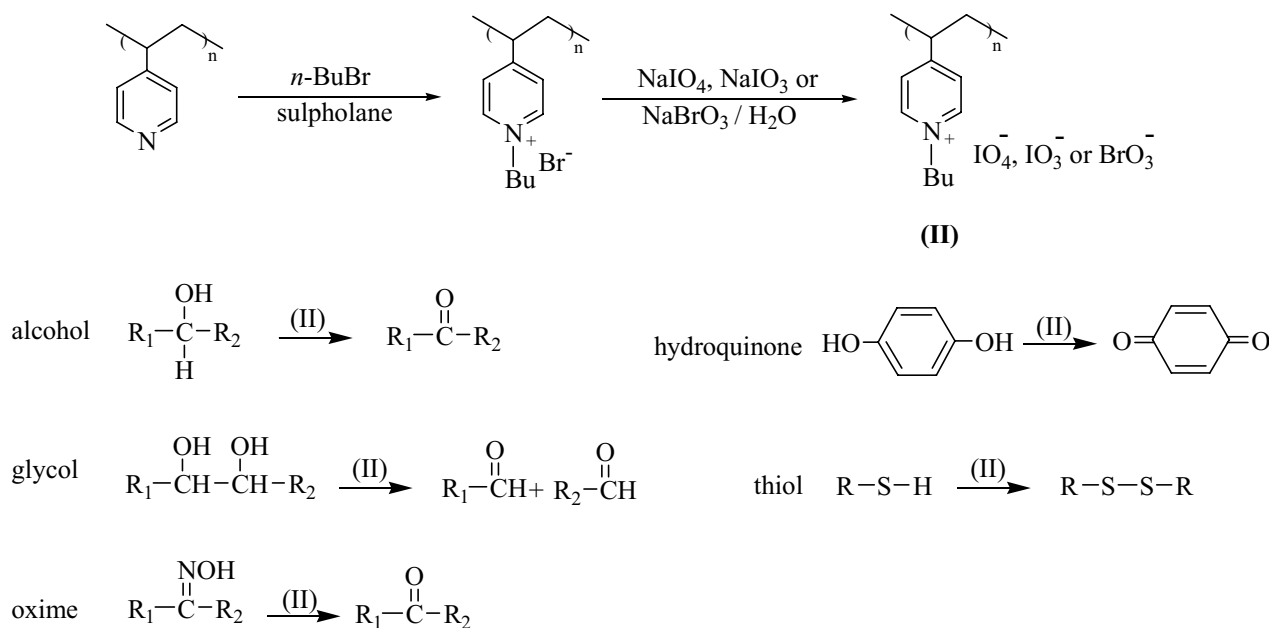
Scheme I. Synthesis and applications of PVPy supported silver dichromate for oxidation of alcohols, oximes, thiols, and aromatic hydrocarbones.

performed in non-aqueous media. Regenerability and easy handling is the chief advantages of these reagents over their unsupported analogue.

As mentioned above, the oxidizing agents can also be fixed on PVPy as a chelation type. Among these PVPy-supported osmium tetroxide (PVPy-OsO₄) has been reported, as a chelation type of polymeric oxidizing agents for hydroxylation and cleavage of olefins in the presence of co-oxidants such as trimethylamine *N*-oxide and *tert*-butyl hydroperoxide (entry 6). PVPy-OsO₄ can be easily prepared by addition of a solution of OsO₄ in cyclohexane to cross-linked PVPy. The use of PVPy-OsO₄ provides the advantage of non-toxicity and an easy work-up as there is no-need of decomposition of the residual tetroxide in the reaction medium. PVPy-OsO₄ can be stored in a bottle without any particular care and it is stable for several weeks. It is important to note that hazardous toxicity is the chief drawback in the use of unsupported-OsO₄. Tamami et al. reported PVPy-supported silver dichromate as a polymeric oxidizing agent (entry 7). In that article, linear and cross-linked P₄VPy and P₂VPy supported silver dichromate are prepared by complexation of the corresponding polymer with silver nitrate and then exchanging the nitrate anions with the dichromate (Scheme I). These dark brown fine powder reagents are stable for months and can be used in equimolar amount for oxidation of different hydroxy compounds to their corresponding carbonyl compounds in aprotic solvents. Oximes,

thiols, and aromatic hydrocarbones can also be oxidized by these reagents. Also, they reported PVPy-supported zinc and ferric dichromate complexes as oxidizing agents (entry 8). The acidity of both reagents is less than that reported for many other reagents such as pyridinium chlorochromate and thus they can be used for the pH sensitive compounds. These polymeric oxidizing reagents are stable, mild and efficient oxidizing reagents for the oxidation of different organic substrates, and they are regenerable.

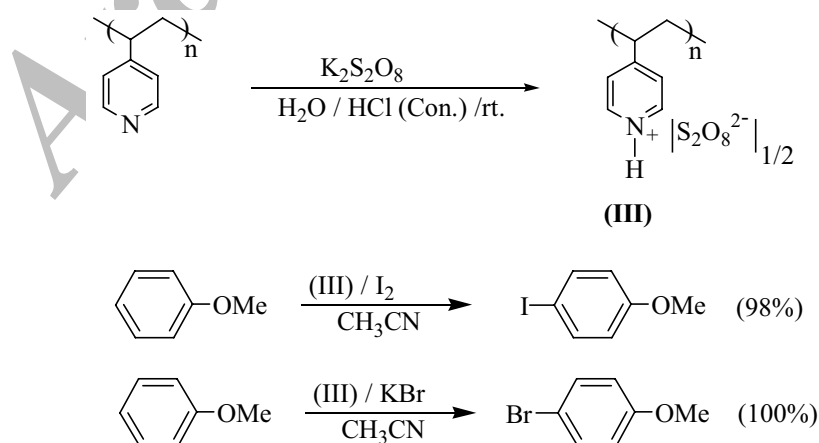
Tamami et al. reported the synthesis of poly(*n*-butyl-4-vinylpyridinium)periodate, iodate, and bromate as polymeric oxidizing agents (entry 14). These reagents are capable of oxidizing different organic compounds, such as primary, secondary, and benzylic alcohols to their corresponding aldehydes and ketones, thiols to disulphides, hydroquinones to quinones, and acyloins, oximes, allylic alcohols, and diols to their corresponding carbonyl compounds in non-aqueous media. It should be noted that solubility properties of iodate and bromate salts such as NaIO₄, NaIO₃, and NaBrO₃ are such that these salts can generally be used only in aqueous media. These polymeric oxidizing agents can be prepared easily by reaction of cross-linked PVPy with an excess of *n*-BuBr followed by an exchange reaction with NaIO₄, NaIO₃, or NaBrO₃ (Scheme II). All these reagents are regenerable. The result showed the order of oxidation activity of these reagents is P₄VPy-IO₄⁻ > P₄VPy-BrO₃⁻ > P₄VPy-IO₃⁻.



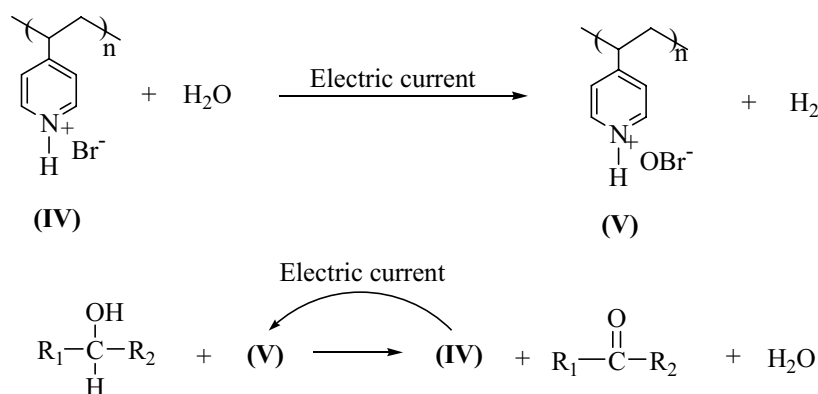
Scheme II. Synthesis and applications of poly(*n*-butyl-4-vinylpyridinium)periodate, iodate, and bromate for oxidation of alcohols, thiols, and oximes.

Very recently it has been reported that poly(4-vinylpyridine)-supported peroxodisulphate can act as a mild oxidant in the presence of iodine and potassium bromide for chemoselective *para*-iodination and *para*-bromination of aromatic compounds, respectively (entries 19-20, Scheme III). As shown in Scheme III, PVPy-supported peroxodisulphate (III) can be prepared easily by reaction of cross-linked PVPy with an excess of potassium peroxodisulphate in distilled water and concentrated hydrochloric acid at room temperature. It is noteworthy that PVPy-

supported peroxodisulphate is a mild oxidizing agent compared to unsupported peroxodisulphate ion. Furthermore, it is also a cheaper oxidizing agent and can be prepared easier compared with the other oxidizing agent used in other comparable reagents reported in the literature. In addition, this polymer-supported oxidant provides the possibility of running the reaction to completion in the presence of more than one equivalent ratio of the reagent to the substrate without serious changes in the reaction products. The reactions were performed in non-aqueous



Scheme III. Synthesis and applications of PVPy-supported peroxodisulphate for chemoselective *para*-iodination and *para*-bromination of aromatic compounds.



Scheme IV. Electrochemical oxidation of alcohols using polymeric oxidizing agent V which is electrochemically generated and recycled in situ.

media and the work-up of the reaction mixture is easy.

The utility of indirect electrochemical reactions using a catalytic electron carrier has been recognized by synthetic organic chemists [52]. Use of electron carrier makes it possible to perform electrochemical oxidations at lower potentials than those required for direct anodic reactions. Although various inorganic and organic carriers have been employed so far, recent development of polymeric electron carriers opens an intriguing aspect of indirect electrochemical reactions. Such polymeric electron carriers enable simple work-up of the reactions and since the exhausted polymeric reagent is regenerated by continuous electrochemical oxidation in situ, the method does not consume any chemical oxidant and does not produce

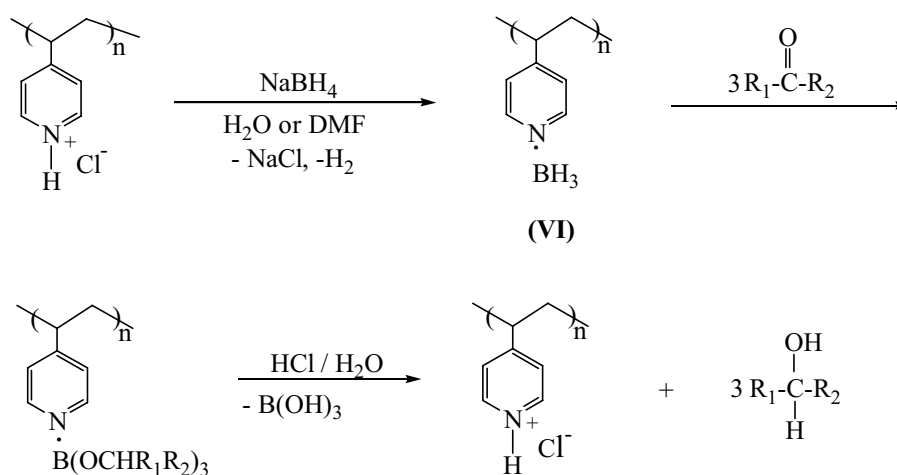
any contaminating reduced product. Polymeric reagents, based on PVPy have been reported as polymeric electron carriers for side chain oxidation of alkylbenzenes, alcohols, olefins, and sulphides (entry 21). For instance cross-linked poly(vinylpyridine) hydrobromide, is an excellent precursor of polymeric reagent for this purpose. Scheme IV shows electrochemical oxidation of alcohols using polymeric oxidizing agent, V, which is electrochemically generated and recycled in situ.

Polymeric Reducing Agents Based on PVPy

Polymer-supported reducing agents have received considerable attention in recent years and a variety of them, while exhibiting the advantages of polymeric

Table 2. Polymeric reducing agents based on PVPy.

Entry	Reagent	Transformation	Ref.
1	N·BH ₃	Reduction of carbonyl compounds	53
2	N	Reduction of aldehydes and ketones	54
3	N·Zn(BH ₄) ₂	-Selective reduction of aldehydes in the presence of ketones	55
4	N·AlCl ₂ BH ₄	-Reduction of aldehydes, ketones, acid chlorides, epoxides and azides	57
		-Regioselective reductive cleavage of terminal epoxides	58
5	N·ZrBH ₄	Reduction of carbonyl compounds	59



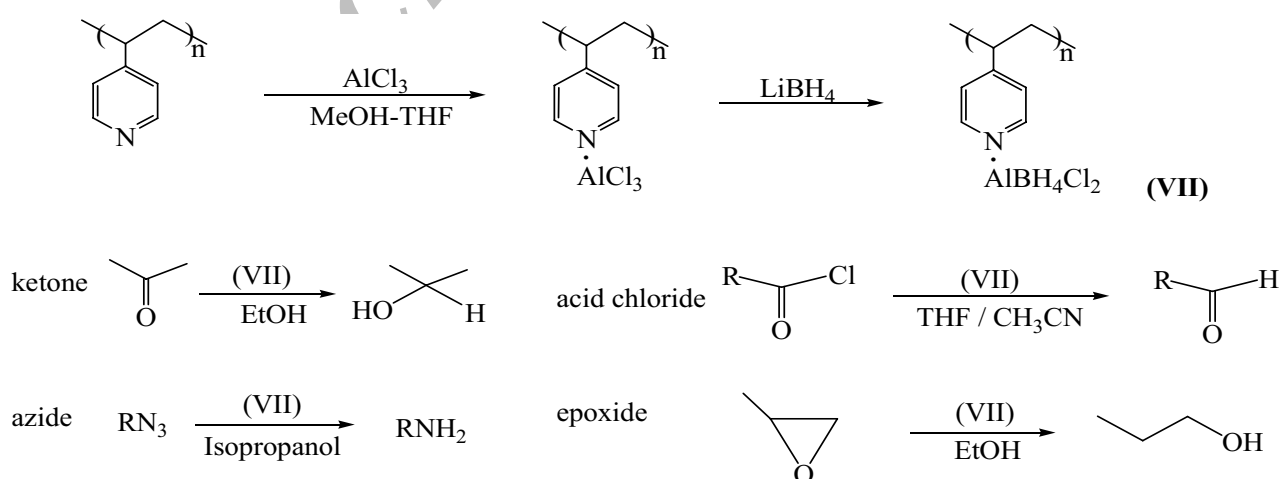
Scheme V. Synthesis and application of poly(4-vinylpyridine)borane for reduction of carbonyl compounds.

reagents, have been used in the mild and selective reduction of organic compounds [10]. PVPy is not only ideally suited for anchoring oxidants but has also been shown to immobilize reducing agents very effectively. Representative polymeric supported reducing agents based on PVPy are summarized in Table 2.

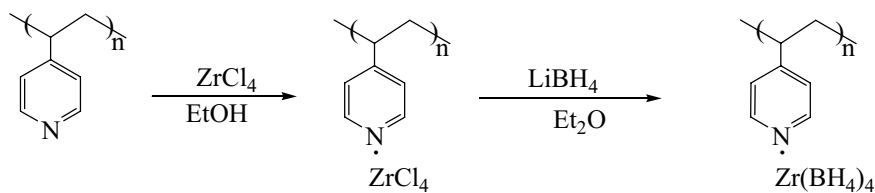
Transition-metal borohydride complexes are volatile unstable solids and as such cannot be used in organic synthesis as reducing agents without modification [60]. One strategy useful to overcome drawbacks of transition-metal borohydride complexes is heterogenization of these complexes on organic polymers. Several types of PVPy-supported borane and borohydride have been reported in literature which

unlike their unsupported analogue are stable, easily prepared, and regenerable polymeric reducing agents. Hallensleben et al. synthesized poly(4-vinylpyridine)borane (Table 2, entry 1) as a polymeric reducing agent. Though the reduction yields with this polymer were generally low, the supported borane is stable and it can be used in a column and is regenerable. Scheme V shows the synthesis and application of this polymeric reducing agent (VI) for reduction of carbonyl compounds.

Zinc borohydride is one of the transition-metal borohydride complexes which has been used frequently in reduction reactions, however because of its instability it should always be used as its freshly pre-



Scheme VI. Synthesis and applications of PVPy-supported chloroaluminium tetrahydroborate in reduction of aldehydes, ketones, acid chlorides, azides, and regioselective reductive cleavage of terminal epoxides.



Scheme VII. Synthesis of PVPy-supported zirconium borohydride.

pared ethereal solutions. Tamami et al. reported the stabilization of zinc borohydride on a polymeric ligand, cross-linked P₄VPy, and its use as a new bench top, stable, efficient and regenerable polymer supported transition-metal borohydride reducing agent for selective reduction of aldehydes in the presence of ketones in high yields (entry 3). It was also found that PVPy-supported chloroaluminium tetrahydroborate can act as stable polymeric reducing agent (entry 4). Scheme VI shows the preparation steps of this polymeric reducing agent. This reagent is able to reduce aldehydes, ketones, acid chlorides, and azides and also is able of regioselective reductive cleavage of terminal epoxides to the less substituted alcohols.

Tamami et al. reported also the synthesis of cross-linked PVPy-supported zirconium borohydride (PVPy-Zr(BH₄)₄), as a polymeric reducing agent for the reduction of carbonyl compounds (entry 5). This polymer is prepared by the exchange reaction between PVPy-supported zirconium chloride complex and lithium borohydride in dimethyl ether (Scheme VII). PVPy-Zr(BH₄)₄ is a white-cream, stable, non-hygroscopic powder, regenerable, and can be kept for months without significant change in its efficiency. One point worth mentioning is that Zr(BH₄)₄ itself is a highly volatile solid, decomposing ambient room temperature, inflaming in air and hydrolyzing explosively.

Polymeric Halogenating Agents Based on PVPy

Halogenation of organic compounds is a crucial step in the preparation of various synthetic intermediates or products. Therefore, it is not surprising that several polymer-bound halogenating reagents have been established since 20 years ago in the early days of functionalized polymers. In most cases cross-linked polystyrene, cross-linked PVPy or cross-linked copolymers of styrene and 4-vinylpyridine have been

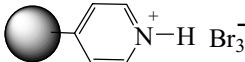
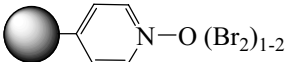
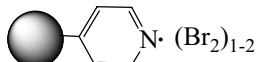
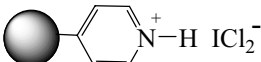
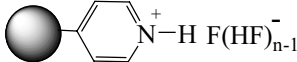
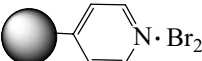
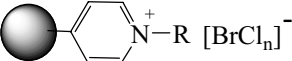
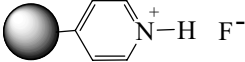
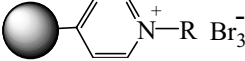
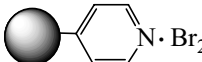
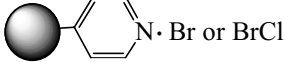
used as polymeric supports for halogenating reagents. Most of these reagents are based on ion-exchange resins, often loaded with perbromide making them well suited for bromination reactions. It has also been shown that the cross-linked copolymer of 4-vinylpyridine with styrene formed various types of complexes with halogens, and its bromine complexes have been found to be able to introduce bromine into alkenes, ketones, and side chains in alkyl substituted aromatic molecules. Representative polymeric halogenating agents based on PVPy are summarized in Table 3.

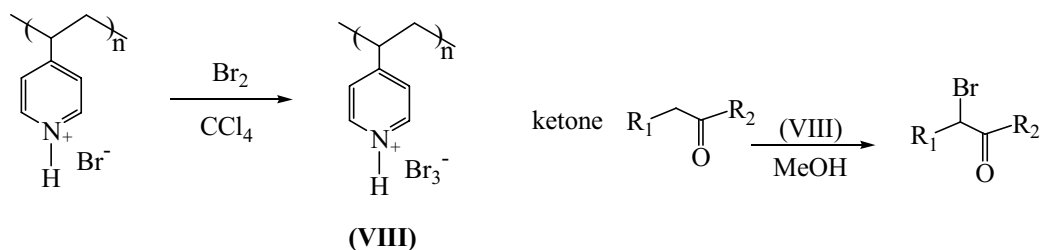
Frechet et al. reported the synthesis of poly(vinylpyridinium hydrobromide perbromide) as a polymeric halogenating reagent (Table 3, entry 1) [61]. This polymeric reagent can be used instead of free bromine for the bromination of ketones. The reagent is easier to handle than liquid bromine and can be handled more accurately in micro quantities; in addition it is often more selective than bromine. This polymeric reagent was prepared by reaction of the PVPy beads with an excess of hydrogen bromide, followed by reaction with bromine (Scheme VIII).

Zupan et al. reported the synthesis of PVPy-supported bromine complexes as stereoselective brominating agents (entry 2, Scheme IX). Reactions of alkenes with these polymeric reagents resulted in a high degree of anti-stereoselectivity. Easy work-up and handling of the polymeric reagents are the obvious advantages of the present method. The use of these reagents has resulted in a reduction in the unwanted and hazardous waste that is produced during conventional homogeneous processes. These polymeric reagents can be recovered unchanged and used again several times without any loss in their activity. The reactivity increases from IX to XI.

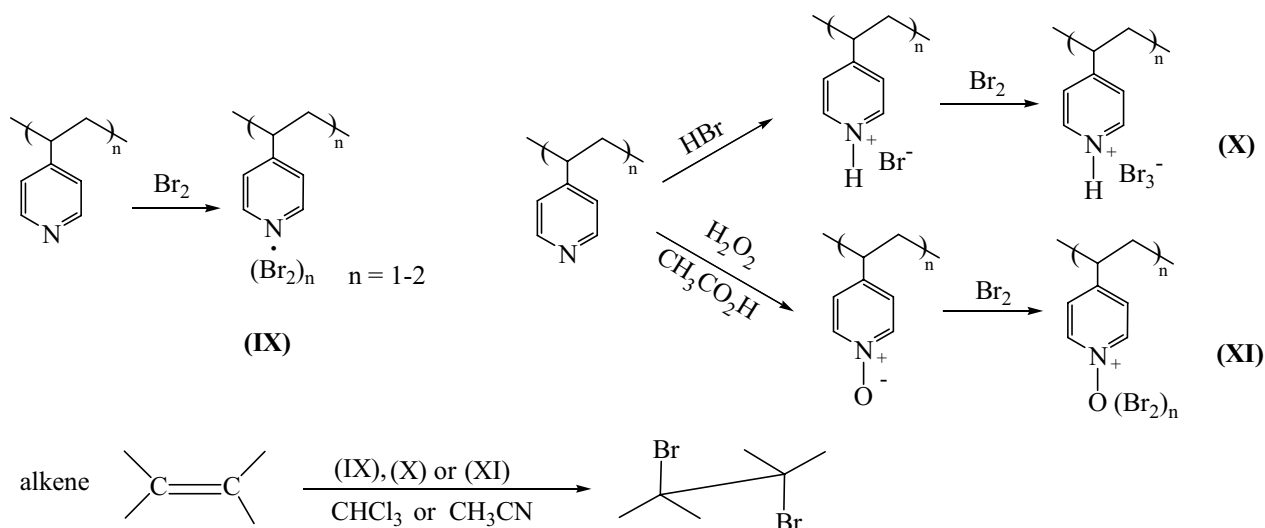
Another polymeric halogenating reagent based on PVPy is cross-linked poly(styrene-4-vinylpyridinium dichloriodate) for regioselective iodination of aro-

Table 3. Polymeric halogenating agents based on PVPy.

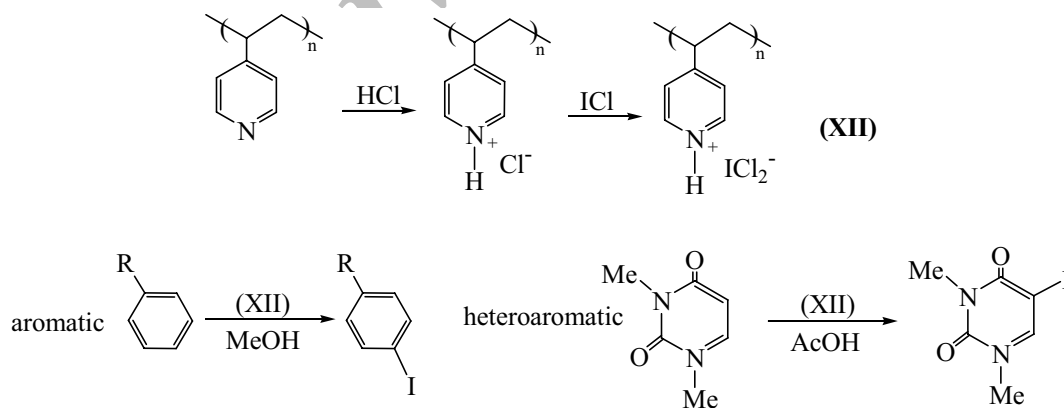
Entry	Reagent	Transformation	Ref.
1		- α -Bromination of ketones	61-64
2		Bromination of alkenes with a high degree of anti-selectivity	65
			
3		-Regioselective iodination of aromatic and heteroaromatic molecules	66-67
4		-Hydrofluorination and bromofluorination of alkenes and alkynes and fluorination of alcohols	68
		-Transformation of hydrazines into gem-difluoro compounds in the presence of <i>N</i> -bromosuccinimide	69
5	 Copolymers with (-)-menthyl acrylate or (-)-menthyl methacrylate	Chiral polymeric halogenating agent: regioselective bromination of mono-olefines and diens	70
6	 R = H, C ₂ H ₅ , n-C ₄ H ₉ , n-C ₆ H ₁₃ , n-C ₁₂ H ₂₅	Bromination and chlorobromination of alkenes and study of the polymeric backbone on the reactivity of polymer supported reagent	71
7		-Iodofluorination of alkenes and alkynes in the presence of <i>N</i> -iodosuccinimide	72
8	 R = n-C ₆ H ₁₃ R = Bu	-Bromination of aromatic molecules	73
		-Dibromination of alkenes and alkynes and α -bromination of ketones	74
9		-Bromination alkenes and aromatic compounds and side chain bromination of aromatic compounds in the presence of dibenzoyl peroxide	75
		- α -Bromination or α,α -dibromination of ketones in the presence of dibenzoyl peroxide	76
		-Side chain bromination of aromatic compounds in the presence of dibenzoyl peroxide	77
10		- α -Bromination of the functionality in synthesis of piperidino-thiomorpholines	78
		Halogenation of olefinic and acetylenic bonds	79



Scheme VIII. Synthesis and applications of poly(vinylpyridinium hydrobromide perbromide) for the bromination of ketones.



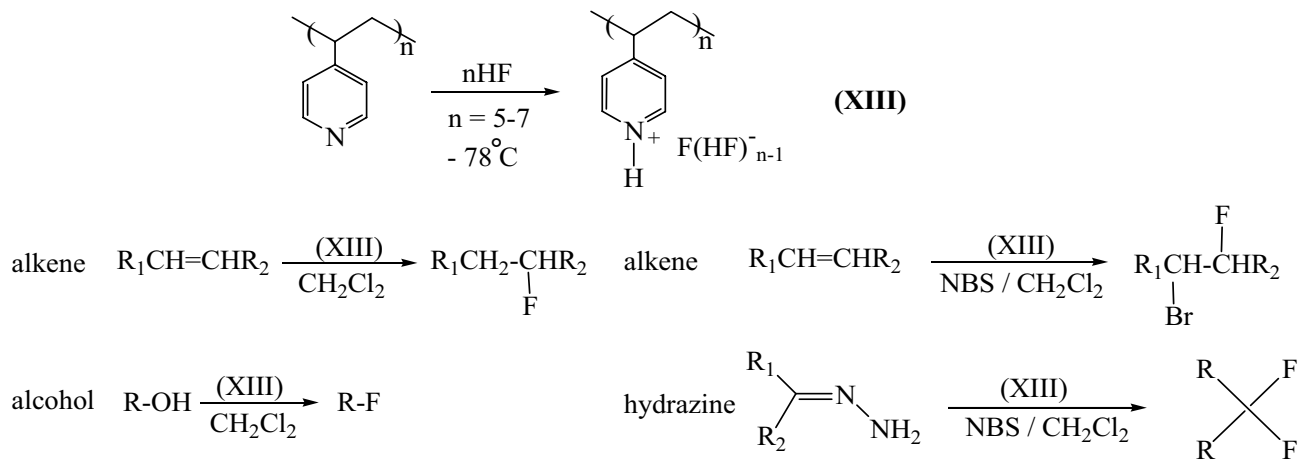
Scheme IX. Synthesis and application of PVPy-supported bromine complexes for stereoselective bromination of alkenes.



Scheme X. Synthesis and applications of poly(styrene-4-vinylpyridinium dichloroiodate) for regioselective iodination of aromatic and heteroaromatic molecules.

matic and heteroaromatic molecules (entry 3). This polymeric reagent was prepared by reaction of PVPy with hydrogen chloride, followed by the reaction with an equivalent amount of iodine chloride (Scheme X).

Poly(4-vinylpyridinium) polyhydrogen fluoride, a solid polymeric poly(hydrogen fluoride), has been reported and used as a fluorinating agent for hydrofluorination and bromofluorination of alkenes and

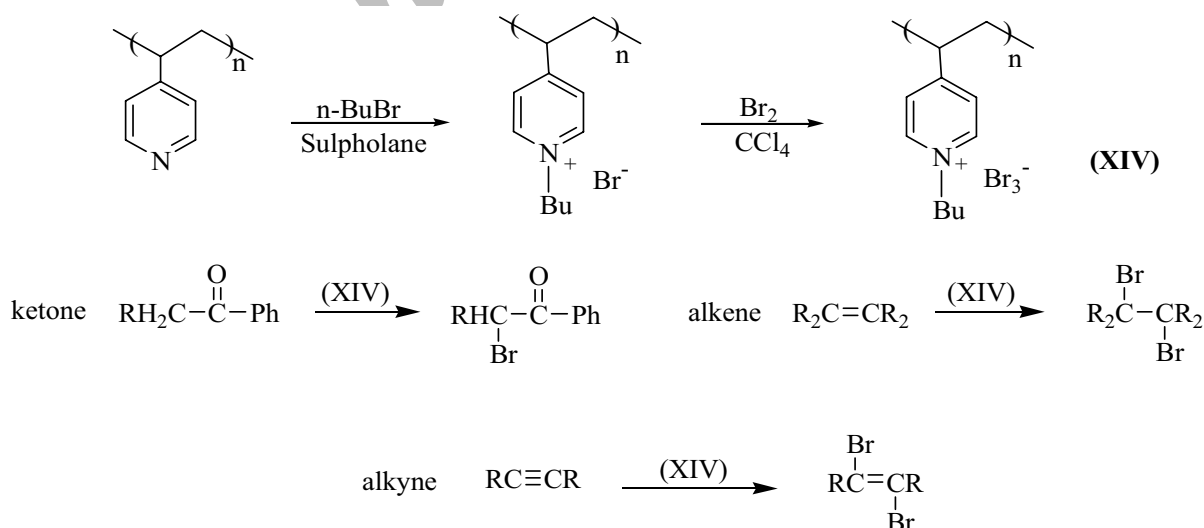


Scheme XI. Synthesis and applications of poly(4-vinylpyridinium) polyhydrogen fluoride for hydrofluorination and bromofluorination of alkenes, fluorination of alcohols, and transformation of hydrazines into gemdifluoro compound in the presence of *N*-bromosuccinimide.

alkynes and for fluorination of alcohols (entry 4). The reagent was prepared by reaction of commercially available cross-linked PVPy with anhydrous hydrogen fluoride at low temperature without use of solvent. The advantage of this reagent is its easier handling compared to anhydrous hydrogen fluoride or the liquid hydrogen fluoride. In the latter case, separation of the products from the reaction mixture containing excess reagent can be rather tedious. This reagent has been used for transformation of hydrazines into gemdifluoro compound in the presence of *N*-bromosuccinimide (Scheme XI). Although this reaction can

also be carried out in anhydrous hydrogen fluoride, poly(4-vinylpyridinium) polyhydrogen fluoride is more convenient alternatives to anhydrous hydrogen fluoride which has a low boiling point (19.6°C).

Parvanak found that poly(*n*-butyl-4-vinylpyridinium) tribromide can act efficiently as a brominating agent for α -bromination of ketones and dibromination of alkenes and alkynes (entry 8). This reagent was prepared by quaternization of the P₄VPy beads with an excess of *n*-BuBr in sulfolane as solvent, followed by reaction with a solution of bromine in carbon tetrachloride to result orange beads (Scheme XII).



Scheme XII. Synthesis and applications of poly(*n*-butyl-4-vinylpyridinium) tribromide for α -bromination of ketones and dibromination of alkenes and alkynes.

The resin is stable and can be stored on a bench for several months without any loss in its activation. In addition, this reagent can be regenerated and reused.

CONCLUSION AND OUTLOOK

The use of supported reagents in chemistry offers many potential environmental advantages compared to traditional reagents. PVPy-supported reagents are active for various organic reactions including oxidations, reductions, and halogenations. The relative ease of anchoring various reagents on PVPy, simple recovery from reaction mixtures, their reusability, compatibility with a wide range of solvents, physical stability, and their toleration of a great number of reaction conditions bodes well for the future of PVPy-supported reagents in which their properties can be fine-tuned for specific chemical transformations. Although great strides have been made in the use of PVPy as support for reagents and catalysts, considerable research work remains to be done. We hope this article will help researchers of the field plan syntheses using supported reagents based on PVPy. We confess that the present article is not a comprehensive of all the works related to the topic, and we apologize to those investigators whose work could not be summarized herein.

ACKNOWLEDGEMENT

The authors are thankful to the Research Councils of Shiraz University and Shahrekord University for their partial support of this work. We are grateful to Dr. Abdulhamid Fadavi for his assistance in the preparation of this manuscript.

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