CHAPTER 2

POLYMER SUPPORTED REAGENTS:
AN OVERVIEW
2.1 Introduction

After Merrifield's revolutionary invention of the solid-phase peptide synthesis,\(^1,2\) an increasing number of polymeric reagents have been developed for use in organic synthesis,\(^3-7\) ion-exchangers,\(^8-13\) synthesis of heterocycles,\(^14,15\) catalysis,\(^6,7\) synthesis of therapeutics,\(^7\) and synthesis of natural products.\(^7\) Among them those based on cross-linked polymers have become popular because of ease of handling and reaction work-up. Most polymeric reagents can be removed by simple filtration upon completion of a reaction and can be recycled several times over following their use without appreciable loss of reactivity. The reactions can often be driven to completion by using excess of these cross-linked reagents without the fear of separating the unspent reagents or the polymeric by-products from the desired reaction products. A polymeric reagent is a system that combines the unique properties of conventional reactive moieties bound to it and those of high molecular weight polymer. The chemistry and applications of these polymeric reagents depend largely on the characteristics of the bound functional group, which in turn depend on the structural characteristics of the macromolecules. This interdependence of the polymer structure and reactivity of bound functional groups in polymeric reagents finds the applications of such systems in a number of areas. The reactivity of a functional group bound to a polymer backbone depends on the nature of the polymer backbone, the conformation of the polymer chain, the microenvironment of the reactive functional groups, the relative occurrence of the functional groups in the chain, the stereochemistry around the functional group, the
overall topology of the macromolecular matrix and the solvation and swelling characteristics.

### 2.2 Functionalisation of Polymer Supports

A functional polymer is a macromolecule on which reactive functions are anchored either by physical interaction or through chemical bonds. The macromolecule can either be a linear, which is soluble or a cross-linked, which is insoluble but swellable in solvents. The required reactive functional group can be attached on to the polymeric support either by the polymerisation of the monomer having the desired functional group or by the chemical modification of the preformed polymer. Since a good control over the degree of functionalisation is possible, the more accepted method is the chemical modification of the preformed support. Because of the difference in the chemical environment of the functional groups on the support, their chemical reactivity varies with their position in the matrix. For instance, the reactivity of a functional group near the cross-links differs from that of a group away from the cross-links, in the case of cross-linked supports.

Since the polystyrene matrix satisfies many of the requirements of a solid support, most of the work involving functional polymers has been carried out on cross-linked polystyrene resins. Chloromethylation and lithiation are the two most important methods of chemical modification of polystyrenes. Chloromethylation is carried out using chloromethyl methyl ether and a Lewis acid such as stannic chloride\textsuperscript{16} or zinc chloride\textsuperscript{17}. Another method developed by Nugiel et al in 1997 for the preparation of chloromethylated polystyrenes uses methanesulfonyl chloride and Hunig's base\textsuperscript{18}. Sheng et al developed, in 1997, an yet another new
route to (chloromethyl)styrene polymers\textsuperscript{19}. Lithiation can be carried out either directly using n-butyllithium and tetramethylethylenediamine\textsuperscript{20} or indirectly by lithium-bromine exchange\textsuperscript{21}. In this exchange reaction the support is first treated with bromine in presence of a Lewis acid followed by n-butyllithium. Both chloromethylated and lithiated polystyrenes are precursors to numerous other functional polymers based on polystyrene\textsuperscript{22}. Friedel-Crafts reactions can also be used in the chemical modification of polystyrene based supports\textsuperscript{23, 24}.

The reagents based on the complexes of poly(vinylpyridine)-based supports with bromine and bromine chloride can be used in the oxidation and addition reactions. One method of preparation of poly(vinylpyridine)-bromine complex involves the pouring of liquid bromine on dry poly(vinylpyridine) with vigorous shaking and removal of excess bromine by aeration\textsuperscript{25}. Another method involves the treatment of swollen poly(vinylpyridine), swelled in CCl\textsubscript{4} or a hydroxylic solvent, with bromine solution prepared with the same solvent\textsuperscript{25}. The method of preparation of poly(vinylpyridine)-bromine chloride complex is: Chlorine is bubbled into a halogenated solvent such as CH\textsubscript{2}Cl\textsubscript{2}, CHCl\textsubscript{3} or CCl\textsubscript{4} at \(-10^\circ\text{C}\). To which bromine is added and the solution is stirred in presence of light. The previously swollen poly(vinylpyridine) is added to this solution and stirred until the complexation is over\textsuperscript{25}. The linear as well as the cross-linked poly(vinylpyridine)-supported silver dichromates can be used as versatile, mild and efficient oxidants for different organic compounds. The linear reagent is prepared by adding a solution of poly(vinylpyridine) in methanol to a solution of silver nitrate in methanol. The white precipitate obtained is treated with a solution of potassium dichromate in water to afford the reagent. For cross-linked reagents, the resin is stirred with an
aqueous solution of silver nitrate and the white precipitate obtained is treated with potassium dichromate solution in water to afford the reagent\textsuperscript{26}. Poly(vinylpyridine)s can be functionalised with dichromate function by the reaction of the resin with CrO\textsubscript{3} in water at room temperature. Similarly, permanganate function can also be introduced by treating the resin with acidic KMnO\textsubscript{4} solution at 0\textdegree C\textsuperscript{27}. The reagent poly(N-bromoacrylamide) can be used as an oxidising and brominating reagent and is prepared by treating polyacrylamide with bromine in CCl\textsubscript{4} followed by the addition of potassium hydroxide solution\textsuperscript{28}. The halogen complexes of poly(vinylpyrrolidone)-based polymers can be used in oxidation and halogenation reactions. The halogen function is introduced by treating the support with a solution of the halogen in CCl\textsubscript{4}\textsuperscript{29,91}.

2.3 Characterisation of Functional Supports

The usual methods of qualitative and quantitative analysis applied to low molecular weight compounds can also be applied in the characterisation of functional polymers. The detection of elements such as nitrogen, halogens, sulphur and phosphorous can be done by elemental analysis. The presence of different functional groups can be detected qualitatively by the general chemical tests. The quantitative analysis includes the ordinary method of volumetric titrations. For instance, the quantitative analysis of chloromethylated resins can be done using the modified Volhardt's method\textsuperscript{30}. The capacity of permanganate function on a resin can be determined by direct titration of a known amount of the resin suspended in dilute H\textsubscript{2}SO\textsubscript{4} with standard ferrous ammonium sulphate solution. The capacities of chromate, dichromate and chlorochromate resins can be determined by titration of the chromate displaced from the resin.
by reaction with aqueous 2N KOH. The titration is conducted in acid medium against standard ferrous ammonium sulphate solution using N-phenylantranilic acid as indicator. The iodine function on a reagent can be quantitatively characterised by direct titration of the liberated iodine from the reagent in dimethylformamide at 0°C with standard sodium thiosulphate solution. The complexed bromine can be determined quantitatively as follows. To a suspension of the resin in ice-cold dimethylformamide, KI is added and the liberated iodine is titrated against standard sodium thiosulphate solution25.

IR spectroscopy and NMR technique are used in the structural characterisation of functional polymers. IR spectroscopy can also be used for following the chemical reactions carried out on cross-linked polymers. The structural characterisation of cross-linked polymers makes use of solid state high resolution CP-MAS NMR technique. Connor et al recently reported the application of 1H NMR in the characterisation of swelling in cross-linked polymer systems50.

The size and shape of polymer beads and the nature and distribution of pores on the surface of beads, can be characterised by Scanning Electron Microscopic analysis. The thermal stability of supports is usually studied using TG-DTG analysis.

2.4 Swelling Behaviour of Functionalised Polymers

In a chemical reaction, at least in the case of cross-linked polymers, the availability of functional groups present on the support depends on the phenomenon of swelling of the support. Since a linear support dissolves in almost all the solvents to form
homogeneous solutions, the phenomenon of swelling does not have any role in the availability of bound functions on it. The chemical nature of the polymer backbone and cross-link density together decide the swelling properties of the matrix. The support should have a backbone compatible with solvents. A hydrophilic-hydrophobic balance of the backbone can be achieved by the proper selection of the cross-linking agent. Thus the more hydrophobic backbone of polystyrene becomes less hydrophobic through the incorporation of hydrophilic cross-linkers, which in turn improves the swelling properties of the backbone. For copolymers, such a balance can be attained by changing the nature and ratio of the co-monomer units, as in poly(vinylpyrrolidone-styrene), poly(vinylpyridine-styrene) and poly(acrylamide-styrene). In a given solvent, as the degree of cross-linking increases the extent of swelling decreases and vice versa\textsuperscript{31}, even if both backbone and cross-links are compatible with the solvent. At low cross-link density the solvent-swollen polymer resembles a homogeneous solution. But as cross-link density increases, the tendency of the polymer backbone to expand in “good” solvents decreases and penetration of the reagents into the interior becomes difficult. Thus swelling studies are important for identifying the appropriate solvents to select the suitable reaction medium for performing reactions on polymer supports.

The oxidation reactions using poly(N-bromoacrylamide)s depend on the polarity of the solvent and that of the polymer backbone\textsuperscript{32}. Highly polar solvents have a pronounced effect on rate of oxidation in the case of NNMBA cross-linked reagents\textsuperscript{33}. If the polarity of the solvent used and that of the polymer backbone match each other, the yields of products are maximum. In the aminolysis of poly(N-2-aminoethylacrylamide)s, the reactivity of the DVB cross-
linked system is lower than the NN MBA and TEGDA cross-linked systems\textsuperscript{34}. The DVB cross-linking makes the resin more rigid and hydrophobic and the compatibility of the cross-linked support with the solvent becomes reduced. This increased rigidity and decreased swelling are the reasons for its diminished reactivity. The hydrophilicity of the polymer supports plays an important role in binding metal ions from aqueous solution\textsuperscript{35}. In the complexation of polyacrylamide-supported ligands with metal ions, the hydrophilicity and flexibility of the cross-linker determine the diffusion of the aqueous metal salt solution into the interior of the polymer matrix. The diffusion becomes difficult with increasing cross-linking as swelling decreases\textsuperscript{36}.

\section*{2.5 Spacer Handles and Their Effects}

One of the serious drawbacks of the polymeric reagent concept is the slow reaction rate. The polymer-supported heterogeneous reactions are slow and require drastic conditions when compared to homogeneous reactions. The close proximity of the macromolecular matrix causes this decrease in reactivity of functional groups. This "polymer effect" is more prominent in the case of cross-linked supports, since the active functional groups are flanked by the cross-links or buried in the interior of the polymer matrix. The functional groups in these systems are not easily available to substrates present in the reaction medium. The reactivity of the functional groups can be considerably enhanced if the active site is separated from the polymer matrix\textsuperscript{37,38}. In most cases one or more methylene or ethylene oxide groups in between the polymer matrix and functional group serve this purpose of separation, which make the active function to project from the matrix into the reaction medium where it is more accessible to substrates.
and solvent. Now the methylene or ethylene oxide group is termed “spacer handle” or “spacer arm”.

Many cases of increased reactivity were reported where the functional groups are separated from the polymer backbone by a flexible spacer arm. The extent of immobilisation of enzymes was found to increase with the length of the spacer arm in DVB cross-linked polystyrene\(^3\). It is because of the decrease in steric effect caused by the cross-linked polymer backbone with increasing length of the spacer arm. Divinylbenzene cross-linked polystyrene-supported tert-butyl hypochlorite containing a trimethylene spacer between the support and the tert-butyl hypochlorite group oxidises alcohols in higher yields. The oxidising efficiency of this reagent was found to be greater than that of the reagents with only one methylene spacer and no spacer between the active function and the support\(^4\). The effect of spacer arm on chromate capacity and oxidising efficiency of DVB cross-linked polystyrene-supported tert-butyl chromate reagents was reported recently. In this case, both chromate capacity and oxidising efficiency increase with the length of the spacer group\(^5\). Heterogeneous phase transfer catalysts like phosphonium salts and crown ethers supported on a polystyrene matrix show an increase in efficiency when they were separated from the polymer backbone with spacer handle\(^6\). The immobilised enzymes supported on ion-exchange resins can be used as biocatalysts for asymmetric synthesis\(^7\). The use of spacer arms between the active site and the polymer backbone was found to facilitate the ion-exchange.
2.6 Microenvironmental Effects

It has been assumed that functional groups anchored to a polymer are in a different local environment than in free solution. The results from a number of studies indicate that the groups or the microenvironment surrounding an active site in a polymer-supported reagent can play an important role in deciding the rate and yield of product formation, the so called microenvironmental effect\textsuperscript{43,44}. The reaction of cumene with the homopolymer, poly(N-bromomaleimide) differs depending upon whether the homopolymer or the copolymer, poly(N-bromomaleimide-styrene) was used\textsuperscript{45}. In another example, the efficiency of polystyrene-supported (dialkylamino)pyridine ligands as an acylation catalyst was found greater when the degree of functionalisation is less than 50% due to a more hydrophobic environment around each ligand\textsuperscript{46}. The microenvironmental effect affects the ionic recognition properties of polymer-supported reagents. The binding constants of Cu\textsuperscript{2+} and Co\textsuperscript{2+} to a series of copolymers based on N-vinylimidazole and ethyl acrylates were found to depend on the ratio of the two monomers in the support\textsuperscript{47}. The involvement of the neighbouring groups, the microenvironmental effect, plays an important role in the ionisation of carboxylic acid groups of polyacrylic acid. The ease of ionisation decreases as the degree of ionisation increases because the polymeric backbone becomes progressively more negatively charged\textsuperscript{48}. The same effect also arises in the protonation and alkylation of poly(vinylpyridine)s\textsuperscript{48}. Another example involves the oxidation of alcohol using poly(methyl methacrylate)-supported isoxazolinium Cr(VI) reagents. The reaction is faster with NN MBA cross-linked reagent when compared with DVB cross-linked reagent\textsuperscript{49}. The reason for the increased reactivity is attributed to the presence of hydrophilic and flexible NN MBA in the polymer
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matrix, which reduces the rigidity and enhances the swelling property of the system.

The microenvironmental effect with in a polymer-supported reagent can be tailored to a given reaction in order to maximise reaction rates and product yields. Alexandratos et al reported how the microenvironmental effect can be used to maximise reaction rates and product yields using the Prins reaction between formaldehyde and styrene\textsuperscript{43} and also using the Mitsunobu reaction\textsuperscript{44}.

2.7 Direct Monitoring of Reactions on A Solid Polymer Support

Organic synthesis on polymeric supports provides several advantages over solution-based synthesis, including the use of reagents in large excess, the ease of isolation of products and the use of solvents in which the reactants alone would be insoluble. However, the difficulty associated with monitoring the progress of reactions and characterising resin-bound reaction products is the serious drawback of using insoluble supports. Even though NMR\textsuperscript{51-53} and IR\textsuperscript{54-56} techniques have been used with some success to characterise polymer-supported molecules, there are no convenient and general methods for the monitoring of organic reactions on the solid-phase. The mass spectrometry has recently been utilised for the analysis of polymer-bound molecules\textsuperscript{57-59}. However its application has been limited by the need for cleavage of the molecules from the resin\textsuperscript{60-63} and the inefficient ionisation of the analytes\textsuperscript{64,65}. Fitzgerald et al described a method where polymer beads with a photocleavable linker, from which a peptide chain was built up, could be analysed directly using MALDI-MS\textsuperscript{66}. Although
this method did not require removal of peptides from the bead prior to MALDI analysis, it failed in the case of fully protected peptides since they lack sufficient protonation sites to effect ionisation during MALDI analysis.

Amine colour tests\textsuperscript{67-69} are frequently used as qualitative tests when amines are involved in the solid-phase organic synthesis. The techniques such as KBr pellet method\textsuperscript{70}, FT Raman\textsuperscript{71}, diffuse reflectance infrared Fourier transform spectroscopy\textsuperscript{72}, photoacoustic FTIR spectroscopy\textsuperscript{55} and FTIR microspectroscopy on a single resin bead\textsuperscript{54,73} are also employed in qualitative monitoring. The conventional combustion elemental analysis, acid-base titration and FTIR can provide semiquantitative information\textsuperscript{75}. Gravimetric analysis provides quantitative informations, but in most cases they are misleading\textsuperscript{75}.

Carrasco et al developed a simple and general method for the real time analysis of organic reactions on solid supports\textsuperscript{74}. Here, an ionisation tag sequence was anchored to the polymer support through a photocleavable linker and then a chemically cleavable linker was attached to the ionisation tag sequence. The free end of the chemically cleavable linker was utilised to synthesis the target molecules. The combination of the photocleavable linker and the ionisation tag sequence helped direct analysis of the resin beads by MALDI-MS regardless of whether the attached reactants or products contain protonation sites to effect ionisation during MALDI analysis. Thus this technique overcame the limitation of the method described by Fitzgerald et al\textsuperscript{66}.

Single-bead FTIR spectroscopy is a powerful technique for real time monitoring of solid-phase reactions\textsuperscript{75}. Marti et al
demonstrated its application in the solid-phase oxazolidinone ring opening reactions using primary amines to provide the corresponding amides\textsuperscript{76}. Warrass et al very recently reported the application of high resolution magic angle spinning NMR spectroscopy in the quantitative monitoring of polymer-supported Horner-Emmons reaction\textsuperscript{77}.

### 2.8 Advantages of Polymer-supported Reactions

The advantages of polymer-supported strategy include the following.

a) Operational simplicity: In the classical solution-phase reactions, the isolation and the purification of the product is time-consuming and the yield of the product will be poor due to mechanical losses during the reaction work-up. In supported reactions, the reaction work-up is simplified because the supported species are easily separated from the soluble reagents by filtration, if the support is cross-linked. In the case of soluble linear supports ultrafiltration or selective precipitation of the support is employed. This avoids tedious chromatographic separation in each step as in the case of step-wise solution-phase synthesis.

b) An excess of reagents based on cross-linked supports can be used without causing separation problems in order to drive the reaction to completion so that the yield of the final product can be increased. It is not always possible in the ordinary solution-phase synthesis.
c) In most supported reactions the spent resin can be regenerated as such or by some chemical modification and can be reused. It is very important in the economic point of view.

d) When the supported reaction takes place virtually to completion and if the work-up involves only simple filtration and washing of the supported species, the whole procedure can be automated which is of great industrial attraction.

e) Since the reactive functions are immobilised on the support, the supported reagents are non-volatile, non-hazardous and odourless. Thus the polymer-supported strategy offers a superior method for carrying out reactions with poisonous reagents such as arsenic or selenium compounds.

f) The polymer backbone can impose certain definite steric requirements on molecules diffusing into it, which is determined by the rigidity, the porous structure, presence of substituents and separation of the reactive function from the polymer backbone. By varying these structural parameters, giving tailor-made reaction environments, some selectivity can be achieved.

2.9 Limitations of Polymer-supported Reactions

The main limitations of polymer-supported method include the following.

a) The method requires additional time and cost in synthesising the support.

b) If the degree of functionalisation or loading is low then the total volume of the reaction mixture will be large.
c) Non-equivalence or inaccessibility of the functional group causes serious problems in peptide synthesis leading to truncated and failure sequences.

d) Lower degree of functionalisation, slower reaction rates and poor yield are encountered in certain cases.

e) When vigorous conditions are used for the cleavage of the final product from the support, it may result in the degradation of the polymer.

f) The kinetics of supported reactions are different from low-molecular weight chemistry and in many cases these are very complex.

g) The occurring of side reactions during functionalisation and subsequent reaction results in a polymer-bound product which is difficult to remove and this can interfere in further use with the reagent.

2.10 Polymer-supported Oxidising Reagents

Polymer-supported reagents find wide spread applications in many areas and those developed in 1970s and 1980s are commercially available. A large number of polymer-bound oxidants has been developed and successfully applied to synthetic organic chemistry. Many of them are based on polystyrene supports. However, oxidants based on other supports such as poly(vinylpyrrolidone)s, poly(vinylpyridine)s, polyacrylamides, poly(methyl methacrylate)s and poly(ethylene glycol) have been reported and successfully applied. The following takes a brief discussion on the supported oxidants.
2.10.1 Polystyrene-based oxidants

Kessat et al reported oxidation of alcohols to carbonyl compounds using polyvinylthiazolium hydrotribromide in aqueous sodium hydroxide. The resin was synthesised from styrene (60%), 4-methyl-5-vinylthiazole (30%) and divinylbenzene (10%), followed by treatment with HBr and bromine. V.N.R Pillai et al reported polystyrene-supported tert-butyl hypochlorite and hypobromite to effect oxidation of alcohols to carbonyl compounds. The oxidants with a trimethylene spacer between the support and the tert-butyl hypochlorite function were found to be more efficient than those with zero and one methylene spacer. It was shown by the same group the utility of chloramine-T and bromamine-T supported on polystyrene in the oxidation of alcohols. Sreekumar et al developed polystyrene-supported tert-butyl chromate reagents for oxidising alcohols to corresponding carbonyl compounds. The reagent prepared from 2% DVB cross-linked polystyrene was most efficient in terms of reaction time and product yield. Polystyrene-supported peracids were reported in 1970s for the oxidation of alkenes, penicillin derivatives and sulphides. Polystyrene-supported benzyltriethylammonium dichloroiodate and dibromoiodate were reported as polymeric anionic oxidants. Carbodiimide anchored to cross-linked polystyrene, reported in 1970s, was used in the Moffat oxidation of alcohols to carbonyl compounds.

2.10.2 Poly(vinylpyridine)-based oxidants

Tamami developed a number of polymer-supported oxidants including poly(vinylpyridine N-oxide)-supported dichromate and poly(vinylpyridine)-bound silver dichromate. The latter oxidant was found to oxidise many organic compounds such as hydroxy...
compounds, oximes, amines, thiols and aromatic hydrocarbons. Studies from our laboratory reported permanganate and chromate functions supported on poly(4-vinylpyridine)s as oxidising agents for alcohols. Frechet developed poly(vinylpyridine)-supported chlorochromate as an oxidising reagent as early in 1970s. A polymeric reagent electrochemically produced from cross-linked poly(4-vinylpyridine)-supported hydrobromide was found to oxidise secondary alcohols to corresponding ketones.

2.10.3 Poly(vinylpyrrolidone)-based oxidants

Bromo derivatives of poly(vinylpyrrolidone)s were reported as oxidising reagents for the oxidation of alcohols. The same group reported permanganate and chromate species bound on poly(vinylpyrrolidone)s as oxidants for alcohols.

2.10.4 Polyacrylamide-based oxidants

Sreekumar et al developed a series of polymeric oxidants based on a copolymer of acrylamide and divinylbenzene for oxidising primary and secondary alcohols to aldehydes and ketones, respectively. He could succeed in binding the active functions $\text{ICl}_2^-$, $\text{ICl}_4^-$ and $\text{IBr}_2^-$ on these acrylamide-based supports. Polyacrylamide-bromine complexes were developed as oxidants and observed that highly polar solvents enhanced reaction rate in the case of NN MBA cross-linked reagents.

2.10.5 Miscellaneous polymeric oxidants

Ley described polymeric tetrapropylammonium perruthenate for the oxidation of alkyl and aryl alcohols. This oxidant was prepared by treating Amberlyst IR 27 anion exchange resin with an
aqueous solution of potassium perruthenate. Vederas reported the use of poly(ethylene glycol)-supported sulfoxide in Swern oxidation. Hassanein described poly(vinylbenzyltriphenyl) phosphonium dichromate as an oxidising agent. McKillop developed an oxidant for the oxidation of alcohols using iron (III) nitrate impregnated on K-10 bentonite clay. Silica gel-supported pyridinium chromate was developed for the oxidation of alcohols containing acid labile functions. Sreekumar described poly(methyl methacrylate)-supported isoxazolinium chromium(VI) oxidant for the oxidation of alcohols. Murugesan et al reported quinolinium fluorochromate supported on alumina as a new and selective oxidant for primary and secondary alcohols.

2.1.1 Polymer-supported Halogen Containing Reagents in Addition and Halogenation Reactions

The halogen containing reagents based on the polymers such as polystyrenes, polyacrylamides, poly(vinylpyrrolidone)s, poly(vinylpyridine)s and poly(vinylpyridine-styrene)s were developed for using in addition and halogenation reactions.

Polystyrene-supported tert-butyl hypochlorite and hypobromite reagents were reported as non-toxic, non-hazardous and versatile halogenating reagents. Polystyrene-supported chloramine-T and bromamine-T were also reported from the same group as halogenating agents for ketones. Zupan reported the use of poly(4-vinylpyridinium-styrene)-supported dichloroiodate for the addition reactions of alkenes.

Poly(N-bromoacrylamide)s were developed as polymeric recyclable reagents for bromination and addition reactions. The same reagent was also used in the bromination of carbonyl compounds.
Sinisterra described the use of poly(N-bromoacrylamide)s as heterogeneous reagents for alpha halogenation of ketones. With poly(N-chloroacrylamide)s, yields were poor. Bromo derivatives of poly(vinylpyrrolidone)s have also been reported for the bromination of carbonyl compounds.

Zupan described the use of bromine complex of vinylpyridine copolymer for side chain bromination of aromatic compounds. The complexes of bromine with poly(vinylpyridine-styrene), poly(vinylpyridine oxide-styrene) and poly(vinylpyridinium bromide-styrene) were used in addition reactions of double bond containing compounds. These reagents showed stereospecificity in the addition (anti adduct) and the latter was the most reactive. Zabicky et al developed complexes of bromine and bromine chloride with poly(4-vinylpyridine)s to use in the addition reactions with alkenes and alkynes.
REFERENCES


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79. Sigma-Aldrich catalogue: Combinatorial Chemistry Products.


