

PROJECT COMPLETION REPORT

**Preparation and studies on polymer anchored transition metal compounds.
Towards development of biorelevant complexes and active oxidation
catalysts**

DST Reference No: DST No. SR/SI/IC-31/2009 . Dt. 8th February, 2010

Principal Investigator: Dr. Nashreen S. Islam

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1. **Title of the Project:** *Preparation and studies on polymer anchored transition metal compounds. Towards development of biorelevant complexes and active oxidation catalysts*

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2. **Name of the Investigators:** Dr. Nashreen S. Islam (PI)

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Tezpur University, Tezpur 784 028

Co-investigator : Dr. Sashi Baruah, Professor Department of Molecular Biology and Biotechnology, Tezpur University, Tezpur 784 028

3. **Implementing Institution:** Tezpur University, Tezpur, Assam

4. **Date of commencement of the project :** from 1.03.10

5. **Planned date of completion:** 28.2.2013

6. **Actual date of completion:** 31.8.13.

7. **Original objectives (quoted from project proposal):**

(1) to develop new macro complexes by anchoring peroxo species of vanadium(V), molybdenum(VI) or tungsten(VI) to soluble as well as insoluble polymer matrices with appropriate pendant functional groups and to characterize them.

(2). to study the stability of the compounds towards decomposition in the solid state as well as in solution.

(3). to explore the efficacy of the compounds synthesized as catalytic oxidant in organic oxidations viz., halide and sulphide oxidation, olefin epoxidation and hydroxylation, under mild reaction condition.

(4). to explore biochemical properties of the polymer-bound complexes, particularly involving their effect on key enzymes like phosphatases, PTPasee, Gl-6-phosphatase, nuclease, peroxidase, NADPH oxidase, and interaction with catalase.

8. **Deviation made from the original objectives, if any, while implementing the project and reasons thereof :** None

9. Experimental work giving full details of experimental set up, methods adopted, data collected etc. : Please see Annexure 1

10. Detailed Analysis of results indicating contributions made towards increasing the state of knowledge in the subject: Please see Annexure 1

11. Conclusions summarizing the achievements and indication of scope for future work:
Annexure I

12. S& T benefits accrued: **List of Publications from this Project** (including title, authors, journals & year):

(A) Papers published in cited Journals (SCI) : 5 (one)

Sl. No	Authors	Title of paper	Name of Journal	Volume	Pages
1.	J.J. Boruah, D. Kalita, S. P. Das, S. Paul, N. S. Islam	Polymer Anchored Peroxo Compounds of Vanadium(V) and Molybdenum(VI) : Synthesis, Stability and Their Activities with Alkaline Phosphatase and Catalase	Inorg.Chem	50	8045-8062
2.	S. P. Das, J.J. Boruah, H.Chetry and N S. P. Das, J.J. Boruah, H.Chetry and N. S. Islam	Selective oxidation of organic sulfides by mononuclear and dinuclear peroxo tungsten complexes	Tetrahedron Letters	35	1163-1168
3.	J. J. Boruah, S. P. Das, R. Borah, S. R. Gogoi and N. S. Islam	New Polymer –immobilized peroxotungsten compounds as an efficient catalyst for selective and mild oxidation of sulfides by hydrogen peroxide	J.Mol.Catalysis A: Chemical	653	36-45
4.	Boruah J J, Das S P, Gogoi S R and Islam N S	Polymer-anchored Peroxo Compounds of Molybdenum and Tungsten as Efficient and Versatile Catalysts for Mild Oxidative Bromination	Polyhedron (Warner Special Issue)	52	246
5.	Boruah J J, Das S P, Ankireddy S R, Gogoi S R and Islam N S	Merrifield resin supported peroxomolybdenum(VI) compounds: new recoverable heterogeneous catalysts for efficient, selective and mild oxidation of organic sulfides with H ₂ O ₂	Green Chemistry	15	2944

(II) Manpower trained on the project

A) Research Scientists or Research Associates: None

B) No. of Ph.D produced: 1

(III) Patents taken: none

13. Financial Position:

No	Budget Head	Funds sanctioned	Expenditure	% of total cost
I	Salaries/ Manpower costs	4,90,000/-	4,81,600/-	98
II	Equipment	5,00,000/-	4,72,554/-	95
III	Supplies & materials	6,00,000/-	5,99,321/-	99.9
IV	Contingencies	1,00,000/-	1,00,000/-	100
V	Travel	90,000/-	58,842/-	65
VI	Overhead Expenses	3,00,000/-	3,00,000/-	100
VII	Others, if any	Nil	Nil	
	Total	20,80,000/-	20,12,507/-	97

14. Procurement/ usage of equipment

Major Equipment (Model and Make)					
SL.No	Name of Equipment	Model and make	Cost : Rs.	Working (Yes /No)	Utilisation rate (%)
1.	Peltier Cell holder with pump (Accessory for CARY 100 spectrophotometer)	Yes. Varian Peltier 1x1 cell holder	2,57,075/-	Yes	100%
2.	PC with scanner and printer	Sony (Laptop) (VPCYA15FG/B)	39,990/-	Yes	
		Scanner Canon (CS 5600F)	11,995/-		
3.	Water bath shaker	Printer HP (CP 1515n)	24,999/-	Yes	
4.	Digital magnetic stirrer + Hot plate	IKON (IK - 132)	1,04,420/-	Yes	
		Tarson	34,075/-		
	Total		4,72,554/-		

b) Plans for utilizing the equipment facilities in future: The equipment are to be used routinely for research as well as PG laboratory courses.

Name and Signature with Date

a. N.S. Salam
24.1.14
(Principal Investigator) (Nashreen S. Salam)

b. _____
(Co-investigator)

ANNEXURE - I

1. Experimental work giving full details of experimental set up, methods adopted, data collected supported by necessary table, charts, diagrams

1.1 Synthesis of novel peroxo compounds of Mo (VI) and W (VI) anchored to water soluble polymer (WSP) matrices

Series of new water soluble polymer bound diperoxomolybdate complexes of the type $[\text{Mo}_2\text{O}_2(\text{O}_2)_4(\text{carboxylate})]-\text{PA}$ [PA = poly(sodium acrylate), $[\text{MO}(\text{O}_2)_2(\text{carboxylate})]-\text{PMA}$ [PMA = poly(sodium methacrylate)], $[\text{MO}(\text{O}_2)_2(\text{amide})]-\text{PAm}$ [PAm = poly(acrylamide)], and $[\text{MO}(\text{O}_2)_2(\text{sulfonate})]-\text{PS}$ [PS = poly(sodium vinyl sulfonate)] (M = Mo or W) have been synthesized and characterized.

In a representative procedure, molybdic acid or tungstic acid was dissolved in 30% H_2O_2 . To the clear solution obtained, of respective polymer was added in portions with continuous stirring. The mixture was stirred for *ca.* 60 min in an ice bath until all solids dissolved. At this stage the pH of the reaction medium was recorded to be *ca.* 2. The pH of the solution was raised to *ca.* 5 by dropwise addition of concentrated NaOH solution. A red colored pasty mass separated out on adding pre-cooled acetone (*ca.* 50 mL) to this mixture under vigorous stirring. The reaction mixture was allowed to stand for about 30 min and the residue obtained after decanting the supernatant liquid was washed repeatedly with pre-cooled acetone under scratching. The microcrystalline product, separated by centrifugation, was washed with cold acetone and dried in *vacuo* over concentrated sulfuric acid. The compounds were finally dried by heating upto 70 °C under nitrogen atmosphere.

1.2 Synthesis of peroxo compounds of Mo(VI) and W(VI) immobilized on insoluble polymer resins

Synthesis of Merrifield resin (MR) immobilized molybdenum dioxomonoperoxo compounds $[\text{MoO}_2(\text{O}_2)(\text{L})_2]^{2-}-\text{MR}$, [L = valine (MRVMO) or alanine (MRAMO)]

In a typical reaction, H_2MoO_4 was dissolved in 30% H_2O_2 by maintaining the molar ratio at 1: 10 and temperature at 30-40 °C. The pH of the clear solution obtained was recorded to be *ca.* 1. Concentrated sodium hydroxide was then added to the above solution to raise the pH of the reaction medium to 5.0. Keeping the temperature of the reaction mixture below 4 °C in an ice bath, 1.0 g of MRV or MRA was added to it which was pre-swelled in 5 mL ethanol for 1 h. The mixture was kept for 24 h under continuous stirring in an ice bath. The supernatant liquid was then decanted and the yellowish residue was repeatedly washed with pre-cooled acetone. The products were separated by centrifugation and dried in *vacuo* over concentrated sulfuric acid. The compounds were further dried by heating upto 70 °C under nitrogen atmosphere.

Synthesis of $[\text{MO}_2(\text{O}_2)(\text{CN})_2]-\text{PAN}$ [PAN = poly(acrylonitrile)] (M= Mo or W)

Molybdic acid or tungstic acid was dissolved in 30% H_2O_2 in the molar ratio of 1: 10, by maintaining the temperature at 30-40 °C, to obtain a clear solution of pH *ca.* 1. Subsequently, pH of the reaction solution was raised to 5.0, by the addition of concentrated sodium hydroxide solution. 1.0 g of poly(acrylonitrile) was added to it and the reaction mixture was left for 24 h under constant stirring for swelling of the suspended polymer beads. The white residue obtained was separated by decanting off the supernatant liquid and was repeatedly

washed with pre-cooled acetone. The product was dried in *vacuo* over concentrated sulfuric acid.

1.3 Characterization of the synthesized compounds

The compounds were characterized by elemental analysis (CHN and energy dispersive X-ray spectroscopy), spectral studies (UV-Vis, IR, Raman, ^{13}C NMR and ^{95}Mo NMR), thermal (TGA) as well as scanning electron micrographs (SEM) and EDX and XPS analysis.

1.4 Physical and Spectroscopic Measurement

The IR spectra were recorded with samples as KBr pellets in a Nicolet model 410 FT-IR spectrophotometer. The spectra were recorded at ambient temperature by making pressed pellets of the compounds. Spectroscopic determinations of the initial rate of AP and ALP catalyzed hydrolysis of p-NPP were carried out in a Cary model Bio 100 spectrophotometer, equipped with a peltier controlled constant temperature cell. The absorbance values were denoted as e.g., A_{405} at the wavelength indicated. The SEM characterization was carried out by using the JEOL JSM-6390LV Scanning Electron Micrograph attached with energy dispersive X-ray detector. Scanning was done at 10–20 μM range and images were taken at a magnification of 15–20 kV. Data were obtained using INCA software. The standardization of the data analysis is an integral part of SEM-EDX instrument employed. The ^{13}C NMR spectra were recorded in a JEOL JNM-ECS400 spectrometer at carbon frequency 100.5 MHz, 1,31,072 X-resolution points, number of scans 8000, 1.04 s of acquisition time and 2.0 s of relaxation delay with ^1H NMR decoupling method in D_2O . Magnetic susceptibilities of the complexes were measured by the Gouy Method, using $\text{Hg}[\text{Co}(\text{NCS})]$ as the calibrant. Thermogravimetric analysis was done in Perkin Elmer STA 6000 system at a heating rate of $10^\circ\text{C}/\text{min}$ under an atmosphere of nitrogen using aluminium pan. Prior to TGA analysis, the samples were dried by heating under nitrogen atmosphere at 70°C .

1.5 Effect of Catalase on the Complexes

The effect of catalase on complexes was studied by determining the peroxide content of the compounds in a solution containing catalase at specified time intervals. The test solution contained phosphate buffer (50 mM, pH 7.0) and catalase (40 $\mu\text{g}/\text{ml}$). The volume of the reaction solution was kept at 70 ml. The solution was incubated at 30°C . The polymeric compound was then added to the test solution and aliquots of 5 ml were pipetted out and titrated for peroxide content after stopping the reaction by adding it to cold sulfuric acid (0.7 M, 100 ml) at an interval of 5 min from the starting of reaction. Degradation of the compounds with respect to their loss of peroxide was also followed by monitoring the band at ca. 230–250 nm with time. For the polymer bound compounds concentrations were on the basis of actual peroxometal loading (mmol g^{-1}).

1.6 Measurement of Alkaline Phosphatase Activity

Phosphatase activity was assayed spectrophotometrically by using p-NPP as a substrate. The continuous production of p-nitrophenol (p-NP) was determined at 30°C by measuring absorbance at 405 nm in a reaction mixture containing ALP from rabbit intestine (3.3 μg protein/mL), p-NPP (2 mM) in incubation buffer (25 mM glycine + 2 mM MgCl_2 , pH 10.0). The initial reaction rates were obtained by starting the reaction by adding ALP to the reaction solution, which was pre-incubated for 5 min. The initial reaction rate of p-NPP hydrolysis in

the absence of the inhibitors, V_0 was determined which was used as control. The effects of pV, pW and bare ligands were assessed by adding different concentrations of each species in the ALP assay. For the polymer bound compounds concentrations were on the basis of actual peroxometal loading (mmol g^{-1}). The IC_{50} values were graphically determined as the half-maximal inhibitory concentration of the inhibitor species giving 50% inhibition. All the assays were performed in triplicate. The data in figures are presented as the means \pm SE from three separate experiments.

1.7 General procedure for catalytic oxidation of sulfides to sulfoxides

In a representative procedure, organic substrate (5 mmol) was added to a mixture of catalysts (containing 0.005 mmol of Mo) [**MRVMo** (10.86 mg) or **MRAMo** (13.15 mg)] and 30% H_2O_2 (1.13 mL, 10 mmol) in methanol (5 mL), maintaining molar ratio of Mo:substrate at 1:1000 and substrate: H_2O_2 at 1:2, in a 50 mL two-necked round-bottomed flask. The reaction was conducted at room temperature (RT) under continuous stirring. The progress of the reaction was monitored by thin layer chromatography (TLC) and GC. After completion of the reaction, the catalyst was separated by filtration and washed with acetone. The product as well as unreacted organic substrates were extracted with diethyl ether from the filtrate and dried over anhydrous Na_2SO_4 and distilled under reduced pressure to remove excess diethyl ether. The corresponding sulfoxide obtained was purified by column chromatography on silica gel using ethyl acetate and n-hexane (1:9).

2. Detailed analysis of results indicating contributions made towards increasing the state of knowledge in the subject

2.1. Preparation and characterization of novel peroxo compounds of Mo(VI) and W(VI) anchored to water soluble polymer matrices

We have successfully isolated a series of new peroxo complexes of molybdenum(VI) (pMo) and tungsten (VI) (pW) co-ordinated to water soluble polymers viz., poly(acrylate), poly(methacrylate) and poly(acrylamide). The macro complexes of the type, $[\text{M}_2\text{O}_2(\text{O}_2)_4(\text{carboxylate})]_{\text{-PA}}$ [PA = poly (sodium acrylate); M = Mo(VI) [PM1] or W(VI) [PW1], $[\text{MoO}(\text{O}_2)_2(\text{carboxylate})]_{\text{-PMA}}$ [PMA = poly (sodium methacrylate)] [PM2], $[\text{MoO}(\text{O}_2)_2(\text{amide})]_{\text{-PAm}}$ [PAm = poly(acrylamide)] [PM3], have been generated by reacting H_2WO_4 or H_2MoO_4 with H_2O_2 and the respective water soluble macromolecular ligand at near neutral pH.

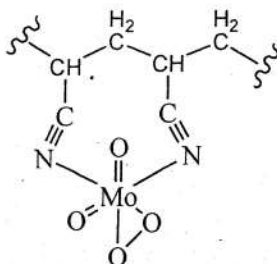
The compounds were characterized by elemental analysis (CHN and energy dispersive X-ray spectroscopy), spectral studies (UV-Vis, IR, ^{13}C NMR and ^{95}Mo NMR), thermal (TGA) as well as scanning electron micrographs (SEM) and EDX analysis.

2.2 Synthesis and characterization of peroxo compounds of Mo(VI) and W(VI) supported on insoluble polymer

Structurally defined peroxomolybdate(VI) as well as peroxotungsten(VI) compounds supported on **insoluble polymer matrix**, of the type $[\text{M}(\text{O})_2(\text{O}_2)(\text{CN})_2]_{\text{-PAN}}$ [PAN = poly(acrylonitrile)]; M=Mo [**PANMo**] or W [**PANW**] have been prepared and characterized by elemental analysis (CHN and EDX analysis), spectral (IR, UV-Vis and ^{13}C NMR, ^{95}Mo NMR), thermal (TGA-DTG) as well as SEM studies. The macro complexes

were obtained by reacting H_2MO_4 with 30% H_2O_2 and the macromolecular ligand, PAN at near neutral pH.

A structure of the type shown in Figure with PANMo as a representative, has been proposed which includes metal atom with a side-on bound peroxy and terminal $\text{M}=\text{O}$ groups, bonded to the polymer matrix via the pendant nitrile groups. Simultaneous bond formation of Mo(VI) to the two neighbouring nitrile groups of the polymer chain appears to complete the hexa co-ordination around each tungsten atom.

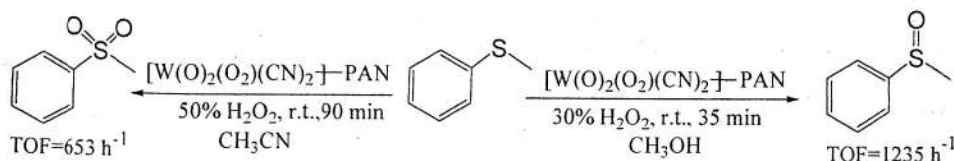


2.3 Stability of the water soluble macro complexes in solution – Stability of the newly synthesized compounds in solution of varying pH has been explored by chemical analysis as well as spectroscopic methods viz., UV-Vis, ^{51}V NMR, ^{13}C NMR, and ^{95}Mo NMR over a time period of 12 hours. Unlike majority of free monomeric pV or pMo compounds which are usually unstable in solution, the polymer anchored compounds retain their structural integrity in solutions of a wide range of pH values.

2.4 Polymer-Immobilized Peroxotungsten Compound as an Efficient Catalyst for Selective and Mild Oxidation of Sulfides by Hydrogen Peroxide

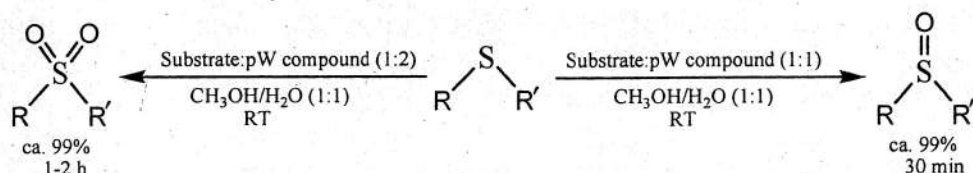
Selective oxidation of organic sulfur containing substrates to sulfoxides or sulfones hold tremendous contemporary interest from both chemical as well as biological perspectives.

Clean conversion of a variety of sulfides and dibenzothiophene (DBT) to the corresponding sulfoxide or sulfone, using H_2O_2 as oxidant, could be achieved in presence of the heterogeneous catalyst PANW, by a variation of reaction conditions. The reactions proceed under mild conditions to afford the resulting products with impressive turn over frequency (TOF). The catalyst exhibit complete chemoselectivity toward sulfur group of substituted sulfides with other oxidation prone functional groups. Easy regeneration and reusability of the catalyst for at least up to seven catalytic cycles with consistent activity and selectivity is an important attribute of the catalyst.



2.5 Safe and Selective Oxidation of Organic Sulfides by Mononuclear and Dinuclear Peroxotungsten(VI) Complexes

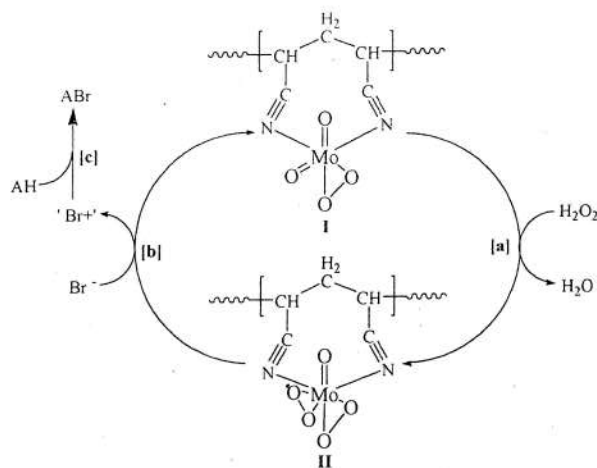
Mononuclear as well as dinuclear diperoxo complexes of tungsten of the type, $[\text{WO}(\text{O}_2)_2(\text{glycyl-glycine})].3\text{H}_2\text{O}$ (**MWG**), $\text{Na}_2[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{glycyl-glycine})_2].3\text{H}_2\text{O}$ (**DWG**) or $\text{Na}_2[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{cystine})].4\text{H}_2\text{O}$ (**DWC**) could serve as stoichiometric reagents for the efficient and selective oxidation of a variety of structurally diverse sulfides to sulfoxides in impressive yields under environmentally clean conditions. The attractive features associated with the protocol are: (i) it can be used for obtaining high purity sulfoxide as well as sulfone by a versatile variation of reagent:substrate stoichiometry; (ii) chemoselectivity of the complexes toward the sulfur group of sulfides with co-existing oxidation prone functional groups; (iii) compounds can be stoichiometrically recovered in the presence of H_2O_2 . Significantly, the compounds could also efficiently catalyze the selective oxidation of sulfides by H_2O_2 to yield sulfone with reasonably good TOF, under mild reaction conditions. The simplicity in the method of preparation of the reagents and redundancy of chlorinated solvents are additional advantages offered by the procedure. The developed methodologies thus conform to several guiding principles of green chemistry.



2.6 Polymer-anchored peroxo compounds of molybdenum and tungsten as efficient and versatile catalysts for mild oxidative bromination

Bromination of organic compounds has been receiving tremendous attention in recent years, mainly owing to the utility of bromo-organics as fine chemicals, therapeutic agents, agrochemicals and also as valuable intermediates for construction of chemically and biologically active molecules. The traditional bromination protocols require elemental bromine and halogenated solvents which are toxic, corrosive and environmentally hazardous[4,5]. Therefore, search for alternative environmentally benign bromination protocols, which can mimic the biological bromoperoxidation for the synthesis of brominated organics continues unabated.

The catalytic activity of **PANMo** and its tungsten containing analogue, **PANW** in oxidative bromination of organic substrates has been explored. Our preliminary investigation has shown that the supported complexes could serve as efficient heterogeneous catalysts for the oxidative bromination of a variety of structurally diverse aromatic compounds, with H_2O_2 as terminal oxidant, to afford bromo organics **in impressive yields under mild conditions**. The catalysts afforded regeneration and could be reused for a minimum of six reaction cycles. The two compounds viz., **PANW** and **PANMo**, having similar macro ligand environment, enabled us to draw comparison on their efficiency as catalyst in the chosen reactions. **PANW** displayed superior activity in comparison to its Mo containing analogue.



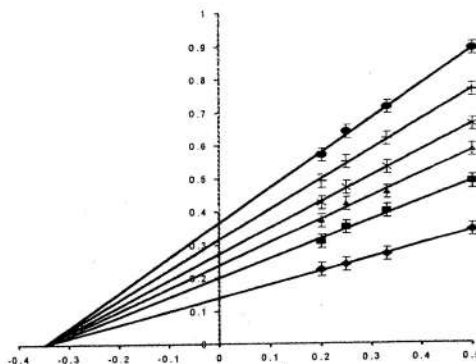
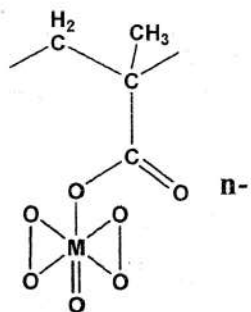
2.7 Activity with Catalase : Catalase is a powerful reactive oxygen (ROS) mopping enzyme responsible for breakdown of H_2O_2 to H_2O and O_2 . H_2O_2 is a significant cellular oxidant needed particularly for action of peroxidases that yield highly active intermediates. The importance of H_2O_2 is increasingly realized as a key signal transducing agent regulating a variety of cellular processes. Fast decomposition of extracellular H_2O_2 is a constraint for studying the signaling activities of H_2O_2 because cells are equipped with catalase and glutathione peroxidase that rapidly deplete H_2O_2 . In order to investigate how the small concentrations of H_2O_2 generated in cells will function in presence of abundant catalase, it is desirable to have peroxide derivatives easily formed and stable to degradation, yet efficient in their action, that can substitute for H_2O_2 .

In the present study, action of catalase on the newly synthesized compounds was observed to be a slow process in contrast to H_2O_2 . Under the effect of catalase the rate of degradation of H_2O_2 with the release of oxygen was reported to be $430 \mu M/min$ from a solution of 0.1 mM concentration. The polymer anchored peroxometal compounds are approximately 100 times weaker as substrate to the enzyme catalase relative to H_2O_2 , its natural substrate.

Table . Catalase Dependant Oxygen Release from Peroxometallates

Compound	Concentration (mg/ml)	Peroxide content (mM)	Loss of peroxide ($\mu M/min$)
PMo_1	0.137	0.4	17.81
PMo_2	0.294	0.4	17.57
PMo_3	0.327	0.4	10.34
DMo_1^a	0.054	0.4	37.60

2.8 Activity with Alkaline Phosphatase: The effect of the title compounds, on rabbit intestine alkaline phosphatase (ALP) has been investigated and compared with effect induced by the corresponding free dperoxometallates. It has been observed that although all the compounds tested are potent inhibitors of the enzyme, the polymer bound and neat complexes act via distinct mechanisms. Each of the macromolecular compounds is a classical non-competitive inhibitor of ALP. In contrast, the action of neat pV and heteroligand pMo compounds on the enzyme function is consistent with mixed type of inhibition.



3. Conclusions summarizing the achievements and indication of scope for future work:

(i) The newly synthesized compounds of W(VI) and Mo(VI) are the first known examples of peroxo compounds of these metals anchored to water soluble polymers.

(ii) The compounds are highly stable in solution of acidic as well as alkaline pH and are relatively resistant to the enzyme catalase.

(iii) It is significant that these compounds are potent non-competitive inhibitors of ALP

(iv) A heterogeneous catalysts have been developed for oxidation of organic sulfides by hydrogen peroxide under mild reaction conditions, by immobilizing peroxotungstate and peroxomolybdate on poly(acrylonitrile) matrix. It is remarkable that the catalyst can be effectively used for obtaining high purity sulfoxide as well as sulfone from the corresponding aryl or alkyl sulfide and DBT in excellent yield and high TOF by a versatile variation of reaction conditions.

(v) Facile oxidation of a variety of sulfides and dibenzothiophene (DBT) to the corresponding sulfoxide or sulfone could be achieved in excellent yield at room temperature, using mononuclear as well as dinuclear diperoxo complexes of tungsten as oxidants, by a versatile variation of reaction conditions. The compounds are recoverable, exhibit chemoselectivity and proceed under mild conditions.

(vi) Polymer anchored pMo and pW complexes could serve as heterogeneous catalysts in oxidative bromination of organic substrates under environmentally benign reaction conditions.

Future prospects:

(a) Polymeric complexes synthesised may emerge as useful additions to the range of biomimetic synthetic oxidants. (b) The water soluble macro complexes are likely to be of biochemical interest in view of their properties such as their stability toward decomposition in solution of a wide range of pH values, and their significant affinity as alkaline phosphatase inhibitor. (c) Acrylonitrile polymers have attracted much attention for their application in diverse areas that include medicine, antioxidants, surface coatings, catalysis, textiles treatment, binders and as adsorbant for removal of heavy metal ions from water. As far as we are aware, the compounds PANW and PANMo are the only example where PAN has been used as polymeric support to obtain an immobilized peroxometal compound. The synthesized catalysts are likely to be useful addition to the range of ecologically suitable oxidation catalysts with the potential for accomplishing some of the goals of green chemistry.