

## Recent Advances in the Syntheses and Characterization of Polymer-anchored Transition Metal Complexes

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**Abstract:** In this review, some important recent works on some transition metal complexes synthesized and characterized by new chemical technology have been presented. The route of preparation for these materials is discussed. Focus on their compositions, structures as well as physicochemical characterization techniques are reported. The results revealed that chloromethylated polystyrene cross linked with divinylbenzene is one of the most widely employed macromolecular supports. Chemical analysis, IR, NMR, electronic and EPR spectroscopy, field-emission scanning electron micrograph (FE-SEM), transmission electron microscope (TEM), energy dispersive X-ray analysis (EDAX) and thermogravimetric studies prove to be essential tools for identifying and characterizing the anchored complexes. Magnetic and BET surface area measurements are not frequently used but are informative.

**Keyword:** Inorganic compounds, Polymers, Transition metal complexes.

### Introduction

Investigation on metal-organic complexes represents one of the most active areas of material science and chemical research due to their interesting properties and potential in various applications as host-guest chemistry, ion exchange and catalysis. Transition metal complexes have wide applications in food industry, dye industry, analytical chemistry, catalysis, agrochemical and biological activities [1]. Research has shown significant progress in utilization of transition metal complexes as drugs to treat several human diseases like carcinomas, lymphomas, infection control, anti-inflammatory, diabetes, malaria and neurological disorders [2]. New dyes especially those used on some of the synthetic fabrics that are difficult to tint, have been made from coordination compounds. Chelated iron is used in fertilizers to provide iron. The long known ability of aqua regia to dissolve gold and platinum depends on the formation of complex ions  $\text{AuCl}_4^-$  and  $\text{PtCl}_6^{2-}$ . The cis isomer of  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  has been used to control tumors and cancers. Dimethylglyoxime (DMG) is used to extract nickel from solution containing other ions such as iron and cobalt. Chlorophyll and hem in red blood cells are two important complexes.

Actually, studies in area of supported transition metal complexes are taking wide attention due to their various advantages. Heterogenization of metal complexes known to be active in homogenous catalysis can be achieved by (i) immobilization of the metal complex on insoluble support e.g., polymers, (ii) encapsulating it in the nanocavity of e.g., zeolites, and (iii) polymerization of metal complexes. Here, the first kind has been discussed.

Supporting transition metal complexes on insoluble materials as polymers solves one of the main problems in industry, which is related to the use of organic solvents with homogenous catalysts. The manufacture, transport,

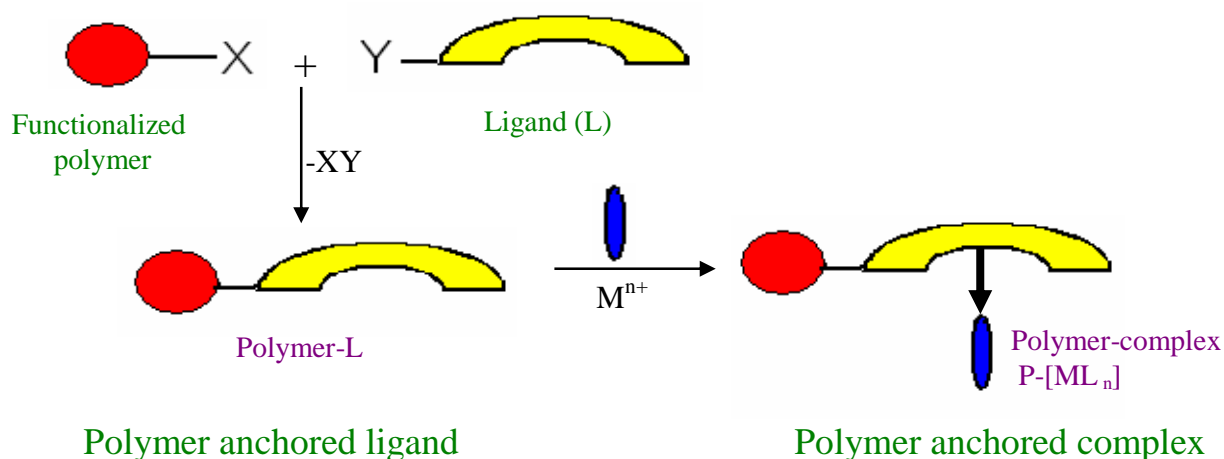
stock, handling and disposal solvents are aspects that demand great care and expense. Indeed, avoiding or minimising use of expensive, flammable and toxic organic solvents is a step in developing green technology.

### Synthesis and characterization of polymer anchored complexes

The reaction of polymer-anchored ligand with metal ions provides an easy route for the synthesis of immobilized transition metal compounds. Polymer-bound ligands and their metal complexes have been synthesized by the stepwise modification of functionalized polymers. Generally, the organic reagents (ligands having nitrogen, oxygen or sulfur as coordinating site) are allowed to react with the functionalized polymer to yield polymer-bound ligands attached to the polymer through covalent bonds. Finally, the polymer-anchored ligands react with a suitable metal to yield the polymer-anchored complexes, Scheme 1. These synthetic polymer-metal complexes have been found to possess high catalytic efficiency, semi-conductivity, heat resistance [3].

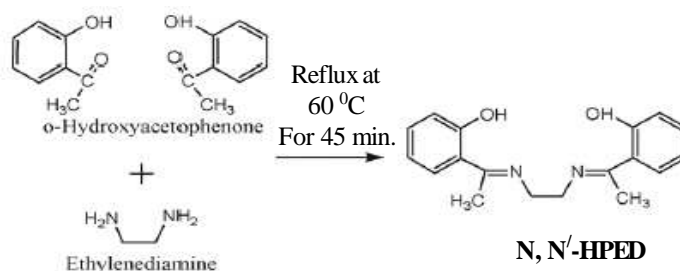
Immobilization of transition metal complexes on insoluble support (mainly organic polymer) appear to be a good way of heterogenizing homogeneous catalytic systems. Such type of heterogenized-homogeneous catalytic systems not only offers the combined advantages of homogeneous (mild conditions) and heterogeneous (easy separation), but also impose extreme shape selectivity in catalytic process. The insoluble cross-linked polymers are used widely as they are inert, non-toxic, thermally stable and easy to be recycled, whereas, linear soluble polymers are of limited value because their separation from reaction mixture is difficult. Similarly, linear insoluble polymer supports are also of limited use as they are not able to increase the turnover number in comparison to cross-linked polymers. Although various inorganic supports such as silica have been used for anchoring catalysts but polymer supports have been found to be more useful as they are able to provide preferential stereochemistry for catalysts and reactants in presence of solvent in comparison to rigid inorganic supports.

In 2007, Gupta and Sutar [4] prepared a polymer anchored transition metal complexes of *N,N'*-bis(*o*-hydroxyacetophenone)ethylenediamine (HPED) Schiff base by reacting *N,N'*-bis(4-amino-*o*-hydroxyacetophenone) ethylenediamine (AHPED) with cross-linked chloromethylated polystyrene beads and then loading of iron(III), cobalt(II) and nickel(II) ions in methanol. The route of preparation for all compounds used under investigation can be summarized in steps as in Scheme 2. The free and polymer supported metal complexes were analyzed for molecular weight (Mw) and composition by elemental analysis. The UV, IR and magnetic measurements of free and polymer supported metal complexes have confirmed the octahedral geometry for iron(III) and square planar geometry for cobalt(II) and nickel(II) ions complexes. The thermal data clearly indicated that iron(III) complexes were more stable in comparison to cobalt(II) and nickel(II) ions complexes. The unsupported HPED Schiff base complexes of metal ions were found to be less stable than supported complex although the trend in their thermal stability was almost same.

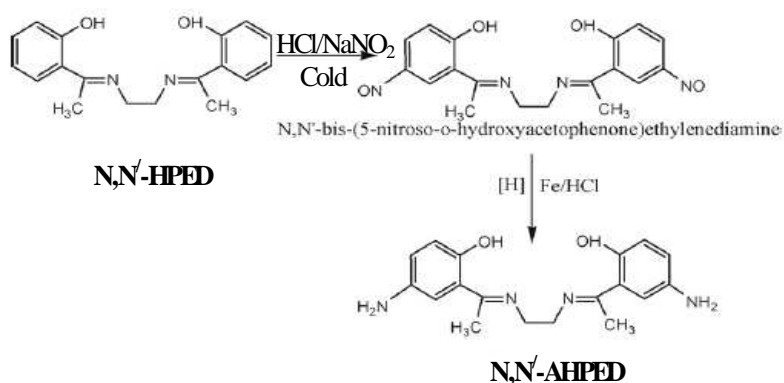


**Scheme 1.** General representation for synthesizing polymer-anchored complexes

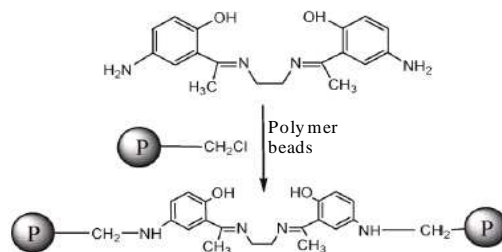
Step1. Synthesis of *N,N'*-bis(*o*-hydroxy acetophenone)ethylene diamine Schiff base (HPED).



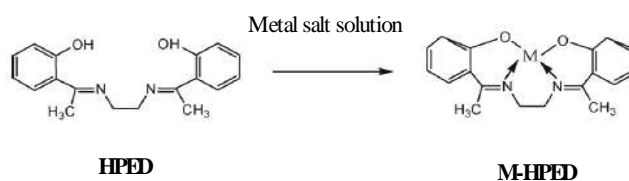
Step 2. Synthesis of *N,N'*-bis(4-amino-*o*-hydroxy acetophenone)ethylene diamine Schiff base (AHPED).



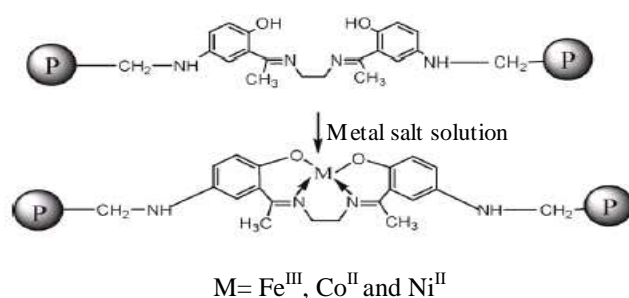
Step 3. Synthesis of polymer anchored Schiff base (P-HPED).



Step 4. Loading of metal ions on unsupported Schiff base (HPED-M).

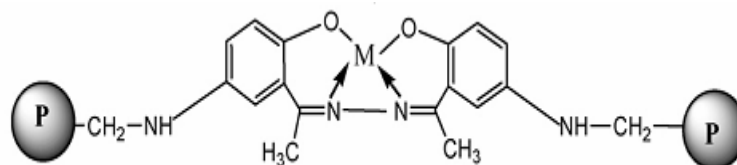


Step 5. Loading of metal ions on polymer supported Schiff base (P-HPEDM).



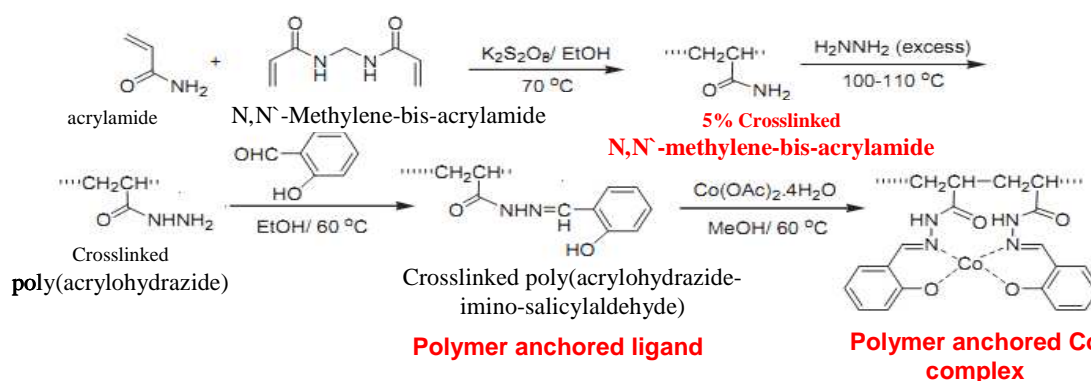
**Scheme 2.** Synthesis of modified polystyrene loaded ligand and metal complexes.

In 2008, The same authors [5] repeated the above study to separate iron(III), copper(II) and zinc(II) complexes of *N,N'*-bis(*o*-hydroxy acetophenone) hydrazine (HPHZ), **Fig. 1**. The HPHZ Schiff base were prepared by anchoring its amino derivative Schiff base on cross-linked (6 wt%) polymer beads and then loading iron(III), copper(II) and zinc(II) ions in methanol. The structural information obtained by spectral, magnetic and elemental analysis has suggested octahedral and square planar geometry for iron(III) and copper(II) ion complexes, respectively, with paramagnetic behavior, but zinc(II) ions complexes were tetrahedral in shape with diamagnetic behavior. The complexation with metal ions increased thermal stability of polymer anchored Schiff base.

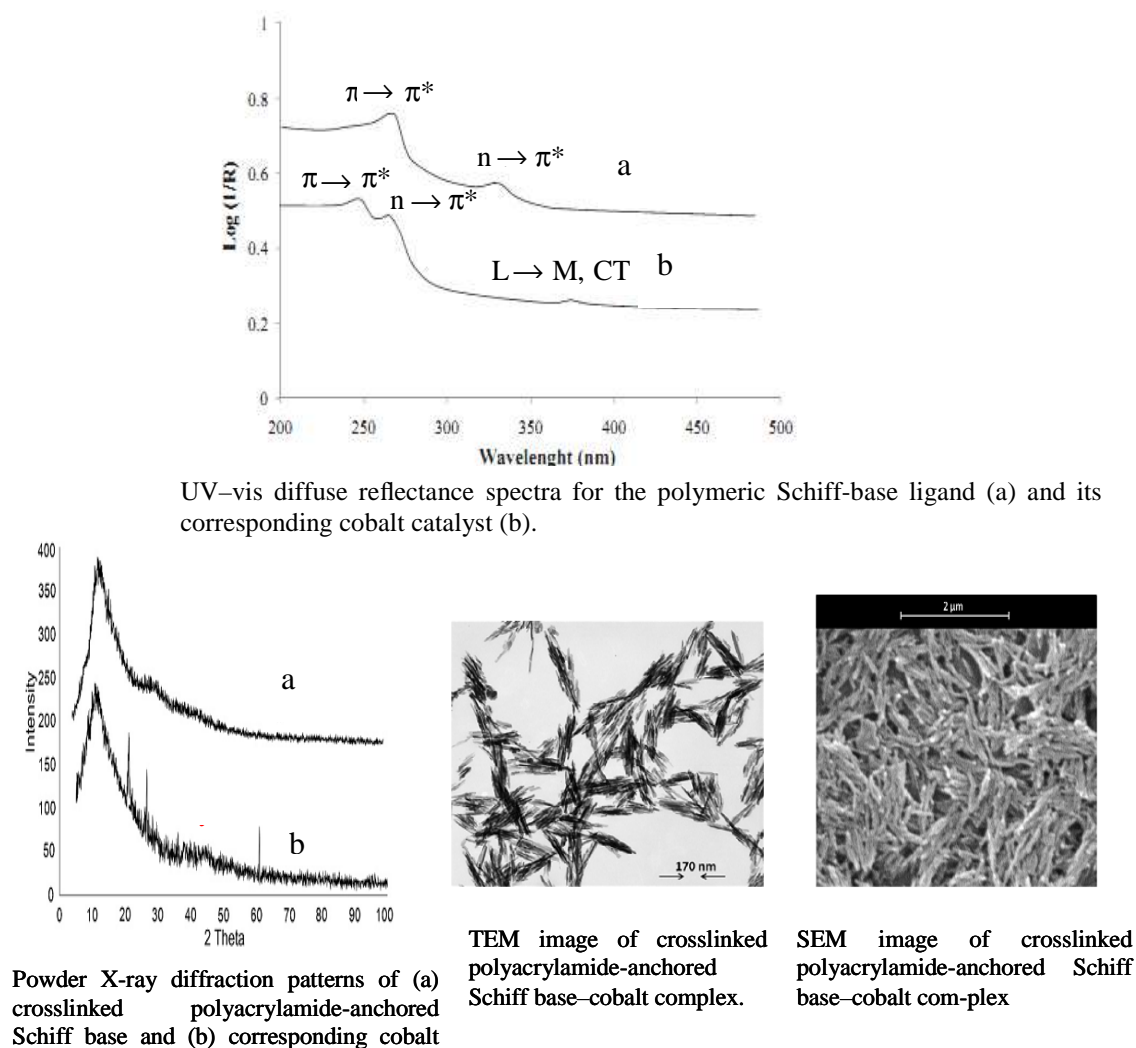


**Fig. 1.** Polymer anchored Schiff base complexes (P-HPHZ-M)

A nanosized polymer-supported Schiff base-cobalt complex on crosslinked poly-acrylamide was synthesized (Scheme 3) and characterized [6]. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of the synthesized material showed nanosize fiber-like image of the polymeric sample. IR spectra of the polymer before and after cobalt loading showed a shift in frequency from 1620 to 1603  $\text{cm}^{-1}$  for  $\nu(\text{C}=\text{N})$  and from 1272 to 1283  $\text{cm}^{-1}$  for  $\nu(\text{C}-\text{O})$ . In addition, IR spectrum of the complex showed two new absorption bands at 450 and 535  $\text{cm}^{-1}$ , which were attributed to the formation of  $\text{M}-\text{N}$  and  $\text{M}-\text{O}$ , respectively. These variations confirmed the coordination of cobalt ion with the azomethine nitrogen and phenolic oxygen of the polymeric Schiff-base ligand. The complexation of cobalt (II) ions with Schiff-base ligand showed a shift in the electronic  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions from 265 to 240 nm and from 328 to 261 nm, respectively, which provided evidence for the coordination of cobalt (II) ions through nitrogen atom of azomethine group. The appearance of a new band at 380 nm for metal complex is attributed to charge transfer process ( $\text{L} \rightarrow \text{M}$ ) from ligand to cobalt (II) ions. No  $d \rightarrow d$  transition was observed for the complex. UV-vis diffuse reflectance spectra for the polymeric Schiff-base ligand and its corresponding cobalt species is presented in Fig. 2. The strongest peak of the XRD pattern of the heterogeneous material (Fig. 2) corresponds to an amorphous polymer matrix. In addition to XRD, scanning electron microscopy (SEM), Fig. 2, showed a nanometer up to micrometer fiber-like images for the polymeric species. Transmission electron microscopy (TEM) image of the catalyst showed that the fiber lengths mostly range from 50 to 250 nm in size (Fig. 2). The BET surface area of the polymeric Schiff-base ligand is significantly increased for its corresponding cobalt sample.



**Scheme 3.** Synthetic strategy for the preparation of modified polyacrylamide loaded cobalt complex.

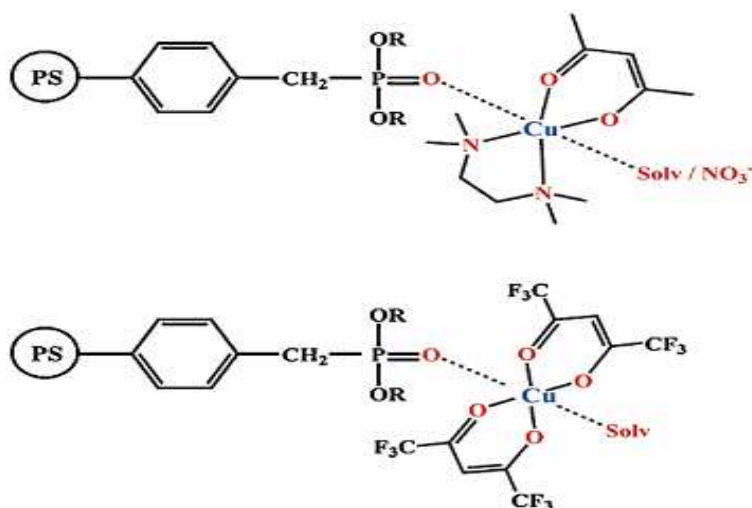


**Fig. 2.** Some resulting spectra of crosslinked polyacrylamide-anchored Schiff base and cobalt complex.

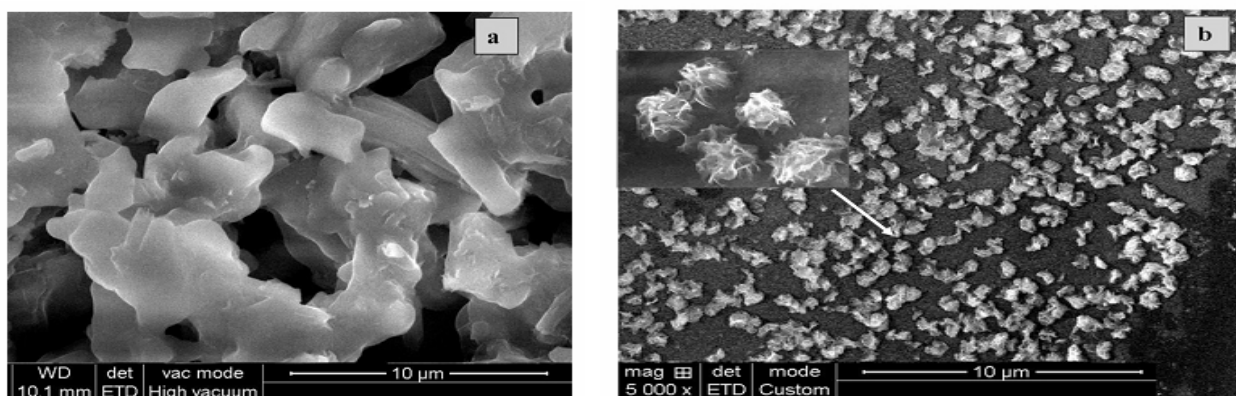
Heterogenized complexes were synthesized by immobilization of neutral and monocationic copper complexes  $\text{Cu}(\text{hfac})_2$  ( $\text{hfac}^-$  = hexafluoroacetylacetonato ligand) and  $[\text{Cu}(\text{acac})(\text{tmen})]\text{NO}_3$  ( $\text{acac}^-$  = acetylacetonato ligand,  $\text{tmen} = \text{N,N,N',N'}$ -tetramethyl-ethylenediamine) on styrene-divinylbenzene copolymer functionalized with four different dialkyl phosphonate moieties typified by  $\text{P-PO}(\text{OR})_2$  (with  $\text{R} = -\text{CH}_3, -\text{C}_2\text{H}_5, -\text{C}_3\text{H}_7$  and  $-\text{C}_4\text{H}_9$ ), Scheme 4. The formation of  $\text{P}(\text{O})(\text{OR})_2$  phosphonate groups has been confirmed by the FT-IR spectra [7]. Thermogravimetric analysis results revealed that the thermal stability of polymer support depends on the functional group attached. The complexes were anchored by coordination interaction between the copper(II) ion and the phosphonate oxygen atom on each of the four functionalized supports and the strength of the  $\text{P}=\text{O} \cdots \text{Cu}^{2+}$  coordination interaction was influenced by the nature of the R group. A very good and homogeneous dispersion of Cu(II) complex particles on the copolymer support was evidenced by SEM microscopy (Fig. 3). It was believed that this sustain the immobilization of the complexes by coordination interaction between the copper(II) ion and the phosphonate oxygen atom of the functionalized supports. The SEM images showed the change of Cu(II) complexes morphology after immobilization. The new Cu(II) complexes on the polymer surface are spherical formations with diameters around 500 nm.

Islam and co-workers [8] prepared polymer supported copper complex by the complexation of copper salts with polymer anchored ligand derived from 2-aminophenol, (Scheme 5). The characterization of the catalyst was done on the basis of infrared spectroscopy, diffuse reflectance spectra of solid, thermogravimetric analysis and by using scanning electron microscope. The metal content in the copper sample was determined by atomic absorption spectroscopy. The modes of attachment of copper metal onto the support were confirmed by FT-IR

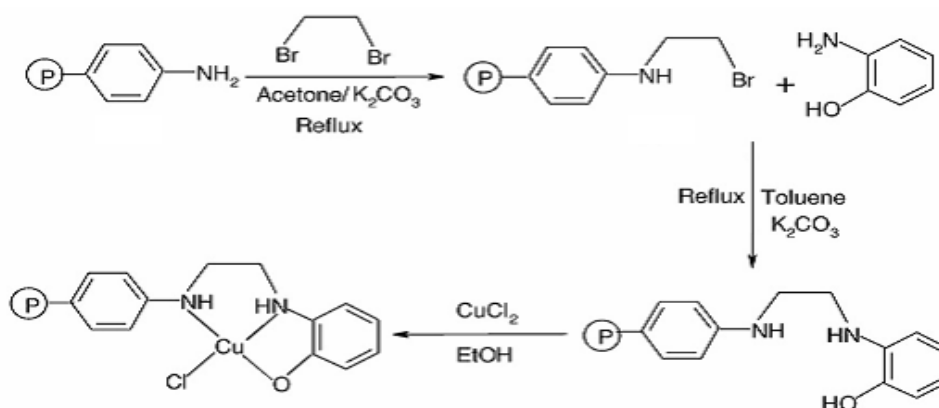
spectral bands. The scanning electron micrographs of polymer anchored ligand and supported copper complex clearly showed the morphological change, which occurred after complexation and suggest the loading of copper metal on the surface of polymer. Energy dispersive spectroscopy analysis of X-rays (EDAX) data for polymer anchored ligand and supported copper complex are given in Fig. 4 (A and B). The EDAX data confirmed the attachment of copper metal on the surface of the polymer matrix. Polymer supported ligand decomposed in the temperature range 310–340 °C. After complexation of copper metal on polymers supported ligand, the thermal stability of the immobilized complex was improved where the polymer supported Cu(II) complex decomposed at 390–410 °C. The electronic spectrum of the immobilized copper sample has been recorded in the diffuse reflectance mode which corresponds to the square-planar geometry.



**Scheme 4.** Immobilization of coordinatively unsaturated metal centers of  $[\text{Cu}(\text{acac})(\text{tmen})]^+$  and  $\text{Cu}(\text{hfac})_n$  complex species on polymer-supported phosphonates (where  $\text{R} = -\text{CH}_3, -\text{C}_2\text{H}_5, -^i\text{C}_3\text{H}_7$  and  $-^n\text{C}_4\text{H}_9$ ).



**Fig. 3.** SEM images of  $[\text{Cu}(\text{acac})(\text{tmen})]\text{NO}_3$  complex before (a) and after immobilization on PS- $\text{PO}(\text{O}^n\text{C}_4\text{H}_9)_2$  polymeric support (b).



Scheme 5. Synthesis of polymer anchored copper(II) complex.

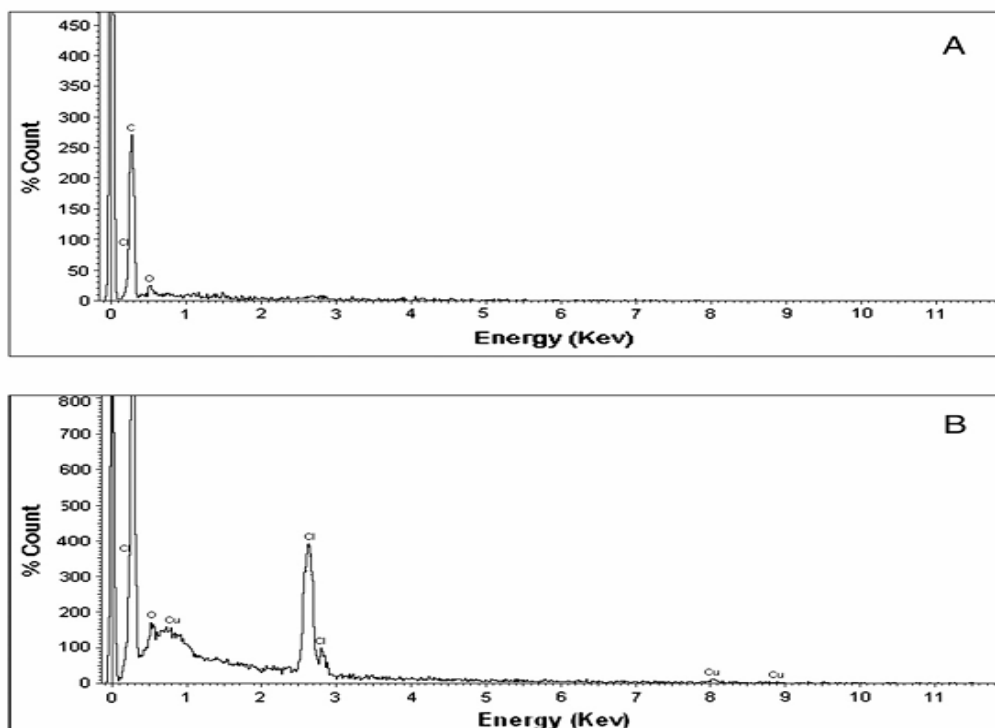
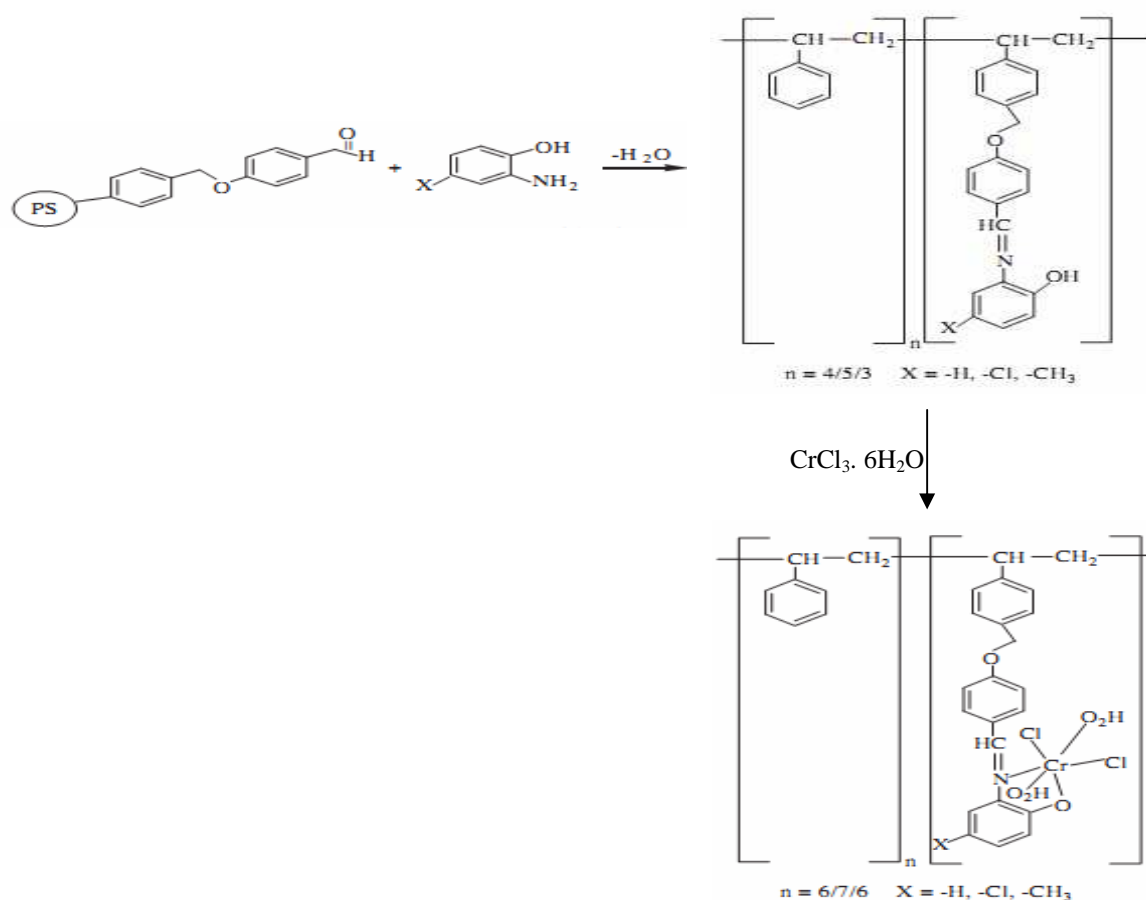


Fig. 4. EDAX data of polymer anchored ligand (A) and polymer anchored Cu(II) sample (B).

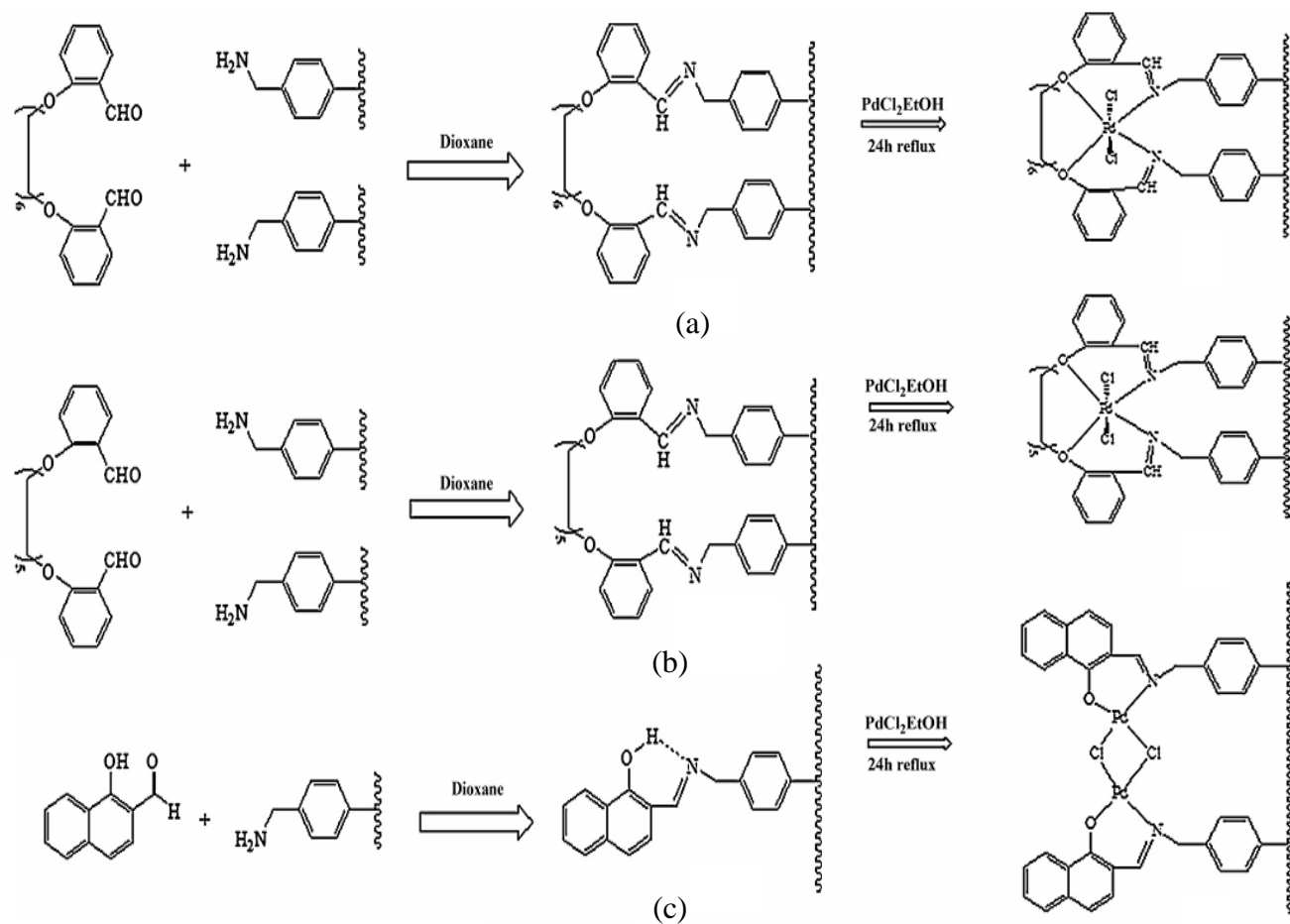
Polymer-bound Schiff bases and Cr(III) complexes have been synthesized by the reaction of 4-benzyl-oxybenzaldehyde, polymer-bound with 2-aminophenol, 2-amino-4-chlorophenol and 2-amino-4-methyl-phenol, **Scheme 6**, [9]. The structure of polymeric-Schiff bases and their Cr(III) complexes have been characterized by elemental analyses, magnetic measurements, IR, UV-Vis, TG-DTA and  $^1\text{H-NMR}$ . The average molecular weights (Mw) of polymeric-Schiff bases were suggested from the elemental analyses. According to the values of magnetic susceptibility of polymeric-Schiff base Cr(III) complexes, octahedral geometry was assigned to Cr(III) complexes. All these compounds have also been investigated for antibacterial activity where it was noticed that the biological activity of polymeric-Schiff bases is higher than their Cr(III) complexes. Some of the properties may have affected their antimicrobial activity such as molecular weight, space length between active site and polymer, chelation and concentration. Polymeric antimicrobial agents have the advantage that they are nonvolatile and chemically stable and do not permeate through skin.

Schiff bases (1,6-bis(2-carboxy aldehyde phenoxy)hexane (a); 1,5-bis(2-carboxy aldehyde phenoxy)pentane (b); 2-hydroxy-1-naphthaldehyde (c)) of amino methylated polystyrene and their metal complexes were synthesized (Scheme 7) and characterized by thermal analysis, IR, UV-vis spectral analysis, SEM and EDX studies [10]. Analytical data of the complexes show 1L:1M geometry. The IR spectra of the polymer anchored Schiff bases showed peaks at 1634–1621  $\text{cm}^{-1}$  characteristic of the C=N group. In all the complexes, the  $\nu(\text{C}=\text{N})$  group absorption shifted to lower frequency by 30–15  $\text{cm}^{-1}$ , indicating coordination of the imine nitrogen atoms of the Schiff bases. From the different microanalytical and spectral data, the structure for the polymer-anchored Pd(II) complex is proposed. Thermo-gravimetric analysis showed stability of the polymer-anchored complexes up to 300 °C, above which there is a continuous weight loss, which extends to 600 °C. DTA analysis revealed that all the decomposition stages are exothermic in nature. As it was clear from the data, the complexation of the polymer supported Pd(II) compounds has shown a dramatic increase in thermal stability which has clearly indicated that these complexes could be used as catalysts for high temperature reactions. SEM was used to detect the presence of the complex on the surface of the polymer. Scanning electron micrographs (SEM), [assigned to ligand (c), for instance, Fig. 5, were recorded taking single bead of each to understand the morphological changes. A light roughening of the top layer of beads having polymer-anchored ligand compared to relatively smooth and flat surface of neat polystyrene bead suggests the change of nature of beads on covalent bonding. Images of metal complexes beads show further roughening of the top layer which is possibly due to interaction of metal ions with ligand to arrange in the fixed geometry of the complex. According to the EDAX spectra it was seen that only C and N were present in the ligands, while, the polymer-anchored metal complex contained Pd along with C, N and Cl.



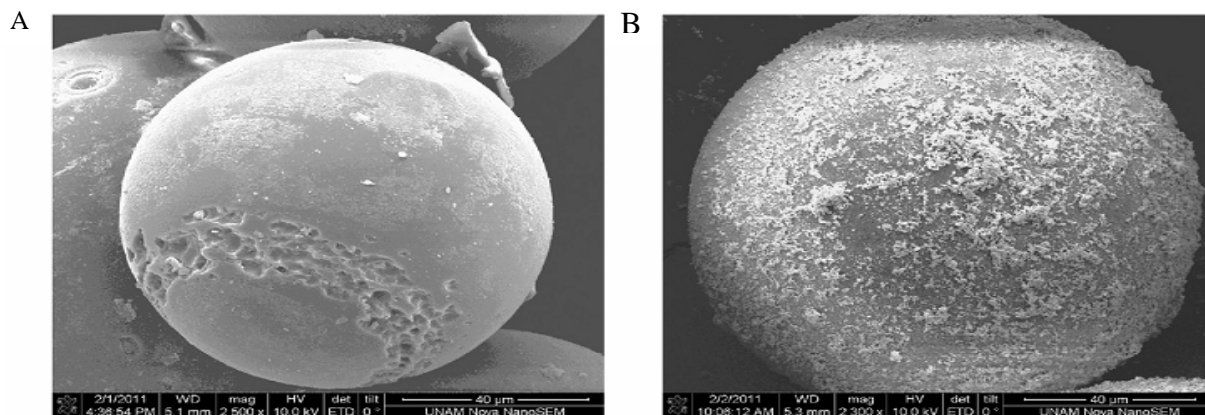
**Scheme 6.** Synthesis and structures of synthesized polymeric-Schiff bases and their Cr(III) complexes.





- (a) 1,6-bis(2-carboxy aldehyde phenoxy)hexane Schiff base of amino methylated polystyrene; (b) 1,5-bis(2-carboxy aldehyde phenoxy)pentane Schiff base of amino methylated polystyrene; (c) 2-hydroxy-1-naphthaldehyde Schiff base of amino methylated polystyrene.

**Scheme 7.** Preparation of polymer-anchored ligands and their polymer-anchored Pd(II) complexes.



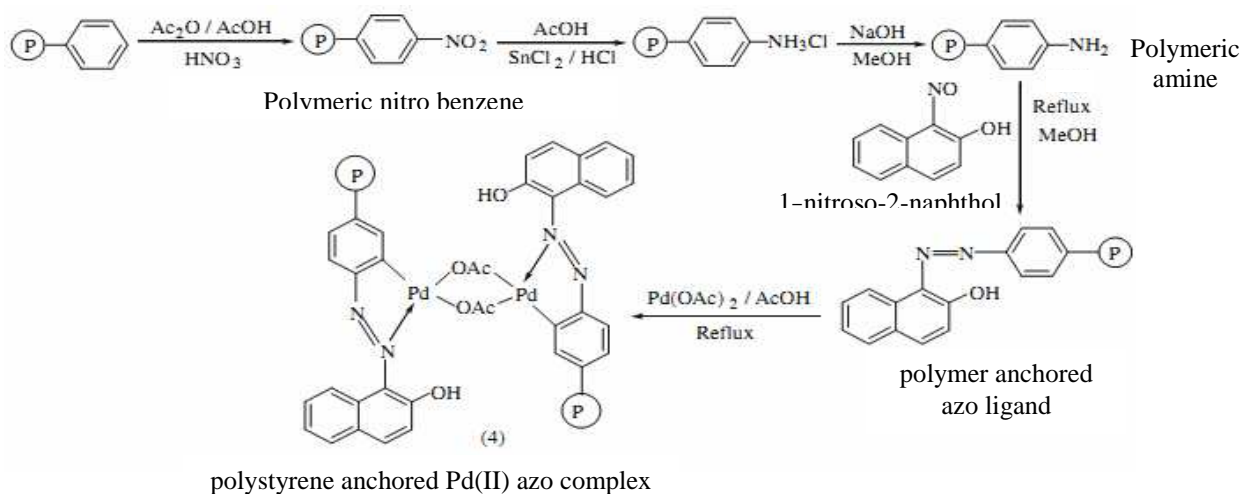
**Fig. 5.** SEM spectra of (A) polymer anchored ligand (c) and (B) polymer anchored Pd(II) complex.

Islam and co-workers [11] isolated and characterized polystyrene anchored Pd(II) azo complex. The preparation procedure followed to obtain the solid material is indicated in Scheme 8. Due to insolubility of the different functionalized polystyrene and the corresponding polystyrene anchored Pd(II) complex in all common solvents, their structural investigations were limited only to their physico-chemical properties, SEM, TGA-DTA, IR, and UV-vis spectral data. The polystyrene anchored azo ligand showed a sharp peak at  $1452\text{ cm}^{-1}$  due to the N=N bond which on complexation with Pd disappeared and appeared as a band at  $1440\text{ cm}^{-1}$ . The lowering in frequency of N=N peak indicated an effective coordination interaction between the ligand and Pd center. The polystyrene anchored Pd(II) azo complex exhibited important IR peaks at  $1585$  and  $1430\text{ cm}^{-1}$  (vCOO bridged),  $530\text{ cm}^{-1}$  (v Pd-C),  $722\text{ cm}^{-1}$  (orthometallation) and  $455\text{ cm}^{-1}$  (v Pd-N).

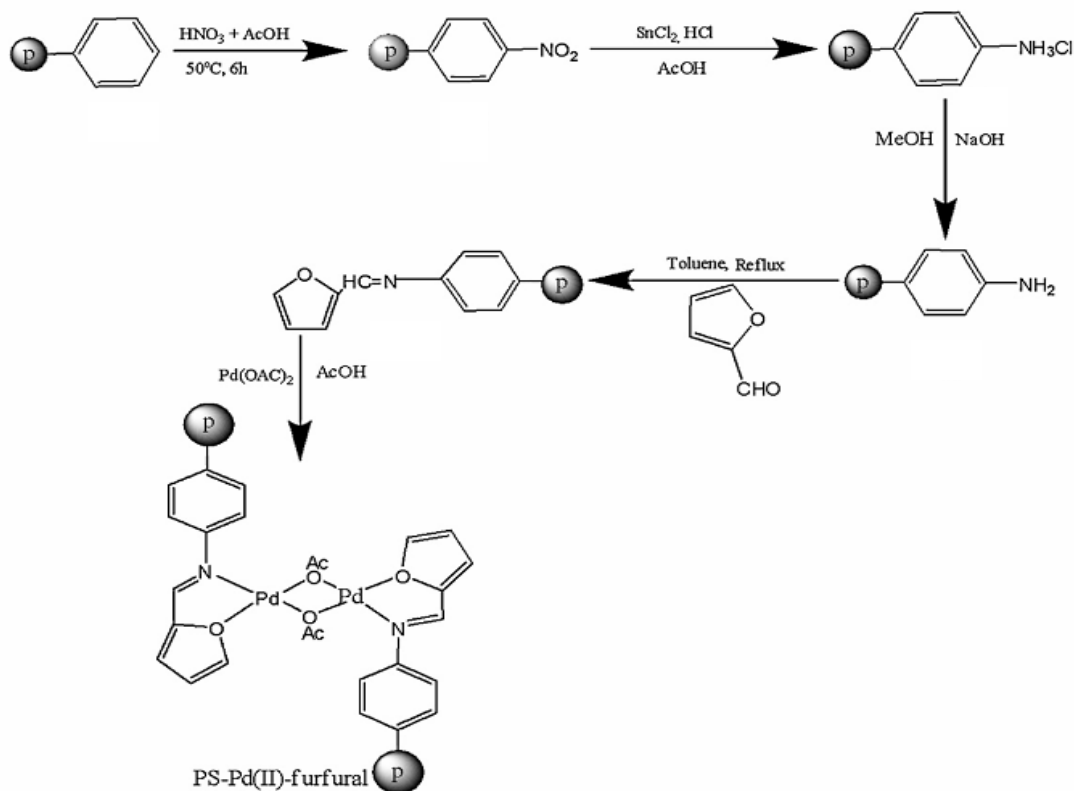
Extending to the work of Islam et al. attributed to the polymer anchored palladium complexes {11}, inexpensive, air-moisture stable and reusable PS-Pd(II)-furfural complex was synthesized by reacting polymeric amine with furfural to get polymer anchored ligand which was then reacted with Pd(OAc)<sub>2</sub> to get polymer anchored complex, Scheme 9. Due to insolubility of this polymer anchored Pd(II) complex in all common organic solvents, Islam and co-workers [12] characterized the synthesized complex by the same above mentioned physicochemical techniques reported in Ref. 11. SEM images of the polymer anchored Schiff base ligand and the immobilized palladium complex on modified polystyrene showed a morphological difference between the free Schiff base ligand and the hybrid material. EDX data also support the metal attachment on the surface of polymer matrix.

The reaction of 2-thiomethylbenzimidazole (Htmbmz) with chloromethylated polystyrene yielded a product designated by (PS -ligand), which corresponds mostly to the tmbmz bound to the polystyrene matrix by the sulfur atom, Scheme 10, [13]. [VO(acac)<sub>2</sub>], [MoO<sub>2</sub>(acac)<sub>2</sub>] and Cu(CH<sub>3</sub>COO)<sub>2</sub> react with the PS-ligand to give PS-[VO(ligand)<sub>n</sub>], PS-[MoO<sub>2</sub>(ligand)<sub>n</sub>] and PS-[Cu(ligand)<sub>n</sub>], respectively, with  $n \cong 2$ . Non-polymer-bound complexes [VO(tmbmz)<sub>2</sub>], [MoO<sub>2</sub>(tmbmz)<sub>2</sub>] and [Cu(tmbmz)<sub>2</sub>] have also been prepared similarly. The anchored complexes were characterized by elemental analysis, IR, electronic and EPR spectroscopy, field-emission scanning electron micrograph (FE-SEM), energy dispersive X-ray analysis (EDAX) and thermogravimetric studies. EPR was particularly useful to characterize the binding modes in PS-[VO(ligand)<sub>n</sub>] and PS-[Cu(ligand)<sub>n</sub>], confirming that the vanadium and copper centers are well dispersed in the polymer matrix and supporting the presence of N<sub>2</sub>O<sub>2</sub> binding modes in both cases. All polymer-anchored complexes are stable up to ca. 180 °C and thereafter they decomposed in two major steps giving the corresponding metal oxides as end products at ca. 600 °C. Field emission-scanning electron micrographs were detected for single beads and showed that the pure polystyrene bead has a smooth surface. Introduction of ligands into polystyrene beads through covalent bonding causes the light roughening of the top layer of polymer-anchored beads. Images of metal-complex beads show further roughening of the top layer, probably due to the changes that occur during the rearrangement of the chains to adapt the bound ligand to the fixed geometry of the complex. EDAX supports this conclusion in that ca. 19% chlorine content has been found in the pure polystyrene beads, while beads having anchored ligand showed only ca. 1% Cl along with ca. 6.5 % nitrogen and ca. 9.2 % sulfur. The polystyrene beads of immobilized metal complexes contain metal along with nitrogen and sulfur, suggesting the formation of metal complexes with the anchored ligand at various sites.

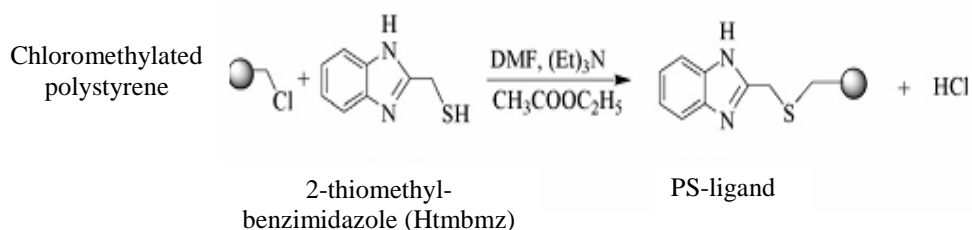
The preparation of polystyrene anchored orthometallated ruthenium(II) complex, P-[(azb)(CO)<sub>2</sub>Ru.Cl]<sub>2</sub> (P = polystyrene backbone and H-azb = azobenzene) is shown in Scheme 11. The complex was prepared by reacting polymer anchored azobenzene ligand with (i) [Ru(CO)<sub>2</sub>Cl<sub>2</sub>S<sub>2</sub>] or (ii) RuCl<sub>3</sub> .3H<sub>2</sub>O under high P<sub>CO</sub> [14]. The resulting ruthenium(II) species is insoluble in all common solvents, thermally stable up to 200 °C and XRD pattern suggested its non-crystalline nature. Rigid structure of the polymer matrix allows only suitably positioned azobenzene moieties to form chloro or carbonyl bridged complexes.



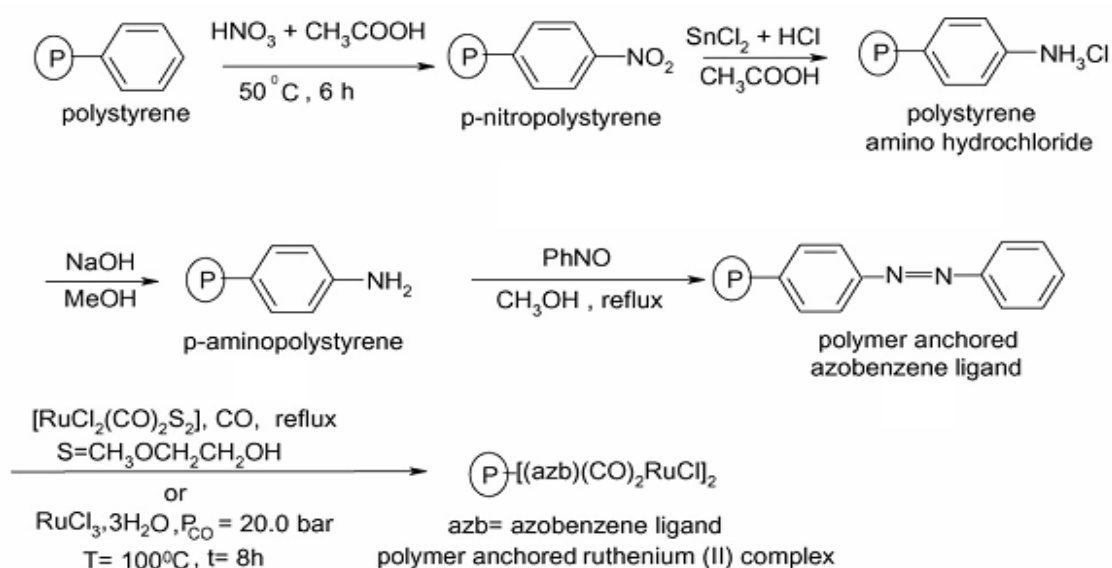
**Scheme 8.** Preparation of polystyrene anchored Pd(II) azo complex.



**Scheme 9.** Preparation of polystyrene anchored PS-Pd(II)-furfural complex.



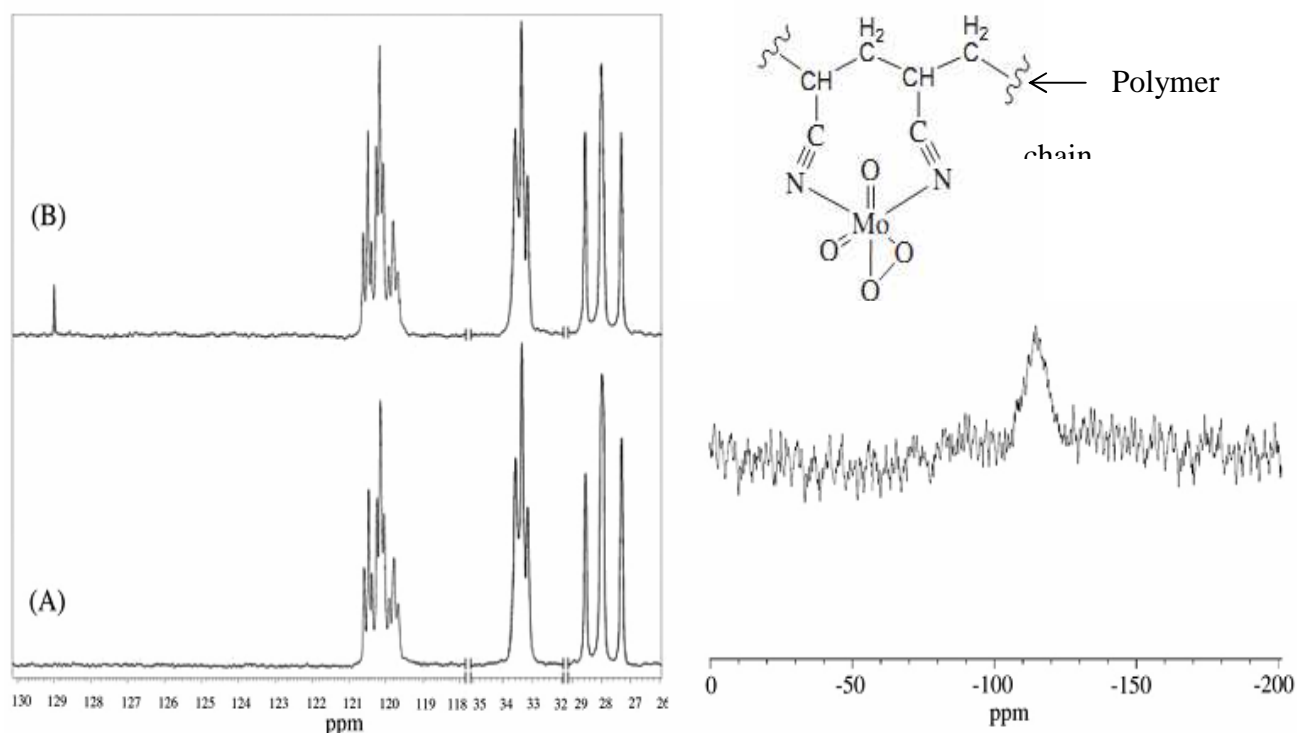
**Scheme 10.** Reaction of Htmbmz with chloromethylated polystyrene; the ball represents the polymer backbone.



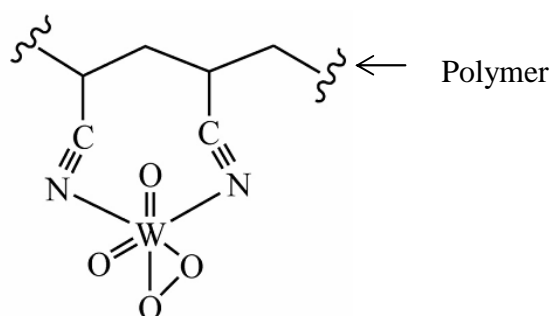
**Scheme 11.** Preparation of polymer anchored Ru(II) complex.

In 2013, A polymer supported peroxomolybdate(VI) compound of the type  $[\text{MoO}_2(\text{O}_2)(\text{CN})_2]\text{-PAN}$ , (PAN = poly(acrylonitrile)) (PANMo) was obtained by reacting  $\text{H}_2\text{MoO}_4$  with 30%  $\text{H}_2\text{O}_2$  and the macromolecular ligand, PAN at near neutral pH. The macro-complex has been characterized by elemental analysis (CHN and EDX analysis), spectral (IR, UV-Vis and  $^{13}\text{C}$  NMR,  $^{95}\text{Mo}$  NMR), thermal (TGA-DTG) as well as SEM studies [15]. Information regarding the change in particle size, as well as morphological changes occurring on the surface of the polymer after incorporation of the peroxomolybdates into the polymer matrix, was derived from scanning electron microscopic study. It was evident from the micrograph that the metal ions are distributed across the surface of the polymeric peroxometal compound, PANMo, leading to considerable roughening of its surface in contrast to the smooth and flat surface of the pristine polymer. Also, enhancement of the average particle size after incorporation of the peroxo-molybdenum (pMo) moieties into the polymer beads in comparison to the size of the PAN beads was noted. The polymer-anchored complex PANMo displayed characteristic spectral patterns in the infrared region involving absorptions due to  $\nu(\text{Mo}=\text{O})$  and coordinated peroxide ligand. The IR spectrum of PANMo resembled closely the spectral pattern observed for PANW. The  $^{13}\text{C}$  NMR spectra of the pristine PAN and the compound PANMo are presented in Fig. 6. The  $^{95}\text{Mo}$  NMR spectrum of PANMo displayed a lone resonance at -114 ppm (relative to  $[\text{MoO}_4]^{2-}$ ) characteristic of monoperoxomolybdate species, in agreement with the formula assigned to the compound (Fig. 6). The appearance of a single characteristic peak in the  $^{95}\text{Mo}$  NMR spectrum of the compound confirmed the presence of a single coordination environment for the peroxomolybdenum species present in solution. The proposed structure of PANMo is shown schematically in Fig. 6, that includes a dioxomonoperoxo molybdenum(VI)

moiety bonded to the polymer matrix via the N atom of the pendant nitrile group. Similarly, A polymer-bound peroxotungstate(VI) complex of the type  $[W(O)_2(O_2)(CN)_2]$ -PAN, (PANW) was also prepared by reacting  $H_2WO_4$  with 30%  $H_2O_2$  and the macromolecular ligand, PAN at pH 5.0 [16]. The compound was also characterized by the same physicochemical techniques forming a structure (Fig. 7) similar to PANMo.



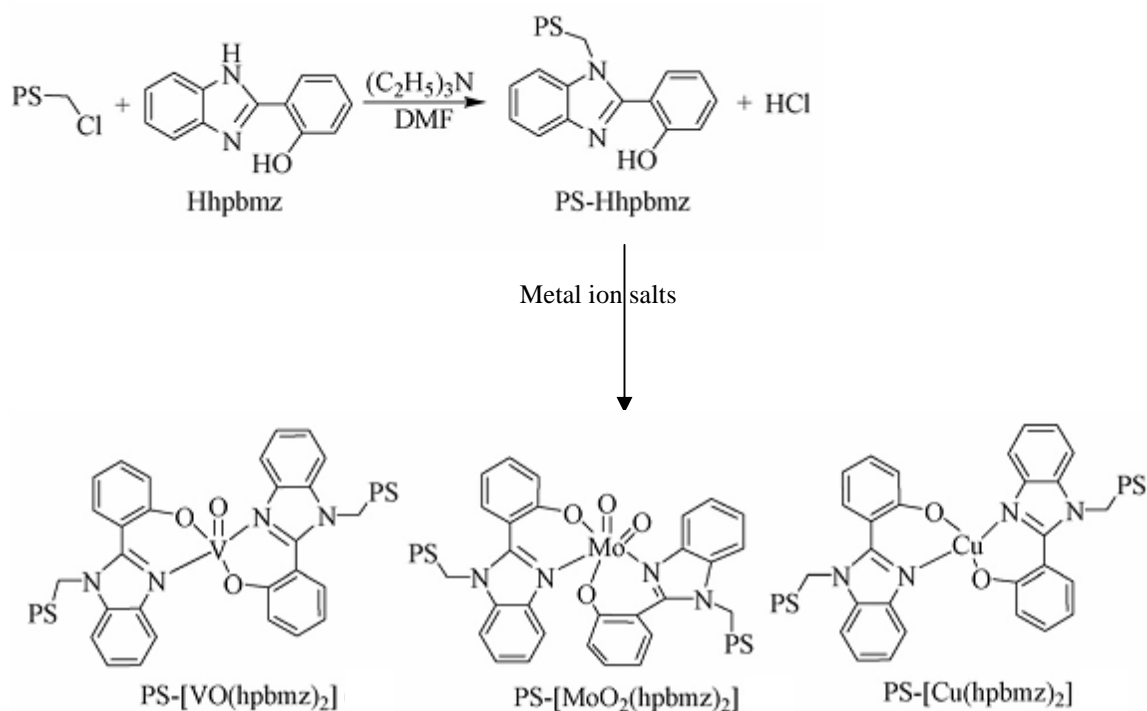
**Fig. 6.**  $^{13}C$  NMR (left) and  $^{95}Mo$  NMR (right) of (A) PAN and (B) PANMo in DMSO-d + DMF (1:4).



**Fig. 7.** Proposed structure of PANW.

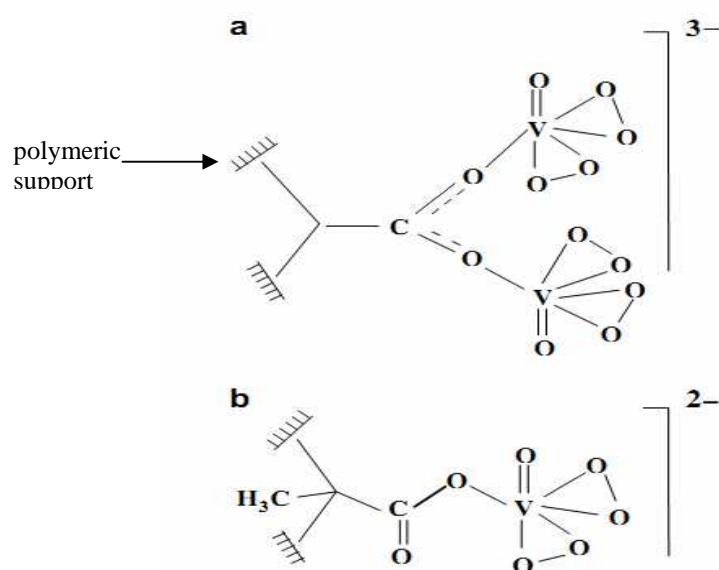
Monobasic bidentate ligand 2-(2'-hydroxyphenyl)benzimidazole (Hhpbmz) has been covalently bonded to the chloromethylated polystyrene cross-linked with 5% divinylbenzene. Treatment of the resulted chelating resin, abbreviated as PS-Hhpbmz, with  $[VO(acac)_2]$ ,  $[MoO_2(acac)_2]$  (Hacac = acetylaceton) and  $Cu(CH_3COO)_2 \cdot H_2O$ , gave polymer-anchored complexes PS- $[VO(hpbmz)_2]$ , PS- $[MoO_2(hpbmz)_2]$  and PS- $[Cu(hpbmz)_2]$ , respectively. During this process  $-CH_2Cl$  group of the functionalized polymer reacts with imine nitrogen of the benzimidazole moiety as shown in Scheme 12. The corresponding neat complexes with Hhpbmz have also been prepared similarly. Structures of these complexes have been established on the basis of elemental analyses, scanning electron micrographs and spectroscopic (infrared and electronic) as well as

thermogravimetric studies [18]. The polymer-anchored complexes were stable up to 150 °C and thereafter they decomposed in several small fragments with exothermic weight loss. Disappearance of the  $\nu(\text{NH})$  band (in the IR spectra) on anchoring with chloromethylated polystyrene suggests the covalent bond formation of ligand through imine nitrogen (Scheme 12). On the other hand, a shift of the  $\nu(\text{C}=\text{N})$  (ring) stretching band to lower frequency and absence of the  $\nu(\text{OH})$  band in all the complexes suggested the coordination of the azomethine nitrogen and phenolic oxygen of the ligand to the metal.

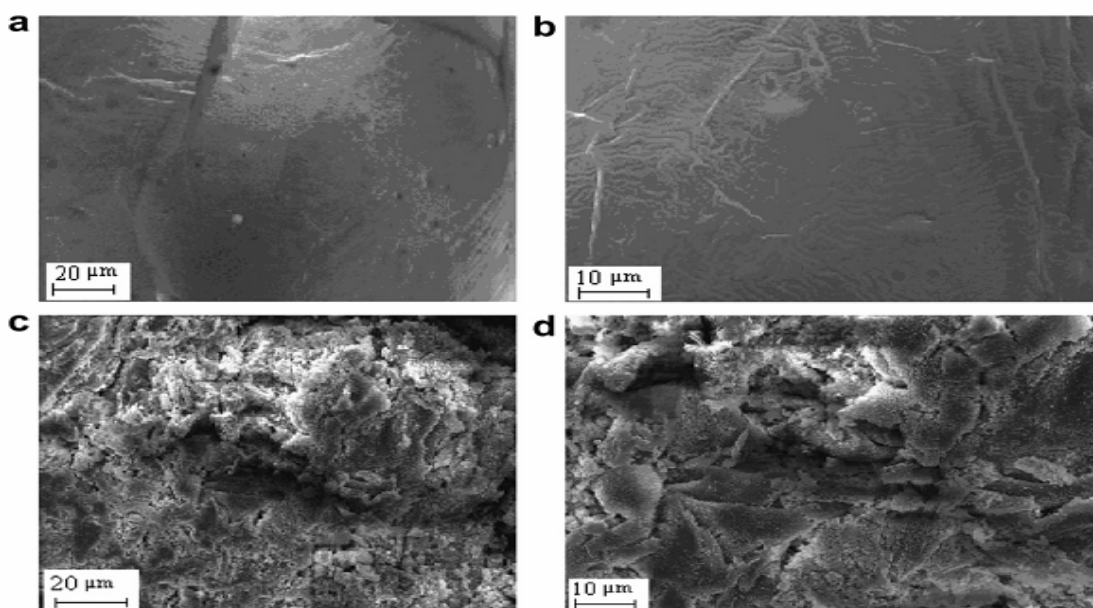


**Scheme 12.** Synthesis of polymer anchored metal complexes.

Islam et al. [19] synthesized a peroxovanadate (pV) complexes anchored to soluble polymers of the type, Na<sub>3</sub>[VO<sub>2</sub>O<sub>2</sub>]<sub>4</sub>(carboxylate)-PA, [PA=poly(acrylate)](PAV) and Na<sub>2</sub>[VO(O<sub>2</sub>)<sub>2</sub>(carboxylate)]-PMA [PMA = Poly(methacrylate)] (PMAV) by the reaction of V<sub>2</sub>O<sub>5</sub> with H<sub>2</sub>O<sub>2</sub> and the sodium salts of the respective macromolecular ligands at pH ca. 6. The compounds were characterized by elemental analysis, SEM, EDX, TGA and spectral studies confirming the proposed structures shown in Fig. 8. In PMAV, the pV moieties are anchored in monomeric form to the polymer chain through unidentately coordinated O(carboxylate) atoms. Carboxylate groups of PA chain coordinate to V(+5) centres, in a bridging bidentate fashion leading to the formation of dimeric pV structures in PAV. The elemental analysis data of the compounds PAV and PMAV indicated the presence of two peroxide groups per metal center. The electronic spectra of the compounds PAV and PMAV in aqueous solution displayed a weak intensity broad band at 320 nm which was assigned to peroxo to vanadium (LMCT) transition. SEM was used and demonstrated that, in contrast to the smooth and flat surfaces of the pure poly(acrylate) or poly(methacrylate) polymers, the surfaces of the polymer anchored complexes exhibited a considerable roughening (Fig. 9). EDX spectroscopy of the compounds, which provides in situ chemical analysis of the bulk, clearly showed V,C,O and Na as the constituents of the anchored complexes. Moreover, the EDX spectral data obtained on the composition of the compounds were in good agreement with the elemental analysis values.



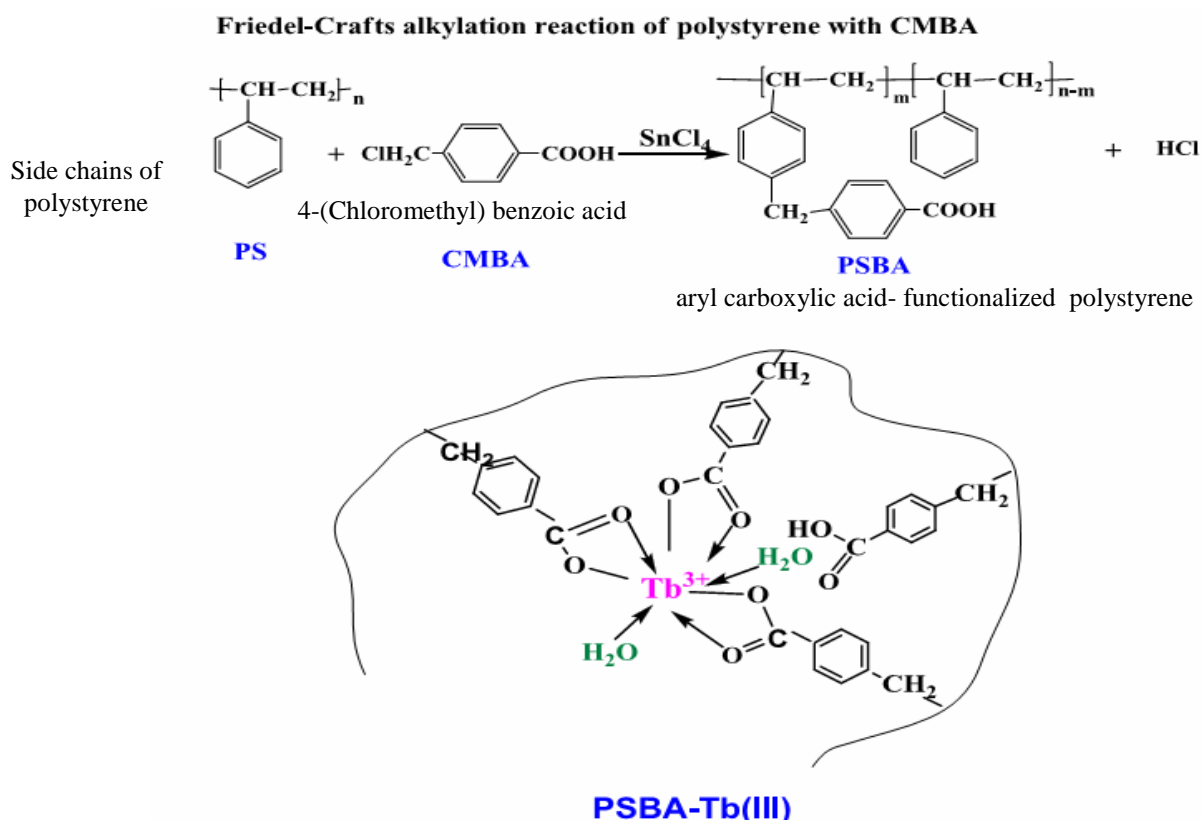
**Fig. 8.** Proposed structures of (a)  $\text{Na}_3[\text{VO}_2\text{O}_2]_4(\text{carboxylate})\text{-PA}$  (PAV) and (b)  $\text{Na}_2[\text{VO}(\text{O}_2)_2(\text{carboxylate})\text{-PMA}$  (PMAV).



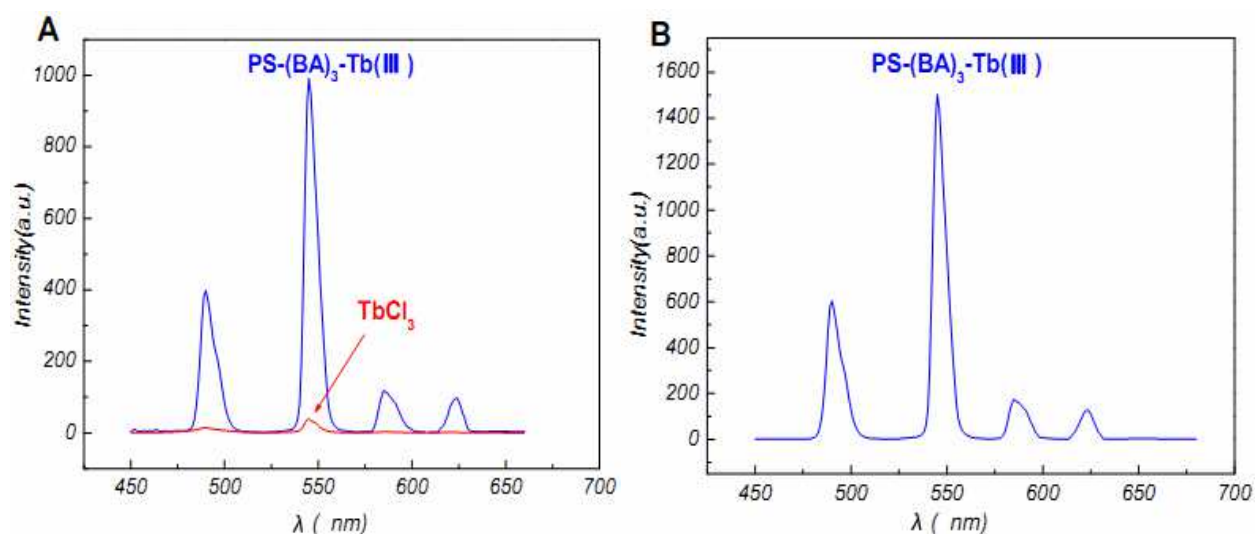
**Fig. 9.** Scanning electron micrographs of (a) sodium poly(acrylate), (b) sodium poly(methacrylate), (c) PAV and (d) PMAV.

4-(Chloromethyl) benzoic acid (CMBA) was bonded onto the side chains of polystyrene (PS) via a polymer reaction, Friedele Crafts alkylation reaction, and aryl carboxylic acid- functionalized polystyrene (PSBA) was generated. The functionalized polystyrene was used to prepare rare earth metal complexes. By using PSBA as macromolecule ligand, the binary polymer-rare earth complexes,  $\text{PS}-(\text{BA})_n\text{-Tb(III)}$ , were prepared, Scheme 13, [20]. The complexes were fully characterized using FTIR and proton NMR spectroscopy. Both ultraviolet absorption and fluorescence emission spectra for the complexes were recorded. Fluorescence spectra of  $\text{PSF}-(\text{BA})_3\text{-Tb(III)}$  and  $\text{TbCl}_3$  are shown in Fig. 10. where the following facts can be found: (1) The emission spectrum of the binary complex  $\text{PS}-(\text{BA})_3\text{-Tb(III)}$  is similar to that of  $\text{TbCl}_3$  in the spectrum shape and band positions, suggesting that the emission peaks exhibiting in the complex spectrum are the characteristic

emissions of  $Tb^{3+}$  ion. In the spectrum, four main emission peaks at 490, 545, 585 and 623 nm are displayed. The first is assigned to the transition of  ${}^5D_4 \rightarrow {}^7F_6$ , the second is ascribed to the transition of  ${}^5D_4 \rightarrow {}^7F_5$ , the third is attributed to the transition of  ${}^5D_4 \rightarrow {}^7F_4$ , and the last is corresponding to the transition of  ${}^5D_4 \rightarrow {}^7F_3$ . (2) Among these transitions, the  ${}^5D_4 \rightarrow {}^7F_5$  at 545 nm is the strongest emission as shown in Fig. 10. Besides, the fluorescence emission peak of the complex PS-(BA)<sub>3</sub>-Tb(III) at 545 nm is very narrow, implying good color purity. Under the condition of this investigation ( $Tb^{3+}$  ion concentration was  $1.06 \times 10^{-4}$  mol/L), the fluorescence emission of the complex PS-(BA)<sub>3</sub>-Tb(III) is far stronger than that of  $TbCl_3$ , and the intensity increases by 28 times. (3) The film of PS-(BA)<sub>3</sub>-Tb(III) can also emit strong fluorescence.



**Scheme 13.** Schematic expressions of structures of PSBA and binary complex PS-(BA)<sub>n</sub>-Tb(III).



**Fig. 10.** (A) Fluorescence spectra of PSF-(BA)<sub>3</sub>-Tb(III) and  $TbCl_3$ , Solvent: DMF, concentration of  $Tb^{3+}$ :  $1.06 \times 10^{-4}$  mol/L. (B) Film fluorescence spectrum of PSF-(BA)<sub>3</sub>-Tb(III).



New polystyrene supported coordination compounds have been synthesized by the reaction of metal salt with the polystyrene supported base (PS-LH<sub>2</sub>) (obtained by the reaction of chloromethylated polystyrene, 3-formylsalicylic acid and ethanolamine). The compounds have the formulae:- PS-TiCl<sub>2</sub>DMF, PS-VCl<sub>2</sub>DMF, PS-MnCl<sub>2</sub>DMF, PS-FeCl<sub>2</sub>DMF, PS-RuCl<sub>2</sub>DMF, PS-Ru<sub>3</sub>DMF, PS-MoO<sub>2</sub>.DMF, PS-MoOCl.DMF, PS-UO<sub>2</sub>.DMF and PS-CoCl<sub>2</sub>DMF (DMF = dimethylformamide). The compounds have been characterized by elemental analyses, IR, electronic and magnetic susceptibility measurements [21]. The Ti(III), V(III), Mn(III), Fe(III), Ru(II) and Mo(V) compounds are paramagnetic while Mo(VI) and U(VI) compounds are diamagnetic. The shifts of the (C=N) (azomethine), (C-O) (phenolic) and (C-O) (alcoholic) stretches have been monitored to find out the donor sites of PS-LH<sub>2</sub>. Octahedral structures for all the compounds have been suggested for the compounds.

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