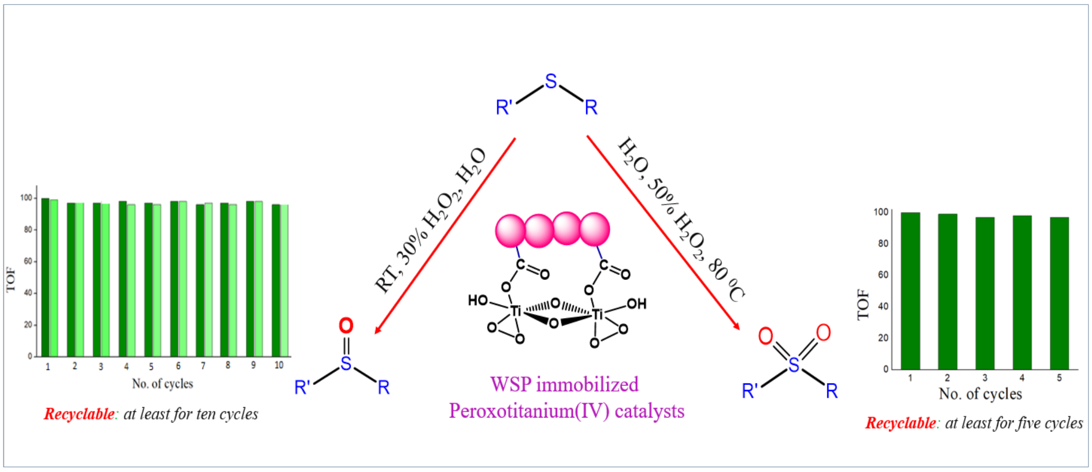
CHAPTER 3

Water-soluble polymer anchored peroxidotitanates as recyclable catalysts for environmentally clean and selective oxidation of sulfides with H_2O_2 in water



3.1 Introduction

Water soluble peroxidotitanates have been for the past several years object of intense investigation for a variety of reasons including their utility as ideal environmentally benign precursors for preparation of titanium-containing functional materials by water-based synthesis methods [1]. Most importantly, Ti(IV)–peroxido systems have proved to be excellent and versatile oxidation catalysts, as elegantly exemplified in a wide range of oxygen transfer processes such as asymmetric epoxidation [2-8], phenol hydroxylation [3-11], ammoximation of ketone [9,12-14], as well as selective transformation of sulfides to sulfoxides or sulfones [15-35].

It has been the pioneering work of Kagan [36,37] and Modena [38], which showed the use of titanium(IV) isopropoxide-diethyltartrate catalyst systems, also known as "modified Katsuki-Sharpless reagents" for asymmetric oxidation of prochiral sulfides by alkylhydroperoxides [15]. However, as the growing ecological concerns triggered an uninterrupted exploration of alternative non-polluting and sustainable oxidation protocols in recent years, aqueous H_2O_2 has emerged as an ideal clean, ecologically acceptable cost effective oxidant among the plethora of traditional oxidants available for organic oxidations [39-43]. Numerous innovative and promising transition metal homogeneous and heterogeneous catalysts with metals like vanadium [44-48], molybdenum [49-55], Iron [56-62], manganese [63-65] etc. have been reported for sulfide oxidation with H_2O_2 as terminal oxidant. A large number of catalytic systems based on well characterized salen-titanium complexes [66,67], Ti(IV) compounds with polydentate Schiff bases [68,69], other highly active systems bearing tetradentate ligands such as trialanolamine [70] and triphenolamine [71] have been developed and used as homogeneous catalysts for the oxidation of sulfides to the corresponding sulfoxides. In fact, as revealed by a survey of literature, majority of existing procedures still rely upon the use of hazardous and volatile organic solvents as reaction medium [17,68,71-78] due to which the important criterion of environmental sustainability remains a challenging issue to address. Difficulty in catalyst regeneration is another limitation with respect to many of the otherwise efficient catalytic sulfoxidations, particularly in case of homogeneous systems [69,72,73,79-81]. It is notable in this context that, we have come across only few reports dealing with titanium based catalytic oxidation of sulfide that have used water as reaction medium [82-84].

Water has already been widely recognized as a natural solvent with obvious benefits of cost efficiency, nontoxicity, nonflammability, abundance and environmental compatibility, of vital importance for organic synthesis [85-94]. Apart from reducing the environmental impact, use of water as a reaction medium often facilitates simple separation and quantitative recovery of a water soluble catalyst through easy phase separation due to poor solubility of organic products in water [93,94]. A variety of commercially important processes, including hydroformylation, carbonylation, hydrogenation, olefin metathesis, polymerization etc. have already been carried out in aqueous medium at industrial scale [90-92]. The recent upsurge in activity in the area of water-centered organic synthesis has stimulated a concomitant rise in the demand for water-tolerant and water compatible catalysts to support aqueous phase organic reactions [85,94].

In the recent past, our group has documented a series of d^0 transition metals peroxido complexes immobilized on different polymer supports including water soluble polymers [45,49-51,95-100], which displayed excellent catalytic activity in a variety of selective organic oxidations under mild condition [98]. It is somewhat surprising that the idea of using linear WSP as support to generate catalytically active metal complexes appears to have received scant attention, although Merrifiled and Letsinger utilized soluble polymers during their pioneering work on peptide synthesis [104-106], which paved the way towards preparing immobilized homogeneous catalysts [107,108].

Encouraged by the aforementioned observations in the present study, we focused on developing convenient and stable peroxido compounds of titanium, a non-toxic and cheap metal, that can be used as environmentally safe, water-compatible recyclable catalysts to accomplish organic oxidation in aqueous medium [15]. There is a paucity of reports on activity of well-defined synthetic peroxidotitanium complexes (PTC) in sulfide oxidation [75,82] as majority of the Ti mediated sulfoxidation reactions have been performed *via in situ* generated peroxidotitanium species using Ti complexes as pre-catalysts [35,74].

In this Chapter we describe the preparation and characterization of a set of peroxido-Ti(IV) compounds anchored to water soluble polymer matrices, poly(sodium acrylate) (**PA**), poly(sodium methacrylate) (**PMA**) and poly(sodium styrene sulfonate) (**PSS**) and their activity in controlled oxidation of sulfides with H_2O_2, with respect to selectivity, TOF, reusability and eco-compatibility. These polymers were chosen for the purpose of this study mainly owing to their chemical stability, ready availability and in particular, due to the presence of pendant functional groups such as carboxylate or sulfonate in the polymer matrices which are capable of forming facile attachment with the Ti(IV) centres. In addition, the chosen polymer supports are biocompatible and non-toxic as evident from their extensive use in development of pharmaceutical formulations [109,110]. To the best of our knowledge, this is the first report dealing with synthesis of well defined **pTi** complexes in macroligand environment comprising of poly(acrylate) based WSP and their application as catalysts for organic oxidations.

3.2 Experimental section

3.2.1 Synthesis of water soluble peroxidotitanium complexes, $Ti_2(O_2)_2O_2(OH)_2$(carboxylate)]-PA (PATi) (3.1), [$Ti_2(O_2)_2O_2(OH)_2$(carboxylate)]-PMA (PMATi) (3.2) and [$Ti_2(O_2)_2O_2(OH)_2$(sulfonate)]-PSS (PSSTi) (3.3)

$TiCl_4$ (1.72 mL, 10 mmol) in 20 % HCl solution was placed in a 100 mL beaker maintaining temperature below 4 ^{0}C in an ice bath. To this, 8M NaOH solution was added dropwise with stirring until no further precipitation occurred. The titanic acid thus obtained was filtered and washed repeatedly with water to remove chloride as well as excess NaOH. The absence of chloride in the filtrate was confirmed by silver nitrate test. To the obtained precipitate, 30% H_2O_2 (2.26 mL, 20 mmol) was added dropwise with constant stirring until a clear yellow solution was obtained. The pH of the solution was *ca.* 2. To this yellowish solution, 1 g (for **PATi**) or 2 g (for **PMATi**) or 4 g (for **PSSTi**) of the soluble polymer was then added in portions with continuous stirring. The pH of the system was recorded to be *ca.* 4 at this stage. The resulting solution was allowed to stand in an ice bath for 12 h. Subsequently, 50 mL of acetone was added to the mixture under stirring and the system was kept as such for another 2 h below 4 ^{0}C. A pasty mass separated out on adding pre-cooled acetone to this mixture under vigorous stirring. The supernatant liquid was decanted off and pale yellow residue was treated repeatedly with acetone under scratching. The microcrystalline product obtained was separated by centrifugation and dried *in vacuo* over concentrated sulfuric acid.

3.2.2 Elemental analysis and physical measurements

The titanium, peroxide, carbon, hydrogen, nitrogen and sodium content in the synthesized compounds were quantitatively determined by procedures described in Chapter 2. The analytical data of the compounds are summarized in **Table 3.1**. The methods employed for thermogravimetric analysis, scanning electron micrographs (SEM) and EDX analysis, as well as spectroscopic measurements have been outlined in Chapter 2. Structurally significant IR bands and their assignments are listed in **Table 3.2**. Presented in **Table 3.3**, are the ^{13}C NMR chemical shift values for the complexes and their respective free polymers. TGA data of the complexes are reported in **Table 3.4**.

3.2.3 Computational details

In the present work, we have performed all the computation as in Dmol^3 program package [111,112]. Local Density Approximation (LDA) [113] using (PWC) functional has been used to optimize the electronic structures of the complexes with double numerical with polarization (DNP) [114, 115] basis set for our calculations. DNP basis set used for our calculations is comparable to Gaussian 6-31G**, but DNP is more accurate than a Gaussian basis set of the same size [116, 117]. For the vibrational frequency calculations, same level of theory was used. We have obtained stable minima which correspond to the real and positive values. To improve computational performance, a global orbital cutoff of 4.5 Å was employed. Self-consistent field (SCF) procedures are done with tolerances of the energy, gradient, and displacement convergences: $1.0*10^{-5}$ Ha, $2*10^{-3}$ Ha Å, and $5*10^{-3}$ Å, respectively.

3.2.4 General procedure for catalytic oxidation of sulfides to sulfoxides

In a typical procedure, the sulfide oxidation reaction was carried out by placing organic substrate (5 mmol), catalyst containing 0.005 mmol of Ti [**PATi** (1.40 mg) or **PMATi** (1.88 mg) or **PSSTi** (2.9 mg)], 30% H_2O_2 (2.26 mL, 20 mmol) in 5 mL of water in a round bottom flask. The molar ratio of Ti : substrate was maintained at 1:1000 and substrate : H_2O_2 at 1:4. Reaction was conducted at ambient temperature under magnetic stirring. The progress of the reaction was monitored by thin layer chromatography (TLC) and GC. After completion of the reaction, the oxidised product along with unreacted organic substrates were extracted with diethyl ether, dried over anhydrous sodium sulfate and distilled under reduced pressure to remove excess diethyl ether. The product was then purified by column chromatography on silica gel with ethyl acetate-hexane (1: 9 v/v) as the eluent. The product obtained was characterized by IR, ^{1}H NMR, ^{13}C NMR spectroscopy and melting point determination (for solid products) (**Appendix I**).

3.2.5 General procedure for catalytic oxidation of sulfides to sulfones

To a stirred solution of 5 mmol sulfide in 5 mL water, 0.01 mmol of Ti containing catalyst [**PATi** (2.81 mg) or **PMATi** (3.77 mg) or **PSSTi** (5.95 mg)] was added, followed by addition of 50% H_2O_2 (1.36 mL, 20 mmol) in a round bottom flask. The Ti : substrate molar ratio was maintained at 1:500 and the substrate:H_2O_2 molar ratio at 1:4. The reaction was conducted at 80 ^{0}C temperature. The reaction was monitored by thin-layer chromatography (TLC) and GC. After completion of the reaction, the system was allowed to cool to room temperature. The sulfone obtained was then isolated, purified and characterized by following similar procedure as mentioned under above section.

3.2.6 Regeneration of the catalyst

The recyclability of the catalyst was tested employing methyl phenyl sulfide (MPS) as the model substrate. After completion of the reaction, the product and the unreacted substrates were extracted by diethyl ether. To this spent reaction mixture, fresh batch of MPS (5 mmol) was added followed by addition of 30% hydrogen peroxide (2.26 mL, 20 mmol). The progress of the reaction was monitored by thin layer chromatography (TLC) as well as by GC and the process was repeated under optimized reaction condition for minimum of ten reaction cycles. The regenerated catalyst could also be recovered as solid by adding pre-cooled acetone to the spent reaction mixture that was kept on an ice bath after the completion of the reaction and extraction of the product.

3.3 Results and discussion

3.3.1 Synthesis and characterization

The synthesis of water soluble macromolecular peroxidotitanium complexes **PATi**, **PMATi** and **PSSTi** were achieved by reacting freshly prepared titanic acid with 30 % H_2O_2 in presence of the respective WSP, poly(sodium acrylate) (**PA**) or poly(sodium methacrylate) (**PMA**) or poly(sodium 4-styrene sulfonate) (**PSS**). Titanic acid was obtained by employing a procedure introduced by Kakihana *et al*. [1], based on the reaction of $TiCl_4$ in 20% HCl with NaOH. The maintenance of pH of *ca.* 4 was found to be crucial for the formation of the µ-oxido peroxidotitanium(IV) complexes and their co-ordination to the pendant carboxylate groups of the polymer chain. In a similar manner, the synthesis of peroxido titanium complex anchored to soluble polymer (PSS) with the sulfonate group was carried out. The peroxido-hydroxido titanium complexes formed in an acidic solution have been known to undergo facile dimerization to afford stable oxido-bridged di-titanium complexes with Ti_2O_2 core [118-122]. Ligands possessing carboxylate groups have been reported to stabilize peroxidotitanium species, leading to the development of a host of highly stable peroxidotitanium complexes with carboxylate containing co-ligands [123-126]. One of the advantages of using water soluble polymeric ligands, which are essentially polychelatogens, is the convenience of adopting synthetic procedures used for obtaining their monomeric analogues. The immobilized complexes **PATi**, **PMATi** and **PSSTi**, finally obtained as solids by solvent induced precipitation, remain stable and can be stored dry at ambient temperature for several weeks.

The elemental analysis data of the complexes revealed the ratio of $Ti:O_2^{2-}$ content to be unity, showing that the anchored **pTi** moieties occur in the complexes in their monoperoxido configuration. The metal : ligand ratio for the complexes **PMATi**, **PATi** and **PSSTi** was found to be 1:2, 1:1.5 and 1:2, respectively. Magnetic susceptibility measurements revealed the diamagnetic nature of the compounds, testifying to the occurrence of Ti in its +4 oxidation state in each of them.

3.3.1.1 SEM and energy dispersive X-ray (EDX) analysis

The scanning electron micrographs of the polymer anchored complexes showed noticeable alteration of their surfaces in comparison to the even surfaces of the pure polymers (**Fig. 3.1** 1a, 1c and 1e). That the metal ions are distributed across the surface of the polymer was evident from the morphological changes occurring on the polymers after metal incorporation (**Fig. 3.1** 1b, 1d and 1f).

From the energy dispersive X-ray (EDX) spectroscopic analysis, carried out by focusing regions over the surface of the compounds, it was further confirmed that Ti, C, O, Na are the constituents of the complexes (**Fig. 3.2**). The EDX analysis data obtained on the composition of the compounds were in good agreement with the elemental analysis values (**Table 3.1**).

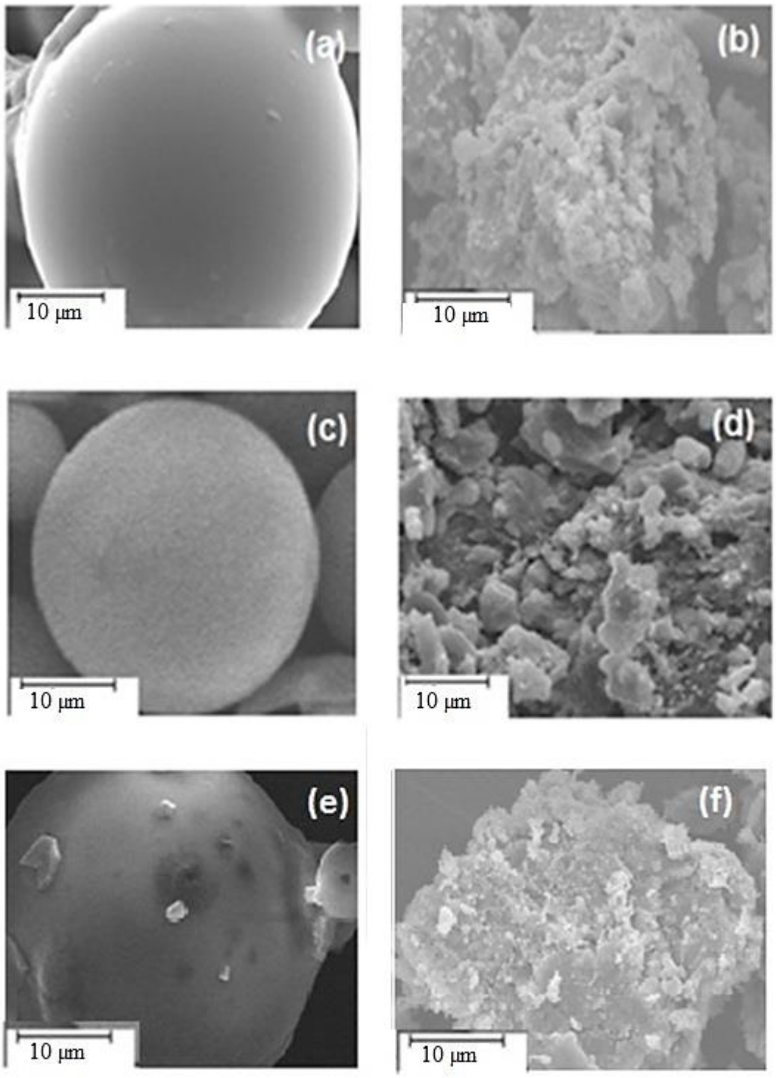


Fig. 3.1 Scanning electron micrographs of (a) PMA**,** (b) **PMATi**, **(**c) PA**,** (d) **PATi**, (e) PSS and (f) **PSSTi**.

Table 3.1 Analytical data for the synthesized peroxido-titanium complexes **PMATi, PATi** and **PSSTi**

Compound	% found from elemental analysis (% obtained from EDX)						Metal loading[a] (mmolg^{-1} of polymer)
	C	H	Na	S	Ti	O_2^{2-}	
PMATi	25.59	3.10	18.26	--	12.41[b]	9.24	2.65
	--	--	--		12.69[c]	--	
	(25.41)	--	(18.11)		(12.70)	--	
PATi	16.40	1.81	17.69	--	16.83[b]	12.41	3.56
	--	--	--		16.91[c]	--	
	(16.28)	--	(17.41)		(17.03)	--	
PSSTi	31.38	3.3	12.30	13.87	8.04[b]	5.1	1.68
	--	--	--	--	8.22[c]	--	
	(33.55)	--	(12.01)	(14.11)	(8.14)	--	

$$^{a}\text{Titanium loading} = \frac{\text{Observed metal } \% \times 10}{\text{Atomic weight of metal}}$$

[b] Determined by AAS.

[c] Determined by ICP-OES.

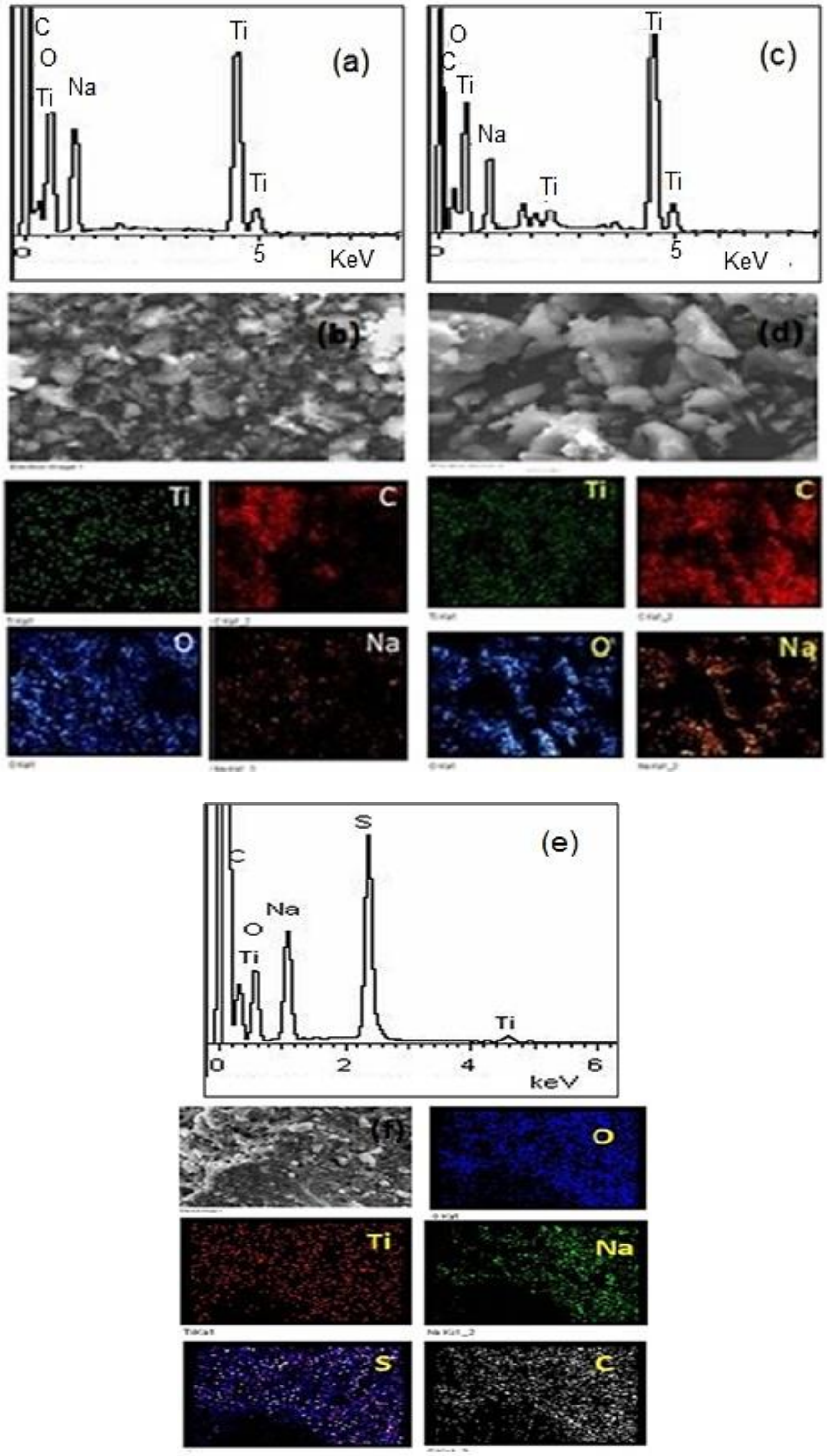


Fig. 3.2 EDX spectra (a, b) **PMATi**, (c, d) **PATi** and **(**e, f) **PSSTi**.

3.3.1.2 FTIR and Raman spectral studies

Raman and IR spectra of each of the compounds displayed typical absorption in the vicinity of *ca*. 860 cm^{-1} attributable to ν(O-O) mode of coordinated peroxido group, in addition to the complementary $\nu_{asym}(Ti\text{-}O_2)$ and $\nu_{sym}(Ti\text{-}O_2)$ modes, as has been expected, in the 500-600 cm^{-1} region [118,127-138]. The IR spectra of **PMATi**, **PATi** and **PSSTi** are presented in **Fig. 3.3-Fig. 3.5** and the corresponding Raman spectra are shown in **Fig. 3.6(a)-Fig. 3.6(c)** respectively.

The significant IR and Raman spectral data for the compounds are summarized in **Table 3.2**. The weak intensity band observed in the 750-780 cm^{-1} region in the IR spectra has been assigned to Ti-O-Ti stretching vibration of μ-oxidotitanium dimer [82,121,135,137]. The corresponding absorption appeared as a sharp band in the Raman spectra of the compounds at *ca.* 790 cm^{-1}. The Ti-OH bending mode corresponding to the terminal –OH groups of the complexes manifested at 1104 cm^{-1} in **PATi**, at 1120 cm^{-1} in **PMATi** and 1127 cm^{-1} in **PSSTi**, corresponding to Raman band at *ca*. 1109, 1138 and 1098 cm,$^{-1}$ respectively [128,131,136]. The ν(OH) modes appeared as a broad band in the spectrum of each of the complexes in the 3300-3500 cm^{-1} [127-138].

The intense band observed in the IR spectrum of the poly(acrylate) bound complex, **PATi** at 1626 cm^{-1} and a weak absorption occurring at 1391 cm^{-1} have been ascribed to ν_{asym} and ν_{sym} stretching vibrations, respectively of deprotonated and coordinated carboxyl groups [139,140]. The corresponding bands in the poly(methacrylate) anchored compound **PMATi** were observed at 1647 and 1407 cm^{-1}, respectively. The observed shift of ν_{asym}(COO) to a higher frequency and that of ν_{sym}(COO) to a lower frequency in the complexes relative to the free polymer values (**Table 3.2**), resulting in the magnitude of wavenumber difference of *ca.* 230 cm^{-1}, provided clear indication of unidentate co-ordination of COO^- groups in each of the compounds [98,139,140]. The IR and Raman spectra also indicated the presence of free –COOH in the compounds showing absorptions at *ca*. 1710 cm^{-1} [139,140].

For the complex **PSSTi**, the IR spectrum shows broad bands at 1212 cm^{-1} and 1183 cm^{-1} along with the symmetric vibration of S-O at 1035 cm^{-1} [141-145]. In case of the pure polymer, S-O asymmetric and symmetric stretching of SO_2 group was observed at 1197 cm^{-1} and 1039 cm^{-1} respectively [141,142]. The appearance of the new bands in the complex can be assigned as S-O stretching vibrations that originates due to the

Table 3.2 Infrared (IR) and Raman (R) spectral data (cm^{-1}) for **PMATi, PATi** and **PSSTi** compounds[a]

Assignment		**PMA**	**PMATi**	**PA**	**PATi**	**PSS**	**PSSTi**
v(O-O)	(IR)		848(s)		863(s)		839(s)
	(R)		839(vs)		879(vs)		820(s)
v_{sym}(Ti-O$_2$)	(IR)		531(m)		525(m)		576(m)
	(R)		523(s)		527(m)		546(s)
v_{asym}(Ti-O$_2$)	(IR)		614(m)		619(w)		620(m)
	(R)		607(s)		613(m)		647(s)
v(Ti-OH)	(IR)		1120(m)		1104(s)		1127(s)
	(R)		1138(m)		1109(s)		1098(m)
v(Ti-O-Ti)	(IR)		753(w)		766(w)		775(m)
	(R)		815(s)		795(s)		754(w)
v_{asym}(COO)	(IR)	1540(s)	1701(s), 1647(br,s)	1565(s)	1710(s),1626(br,s)		
	(R)		1708(m), 1643(m)		1710(m), 1592(w)		---
v_{sym}(COO)	(IR)	1415(s)	1407(w)	1409(s)	1391(w)		---
	(R)		1405(m)		1347(s)		
v_{asym}(S-O)	(IR)		---		---	1197 (m),1039 (s)	1212(sh),1183(s)
	(R)						1214(m), 1147(s)

[a]s, strong; m, medium; vw, very weak; sh, shoulder; br, broad

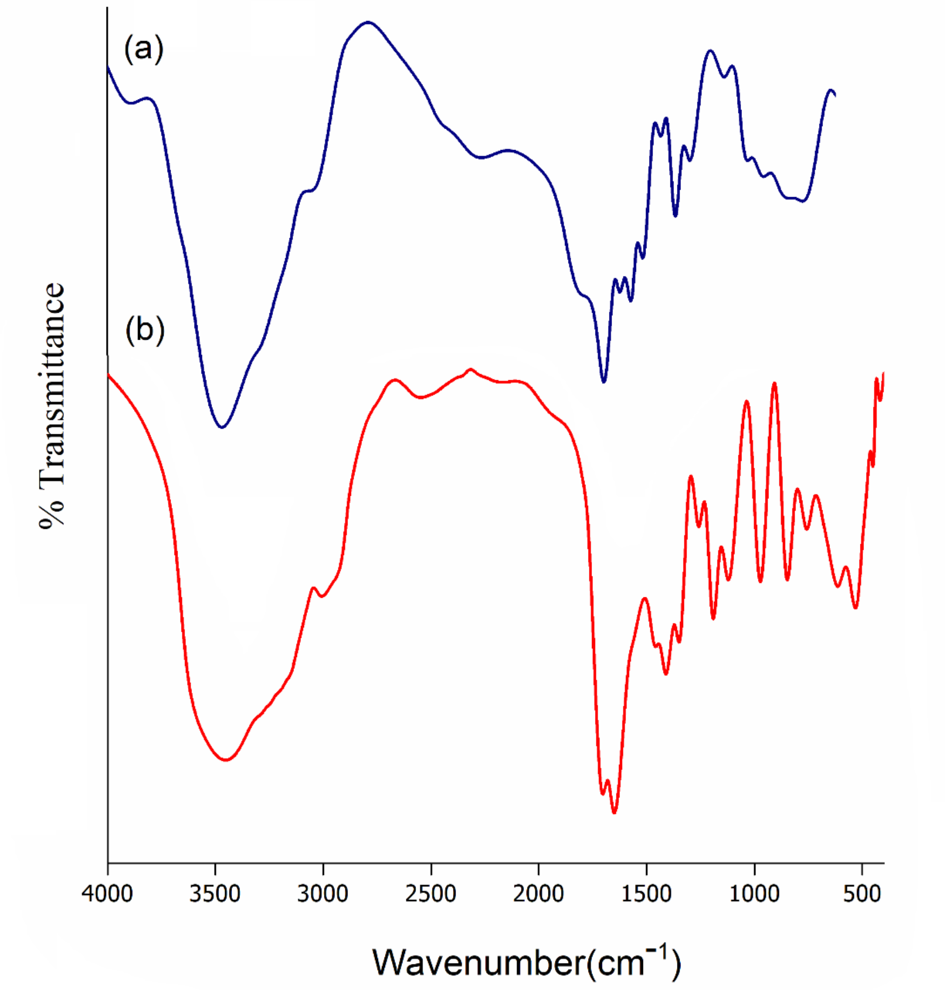


Fig. 3.3 IR spectra of (a) **PMA** and (b) **PMATi**.

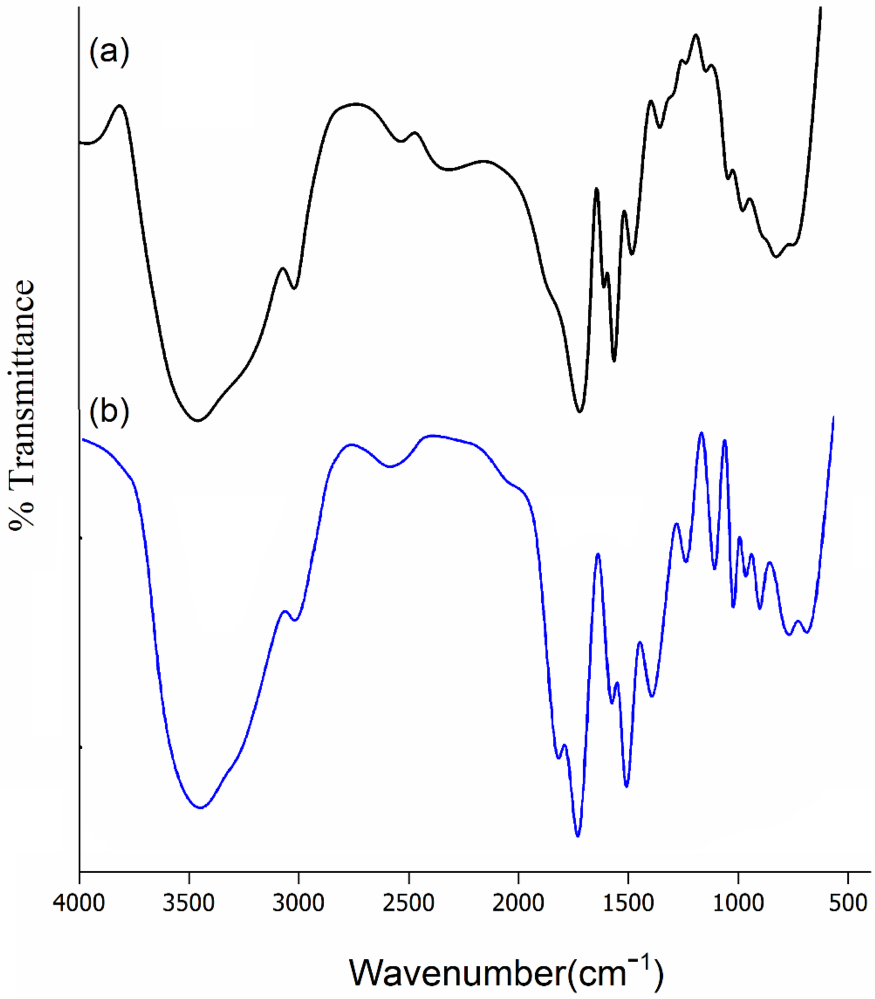


Fig. 3.4 IR spectra of (a) **PA** and (b) **PATi**.

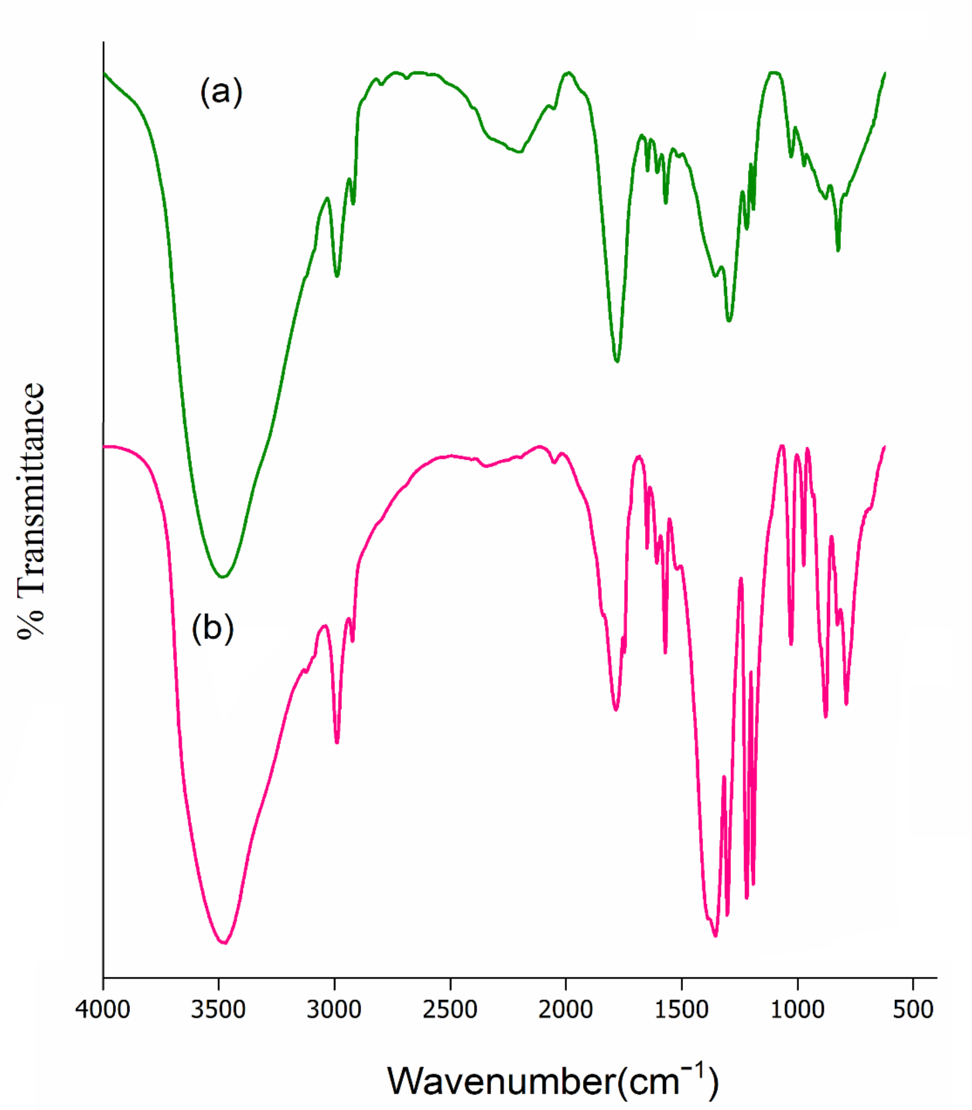


Fig. 3.5 IR spectra of (a) **PSS** and (b) **PSSTi**.

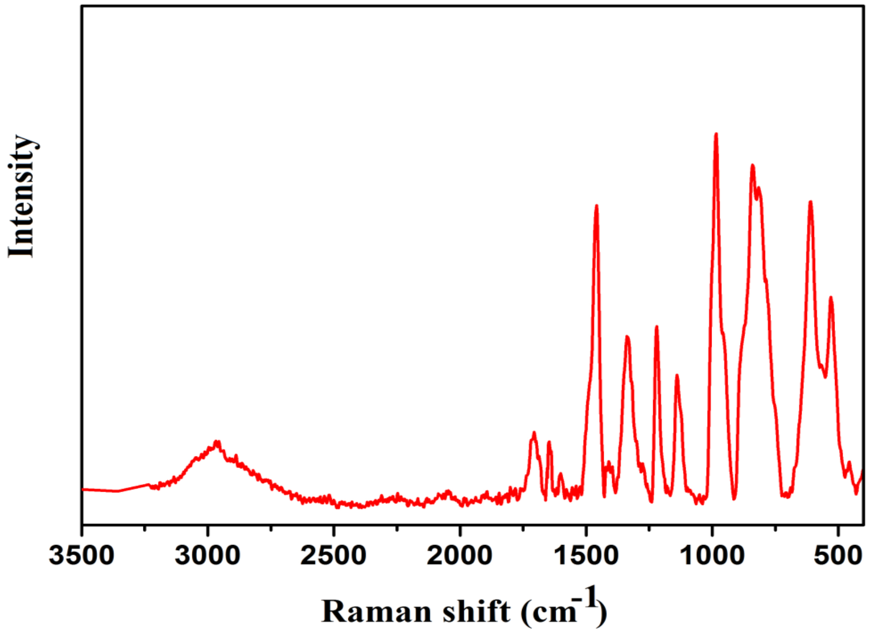


Fig. 3.6 Raman spectrum of **PMATi**.

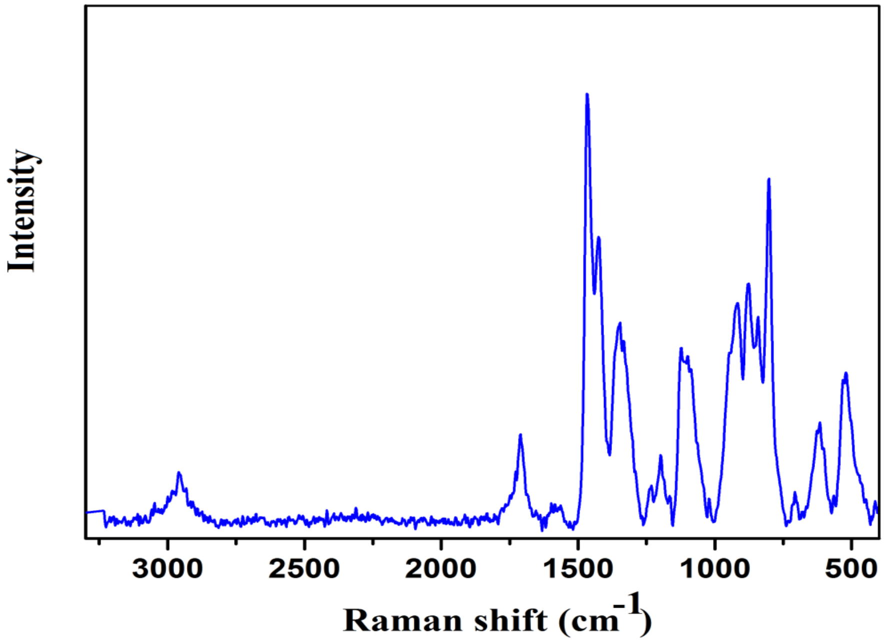


Fig. 3.7 Raman spectrum of **PATi.**

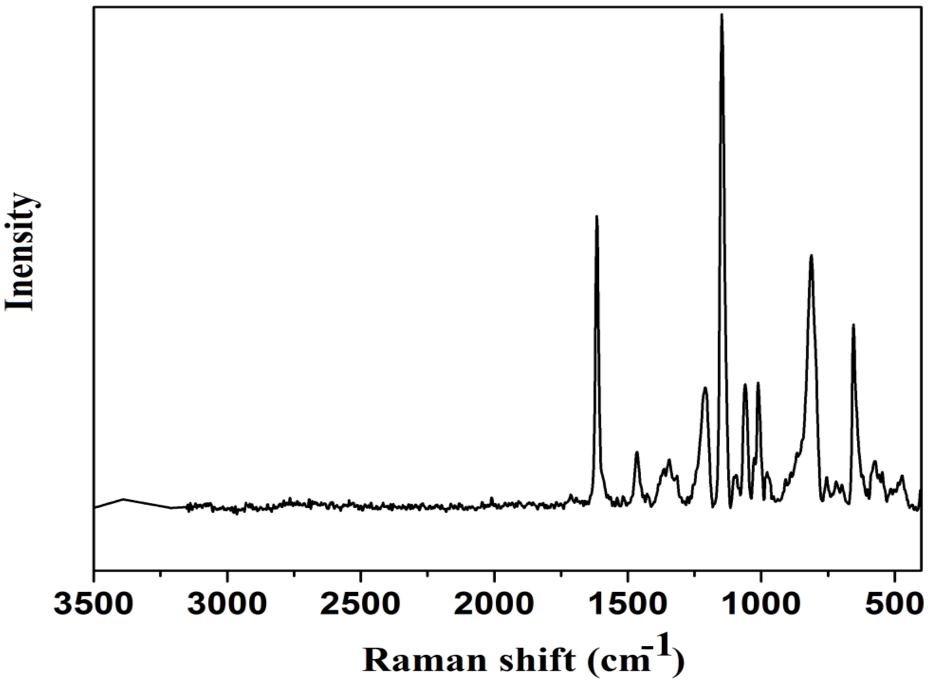


Fig. 3.8 Raman spectrum of **PSSTi**.

complexation of sulfonate group to the metal. In addition to this, the IR spectrum of **PSSTi** shows absorption bands for the phenyl group and bending CH_2 at *ca.* 1631 and 1499 cm^{-1} respectively [141,143,146] which show no alternation of value in comparison to the pristine polymer and thus signifying non-involvement of these groups in any bond formation in the complex.

3.3.1.3 Electronic spectral studies

The electronic spectra of the complexes **PATi**, **PMATi** and **PSSTi**, recorded in H_2O showed a well resolved broad band at 350-360 nm region, in addition to a sharp and intense absorption at 215 nm (**Fig. 3.9-3.11**). In line with the previous literature on peroxidotitanium(IV) complexes [125,127,147], the weaker band at 350-365 nm could be attributed to $\pi_v^* \rightarrow d$ peroxido to metal charge transfer (LMCT) transition, whereas the intense peak appearing at higher energy at 215 nm has been assigned to $\pi_h^* \rightarrow d\sigma^*$ LMCT transition.

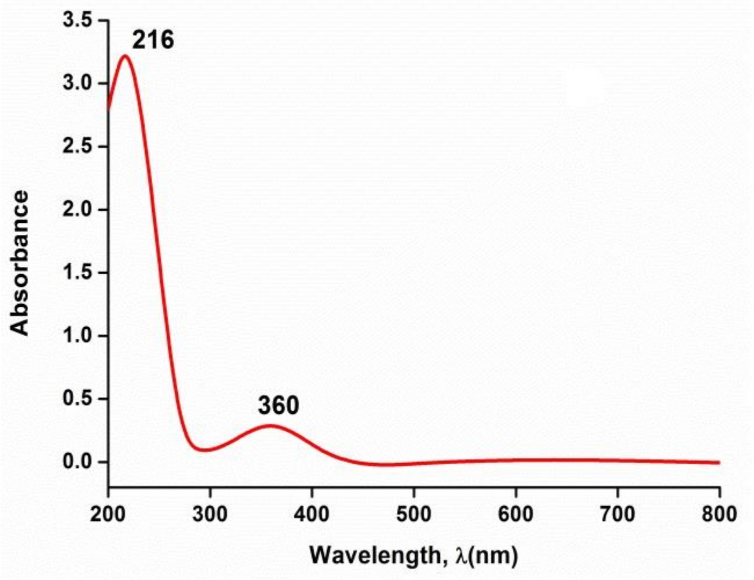


Fig. 3.9 UV-Vis spectrum of complex **PMATi.**

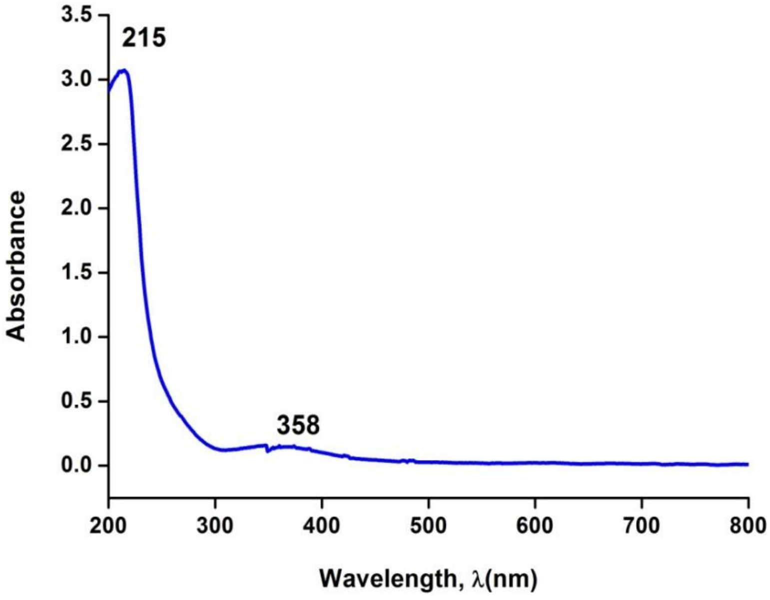


Fig. 3.10 UV-Vis spectrum of complex **PATi**.

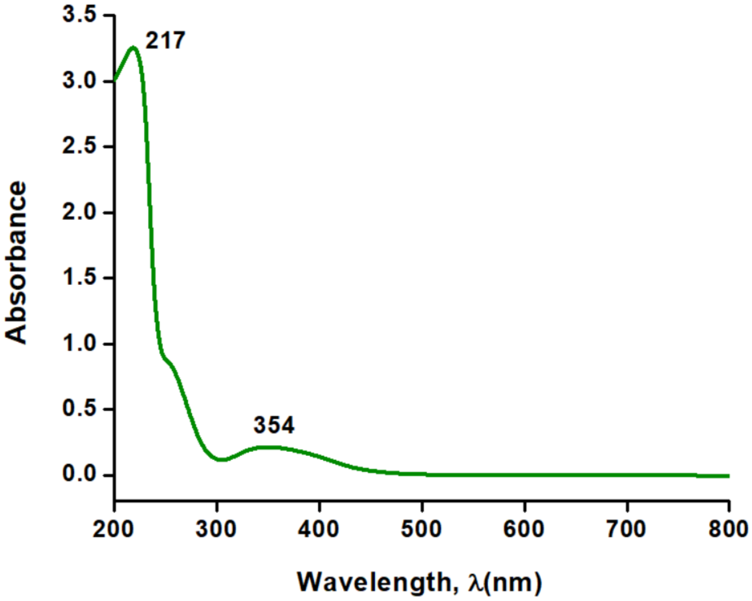


Fig. 3.11 UV-Vis spectrum of complex **PSSTi**.

3.3.1.4 ^{13}C NMR studies

The ^{13}C NMR spectra of the complexes and the respective pristine polymers, **PA, PMA** and **PSS** are presented in **Fig. 3.12**-**Fig. 3.14**. The spectral pattern along with the corresponding chemical shift data listed in **Table 3.3**, provided complementary information indicating modification of carbon resonances of the polymer support to varying degrees after anchoring of Ti(IV) species. The major resonances have been assigned on the basis of available literature [148-157]. The spectra of the free polymers **PA** and **PMA** showed carboxylate carbon resonances at lower end of the field at 187 and 184 ppm, respectively [148-151], apart from the expected signals corresponding to the chain carbon atoms. The spectra of the Ti anchored macro complexes on the other hand displayed an additional peak at much lower field of *ca.* 215 ppm which may be ascribed to the C atom of the metal coordinated carboxylate group. The observed large downfield shift, $\Delta\delta$ ($\delta_{complex}$ - $\delta_{free\ carboxylate}$) of 28 ppm in **PMATi** and 31 ppm in **PATi** suggested presence of strong metal ligand interactions in the macromolecular complexes, as has been reported earlier [49,98,99,140].

Table 3.3 ^{13}C NMR chemical shift data for polymer-anchored peroxidotitanium complexes and free polymer

Compound	Chemical shift (ppm)										
	Carboxylate carbon					Ring carbon					
	Free	Complexed	CH	CH_2	CH_3	C1	C2	C3	C4	C5	C6
PMA	187.4	---	---	17.3	56.5	---	---	---	---	---	---
PMATi	187.4	215.5	---	17.2	55.6	---	---	---	---	---	---
PA	184.5	---	45.5	36.1	---	---	---	---	---	---	---
PATi	184.5	215.4	45.5	35.9	---	---	---	---	---	---	---
PSS	----	---	40.5	44.1	---	140.3	128.8	125.5	148.5	125.3	128.1
PSSTi	---	---	40.1	42.8	---	140.3	128.1	125.5	148.6	125.2	128.2

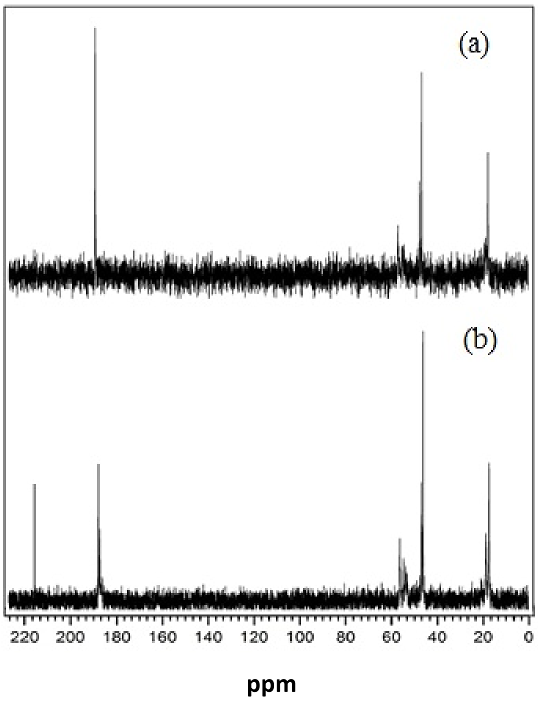


Fig. 3.12 ^{13}C NMR spectra of (a) **PMA** and **(**b) **PMATi.**

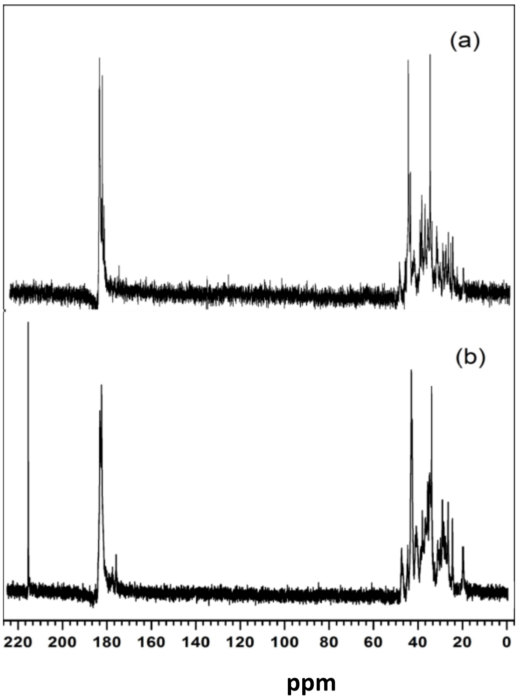


Fig. 3.13 ^{13}C NMR spectra of (a) **PA** and (b) **PATi.**

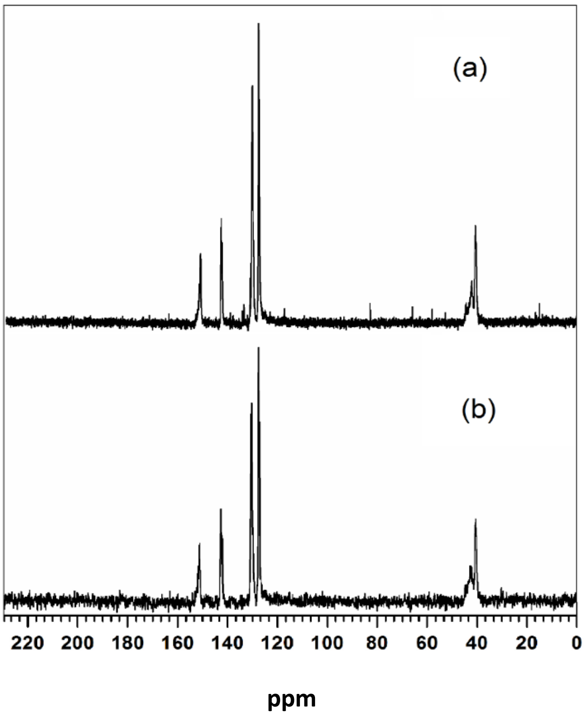


Fig. 3.14 ^{13}C NMR spectra of (a) **PSS** and (b) **PSSTi**.

In the spectrum of **PSSTi,** the peaks at 40.5 and 44.1 of CH and CH_2 groups of the pure polymer poly(sodium styrene sulfonate) were observed almost unchanged. This is not unexpected as Ti(IV) is bound to the polymer through the sulfonate groups which is well separated from the chain carbon as well as ring carbon atoms of the polymer support.

3.3.1.5 TGA-DTG analysis

The TGA-DTG profile of the complexes (**Fig. 3.15-Fig. 3.17**) show multistage of degradation with major break down processes that reveal the compound compositions and phase transition in each of the complexes (**Table 3.4**). The first step of weight loss due to the liberation of physisorbed water molecules from the complexes occurred between room temperature and *ca.*108 ^{0}C. The second degradation stage in the temperature range of 170-303 ^{0}C in **PMATi**, 166-220 ^{0}C in **PATi** and 146-213 ^{0}C in **PSSTi** is attributable to the decomposition and loss of co-ordinated peroxido groups of peroxidotitanium moieties anchored to the polymer [129,158-161]. The absence of peroxide group in the decomposition product, isolated at this stage, was also verified by its IR spectrum. The subsequent step occurred between the range of 221-280 ^{0}C in **PATi** with a weight loss of 6.5 % which may be ascribed to the decomposition of terminal -OH group by analogy with previous reports on some dimeric hydroxido-peroxido Ti(IV) complexes possessing terminal Ti-OH group [128,131,161]. The observed weight loss is in good agreement with the value of 6.4 % calculated for the compound **PATi**. The corresponding degradation step in the compound **PSSTi** was found at 214-274^{0}C with a weight loss of 2.3 %, close to the calculated value 2.8%. For **PMATi,** the degradation was observed at a relatively higher temperature range of 329-388 ^{0}C with a weight loss of 5.6 % which is close to the calculated value of 5.55%. On increasing the temperature further, degradations attributable to decarboxylation of carboxylate functional groups accompanied by rupture of polymers chain occurs in the broad temperature range of 394 to 538 ^{0}C for **PMATi** and for **PATi**, in the temperature range of 359 ^{0}C upto 520 ^{0}C, respectively [99,140]. In case of **PSSTi**, a two stage weight loss was observed in the range of 278-576 ºC. This degradation was probably due to loss of the sulfonate group and rupturing of polymers. From the available literature data on TGA analysis for poly(vinyl sulfonate), the weight loss at this range of temperature have been ascribed to loss of sulfonate group and rupturing of the polymer accompanied by evolution of ethylene, water, SO_2 and CS_2 [162].

T**able 3.4** TGA data of polymer anchored peroxidotitanium complexes, **PMATi, PATi** and **PSSTi**

Compound	Temperature range (^{0}C)	Observed weight loss (%)	Final residue (%)
PMATi	37-108	13.7	48.6
	170-303	9.4	
	329-388	5.6	
	394-538	22.7	
PATi	36-103	9.2	42.6
	166-220	12.9	
	221-280	6.5	
	359-520	28.8	
PSSTi	30-107	12.1	45.4
	146-213	6.3	
	214-274	2.3	
	278-513	11.9	
	513-576	22.0	

The residue remaining after the complete degradation of the polymer immobilized compounds was found to be oxidotitanium species. This was further confirmed from the IR spectra recorded after heating the compounds separately up to the final decomposition temperature which revealed complete disappearance of absorptions attributable to peroxido and terminal Ti-OH stretching as well as the strong peaks originating from υ(COO) and of the original compounds. Thus, the TGA- DTG analysis data furnished additional evidence in support of the composition and formula assigned to the macrocomplexes.

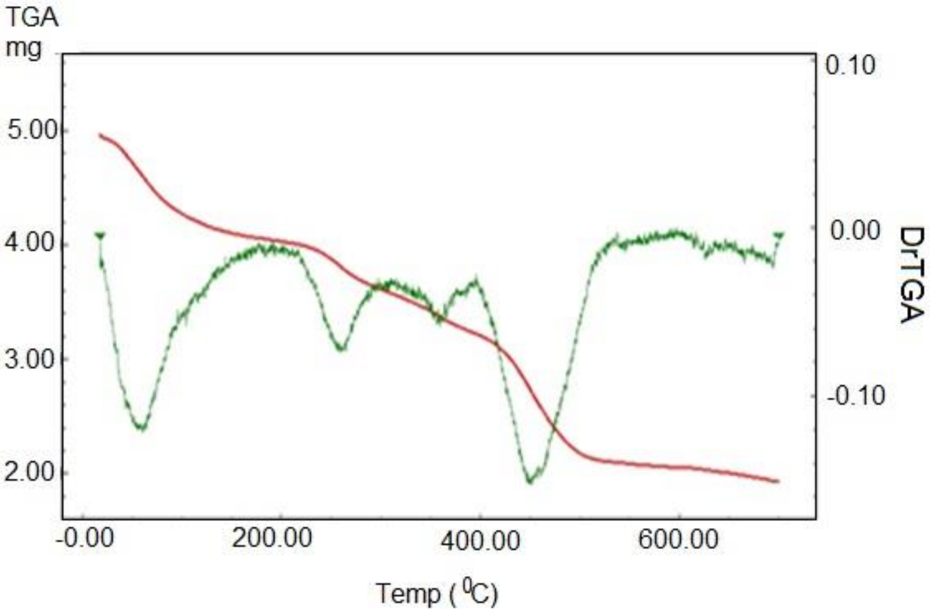


Fig. 3.15 TGA-DTG plot of **PMATi**.

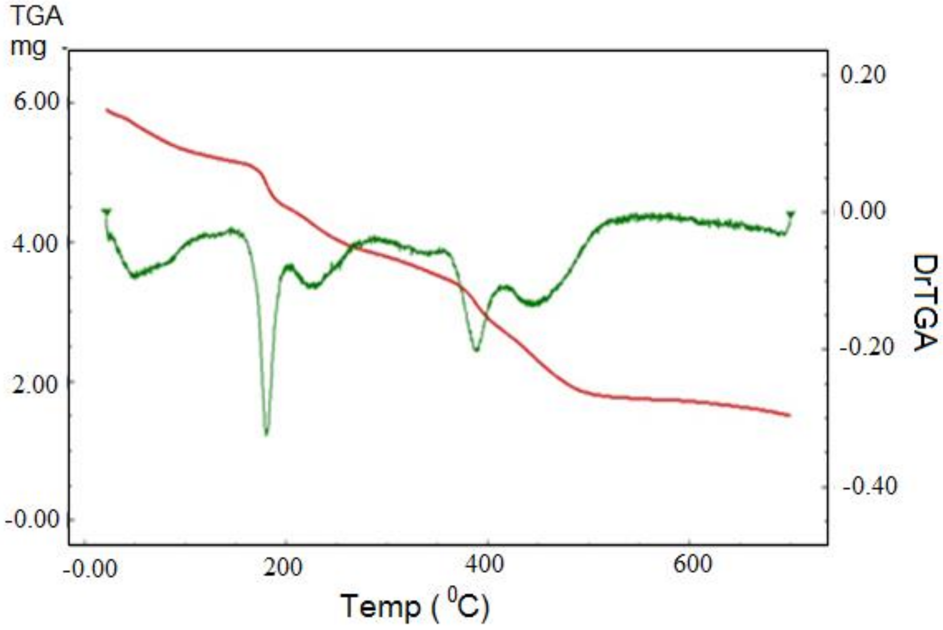


Fig. 3.16 TGA-DTG plot of **PATi.**

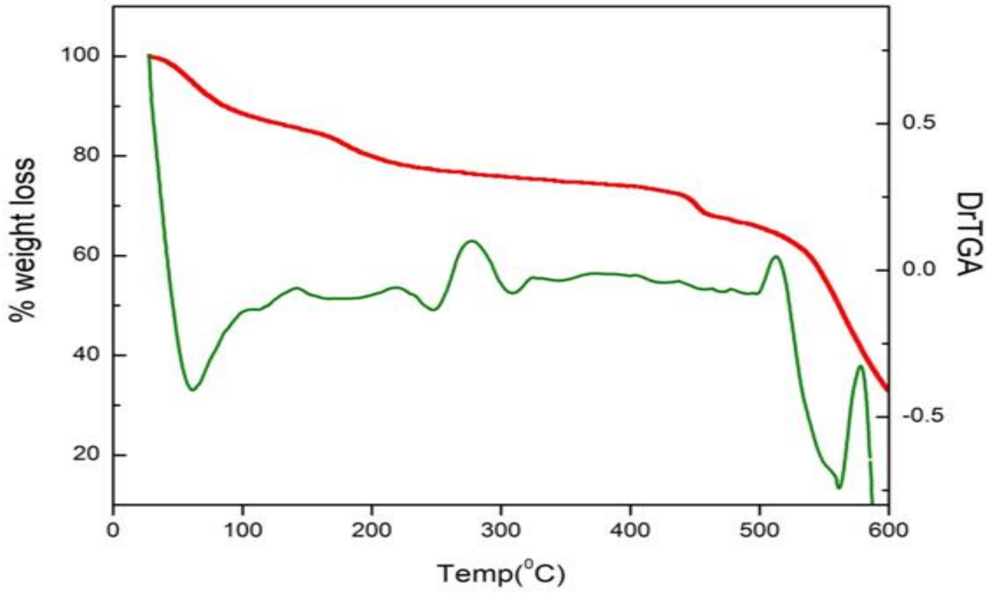


Fig. 3.17 TGA-DTG plot of **PSSTi.**

Bringing together all the above experimental evidences, structures of the type shown in **Fig. 3.18** and **Fig.3.19** have been envisaged for the **pTi** complexes. The proposed structures consist of a dimeric hydroxido-peroxido Ti(IV) moiety with a Ti_2O_2 core linked to the polymer chain *via* its pendant carboxylate groups for compound **PATi** and **PMATi**. For the compound **PSSTi**, the Ti_2O_2 core has proposed to linked to the polymer chain through the sulfonate groups. Thus the co-ordination sphere around each Ti(IV) centre is completed by oxygen atoms belonging to the μ-oxido, η^2-peroxido, hydroxido and unidentately bound carboxylate groups of the polymer chain. Di-μ-oxido titanium complexes with Ti_2O_2 core have been reported in variety of ligand environment which is known to impart stability to the peroxidotitanium(IV) complex species [6,118-122].

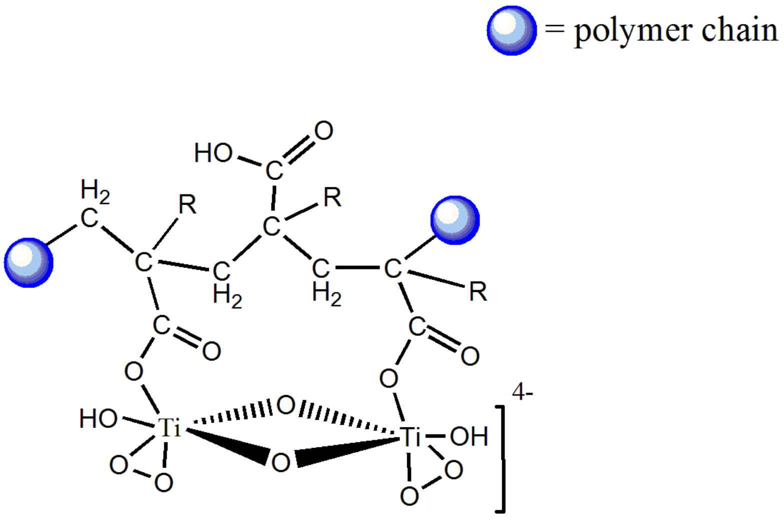


Fig. 3.18 Proposed structure of peroxidotitanium complexes **PATi** and **PMATi**. [R= H for poly(sodium acrylate) (**PA**) or R= CH_3 for poly(sodium methacrylate) (**PMA**)].

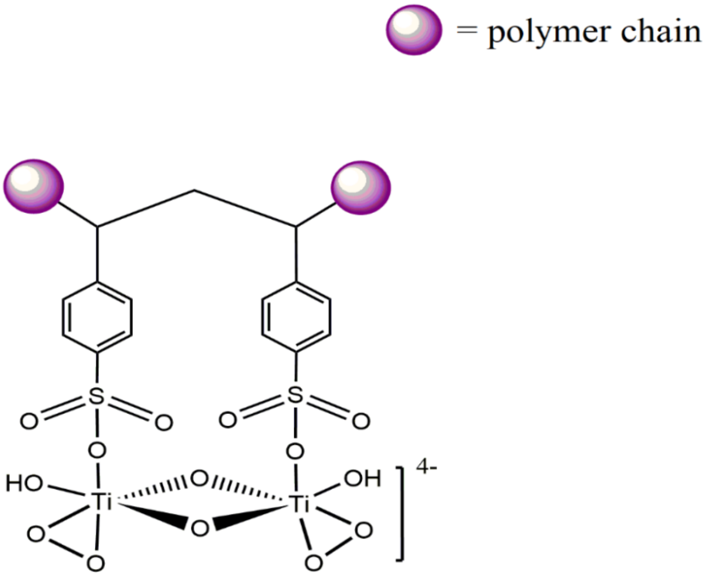


Fig. 3.19 Proposed structure of peroxidotitanium complex **PSSTi**.

3.3.1.6 Density functional studies

We have carried out theoretical investigations employing the density functional theory (DFT) method with an aim to examine the feasibility of structures proposed for the polymer anchored **pTi** complexes. A model complex has been generated corresponding to a section of the poly(acrylate) anchored **pTi** complex **PATi**, on the basis of experimentally derived structural information (FTIR, Raman, ^{13}C NMR, TGA, EDX and elemental analysis). DFT calculations were performed on the model complex at PWC/DNP level of theory [113-115]. The optimized structure of the complex presented in **Fig. 3.20** shows three repeating unit of the polymer with one dinuclear peroxidotitanium(IV) complex with di-µ-oxido Ti_2O_2 core bonded to the polymer chain through its carboxylate groups. Bonding of O atom of terminal –OH group completes hexa co-ordination around each of Ti(IV) centers as has been observed in a majority of the reported **pTi** complexes. The structure also indicated participation of –OH groups in H-bond formation with neighbouring –COOH groups as well as one of the metal bound peroxido ligands.

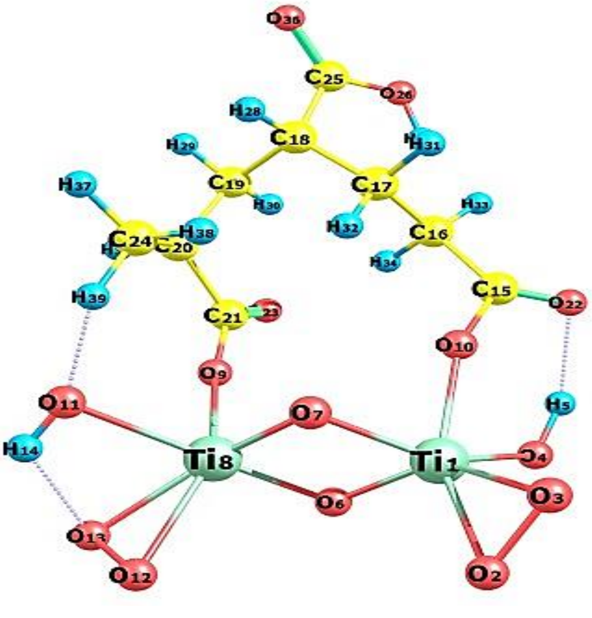


Fig. 3.20 Optimized geometry for complex **PATi**. The numerical numbers represent the labelling of the atoms as in **Table 3.6**.

After optimization of the structure vibrational frequencies were calculated to conform to the stability of the complex. Absence of negative vibrational frequency (imaginary frequency) in the vibrational frequency calculations implied that the complex represents a stable structure. Moreover, the vibrational frequencies calculated for the optimized geometry (**Table 3.5**) were observed to simulate well with the experimentally determined IR spectral data. The selected geometrical parameters such as bond lengths and bond angles obtained from the theoretical calculations listed in **Table 3.6** have been found to be in good agreement with the reported crystallographic parameters corresponding to heteroleptic monoperoxidotitanium complexes [122,163-166]. Thus, the mutually consistent findings of our theoretical studies and experimental results completely validate the predicted structures of the synthesized complexes.

Table 3.5 Experimental and theoretical infrared (IR) spectral data (cm^{-1}) for peroxido titanium complex **PATi**

Assignment		**PATi**
ν_{asym}(COO)	Exp.	1626
	Cal.	1640
ν_{sym}(COO)	Exp.	1391
	Cal.	1380
ν(O-O)	Exp.	863
	Cal.	860
ν_{sym}(Ti-O_2)	Exp.	525
	Cal.	529
ν_{asym}(Ti-O_2)	Exp.	619
	Cal.	614
ν(Ti-OH)	Exp.	1104
	Cal.	1102
ν(Ti-O-Ti)	Exp.	766
	Cal.	771

Table 3.6 Selected bond lengths (Å) and bond angles (degree) for **PATi** calculated using density functional theory (DFT) as implemented in DMol^3 package

Complex **PATi**

Structural index[a]	Calculated values	Structural index[a]	Calculated values
Ti1-O2	1.889	Ti8-O9	2.138
Ti1-O3	1.988	C15-O10	1.256
O2-O3	1.437	∠O12-Ti8-O13	41.32
Ti1-O6	1.854	∠Ti8-O13-O12	62.16
Ti1-O7	1.956	∠Ti8-O12-O13	76.52
C21-O9	1.258	∠Ti8-O11-H14	86.58
O4-H5	0.985	∠Ti1-O2-O3	71.96
Ti1-O4	1.914	∠Ti1-O3-O2	64.63
Ti8-O12	1.916	∠O2-Ti1-O3	43.41
O12-O13	1.431	∠Ti1-O4-H5	112.38
Ti8-O6	1.889	∠Ti1-O7-Ti8	97.12
Ti8-O7	1.810	∠Ti1-O6-Ti8	97.99
Ti8-O11	2.062	∠O7-Ti1-O6	80.95
O11-H14	0.986	∠O7-Ti8-O6	83.92

[a] See Fig. 3.20 for the atomic numbering.

3.3.2 Catalytic activity of the synthesized complexes PMATi, PATi and PSSTi in oxidation of sulfides

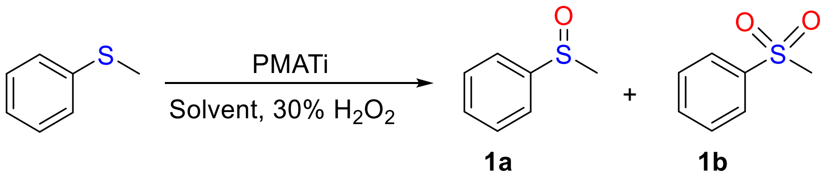
3.3.2.1 Oxidation of sulfides to sulfoxides– Optimization of reaction condition

In order to assess the catalytic potential of the peroxido titanium macro complexes we first examined the sulfoxidation of methyl phenyl sulfide (MPS) as a model substrate using **PMATi** as a representative catalyst with 30% H_2O_2 as oxidant. To screen the optimal reaction condition, a preliminary experiment was conducted maintaining catalyst: MPS and MPS : H_2O_2 molar ratio as 1:500 and 1:2, respectively. The reaction was carried out in water at ambient temperature under magnetic stirring in complete absence of organic solvent. It was gratifying to note that oxidation of thioanisole was virtually quantitative under these conditions and provided the corresponding sulfoxide with complete selectivity and a good TOF within an hour (**Table 3.7**, entry 1). We have subsequently proceeded to optimize the reaction by assessing the influence of various reaction parameters *viz.*, solvent type, catalyst concentration, oxidant: substrate stoichiometry and reaction temperature as shown in **Table 3.7**.

The influence of catalyst amount

We have examined the reaction under three different catalyst concentrations, in addition to conducting a blank run in absence of the catalyst, under otherwise identical reaction conditions. The role of the catalyst is very much evident when the conversions were compared to the result of the control run which provided poor conversion not exceeding 13%, under identical condition (**Table 3.7**, entry 11). From the data presented in **Table 3.7** (entries 1-3), it is noticeable that increasing the catalyst amount elevated the reaction rate considerably without affecting the sulfoxide selectivity, although no significant improvement was seen with respect to TOF at higher catalyst concentration. On the other hand, a reasonably good TOF was obtained along with sulfoxide selectivity (**Table 3.7**,entry 3) even at a low catalyst: substrate ratio of 1:2000.

Table 3.7 Optimization of reaction conditions for **PMATi** catalyzed selective oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide by 30% H_2O_2[a]



Entry	Molar ratio (Ti:MPS)	H_2O_2 Equiv.	Solvent	Temp.	Time (min)	Isolated yield (%)	1a:1b	TON[b]	TOF[c] (h^{-1})
1	1:500	2	H_2O	RT	35	94	100:0	470	806
2	1:1000	2	H_2O	RT	65	96	100:0	960	887
3	1:2000	2	H_2O	RT	150	96	100:0	1920	768
4	1:1000	3	H_2O	RT	40	96	100:0	960	1440
5	**1:1000**	**4**	**H_2O**	**RT**	**15**	**97**	**100:0**	**970**	**3880**
6	1:1000	4	MeOH	RT	25	98	100:0	980	2352
7	1:1000	4	CH_3CN	RT	35	96	100:0	960	1646
8	1:1000	2	H_2O	60 ^{0}C	35	95	100:0	950	1626
9	1:2000	2	MeOH	65 ^{0}C	10	95	100:0	1900	11400
10	1:2000	4	H_2O	RT	75	96	100:0	1920	1536
11[d]	--	4	H_2O	RT	15	13	100:0	--	--

[a] All the reactions were carried out with 5 mmol of substrate in 5 mL of solvent. Catalyst amount = 1.8 mg for 0.005 mmol of Ti.

[b] TON (turnover number) = mmol of product per mmol of catalyst.

[c] TOF (turnover frequency) = mmol of product per mmol of catalyst per hour.

[d] Blank experiment without any catalyst.

Effect of H_2O_2 concentration

Next, a concentration dependent study was carried out with respect to the oxidant:substrate stoichiometry, using three different equivalents of 30% H_2O_2 under analogous reaction conditions. As demonstrated by the data (**Table 3.7**, entries 2, 4 and 5), increasing oxidant concentration from 2 to 4 equivalents accelerated the reaction considerably, leading to nearly 5-fold enhancement of TOF with 4 equivalents of H_2O_2. It is also notable that the sulfoxide selectivity remained unaffected and no overoxidation to sulfone occurred even at relatively higher oxidant concentration used. The above findings collectively indicated that a substrate:H_2O_2 of 1:4 with Ti:substrate molar ratio maintained at 1:1000 was optimal to achieve best results in terms of selectivity as well as TOF.

Effect of solvent

The impressive results achieved in aqueous medium prompted us to screen the water-soluble catalyst for its compatibility with some common organic solvents. Significantly, despite of the insolubility of the catalysts in the neat organic solvents, the compounds dissolved completely in water miscible organic solvents, methanol and acetonitrile in presence of aqueous H_2O_2, leading to homogeneity of the catalytic process. Pertinent here is to mention that we have avoided the use of hazardous chlorinated solvents in our present work. As seen from data in **Table 3.7** (entries 6 and 7), the catalysts are compatible with the chosen organic solvents as well. To our pleasure however, water emerged to be the best solvent providing maximum catalyst efficiency in terms of both product selectivity as well as superior rate (**Table 3.7**, entry 5). The observation is not surprising as it has been amply demonstrated by Sharpless and co-workers [87], followed by reports from some other laboratories [167,168], that for reactions to occur optimally in neat water, solubility of the organic reagents is not a fundamental requirement. Furthermore, our findings are in agreement with previous reports showing the favourable effect of polar protic solvent with ability to form H-bond, on chemoselective sulfoxidation [52,98,167-169].

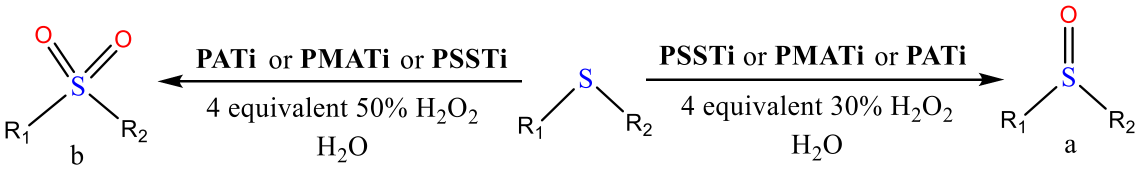
Effect of reaction temperature

A further striking feature of the protocol is the remarkable improvement of the rate of reaction achieved on increasing the reaction temperature from RT to 60 ^{0}C in water and 65 ^{0}C in methanol without affecting the selectivity. Thus, the TOF could be elevated to a high value of (11400 h^{-1}) with 100 % sulfoxide selectivity in refluxing methanol (**Table 3.7**, entry 9). Nevertheless, we preferred to carry out the reactions at room temperature due to the environmentally benign aspect. It has also been ascertained that neither light nor air had any observable influence on the rates of the catalytic oxidations.

3.3.2.2 Selective sulfoxidation catalyzed by PATi (3.1), PMATi (3.2) and PSSTi (3.3)

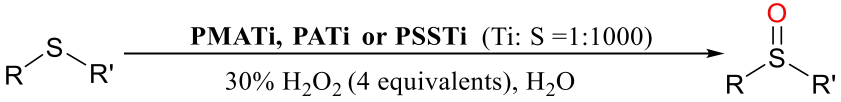
Having standardized the appropriate conditions for sulfoxidation of MPS (**Scheme 3.1**), we proceeded to establish the scope of the catalysts and the developed protocol using a wide variety of substrates. The reactivity data summarized in **Table 3.8** demonstrate that clean conversion of the chosen aliphatic or aromatic substrates to the corresponding sulfoxide occurred in presence of each of the catalysts within a reasonably short time, providing excellent yield and TOF (**Table 3.8**, entries 1-10). Previous work has already established that sulfide oxidation by H_2O_2 generally occurs *via* an electrophilic addition reaction of oxygen atoms, due to which sulfides with higher electron density on sulfur atom are expected to react faster [170,171]. The observed sequence in the present study (**Table 3.8**, entries 1-10) indicating the oxidation of aliphatic sulfides to be more facile in comparison to aromatic sulfides as well as other conjugated systems *viz.*, allylic or vinylic sulfides is thus in accord with the decreasing nucleophilicity of the tested substrates, owing to conjugation of sulfur lone pair of electrons of the aromatic and allylic sulfides.

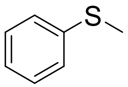
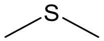
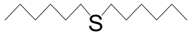
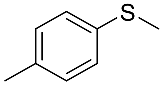
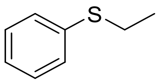
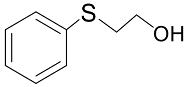
The catalyst **PMATi** displayed consistently superior activity compared to the **PATi** and **PSSTi**. In fact, considering the mild reaction conditions the TOF values obtained in the present study, reaching up to a highest value of 11,280 h^{-1} (**Table 3.8**, entry 2), are indeed remarkable in comparison to most of the water-based catalytic sulfoxidations reported so far [52,83-85,172-175]. The synthesized catalysts displayed high functional group tolerance towards sensitive groups such C=C and OH. Thus, allylic and alcoholic



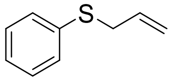
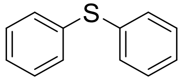
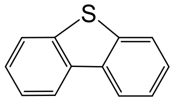
Scheme 3.1 Optimized reaction conditions for the selective oxidation of sulfides to sulfoxides or sulfones by **pTi** compounds.

Table 3.8 Selective oxidation of sulfides to sulfoxides catalyzed by **PMATi, PATi** and **PSSTi** with 30% H_2O_2 using water as solvent[a]



Entry	Substrate	**PMATi**				**PATi**				**PSSTi**			
		Time (min)	Isolated yield (%)	TON[b]	TOF[c] (h^{-1})	Time (min)	Isolated yield (%)	TON[b]	TOF[c] (h^{-1})	Time (min)	Isolated yield (%)	TON[b]	TOF[c] (h^{-1})
1		15	97	970	3880	20	98	980	2940	70	98	980	840
			94[d]	940	3760		95[d]	950	2850		96[d]	960	822
2		5	94	940	11280	9	97	970	6466	25	97	970	2328
3		10	97	970	5820	15	94	940	3760	40	98	980	1470
4		10	95	950	5700	17	95	950	3353	45	96	960	1280
5		15	92	920	3680	20	96	960	2880	65	98	980	904
6		25	96	960	2304	35	95	950	1632	90	98	980	653
7		70	94	940	806	100	94	940	564	130	96	960	443

Continued…

		PMATi				**PATi**				**PSSTi**			
Entry	Substrate	Time (min)	Isolated yield (%)	TON[b]	TOF[c] (h^{-1})	Time (min)	Isolated yield (%)	TON[b]	TOF[c] (h^{-1})	Time (min)	Isolated yield (%)	TON[b]	TOF[c] (h^{-1})
8		55	95	950	1036	80	96	960	720	105	97	970	554
9		190	94	940	297	205	95	950	278	265	96	960	217
10[e]		12h	90	90	7.5	12h	85	85	7	12h	76	76	6.3

[a] All reactions were carried out in 5 mmol substrates, 20 mmol 30% $H_2O_2$and catalyst (0.005 mmol of Ti) in 5 mL H_2O at RT, unless otherwise indicated.

[b] TON (turnover number) = mmol of product per mmol of catalyst.

[c] TOF (turnover frequency) = mmol of product per mmol of catalyst per hour.

[d] Yield of 10th reaction cycle.

[e] Reaction condition: 5 mmol substrate, 20 mmol 30% H_2O_2 and catalyst (0.05 mmol of Ti) at 65 °C in refluxing methanol.

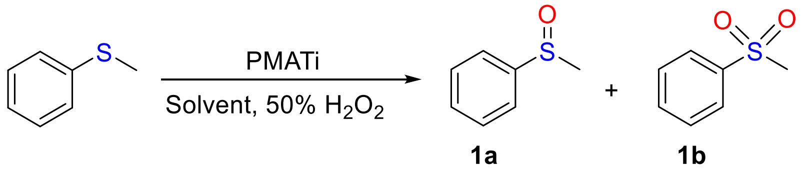
sulfides were chemoselectively oxidized to yield targeted sulfoxide without affecting any other functional group transformation under the optimized condition.

Versatility of the developed catalysts is further evident from the fact that, a least nucleophilic and refractory sulfide like dibenzothiophene (DBT) could also be selectively oxidized to sulfoxide in presence of the catalysts by modification of reaction condition. As the DBT oxidation was too slow in water, it was advantageous to make use of the compatibility of the catalysts in organic medium to attain the intended oxidation by performing the reaction in MeOH.

3.3.2.3 Oxidation of sulfides to sulfones

Subsequently, we have directed our efforts towards developing methodology to attain selective oxidation of sulfide to sulfone using the same catalysts. Our initial attempts to obtain the targeted sulfone from the model substrate, thioanisole using 30% H_2O_2 in a reaction conducted in water, was unsuccessful. However, taking cues from our past experience pertaining to sulfide oxidation with polymer supported peroxidometal catalysts [49], we could finally accomplish complete conversion of MPS, to pure sulfone in aqueous medium at ambient temperature using 4 equivalents of 50% H_2O_2 (**Table 3.9**, entry 3) with catalyst:substrate molar ratio maintained at 1:500. Although the reaction was rather sluggish at room temperature, the reaction rate and hence the TOF could be substantially improved without affecting the selectivity, by increasing the reaction temperature gradually to 80 ^{0}C (**Table 3.9**, entry 6). After investigating the solvent effect on the rate of the oxidation (**Table 3.9**, entries 8 and 10), it was satisfying to note that the catalyst was most potent in water as has been observed in case of sulfoxidation reaction. In methanol and acetonitrile, the catalyst displayed comparable activity at RT.

Table 3.9 Optimization of reaction conditions for **PMATi** catalyzed oxidation of methyl phenyl sulfide to methyl phenyl sulfone by 50% H_2O_2[a]



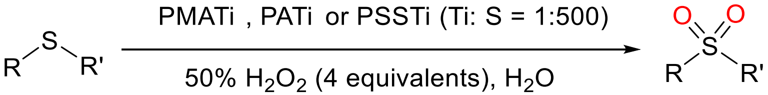
Entry	Molar ratio (Ti:MPS)	H_2O_2 Equiv.	Solvent	Temp.	Time (h)	Isolated yield (%)	1a:1b	TON[b]	TOF[c] (h^{-1})
1	1:1000	2	H_2O	RT	10	93	77:23	930	93
2	1:500	2	H_2O	RT	9	94	41:59	470	52
3	1:500	4	H_2O	RT	7.6	98	0:100	490	64
4	1:500	4	H_2O	60 ^{0}C	6	96	0:100	480	80
5	1:500	4	H_2O	70 ^{0}C	4.5	98	0:100	490	108
6	**1:500**	**4**	**H_2O**	**80 ^{0}C**	**3**	**98**	**0:100**	**490**	**163**
7	1:100	4	H_2O	80 ^{0}C	1.3	97	0:100	485	72
8	1:500	4	CH_3CN	RT	24	94	40:60	470	19
9	1:500	4	CH_3CN	78 ^{0}C	9	98	0:100	490	55
10	1:500	4	MeOH	RT	24	95	55:45	475	20
11	1:500	4	MeOH	60 ^{0}C	20	99	0:100	495	25

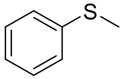
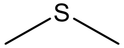
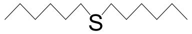
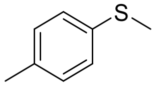
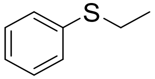
[a] All the reactions were carried out with 5 mmol of substrate in 5 mL of solvent. Catalyst amount = 3.7 mg for 0.01 mmol of Ti.

[b] TON (turnover number) = mmol of product per mmol of catalyst.

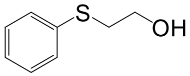
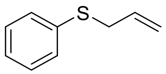
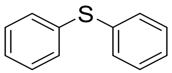
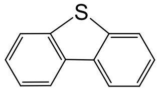
[c] TOF (turnover frequency) = mmol of product per mmol of catalyst per hour.

Table 3.10 Selective oxidation of sulfides to sulfones catalyzed by **PMATi, PATi** and **PSSTi** with 50% H_2O_2 using water as solvent[a]



Entry	Substrate	PMATi				PATi				PSSTi			
		Time (min)	Isolated yield (%)	TON[b]	TOF[c] (h^{-1})	Time (min)	Isolated yield (%)	TON[b]	TOF[c] (h^{-1})	Time (min)	Isolated yield (%)	TON[b]	TOF[c] (h^{-1})
1		180	98	490	163	205	97	485	142	255	98	490	115
			90[d]	450	150		92[d]	460	134		88[d]	455	103
2		50	96	480	578	65	96	480	444	80	97	485	363
3		75	98	490	392	85	97	485	342	95	98	490	309
4		80	97	485	364	85	98	490	347	115	96	480	250
5		180	97	485	162	195	96	480	148	250	97	485	116
6		225	96	480	128	230	97	485	127	320	97	485	91

Continued…

		PMATi				PATi				PSSTi			
Entry	Substrate	Time (min)	Isolated yield (%)	TON[b]	TOF[c] (h^{-1})	Time (min)	Isolated yield (%)	TON[b]	TOF[c] (h^{-1})	Time (min)	Isolated yield (%)	TON[b]	TOF[c] (h^{-1})
7		380	93	465	73	395	95	475	72	425	96	480	67
8		350	95	475	81	370	97	485	78	395	94	470	71
9		8.5h	94	470	55	8.9h	96	480	53.8	9.8h	97	485	49
10[e]		12h	85	85	7	12h	80	80	6.7	12h	72	72	6

[a] All reactions were carried out in 5 mmol substrates, 20 mmol 50% H_2O_2 and catalyst (0.01 mmol of Ti) in 5 mL H_2O at 80 °C, unless otherwise indicated.

[b] TON (turnover number) = mmol of product per mmol of catalyst.

[c] TOF (turnover frequency) = mmol of product per mmol of catalyst per hour.

[d] Yield of 5th reaction cycle.

[e] Reaction condition: 5 mmol substrate, 20 mmol 50% H_2O_2 and catalyst (0.05 mmol of Ti) at 78 °C in refluxing acetonitrile.

In addition to thioanisole, as shown in entries 1-10 of **Table 3.10**, the developed oxidation protocol could be conveniently applied to variously substituted aromatic and aliphatic sulfides, regardless of the catalyst used. For DBT oxidation, however, we could achieve the desired results by conducting the reaction in acetonitrile at 78 ^{0}C, instead of water, using a higher amount of catalyst (substrate: catalyst = 1:100 molar ratio). Most importantly, despite the presence of excess of 50% H_2O_2 and a relatively higher reaction temperature maintained, the oxidation of sulfide to sulfone proceeded with complete chemoselectivity (**Table 3.10**, entries 7 and 8) leaving the co-existing alcohol and C=C groups unaffected.

3.3.2.4 Recyclability of the catalysts

Stability of a catalyst and its recyclability are crucial for its practical utility in a catalytic process. The recyclability of the synthesized catalysts were tested up to 10 reaction cycles using MPS as the model substrate in water under optimized reaction conditions. The catalysts could be recycled by adding fresh batch of oxidant and substrate to the aqueous phase of the spent reaction mixture on completion of each catalytic cycle. The recycling performances of the catalysts presented in **Fig. 3.21** demonstrated the impressive reusability of the catalyst at least up to 10 catalytic cycles with consistent activity and selectivity. The approach of *in situ* recycling of the catalyst is definitely more convenient as the troublesome separation and purification steps usually associated with soluble catalyst could greatly be avoided. The redundancy of these steps further helped in limiting the use of organic solvents during the process.

We have also characterized the regenerated catalysts after isolating it as solid, by elemental and spectral analysis in order to further confirm that the catalysts remain intact during the cycles of oxidations. The FTIR and Raman spectra of the regenerated catalysts displayed the characteristic peaks that are present in the pristine catalyst.

As revealed by elemental analysis and EDX data, no significant decrease in peroxide content or metal loading occurred, ruling out the possibility of metal leaching out of the polymer support during the catalytic process. Thus, it has been established that the catalysts are structurally robust reflecting the strong attachment of the **pTi** species to the polymer chain.

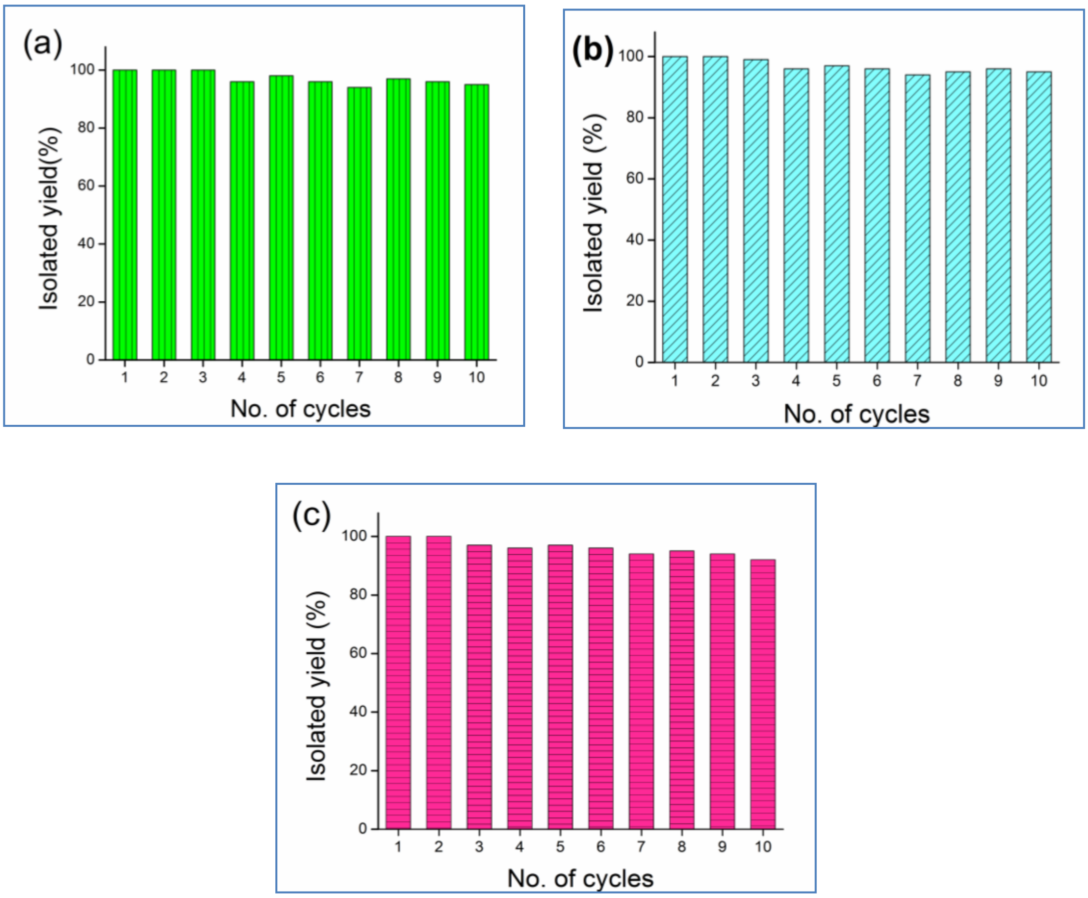


Fig. 3.21 Recyclability of catalysts (a) **PMATi**, (b) **PATi** and (c) **PSSTi** for the selective oxidation of sulfide to sulfoxide in water.

The reusability of the catalysts in oxidation of sulfide to sulfone was also examined following a similar methodology. **Figure 3.22** shows the no. of cycles vs. % yield in the selective oxidation reaction of sulfide to sulfone. Both the catalysts showed good activity retaining the selectivity upto nearly fifth reaction cycles. However, a gradual fall in % conversion was observed in the subsequent cycles indicating possible degradation of the catalyst. This may not be unusual keeping in view the relatively higher reaction temperature maintained as well as longer reaction time required for the complete conversion of sulfides to sulfones.

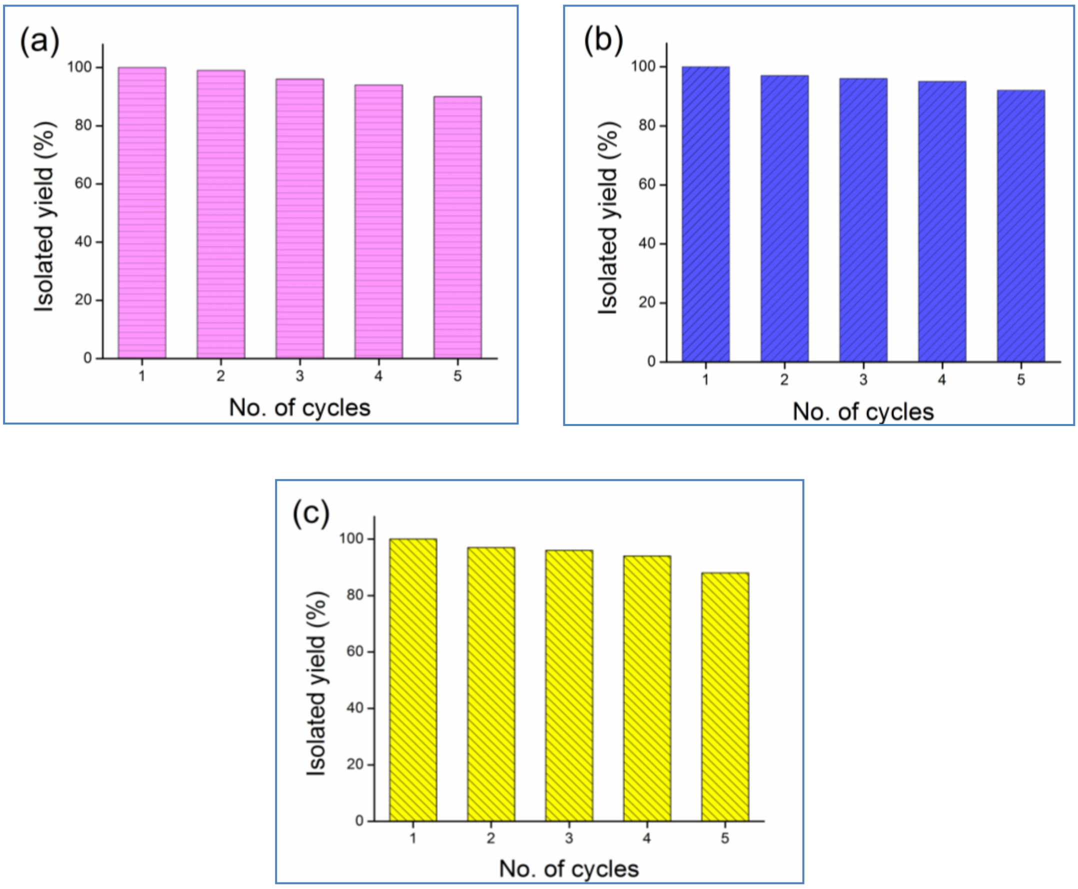


Fig. 3.22 Recyclability of catalysts (a) **PMATi**, (b) **PATi** and **(c) PSSTi** for the oxidation of sulfide to sulfone in water.

A comparative report on selective oxidation of MPS by some of the reported homogeneous Ti based catalyst systems is presented in **Table 3.11**, which demonstrate the merit of the developed **pTi** catalysts in terms of conversion rate, selectivity, reusability and reaction conditions employed.

Table 3.11 Comparison of catalytic performance of **PATi** or **PMATi** or **PSSTi** with literature reported titanium based homogenous catalytic systems for oxidation of sulfides using H_2O_2 as oxidant[a]

Entry	Catalyst	Reaction condition	Time (min)	%Conversion (% yield) / selectivity	Recycling Run/no. of recycling	Ref.
1	PMATi	Water, RT	15	100/100 (TOF=3880)	Yes/10	This Work
2	PATi	Water, RT	20	100/100 (TOF=2940)	Yes/10	
3	PSSTi	Water, RT	70	100/100 (TOF=840)	Yes/10	
4	$K_{16}[Ti_{20}(\mu\text{-}O)_8(HO_2)_8(O_2)_{12}(R,R\text{-}tart)_{12}]\cdot 52H_2O$	Water, RT	90	89.4/91.6	No	83
5	$PN_{68}(IS)_4$	Water, 25 ^{0}C	60	99/95	Yes/7	84
6	Ti(IV) complexes bearing a chiral polydentate ligand based on α-pinene	MeOH, RT	5	99/100	No	69
7	TOC-1	MeOH, 40 ^{0}C	15	98/99	Yes/4	79
8	TOC-2	MeOH, 40 ^{0}C	15	93/96	No	
9	$Ti(Phen)(OC_2H_5)_2Cl_2$	MeOH, RT	20	99/98 (TOF=1182)	Yes/8	75
10	$Ti(Oi\text{-}Pr)_4$ + Schiff base ligand	MeOH and water mixture, dry DCM, N_2 atm, 0 ^{0}C	90	95/94	No	164

Continued…

Entry	Catalyst	Reaction condition	Time (min)	%Conversion (% yield) / selectivity	Recycling Run/no. of recycling	Ref.
11	$Ti(Oi\text{-}Pr)_4$+ Shiff base	Dry dichloro methane, 0 ^{0}C	600	92/93	No	**73**
12	Ti (IV) amino triphenolate complexes	Chloroform, 28 ^{0}C	120	97/98	No	**71**
13	Ti(IV)–Isopropoxide complexes	MeOH, N_2atm, RT	30	90/91	No	**35**
14	Ti(IV)–Amino triphenolate complexes	MeOH, 28 ^{0}C	20	96/98	No	**81**
15	Titanium substituted heteropolytung state	Dichloro ethane, 25 ^{0}C	90	72/86	No	**82**

^{a}Substrate considered is methyl phenyl sulfide (MPS).

Although a precise comparison of the efficiency of the catalysts **PATi**, **PMATi** and **PSSTi** in terms of TON or TOF obtained with different reported examples is not possible in absence of sufficient reported kinetic data, nevertheless it is evident from our findings that, **pTi** compounds provide benefits of both homogeneous and heterogeneous catalysts by displaying excellent activity along with good recyclability which demonstrate the synthetic value of the protocol [35,69,71,72,74,78,80-83,176,177]. These results are especially significant considering the truly mild reaction conditions under which the reactions have been accomplished using green solvent water as reaction medium at ambient temperature.

3.3.2.5 The proposed catalytic cycle

The mechanism of action of titanium-based catalysts in H_2O_2 induced oxygen transfer processes such as sulfoxidation, epoxidation, oxidation of allylic alcohol has been extensively investigated [35,134,138,178-183]. It has been known to proceed by *in situ* activation of peroxide *via* formation of an active peroxidotitanium species, in which peroxido group is usually η^2 co-ordinated to Ti(IV) [35,138,178-183]. Based on these observations along with findings of our present study, we propose a credible catalytic cycle for selective oxidation of sulfides to sulfoxide or sulfone shown in **Fig. 3.23**.

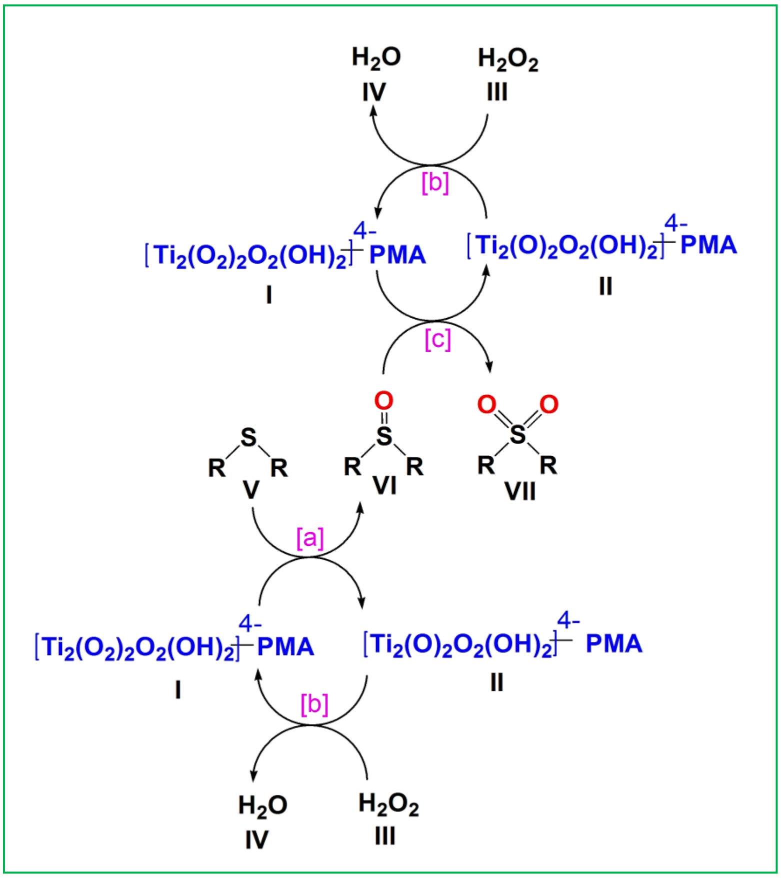


Fig. 3.23 Proposed catalytic cycle.

In the present case the first step is expected to be the transfer of electrophilic oxygen from the monoperoxido Ti(IV) complex **I** of the catalyst to organic sulfide **V**, to yield the corresponding sulfoxide **VI** (reaction a) with concomitant formation of a oxidotitanium intermediate **II**. Formation of such an oxidotitanium intermediate subsequent to electrophilic oxygen transfer from a **pTi** complex to sulfides, has been documented in the literature [35,138,178-183]. The intermediate **II** subsequently combines with oxygen of H_2O_2 to regenerate the starting catalyst (reaction b) thus completing a catalytic cycle. The sulfoxide produced may undergo further oxidation to yield sulfone **VII** (reaction c) in a separate catalytic cycle of reaction.

3.4 Conclusions

In summary, this work highlights the synthesis and characterization of new well defined water-soluble peroxidotitanium(IV) compounds anchored to linear macromolecular supports, and their successful application as highly efficient water-compatible catalysts to obtain selective conversion of sulfides to their respective sulfoxide or sulfone with H_2O_2 in aqueous medium. The oxidation protocol being operationally simple and free from halogenated solvents or any other hazardous additive, offers the additional benefits of safety and ease of handling. Catalysts are remarkably robust in the reaction medium as evident from their easy recyclability up to 10 reaction cycles of sulfoxidation without significant change in activity. Thus, these immobilized catalysts comprising of Ti, low cost, non-toxic metal and environmentally safe water-soluble polymer supports, appear to combine the advantages of selectivity and efficiency of homogeneous catalysts with the stability and recyclability benefits of heterogeneous catalysts, making them potentially attractive for practical applications.

The work on applications of this efficient catalyst system to some other important oxidative transformations such as olefin epoxidation and oxidation of biomass derived substrate, 5-hydroxymethyl-2-furfural (HMF) are presented in Chapter 6 of the thesis.

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