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ORIGINAL PAPER

Iron(III) porphyrin catalyzed polymerization of acrylamide in ionic liquids

Anchal Singhal[1] · **S. M. S. Chauhan**[1]

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Abstract

Iron(III) porphyrin is advocated as catalyst for polymerization of acrylamide with hydrogen peroxide in ionic liquid medium. Reaction conditions were optimized using different porphyrins, solvents, oxidants and initiators. The polymer products were characterized by using ^{1}H NMR, FT-IR, GPC and Mass spectrometric techniques. The recyclability of catalyst and ionic liquids, high yields, high molecular weights and simple work-up procedure are the important attributes of this protocol and contribute as an attractive addition to polymer chemistry.

Keywords Polyacrylamide · Porphyrin · Ionic liquids · Catalysis · Hydrogen peroxide

Introduction

The acrylamide polymerizes to give a hydrophilic polymer, polyacrylamide (PAM), which finds widespread applications in different fields such as fractionation of proteins, nucleic acids and other biomolecules by electrophoresis [1], clarify wastewater [2], recover tailings [3], flocculate ores in mineral processing [4], binder of bone cement [5], oil recovery [6], sugar refining [7, 8], water-based drilling fluids [9], water-based paints for pigment suspension and flow [10], textile industry [11], agriculture and maintenance of soil quality [12]. In recent years, PAM is getting an upsurge of interest due to its potential use as biomaterials [13] and other applications [14, 15]. PAM-based matrices have been used in toxin removal modalities, body contouring in reconstruction surgery and other cosmetic applications. PAM possesses the remarkable property of acting as smart materials and hence finds use in drug delivery system [13]. Owing to its important contributions in different fields, the synthesis of PAM attracts the central interest of researchers. Various methods have been employed for the synthesis of polyacrylamide including enzymatic [16], free radical [17], frontal [18], living radical [19], photocatalytic [20], nitroxide-mediated (NMP) [21], reverse addition fragmentation (RAFT) [22], electrochemical [23], coordination [24], block and statistical polymerization [25, 26] but harsh reaction conditions such as corrosive chemicals, prolonged reaction time and prolonged heating were employed in all these methods. Hence, mild conditions were required for the synthesis of polymer products.

HRP and related enzymes have been used frequently to polymerize vinylic and other monomers under milder conditions in the presence of β-diketones, but these enzymes possess low stability under physiological conditions and hence suitable polymer synthetic route is still in demand [27]. The iron(III)porphyrins in presence of various monooxygen donors mimic the reactions of cytochrome P450, peroxidase and related monooxygenases in milder conditions [28–30]. Metalloporphyrins offer cheaper, stable and more promising aspects for different applications. In particular, the reactions of metalloporphyrins with hydrogen peroxide are considered more appealing as hydrogen peroxide is environmentally clean oxidant and biologically important and produces water as the side product. However, the role of metalloporphyrins in polymerization reactions has been elaborated very little so far [31] though transition metal complexes have been frequently used in atom transfer radical polymerizations [32]. Earlier, we have reported the use of water−soluble metalloporphyrins in free−radical polymerization of acrylamide in the presence of β − diketones in an organic and organized reaction media [33]. Recently, we have stated the employment of iron(III)porphyrin in the polymerization of methyl methacrylate [34] and copolymerization of acrylamide and vinylpyrrolidone in ionic liquids as reaction media [35].

✉ Anchal Singhal
singhal.anchal@gmail.com

[1] Department of Chemistry, University of Delhi, Delhi 110007, India

ILs have attracted considerable attention as potential alternatives to conventional organic solvents in a variety of synthetic, catalytic and electrochemical applications [36]. Recently, there have been several investigations into polymerization in ionic liquids such as free radical [24], coordination [37], cationic [38], group transfer [39], enzymatic [40], electrochemical [41], step-growth [42] and other polymerizations [43]. Hence in continuation of development of catalytic applications of iron(III)porphyrins, we present the polymerization of acrylamide catalyzed by iron(III)porphyrins immobilized in ionic liquids in presence of hydrogen peroxide without using mediators.

Experimental procedure

Materials

Benzaldehyde and 4-chlorobenzaldehyde were obtained from SRL, India. 2,6-dichlorobenzaldehyde and pyrrole were obtained from Acros. 1-methylimidazole, n- butyl bromide, sodium tetrafluoroborate, hexafluorophosphoric acid and lithium bis(trifluoromethyl sulphonyl) amide were obtained from Sigma-Aldrich, USA. Acrylamide was obtained from Biochemicals unit, India, and was recrystallized with methanol before use. Hydrogen peroxide (30%, *v*/v) was obtained from the Merck and used as received. 2,4-Pentanedione and acetylacetone was obtained from Aldrich. Cetyltrimethylammonium bromide and sodium dodecylsulphate were obtained from Aldrich and SRL Pvt. Ltd., India respectively and recrystallized before use. Hydroquinone was obtained from Merck and used as such. Dichloromethane, acetonitrile, tetrahydrofuran and methanol were of analytical grade, Spectrochem, India and used as received. 2,3-dichloro-5,6-dicyanobenzoquinone was obtained from Sigma-Aldrich, USA. Iodobenzenediacetate was obtained from Merck and was used to synthesize iodosylbenzene. t-Butyl hydroperoxide was obtained from Spectrochem, India and used as received.

Representative procedure for the synthesis of polyacrylamide

Acrylamide (**1**) (398 mg, 5.6 mmol) was added to iron(III)porphyrin, 5,10,15,20-tetrakis-(2′,6′-dichlorophenyl) porphyrin [Cl_8TPPFe(III)Cl] (**3c**) (0.24 mmol) dissolved in dichloromethane (2 ml) under nitrogen atmosphere. Hydrogen peroxide (30%, 160 μL, 1.3 mmol) was added to the above acrylamide solution. The reaction mixture was stirred for 6 h at an ambient temperature (25 °C). The white precipitate obtained by quenching the reaction with a large excess of methanol, was filtered off, washed with methanol and dried under vacuum at 50 °C.

Characterization

In the ^{1}H NMR spectra of polyacrylamide [44], the disappearance of peak for olefinic protons at δ 5.10 and the

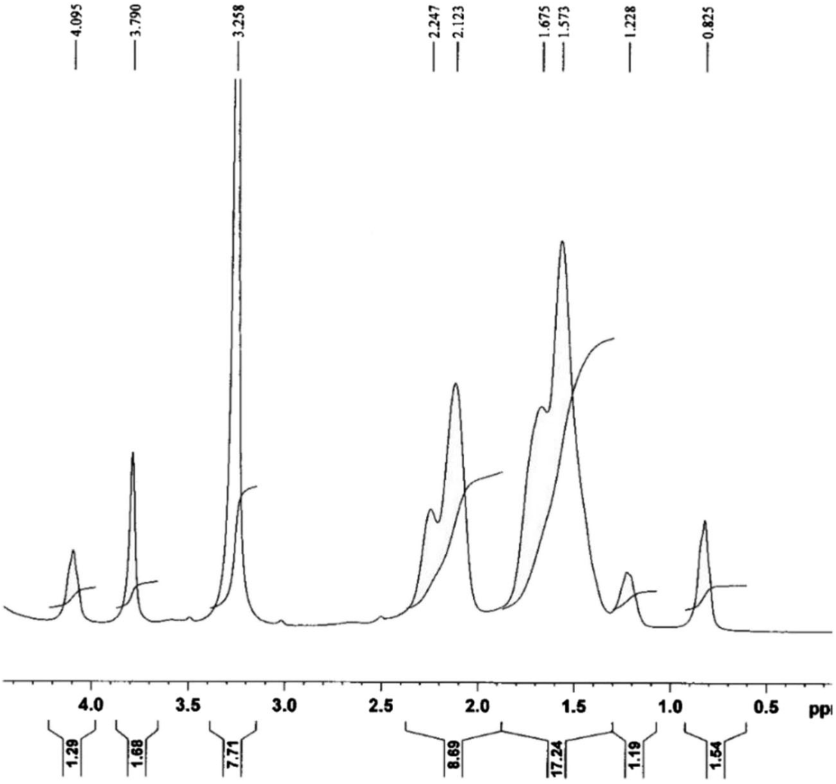


Fig. 1 ^{1}H NMR spectra of polyacrylamide (2)

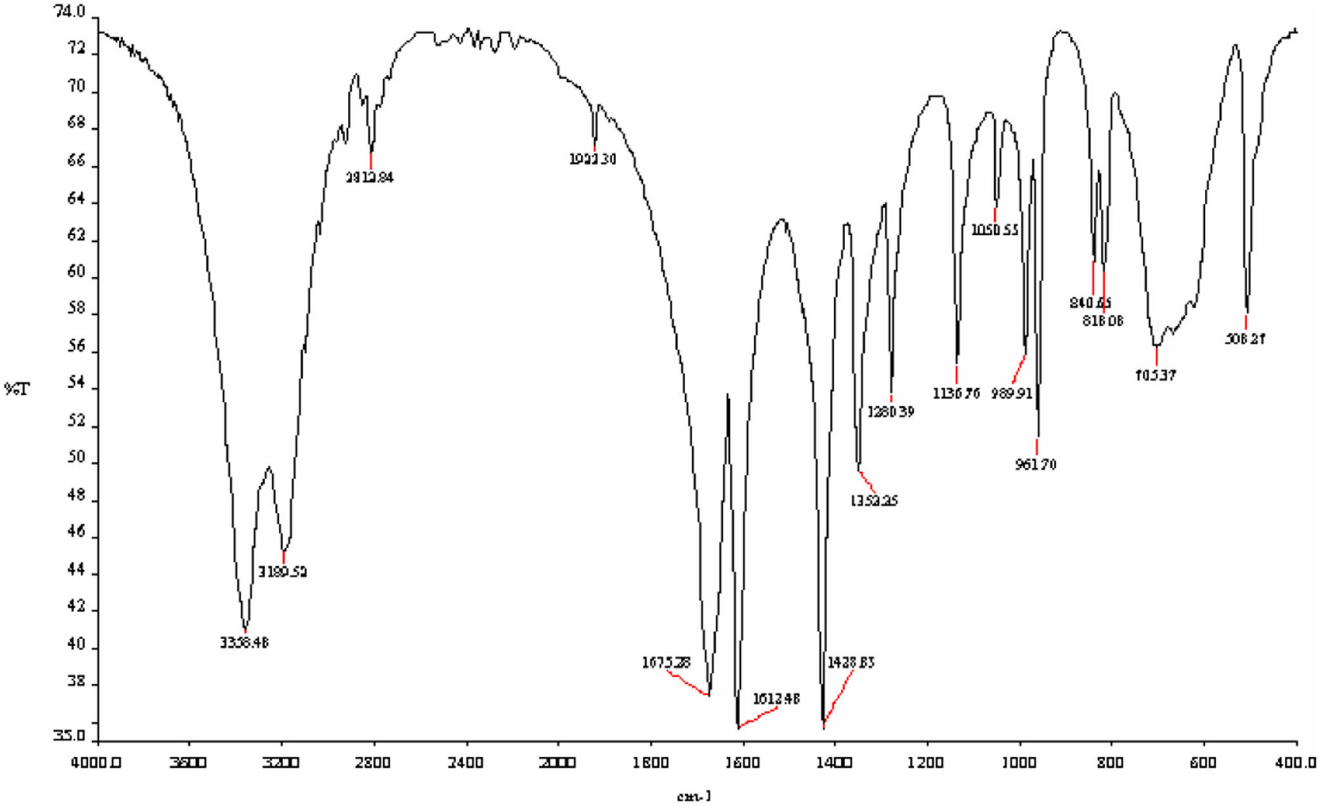


Fig. 2 IR spectra of acrylamide (1)

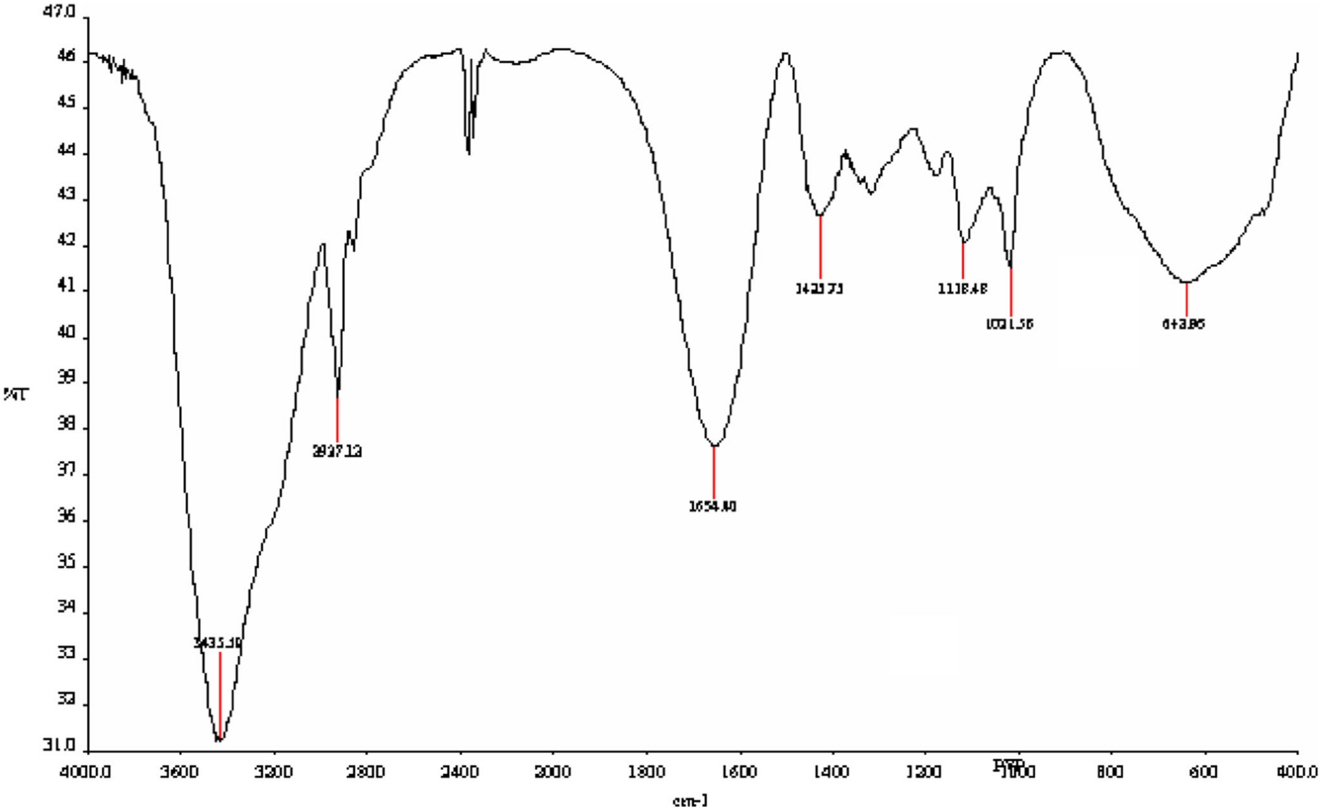


Fig. 3 IR spectra of polyacrylamide (2)

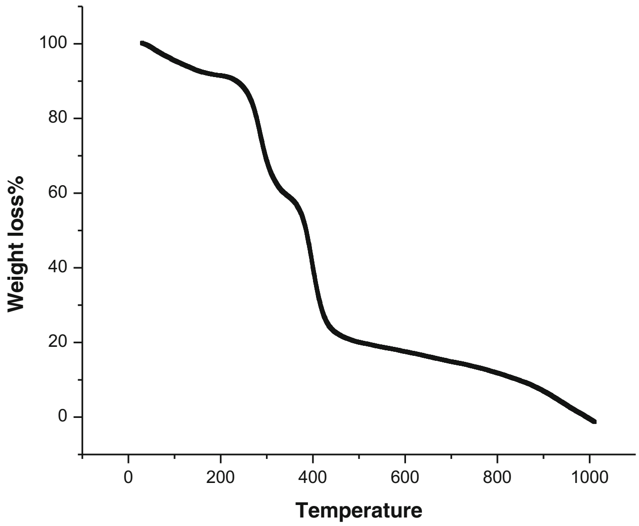


Fig. 4 TGA spectra of 2

appearance of characteristic broad peaks at δ 1.59 and δ 2.15 corresponding to the methylene and methine protons, respectively confirmed the formation of **2** (Fig. 1). A comparison of the FT-IR spectrum of polymer [45] (**2**) with that of the monomer (**1**) indicated that the monomer spectral peak at 1612 cm^{-1} for olefinic stretching disappeared after polymerization confirming the formation of polymer through C-C single bonds. The shift of the carbonyl peak from 1672 to 1654 cm^{-1} in the FT-IR spectra of **2** compared to that of **1** was also observed (Figs. 2 and 3). The complete thermal degradation of **2** occurred in two stages when synthesized in organic solvent and in single stage, when synthesized in ionic liquids (Fig. 4).

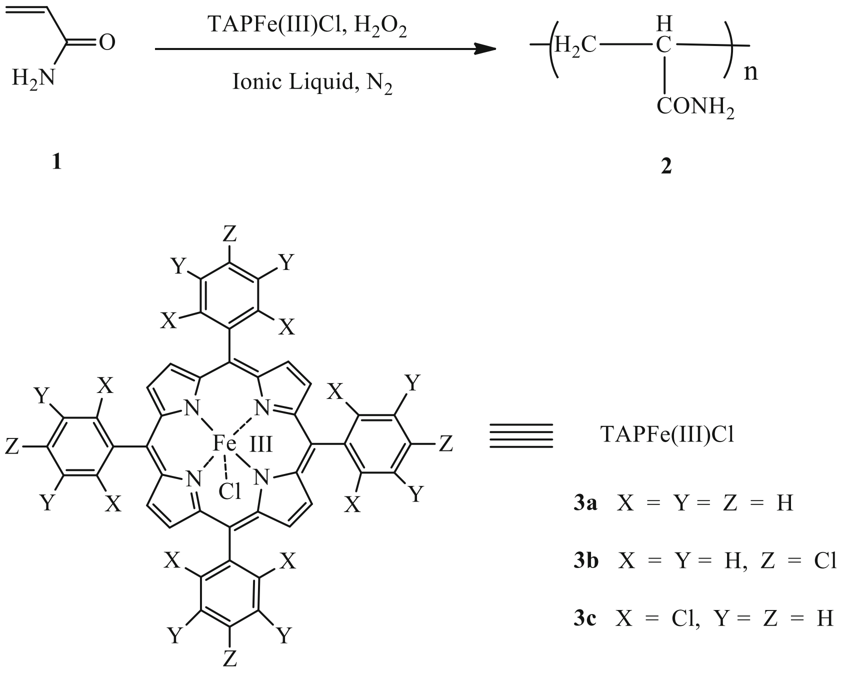
Results and discussion

Effect of different solvents on the polymerization of acrylamide

The reaction of acrylamide (**1**) with hydrogen peroxide in the presence of iron(III) porphyrin, 5,10,15,20-tetrakis-(2′,6′-dichlorophenyl) porphyrin [Cl_8TPPFe(III)Cl] (**3c**) as the catalyst was carried out in dichloromethane (Scheme 1). The reaction mixture became viscous and led to sticky and rubbery product in 60% yields on addition of methanol to it whereas the similar reaction in the presence of acetonitrile and tetrahydrofuran gave 65 and 75% yield respectively (Fig. 5). The increase in yield of polymer **2** on using THF could be attributed to its coordinating nature, which is responsible for radical stabilization by forming complex with solvent and propagation of radical chain during the polymerization reaction.

Realizing the importance of solvents in polymerization of acrylamide, ionic liquids were employed as reaction media and polyacrylamide (**2**) was obtained in 93% yield in the presence of [bmim][BF_4] (**4**) under otherwise similar reaction conditions. This demonstrated

Scheme 1 Polymerization of acrylamide (1) with H_2O_2catalyzed by iron(III)porphyrins



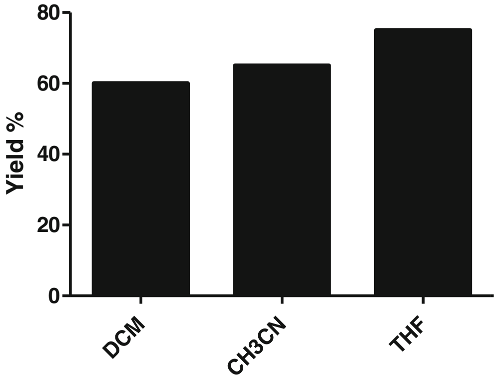
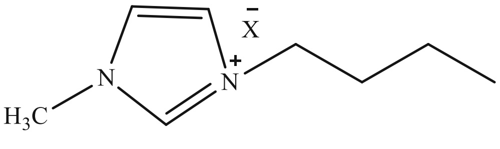


Fig. 5 Effect of different solvents on the yield of 2

that ionic liquids provide better reaction medium for the polymerization of acrylamide. Further, the polymerization of acrylamide was carried out in different ionic liquids such as [bmim][Br] (**5**), [bmim][PF_6] (**6**) and [bmim][Tf_2N] (**7**) (Scheme 2) to afford **2** in 81–93% yield respectively.

Effect of different iron(III)porphyrins on the yield of polyacrylamide

The reaction of acrylamide with hydrogen peroxide in ionic liquid, [bmim][BF_4] gave polyacrylamide in 72, 75 and 93% yields in the presence of the catalysts TPPFeCl, TCPPFeCl and TDCPPFeCl respectively (Fig. 6) (Table 1, entry 3, 4 & 5). The higher yield obtained in case of TDCPPFe(III)Cl (**3c**) shows the better catalytic activity of latter among other porphyrins used, in the polymerization reaction of **1** with H_2O_2. This is due to presence of electron withdrawing group on the phenyl ring of porphyrin, which makes it more resistant to oxidative degradation and more reactive towards radical stabilization compared to metalloporphyrins with electron donating substituents. Along with, high molecular weights and low polydispersity (PDI) was observed on using TDCPPFe(III)Cl with hydrophilic ionic liquids **4** and **5** (Table 1). Hence TDCPPFe(III)Cl is selected to be used as catalyst to carry out further reactions.



4 = X = Br
5 = X = BF_4
6 = X = PF_6
7 = X = TF_2N

Scheme 2 Structure of ionic liquids

Effect of different ionic liquids on the polymerization reaction of acrylamide

The reaction of acrylamide with hydrogen peroxide in the presence of TDCPPFe(III)Cl gave 93, 90, 87 and 81% yield in IL **4**, **5**, **6** and **7** respectively (Fig. 7). The higher yield obtained on using 5 as reaction medium was due to hydrophilic nature of ionic liquid which is compatible with the hydrophilic nature of monomer. Also, the tetrafluoroborate anion forms complex with the free radical thus stabilizing it causing higher propagation of the reaction. The IL **7** being hydrophobic in nature resulted in lower yield of the polyacrylamide.

Further, it was observed that on using TPPFe(III)Cl as catalyst, the addition of organic solvent to the ionic liquid used, resulted in increased yield of polymer due to increased solubility of catalyst in the reaction medium. The above reaction in the presence of TPPFe(III)Cl in 1:1 ratio of **5** and tetrahydrofuran gave 78% yield respectively.

Effect of different monooxygen donors on the polymerization of acrylamide

The polymerization of acrylamide using iron(III)porphyrins was studied with various monooxygen donors to determine the role of oxidant in the polymerization reactions. It was observed that hydrogen peroxide was more suitable for the polymerization of acrylamide as it gives higher yield as compared to iodosyl benzene and t-butyl hydroperoxide, though their use as oxidant in the polymerization of **1** were also acceptable as they were also giving moderate yields (Table 2).

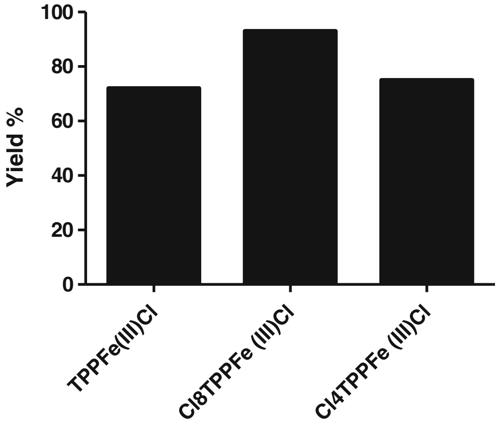


Fig. 6 Effect of iron(III)porphyrins on the yield of polyacrylamide

Table 1 Free-radical polymerization of acrylamide with hydrogen peroxide catalyzed by iron(III) porphyrins in imidazolium ionic liquids under nitrogen atmosphere

S. No.	IL	Porphyrin	H_2O_2 (mol %)	yield[a]	Mn[b]	Mw	PDI
1.	[bmim][BF_4]	Cl_8TPPFe(III)Cl	23.2	–	–	–	–
2.	[bmim][BF_4]	–	23.2	–	–	–	–
3.	[bmim][BF_4]	Cl_8TPPFe(III)Cl	23.2	93	54,670	75,940	1.138
4.	[bmim][BF_4]	Cl_4TPPFe(III)Cl	23.2	75	35,407	44,870	1.238
5.	[bmim][BF_4]	TPPFe(III)Cl	23.2	72	15,290	23,800	1.350
6.	[bmim][Br]	Cl_8TPPFe(III)Cl	23.2	90	52,450	64,090	1.151
7.	[bmim][PF_6]	Cl_8TPPFe(III)Cl	23.2	87	15,901	24,877	1.529
8.	[bmim][TF_2N]	Cl_8TPPFe(III)Cl	23.2	81	13,251	21,458	1.501

Iron(III) porphyrin: H_2O_2: monomer::1:250:1000 in IL (1 cm^3)

[a] yield corresponds to weight of 2 to weight of 1 used

[b] based on GPC analysis

Effect of different additives in the reaction of acrylamide with hydrogen peroxide catalyzed by iron(III)porphyrins

The effect of different additives such as 2,4-PD (2,4-Pentanedione), surfactants, quenchers, and methanol on the reaction has been studied and compiled in this section.

Effect of 2,4-Pentanedione and acetylacetone

The polymerization of acrylamide with hydrogen peroxide using TDCPPFe(III)Cl (**3c**) in IL **5** was done to give polyacrylamide in the presence of β-diketone moieties such as 2,4-PD and acetylacetone. The addition of β-diketones significantly increases the yield of **2** and it was observed that the increase in yield is much more significant in case of acetylacetone as compared to 2,4-PD. The addition of acetylacetone to the reaction of acrylamide with H_2O_2 in the presence of TDCPPFe(III)Cl increases the yield of polymer from 93% to 98% while 95% yield was obtained on the addition of 2,4-PD.

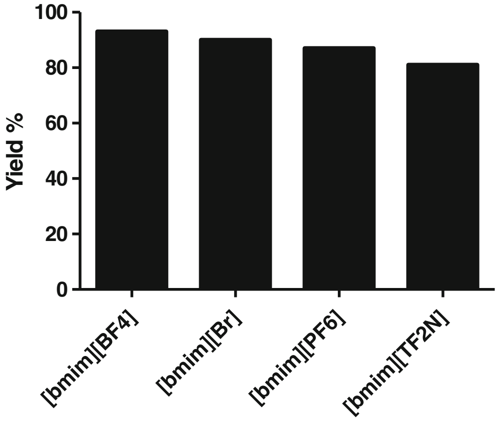


Fig. 7 Effect of different ILs on the yield of 2

Effect of surfactants

The effect of surfactants, sodium dodecyl sulfate (SDS) and cetyl trimethylammonium bromide (CTAB) on the above reaction was studied. In the HRP-catalyzed acrylamide poymerization carried out in the presence of surfactants, both anionic (SDS) and cationic (CTAB) accelerates the reaction kinetics, although there are no clear reasons to validate this observation [46]. In the acrylamide polymerization catalyzed by either potassium permanganate/glyceric acid or perphosphate/activator redox system in aqueous media, the reaction rate accelerates appreciably in the presence of anionic surfactants, while it decreases in the presence of cationic surfactants [47, 48]. The dissociation of anionic surfactants provides negatively charged ionic micelles that probably exerts a repelling force between the growing polymer chains and decreases the possibility of bimolecular termination. The positively charged micelles produced by the cationic detergent favors the orientation of the growing chain for termination

Table 2 Effect of "oxygen surrogate" and its concentration on TAPFe(III) catalyzed polymerization of acrylamide

Oxygen Surrogate	Concentration (mol %)	% yield of 2
H_2O_2	23.2	93
	18.5	58
Iodosyl benzene	23.2	81
	18.5	55
TBHP	23.2	66

Table 3 Effect of surfactants on the yield of **2**

S.No.	Surfactant	%yield
1.	–	93
2	SDS	98
3.	CTAB	85

and hence the retardation of the reaction occurs. Thus, the present study is in alignment with the chemical catalyst in terms of the response of the detergents in acrylamide polymerization. The reaction of acrylamide with hydrogen peroxide in the presence of TDCPPFe(III)Cl in ionic liquid **5** gave lower yield of polymer, 85% in the presence of CTAB whereas the addition of SDS to the above reaction resulted in slightly higher yield, 98% respectively (Table 3). Thus, the conditions have been standardized to increase the yield of polymer **2** in the presence of iron(III)porphyrins as catalyst.

Effect of quenchers (hydroquinone and methanol)

The reaction of **1** was carried out in the presence of excess of hydroquinone and it was found that the reaction mixture turned dark-brown, and no polymer was formed even after 48 h of the reaction. This could be explained in terms of reactivity difference that in the competition of reaction of oxoiron(IV)radical cation of porphyrin with hydroquinone and **1**, hydroquinone was oxidized to quinone first and the reaction with **1** was quenched. This suggested that the principal species for the reaction was oxoiron(IV)radical cation, confirming the free radical behavior of the polymerization. The reaction of **1** with H_2O_2 in the presence of iron(III)porphyrin was carried out in dry methanol instead of ionic liquid, and found that no polymer was formed even after 30 h of the reaction. This could be attributed to fact that the build-up of iron(IV)oxo species during reaction of iron(III)porphyrin with oxidants in methanol, takes much longer time and large excess of oxidant to bring out the complete conversion [49]. The formation of dimethoxy species of porphyrin may also occur which is inactive for catalysis. This could be the reason for quenching of polymerization of 1 in methanol [50].

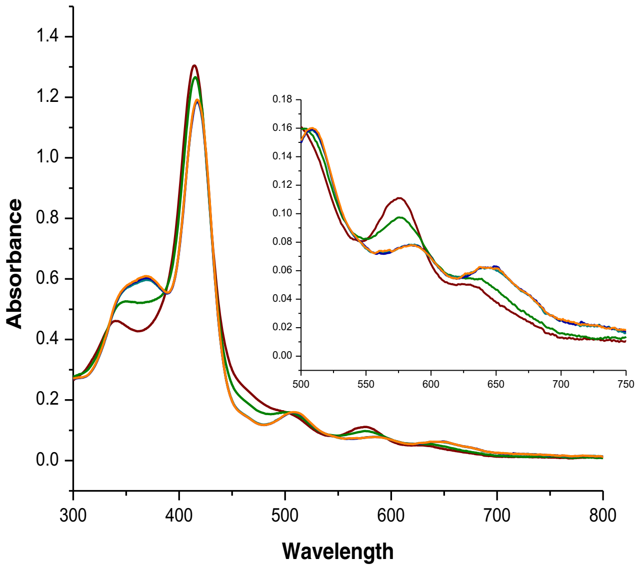
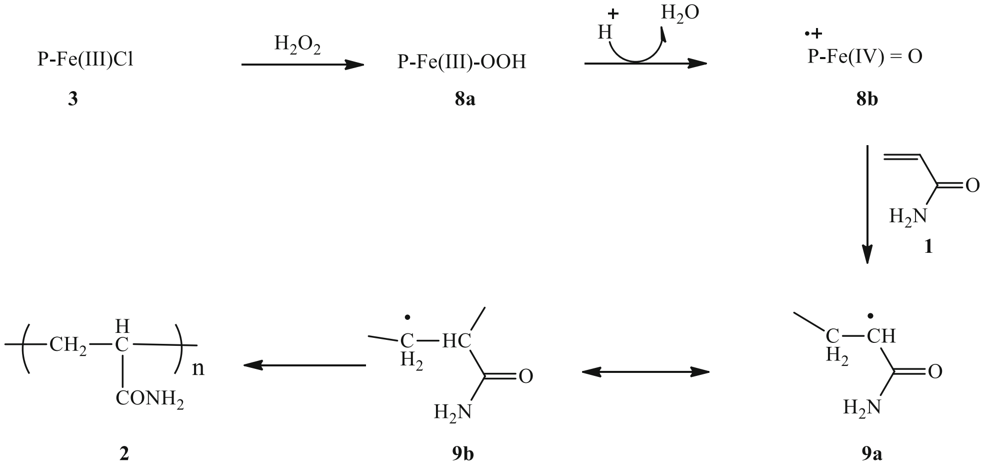


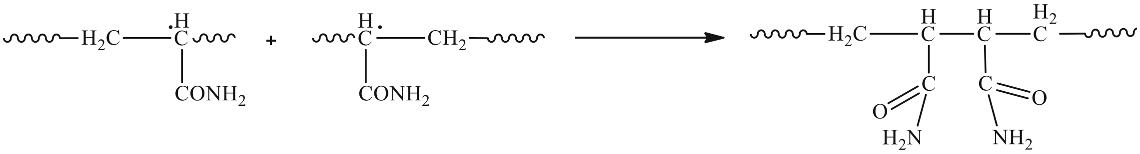
Fig. 8 UV-Vis spectra of formation of iron(III)porphyrin reactive intermediate during the reaction of iron(III)porphyrin with H_2O_2. Inset shows the change in peak intensity in the region of 500–750 nm

Reaction mechanism

The reaction of iron(III) porphyrins and hydrogen peroxide produces oxo iron(IV) porphyrin π-radical cation as the intermediate species in oxidative transformations. This active species is kinetically favored in these

Scheme 3 Proposed mechanism for the formation of reactive intermediate during polymerization of 1 with H_2O_2catalyzed by iron(III)porphyrin 3c





Scheme 4 Termination mechanism for the polymerization of acrylamide

reactions. The formation of oxo iron(IV) porphyrin radical cation during the oxidation of tetramesityl porphyrin with pentafluoroiodosylbenzene at −40 °C supports this dynamic intermediate [51, 52]. The same species is formed with hydrogen peroxide in the similar reaction conditions. Thus, the species may be attributed to be responsible for the oligomer formation in the lipophilic iron(III) porphyrin-catalyzed reaction of acrylamide (**1**) with hydrogen peroxide in dichloromethane (Scheme 3). The oxo iron(IV) porphyrin π-radical cation is produced in the reaction of iron(III) porphyrin with hydrogen peroxide in the presence of ionic liquids. Since no epoxide was observed in the reaction, the reaction certainly proceeds via oxidation of 1 rather than oxygenation path. Moreover, the ratio of iron(III) porphyrin: H_2O_2: monomer (**1**) (1:250:1000), which is different than the normal epoxidation reactions, suggests the path different than that of epoxidation. In the absence of any of the component, either porphyrin or H_2O_2, no polymerization took place. This emphasizes the involvement of oxo iron(IV) porphyrin π-radical cation as the reactive intermediate in the reaction. The formation of oxo iron(IV) porphyrin π-radical cation as reactive intermediate [53] during the reaction is further confirmed by the UV-Vis studies. In the Fig. 8, the Soret peak of 5,10,15,20-tetrakis-(2′,6′-dichlorophenyl) porphyrinato iron(III) chloride (**3c**) appeared at 414 nm. On the addition of stoichiometric amount of hydrogen peroxide to this solution, the Soret band was red shifted with decrease in absorbance and significant changes in the Q-bands has also been observed. In the Q band, the peak at 574 nm (the region of 500–600 nm) was disappeared and a new peak at 648 nm (Fig. 8) was generated which can be assigned for the formation of oxoiron(IV)π-radical cation responsible for the polymerization of acrylamide during the reaction [54]. The possible mechanism can be proposed as the species -Fe(III)(OOH) (**8a**) is generated on the addition of H_2O_2 to **3** which spontaneously produces the highvalent oxoiron(IV)porphyrin π- radical cation (**8b**) as the reactive intermediate [30]. The intermediate **8b** initiates the formation of acrylamide radical **9a** and **9b**, which attacks the other acrylamide molecule to form another free radical and hence the reaction further propagates to give the polymer **2** (Scheme 3). The reaction is terminated either by the combination of two bigger radicals or by abstraction of a proton from another monomer molecule (Scheme 4). The use of large excess of methanol resulted in the formation of stable dimethoxyiron(IV) porphyrin species by the reaction of iron(III)porphyrin with H_2O_2 [55] (Fig. 8). Hence the polymerization of **1** is quenched by the addition of large excess of methanol. The formation of intermediate **8b** could be explained only by the heterolytic cleavage of H_2O_2, which leads to the polymerization reactions. This was confirmed as no polymer was obtained in the presence of H_2O_2 and absence of iron(III)porphyrin. The intermediate 8b initiates the polymerization reaction by transferring radical to monomer substrate and gets converted to resting state of heme (Fe(IV) = O) [30].

Recycling of catalyst and ionic liquid

In order to demonstrate the recyclability of catalyst and ionic liquid, the porphyrin immobilized in ionic liquid was reused for polymerization reaction. Polymer was separated from the reaction mixture followed by evaporation of the solvent under reduced pressure. The porphyrin residue mixed with ionic liquid was vacuum dried and recycled for further polymerization reaction with slight product loss being noted (Table 4).

Table 4 Recycling of catalyst

S. No.	IL	Porphyrin	H_2O_2(mol %)	% yield	Mnd	Mw	PDI
1.	[bmim][BF_4]	Cl_8TPPFe(III)Cl	23.2	93	54,670	75,940	1.138
2[a].	[bmim][BF_4]	Cl_8TPPFe(III)Cl	23.2	85	45,587	58,269	1.281
3[b].	[bmim][BF_4]	Cl_8TPPFe(III)Cl	23.2	70	32,641	44,261	1.320

[a] second use

[b] third use

Conclusions

An application of iron(III)porphyrin is advocated as a catalyst for the polymerization of acrylamide with hydrogen peroxide in the presence of ionic liquids. Ionic liquids facilitated the easy isolation of polymer product from the reaction mixture leaving behind the porphyrin catalyst immobilized in it. The use of iron(III) porphyrin afforded the mild polymer synthetic route with good yields and resulted in high molecular weights and narrow dispersity of polymer obtained.

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