

## Chapter 3

### Synthesis of 1,4-disubstituted 1,2,3-triazoles using Cu(I) stabilized on N,N'-methylene bis-acrylamide cross linked polyvinylpyrrolidone

#### 3.1 Introduction

Polymer supported metal complexes are a class of compounds in which metal precursors are implanted over a polymer support. It binds the metal ions through coordinate bond using heteroatoms like oxygen or nitrogen and stabilized on the polymer matrix. Microenvironment of the ligand is an important factor that affects the complexation. During metalation, changes occur in both polymer and metal precursor. One of the important applications of polymer-metal complexes is in catalysis which coalesce the advantages of both homogenous and heterogeneous catalysts. Copper(I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction was independently introduced by Sharpless<sup>1</sup> and Meldal.<sup>2</sup> Various methods have been developed in order to increase the efficiency of the reaction which includes the introduction of different catalytic systems like homogeneous, heterogeneous and magnetic heterogeneous catalysts,<sup>3-5</sup> nanoparticles,<sup>6-8</sup> one pot procedures<sup>9</sup> and using water as reaction media.<sup>10,11</sup> The copper catalyzed version of click reaction is the most commonly used one for the regioselective synthesis of 1,4-disubstituted 1,2,3-triazoles.<sup>12,13</sup> Nitrogen containing ligands are known to stabilize the Cu(I) active species in reaction media even in water.<sup>14</sup> It was observed that CuAAC accelerated by the ligands such as tris(2-aminoethyl)amine derivatives, acryl amide can minimize the amount of Cu(I) catalyst to an order less than 1%.<sup>15,16</sup> Poly(*N*-vinyl-2-pyrrolidone) (PVP) is widely used as reducing agent, stabilizer and growth modifier in nanoparticle synthesis.<sup>17-20</sup> These nanoparticles are also used as catalysts for 1,3-dipolar cycloaddition reactions for the synthesis of 1,2,3-triazoles.<sup>21</sup>

### **3.2 Review of literature**

In recent years, polymer supported metal complexes have achieved great attention due to their wide application in bioinorganic and synthetic chemistry. Merrifield in 1963 introduced “solid phase technique” for the synthesis of peptides using insoluble cross linked macromolecules as supports. Such functionalized polymers were used as catalysts and protecting groups in the synthesis of pharmaceuticals, agricultural, dyes etc. Application of functional polymers depends on the chemical modification made, such that the polymers have characteristic physical properties of polymer and chemical reactivities of the incorporated functional groups. Functionalized polymers found out their application as reducing agents,<sup>22</sup> to understand biological reactions of macromolecules,<sup>23</sup> photoconductive polymers<sup>24</sup> and polymeric surfactants.<sup>25</sup> Polymer metal complexes belong to coordination compounds in which the central metal atom or ion is attached with molecules or ions. They have application in diverse fields like organic synthesis,<sup>26,27</sup> waste water treatment,<sup>28</sup> hydrometallurgy,<sup>29</sup> polymer drug grafts,<sup>30</sup> environmental protection<sup>31</sup> and nuclear chemistry.<sup>32</sup> The polymer – metal complexes possess characteristic structure in which the central metal ions are surrounded by a giant polymer chain bound to metal ion through coordinate bonds. Here the polymer chain is obtained by the polymerization of monomer units containing coordinating atoms like N, O and S. Polymer supported metal complexes have various advantages like easy recovery by simple filtration, recyclability etc. Therefore, it can be reused and hence economic.

Polymeric metal complexes are classified depending on the preparation methods

1. Complexation of polymeric ligand with metal ion; which is again subdivided into
  - 1.1 Pendent polymer metal complexes and
  - 1.2 Inter/ intra molecular bridged polymer complex
2. Complexation of metal ions with multifunctional polymer ligands
3. Polymerization of metal containing monomer units.

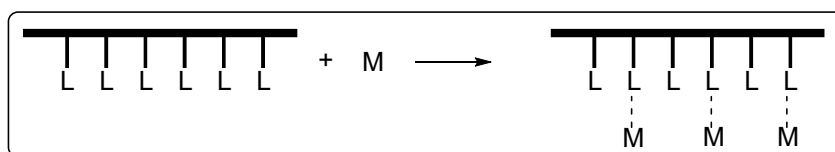
Complexation of polymeric ligands with metal ion results in different types of coordination structures which are divided into Pendent and Inter and/or Intramolecular bridged polymers.

## 1.1 Pendent Polymer metal complexes

In this type, the metal ion is attached to the polymer ligand through the functional group which is tagged on the polymer chain. Pendent complexes are classified as monodentate and polydentate depending on the chelating abilities of the ligands.

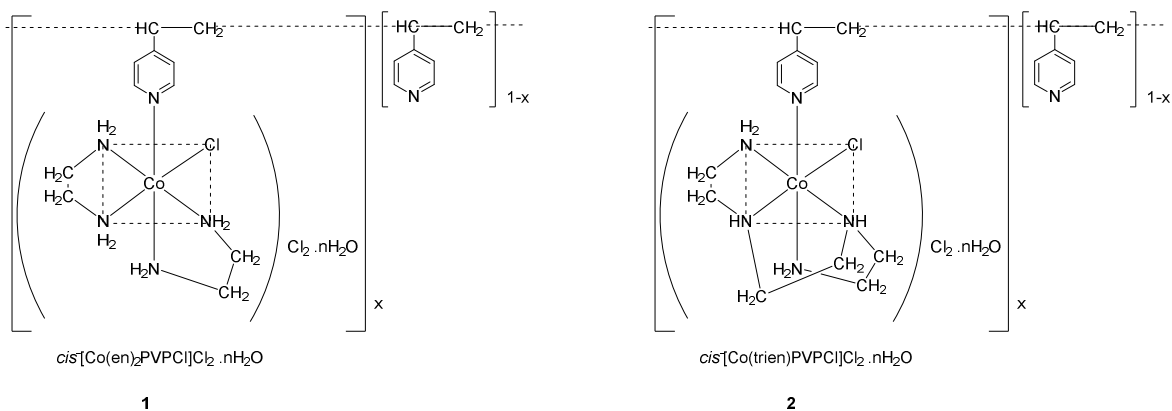
## 1.1.1. Monodentate pendent polymer complexes

Here metal ion or metal complex is attached to the one labile ligand which is substituted by the polymeric ligand (**Scheme 1**)



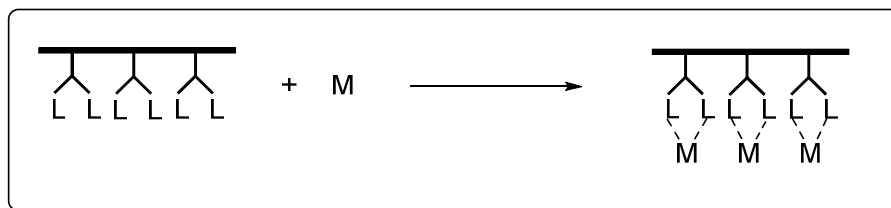
Scheme 1

Kurimura<sup>33</sup> and Tsuchide<sup>34</sup> reported the synthesis of poly-4-vinylpyridine complexes (**1** and **2**) with various metal chelates belonging to monodentate type.



## 1.1.2. Polydentate pendent polymer complexes

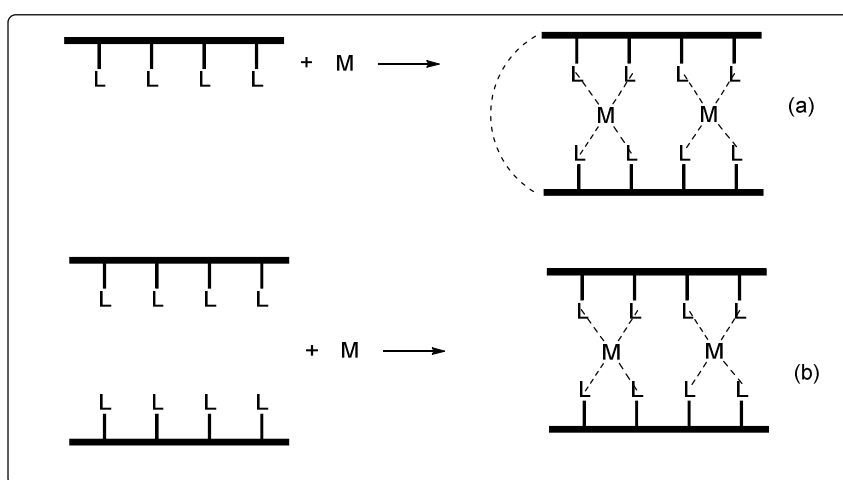
Polydentate ligand on complexation results in the formation of bridged structures (**Scheme 2**)



Scheme 2

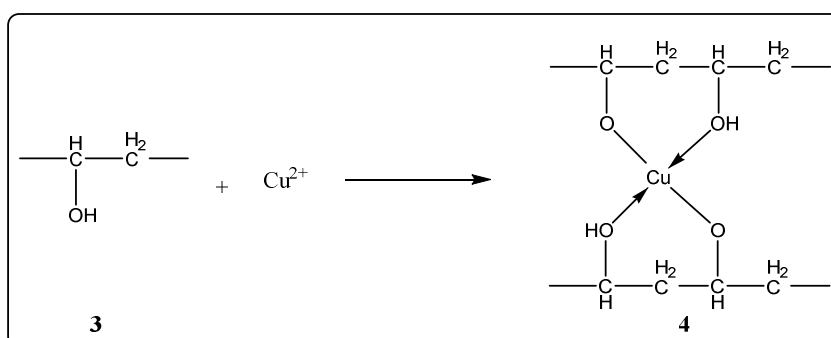
## 1.2. Inter and/or intra molecularly bridged polymer metal complexes

This type of complexes results after the reaction of metal ion with polymeric ligand that has four or six coordinating bonding hands (**Scheme 3**).



Scheme 3 M= metal ion, a)intra polydentate b) inter polydentate

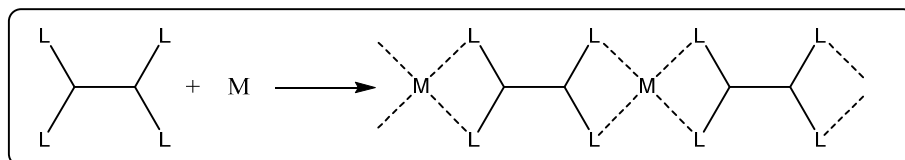
Poly(vinyl alcohol)(PVA) copper(II)complex is the simplest example belonging to the above category<sup>35</sup> (**Scheme 4**).



Scheme 4

## 2. Complexation of metal ions with multifunctional polymer ligand

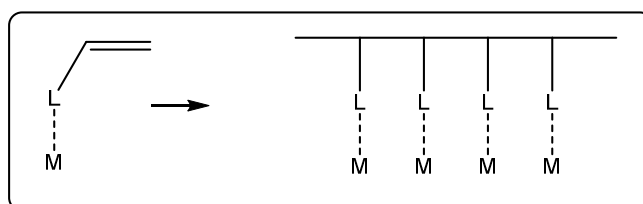
Polymer chain in this type is composed of coordinate bonds and ligands that act as bridging unit. Multidentate ligands tend to form this type of polymer metal complex (**Scheme 5**).



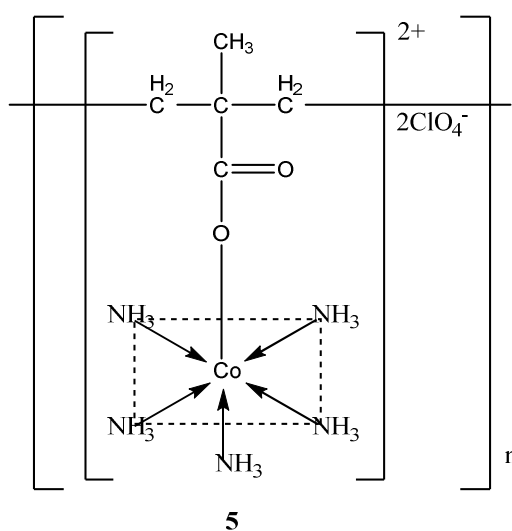
Scheme 5

## 3. Polymerization of metal containing monomer unit

This type of polymer metal complex is formed by the polymerization of functionalized ligand units. Most studied example of this type complex is vinyl complexes which polymerize through radical polymerization of vinyl monomer containing transition metal ions (**Scheme 6**).



Scheme 6



**Application of Polymer-metal complexes as catalysts**

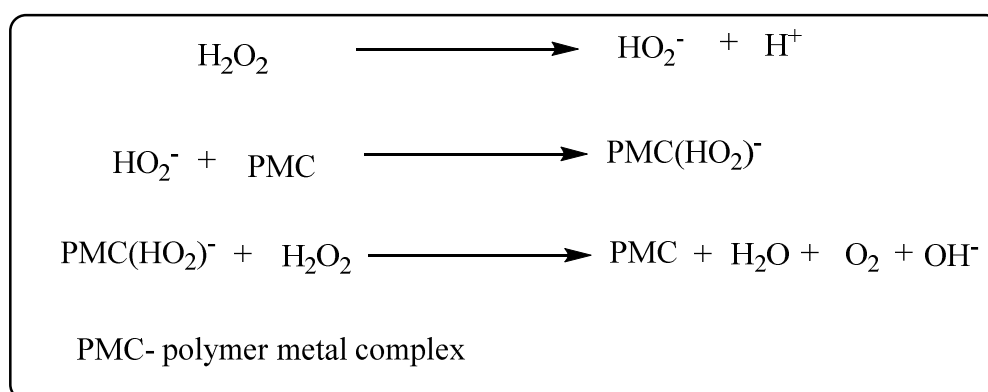
Catalysts are the substances that increase the rate of a chemical reaction by providing an alternative pathway with a lower energy of activation compared to uncatalyzed reaction. Reactions can be catalyzed homogeneously and heterogeneously. In homogeneous catalysis, both reactants and catalyst are in the same phase whereas in heterogeneous reactions they are in different phases. Heterogeneous catalysts gained more attention in organic synthesis because of their good thermal stability, good selectivity, and they are insoluble in reaction media facilitating easy recovery of catalyst by filtration or centrifugation. The advantages of homogeneous catalysts are better reproducibility, selectivity and requirement of less drastic conditions. But the major disadvantage was the difficulty in recovery of the catalyst from the reaction media which can be avoided by binding homogeneous catalyst to inorganic carrier or organic polymer. Therefore, when incorporating a transition metal ion or complex into polymer support, we get a polymer supported catalyst and the recovery and recyclability of the catalyst became easy because of the insoluble support. Such catalysts can be renamed as “Heterogeneously homogeneous” catalyst. The catalytic activity of polymer metal complexes is affected by

- i. Porosity and surface area
- ii. Nature of polymer support and extent of cross linking
- iii. Spacer effect
- iv. Swelling and solvation of polymer matrix

The pore size and surface area is largely affected by the nature and degree of cross linking. Greater the porosity, greater will be the solvent flow and higher will be the catalytic activity. To increase the reaction rate, the catalyst must be highly porous and the active species should be largely distributed over the interior of the catalyst. Cross linked polymer support offers better stability to metal complex compared to the linear one. Nature and extent of cross linking in polymer matrix strongly affect the complexation process; as the degree of cross linking increases, lesser will be the metal ion intake which lowers the stability of polymer metal complex as the polymer became more rigid.

Varghese *et.al* reported the effect of molecular interaction on the structure of polymer metal complex.<sup>36</sup> Length of the pendent chain largely affects the amount of metal complexed and the structure of metal complex. Steric hindrance of functional groups arises due to the shorter distance which decreases the efficiency of complex formation. The reactivity of functional groups will be less because of steric hindrance occurred by the interference of polymer chains. To increase the reactivity of functional groups there must be a separation between from the active site and polymer matrix.<sup>37</sup>  $\alpha,\omega$ -Dibromoalkanes,<sup>38</sup>  $\omega$ -bromoalkane,<sup>39</sup> triethylamine<sup>40</sup> are commonly used spacers. The degree of cross linking has major effect on swelling nature of the polymer back bone. As the degree of cross linking increases the extent of swelling decreases. Different factors that made difficulties in the swelling nature are length of polymer chain, chain entanglement, efficiency of cross link formation, nature and proportion of monomer to diluent ratio used during the polymer matrix synthesis. Gel type polymer supports with microporous nature and lesser cross linking are widely used as polymer support and catalyst. Upon swelling the gel supports exposes the reactive site towards the reactants.

Polymer supported catalysts can catalyze different types of reactions. For example, poly( $\beta$ -diketone)Cu(II)<sup>41</sup> in the oxidation of L-ascorbic acid, poly(vinylalcohol)<sup>42</sup> and NNMBA cross linked polyacrylamides with glycine functionalities<sup>43</sup> exhibit catalytic activity towards the decomposition of  $H_2O_2$ (Scheme 7).

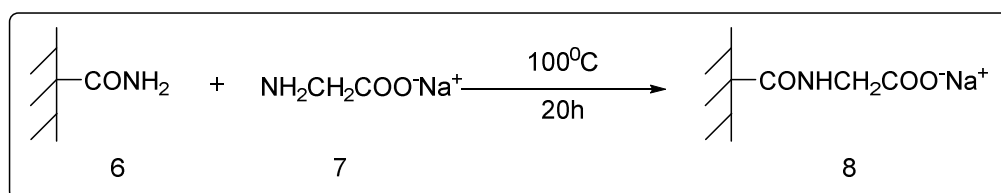


Scheme 7

Cobalt containing polyvinyl pyrrolidone complexes was synthesized by Musin in 1988.<sup>44</sup> Alcoholic solution of  $CoCl_2$  was added to PVP solution. Stirred for half an

hour, solvent evaporated by rotary evaporator and dried in vacuum oven at 60-80°C. Cobalt containing coordination compounds have biological relevance, like vitamin B<sub>12</sub>. They investigated the biological action of Cobalt-PVP complex. The cobalt complex reduces the cardiotoxic action, which was due to the known nature of PVP in improving the blood flow. Metal complexation of cross linked polyacrylamide supported dithiocarbamates was reported in 1992 by Pillai.<sup>45</sup> Kannan and coworkers reported the oxidation of cyclohexanol to cyclohexanone was done by poly(2-hydroxy-4-acryloyloxybenzaldehyde)-Cu(II)/Ni(II) complexes.<sup>46</sup>

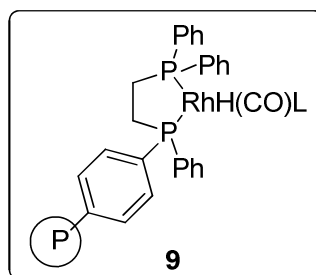
Hydrolytic dehydrogenation of ammonia borane was catalyzed by PVP stabilized Ni(II) catalyst.<sup>47</sup> Later in 1998 B. Mathew reported the synthesis of NNMBA cross linked polyacrylamide supported glycine.<sup>48</sup> Cross links were introduced by free radical polymerization using potassium persulfate as initiator. Glycine functions were incorporated by transamidation using excess sodium salt of glycine at 100°C for 24h (Scheme 8).



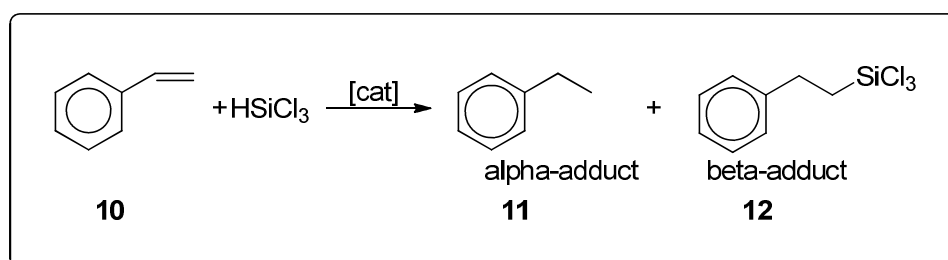
Scheme 8

Seguel reported the synthesis and characterization of Cu(II), Co(II), Ni(II) and Zn(II) complexes of poly(maleic acid).<sup>49</sup> Hydrogenation of olefins catalyzed by poly(acrylic acid) Ru(II) complexes was reported by Hirai in 1974.<sup>50</sup> Using polymer supported Rh(I) catalyst, Grubbs reported the rate of hydrogenation of olefins.<sup>51</sup> Hydrogenation of alkenes and alkynes were catalyzed by poly(styryl)bipyridinePd(II) acetate.<sup>52</sup> Catalyst reduces more crowded or sterically hindered alkenes rather than less hindered ones. Nayak reported the reduction of alkenes and alkynes under mild conditions using polystyrene supported Pd(II) species.<sup>53</sup> The rate of hydroformylation reaction was found to be increased when the catalyst was bound to a polymer matrix. The hydroformylation reaction of 1-pentene was carried out using polymer anchored rhodium complex **9**.<sup>54</sup>



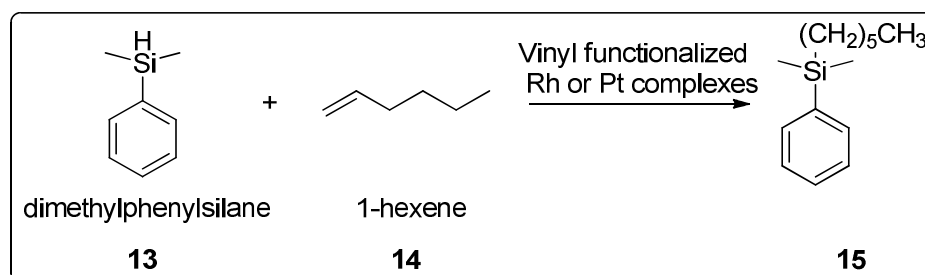


Hydrosilylation of phenylacetylene was catalyzed by polyamide supported metal complexes.<sup>55</sup> Polymer supported ferrocene derivatives of platinum and palladium complexes shows excellent catalytic activity for the hydrosilylation of olefins by trichlorosilane. The catalyst can be reused without any significant loss in catalytic activity<sup>56</sup> (Scheme 9).



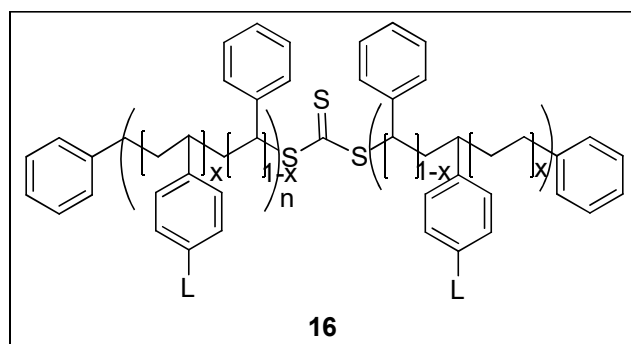
Scheme 9

Tetraamineplatinum(II) chloride on silica supported polyethylene glycol is an example of supported liquid-phase catalyst (SLPC)<sup>57</sup> in which the catalyst component dissolved in a liquid phase and coated over a porous material. The catalyst shows high activity towards the hydrosilylation of phenylacetylene and found to be stable under all the reaction conditions they had studied. Hydrosilylation of terminal olefins catalyzed by both rhodium and platinum complexes of vinyl functionalized polysiloxanes was reported by Michalska in 2004<sup>58</sup> (Scheme 10).



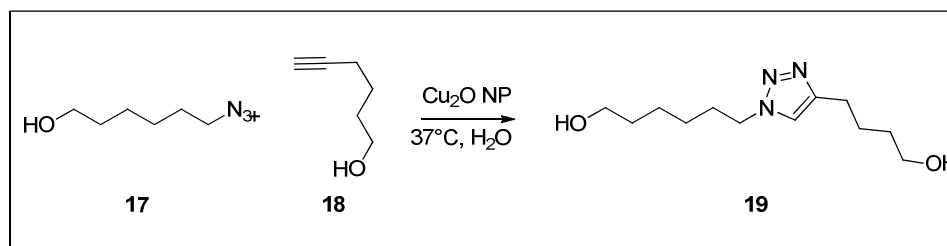
Scheme 10

Jiang reported the synthesis and catalytic activity of poly- $\gamma$ -mercaptopropylsiloxane-platinum complex in the hydrosilylation of 1-hexene and acetylene.<sup>59</sup> Addition of triethoxysilane to 1-hexene at 80°C or at room temperature using the catalyst provides n-hexyltriethoxysilane only whereas the addition towards acetylene provides vinyltriethoxysilane and bis(triethoxysilyl) ethane in good yields. Epoxidation of cyclohexene has been studied by Tempesti in 1987<sup>60</sup> in which molybdenum-boron mixed oxo derivatives were immobilized on to the polymeric support and carried out the epoxidation using t-butyl or ethylbenzenhydroperoxide. The catalyst provides a comparable result with that of bimetallic boron-molybdenum catalyst. They concluded that the grafting on the polymer support didn't negatively affect the reaction. Similar work was done by Stamenova<sup>60</sup> and Sherrington<sup>61</sup> using polymer supported molybdenum and vanadium catalyst with different polymer supports. Polymer matrices containing Mn(III) salen complexes were synthesized and the catalytic activity in epoxidation has been studied by Sivaram.<sup>62</sup> Catalytic oxidation of phenol using PVP or chitosan stabilized copper catalyst<sup>63</sup> provided 80% phenol conversions compared to commercially available CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under similar reaction conditions. Prez *et.al* reported the synthesis and catalytic activity of styrene functionalized TBTA (Tris((1-benzyl-4-triazolyl)methylamine) monomer which copolymerized via RAFT (Reversible addition-fragmentation chain-transfer) polymerization to afford the catalyst support **16**. This was used for the complexation with copper(I) source providing a reusable catalyst<sup>64</sup> for the click synthesis of 1,2,3-triazoles. They checked the reusability of the catalyst and it can be reused for 6 times without any loss in the catalytic activity.



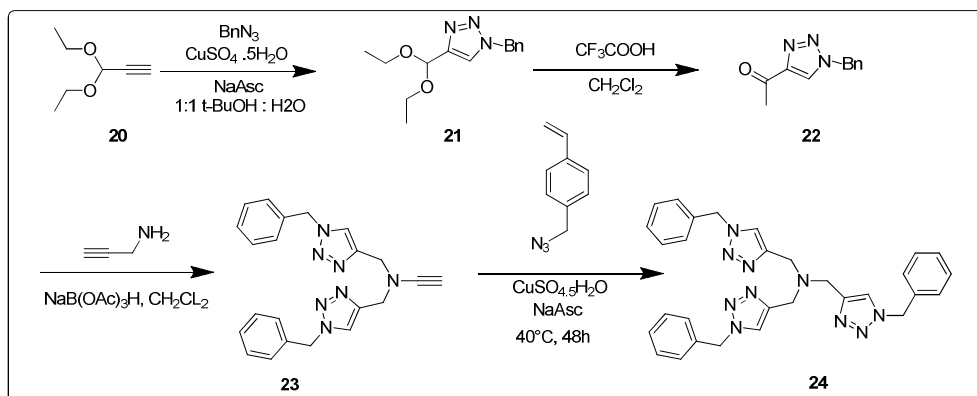
Suzuka reported the synthesis of polymer supported 2,2'-biarylpyridine copper complexes for cycloaddition reaction.<sup>65</sup> Chen reported the synthesis of PVP coated

$\text{Cu}_2\text{O}$  catalyst which shows good catalytic activity for azide-alkyne click reaction in water<sup>66</sup>(Scheme 11).



Scheme 11

Prez and coworkers first synthesized TBTA based monomer **23**(Scheme 12) in a method developed by Fokin *et.al.*<sup>67</sup> They used CuAAC scheme for the monomer preparation and RAFT instead of ATRP because the transition metal ion used as the catalyst will react with TBTA monomer and leads to uncontrollable polymerization. Using TBTA/Cu polymer they conducted model reaction of CuAAC using benzyl chloride and phenyl acetylene.



Scheme 12

Magnetic poly(imidazole/imidazolium)-supported  $\text{Cu}(\text{II})$  complex were prepared and its catalytic activity for CuAAC was studied by Pourjavadi.<sup>68</sup> After the synthesis of MNPs it was further functionalized using 3-(trimethoxysilyl)propylmethacrylate. Monomer ([EVim][ $\text{BF}_4$ ]) was obtained by heating 1-vinylimidazole and ethyl bromide in methanol at 60 °C for 20 h and the solid was separated by simple decantation and dried in vacuum. Copper was introduced to the catalyst using  $\text{CuSO}_4$  in water by vigorous stirring continuously for 3 days at 70 °C.  $\text{Cu}(\text{I})$ -poly(2-aminobenzoic acid) ( $\text{Cu}(\text{I})$ -pABA) was prepared by dissolving 2-aminobenzoic acid in Milli-Q water at 60

°C,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  dissolved in DMF was added to the above solution with continuous stirring. This catalyst was used for click reaction in aqueous media.<sup>69</sup>

### **Scope of the present work**

There are a number of reports on CuAAC reactions catalyzed by heterogeneous catalyst having various advantages like easy recovery, simple product isolation etc. Most of the heterogeneous system uses copper(I) as the metal precursor which is the catalytically active species in CuAAC reaction. Polymer metal complexes with application in CuAAC reaction using copper(I) source were found to be less. Herein, we have developed a catalytic system containing catalytically active copper(I) species stabilized within the polymeric matrix for the CuAAC reaction.

### **3.3.1 Reagents and Materials**

- Anhydrous sodium sulphate, glacial acetic acid, copper sulfate and sodium dihydrogen phosphate, N,N'-methylene bisacrylamide, phenyl acetylene and 4-ethynyl toluene were purchased from Sigma Aldrich, Bangalore.
- N-vinyl pyrrolidone, benzyl chloride, 4-chlorobenzyl chloride, 2,4-dichlorobenzyl chloride, 4-nitro benzyl bromide, N-butyl bromide, allyl bromide, 1-chloromethyl naphthalene, cyclopentyl bromide and 2-bromoethyl benzene were purchased from Spectrochem, Mumbai
- Sodium azide from Nice chemicals, Kochi
- Ethanol, Distilled water

### **3.3.2 Instruments**

- IR spectra was recorded on a Shimadzu IR Affinity- 1 Spectrometer using KBr pellets
- SEM performed on JEOL Model JSM-7600F along with identification of chemical composition of sample using energy dispersive X-ray spectroscopy.
- Powder X-ray diffraction pattern was recorded on Bruker AXS, D8 Advance. operating at 20kV using Cu-K $\alpha$  radiation( $\lambda = 0.1542\text{nm}$ )
- TG-DTA results obtained from Perkin Elmer, Diamond TG/DTA
- X-ray photoelectron Spectroscopy (XPS): Kratos Analytical U K Model Axis Ultra AL K alpha
- NMR – Bruker Avance III, 400MHz
- GC-MS – Thermo Fisher Scientific
- Buchi Rotavapour
- Mechanical overhead rotator

### 3.4 Results and Discussion

N,N'-methylene bisacrylamide (NNMBA) cross linked polyvinylpyrrolidone copolymer(PVPNNMBA) was synthesized by suspension polymerization of N-vinyl pyrrolidone using NNMBA as cross linking agent and AIBN used as radical initiator. To maintain the optimum rigidity and swelling properties, the degree of cross linking was maintained to 4%. Immobilization of copper ions into the polymer matrix (CuPVPNNMBA) was done by swelling the polymer in glacial acetic acid followed by heating the polymer with copper(II) sulphate in glacial acetic acid.

Reduction of copper(II) to copper(I) takes place in the presence of polyvinyl pyrrolidone(PVP) which can act as a mild reducing agent.<sup>70,71</sup> This reducing power of PVP was attributed by the presence of end hydroxyl group.<sup>72</sup> NNMBA plays a dual role as cross linking agent and the amide moiety can facilitate coordination to copper.<sup>73</sup> Further reduction of copper(I) to copper(0) was prevented by the coordination of copper(I) with the oxygen atom of pyrrolidone and nitrogen atom of NNMBA which stabilize Cu(I) in the polymer matrix. These observations were affirmed by different characterization techniques.

#### 3.4.1 Infrared spectral studies of PVPNNMBA and CuPVPNNMBA

Comparison of the FTIR spectrum of PVPNNMBA and CuPVPNNMBA helps to differentiate them and can be used as the primary evidence for the incorporation of copper into the polymer matrix (**Table 1** & **Fig 1**). The free N-vinyl pyrrolidone exhibited  $\nu_{\text{CH}_2}$  wagging of vinyl bond around  $850\text{cm}^{-1}$ ,  $\nu_{\text{C=C}}$  at  $1630\text{cm}^{-1}$  and  $1426\text{cm}^{-1}$  corresponds to vinyl scissoring. These peaks were absent in PVPNNMBA and CuPVPNNMBA spectrum. This confirms the formation of PVPNNMBA and CuPVPNNMBA sacrificing the vinylic bond. Peak at  $629\text{cm}^{-1}$  is characteristic of  $\text{Cu}_2\text{O}$ . Due to the interaction with copper ions in the polymer, the characteristic peak of carbonyl shifted from  $1656\text{cm}^{-1}$  to  $1614\text{cm}^{-1}$ (**Fig 1**). Similar shifting of peaks were noticed at  $1446\text{cm}^{-1}$  to  $1438\text{cm}^{-1}$ ,  $3360\text{cm}^{-1}$  and  $3110\text{cm}^{-1}$  to  $3376\text{cm}^{-1}$  and  $3273\text{cm}^{-1}$ ,  $1547\text{cm}^{-1}$  to  $1558\text{cm}^{-1}$  corresponding to C-N-C stretching, secondary amide, N-H bending vibrations respectively.

Table 1. FTIR absorption bands

FTIR absorption ( $\text{cm}^{-1}$ )						
Sample	Vinyl Scissoring & $=\text{CH}_2$ wagging	Amide	N-H Bend	N-H Str	C-H Str	M-O
PVPNNMBA	Absent	1655	1547	3441	2882	Absent
CuPVPNNMBA		1626	1516	3429	2883	683

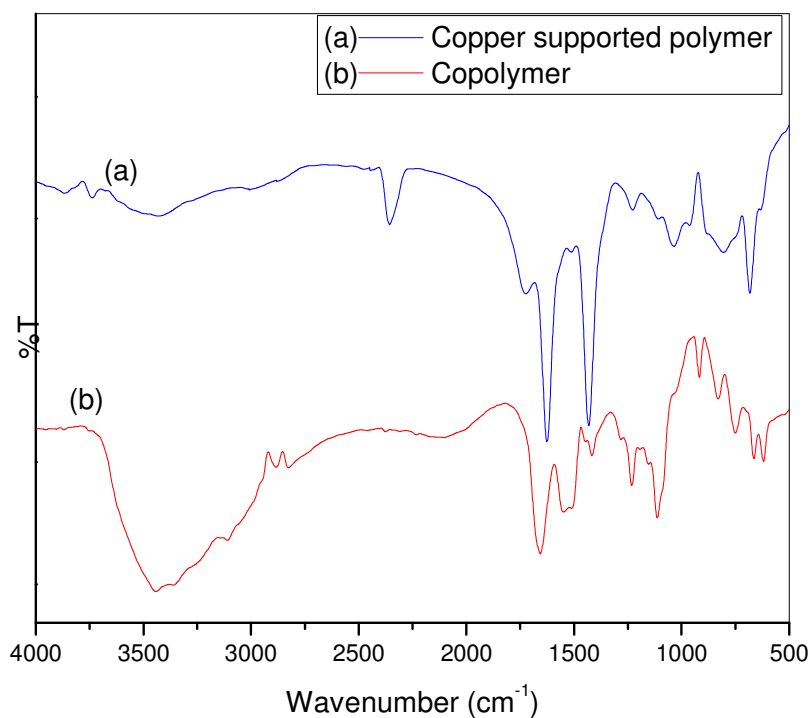
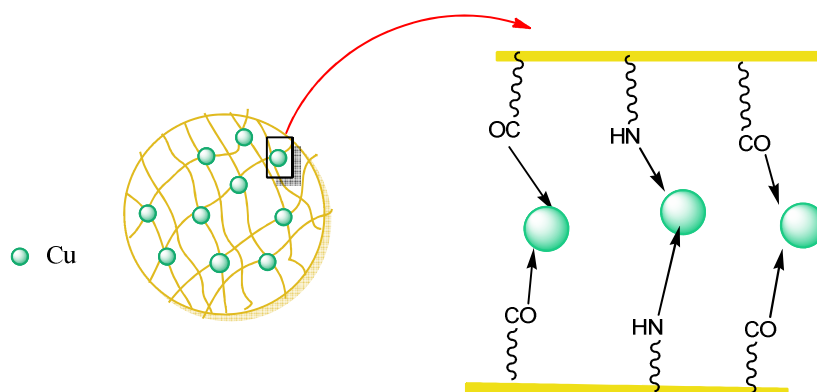


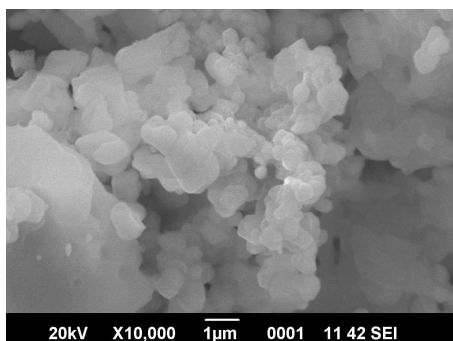
Fig.1 FTIR of Copolymer and CuPVPNNMBA



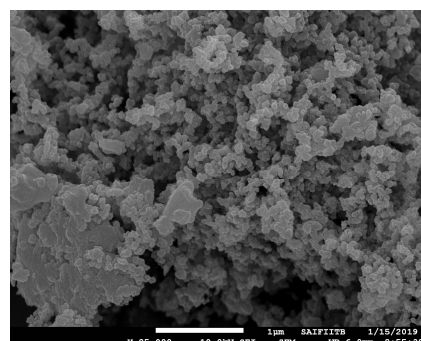
**Fig .2** Schematic representation of incorporation of metal ion in the polymer matrix

### **3.4.2 Morphological and elemental composition studies**

Scanning electron micrographs provides information about nature of the surface and size of particles. An X-ray beam emitted from the sample during SEM analysis makes use for the elemental analysis termed as energy dispersive X-ray spectroscopy (EDX). The emitted X-ray beam will be a characteristic of each element present in the sample. The changes occurred in the surface morphology of the copolymer during the metal complexation can be identified using this technique. In the present work, we have studied the morphological features of 4mol% NNMBA cross linked polyvinyl pyrrolidone and its copper complex. The SEM image of the cross linked polymer and copper complex are given (**Fig. 3**). Compared to pure polymer, copper added polymer adopts particle nature after complexation.



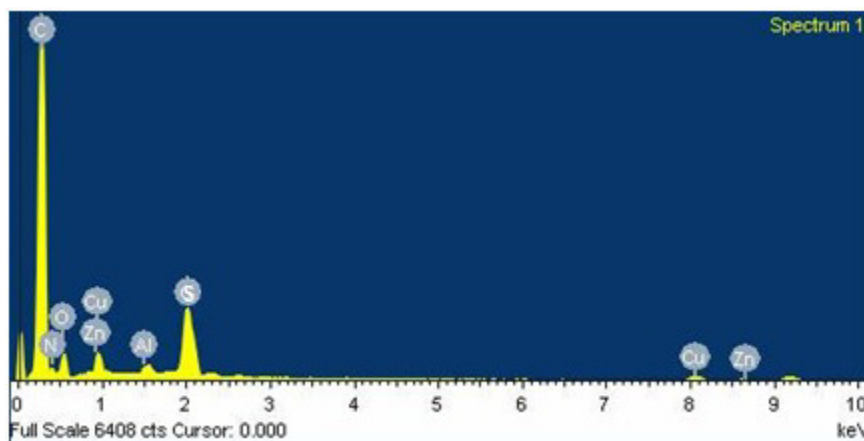
**Fig:3 I** SEM image of PVPNNMBA



**II.** SEM image of CuPVPNNMBA



Elemental composition of the polymer metal complex (CuPVPNNMBA) can be studied using EDS spectra (**Fig.4**). It confirms the presence of copper providing its characteristic peaks at 0.94 and 8.1keV corresponds to CuL $\alpha$  and CuK $\alpha$  respectively. Peak at 2.34keV indicate the presence of sulphur whereas the presence of oxygen was confirmed by the peak at 0.52keV corresponds to CuK $\alpha$  and presence of carbon provides peak at 0.28keV of CuK $\alpha$ . Peak at 0.39keV corresponds to nitrogen.

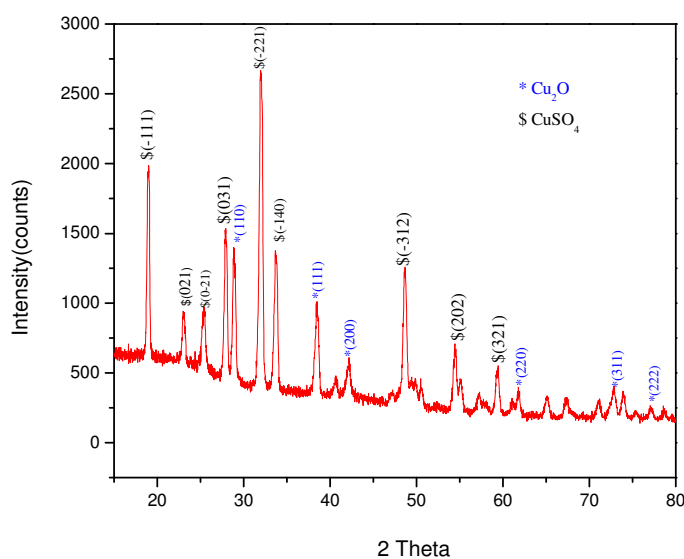


**Fig.4** EDS Spectra of CuPVPNNMBA

Inductively coupled Atomic Emission Spectroscopy (ICP-AES) also supports the EDX result which substantiates that the 1.23wt% of copper impregnated on the polymer support.

### 3.4.3 Powder X-ray diffraction

The X-ray diffraction pattern provides information about the phases, unit cell dimensions, orientation and chemical composition of the sample. X-ray diffraction is a non-destructive analytical technique, which produces monochromatic X-rays as a result of bombardment of accelerated electron with heavy metals like Cu. XRD pattern of CuPVPNNMBA given in **Fig.5**. The XRD pattern confirms the presence of copper in both oxidation state +1 and +2 in the polymer and its existence as  $\text{Cu}_2\text{O}$  and  $\text{CuSO}_4$ , supporting the EDX result. The major peaks at  $28.8^\circ$ ,  $38.4^\circ$ ,  $42.1^\circ$ ,  $61.8^\circ$  and  $73.6^\circ$  are related to the corresponding (110), (111), (200), (220) and (311) planes of  $\text{Cu}_2\text{O}$  (Cubic, JCPDS Card No. 05-0667). Peaks at  $2\theta = 18.9$ , 23, 25.4, 27.9, 32, 33.7, 48.7, 54.4 and  $59.3$  can be assigned to (-111), (021), (0-21), (031), (-221), (-140), (-312), (202) and (321) phases of  $\text{CuSO}_4$  respectively (triclinic, JCPDS File No. 77-1900).

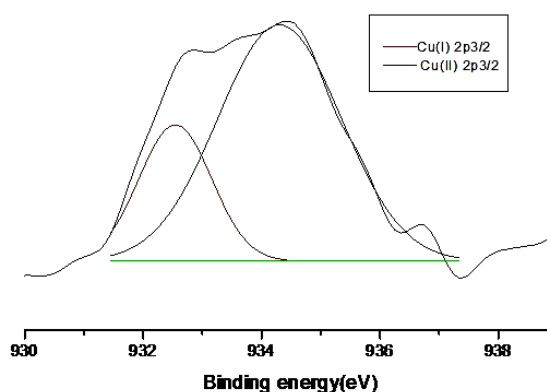


**Fig.5** XRD pattern of CuPVPNNMBA

### 3.4.4 X-ray photoelectron spectroscopy

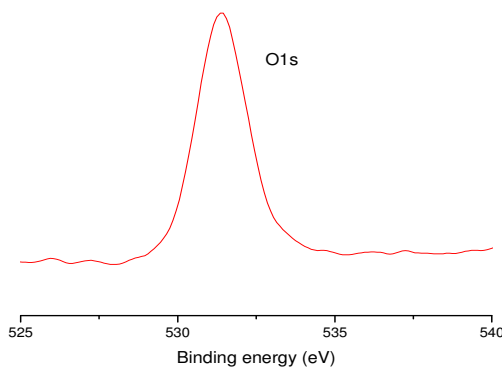
X-ray photoelectron spectroscopy can be used for the detection and quantification of elements present in a sample. When the sample surface was irradiated with beam of X-rays commonly Al K $\alpha$  or Mg K $\alpha$ , core level electrons absorb the energy and get ejected. The outer electron fills the vacancy created by the core electron. During this process energy is emitted and the instrument measures this energy. In the present study the sample was characterized by XPS technique and confirms the presence of both Cu<sup>+</sup> and Cu<sup>2+</sup>. **Fig.6.1** XPS spectra of Cu 2p core level spectra of CuPVPNNMBA. Spin orbit doublet of Cu 2p core level produces two states 2p<sub>3/2</sub> and 2p<sub>1/2</sub>. Following conclusions have been made:

- The Cu (2p<sub>3/2</sub>) analysis reveals the presence of peak at 934.3eV which arises due to the ligand to metal charge transfer during the photoemission process and accompanying with weak satellite peaks at 940.4, 941.8, 943.1 eV due to 3d<sup>9</sup>L configuration,<sup>74</sup> confirms the presence of Cu<sup>2+</sup>. Peak at 953eV corresponds to Cu (2p<sub>1/2</sub>) level.
- The satellite peaks are found to be 6-10eV greater than the core level peak.
- The main Cu 2p<sub>3/2</sub> peak at 932.5 eV and its corresponding weak satellite peak at 948.9 eV indicate the presence of Cu<sup>+</sup>. The presence of such weak satellite peak was explained by Harmer that it could be from the minor contributions from Cu d<sup>9</sup> initial state configuration<sup>75</sup>.
- Area under the curve indicates that Cu(I) and Cu(II) are present in approximate ratio 1:2



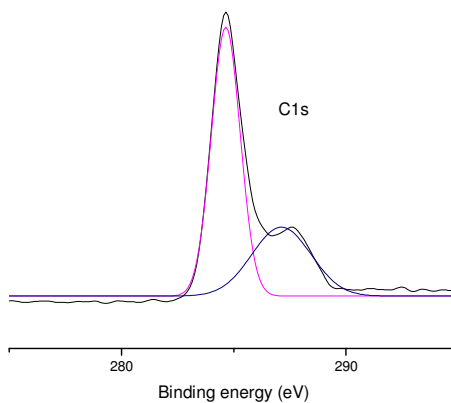
**Fig 6.1** Cu2p core level spectra of CuPVPNNMBA

- O1s Peak at 531.3 eV in XPS spectra confirms the presence of Cu<sub>2</sub>O (Fig.6.2).



**Fig 6.2** O1s XPS spectra of CuPVPNNMBA

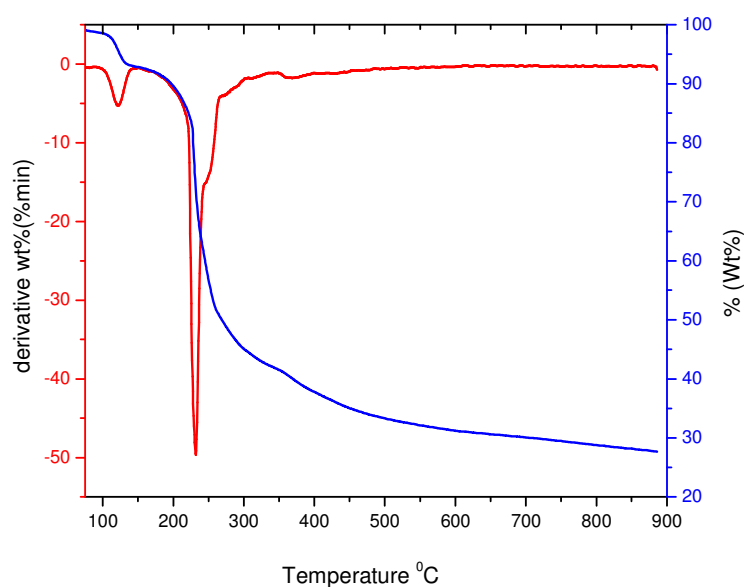
- The C1s spectra contains two major peaks; one at 284.6eV corresponds to polymeric hydrocarbons whereas the second one at 287.1eV belongs to C-OH<sup>76</sup> (Fig 6.3).



**Fig 6.3** C1s XPS spectra of CuPVPNNMBA

### 3.4.5 Thermogravimetric analysis

Thermal stability and decomposition pattern of cross linked polymers were studied using thermogravimetric analysis. The TG and DTA curve of 4mol% NNMBA cross-linked polyvinylpyrrolidone was examined and shown in Fig 7. It shows that the sample is stable up to 232°C. Initial weight loss at 121°C represents loss of water, solvent etc.



**Fig.7** TG and DTA curve of CuPVPNNMBA

The first stage of decomposition occurs from 100°C to 138°C with a weight loss of 5.18% due to the extrusion of absorbed and coordinated water molecules. The second stage starts at 185°C and continued up to 265°C. In this region, 49.4% weight loss occurs due to the rupture of polymer copper coordination bonds. Rupture of cross linking and polymeric linkages occurs from 337°C to 396°C with a weight loss of 1.73%.

### 3.5 Synthesis of 1,4-disubstituted 1,2,3-triazole using CuPVPNNMA as heterogeneous catalyst

Heterogeneous catalysts gained more attention in catalysis chemistry because of easiness in handling, reusability and recyclability. Girard and coworkers were the first to report the heterogeneous version of copper catalyzed azide-alkyne cycloaddition.<sup>77</sup> They used CuI immobilized on Amberlyst A-21 with dimethyl-aminomethyl functionality which can act as both chelating agent as well as base. To date there were enormous heterogeneous copper catalysts reported for the click reaction including those supported over biomaterials, dendrimers, mesoporous silica, magnetite etc.

Here, the catalytic activity of prepared CuPVPNNMBA was investigated in CuAAC using alkyl/ aryl halides, alkynes and sodium azide. Optimization of reaction conditions like temperature, catalyst loading, and solvent were studied by carrying out the reaction between benzyl chloride, sodium azide and phenyl acetylene (Scheme 13). Table 2 shown below represents the solvent, catalyst amount and temperature optimization studies.

**Table 2.** Optimization of the reaction conditions for the reaction of benzyl chloride, sodium azide and phenyl acetylene



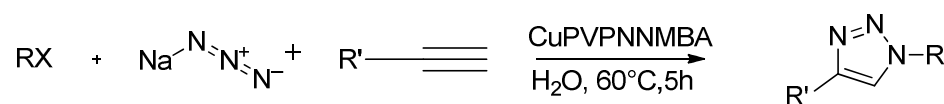
**Scheme 13**

Entry	Catalyst loading	Solvent	Temperature	Yield %
1	10mg	<sup>t</sup> BuOH	rt	70
2	10mg	Ethanol	rt	65
3	10mg	THF	rt	84
4	10mg	THF/H <sub>2</sub> O	rt	92
5	10mg	H <sub>2</sub> O	rt	92

<b>6</b>	10mg	H <sub>2</sub> O	60°C	97
<b>7</b>	20mg	H <sub>2</sub> O	60°C	98
<b>8</b>	5mg	H <sub>2</sub> O	60°C	88
<b>9</b>	No catalyst	H <sub>2</sub> O	60°C	Nil
<b>10</b>	10mg	CH <sub>3</sub> CN	rt	78
<b>11</b>	10mg	DCM	rt	75
<b>12</b>	10mg	DMF	rt	60

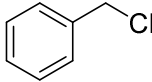
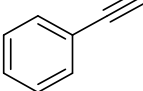
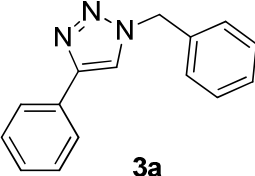
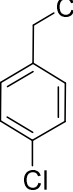
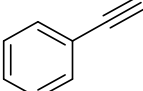
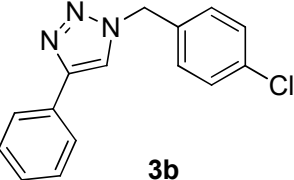
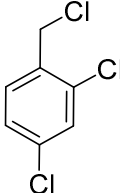
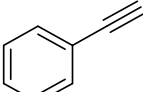
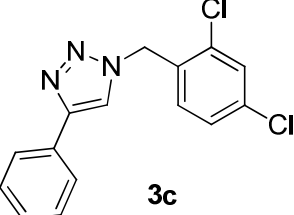
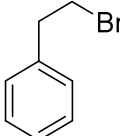
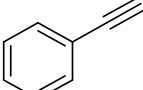
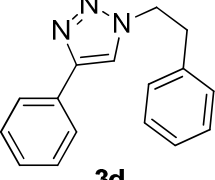
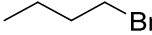
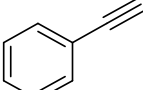
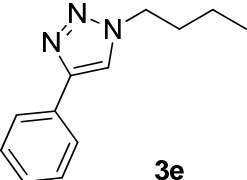
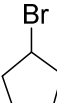
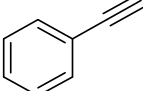
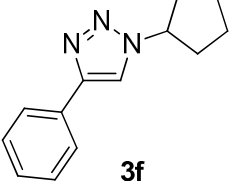

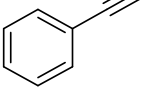
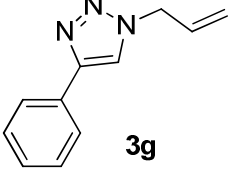
Reagents used: benzyl chloride(1 mmol), NaN<sub>3</sub> (1.5 mmol), phenyl acetylene (1.5 mmol) and solvent (5 ml)

To explore the effect of catalyst amount on the conversion yield, the catalyst loading was increased from 5 to 20 mg. At room temperature, using 10mg of the catalyst in different solvents such as DMF, acetonitrile, DCM, THF, ethanol, *t*-butanol afforded low yield of the product compared to water. By increasing the reaction temperature to 60 °C in water provides better yield. Thus, an optimum condition of 10 mg of catalyst loading in water as solvent at 60 °C, the triazole was obtained in 97% yield (**Table 2, entry 6**). Increasing the amount of catalyst to 20 mg doesn't make any significant improvement while decreasing the catalyst amount to 5 mg reduced the yield of products (**Table 2, entry 7& 8**). In the absence of catalyst there was no sign of formation of the product 1-benzyl-4-phenyl-1H-1,2,3-triazole. Having the optimized reaction conditions in hand, the scope of this catalyst in triazole synthesis was studied using different alkyl/aryl halides with sodium azide and phenyl/*p*-tolylacetylene in water at 60 °C (**Table 3**). The product was extracted using ethyl acetate, dried using Na<sub>2</sub>SO<sub>4</sub>. Solvent was removed under vacuum and the product was further purified by simple recrystallization from ethanol.

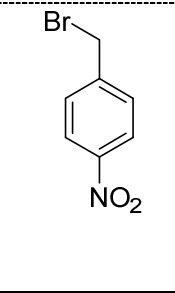
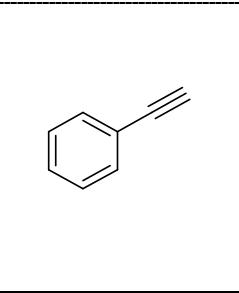
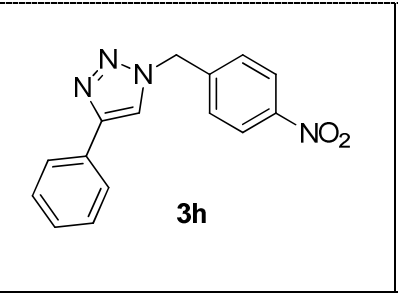
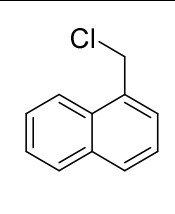
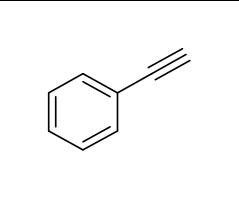
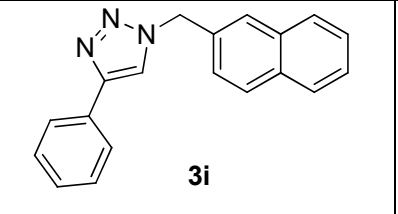
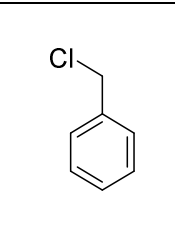
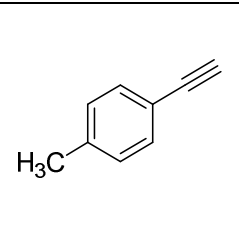
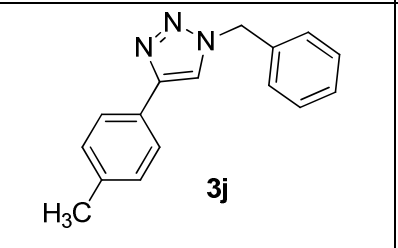
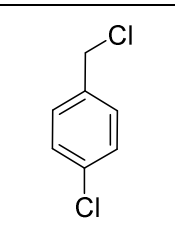
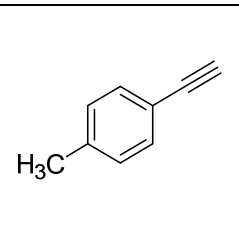
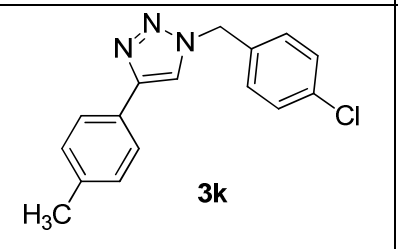
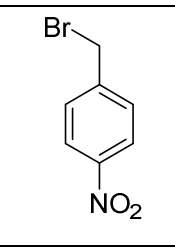
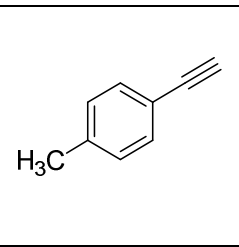
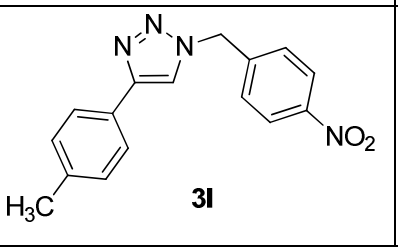
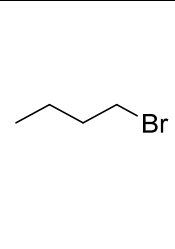
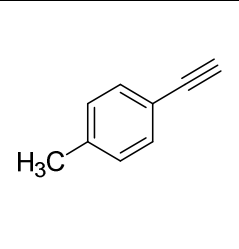
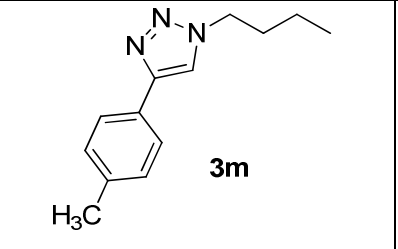


**Scheme 14**

**Table 3.** Synthesis of 1,4-disubstituted 1,2,3-triazoles with different halides and alkynes\*

Sl No.	RX	R'	Product	Yield(%)
1			 <b>3a</b>	97
2			 <b>3b</b>	94
3			 <b>3c</b>	92
4			 <b>3d</b>	97
5			 <b>3e</b>	88
6			 <b>3f</b>	82
7			 <b>3g</b>	92



8			 <b>3h</b>	96
9			 <b>3i</b>	90
10			 <b>3j</b>	93
11			 <b>3k</b>	95
12			 <b>3l</b>	93
13			 <b>3m</b>	88

Reagents and conditions: organic halide(1 mmol),  $\text{NaN}_3$  (1.5 mmol), alkyne (1.5 mmol) and CuPVPNNMBA (10 mg) in water (5 ml) temperature 60 °C, time 5h

In 2010, Hein and Fokin reported the generation of organic azide by an *in situ*  $\text{S}_\text{N}^2$  reaction between organic halide and sodium azide which was immediately used in the cycloaddition reaction with copper acetylide to yield triazole.<sup>78</sup> Presence of substituents in both organic azide and alkyne may influence the yield of product to

some extent. Electron withdrawing group slightly reduces the yield in which chlorine displays more compared to nitro group (**Table 3, entry 2,3 & 8**). Alkyl azides are less reactive compared to aryl azides (**Table 3, entry 5 & 6**). Similarly, substituent on alkyne can also affects the yield of the reaction. Electron donating methyl group in *p*-tolylacetylene diminishes the yield compared to phenylacetylene (**Table 3, entry 10, 11 & 12**).

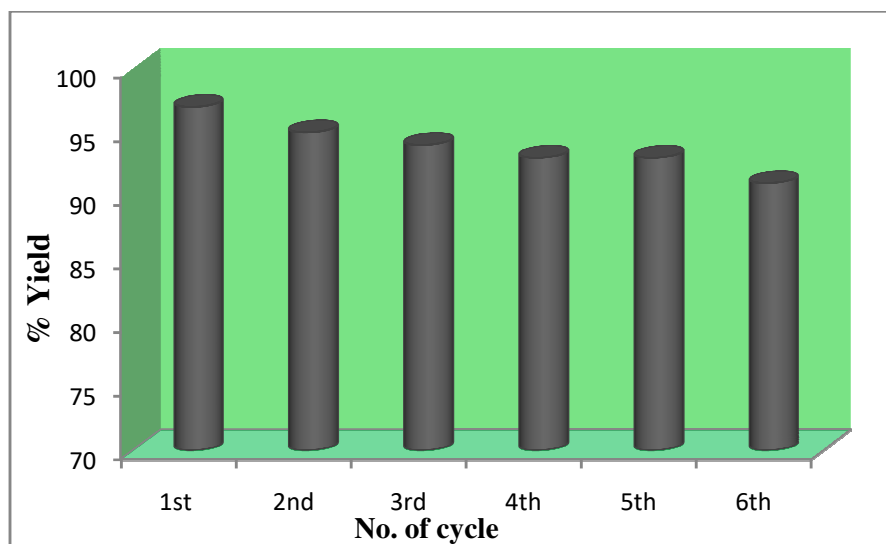
Recent reports have demonstrated the catalytic activity of mixed valence dinuclear copper catalyst in azide alkyne cycloaddition reaction.<sup>79,80</sup> During the catalytic process Cu(I) is oxidized to Cu(II) which in turn is reduced to Cu(I) by the PVP backbone and the catalytic cycle goes on.

The benefit of heterogeneous catalyst over homogeneous is the recyclability of the catalyst. This was examined using phenyl acetylene, benzyl chloride and sodium azide as model reactants under the same reaction conditions discussed above. After the 1<sup>st</sup> run the catalyst in the aqueous layer recovered by simple filtration and washed with ethanol and acetone and then dried in vacuum oven at 70 °C for 3 h before reuse. The residual catalyst was reused for five times (**Table 4**) and found no significant dampening in catalytic activity (**Fig. 8**).

**Table 4.** Reusability of CuPVPNNMBA

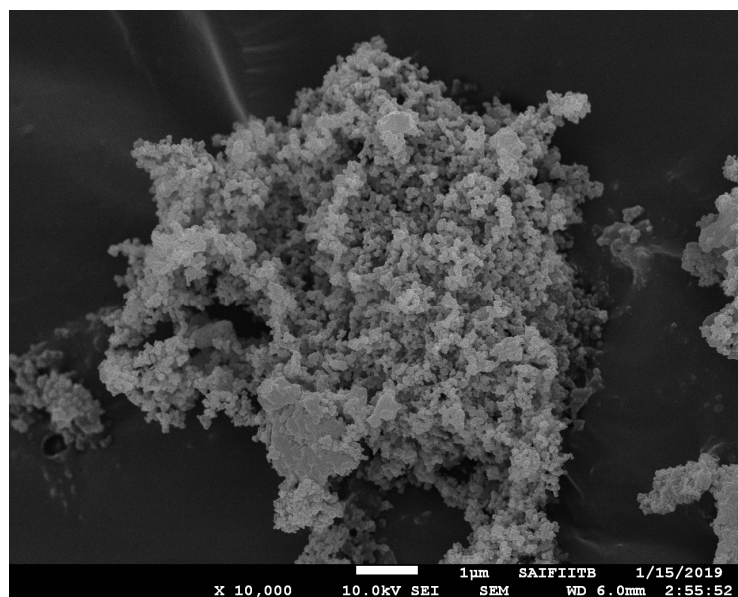
Cycle	Yield (%)
Native	97
1	95
2	94
3	93
4	91
5	91

Reaction conditions: benzyl chloride(1 mmol), NaN<sub>3</sub> (1.5 mmol), phenyl acetylene (1.5 mmol) and CuPVPNNMBA (10 mg) in water (5 ml) at 60 °C for 5h

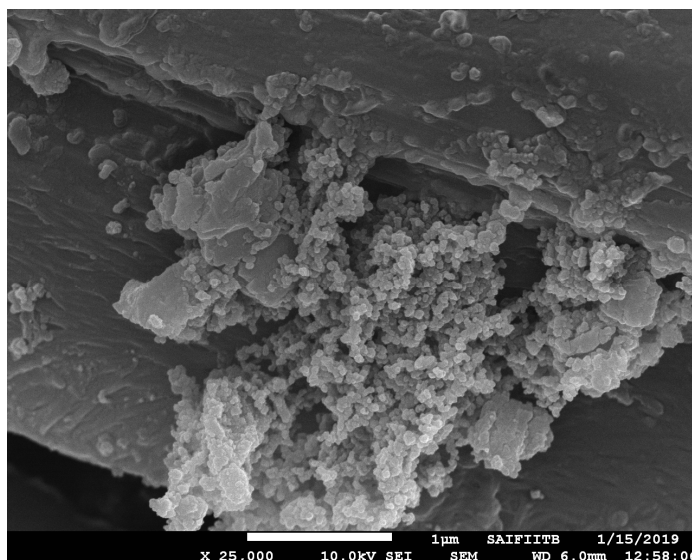


**Fig. 8** Reusability of the catalyst

To get more insight into the reused catalyst it was subjected to SEM and EDX characterization after 5<sup>th</sup> run. SEM image of the reused catalyst showed only slight change in morphology and composition relative to the original catalyst. (**Fig 9**)

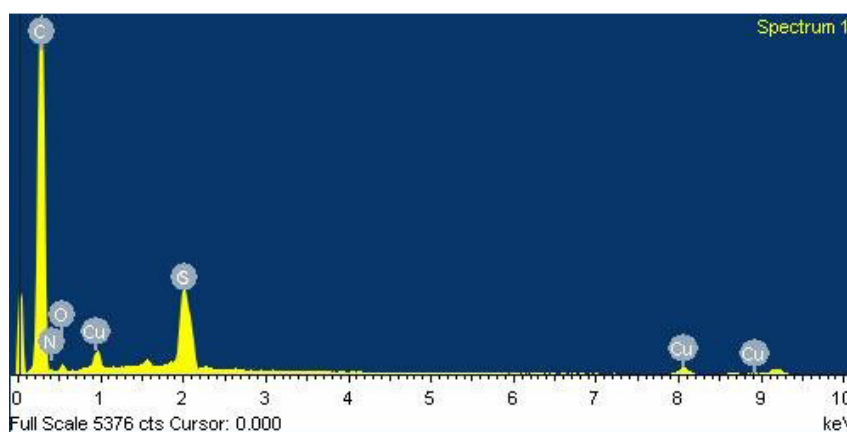


**Fig. 9** I SEM image of CuPVPNNMBA



**Fig 9 II** SEM image of reused catalyst

Copper in the original catalyst was found to be 1.23 wt% (**Fig 4**) while that in the reused one was found to be 1.22 wt% (**Fig 10**). This implies that there is any significant loss in the copper content after reuse.

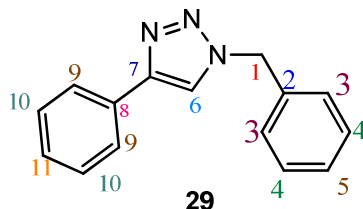


**Fig. 10** EDS spectrum of reused catalyst

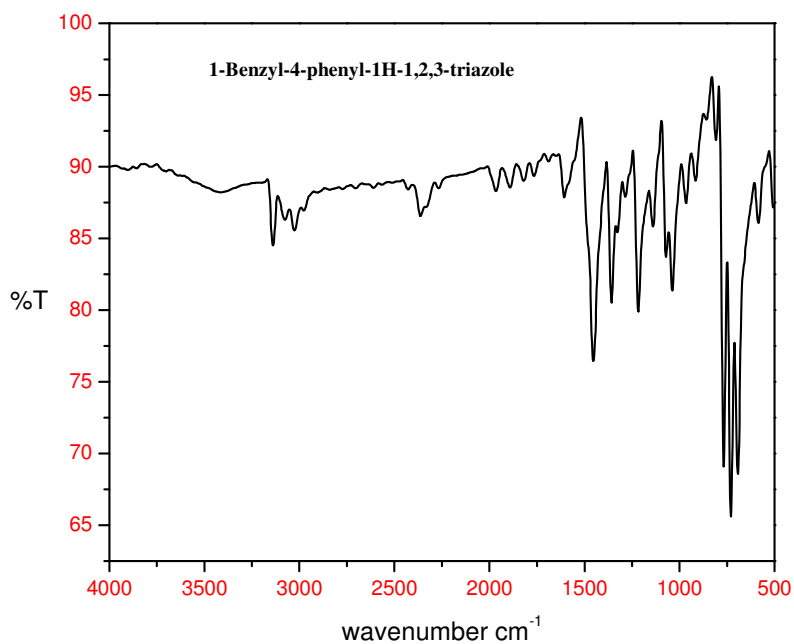
The scaling up of the reaction was carried out by increasing the amount of reactants by ten-fold keeping the same reaction conditions like temperature, solvent and catalyst loading. Using 10 mg of catalyst the 97% yield of product obtained only after 7 h whereas by increasing the catalyst loading to 20 mg can reduce the reaction time to 5 h to get same yield of the product.

### 3.6 Characterization of 1,4-disubstituted 1,2,3-triazoles

**1-Benzyl-4-phenyl-1H-1,2,3-triazole (29)** was taken as a representative molecule for the general discussion.



The FT-IR spectrum of the triazole gives major absorptions at 1467, 1217, 806  $\text{cm}^{-1}$  corresponds to  $-\text{CH}_2$ ,  $\text{N}=\text{N}=\text{N}$ - and  $=\text{C}-\text{H}$  of the triazole ring (**Fig 11**).



**Fig11** FT-IR spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole

The structure of triazole was confirmed by  $^1\text{H}$  NMR spectrum (**Fig. 12**). The  $-\text{CH}_2$  proton of benzyl is observed as two proton singlet at  $\delta$  5.57. Protons at positions C3 and C5 provide multiplet at  $\delta$  7.25-7.32. The characteristic  $=\text{C}-\text{H}$  proton provides peak at  $\delta$  7.66. C4, C10 & C11 gives peak at  $\delta$  7.36-7.41 and C9 protons gives doublet at  $\delta$  7.79.

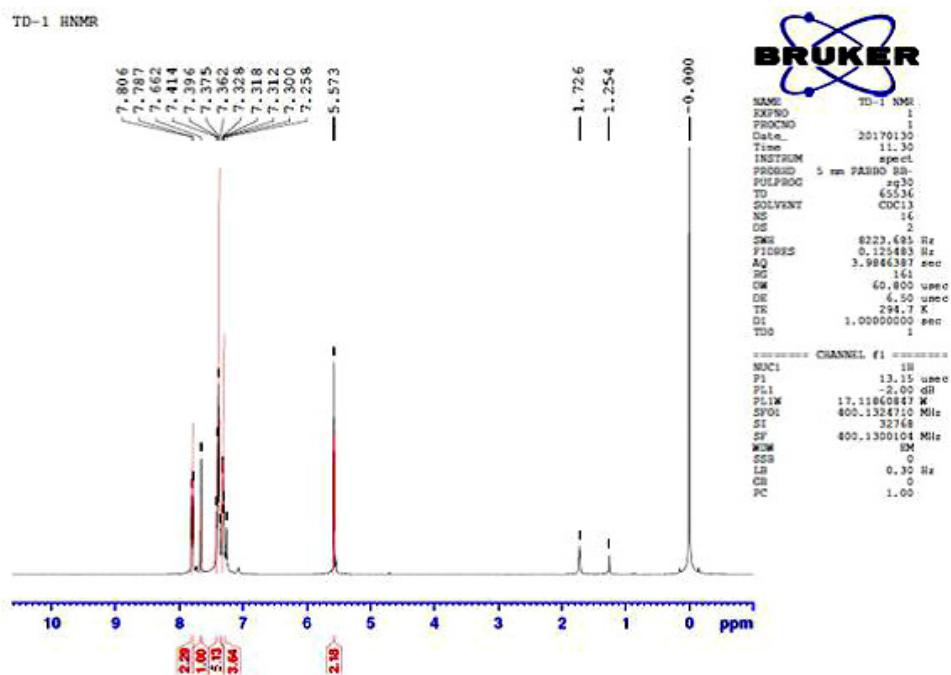
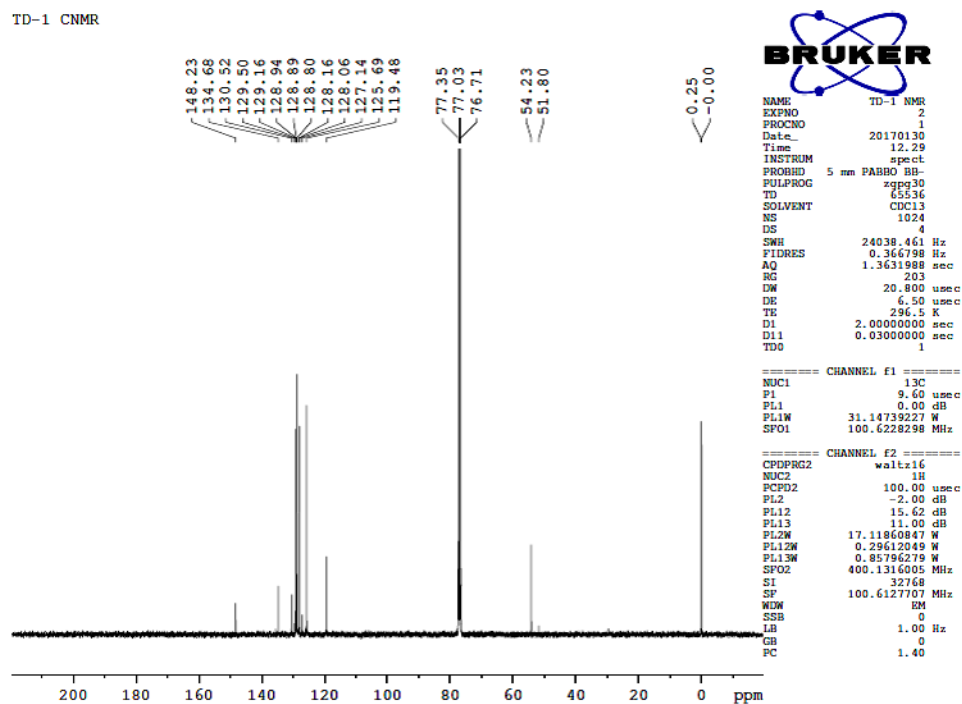


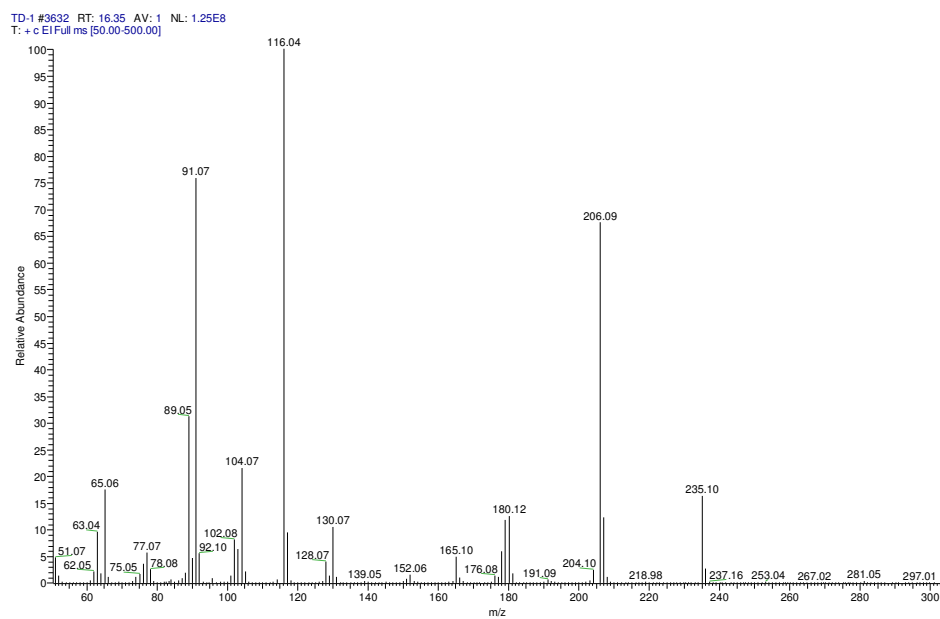
Fig 12  $^1\text{H}$  NMR spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole

The  $^{13}\text{C}$  NMR spectrum (Fig. 13) spectrum is in agreement with both  $^1\text{H}$  NMR and FT-IR data. The downfield peak at  $\delta$  148.2 is due to the carbon at the position C7. The characteristic peak of triazole carbon (C6) that is directly bonded to hydrogen was observed at  $\delta$ 119.4 confirming the formation 1,4-disubstituted triazoles.<sup>81</sup> The benzylic carbon C1 gives peak at  $\delta$ 54.2 and the values at 134.6, 127.1, 128.1, and 128.9 attributed to the benzyl carbons C2, C3, C4 and C5 carbons. The signal at 130.5 corresponds to the phenyl carbon C8 that is connected to the triazole ring. Other peaks at 125.6, 129.1 and 129.5 belong to ortho, meta and para carbons of phenyl ring.



**Fig 13**  $^{13}\text{C}$  NMR spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole

The structure of the compound was further confirmed by mass spectral analysis. In the mass spectrum, the molecular ion peak ( $M^+$ ) was observed at  $m/z$  235.08 (**Fig. 14**). The signal at  $m/z$  corresponds to  $M-N_2$  and the base peak at  $m/z$  116 & 91 belongs to  $M-C_8H_7N_2$  and  $M-C_8H_6N_3$  respectively.

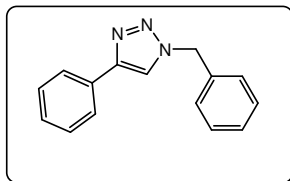


**Fig. 14** Mass spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole



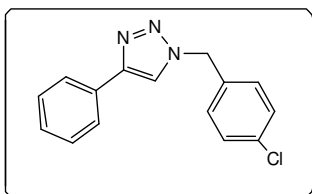
### 3.7 Spectral data of the triazoles synthesized

#### 1. 1-benzyl-4-phenyl-1*H*-1,2,3-triazole (3a)



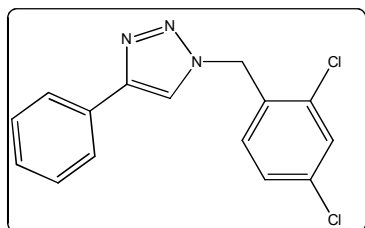
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.57(s,2H), 7.30-7.32 (m, 4H), 7.36-7.41 (m, 3H), 7.66(s, 1H), 7.79 (d, 2H,  $J=7.6\text{Hz}$ ).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  54.2, 119.4, 125.6, 127.1, 128.1, 128.9, 129.1, 129.5, 130.5, 134.6, 148.2. Mass  $m/z$  (%): 235 ( $\text{M}^+$ , 20), 116 (100), 91 (75), 206 (70). FTIR (KBr): 3139, 3024, 2362, 1606, 1452, 1216, 1037, 767, 727, 691,  $584\text{ cm}^{-1}$

#### 2. 1-(4-chlorobenzyl)-4-phenyl-1*H*-1,2,3-triazole (3b)



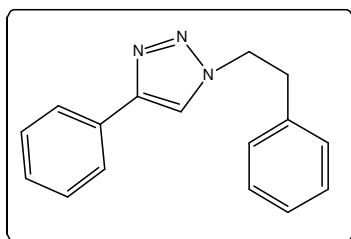
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.53(s,2H), 7.23(d,3H,  $J=7.2\text{Hz}$ ), 7.41-7.34(m,6H), 7.88(s,1H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  53.4, 119.4, 125.7, 128.2, 128.8, 129.3,130.3, 132,133.2, 134.8, 148.4. Mass  $m/z$  (%): 269 ( $\text{M}^+$ , 10), 271 ( $\text{M}^{++2}$ , 4), 116 (100), 125(44). FTIR (KBr): 3107, 3082, 3064, 3034, 2933, 1492, 1462, 1411, 1350, 1220, 1143,1091, 1080, 1016, 975, 819, 804, 763, 688,  $495\text{ cm}^{-1}$

#### 3. 1-(2,4-dichlorobenzyl)-4-phenyl-1*H*-1,2,3-triazole (3c)



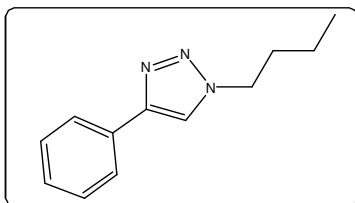
$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.67 (s 2H), 7.16 (s, 1H), 7.25–7.46 (m, 4H), 7.88 (s, 3H).  $^{13}\text{C}$  NMR (100.6MHz,  $\text{CDCl}_3$ )  $\delta$ : 50.8, 119.8, 125.7, 127.9, 128.2, 128.8, 129.7, 130.3, 131,131.3, 134.1, 135.5, 148.2; Mass  $m/z$  (%): 303 ( $\text{M}^+$ , 5), 305 ( $\text{M}^{++2}$ , 3), 240, 158, 116 (100).

## 4. 4-phenyl-1-(2-phenylethyl)-1H-1,2,3-triazole (3d)



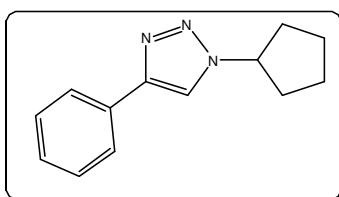
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.24 (t, 2H,  $J = 7.2\text{Hz}$ ), 4.62 (t, 2H,  $J = 7.6\text{Hz}$ ), 7.13 (d, 1H,  $J=6.8$ ), 7.25–7.30 (m, 3H), 7.39 (t, 2H,  $J = 7.2\text{Hz}$ ), 7.48 (s, 1H), 7.76 (d, 2H,  $J = 6.8\text{Hz}$ ).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ )  $\delta$ : 51.7, 36.8, 119.8, 120.0, 125.7, 127.1, 128.1, 128.7, 128.8, 130.7, 137.1, 147.5. Mass  $m/z$  (%): 249 ( $\text{M}^+$ , 35), 220 (18), 193 (13), 179 (8), 130 (34), 118 (71), 105 (100), 77 (42), 51 (8). FTIR (KBr): 3107, 3028, 1683, 1483, 1450, 1365, 1220, 1080, 1043, 94, 910, 844, 734, 690  $\text{cm}^{-1}$

## 5. 1-Butyl-4-phenyl-1H-1,2,3-triazole (3e)



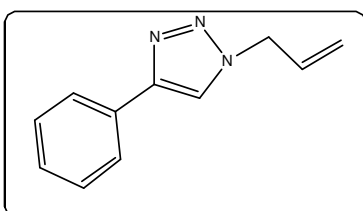
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.96 (t, 3H,  $J = 7.2\text{Hz}$ ), 1.36–1.41 (m, 2H), 1.90–1.94 (m, 2H), 4.39 (t, 2H,  $J = 7.2\text{Hz}$ ), 7.33 (d, 1H,  $J=7.2\text{Hz}$ ), 7.41 (t, 2H,  $J=7.2\text{Hz}$ ), 7.74 (s, 1H), 7.83 (d, 2H,  $J=7.2\text{Hz}$ ).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.4, 19.7, 32.3, 50.1, 119.4, 125.6, 128.0, 128.8, 130.7, 147.8. Mass  $m/z$  (%): 201 ( $\text{M}^+$ , 33), 145 (16), 117 (100), 90 (24). FTIR (KBr): 3062, 2947, 2870, 1460, 1367, 1215, 1066, 761, 692  $\text{cm}^{-1}$

## 6. 1-Cyclopentyl-4-phenyl-1H-1,2,3-triazole (3f)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.76–1.8 (m, 2H), 1.91–1.95 (m, 2H), 2.05–2.12 (m, 2H), 2.26–2.31 (m, 2H), 4.94–5.01 (m, 1H), 7.31 (t, 1H,  $J = 7.2\text{Hz}$ ), 7.39 (m, 2H), 7.82 (s, 1H), 7.83 (dd, 2H,  $J=7.7, 1.55$ ).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  24.1, 33.4, 61.8, 118.0, 125.6, 128.0, 128.7, 130.8, 147.5. Mass  $m/z$  (%): 213 ( $\text{M}^+$  33), 184, 156, 117 (100).

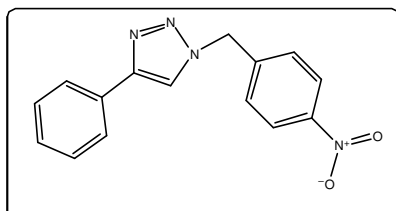
## 7. 1-Allyl-4-phenyl-1H-1,2,3-triazole (3g)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.02 (dd, 1H,  $J = 16.4\text{Hz}$ ), 5.36 (dd, 1H,  $J= 10\text{Hz}$ ), 6.01–6.11 (m, 1H),

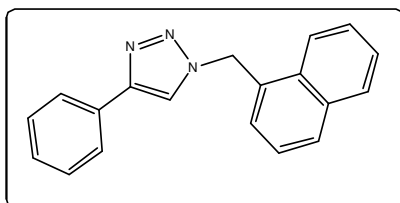
7.31–7.44 (m, 3H), 7.76 (s, 1H), 7.83(d, 2H,  $J = 7.6\text{Hz}$ ).  $^{13}\text{C}$  NMR(100.6MHz,  $\text{CDCl}_3$ ):  $\delta$  52.7, 119.4, 120.2, 125.7, 128.1, 128.8, 130.5, 131.3, 148.0. Mass  $m/z(\%)$ : 185( $\text{M}^+$ , 19), 116(100). FTIR (KBr): 3120, 3088, 2934, 2854, 1645, 1608, 1460, 1334, 1219, 1166, 1049. 985, 914, 825, 765, 690, 509  $\text{cm}^{-1}$

#### 8. 1-(4-Nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (3h)



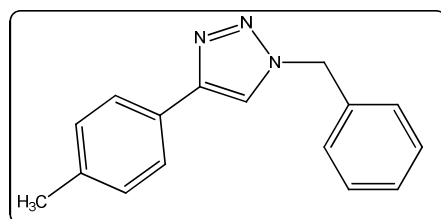
$^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.69 (s, 2H), 7.34–7.45(m,5H), 7.76(s, 1H), 7.80(d, 2H,  $J = 7.6\text{Hz}$ ), 8.22(d, 2H,  $J = 8\text{Hz}$ ).  $^{13}\text{C}$  NMR (100.6MHz, $\text{CDCl}_3$ ):  $\delta$  53.1, 119.7, 124.3, 125.7, 128.5, 129.2,129.9, 130.0, 141.7, 148.07,148.7. Mass, $m/z$  (%): 281 ( $\text{M}^+$ , 19), 207 (44), 116 (100), 106 (24), 89 (43). FTIR (KBr): 3118, 3080, 2939, 2857, 1600, 1517, 1429, 1346, 1209, 1107, 1074, 1305, 844, 815, 761, 729, 686  $\text{cm}^{-1}$

#### 9. 1-(Naphthyl)-4-phenyl-1H-1,2,3-triazole (3i)



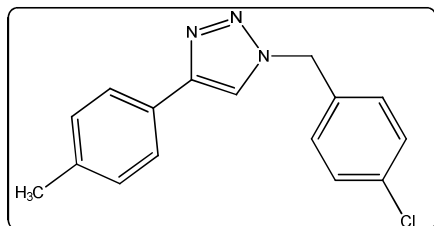
$^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.91(s, 2H), 7.37–7.44 (m, 5H), 7.65 (m, 2H),7.81 (m, 2H), 7.90 (m, 3H) 7.91 (s, 1H).  $^{13}\text{C}$  NMR (100.6MHz,  $\text{CDCl}_3$ ):  $\delta$  52.5,119.7, 122.9, 125.4, 125.7, 126.4, 126.7, 127.9, 128.2, 129.2, 129.7, 130.1, 130.2, 131.2,131.94, 133.96. Mass  $m/z$  (%): 284 ( $\text{M}^+$ , 5), 253 (10), 207 (98), 115 (90), 84(100). FTIR (KBr); 3115, 2924, 2848, 1454, 1431, 1344, 1307, 1211, 114, 1080, 1037, 974, 912, 842, 771, 688  $\text{cm}^{-1}$

#### 10. 1-(Benzyl)-4(p-tolyl)-1H-1,2,3-triazole (3j)



$^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.38 (s, 3H), 5.58 (s, 2H), 7.22 (d, 2H,  $J = 7.6\text{Hz}$ ), 7.32–7.41(m, 5H), 7.66 (1H, s), 7.71 (d, 2H,  $J = 8.4\text{Hz}$ ).  $^{13}\text{C}$  NMR (100.6MHz,  $\text{CDCl}_3$ ):  $\delta$  148.14, 138.18, 134.62,129.52, 129.17, 128.82, 128.1, 127.41, 125.68, 54.33, 21.33. Mass  $m/z$  (%): 249( $\text{M}^+$ , 15),220(63), 130(100), 91(72), 77(18) FTIR (KBr): 3138, 3008, 2902, 1446, 1342, 1213, 1122, 1045, 968, 788, 713, 584, 512  $\text{cm}^{-1}$

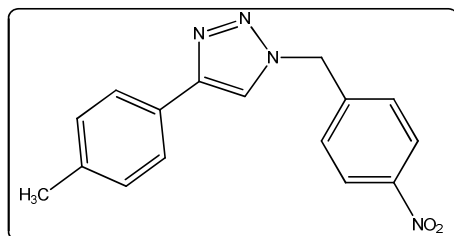
## 11. 1-(4-Chlorobenzyl)-4-(p-tolyl)-1H-1,2,3-triazole (3k)



$^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.38 (s, 3H), 5.55 (s, 2H), 7.22-7.28(m,3H) 7.37(d,2H,  $J= 8.4\text{Hz}$ ), 7.67 (s, 1H), 7.71 (d, 2H,  $J=8\text{Hz}$ ) $^{13}\text{C}$  NMR (100.6MHz,

$\text{CDCl}_3$ ):  $\delta$  21.3, 53.5, 125.68, 127.2,129.3, 129.4, 129.5, 133.1, 134.8, 138.3, 148.3. Mass  $m/z$  (%): 283 ( $\text{M}^+$ , 12), 254 (35), 130(100). FTIR (KBr): 3113, 3012, 2953,1485, 1436, 1334, 1207, 1080, 1033, 808, 750, 507  $\text{cm}^{-1}$

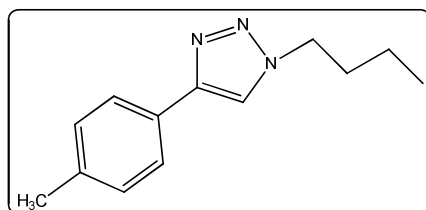
## 12. 1-(4-Nitrobenzyl)-4-(p-tolyl)-1H-1,2,3-triazole (3l)



$^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.39 (s, 3H), 5.71 (s, 2H), 7.24 (d, 2H,  $J = 7.6\text{Hz}$ ), 7.46 (d,2H,  $J = 8.4\text{Hz}$ ), 7.72 (d, 2H,  $J = 8\text{Hz}$ ), 7.77 (s, 1H) 8.24 (d, 2H,  $J$

$= 8.4\text{Hz}$ ).  $^{13}\text{C}$  NMR(100.6MHz,  $\text{CDCl}_3$ ):  $\delta$  21.3, 53.2, 124.3, 125.74, 126.9, 128.6, 129.64, 138.6, 141.6, 148.1. Mass  $m/z$  (%): 294( $\text{M}^+$  9), 281 (25), 207 (70), 130 (100). FTIR (KBr): 3088, 3034. 2924, 2856, 1602, 1516, 1444, 1344, 1213, 1101, 1039, 972, 810, 723, 513  $\text{cm}^{-1}$

## 13. 1-Butyl-4-(p-tolyl)-1H-1,2,3-triazole (3m)



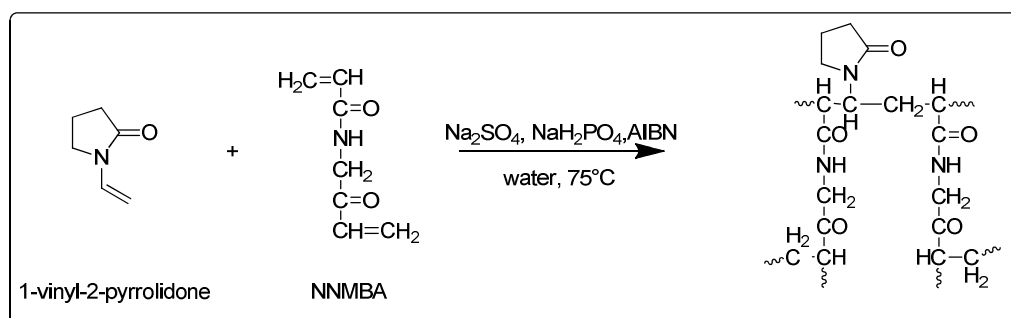
$^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.89 (t, 3H,  $J= 7.2\text{Hz}$ ), 1.29-1.34 (m, 2H), 1.87 (m,2H), 2.30 (t, 3H,  $J=6.4\text{Hz}$ ), 4.34

(s,3H),7.06-7.18(m, 3H), 7.33 (m,2H), 7.73(s,1H). $^{13}\text{C}$  NMR (100.6MHz,  $\text{CDCl}_3$ ):  $\delta$  13.4, 19.7,21.3, 32.2, 50.62, 118.7, 125.6, 127.5, 129.2, 132.3, 138.2. Mass  $m/z$  (%): 215 ( $\text{M}^+$ , 40), 159(30), 144 (35), 131(100).

### 3.8 Experimental details

#### 3.8.1 Synthesis of 4mol% NNMBA crosslinked polyvinylpyrrolidone (PVPNNMBA)

A solution of  $\text{NaH}_2\text{PO}_4$  (0.43 g) and  $\text{Na}_2\text{SO}_4$  (20 g) in 120 ml water was heated to 70 °C with stirring for 15 min. Nitrogen gas was purged through the solution for 10 min followed by the addition of monomer pyrrolidone (5.4 g), NNMBA (0.752 g) and initiator AIBN(100 mg). Heating and stirring was continued for 5 h at 75 °C (**Scheme 15**). The reaction mixture was then cooled to room temperature and the product was filtered, washed with water and acetone dried in vacuum oven at 60 °C to afford the polymer beads. They were further purified by soxhlet extraction using acetone: methanol (1:1) mixture and sieved to 120-200 mesh size.



**Scheme 15** Synthesis of NNMBA crosslinked polyvinyl pyrrolidone

#### 3.8.2 Incorporation of copper into the polymer matrix

The cross linked polymer(1 g) was kept for swelling in glacial acetic acid (20 ml) for 5 h. Copper sulphate pentahydrate (1 g) dissolved in glacial acetic acid (15 ml) was added to the above mixture and heated at 80 °C for 1 h followed by refluxing for 4 h. The reaction mixture was cooled to room temperature and filtered, washed with water, ethanol and dried in vacuum oven at 60 °C.

### **3.8.3 General procedure for Azide-Alkyne Cycloaddition**

For the copper catalyzed azide alkyne cycloaddition reaction, organic halide(1 mmol), alkyne (1.5 mmol) and sodium azide (1.5 mmol) were taken in a 50 ml round bottom flask. To this water (5 ml) and the catalyst CuPVPNNMBA (10 mg) were added. The resulting reaction mixture was heated at 60 °C for 5 h and then cooled to room temperature. The product was extracted with ethyl acetate, dried and the solvent was removed under vacuum. Recrystallization from ethanol to afford 1,4-disubstituted 1,2,3-triazoles in excellent yields. These triazoles were characterized using <sup>1</sup>H NMR, <sup>13</sup>C NMR and GCMS analysis.

### **3.9 Conclusion**

We have synthesized NNMBA cross linked polyvinyl pyrrolidone by suspension polymerization of monomers *N*-vinyl pyrrolidone and NNMBA. The copolymer was then loaded with copper by treating with copper sulphate. Both the copolymer and its copper supported material have been fully characterized. From analysis, we observed that the polymer matrix contain both Cu(I) and Cu(II) in 1:2 ratio. The copper ions are *in situ* reduced by the PVP back bone which in turn is stabilized on the polymer matrix. The copper supported polymer material was found to be a good catalyst for one pot, multicomponent strategy towards the click reaction between azide, alkyne and halides to afford 1,4-disubstituted 1,2,3-triazoles in a regioselective manner and in excellent yields. The robustness of the catalyst includes (a) high catalytic activity, (b) cheapness, (c) easily recoverable and recyclability, (d) low catalyst loading and (e) resistance to oxidation on air and water.

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