

# Synthesis and Amphiphilic 4-Vinyl Pyridine and *n*-Vinyl Pyrrolidone Copolymer Beads

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**ABSTRACT:** Copolymer beads of 4-vinyl pyridine (4VP) and *n*-vinyl pyrrolidone (NVP) [Poly(4VP-*co*-NVP)] were synthesized by suspension polymerization with various compositions of 4VP:NVP (10:0, 9:1, 8:2, 7:3, 6:4, and 5:5). The spherical shape and the macroporous nature similar to the 4VP homopolymer was noticed in copolymers of 6:4 and 5:5, while others were nonporous. The copolymer beads were characterized by FTIR, NMR, SEM, TGA, and dilute solution viscosity. Equilibrium sorption percentages in water were proportional to the content of NVP in the copoly-

mer. The copolymers displayed higher Cu<sup>2+</sup> metal uptake capacity because of their amphiphilic nature. Such copolymer beads with higher ion chelating capacity and improved hydrophilicity may be more suitable for protein immobilization, catalysis, drug delivery etc. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 192–197, 2006

**Key words:** 4-vinylpyridine; *n*-vinyl pyrrolidone; copolymerization; metal-polymer complex; morphology; equilibrium sorption percentage

## INTRODUCTION

Increased attention is currently directed to the synthesis of polymers containing both hydrophilic and hydrophobic groups. The interest stems from the need to understand the stability and interactions they can offer, mainly because of the possibility of producing a chemically homologous series of surfaces varying principally in hydrophilicity. The copolymerization reaction is rather difficult because of the different solution behavior of the monomers. The properties of the copolymers depend not only on the nature of the comonomers but also on their overall composition. Copolymers containing NVP are of interest due to the water-soluble property of the parent homopolymer, and copolymers containing NVP and 4VP result in amphiphilicity depending on the monomer composition and their behavior in water. The presence of basic units of 4VP along the main chain is of particular interest due to the possibility of interpolymer hydrogen bonding interactions and chelating ability with metals.

The effect of hydrophobic unit on the solution properties of vinyl pyrrolidone and vinyl acetate copolymer<sup>1</sup> was studied by Yuanzhen and Phil, who found that the copolymer had shown more homogeneous nature with better solubility in water when the ratio of the copolymer was close to unity. Copolymers con-

taining 2VP/4VP with NVP were synthesized via bulk polymerization by Nicholas et al.<sup>2</sup> They estimated the reactivity ratios of the two monomers, using the classical Finemann Ross and Kele Tüdös linear procedure. Poly(4VP-*co*-NVP) was prepared by solution polymerization by Shengang et al.<sup>3</sup> The copolymer palladium complex was used as a homogeneous catalyst in hydrogenation of nitrobenzene and nitroanisole and was found to improve performance in comparison with the Poly(4VP)-Pd complex. Pd complexes of copolymers of 4VP and acrylic acid were also reported by the same authors and found that introduction of spacer units within pyridine units in the molecular chain through copolymerization leads to improved performance as a homogeneous catalyst owing to the decrease in the intermolecular chain interaction. However, the 4VP and NVP copolymers reported earlier were mostly synthesized either by solution or bulk polymerization methods and focused mainly on their performance.<sup>4</sup> Characterization, study of surface morphology, and solution properties of such polymers gives insight into the reasons for improved performance when applied in catalysis, protein immobilization etc.

In this paper, we have reported the synthesis and characterization of copolymer beads of 4VP and NVP by free radical suspension polymerization. The extent of hydrophilicity of the copolymers was estimated by studying the equilibrium sorption of water in different pH values. The surface morphology of the beads was studied in detail and the structures were correlated to the degree of amphiphilicity. Intrinsic viscosities of the polymers in methanol were determined. The cop-

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per metal uptake capacities were estimated in aqueous medium.

## EXPERIMENTAL

### Materials

4VP and NVP were purchased from Aldrich and purified by distillation under vacuum before polymerization. 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Reagent grade cyclohexane, methanol, copper sulfate, and poly vinyl pyrrolidone (PVP) were used as obtained from SD Fine Chemicals, India.

### Synthesis of P4VP and poly(4VP-co-NVP) polymer beads

Polymerizations were carried out by suspension polymerization method under nitrogen atmosphere. Into a four-neck resin kettle, fitted with a half moon Teflon blade agitator, nitrogen purge adapter and a reflux condenser, water with PVP (0.7%) and NaCl (7.5%) was taken. An organic phase consisting of a mixture of 4VP or 4VP and NVP in corresponding weight ratios, cyclohexane (100% of the monomers) and AIBN (1% of the monomers), was added dropwise into the aqueous phase (1:8, organic:aqueous) while operating the blade agitator at 200 rpm at room temperature. A drop of ammonia is added to the medium to maintain the basic pH. The basic pH of the medium and NaCl helps in keeping the NVP confined to the organic phase during the reaction. The temperature of the mixture was raised to 90°C and the reaction was carried out for 12 h. The resultant nonsticky beads were filtered and washed several times with hot water and then dried under vacuum at 60°C for 24 h.

### Instrumentation

Fourier transform infrared spectroscopy was performed on GC FTIR 740 NICOLET spectrophotometer for KBr pellets of the polymers. The compositions of the copolymers and their metal complexes were determined by BECKMANN DU 7400-UV-VIS Spectrophotometer in methanol by using respective calibration curves of 4VP and NVP. The Poly (4VP-co-NVP) copolymer and P4VP beads were mounted on aluminum stubs with double sided adhesive tape and gold coated and observed on Hitachi 5S 520 Scanning electron microscope under a high vacuum of 0.1 Torr and a high voltage of 1.2 kV. The viscosities of the polymer solutions were determined at 25°C with a 0.47 mm SCHOTT GERATE CT150 UBVELOHDE Viscometer. Thermogravimetric analysis was performed using the 851 Mettler Toledo TGA instrument. The samples were heated from RT to 500°C at a rate of 10°C/min

and a nitrogen purge was employed at a flow rate of 100 mL/min. The <sup>1</sup>H NMR spectra of 9:1 copolymer was done in deuterated methanol on GEMINI-200 Varian spectrophotometer.

### Swelling analysis

To determine the swelling percentage, 1 g of homopolymer and copolymer beads were put into aqueous solutions of pH 4.0, 7.0, and 9.0 at room temperature until equilibrium swelling percentage was attained. The wet weight of the swollen beads was determined by first blotting the beads with filter paper to remove surface water, and then weighed immediately on an electronic balance. The swelling percentage of the beads in the media was calculated as follows:

$$\text{Equilibrium swelling percentage} = \frac{W_t - W_i}{W_i} \times 100$$

Where,  $W_t$ , Weight of the sample at time  $t$  and  $W_i$ , Weight of the initial dry sample. Each swelling experiment was repeated three times and the average value was taken as the swelling percentage.

### Metal uptake capacity of the beads

The complex formation of the beads with  $\text{Cu}^{2+}$  ions was carried out by placing the known weight of the beads into a  $\text{CuSO}_4$  solution and allowed to equilibrate for 72 h. A calibration curve was made with Optical Density (OD) values of known concentration of  $\text{CuSO}_4$  solutions using UV-VIS spectrophotometer. The percentage of metal uptake by the polymer was estimated by subtracting the concentration of metal left in the filtrate solution after complex formation, using the calibration curve.

## RESULTS AND DISCUSSION

### Polymer synthesis and characterization

Amphiphilic copolymers were prepared by suspension polymerization of 4VP and NVP (Fig. 1). The copolymers with 4VP/NVP ratios of 9:1 (b), 8:2 (c), 7:3 (d), 6:4 (e), and 5:5 (f) were prepared with AIBN as the free radical initiator and cyclohexane as the diluent system. Cyclohexane dissolves the monomers/AIBN but not the polymer, resulting in its release from the beads causing porosity. A homopolymer, P4VP (a), was also prepared following the same procedure for comparative study. The copolymer synthesis is rather difficult due to the large difference in the reactivity ratios (4VP/NVP = 9.06:0.05).<sup>2</sup> Nevertheless, their synthesis by bulk<sup>2</sup> and solution polymerization<sup>3</sup> methods, yielding powder samples, was reported. The

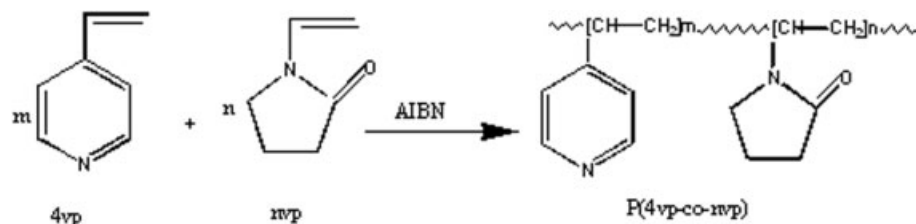


Figure 1 Schematic illustration for the synthesis of 4VP-NVP copolymer beads.

aqueous medium was maintained at pH 9 by addition of ammonia, and NaCl was added to keep the suspension stable and to reduce the monomer (NVP) from escaping into the aqueous medium.<sup>5</sup> UV-Vis spectroscopic data confirmed the composition of the copolymers to be close to the feed ratio. The comonomer feed ratios, and yield percentages are listed in Table I. Figure 2 (curves a–e) shows the IR-spectra of the Poly(4VP-co-NVP) copolymers, wherein the bands at 1593, 1554, 1491, and 1412  $\text{cm}^{-1}$  are assigned to the characteristic vibrations of the pyridine ring<sup>6</sup> and the band at 1665  $\text{cm}^{-1}$  is assigned to that of C=O of the pyrrolidone ring. An additional band at 1665  $\text{cm}^{-1}$  present in all the copolymers confirms the copolymerisation [Fig. 2(a)]. The increase in the intensity of the band was proportional to the NVP content of the copolymer. A  $^1\text{H}$  NMR spectrum of 9:1 copolymer (Fig. 3) further confirms the copolymer formation even at the lowest concentration of NVP. The spectrum shows peaks at  $\delta = 8.2$  and 6.8 corresponding to 4VP protons and at  $\delta = 4.0$ , 3.3, and 2.2 for the protons of NVP. TGA curves of the copolymers are shown in Figure 3. Degradation occurs at 395°C in one degradation step and such a weight loss behavior also proves that the product is a copolymer and not a blend (Fig. 4).

### Morphology of the polymer beads

Normally, porogens or diluents that are inert to the polymer but soluble in the monomer mixture are used to obtain porous beads. The porous nature, shape, and the size of the beads could be best monitored with the

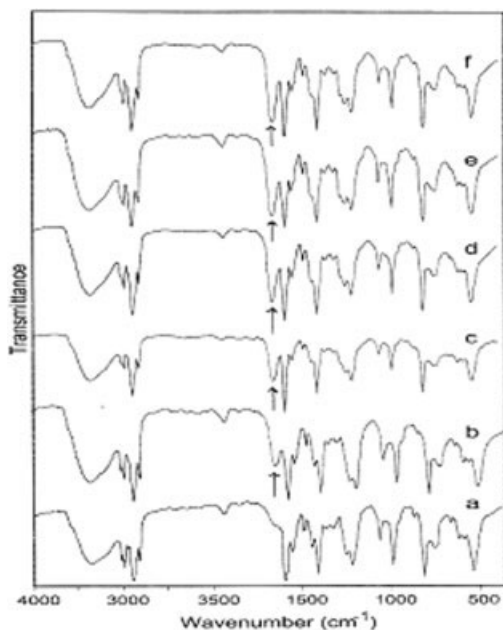
help of SEM [Figs. 5(a–f) and Figs. 6(a–f)]. The homopolymer (P4VP) beads are spherical with approximately 1 mm size, having pores of the order of  $\sim 5 \mu\text{m}$ . On copolymerization, the spherical shape is lost due to the appearance of globular extensions on the beads in b and c, which are slightly less for d, showing rough and fibrous surface. However, e and f copolymer beads were found to be spherical, similar to the homopolymer with a reduction in size to 250  $\mu\text{m}$  having porous and smooth surface. It is probably the incompatibility between the comonomers that results in extensions and a fibrous rough surface morphology on the beads,<sup>7</sup> which becomes smoother as the ratio of the monomers gets close to unity. The difference in the reactivity ratios of the comonomers may lead to initial copolymer containing a preponderance of 4VP until the majority of 4VP has been polymerized. The copolymer formed late in the polymerization might contain significantly higher levels of NVP. This would lead one to suggest that the core of the beads to be mostly 4VP and the shell of the beads mostly of NVP at a 5:5 feed ratio. We therefore propose that f copolymers might experience a kind of balance in the hydrophobic and hydrophilic forces in the aqueous medium, resulting in spherical shape, smooth surface, and porosity similar to the homopolymer.<sup>8</sup>

### Viscosity of the polymer dilute solutions

Intrinsic viscosities of the homopolymer and copolymers are measured by calculating the flow time of the dilute solutions in methanol and the results obtained are tabulated (Table I). The intrinsic viscosity was

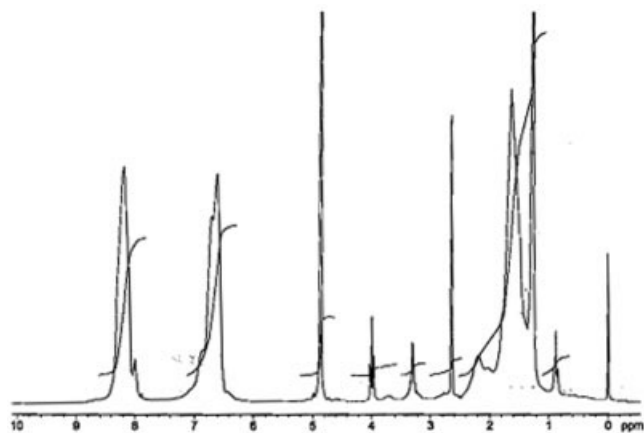
TABLE I  
Properties of the P(4VP) and Poly(4VP-co-NVP)

Polymer type	Monomer feed ratios (4vp:nvp)	% Yield	IR band intensity (C=C/C=O)	Intrinsic viscosity, $\eta$ ( $\text{dg}^{-1}$ )	Amount of Cu (II) complexed ( $10^{-3}$ g/mol/g)	% Swelling at pH 7 and RT
a	10:0	97	3.4	1.57	3.6	101
b	9:1	95	3.0	2.25	6.6	136
c	8:2	93	2.1	2.65	9.1	164
d	7:3	92	1.5	1.20	11.2	187
e	6:4	89	1.4	1.00	12.8	222
f	5:5	90	1.3	0.45	16.0	253

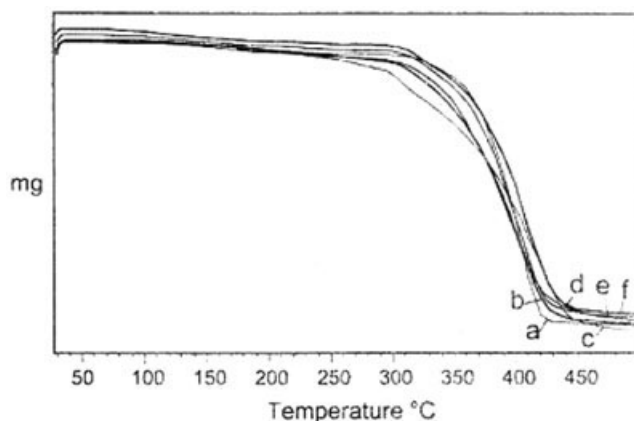


**Figure 2** FTIR Spectra of (a) P(4VP) and P(4VP-co-NVP), (b) 9:1, (c) 8:2, (d) 7:3, (e) 6:4, and (f) 5:5.

found to increase from the homopolymer a to c copolymers, indicating the enhanced polymer-solvent interactions causing an increase in the hydrodynamic volume of the polymer. The copolymers from d to f show a decrease in the intrinsic viscosity values as the ratio of the comonomers get close to unity, which could be due to improved homogeneity due to enhanced intramolecular interactions within the copolymer. Reduced viscosities<sup>9,10</sup> of these polymers in methanol behave similar to nonionic polymers following Flory Huggins equation. Such copolymers help maintain the viscosity of the medium during their application as homogeneous catalysts in alcoholic solvents.



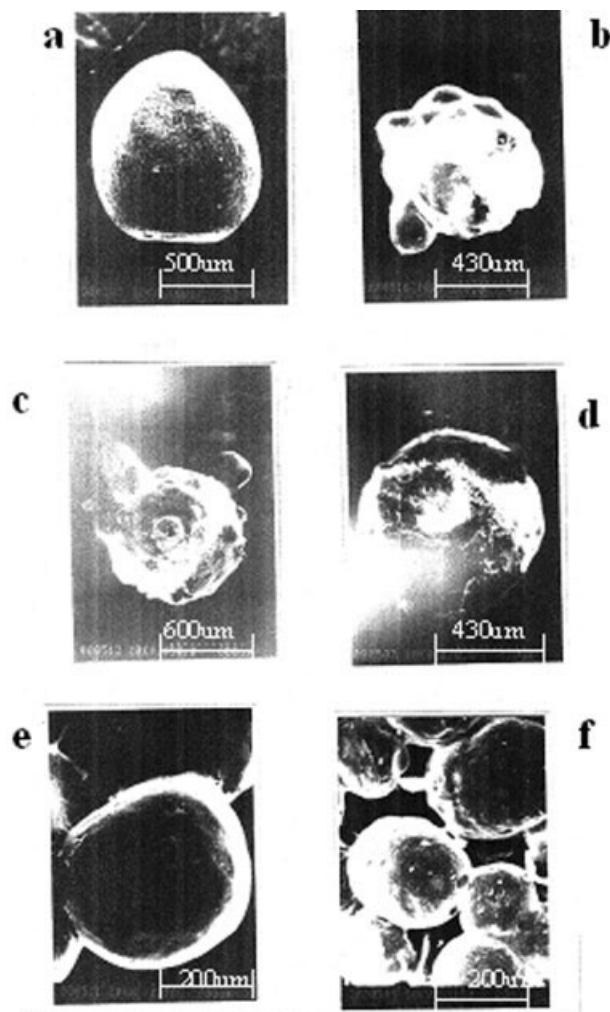
**Figure 3** <sup>1</sup>H-NMR spectra of P(4VP-co-NVP) of 9:1 ratio.



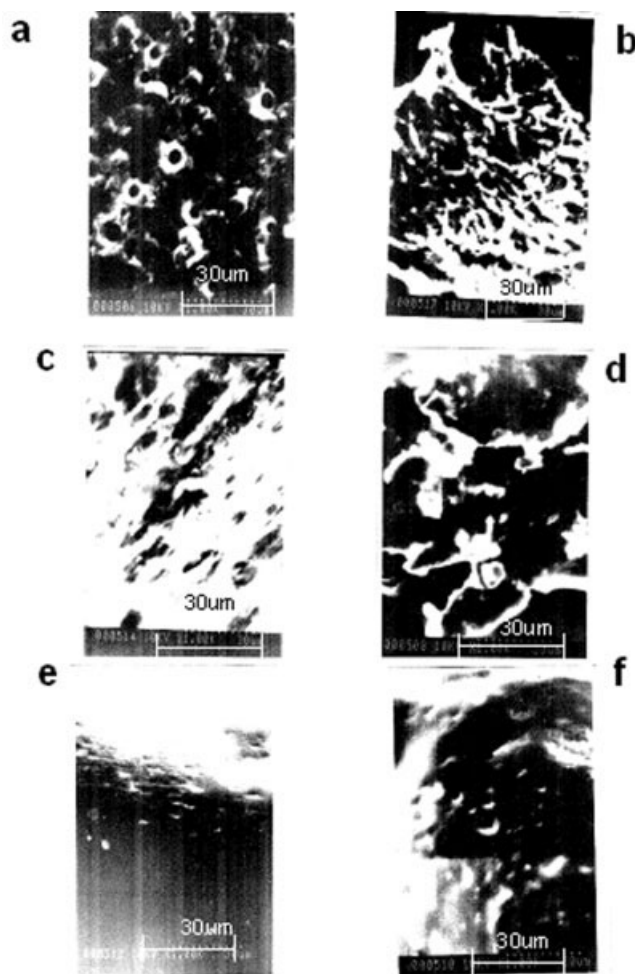
**Figure 4** TGA thermograms of (a) P(4VP) and P(4VP-co-NVP), (b) 9:1, (c) 8:2, (d) 7:3, (e) 6:4, and (f) 5:5.

### Swelling studies

The extent of swelling depends on the solvent-polymer interactions, which are determined not only by



**Figure 5** Scanning electron micrographs of (a) P(4VP) and P(4VP-co-NVP), (b) 9:1, (c) 8:2, (d) 7:3, (e) 6:4, and (f) 5:5.



**Figure 6** SEM images of the polymer bead surfaces: (a) P(4VP) and P(4VP-co-NVP), (b) 9:1, (c) 8:2, (d) 7:3, (e) 6:4, and (f) 5:5.

the nature of the solvent but also on the active groups present on the polymer. The presence of hydrophobic or hydrophilic groups would lead to various solution and swelling characteristics. In the present study, the degree of swelling of the polymer in water is represented as the equilibrium water sorption percentage.

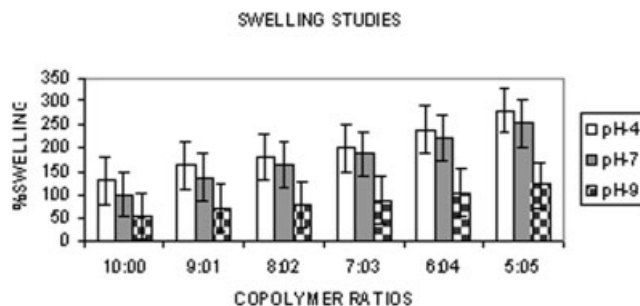
The copolymer beads have shown maximum water uptake in acidic medium in comparison with neutral and basic media. The equilibrium sorption percentages of all the polymer beads are shown in Figure 7 in acidic, basic, and neutral pHs. In acidic medium, equilibrium sorption of P4VP beads is minimum due to its hydrophobic nature that increases and shows maximum for the copolymer with ratio close to unity in all the pH values tested. The increase in the swelling ratio was found to be proportional to the NVP content. However, a remarkable difference in the time taken for the equilibrium sorption was noticed for the e and f copolymers i.e., 24 h instead of 1 h for the homopolymer and other copolymers. This behavior is supported by the SEM pictures in Figure 6, where the surface

morphology of the beads up to d show a network-like surface presenting more free volume, causing quick sorption (1 h). Whereas, e and f copolymers present improved homogeneity in comparison with the others, which could be due to the balanced hydrophobic and hydrophilic forces of the copolymer in water, resulting in time delay for equilibrium sorption and supports the discussion in the section Morphology of the Polymer Beads.

### Metal uptake capacity

P4VP contains basic nitrogen that can form complexes with metals. Macromolecule-metal complexes as catalysts have been extensively studied for many years, and many excellent results were achieved.<sup>11</sup> The catalytic activity of the complex depends on the surface and activation sites it provides for the substrate. The  $\text{Cu}^{2+}$  metal uptake capacities of the copolymers and homopolymer beads from aqueous solutions was investigated and are listed in Table I. Metal uptake is a process by which certain inorganic metal ions co-ordinate with organic functional groups through ionic bonds, co-ordination bonds and ion dipole interactions to form organometallic hybrids having many interesting properties and applications.<sup>9</sup>

The percentage of metal uptake was calculated by an indirect method of estimating the copper content left in the filtrate by UV-Vis spectroscopy. It was found that the extent of copper uptake was lower by the homopolymer, which also has lower water sorption capacity as discussed in the section Viscosity of the Polymer Dilute Solutions. The percentage of metal uptake was found to be maximum for f copolymer with 5:5 ratio in comparison with other copolymers. This is mainly because of the higher water uptake capacity of the copolymer, enabling access to most of the nitrogen atoms on the pyridine ring to coordinate with the metal. Metals coordinated to such copolymers would be in a better state for the activation of the substrate, imparting improved activity during catalytic applications.



**Figure 7** Equilibrium swelling percentages of the polymer beads in aqueous medium at different pH values: (a) P(4VP) and P(4VP-co-NVP), (b) 9:1, (c) 8:2, (d) 7:3, (e) 6:4, and (f) 5:5.

## CONCLUSIONS

Macroporous copolymer beads of 4VP and NVP presenting amphiphilicity were synthesized using suspension polymerization technique. The proof of copolymerization with the ratio of monomers as taken in the feed was confirmed by FTIR, NMR, and TGA. The morphology of the beads with spherical shape, finite pores, and smooth surface similar to that of homopolymer was found for the copolymers (**e** and **f**) with ratio close to unity. The swelling percentages in water and copper metal uptake capacities in aqueous medium were found to be highest for the copolymer **f**, which is mainly due to better hydrophilic and hydrophobic balance in of the copolymer at that ratio. These polymers also had lower viscosities in alcoholic solvents. Such copolymers would be more suitable for application in homogeneous/heterogeneous catalysis, protein immobilization, and drug delivery.

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