

# Synthesis of Full and Semi Interpenetrating Hydrogel from Polyvinyl Alcohol and Poly (acrylic acid-co-hydroxyethylmethacrylate) Copolymer: Study of Swelling Behavior, Network Parameters, and Dye Uptake Properties

Bidyadhar Mandal,<sup>1</sup> Samit Kumar Ray,<sup>2</sup> Ruma Bhattacharyya<sup>2</sup>

<sup>1</sup>Department of Chemistry, Bijoy Krishna Girls' College, Howrah, India

<sup>2</sup>Department of Polymer Science and Technology, University of Calcutta, 92 A.P.C Road, Kolkata 700009, India

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**ABSTRACT:** Semi and full interpenetrating network (IPN) hydrogels were synthesized by allowing free radical copolymerization of acrylic acid (AA) and hydroxyethyl methacrylate (HEMA) in the matrix of polyvinyl alcohol (PVOH). Accordingly, four different semi IPN hydrogels were prepared with PVOH: copolymer mass ratio of 1 : 1, 1 : 0.75, 1 : 0.5, and 1 : 0.25. These hydrogels were designated as SEMIIPN1, SEMIIPN2, SEMIIPN3, and SEMIIPN4, respectively. In all of these SEMIIPN, after polymerization PVOH was crosslinked with 2 mass % glutaraldehyde to form the semi IPN structure. In a similar way, sequential full IPN were prepared from PVOH and copolymer of AA and HEMA (designated as PAAHEMA) with same composition except in this case apart from crosslinking of PVOH by 2 mass % glutaraldehyde the PAAHEMA copolymer was further crosslinked with

*N,N'*-methylenebisacrylamide (NMBA) to produce four full IPN hydrogels designated as FULLIPN1, FULLIPN2, FULLIPN3, and FULLIPN4. All of these semi and full IPN type hydrogels were characterized by carboxylic %, FTIR, UV, DTA-TGA, XRD, SEM, and mechanical properties. The network parameters, swelling and diffusion characteristics of these hydrogels were also studied. The performance of these semi and full IPNs were compared in terms of their relative abilities for removing varied concentration of rhodamine B (RB) and methyl Violet (MV) dyes from water. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2250–2268, 2012

**Key words:** crosslink copolymer; superabsorbent; IPN hydrogel; characterization; network parameter; swelling; dye removal

## INTRODUCTION

Hydrogels are crosslinked hydrophilic polymer capable of showing extensive swelling in water. However, these “water hungry” macromolecules are not soluble in water because of its network type structure due to crosslinking. The hydrophilicity of hydrogel molecules are due to presence of various functional groups like COOH, OH, NH<sub>2</sub>, etc, in its structure which ionizes in water or form hydrogen bond with water molecules. In the present study pH responsive hydrogel polymers were synthesized from PVOH and copolymer of acrylic acid and HEMA. In recent times PVOH is being extensively used for making hydrogel

because of its very low toxicity, high degree of swelling in water, biocompatibility, good mechanical properties, and ability to be easily crosslinked by various chemical agents like multifunctional aldehydes or acids and also physical crosslinking by repeated freeze thawing method.<sup>1,2</sup> This polyhydroxyl compound is not degradable in most physiological situations.<sup>3</sup> Thus, PVOH-based hydrogels are broadly applied in tissue engineering, because of its excellent mechanical strength, good film formation property, minimal protein, and cell adhesion.<sup>4,5</sup> PVOH may be chemically modified to make it pH-responsive hydrogel by grafting anionic or cationic monomer with PVOH or forming semi or full interpenetrating network within matrix of PVOH. Peppas and Wright<sup>6</sup> studied in detail the diffusion of solutes through a full IPN of PVOH and polyacrylic acid at pH 3 and 6. This full IPN was synthesized by crosslinking PVOH with glutaraldehyde and *in situ* crosslink copolymerization of acrylic acid and crosslinker comonomer ethylene glycol dimethacrylate. It was found that binding of solutes like vitamin B<sub>12</sub>, myoglobin, and theophylline

Correspondence to: S. K. Ray (samitcu2@yahoo.co.in).

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occurs only in ionized state. Gudeman and Peppas<sup>7</sup> synthesized semi IPN of PVOH and PAA by *in situ* free radical polymerization of acrylic acid in the matrix of PVOH followed by crosslinking of PVOH with glutaraldehyde. Permeation of various solutes like urea, guaiacol glyceryl ether, L-tryptophan, vitamin B<sub>12</sub> and some selected dextrans through these hydrogels were studied as a function of mesh size and pH. Yun and Kim<sup>8</sup> synthesized microparticles of PVOH-PAA IPN by emulsion polymerization with *in situ* incorporation of vitamin B<sub>12</sub>. The microparticles show fast release of this vitamin. Full IPN of PVOH and PAA was also synthesized<sup>9</sup> by crosslinking PAA with NMBA and crosslinking PVOH with repeated freeze-thaw (F-T) cycles. Vinyl acetate and acrylic acid was copolymerized and hydrolyzed to produce poly(vinyl alcohol-co-acrylic acid) copolymer. pH responsive hydrogel was prepared from this copolymer by thermal crosslinking. This hydrogel showed high swelling in water and good release of theophylline (THO) and a model protein bovine serum albumin (BSA).<sup>10</sup> Full sequential IPN of PVOH and polyacrylamide was prepared by crosslinking PVOH with glutaraldehyde and acrylamide with NMBA. These hydrogels selectively permeate water from mixtures of water and ethanol.<sup>11</sup> Thermo responsive semi-IPN type hydrogels of PVOH and poly (*N*-isopropyl acrylamide) was reported to show enhanced response properties like swelling characteristic or LCST in comparison to poly (*N*-isopropyl acrylamide).<sup>12</sup>

From the above discussion it appears that hydrogels based on polyvinyl alcohol and polyacrylic acid or polyacrylamide have been synthesized by different methods like semi or full IPN, grafting and blending using free radical polymerization in aqueous medium or forming microspheres by emulsion polymerization. In the present work, in a similar way both semi and full IPN of PVOH and PAAHEMA copolymer were synthesized. The objective of the study was two folds i.e., synthesis and characterization of semi and full IPN type hydrogels and evaluating its swelling characteristics, network parameters and dye uptake properties. Hydrogels from HEMA have also been reported<sup>13,14</sup> to show high degree of swelling in water. Thus, these hydrogels have been synthesized and evaluated in terms of its swelling characteristics, crosslink density and mesh size. These hydrogels have also been used for removal of two important industrial dyes i.e., rhodamine-B (RB) and methyl violet (MV) at different feed concentration and pH.

## EXPERIMENTAL

### Materials

Monomers i.e., acrylic acid (AA, from Fluka), hydroxyethylmethacrylate (HEMA, from Fluka),

*N,N'*-methylenebisacrylamide (NMBA, from Fluka), redox initiator pair i.e., ammonium persulfate (APS, from Fluka) and sodium metabisulfite (SMBS, Merck), were of analytical grade and used without further purification. Polyvinyl alcohol (PVOH) of number average molecular mass 1,25,000 and degree of hydrolysis of 98–99% was obtained from S.D. fine chemicals, Mumbai and used as obtained. Rhodamine B (RB) and methyl violet (Basic Violet 1, MV) dye used in sorption studies, were purchased from SRL Chemical, India.

### Preparation of semi and full IPN hydrogels

The four semi IPN i.e., SEMIIPN1, SEMIIPN2, SEMIIPN3, and SEMIIPN4 were synthesized by solution polymerization in a three-necked reactor at 65°C for 3 h using ammonium persulfate and sodium metabisulfite (each, 0.5 mass % of the total monomer mass) as redox pair of initiators. In all of this synthesis 10 : 1 *M* ratio of acrylic acid and HEMA was used. The reactor was fitted with a stirrer, a thermometer pocket and a condenser. At first 5 mass % PVOH solutions was made in deionized water in a 250-mL glass beaker by gradual addition of required amount of PVOH to boiling water in several intervals with constant stirring to obtain a viscous clear PVOH solution. Required amounts of acrylic acid and HEMA were then added to the three neck flask placed on a constant temperature bath. Temperature was raised to 65°C and aqueous solution of initiators was added to the reactor. After 3 h of polymerization the reaction mixture was cooled to ambient temperature and mixed with 25% aqueous solution of glutaraldehyde, 10% solution of H<sub>2</sub>SO<sub>4</sub> (to catalyze the reaction), 50% aqueous methanol (to quench the reaction), and 10% solution of acetic acid (pH controller).<sup>15</sup> Thus, for 2 mass % crosslinking of PVOH and its IPNs the aqueous polymer solution was mixed with 0.4 mL glutaraldehyde, 0.2 mL sulfuric acid, 0.6 mL acetic acid, and 0.4 mL methanol. The gelled mass resulting from addition of crosslinking agent and catalyst were immersed in cold deionized water and kept for 3 days to remove water soluble oligomer, uncrosslink polymer, and unreacted monomers from the gel. The gel obtained was dried in a vacuum oven at 70°C to a constant weight. The dried gel was then disintegrated in a blender. Full IPN were prepared in a similar way except in this case *N,N'*-methylene bis acrylamide (NMBA) was added to the reaction mixtures for crosslinking the copolymer.

### Gel content of the hydrogel

The hydrogels as synthesized by the above method was dried in a vacuum oven at ambient temperature

( $\sim 30^\circ\text{C}$ ) for 2 days to a constant weight ( $W_i$ ). The dried sample was then kept in deionized water for another 2 days with occasional shaking to remove the water soluble part from the gel. It was then taken out from water. This water insoluble gel sample was further dried in vacuum oven to a constant weight ( $W_d$ ). Gel content is defined as

$$\text{Gel content(\%)}j = \frac{W_d}{W_i} \times 100 \quad (1)$$

### Characterization of the hydrogels

The synthesized hydrogels were characterized by the following methods.

#### Determination of carboxylic group of the hydrogel

A specific amount ( $w$ , around 0.5 g) of hydrogel sample was taken in a conical flask containing 25 mL 0.1M NaOH solution and mixed under magnetic stirring for 2 h. It was then titrated with 0.1M HCl solutions.

The mass % of carboxylic group in the hydrogel sample was calculated as

$$\text{COO}^- \% = [(C_{\text{NaOH}} \times V_{\text{NaOH}} - C_{\text{HCl}} \times V_{\text{HCl}}) \times 45 \times 10^{-3}/w] \times 100 \quad (2)$$

### FTIR spectroscopy

Fourier transform infrared (FTIR) spectra of the semi and full IPN hydrogels were recorded on a FTIR spectrometer (Nicolet 670 FTIR, USA), using KBr pellet made by mixing KBr with fine powder of the polymer gel samples (10 : 1 mass ratio of KBr to polymer).

### UV spectroscopy

UV spectra of virgin PVOH and copolymer modified PVOH hydrogel samples were recorded on a UV-visible spectrophotometer (Perkin-Elmer, model lamda25, USA) by inserting thin film of the gel samples in the cuvette to record their absorbance.

### Thermal analysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the polymer samples were carried out in a Mettler instrument in nitrogen atmosphere at the scanning rate of  $10^\circ\text{C min}^{-1}$  in the temperature range of 60–600°C.

### X-ray diffraction (XRD)

Wide angle X-ray diffraction profile of gel samples were studied at room temperature with a diffractom-

eter (model: X'Pert PRO, made by PANalytical B.V., The Netherlands) using Ni-filtered Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and a scanning rate of  $0.005 \text{ deg}(2\theta) \text{ s}^{-1}$ . The angle of diffraction was varied from  $2^\circ$  to  $72^\circ$  to study the comparative change of the crystallinity as well as segmental spacing ( $d$  spacing) of pure PVOH and chemically modified PVOH gel samples.

### Scanning electron microscopy (SEM)

The semi and full IPN gel samples were coated with gold (Au). The morphology of the gels were observed by using SEM (scanning electron microscope, model no. S3400N, VP SEM, Type-II, made by Hitachi, Japan) with the accelerating voltage set to 15 kV.

### Mechanical properties

The tensile strength (TS) and elongation at break (EAB) of the gel samples was determined by an Instron-Tensile tester (Instron 4301, Instron Limited, England). The experiment was performed according to Ref. <sup>16</sup>. In this work, cubic sample of  $2 \text{ mm} \times 2 \text{ mm} \times 80 \text{ mm}$  size was used. The crosshead speed of  $100 \text{ mm min}^{-1}$  was maintained. The cubic samples were elongated at a strain rate of 5%/min. The tensile strength (TS) and elongation at break (EAB) were calculated on the basis of initial cross section area of the sample. The TS and EAB of the hydrogel samples are given in Table II.

### Study of swelling kinetics of the hydrogels

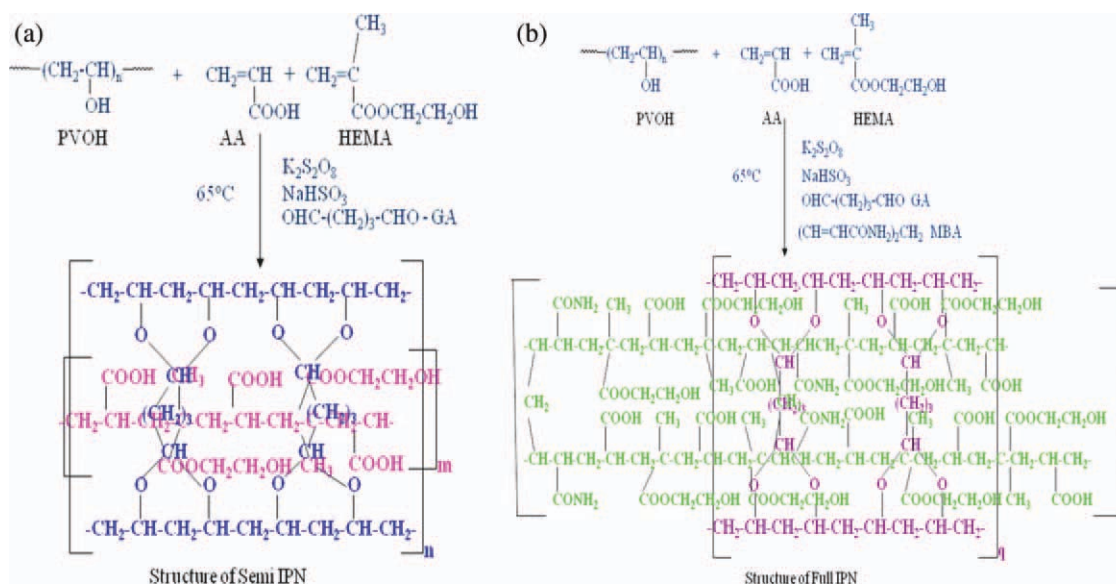
The dynamic swelling properties of the hydrogels were carried out in distilled water at ambient temperature. The mass of the swollen gel was taken at different time intervals until there was no change of mass with time. Each sample was weighed three times and the average values of these three measurements were taken. The water uptake of the hydrogels ( $W_c$ ) was determined by using the following equation.

$$W_c = \frac{W_t - W_d}{W} \quad (3)$$

where  $W_t$  is the mass of swollen hydrogel polymer at time " $t$ " and  $W_d$  is the mass of dry polymers. The amount of water adsorbed by the different hydrogels under equilibrium conditions, also called equilibrium degree of swelling (EDS) was obtained when  $W_t$  did not change any more ( $W_a$ ) with time.

### Study of dye removal capacity of the hydrogels

Solutions of the two kinds of dye i.e., Rhodamine B (RB) and methyl violet (MV) with varied concentration



**Figure 1** Structure of hydrogels. (a) Formation of semi IPN and its structure. (b) Formation of full IPN and its structure. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

range ( $0.25\text{--}3\text{ mg L}^{-1}$ ) were prepared in distilled water at different pH and also in distilled water with varied molar concentration of sodium chloride. About 50 mg of hydrogel was taken in known volume of the dye solution with continuous stirring on a magnetic stirrer until equilibrium was reached. After equilibrium was reached, the dye solution was separated by decantation from the hydrogel. The concentration of dye solutions before and after addition of hydrogel were determined by spectrophotometric measurement from a precalibrated curve of absorbance versus concentrations using Perkin-Elmer lamda 25 UV-visible spectrophotometer. The absorbance of the dye solutions were measured at wavelength of 554 nm for RB and 584 nm for MV dye. The amount of dye uptake (in mg) by unit mass (in g) of the hydrogel at equilibrium ( $Q_e$ ,  $\text{mg g}^{-1}$ ) was calculated using the following equation.

$$Q_e = \frac{(C_0V_0 - C_eV)}{m} \quad (4)$$

Here  $C_0$  and  $C_e$  are initial and equilibrium concentration of dye solution ( $\text{mg L}^{-1}$ ) while  $V_0$  and  $V$  is volume (L) of the initial and equilibrium dye solution containing the hydrogel and  $m$  is mass (g) of the dry hydrogel polymer used for the experiment.

## RESULTS AND DISCUSSION

### Synthesis of IPN hydrogels

In a semi IPN polymer one polymer is crosslinked while in a full IPN both of the constituent polymers are crosslinked. In the present work both semi and

full IPN of PVOH were made by free radical copolymerization of AA and HEMA in the matrix of PVOH followed by crosslinking of only PVOH with glutaraldehyde to produce semi IPN and crosslinking of PVOH with glutaraldehyde and the copolymer with NMBA to produce full IPN. The major drawback of hydrogel of copolymer of AA and HEMA is its poor mechanical properties due to extensive swelling and thus low polymer volume fraction in the gel network. As PAAHEMA copolymer is synthesized in the matrix of PVOH, polymer volume fraction in the gel network increases due to presence of PVOH with increased swelling and mechanical strength. Incorporation of the copolymer PAAHEMA in PVOH matrix also reduces crystallinity of PVOH to give increased swelling in water. Further, the highly hydrophilic PAAHEMA, a water soluble copolymer would give pH responsive hydrophilicity to the modified PVOH hydrogel. The crosslinking of PAAHEMA was fixed at 2 mass % (of AA and HEMA) NMBA while crosslinking of PVOH matrix was fixed at 2 mass % (of PVOH) glutaraldehyde. The comonomer compositions of AA and HEMA were fixed at molar ratio of AA : HEMA of 10 : 1. This molar ratio of comonomer and crosslinker % was earlier reported to produce pervaporation membrane with optimum flux and water selectivity.<sup>15</sup> Thus, in this work hydrogel was made with similar composition. The polymerization reaction was conducted in a nitrogen atmosphere, to prevent oxidative degradation or the formation of copolymers of acrylic acid with oxygen. The hydrogel is formed by crosslink copolymerization of AA, HEMA and NMBA in the matrix of PVOH as shown in Figure 1(a) for semi IPN and Figure 1(b) for full IPN. During polymerization the bifunctional monomer or

**TABLE I**  
Properties of the Polymer Hydrogel

Name of the polymer hydrogel	Composition
PVOH	Polyvinyl alcohol crosslinked with 2 mass % glutaraldehyde
FULLIPN4	Full interpenetrating network of copolymer of acrylic acid-co-hydroxyethyl methacrylate of 10 : 1 molar ratio in PVOH matrix with 1 : 1 mass ratio of copolymer to PVOH. PVOH matrix crosslinked with 2 mass % glutaraldehyde. Copolymer crosslinked with 0.5 mass % NMBA
FULLIPN3	Same as FULLIPN4 except PVOH : copolymer 1 : 0.75
FULLIPN2	Same as FULLIPN4 except PVOH : copolymer 1 : 0.5
FULLIPN1	Same as FULLIPN4 except PVOH : copolymer 1 : 0.25
SEMIIPN4	Same as FULLIPN4 except copolymer is not crosslinked (No NMBA).
SEMIIPN3	Same as SEMIIPN4 except PVOH : copolymer 1 : 0.75
SEMIIPN2	Same as SEMIIPN4 except PVOH : copolymer 1 : 0.5
SEMIIPN1	Same as SEMIIPN4 except PVOH : copolymer 1 : 0.25

crosslinker NMBA undergoes copolymerization with both of the other two monomers i.e., AA and HEMA to form the crosslink copolymer hydrogel. The composition of the four semi and four full IPN hydrogels are given in Table I.

#### Effect of reaction variables on polymer yield, gel content and gel time

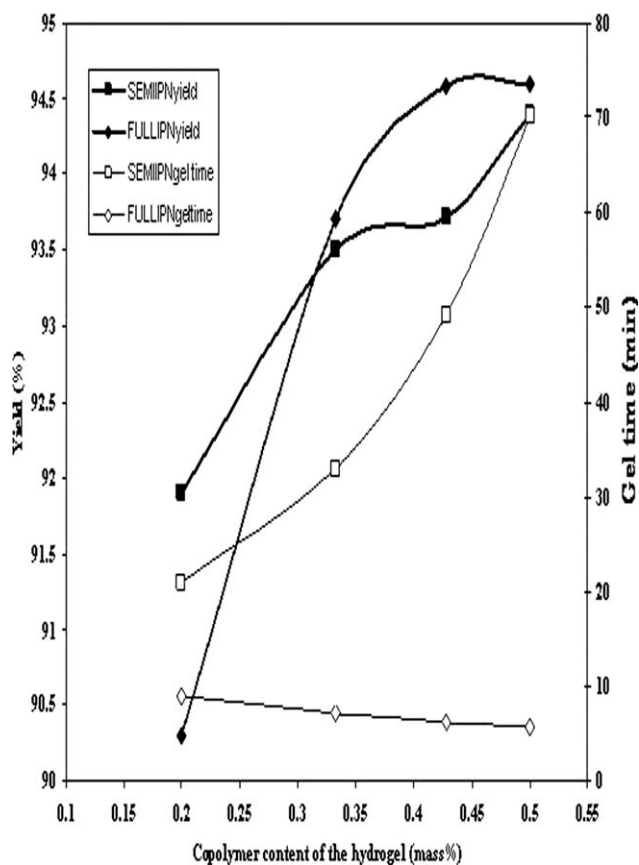
In Figure 2 the gel time and yield is shown as a function of copolymer content in the gel.

#### Gel time and copolymer content

It is observed from the figure that for any copolymer content gel time of semi IPN is higher than full IPN. For full IPN gelling occurs at an early time because of presence of two crosslinkers causing an early gelling. For the semi IPN, with increasing copolymer content gel time increases while for full IPN gel time remains marginally constant with increasing copolymer content. As the amount of PAAHEMA copolymer increases it becomes increasingly difficult for the same amount of glutaraldehyde to crosslink PVOH in semi IPN. However, for full IPN, NMBA is also added to crosslink the copolymer. Hence, for the full IPN the change of gel time with copolymer content is marginal.

#### Yield and copolymer content

From Figure 2 it is also observed that extent of reaction increases with increase in monomer concentra-



**Figure 2** Variation of polymer yield and gel time with copolymer content of the hydrogel: (■) SEMIIPN yield; (◆) FULLIPN yield; (□) SEMIIPN gel time; (◇) FULLIPN gel time.

tion. Hence, for both semi and full IPN yield increases with increasing copolymer content because of increased concentration of comonomers.

#### Gel content and copolymer content

The values of gel content of the hydrogels are shown in Table II. It is observed that the gel content of the

**TABLE II**  
Gel Content, Carboxylic Content and Mechanical Properties of the Hydrogels

Name of the polymer hydrogel	Gel content %	Carboxylic %	Tensile strength (MPa)	Elongation at break (%)
PVOH	98	0	45.32	178.23
FULLIPN4	94.6	23.84	24.51	35.13
FULLIPN3	94.58	20.50	28.79	47.12
FULLIPN2	93.7	16.71	33.13	58.71
FULLIPN1	90.3	9.10	39.15	101.23
SEMIIPN4	94.4	23.79	21.57	47.13
SEMIIPN3	93.72	20.31	26.15	52.33
SEMIIPN2	93.5	16.68	30.27	65.71
SEMIIPN1	91.9	9.26	35.13	113.21

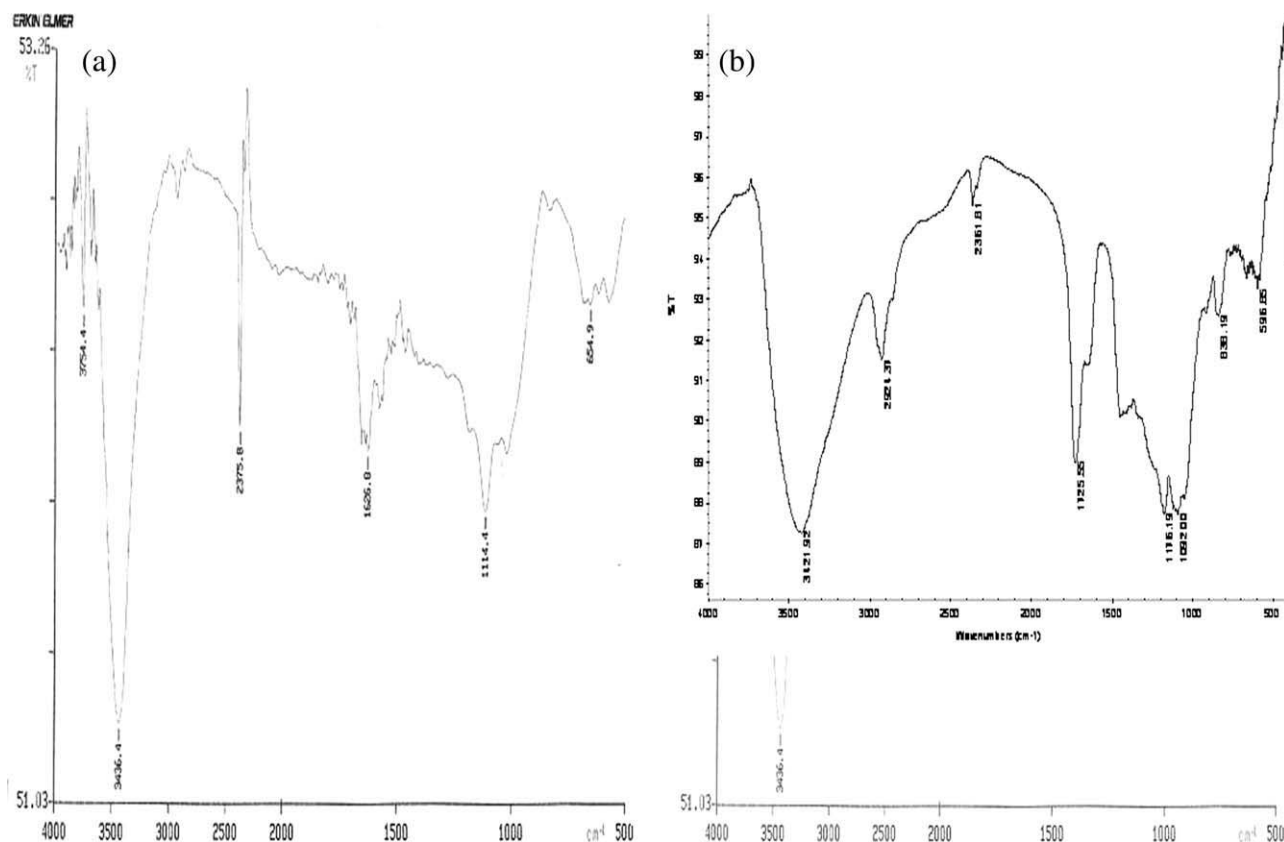


Figure 3 FTIR of hydrogels. (a) SEMIIPN1, (b) FULLIPN1.

full IPN hydrogel polymers is higher than semi IPN polymer for any copolymer content. This may be ascribed to crosslinking of both of the constituent polymer in full IPN resulting in higher gel content. It is also observed that gel content of the full IPN increases from FULLIPN1 to FULLIPN4 while for semi IPN it shows an opposite trend i.e., it decreases from SEMIIPN1 to SEMIIPN4. As the amount of crosslink copolymer increases, networking of the hydrogel samples also increase with greater amount of gel content from FULLIPN1 to FULLIPN4. However, for semi IPN hydrogels, as there is no crosslinking of the copolymer, soluble part increases with increasing amount of copolymer from SEMIIPN1 to SEMIIPN4. However, the semi IPNs also show high gel content because of formation of chemical bonding between hydroxyl functional group of HEMA comonomer and PVOH polymer with carboxyl functional group of AA comonomer.<sup>13</sup> These chemical bonds also increase the insoluble part of the hydrogels.

### Characterization of the hydrogel

#### Amount of carboxyl group in the hydrogel

The carboxyl group comes from acrylic acid in the hydrogel. The amount of free carboxyl group present in the hydrogel was determined by titrating with 0.1M NaOH solutions. The amount of carboxyl

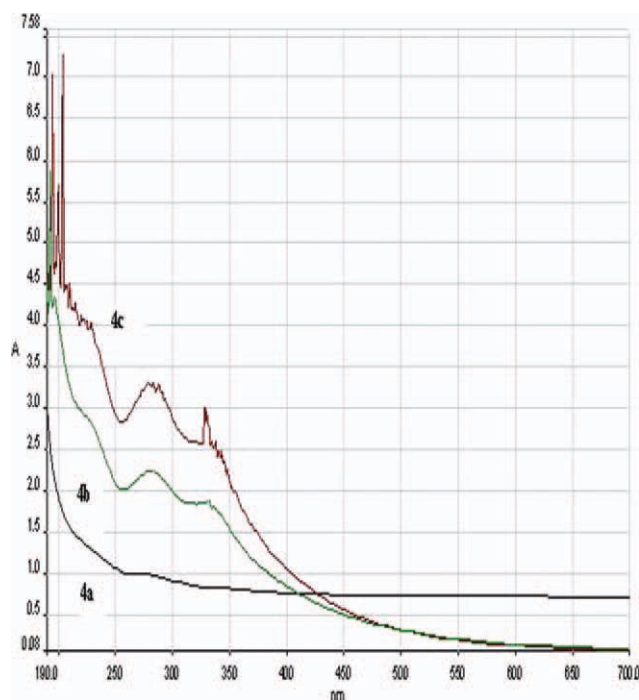
group present in the hydrogel is given in Table II. From the Table it is observed that amount of free carboxyl group increases from IPN1 to IPN4 in both full and semi IPN hydrogel. The amount of free carboxyl is also found to be slightly more in semi IPN than in full IPN. The theoretical amount of carboxylic group in the IPN was calculated by multiplying theoretical copolymer composition with yield %. The theoretical copolymer composition was calculated using the following eq. (5)

$$\frac{d[M_{AA}]}{d[M_{HEMA}]} = \frac{r_{AA}m_{AA}^2 + m_{AA}m_{HEMA}}{r_{HEMA}m_{HEMA}^2 + m_{AA}m_{HEMA}} \quad (5)$$

Here,  $r_{AA}$  and  $r_{HEMA}$  are reactivity ratio of AA i.e., 0.15 and HEMA i.e., 3.52 as obtained from literature.<sup>17</sup>  $m_{AA}$  and  $m_{HEMA}$  are moles of AA and HEMA in comonomer feed.

#### FTIR spectroscopy

The FTIR spectra of SEMIIPN1 and FULLIPN1 hydrogel are shown in Figure 3(a,b), respectively. Similar kind of FTIR was obtained with the other semi and full IPN hydrogels. In the FTIR of SEMIIPN1 a strong band is observed at around 1626.9  $\text{cm}^{-1}$  corresponding to carboxyl (COOH) peak due to



**Figure 4** UV spectra of IPN hydrogels. (a) PVOH, (b) SIPN1, (c) FULLIPN1. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

acrylic acid present in the hydrogel. Similarly, O—H bending vibrations at around  $1114\text{ cm}^{-1}$  correspond to poly vinyl alcohol (PVOH) as well as hydroxyethyl methacrylate comonomer of the copolymer.<sup>18</sup> The bands at around  $3447$  and  $3760\text{ cm}^{-1}$  corresponds to

crosslinked and uncrosslinked hydroxyl group of the hydrogel. These apart, the strong band at around  $770$  and  $2900\text{ cm}^{-1}$  are due to  $(-\text{CH}_2-)$  methylene<sup>19</sup> and C—H alkane group of the copolymer hydrogel.<sup>19</sup> In a similar way, FULLIPN1 shows similar peaks with shifting i.e.,  $2914$  and  $838\text{ cm}^{-1}$  due to  $(-\text{CH}_2-)$  methylene and C—H alkane group of the copolymer,  $3421\text{ cm}^{-1}$  due to crosslinked hydroxyl group and OH bending vibration at  $1176\text{ cm}^{-1}$ . Carbonyl peak is also shifted to  $1725\text{ cm}^{-1}$  in the full IPN. These shifting may be due to chemical crosslinking of both PVOH and the PAAHEMA copolymer.

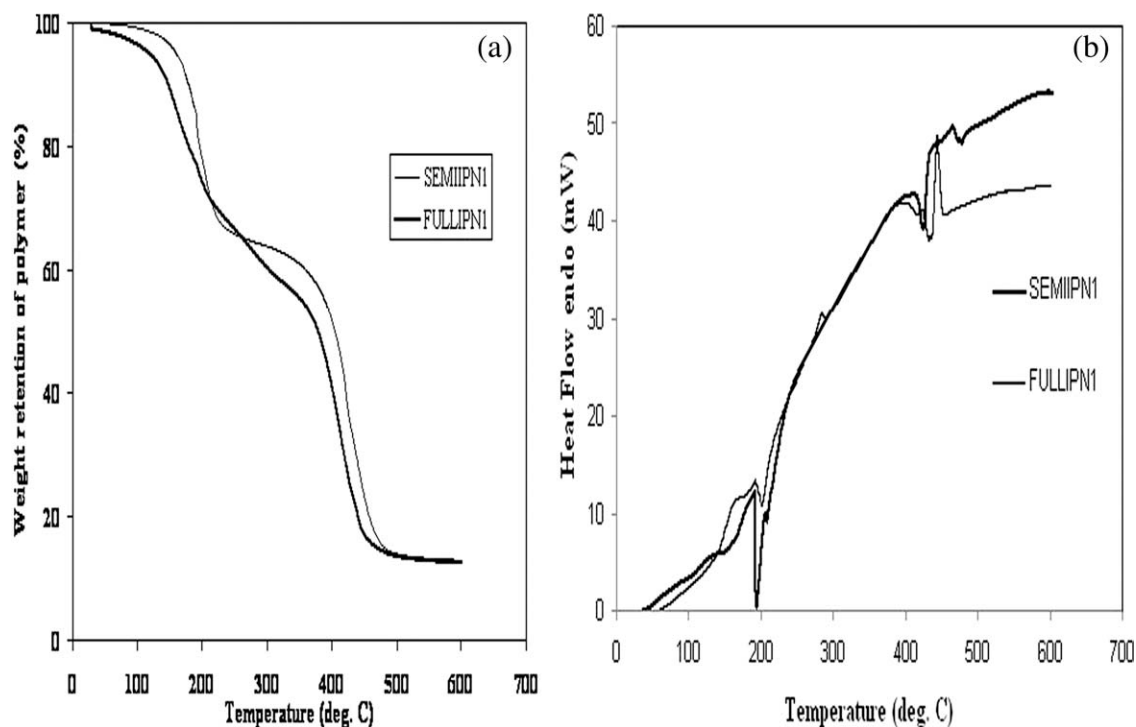
#### UV spectroscopy

The UV absorption spectra of PVOH, SEMIIPN4 and FULLIPN4 are shown in Figure 4. Similar kind of spectra was obtained with the other semi and full IPN hydrogel. From this figure it is observed that no significant peak is available with pure PVOH while SEMIIPN1 shows two distinct peaks at  $281$  and  $331\text{ nm}$ . These peaks are slightly shifted to  $283$  and  $328\text{ nm}$ , respectively, in FULLIPN1. These peaks may be due to  $n$  to  $\pi^*$  transition of carboxylic groups in the hydrogel.<sup>20</sup>

#### Thermal study

##### TGA

TGA of SEMIIPN1 and FULLIPN1 hydrogel are shown in Figure 5(a) while DTA of these hydrogels



**Figure 5** TGA of semi and full IPN, (a) Semi IPN, (b) Full IPN.

are shown in Figure 5(b). Similar kind of TGA and DTA curves were obtained with the other semi and full IPN hydrogel polymers. From Figure 5(a) it is observed that the semi and full IPN hydrogels show two major weight loss regions with onset of maximum weight loss at its melting temperature i.e., at around 160°C which continues up to around 475°C. The weight losses of these IPN polymers in different temperature regions are associated with splitting of the main chain and final decomposition of the polymer. It is also observed that the full IPN hydrogel shows higher thermal stability than the semi IPN which may be due to crosslinking of both of the constituent polymer in full IPN.

#### DTA

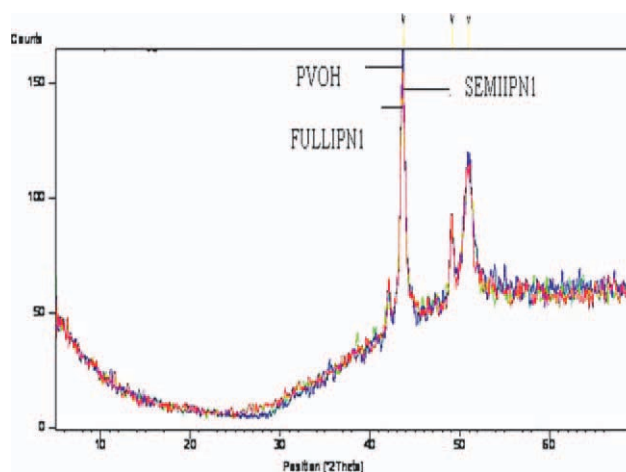
From the DTA of SEMIIPN1 and FULLIPN1 it is observed that the semi and full IPN shows a glass transition temperature ( $T_g$ ) of around 156 and 177°C, respectively. These  $T_g$ s are much higher than  $T_g$  of its constituent homopolymers. Interpenetration and crosslinking restricts segmental motion and thus the IPN hydrogel shows much higher  $T_g$  than homopolymer of its constituent polymer. Between semi and full IPN, the full IPN hydrogel shows higher  $T_g$  because of crosslinking of both of its constituent polymer.

#### XRD studies

The crystallinity of atactic polyvinyl alcohol arises from extensive hydrogen bonding by the small hydroxyl groups occupying *d* and *l* sites in an atactic chain within a single crystal lattice. As this PVOH is crosslinked, there is a change in *d* spacing and peak intensity also decreases due to loss in crystallinity. Copolymerization of AA and HEMA in the matrix of PVOH further reduces the extent of hydrogen bonding and hence crystallinity. Thus, peak intensity decreases from PVOH to semi IPN gel since some of the hydroxyl groups of PVOH form chemical bond (ester) with carboxyl groups of the copolymer and hence, hydrogen bonding between hydroxyl groups of PVOH is reduced. In full IPN hydrogel intramolecular hydrogen bonding responsible for crystallinity of PVOH is also reduced. However, crosslinking of the copolymer make it less accessible in comparison to copolymer of semi IPN which is not crosslinked. Thus, the peak intensity decreases in the following order PVOH > semi IPN > full IPN as shown in Figure 6 for crosslink PVOH, SEMIIPN1 and FULLIPN1 at  $2\theta = 43.6^\circ$ .

#### Scanning electron microscopy (SEM)

SEM studies of the PVOH, SEMIIPN1 and FULLIPN1 are shown in Figure 7(a–c). SEM of a pure



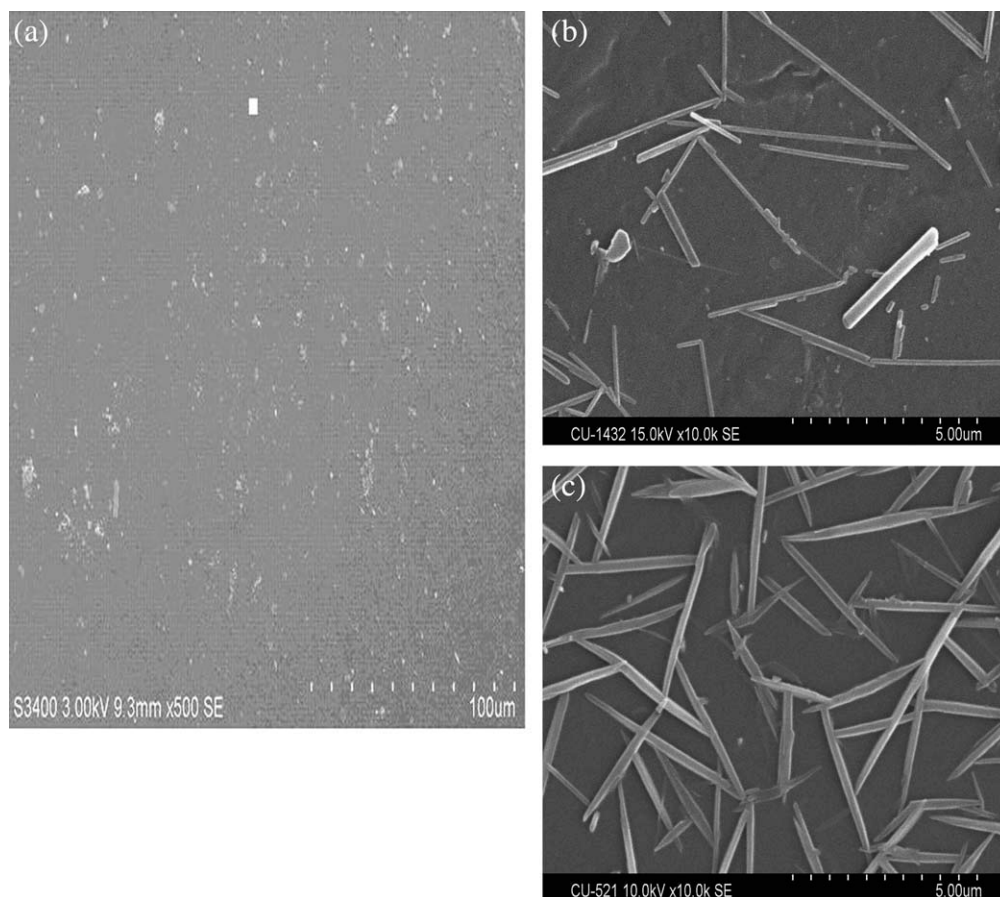
**Figure 6** XRD of the hydrogel samples. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

polymer like PVOH always gives a dense feature as also seen in Figure 7(a). SEM is usually carried out for a polymer blend to evaluate the extent of compatibility in terms of morphology of the blend. The poorer the compatibility, the coarser is the morphology. IPN are different from a blend in that due to interpenetration of the constituent polymers the extent of compatibility is very high in an IPN. Thus, much higher magnification is required (higher than those used for conventional blend) for getting morphology of an IPN through SEM. Hence, SEM of the hydrogel samples was carried out with 10 K magnification (5  $\mu\text{m}$ ) to get morphology of the constituent polymers. The microphase separation of Polymers I and II in an IPN is characterized with needle-like morphology.<sup>21</sup> The relative size and shape of the two different polymer domains (i.e., PVOH and the copolymer) depends on crosslink density as well as on relative proportions of the two polymers.<sup>22</sup> Because of increased crosslinking the full IPN i.e., FULLIPN1 shows morphology [Fig. 7(b)] coarser than SEMIIPN1 [Fig. 7(a)].

#### Mechanical properties

The tensile strength (TS) and elongation at break (EAB) of the semi and full IPN hydrogel polymers are shown in Table II. As shown in this table, the TS and EAB. of IPN hydrogel is found to decrease with increasing amount of copolymer in the matrix of PVOH from IPN1 to IPN4 for both semi and full IPN. Polyvinyl alcohol (PVOH) gel shows high TS because of its crystallinity and it also shows high elongation because of its low  $T_g$ . The increasing amount of acrylic copolymer with high  $T_g$  in PVOH decreases its crystalline structure as well as crosslinking of both PVOH and copolymer reduces chain flexibility of the IPN. Thus, with increasing amount





**Figure 7** SEM of the hydrogel samples. (a) PVOH, (b) SEMIIPN1, (c) FULLIPN1.

of copolymer from IPN1 to IPN4 both TS and EAB of the polymer decreases. It is also observed that for any copolymer content, the full IPN shows higher TS but lower EAB than the semi IPN. This may be due to crosslinking of both of its polymer and tighter entanglement in full IPN.

#### Study of swelling properties of the hydrogels

The water uptake  $W_t$  of the hydrogels in distilled water was calculated from eq. (3). The variation of water uptake% with time for PVOH and semi IPN hydrogels are shown in Figure 8(a) while the same of full IPN hydrogels are shown in Figure 8(b). Similar swelling curves for semi and full IPN hydrogels at varied pH are shown in Figure 9(a,b) for SEMI-IPN4 and FULLIPN4, respectively. From all of these swelling curves it is observed that initially water uptake % increases with time and finally it levels off at an equilibrium value. There is no further increase in water uptake % with time above this equilibrium value. This equilibrium swelling % (ES %) of the hydrogels was obtained from their corresponding swelling curves. Accordingly, the effect of copolymer content and pH on ES % is shown in Figure 10(a,b), respectively.

#### Effect of copolymer content on swelling

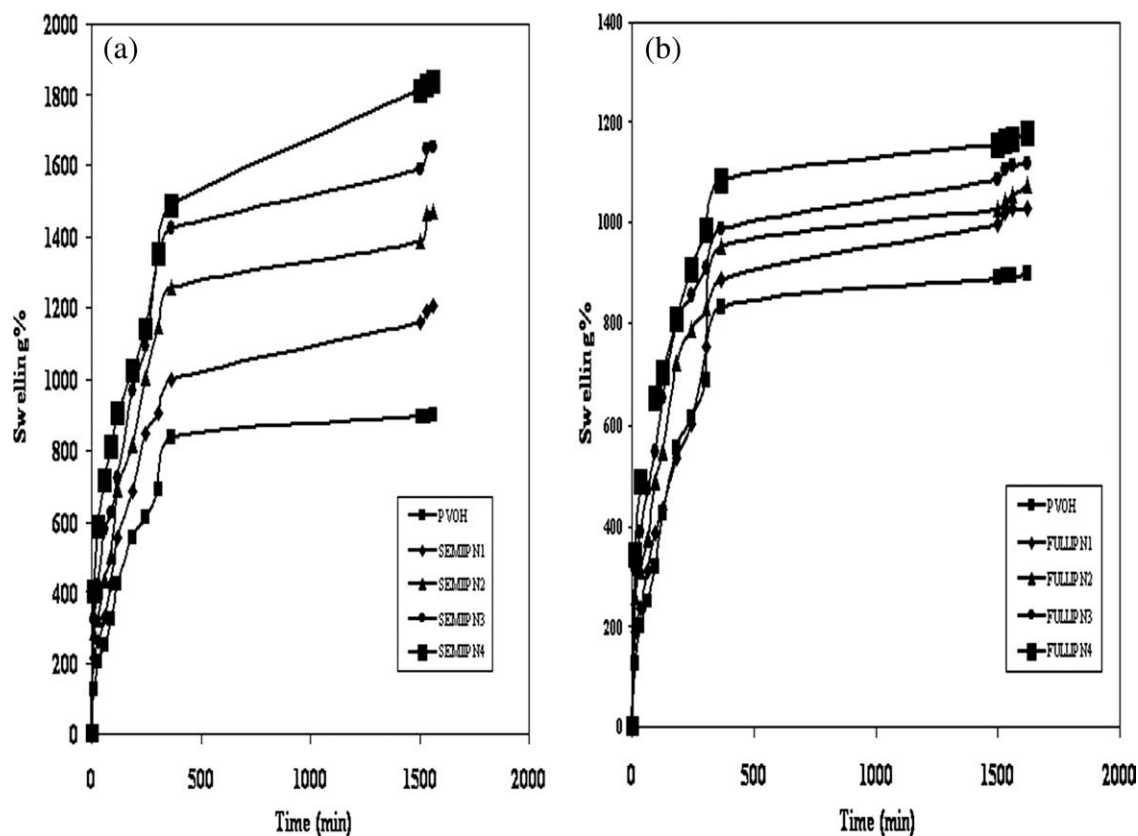
From Figure 8(a,b) it appears that as the total copolymer content in the hydrogel increases water uptake % also increases for both semi IPN [Fig. 8(a)] and full IPN [Fig. 8(b)].

#### Copolymer content and equilibrium swelling time

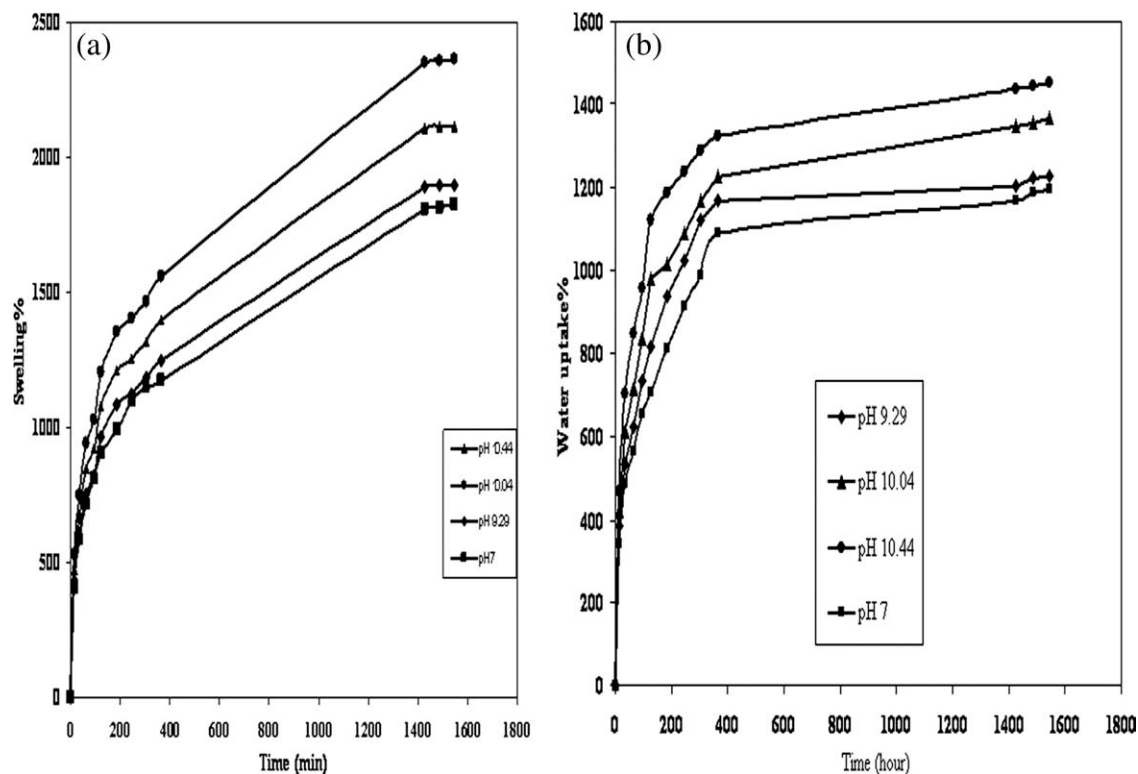
From Figure 8(a,b) it is observed that the time required for reaching equilibrium swelling increases with increasing amount of copolymer from PVOH (0%) to SEMIIPN4/FULLIPN4. The gel network becomes denser at higher concentration of PVOH with less relaxation of polymer chain. This causes much slower diffusion of water in the dense network with an early arrival of equilibrium swelling (ES).<sup>20</sup>

#### Copolymer content and swelling uptake%

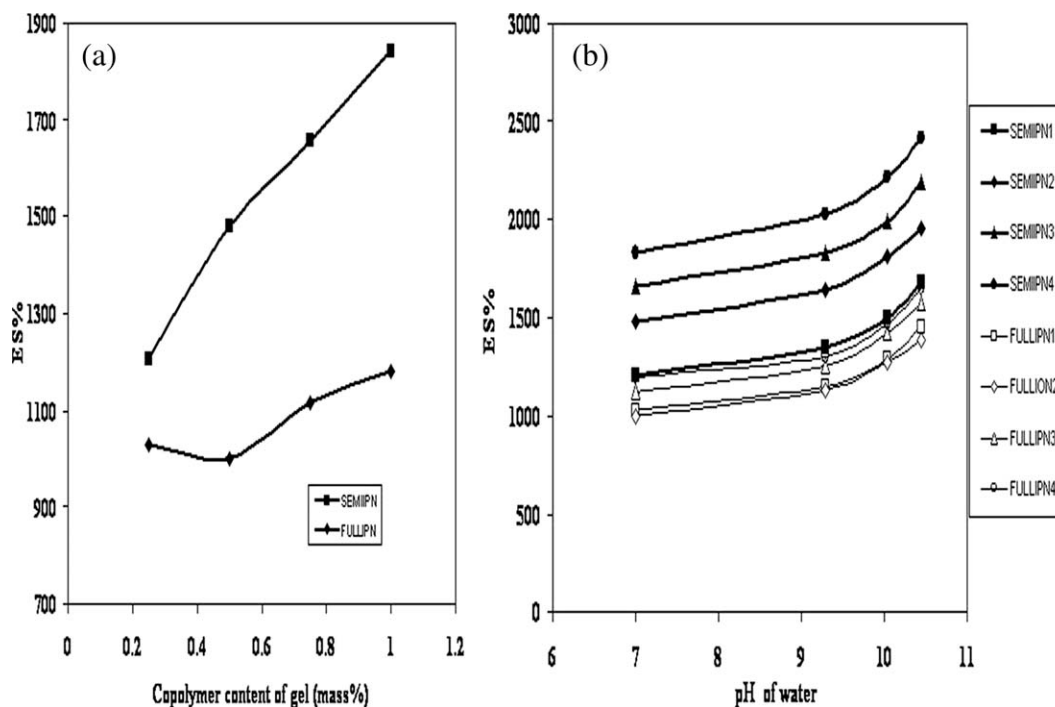
The increasing amount of carboxyl groups from PVOH (0%) to SEMIIPN4/FULLIPN4 (50%) is responsible for increasing water uptake % and ES % in the same order. The ionization of carboxyl group in water causes increased swelling in the copolymer



**Figure 8** (a) Effect of copolymer content on swelling % of the hydrogel at pH 7: (■) PVOH; (◆) SEMIIPN1; (▲) SEMIIPN2; (●) SEMIIPN3; (■) SEMIIPN4. (b) Effect of copolymer content on swelling % of the hydrogel at pH 7: (■) PVOH; (◆) FULLIPN1; (▲) FULLIPN2; (●) FULLIPN3; (■) FULLIPN4.



**Figure 9** (a) Effect of pH on swelling % of SEMIIPN4 hydrogel: (▲) pH 10.44; (●) pH 10.04; (◆) pH 9.29; (■) pH 7. (b) Effect of pH on swelling of FULLIPN4: (▲) pH 10.04; (●) pH 10.44; (◆) pH 9.29; (■) pH 7.



**Figure 10** (a) Effect of copolymer content on ES % of the hydrogel: (■) SEMIIPN; (◆) FULLIPN; (b) Effect of pH on equilibrium swelling % (ES %) of the hydrogel: (■) SEMIIPN1; (◆) SEMIIPN2; (▲) SEMIIPN3; (●) SEMIIPN4; (□) FULLIPN1; (◇) FULLIPN2; (△) FULLIPN3; (○) FULLIPN4.

modified hydrogel. Apart from ionization of carboxyl group density of gel matrix also decreases with decreasing amount of PVOH from PVOH to SEMIIPN4/FULLIPN4 resulting in increased penetration of water molecules in the hydrogels. Peppas and Wright<sup>6</sup> also reported similar swelling behavior for PVOH-PAA blend hydrogel where water uptake % was reported to increase with increasing amount of PAA. Shukla and Bajpai<sup>23</sup> observed decrease of water uptake % with increasing amount of PVOH in acrylamide copolymer modified PVOH hydrogel. Between semi and full IPN, for any concentration of acrylic copolymer full IPN hydrogel is observed to show lower water uptake % because of increased density of its gel network due to crosslinking of both of the constituent polymers.

### Effect of pH on swelling

Both of the semi and full IPN hydrogels were synthesized by incorporating copolymer of acrylic acid in the matrix of PVOH. Thus, these gels become pH responsive. Polyacrylic acid (PAA) is a weak acid with  $pK_a$  value of 4.8. When the pH of water is lower than 4.8, the ionic strength of  $H^+$  is very high which suppress the ionization of carboxyl groups. When the pH of the solution rises above its  $pK_a$  value i.e., above 4.8, the carboxylic groups of the gel network ionize and attract cations in to the gel to replace  $H^+$  ion. With increasing pH, swelling

increases because of increased concentration of free ion within the network. Further, the gel also expands to minimize the repulsion between the ionized carboxylic groups at higher pH. Thus, swelling uptake % and ES % increases with increasing pH from 7 to 10.54.

### Studies of networking in the hydrogels

The size of gel network is usually characterized in terms of average molecular weight between crosslinks,  $M_c$  and mesh size,  $\zeta$ .  $M_c$  can be calculated from the following equation based on network theory of Flory and Rehner.<sup>24</sup>

$$M_c = - \frac{V_s \rho_p (\phi_p^{1/3} - \frac{\phi_p}{2})}{\ln(1 - \phi_p) + \phi_p + \chi \phi_p^2} \quad (6)$$

Here  $V_s$  is molar volume of solvent (water),  $\phi_p$  is volume fraction of polymer in the swollen gel under equilibrium,  $\rho_p$  is density of the polymer, and  $\chi$  is polymer-solvent (water) interaction parameter. The molar volume of water versus experimental temperature (25°C) was calculated (18.18 mL mol<sup>-1</sup>) from its density (0.99 g mL<sup>-1</sup>) and molecular weight (18 g mol<sup>-1</sup>), the density of polymer hydrogel sample,  $\rho_p$ , was calculated from its mass and volume. The volume of the polymer sample was measured by the method reported elsewhere.<sup>25</sup> For equilibrium

**TABLE III**  
**Network Parameter of the Hydrogels at pH 7**

Name of the polymer	Density of polymer g mL <sup>-1</sup>	g of water/g polymer	Volume fraction of polymer in swollen gel	Polymer–water interaction parameter, $\chi$	Swelling ratio, $\phi$	Average molar mass between crosslink, $M_c$	Crosslink density, $\rho_c \times 10^3$	Mesh size of network, $\zeta, A^0$
PVOH	1.78	8.98	0.058	0.174	17.13	10168.44	4.327	243.56
SEMIIPN1	1.58	12.08	0.049	0.159	20.22	11607.79	5.860	211.37
SEMIIPN2	1.43	14.78	0.044	0.152	22.38	12330.29	5.243	232.56
SEMIIPN3	1.31	17.56	0.041	0.145	24.29	12838.78	4.725	253.66
SEMIIPN4	1.24	19.81	0.039	0.141	25.91	13445.97	3.987	285.84
FULLIPN1	1.63	10.29	0.055	0.170	17.98	10069.80	6.755	189.41
FULLIPN2	1.54	10.77	0.056	0.171	17.79	9344.64	6.919	187.68
FULLIPN3	1.41	11.18	0.059	0.175	16.95	7944.34	7.636	177.16
FULLIPN4	1.30	11.81	0.060	0.177	16.45	6968.01	7.693	177.13

swelling of  $m_w$  g water/g dry hydrogel sample, polymer volume fraction in swollen gel under equilibrium,  $\Phi_p$  will be

$$\Phi_p = \frac{1}{1 + \frac{\rho_p}{\rho_i} m_w} \quad (7)$$

Here,  $\rho_p$  and  $\rho_i$  are density of polymer and solvent (water), respectively.

The polymer–solvent interaction parameter,  $\chi$  between water and polymer hydrogel may be obtained using the following eq. (8) based on Flory–Huggins theory

$$\ln a_w = \ln(1 - \phi_p) + \phi_p + \chi \phi_p^2 \quad (8)$$

Here,  $a_w$  is activity of water. The pure component water may be assumed as ideal. Accordingly,  $a_w$  will be unity. The swelling ratio  $\phi$  was calculated from the following eq. (9).<sup>26</sup>

$$\phi = \frac{1}{\Phi_p} \quad (9)$$

The crosslink density in the network,  $\rho_c$  was calculated as

$$\rho_c = \frac{M_0}{M_c} \quad (10)$$

where  $M_0$ , the molar mass of repeating unit per crosslink is defined as

$$M_0 = \frac{n_{\text{VOH}} M_{\text{VOH}} + n_{\text{copolymer}} M_{\text{copolymer}}}{n_{\text{VOH}} + n_{\text{copolymer}}} \quad (11)$$

Here  $n_{\text{VOH}}$  and  $n_{\text{copolymer}}$  are number of moles of repeating unit of PVOH and copolymer in the gel,  $M_{\text{VOH}}$  or molar mass of repeat unit of PVOH is 44,  $M_{\text{copolymer}}$  or molar mass of copolymer in the gel is taken as average from respective contribution of the

comonomer AA (molar mass 72 and HEMA (molar mass 130) in the copolymer.

Ignoring the small amount of NMBA crosslinker and considering binary copolymerization of AA and HEMA to form the copolymer in the matrix of PVOH by free radical polymerization, the approximate copolymer composition ( $d[M_{\text{AA}}]/d[M_{\text{HEMA}}]$ ) of the copolymer hydrogels were calculated using eq. (5). For PVOH there is only one repeating unit i.e., repeating unit of PVOH for which  $M_0$  is 44, for other hydrogels weight average contribution of PVOH and the copolymer was used for calculating  $M_0$ .

The mesh size ( $\zeta$  in  $A^0$ ) of the swollen polymeric network was calculated from the following eq. (12).

$$\zeta = \left[ C_n \left( \frac{2M_c}{M_r} \right) \right]^{1/2} 1\phi_p^{-1/3} \quad (12)$$

The Flory's characteristic ratio,  $C_n$  was taken from literature<sup>20</sup> and C–C bond length; " $l$ " was assumed as 1.54  $A^0$ .  $M_r$ , the molecular weight of repeat unit was calculated as the weight average of the repeat unit of PVOH ( $M_r = 44$ ), PAA ( $M_r = 72$ ), and HEMA ( $M_r = 130$ ). The values of all of these network parameters of the semi and full IPN hydrogels were calculated using eqs. (3)–(14) and these values are given in Table III. Similar values of network parameters were also reported<sup>20</sup> for PVOH grafted acrylamide-*co*-HEMA copolymer. From Table III it is observed that with increasing amount of copolymer from SEMIIPN1 to SEMIIPN4 average molecular mass between the crosslinks,  $M_c$  as well as mesh size of network,  $\zeta$  increases. This effect is accompanied with decrease in crosslink density,  $\rho_c$  and increase in swelling ratio,  $\phi$  of the hydrogel in the same order. PVOH has a dense structure. As it is chemically modified by incorporating the copolymer, the size of the network increases. In fact, the size of the copolymer is bigger than the homopolymer PVOH. Thus, with increase in amount of copolymer

TABLE IV  
Swelling Rate Parameters of the Superabsorbent Copolymer Hydrogel

Name of the polymer	Initial swelling rate $r_0$ (g water/g gel)/min $\times 10^2$	Theoretical equilibrium swelling, $W_\alpha$ (g water/g gel)	Experimental equilibrium swelling, $W_\alpha$ (g water/g gel)	Swelling rate constant, $k_s$ (g gel/g water)/min $\times 10^6$
PVOH	7.50	10.0	8.98	7.50
SEMIIPN1	9.46	12.50	12.08	6.05
SEMIIPN2	11.93	16.66	14.78	4.29
SEMIIPN3	13.81	20.0	16.56	3.45
SEMIIPN4	15.50	20.0	18.42	3.87
FULLIPN1	7.15	11.11	10.29	5.79
FULLIPN2	11.16	11.11	10.77	9.04
FULLIPN3	14.34	11.11	11.18	11.62
FULLIPN4	17.12	12.50	11.81	10.95

from SEMIIPN1 to SEMIIPN4  $M_C$  or mesh size  $\zeta$  of the network increases. Thus, this network of bigger size can hold more of water with increased swelling ratio from SEMIIPN1 to SEMIIPN4. From the data given in Table III it is also observed that the full IPN shows similar trend. Between full IPN and semi IPN, for the same copolymer %, full IPN shows lower  $M_C$  or mesh size ( $\zeta$ ) because of crosslinking of both PVOH and copolymer resulting in tighter network structure with lower swelling ratio.

### Swelling kinetics and diffusion through the hydrogels

#### Swelling kinetics

The mechanism of water permeation through hydrogel polymer depends on different kinds of interactions operating between the functional groups of the polymer and water. A simple second order kinetic equation was reported by many<sup>27</sup> to investigate the swelling of a superabsorbent as given below

$$\frac{dW_t}{dt} = k_s(W_\alpha - W_t)^2 \quad (13)$$

Here " $W_t$ " denotes degree of swelling at time  $t$ ,  $W_\alpha$  is degree of swelling at equilibrium, and  $k_s$  is swelling rate constant.

$$\text{Or } \int_0^t \frac{dW_t}{(W_\alpha - W_t)^2} = k_s \int_0^t dt \quad (14)$$

Integrating eq. (14) with boundary condition of  $W_t = 0$  at  $t = 0$  and  $W_t = W_\alpha$  at equilibrium time  $t$

$$\frac{1}{W_\alpha - W_t} = \frac{1}{W_\alpha} + k_s t \quad (15)$$

Equation (15) may be written in an equivalent linear form

$$\frac{t}{W_t} = \frac{1}{k_s W_\alpha^2} + \frac{1}{W_\alpha} t \quad (16)$$

Further, at  $t = 0$ , eq. (13) reduces to

$$r_0 = k_s(W_\alpha^2) \quad (17)$$

Here  $r_0 = \frac{dW_0}{dt}$  = Initial rate of swelling.  
Hence, eq. (16) reduces to

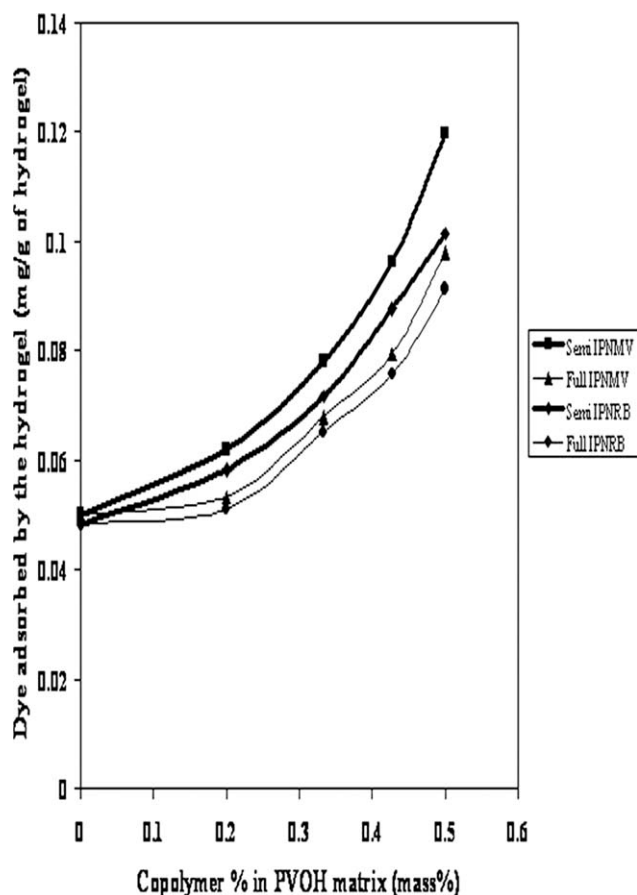
$$\frac{t}{W_t} = \frac{1}{r_0} + \frac{1}{W_\alpha} t \quad (18)$$

A plot of  $t/W_t$  versus  $t$  should give a linear relationship for the applicability of the second order kinetics. The reciprocal of initial rate of swelling ( $r_0$ ) and swelling rate constant ( $k_s$ ) are obtained from the intercept while theoretical equilibrium swelling ( $W_\alpha$ ) can be obtained from reciprocal of slope of the linear plot of  $t/W_t$  versus  $t$ . The initial rate of swelling, swelling rate constant and theoretical equilibrium swelling as calculated for the PVOH, semi and full IPN hydrogels along with the values of regression coefficients for all of these linear trendlines for PVOH and semi IPN hydrogel and full IPN hydrogels are given in Table IV. From this table it is observed that all of the hydrogels show comparable initial rate of swelling as well as rate constant. From this table it is also observed that the swelling data fit well in second order kinetics as evident from regression coefficients of these linear trendlines which is very close to unity for all of these gels. Further, theoretical equilibrium swelling values of the hydrogels are also found to be very close to experimental values signifying close fitting of this second order kinetics.

### Study of dye removal capacity of the hydrogels

#### Effect of copolymer content on dye removal capacity

The effect of copolymer content of the hydrogel on dye removal capacity at solution pH of 7 and feed



**Figure 11** Effect of copolymer content on adsorption of MV and RB dye by the hydrogel for  $1 \text{ mg L}^{-1}$  dye in water: (■) semi IPN MV; (◆) full IPN MV; (▲) semi IPN RB; (●) full IPN RB.

concentration of  $1 \text{ mg L}^{-1}$  of dye is shown in Figure 11. From this figure it is observed that with increasing copolymer content from SEMIIPN1/FULLIPN1 to SEMIIPN4/FULLIPN4 dye removal capacity increases for both MV and RB dye. The MV dye is a basic dye and its cationic amine groups show strong electrostatic attraction for carboxylate anion of the hydrogel polymer. Hence, as the % of carboxylic group increases from SEMIIPN1/FULLIPN1 to SEMIIPN4/FULLIPN4, adsorption of MV dye also increases. RB dye contains a carboxylic group with  $pK_a$  value of 5. Hence, at pH 7 it also ionizes and repels the same group of hydrogels. However, RB dye also contains cationic amine groups which attracts the opposite carboxylate anion of the hydrogel. Further, hydroxy groups of the hydrogel also attract carboxylate group of the RB dye. Because of these two opposing effects, for any copolymer content adsorption of RB dye is lower than MV dye. The full IPN hydrogels are also observed to show lower dye adsorption than the semi IPN hydrogels which may be ascribed to tighter network structure

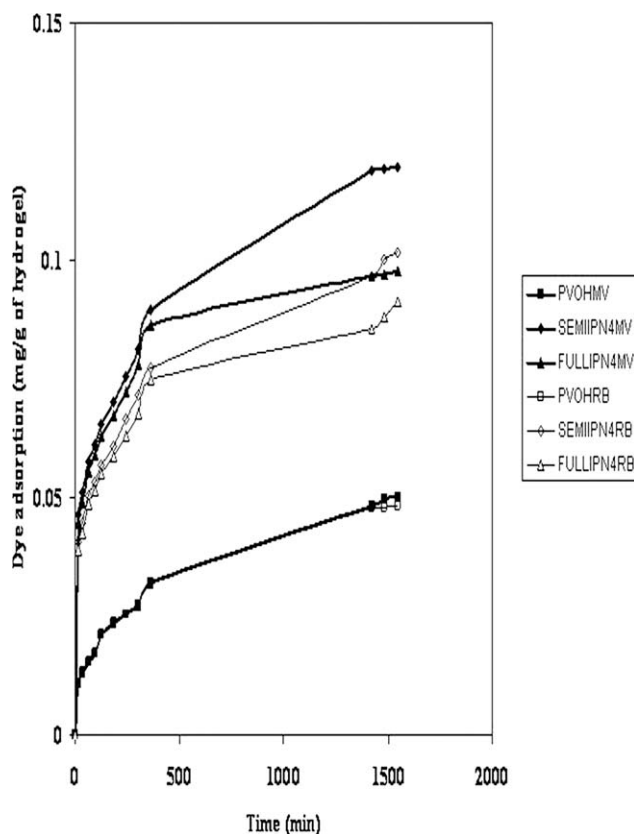
of the full IPN because of crosslinking of both of the constituent polymers.

#### Effect of contact time on dye removal capacity

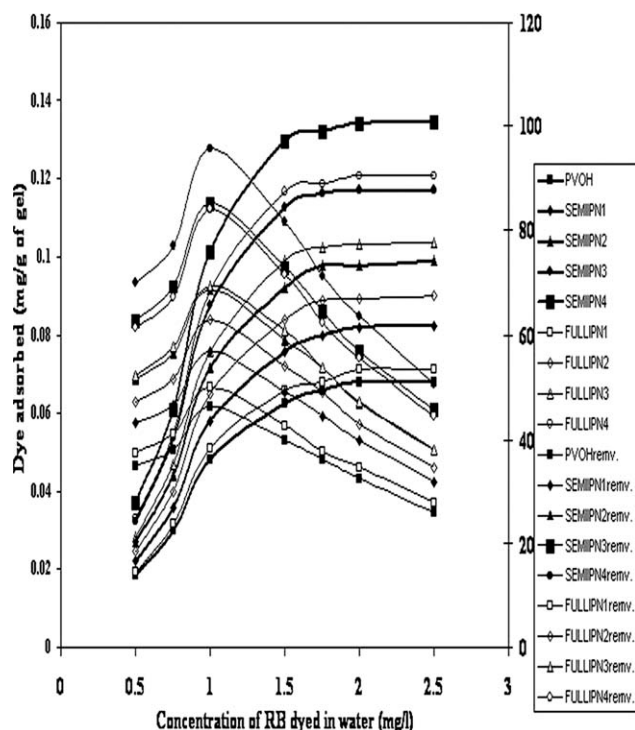
The effect of contact time between dye molecules and the hydrogel polymers was studied at ambient temperature at initial dye concentration of  $1 \text{ mg L}^{-1}$ , and solution pH of 7. It is observed from Figure 12 that like pure water swelling, dye adsorption was also very high and around 50% of the equilibrium value is adsorbed within first three hours of the experiments. As seen in the figure the equilibrium adsorption of dye molecules are achieved within around 10–12 h for all the hydrogels. The other experiments with dye were performed with 24 h contact time to ensure maximum equilibrium adsorption.

#### Effect of initial feed concentration of dye solution

Adsorption experiments were carried out at  $25^\circ\text{C}$  and a pH of 7 for MV and RB dye for PVOH and all of the semi and full IPN hydrogels in the concentration range of  $0.5\text{--}2.5 \text{ mg L}^{-1}$  of dye which is usually found in textile waste. Adsorption isotherm and



**Figure 12** Effect of contact time on dye adsorption: (■) PVOH MV; (◆) SEMIIPN4 MV; (▲) FULLIPN4 MV; (□) PVOH RB; (◇) SEMIIPN4 RB; (△) FULLIPN4 RB.



**Figure 13** Variation of dye adsorption of the hydrogels with initial concentration of dye in water for RB dye: (■) PVOH; (◆) SEMIIPN1; (▲) SEMIIPN2; (●) SEMIIPN3; (■) SEMIIPN4; (□) FULLIPN1; (◇) FULLIPN2; (△) FULLIPN3; (○) FULLIPN4; (■) PVOHremv.; (◆) SEMIIPN1remv.; (▲) SEMIIPN2remv.; (●) SEMIIPN3remv.; (■) SEMIIPN4remv.; (□) FULLIPN1remv.; (◇) FULLIPN2remv.; (△) FULLIPN3remv.; (○) FULLIPN4remv.

removal % of the hydrogels for RB dye is shown in Figure 13. Similar kinds of isotherms were also obtained with MV dye for all of these hydrogels. It is observed that dye uptake of the hydrogel increases with increasing feed concentration of dye and above around  $1 \text{ mg L}^{-1}$  feed dye concentration it tends to level off. The mass transfer resistance of the dye molecules between the aqueous phase and solid (hydrogel) phase is a function of initial concentration of dye in aqueous phase. Hence, a higher initial concentration of dye will increase the adsorption of dye by the hydrogel polymer. For the same dye concentration, adsorption increases with increase in copolymer content from SEMIIPN1/FULLIPN1 to SEMIIPN4/FULLIPN4. PVOH gel is observed to show minimum dye adsorption and removal %. The removal % of the hydrogels is found to increase initially up to  $1 \text{ mg L}^{-1}$  dye concentration and thereafter it decreases for all the hydrogel polymers. Over the used concentration range dye removal % is observed to be the maximum for SEMIIPN4 hydrogel at  $1 \text{ mg L}^{-1}$  ( $95.8\%$ ) and minimum for PVOH ( $46.2\%$ ) at the same concentration. It is also observed from this figure that for any feed concentration the semi IPN hydrogel shows higher dye removing

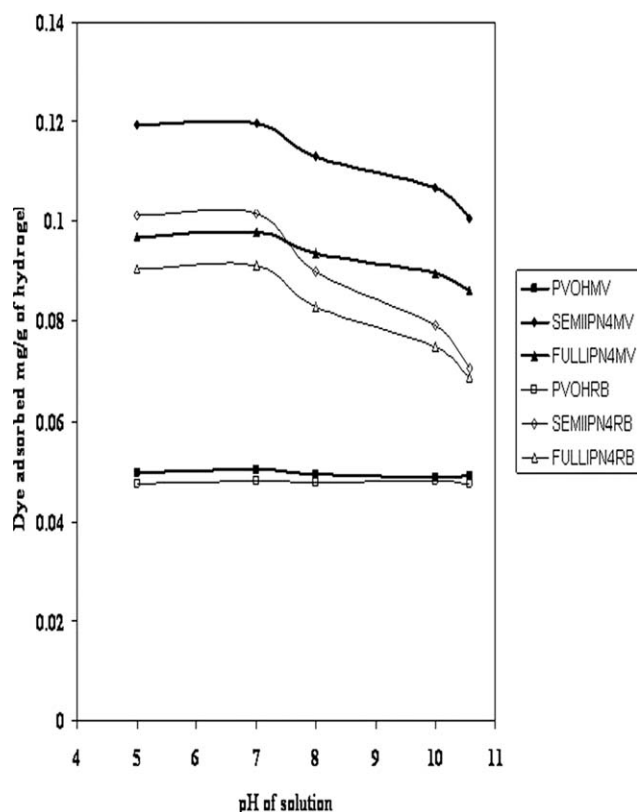
capacity than the full IPN hydrogel. This may be ascribed to tighter network structure of full IPN hydrogel due to crosslinking of both of the constituent polymer. For the same feed concentration adsorption of MV dye was observed to be higher (not shown in the figure) than RB dye. This may be attributed to the difference in molecular structure of the two dyes. The presence of carboxylate anion ( $\text{COO}^-$ ) in the hydrogel shows strong interaction with cationic amine ( $\text{NH}_2^+$ ) group of methylene blue. On the other hand, rhodamine dye contains both cationic substituted amine ( $\text{N}^+$ ) and anionic carboxylate anion ( $\text{COO}^-$ ) group. In this case the cationic amine group attracts the opposite anionic carboxylate group of hydrogel. However, the carboxylate anion of the dye molecules repels the carboxylate anion of hydrogel. Because of these two opposite interaction, overall, all the hydrogel polymers show lower adsorption of rhodamine than methylene blue at the same feed concentration of these two dye molecules.

#### Effect of pH

The pH of the dye solution is very important in that it strongly influences the protonation and deprotonation of the functional groups of the hydrogels and dye molecules. For this experiment the pH was adjusted using dilute HCl and NaOH solution and an initial dye concentration of  $1 \text{ mg L}^{-1}$  was used. The effect of pH on dye adsorption capacity of the hydrogel in the pH range of 5–10 is shown in Figure 14. It is observed that for the basic dye MV the change of dye uptake with feed pH is marginal in the pH range of 5–7. At pH above 8 the primary and secondary amino groups of methyl blue dye become deprotonated<sup>28</sup> and thus due to weak interaction between functional groups of hydrogels and dye molecules, dye uptake capacity of the hydrogel decreases. RB dye contains both substituted cationic amine and carboxylate anion groups showing opposite ionization at higher pH. At higher pH, the decrease in dye adsorption with this dye is much higher than MV dye because of increased ionization of its carboxylate anion which repels the same group of the hydrogel polymer.

#### Effect of ionic strength

The effect of ionic strength on dye adsorption by the hydrogel was evaluated by carrying out similar experiments in presence of sodium chloride. This strong electrolyte is extensively used in textile industries as it promotes adsorption of dyes by the textile fibers.<sup>28</sup> From Figure 15 it is observed that with increasing concentration of sodium chloride, as ionic strength of the solution increases, dye adsorption



**Figure 14** Effect of pH on dye adsorption for  $1 \text{ mg L}^{-1}$  dye concentration. (■) PVOH MV; (◆) SEMIIPN4 MV; (▲) FULLIPN4 MV; (□) PVOHRB; (◇) SEMIIPN4 RB; (△) FULLIPN4 RB.

decreases for both semi and full IPN hydrogel. With increasing ionic strength electrical double layer surrounding the functional hydrogel becomes compressed resulting in decreased adsorption of both of these dyes.

### Adsorption isotherm

The experimental adsorption equilibrium data of dye for different initial feed concentration of dye were fitted to Langmuir [eq. (19)] and Freundlich [eq. (23)] isotherm. The Langmuir adsorption is given by

$$Q_e = \frac{C_e}{\frac{1}{Q_{\max}K_L} + \frac{C_e}{Q_{\max}}} \quad (19)$$

$$\text{Or, } \frac{1}{Q_e} = \frac{1}{Q_{\max}K_L} \cdot \frac{1}{C_e} + \frac{1}{Q_{\max}} \quad (20)$$

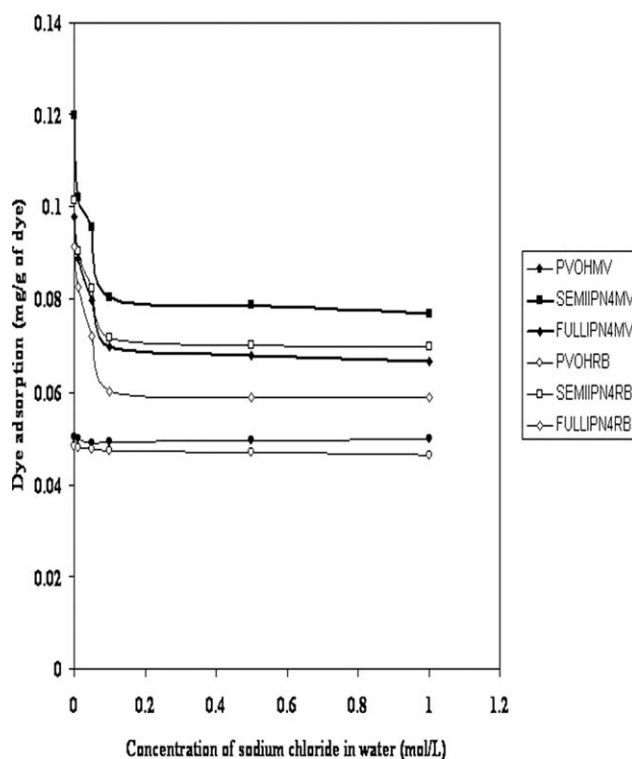
Where  $Q_{\max}$  is the monolayer capacity of the adsorbent hydrogels ( $\text{mg g}^{-1}$ ) and  $K_L$  is Langmuir equilibrium constant ( $\text{L g}^{-1}$ ). From the intercept of the linear plot of  $1/C_e$  against  $1/Q_e$ , the values of  $Q_{\max}$  were obtained. Langmuir constant ( $K_L$ ) was obtained from its slope. Experimental  $Q_e$  was

obtained for various  $C_e$  using eq. (4). Similarly, the Freundlich equation is given by eq. (21)

$$Q_e = K_F C_e^{1/n} \quad (21)$$

$$\text{Or } \ln(Q_e) = \ln K_F + \frac{1}{n} \ln(C_e) \quad (22)$$

where  $K_F$  is Freundlich constant ( $\text{L g}^{-1}$ ).  $n$  is heterogeneity factor.  $n$  is generally greater than unity. The higher the values of  $n$ , the more will be the heterogeneity and the adsorption isotherm will be more nonlinear. The values of  $K_F$  and  $n$  are obtained graphically from intercept and slope, respectively, of a linear plot of  $\ln(Q_e)$  against  $\ln(C_e)$ . For all of the used hydrogels the coefficients of Langmuir and Freundlich for RB and MV dye are given in Table V. The experimental, Langmuir and Freundlich isotherms for RB dye by the SEMIIPN4 and FULLIPN4 hydrogels are shown in Figure 16. From this figure it is observed that Langmuir model fits more closely than Freundlich model to the experimental values. From the values given in Table V it appears that the experimental equilibrium concentration of RB and MV dye fits well in Langmuir model in that regression coefficient ( $r^2$ ) for all of the hydrogels are observed to be  $> 0.95$  for these linear trendlines. For Freundlich isotherms these values are around 0.9 as



**Figure 15** Variation of dye adsorption with concentration of sodium chloride in water: (●) PVOH MV; (■) SEMIIPN4 MV; (◆) FULLIPN4 MV; (○) PVOHRB; (□) SEMIIPN4 RB; (◇) FULLIPN4 RB.



TABLE V  
Langmuir and Freundlich Isotherm Coefficients for RB and MV Dye

Name of the polymer	Langmuir isotherm coefficient for RB dye			Langmuir isotherm coefficient for MV dye			Freundlich isotherm coefficient for RB dye			Freundlich isotherm coefficient for MV dye		
	$K_L$ (L mg <sup>-1</sup> )	$Q_{max}$ mg g <sup>-1</sup>	$r^2$	$K_L \times 10^2$ (L mg <sup>-1</sup> )	$Q_{max}$ mg g <sup>-1</sup>	$r^2$	$K_F \times 10^2$ (mg g <sup>-1</sup> )	$n$ (g L <sup>-1</sup> )	$r^2$	$K_F \times 10^2$ (L mg <sup>-1</sup> )	$n$ (g L <sup>-1</sup> )	$r^2$
PVOH	2.25	1.73	0.956	1.92	2.11	0.956	3.86	1.19	0.908	4.03	1.18	0.908
SEMIIPN1	2.20	2.14	0.957	2.35	2.16	0.957	4.67	1.18	0.909	5.01	1.19	0.910
SEMIIPN2	2.45	2.35	0.959	2.45	2.55	0.959	5.72	1.19	0.900	6.21	1.20	0.900
SEMIIPN3	2.55	2.72	0.946	2.77	2.74	0.945	6.87	1.21	0.886	7.52	1.22	0.884
SEMIIPN4	2.75	2.90	0.945	2.39	3.72	0.932	7.90	1.22	0.884	8.80	1.23	0.860
FULLIPN1	2.14	1.91	0.954	1.99	2.13	0.953	4.06	1.19	0.906	4.24	1.19	0.905
FULLIPN2	2.29	2.29	0.953	2.39	2.27	0.952	5.17	1.20	0.900	5.39	1.20	0.898
FULLIPN3	2.64	2.31	0.949	2.64	2.31	0.949	6.04	1.21	0.893	6.34	1.21	0.893
FULLIPN4	2.68	2.67	0.945	2.67	2.67	0.945	7.09	1.21	0.883	7.60	1.21	0.882

shown in Table V. The Langmuir isotherm can also be expressed in terms of a dimensionless parameter separation factor  $R_L$  as

$$R_L = \frac{1}{1 + K_L C_i} \quad (23)$$

Here  $C_i$  is initial concentration of dye in water. For favorable Langmuir isotherm the values of  $R_L$  should be between 0 and 1.<sup>14</sup> For an initial dye concentration of 0.5–2.5 mg L<sup>-1</sup>, the values of  $R_L$  for all the hydrogels lies between 0.980 and 0.989 signifying favorable adsorption of these two dyes by the used hydrogel polymers. It is also observed that the values of Langmuir coefficient ( $K_L$ ), maximum monolayer adsorption ( $Q_{max}$ ) and Freundlich coefficient ( $K_F$ ) increases from PVOH to SEMIIPN4 while the semi IPN hydrogels show higher values of these coefficients than the full IPN of same copolymer content. In tune with experimental results the values

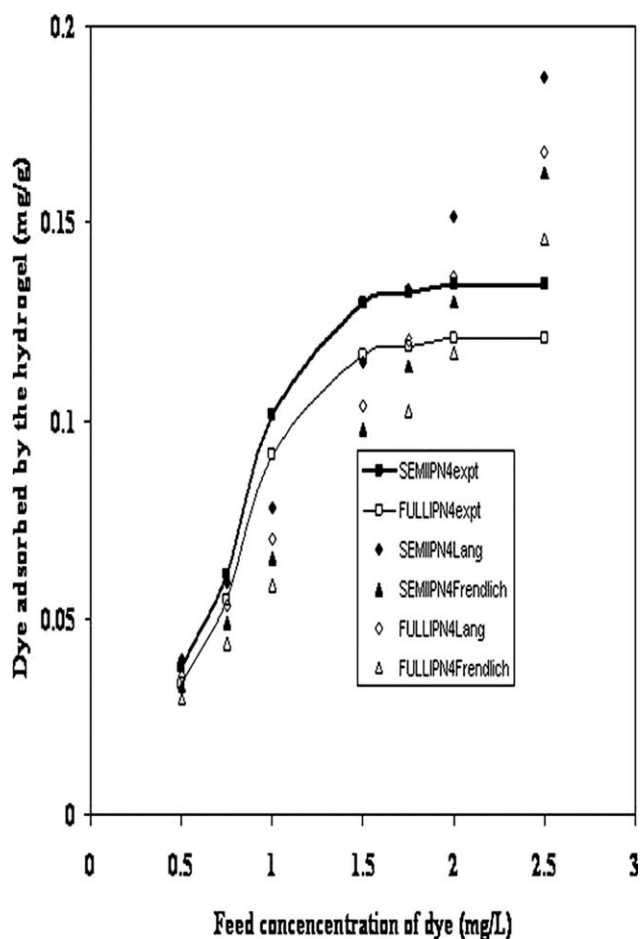


Figure 16 Experimental, Langmuir and Freundlich isotherms for adsorption of MV dye by semi and full IPN hydrogels: (■) SEMIIPN4expt; (□) FULLIPN4expt; (◆) SEMIIPN4 Lang; (▲) SEMIIPN4 Freundlich; (◇) FULLIPN4Lang; (△) FULLIPN4 Freundlich.

TABLE VI  
First Order and Second Order Kinetic Data for Adsorption of RB and MV Dye

Name of the polymer	First order kinetic data for RB dye			First order kinetic data for MV dye			Second order kinetic data for RB dye			Second order kinetic data for MV dye		
	$k_1$ ( $\text{min}^{-1}$ )	$Q_{\text{max}}/Q_{\text{maxEXPT}}$ ( $\text{mg g}^{-1} \times 10^2$ )	$r^2$	$k_1$ ( $\text{min}^{-1}$ )	$Q_{\text{max}}/Q_{\text{maxEXPT}}$ ( $\text{mg g}^{-1} \times 10^2$ )	$r^2$	$k_2 \times 10^6$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$Q_{\text{max}}$ ( $\text{mg g}^{-1} \times 10^2$ )	$r^2$	$k_2 \times 10^6$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$Q_{\text{max}}$ ( $\text{mg g}^{-1} \times 10^2$ )	$r^2$
PVOH	3.20	4.08/4.82	0.995	2.7	4.45/5.02	0.954	9.56	5.38	0.988	8.91	5.56	0.986
SEMIIPN1	3.24	3.91/5.82	0.925	3.3	4.72/6.2	0.995	15.44	6.16	0.997	13.49	6.61	0.996
SEMIIPN2	2.90	5.48/7.16	0.780	2.8	5.68/9.31	0.919	20.85	7.40	0.998	12.78	9.67	0.997
SEMIIPN3	2.69	6.82/8.76	0.828	2.9	7.73/11.0	0.989	12.89	9.16	0.997	8.03	11.64	0.994
SEMIIPN4	2.59	7.50/10.15	0.891	3.4	9.08/11.9	0.987	9.61	10.62	0.995	7.21	12.71	0.994
FULLIPN1	3.46	3.14/5.11	0.887	2.3	3.49/5.33	0.978	20.91	5.27	0.996	16.41	5.60	0.995
FULLIPN2	3.16	4.25/6.51	0.947	2.7	4.51/6.78	0.980	14.38	6.84	0.996	13.65	7.16	0.997
FULLIPN3	3.08	4.57/7.56	0.996	1.5	4.01/7.9	0.853	14.75	7.87	0.997	18.31	7.93	0.996
FULLIPN4	3.46	3.14/9.13	0.887	2.7	5.26/9.7	0.967	13.35	9.41	0.997	15.21	10.11	0.998

of these coefficients for MV dye is greater than RB dye for the same polymers. The values of Freundlich coefficient "n" is also observed to be close to unity for all the hydrogels signifying little heterogeneity and linearity of the isotherms.<sup>28</sup>

### Adsorption kinetics

The kinetics of dye adsorption by the hydrogels were studied using a pseudo first order kinetic model [eq. (24)] and a pseudo 2nd order kinetic model [eq. (25)] by fitting the experimental dye adsorption data in these equations.

The pseudo 1st order equation is

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (24)$$

where  $Q_t$  and  $Q_e$  is adsorption of dye at time  $t$  and at equilibrium ( $\text{mg g}^{-1}$ ) and  $k_1$  is pseudo first order rate constant ( $\text{min}^{-1}$ ). The values of  $k_1$  and  $Q_e$  are obtained from slope and intercept, respectively, of the linear plotting of  $\ln(Q_e - Q_t)$  against  $t$ .

The pseudo second order equation is

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2} \quad (25)$$

where  $k_2$  is pseudo second order rate constant ( $\text{mg}^{-1} \text{g min}^{-1}$ )

The values of  $k_2$  and  $Q_e$  is also obtained in a similar way from the slope and intercept of the linear plot of  $t/Q_e$  versus  $t/Q_t$ . The values of pseudo first order and second order rate constant, equilibrium dye adsorption and regression coefficients for these linear trendlines for all the hydrogels are given in Table VI. The experimental  $Q_e$  values are also given in the same table. It is clearly observed that theoretical  $Q_e$  values based on second order kinetics matches the experimental values more closely than the first order kinetics. Further the values of regression coefficients for second order kinetics are more close to unity. Thus, the dye adsorption by the functional hydrogels may be assumed to follow second order kinetics.

### CONCLUSIONS

Superabsorbent polymer hydrogels were synthesized by free radical crosslink copolymerization of AA and HEMA with NMBA as crosslinker in the matrix of PVOH. Accordingly, four semi IPN and four full IPN hydrogels were synthesized and these hydrogels were characterized by FTIR, UV, XRD, SEM, and mechanical properties. These hydrogel polymers were also characterized by network parameters like mesh size and crosslink density. The full IPN were observed to show higher crosslink density and

lower mesh size than the semi IPN hydrogels. Swelling characteristics of the hydrogels were found to increase with increasing copolymer content and pH of the solution. These hydrogels were also observed to selectively adsorb two industrial dyes i.e., RB and MV from water. The adsorption of dyes was also found to increase with increasing copolymer content from SEMIIPN1/FULLIPN1 to SEMIIPN4/FULLIPN4. However, dye uptake properties were observed to decrease with increasing ionic strength and pH of the solution. Experimental adsorption isotherms of these hydrogels were compared to Langmuir and Freundlich adsorption isotherms. The hydrogels were found to fit Langmuir model more closely than Freundlich isotherm. The swelling % and dye adsorption of semi IPN hydrogels were higher than full IPN while MV dye adsorption was higher than RB dye for all of the hydrogels. These hydrogels may be effectively applied for removal of traces of similar kind of dyes from water.

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