Behavior of Semi IPN Hydrogels Composed of PEG and AAm/SMA Copolymers in Swelling and Uptake of Janus Green B from Aqueous Solutions

Ömer Barış Üzüm, Erdener Karadağ

Department of Chemistry, Fen-Edebiyat Faculty, Adnan Menderes University, TR-09010 Aydin, Turkey

ABSTRACT: Semi-interpenetrating polymer network (semi IPN) hydrogels of poly(ethylene glycol; PEG) were prepared as a water adsorbent for dye (Janus Green B) sorption. For this, PEG and copolymer of acrylamide/sodium methacrylate (AAm/SMA) were prepared by polymerization of aqueous solution of acrylamide (AAm), sodium methacrylate (SMA) using ammonium persulfate (APS)/N,N,N',N'-tetramethylethylenediamine (TEMED) as redox initiating pair in presence of PEG and poly(ethylene glycol)dimethacrylate (PEGDMA) as crosslinker. FTIR spectroscopy was used to identify the presence of different repeating units in the semi IPNs. Some swelling and diffusion characteristics were calculated for different semi IPNs and hydrogels prepared under various formulations. Water uptake and dye sorption properties of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs were investigated as a function of chemical composition of the hydrogels. Janus Green B have used in sorption studies. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: swelling; hydrogel; interpenetrating polymer networks; acrylamide; sodium methacrylate; Janus Green B

INTRODUCTION

Dyeing wastes in some industrials have high color and organic content. Colored waters are also objectionable on aesthetic grounds for drinking and other municipal and agricultural purposes. Effective removal of dye, in connection with waste water treatment strategy, still remains a major topic of present research. Many methods have been proposed for the removal of dyes, heavy metals, and other hazardous materials. Chemical precipitation, membrane extraction, coagulation, solvent extraction, ion change, and adsorption are some of the commonly used process, but each has its own merits and demerits in its applications. Adsorption procedure is a way of one of the most widely used for pollutants such as dyes and organic compounds from industrial effluents. Adsorption is a well-known equilibrium separation process. Recently, new effective, efficient and economic methods for water decontamination applications and for separation analytical purposes have been investigated.[1–10]

In recent years, polymeric gels are the objects of intensive studies. Highly swollen polymers or copolymers are highly hydrophilic, three-dimensional crosslinked polymeric structures that are able to swell in the aqueous environment. The capability of hydrogels to swell in water is due to the hydrophilic groups present in the polymer chains, whereas its mechanical resistance is due in part to the physical or chemical network crosslinking. Hydrogels have special properties due to their intermediate state between a liquid and a solid. The ability to absorb and to store much water and water solutions make hydrogels unique materials for a variety of applications. Hydrogels may be conveniently described as hydrophilic polymers that are swollen by, but do not dissolve in water. They are three-dimensional crosslinked polymeric structures that are able to swell in the aqueous environment. Crosslinked polymers capable of imbibing large volumes of water have found widespread applications in bioengineering, biomedicine, and food industry and water purification and separation process. Because of its swelling ability in water, hydrophilicity, biocompatibility, and no toxicity, hydrogels have been utilized in a wide range of biological, medical, pharmaceutical, environmental applications.[10–17]

Some physical properties of hydrogels may be improved by preparing semi-interpenetrating polymer networks (semi IPN's), when the hydrogel network is prepared in the presence of a previously

made polymer such as poly(ethylene glycol; PEG), polyacrylamide, poly(*N*-isopropyl acrylamide), poly(vinyl pyrrolidione), poly(vinyl alcohol), or poly(acrylic acid), etc. Water sorption property of hydrogels or semi-interpenetrating polymer networks (semi IPN's) accounts for a great number of biomedical and technological applications such as drug delivery systems, artificial implants, contact lens, enzyme immobilization, catheters, wound dressings, biosensors, superabsorbents, and etc.[18–21]

Poly(ethylene glycol; PEG) can be used a linear polymer as mechanical stability agent for semi-interpenetrating polymer networks (semi IPN's). PEG is of great interest in numerous biomedical applications for several purposes. PEG is water-soluble and is non-toxic for body immune system. PEG-based hydrogels have good biocompatibility. PEG-based hydrogel systems have been used at many biotechnological applications.[22–24]

Polyacrylamide based hydrogels have received considerable attention because of their use in many applications. In our previous study, copolymeric hydrogels of acrylamide with some acidic monomers were prepared by free radical solution polymerization and used in separation and adsorption of some dye molecules.[4,7,8,15,16,25,26]

In this study, it was of interest to increase the water absorption capacity of AAm hydrogels with highly hydrophilic functional groups containing chemical reagents such as SMA with PEG via free radical solution polymerization method. It was reported that some groups has been synthesized SMA based crosslinked polymers and/or copolymers.[4,21,26,27] Here, in this study, we have investigated the incorporation of PEG and SMA into AAm hydrogel during free radical solution polymerization synthesis. AAm is a highly hydrophilic monomer, SMA is an anionic monomer and PEG is a linear polymer. The main purpose of this study was to combine both monomers and a polymer in a new polymeric system. In this respect, a series of copolymeric hydrogels were synthesized by changing the content of SMA and PEG. Then, some swelling and some diffusional properties of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs were studied in water by dynamic swelling studies for swelling characterization. Water uptake and dye sorption properties of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs were investigated as a function of chemical composition of the hydrogels.

EXPERIMENTAL

Materials

Acrylamide (AAm) as monomer, sodium methacrylate (SMA) as comonomer, PEG (M_w=4000), poly (ethylene glycol) dimethacrylate (PEGDMA, M_n=330) as crosslinker were supplied from Aldrich, Steinheim, Germany. The initiator, ammonium persulfate (APS) was purchased from Merck, Darmstadt, Germany and the activator N,N,N',N'-tetramethylethylenediamine (TEMED) was purchased from Merck Schuchardt, Germany. Cationic dye, Janus Green B, (JGB) used in sorption studies, were purchased from Fluka, Steinheim, Germany. All chemicals were used as received.

Preparation of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs

To prepare AAm/SMA hydrogel systems, AAm weighing 1.0 g (14.07 mmol) was dissolved in 1.0 mL water. Then, 0 mg, 10 mg/0.0.0925 mmol, 20 mg/0.185 mmol, 30 mg/0.278 mmol, 40 mg/0.370 mmol, 50 mg/0.463 mmol, 60 mg/0.555 mmol, 70 mg/0.648 mmol, 80 mg/0.740 mmol of SMA were added to each AAm solutions, respectively. After these additions, for the synthesis, 0.040 mL/0.133 mmol of PEGDMA and 0.2 mL/0.0438 mmol aqueous solutions of APS (5.0 g APS/0.022 mol/100 mL water) and 0.25 mL/0.0167 mmol 1% concentration of TEMED were added these aqueous solutions. The solutions were placed in PVC straws of 3 mm diameter. After gelation, fresh hydrogels obtained in long cylindrical shapes were cut into pieces of 3–4 mm in length. They were washed 4 days in distilled water to remove unreacted materials, blotted dry with filter paper, dried in air and vacuum, and stored for swelling studies.

To prepare highly swollen AAm/SMA/PEG semi IPNs, same method was used as mentioned above with addition of 0.25, 0.50, 0.75, and 1.00 g PEG to aqueous monomer solution per 1.0 g of AAm.

For dynamic swelling studies, AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs were accurately weighted and transferred into water. Water uptake with respect to time was obtained by periodically removing the samples from water; quickly blot drying, and reweighing. The measurements were conducted at 25 ± 0.1°C in a water bath.
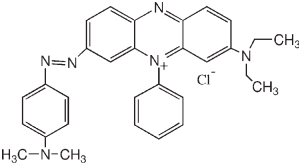
FTIR analysis of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs

For structural characterization, FTIR analysis was made. Spectra were obtained by VARIAN FTS 800 FTIR spectrophotometer using KBr discs.

Swelling studies

A fundamental relationship exists between the swelling of a polymer in a solvent and the nature of the polymer and the solvent. The percentage swelling

TABLE I
Some Properties of Janus Green B

Name	Chemical formula	Molar mass (g/mol)	λ_{max} (nm)	C.I. Nr.
Janus Green B (JGB) (Union Green B)		511.07	660	11050

($S\%$) of the hydrogels in distilled water was calculated from the following relation,

$$S\% = \frac{m_t - m_o}{m_o} \times 100 \qquad (1)$$

Here, m_t is the mass of the swollen gel at time t and m_o is the mass of the dry gel at time 0.

The water absorbed by AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs quantitatively represented by equilibrium water content (EWC), and they can be calculated by below equation.[27–29]

$$EWC = \frac{m_{eq} - m_o}{m_{eq}} \qquad (2)$$

Here, m_{eq} is the mass of the swollen gel at time t (equilibrium), and m_o is the mass of the dry gel at time 0.

Dye sorption equilibrium experimental

Batch sorption studies were proceeding in all sorption experiments. Cationic dye, Janus Green B, (JGB) used in sorption studies and some properties of JGB were given in Table I.

Solutions of JGB concentration range $1.25 \times 10^{-3}M$–$2.00 \times 10^{-3}M$ in distilled water were prepared. AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs containing 60 mg SMA was used in a known volume of dye solution until equilibrium was reached. For SMA effect on the dye sorption, aqueous solution of concentration of $2.00 \times 10^{-3}M$ of JGB was used.

After sorption, dye solution was separated by decantation from the hydrogels. Spectrophotometric method was applied to dye solutions. Spectrophotometric measurements were carried out using a SHIMADZU UV 1601 model UV-VIS spectrophotometer at ambient temperature. The absorbances of these solutions were read at 660 nm for JGB.[30] Distilled water was chosen as the reference. The equilibrium concentrations of the cationic dye solutions were determined by means of precalibrated scales.
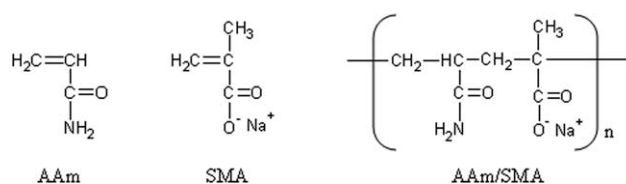

Figure 1 Representative chemical structures of monomers and possible AAm/SMA random copolymer.

RESULTS AND DISCUSSION

FTIR analysis

AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs were prepared by free radical solution polymerization. Chemical structures of monomers and possible AAm/SMA copolymers are presented in Figure 1. The structure of copolymers is random. Dried AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs are glassy and very hard, but swollen gels are soft. The synthesis of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs via radical chain polymerization is a well-established procedure. Upon swelling the hydrogels were strong enough to retain their shape.

For structural analysis of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs during polymerization, FTIR spectra of the hydrogel systems were evaluated and are presented in Figures 2 and 3. In the FTIR spectra of the hydrogels, the broad bands observed between 3600 and 3000 cm^{-1} corresponds to hydrogen bonded O—H and N—H stretching of AAm/SMA and AAm/SMA/PEG units. The bands at 1600–1700 cm^{-1} could be attributed to a shift in stretching vibration associated with hydrogen that is bonded directly to an overtone of the strong carbonyl absorption. The peaks observed between 1600
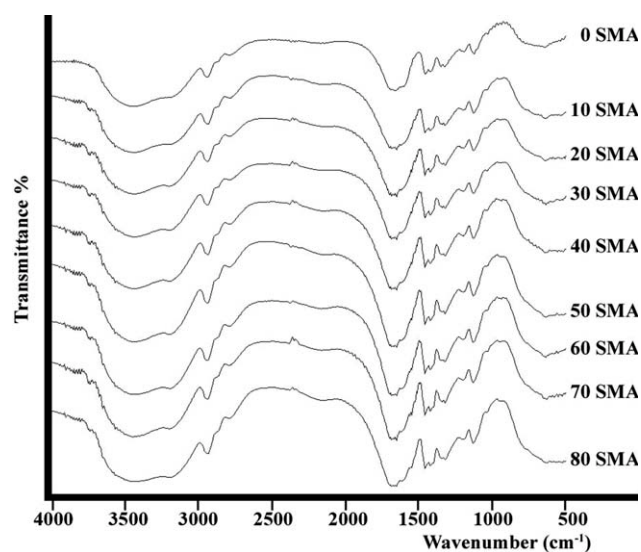

Figure 2 FTIR spectra of AAm/SMA hydrogels including various contents of SMA.
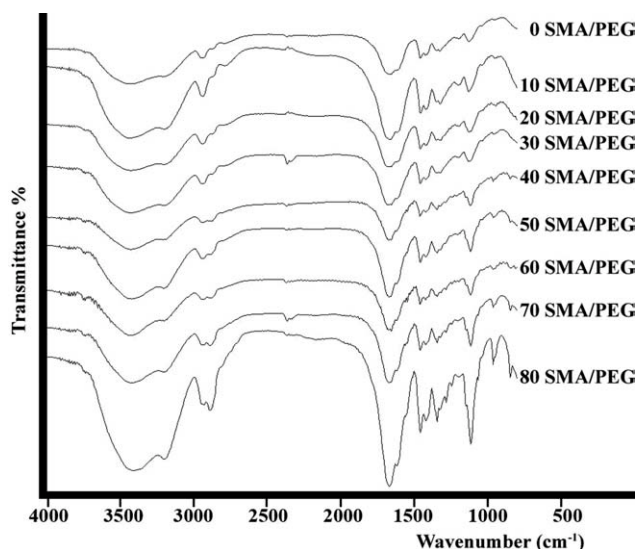
Figure 3 FTIR spectra of AAm/SMA/PEG semi IPNs including various contents of SMA and constant amount of PEG.

and 1700 cm^{-1} corresponding to the vC=O of the methacrylate unit of SMA. The peaks observed this region also corresponding to the vC=O group of AAm. On the other hand, it is thought that the peaks at 1250 cm^{-1} are C—N bands, and the peaks at 2850 cm^{-1} and 1400 cm^{-1} show —CH$_2$— groups on the polymeric chain. The peaks around 3500 and 1100 cm^{-1} are assigned to the terminal hydroxyl group and C—O stretching of polyether, respectively. Broad peaks between 3200 and 3600 and a sharp peak at approximatelly1600–1700 cm^{-1} in the IR spectra of IPN hydrogel can be indicated the presence of the AAm and SMA units along with PEG repeating units in the semi IPN hydrogels.[4,21,26]

Equilibrium swelling studies

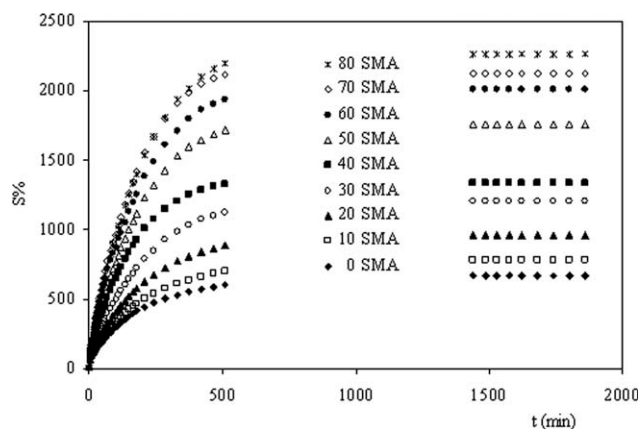The water intake of initially dry hydrogels was followed for AAm/SMA hydrogels and AAm/

SMA/PEG semi IPNs crosslinked by PEGDMA in water, and swelling isotherms of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs crosslinked by PEGDMA are shown in Figures 4 and 5 as representative.

Figures 4 and 5 show that swelling increases with time up to certain level, then levels off. This value of swelling may be called as the equilibrium swelling percent (S_{eq}%). S_{eq}% values of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs are given in Table II.

Table II shows that S_{eq}% of AAm hydrogels is 660%, but S_{eq}% of AAm/SMA are 780–2260% with the incorporation of SMA groups into AAm hydrogels, and S_{eq}% of AAm/SMA/PEG hydrogels are 660–1980% with the incorporation of PEG groups into AAm/SMA hydrogels, while equilibrium swelling percent value of AAm/PEG hydrogels is 580%. In Table II, S_{eq}% of the hydrogels increased with the SMA content in the copolymers. S_{eq}% of AAm/SMA hydrogels is higher than S_{eq}% of AAm hydrogels.

It is well known that the swelling of a hydrogel is induced by electrostatic repulsion of the ionic charges of its network. SMA contains only one ionizable group (—COONa), but SMA groups on the copolymeric chain contain many ionizable groups. The swelling increase is due to an increase in the anionic units. On the other hand, salts of weak acids are decomposed by water with the formation of free acid and free base. The salt group is almost completely ionized, and a large number of hydrophilic groups occur. The hydrophilic group numbers of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs are higher than those of AAm, and so the swelling values of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs are greater than that of AAm swelling values.

The values of EWC of all AAm/SMA hydrogels and AAm/SMA/PEG semi IPN systems were calculated. The values of EWC of the hydrogels are
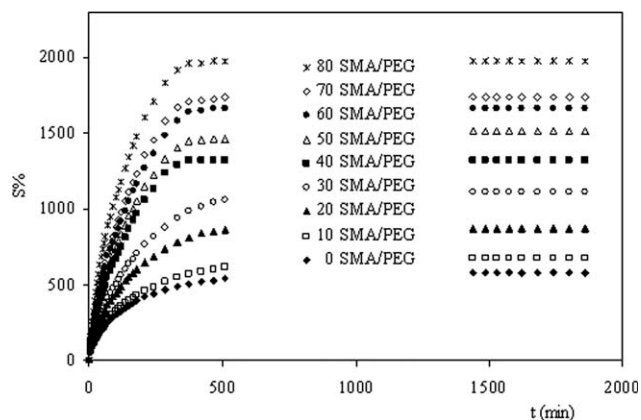

Figure 4 Swelling isotherms of AAm/SMA hydrogels.

Figure 5 Swelling isotherms of AAm/SMA/PEG semi IPNs.

TABLE II
Values of the Equilibrium Percentage Swelling (S_{eq}%) and Equilibrium Water Contents of AAm/SMA Hydrogels and
AAm/SMA/PEG (Containing 0.5 g PEG) Semi IPNs

SMA/mg	0	10	20	30	40	50	60	70	80
Equilibrium swelling percent (S_{eq}%)									
AAm/SMA	660	780	960	1200	1330	1760	2000	2120	2260
AAm/SMA/PEG	580	670	870	1110	1320	1510	1660	1730	1980
Equilibrium water contents (EWC)									
AAm/SMA	0.8698	0.8870	0.9060	0.9235	0.9302	0.9463	0.9526	0.9551	0.9578
AAm/SMA/PEG	0.8533	0.8713	0.8973	0.9178	0.9296	0.9382	0.9434	0.9456	0.9520

tabulated in Table II. It is seen that an increasing of the values of EWC, if SMA have been added to AAm/SMA hydrogels and AAm/SMA/PEG semi IPN systems. Here, the main effect is the hydrophilic character of SMA groups.

Diffusion

When a glassy hydrogel is brought into contact with water, water diffuses into the hydrogel and the network expands resulting in swelling of the hydrogel. Diffusion involves migration of water into pre-existing or dynamically formed spaces between hydrogel chains. Swelling of the hydrogel involves larger segmental motion resulting, ultimately, in increased separation between hydrogel chains.

The following equation is used to determine the nature of diffusion of water into hydrogels.[28,31]

$$F = \frac{M_t}{M_s} = kt^n \tag{3}$$

Here, F is the fractional uptake at time t. Here, M_t and M_s are the mass uptake of the solvent at time t and the equilibrium, respectively. Equation (3) is valid for the first 60% of the fractional uptake. Fickian diffusion and Case II transport are defined by n values of 0.5 and 1.0, respectively. Anomalous transport behavior (non-Fickian diffusion) is inter-mediate between Fickian and Case II. That is reflected by n between 0.5 and 1.0.[28,31] The values of (n) and (k) were calculated from the slope and the intercept of the plot of ln$F$ against ln$t$, respectively.

For AAm/SMA hydrogel and AAm/SMA/PEG semi IPNs, ln$F$ vs. ln$t$ graphs are plotted and representative results are shown in Figures 6 and 7. Diffusional exponents (n) and diffusion constant (k) are calculated and listed in Table III.

Table III shows that the number determining the type of diffusion (n) is over 0.50. Hence, the diffusion of water into the super water-retainer hydrogels is generally found to have a non-Fickian character. When the diffusion type is anomalous behavior, the relaxation and diffusion time are of the same order of magnitude.

The study of diffusion phenomena of water in hydrogels is of value in that it clarifies polymer behavior. For hydrogel characterization, the diffusion coefficients can be calculated by various methods. The diffusion coefficient, D, of the water was calculated using the following equation.[28,32,33]

$$D = \pi r^2 \left(\frac{k}{4}\right)^{1/n} \tag{4}$$

Here, D is in cm^2/min, r is the radius of a cylindrical polymer sample, (n) is the diffusional exponent,
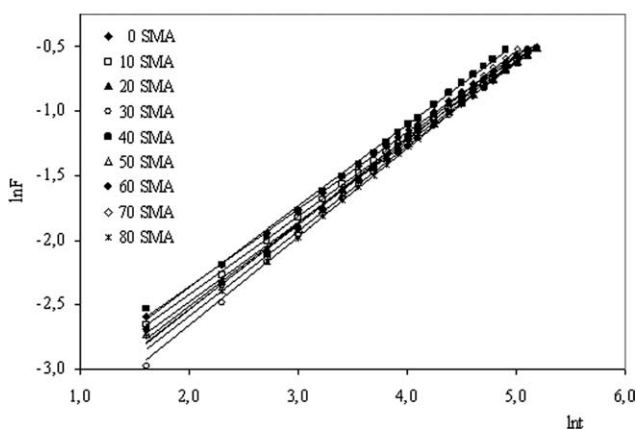

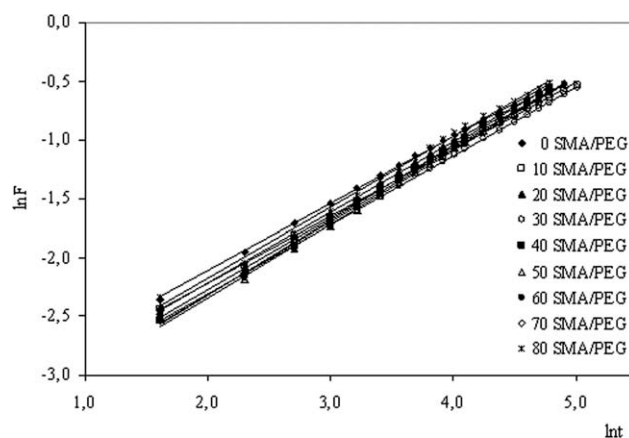Figure 6 Swelling kinetic curves of AAm/SMA hydrogels.

Figure 7 Swelling kinetic curves of AAm/SMA/PEG semi IPNs.

TABLE III
Some Diffusion Parameters of AAm/SMA Hydrogels and AAm/SMA/PEG (Containing 0.5 g PEG) Semi IPNs

SMA/mg	0	10	20	30	40	50	60	70	80
Diffusion exponent, n									
AAm/SMA	0.5986	0.6056	0.6186	0.6833	0.6299	0.6569	0.6456	0.6685	0.6569
AAm/SMA/PEG	0.5673	0.5682	0.5996	0.5870	0.6347	0.6261	0.6206	0.6061	0.6032
Diffusion constant, $k \times 10^2$									
AAm/SMA	2.85	2.63	2.42	1.78	2.65	2.12	2.22	2.08	2.02
AAm/SMA/PEG	3.90	3.51	3.29	3.06	2.77	2.76	2.86	3.08	3.40
Diffusion coefficient, $D \times 10^6$									
AAm/SMA	97	99	139	183	203	246	242	360	325
AAm/SMA/PEG	75	85	121	122	215	207	232	231	280

and (k) is a constant incorporating characteristic of the macromolecular network system and the penetrant. The values of diffusion coefficient determined for AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs are listed in Table III. Table III shows that the values of the diffusion coefficient of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs vary from 75.0×10^{-6} cm^2/min to 360.0×10^{-6} cm^2/min. It was seen that an increasing of the values of the diffusion coefficient of AAm/SMA hydrogels and AAm/SMA PEG semi IPNs by increasing of SMA content. Hydrophilicity of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs becomes greater than that of AAm, so, the diffusion of water of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs is greater than the diffusion of water of AAm hydrogels.

PEG effect on the swelling and diffusion

For investigation of the effect of mass/content of PEG on the swelling properties of AAm/SMA/PEG semi IPNs, the related swelling isotherms of AAm/SMA/PEG hydrogels were constructed and representative swelling isotherms and ln$F$ versus ln$t$ graphs are plotted and representative results are

shown in Figures 8 and 9. PEG effect on some swelling and diffusion parameters of AAm/SMA/PEG semi IPN systems containing 60 mg SMA are tabulated in Table IV.

It was shown that a decreasing of the equilibrium swelling percent (S_{eq}%), EWC, diffusion exponent (n), and diffusion coefficient (D) of AAm/SMA/PEG semi IPN systems when PEG has been added to the hydrogel systems. Incorporation of PEG into the copolymer network leads to lower degrees of swelling. Here, there is no other interaction of PEG with AAm and SMA. Here, PEG chains have been placed into the crosslinked AAm/SMA copolymeric chains. PEG chains have been placed into the crosslinked copolymeric system by "tangled."

On the other hand, also, it is seen that an increasing of diffusion constant (k) of AAm/SMA/PEG hydrogels with increasing content of PEG in hydrogel systems from Table IV. Here, it was said that PEG chains was placed in the crosslinked polymeric systems, in stead of crosslinked AAm and SMA molecules, it was seen that decreasing of the value of the equilibrium swelling percent and related parameters, because of decreasing of hydrophilic character at crosslinked polymeric systems. In addition of this phenomenon, the PEG chains are located in the free
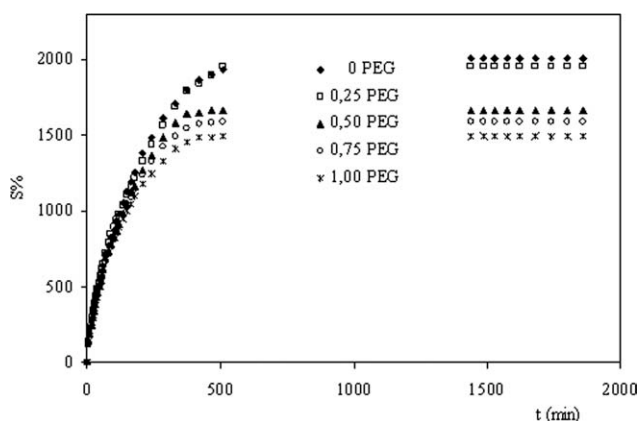

Figure 8 Swelling isotherms of AAm/SMA/PEG semi IPNs with various contents of PEG and containing 60 mg SMA.
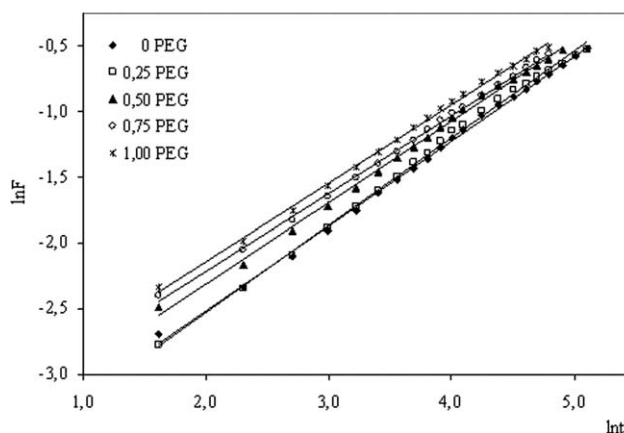

Figure 9 Swelling kinetic curves of AAm/SMA/PEG semi IPNs with various contents of PEG and containing 60 mg SMA.

TABLE IV
Some Swelling and Diffusion Parameters of AAm/SMA/PEG Semi IPNs with Various Contents of PEG (Containing 60 mg SMA)

PEG/g	0	0.25	0.50	0.75	1.00
Equilibrium swelling percent (S_{eq}%)	2000	1950	1660	1580	1490
Equilibrium water contents (EWC)	0.9526	0.9514	0.9434	0.9407	0.9372
Diffusion exponent (n)	0.6456	0.6635	0.6206	0.5936	0.5962
Diffusion constant, $k \times 10^2$	2.22	2.12	2.86	3.33	3.57
Diffusion coefficient, $D \times 10^6$	242	249	232	179	195

space of crosslinked polymer networks; water diffusion is prevented by the PEG chains. This is also caused of decreasing of the equilibrium swelling percent and related parameters.

Equilibrium sorption studies

To observe the sorption of JGB, AAm/SMA hydrogels, and AAm/SMA/PEG semi IPNs were placed in aqueous solutions of JGB and allowed to equilibrate for 4 days at 25°C. At the end of this period, AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs in the JGB solutions showed the dark coloration. But acrylamide hydrogel did not sorb any dye from solution.

In the sorption system at equilibrium, the total solute (dye) concentration; C_o is following equation.[17,34,35]

$$C_o = C_b + C \tag{5}$$

Here, C_b is the equilibrium concentration of the solute (dye) on the sorbent per liter solution (bound solute concentration) and C is the equilibrium concentration of the solute in the solution (free solute concentration). The value of the bound concentration may be obtained by using eq. (5). For a fixed free solute concentration, C_b is proportional to the polymer concentration on the binding system; the amount bound can therefore be conveniently expressed as the binding ratio r, defined by

$$r = C_b/P \tag{6}$$

Thus, with in and P is base mol (moles of monomer units) per liter solute represents the average number of molecules of solute bound each monomer unit at that free solute concentration. To determine the sorption/binding kinetics of JGB into AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs, binding characterization parameters can be investigated.

The binding data was interpreted on the basis of the uniform site-binding (u.s.b.) model, which in statistical-thermodynamic terms corresponds to a formation of an ideal localized one-dimensional monolayer of solute on the polymer chains. This leads to the hyperbolic (Langmuir) from of the binding isotherm, which applies to many polymer/solute (dye molecules) binding system.[17,34,35]

$$r = \frac{n_s KC}{1 + KC} \tag{7}$$

Here, K is the binding constant, that is, the equilibrium constant for the attachment of a molecule of dye onto a site by a specific combination of non-covalent forces. Here, n_s is the site density (the limiting value of r for monolayer coverage), which is therefore of density of the sites along the polymer chain. To reciprocal of n_s is the site-size, u, which may be taken to represent either average number of monomer units occupied by the bound solute molecule, more generally the average spacing of solute molecules when the chain is saturated. The initial binding constant, K_i is the initial slope of the binding isotherm, and therefore the average binding strength of a solute molecule by a single monomer unit on an occupied chain. K_i is equal to the product $n_s K$.

To get the best values for the binding parameters from the experimental data, the linearization methods of eq. (7) have been developed by some researches as Klotz, Scatchard and Langmuir.[17,34,35]

Klotz method

If the isotherm [eq. (7)] is multiplied out and then divided throughout by $CKn_s r$, this gives:

$$\frac{1}{r} = \frac{1}{n_s} + \frac{1}{n_s K}\frac{1}{C} \tag{8}$$

Thus, if this isotherm holds than a plot of $1/r$ versus $1/C$ will be straight line of slope $1/n_s K$, ordinate intercept $1/n_s$. This is very simple method of plotting, with the scatter in the r and C values reflected in the scatter in the ordinate and abscissa values, respectively. Its limitations are that the intercepts may be small and hence difficult to read off.

Scatchard method

Multiplying eq. (7) by $Kn_s r$ and rearranging gives:
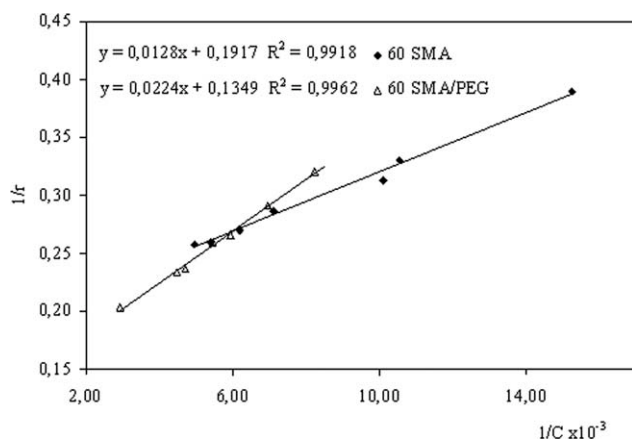
$$\frac{r}{C} = Kn_s - Kr \tag{9}$$

Figure 10 Klotz plots of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs with JGB.

So that in this case a plot of r/C versus r should be a straight line of slope $-K$, ordinate intercept n_sK.

Langmuir method

Multiplying the Klotz form of eq. (7) by C gives:

$$\frac{C}{r} = \frac{1}{n_sK} + \frac{C}{n_s} \qquad (10)$$

So that here a plot of C/r versus C should be a straight line of slope $1/n_s$, ordinate intercept $1/n_sK$.

The Klotz, Scatchard, and Langmuir plots of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs are shown in Figures 10–12, respectively, and the binding parameters for are calculated from the intercept and slopes of the binding isotherm methods.

The binding parameters K_i, K, n_s, and u are listed in Table V for AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs. In Table V, the final column contains the derived values of the Ô, the maximum fractional occupancy attained experimentally,
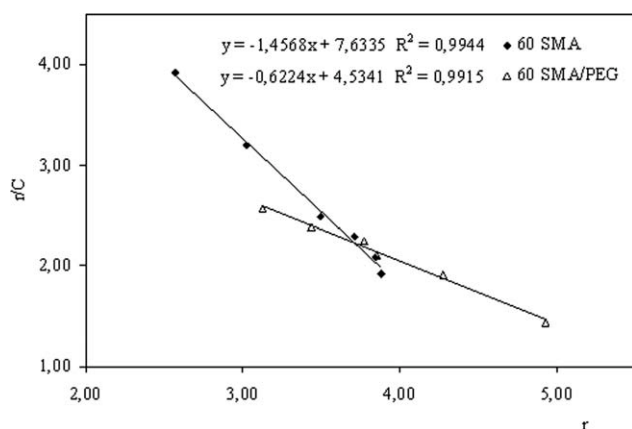
calculated from the definition of fractional occupancy Ô:

$$\hat{O} = r/n_s \qquad (11)$$

Using the value of r at the maximum experimental free dye concentration and with the site-density obtained for the (u.s.b.) model.

The calculated parameters determined by using Klotz, Scatchard, and Langmuir linearization methods are nearly equal to each other (Table V). Then, it was said that related linearization methods such as Klotz, Scatchard, and Langmuir can be used in the hyperbolic binding system for dye-polymers binding process.

There can be many reasons for non-covalent interactions in the binding of JGB by AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs. The main interactions between the hydrogel and the monovalent cationic dye may be hydrophobic and hydrogen bonding. Specially, hydrogen bonding will be expected to occur between amine groups and nitrogen atoms on the dye molecules and the amine and carbonyl groups on the monomer unit of crosslinked polymer. Hydrophobic effects are especially aqueous solutions interactions which in the present case will involve those aromatic rings on the dye molecules and the methine and methyl groups on the gel. There can be some other interactions such as dipole–dipole and dipole-induced dipole interactions between the dye molecules and the hydrogel chains.

In later experiments, for equilibrium sorption studies, the dye removal capacity (q) [mass amount as "mol" of sorption per unit mass (as gram)] of the adsorbent, adsorption percentage (Ads%), and partition coefficient (K_d) can be investigated.

The dye removal capacity (q) of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs were evaluated by using the following equation:
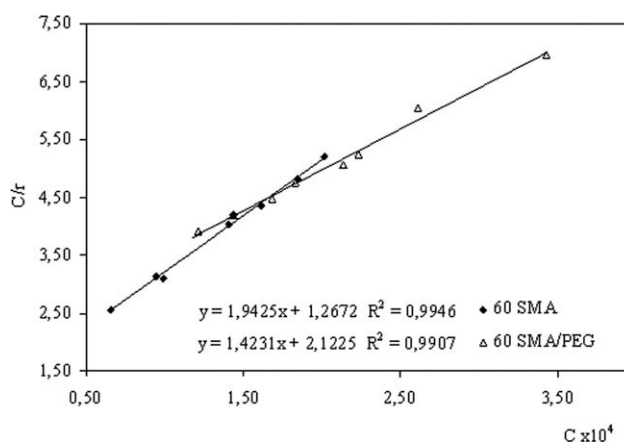

Figure 11 Scatchard plots of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs with JGB.

Figure 12 Langmuir plots of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs with JGB.

TABLE V
Some Binding Parameters of AAm/SMA Hydrogels and AAm/SMA/PEG Semi IPNs with JGB

		$K_i \times 10^{-4}$ (L/mol)	$K \times 10^{-4}$ (L/mol)	n	u	$\hat{O}$
Klotz	AAm/SMA	7.79	1.49	5.22	0.1917	0.7425
	AAm/SMA/PEG	4.47	0.60	7.41	0.1349	0.6648
Scatchard	AAm/SMA	7.63	1.46	5.24	0.1908	0.7397
	AAm/SMA/PEG	4.53	0.62	7.28	0.1373	0.6766
Langmuir	AAm/SMA	7.89	1.53	5.15	0.1943	0.7526
	AAm/SMA/PEG	4.71	0.67	7.03	0.1423	0.7007

$$q = \frac{(C_b)v}{m} \tag{12}$$

where q is the dye removal capacity of AAm/SMA hydrogels and AAm/SMA/PEG semi IPN's (mol/g), v is the volume of the aqueous phase (L), m is the amount of dry AAm/SMA hydrogels and AAm/SMA/PEG semi IPN's. C_b was defined in eq. (5).

Adsorption percentage (Ads%) of AAm/SMA hydrogels and AAm/SMA/PEG semi IPN's was calculated by following equation.

$$\text{Ads}\% = \frac{C_o - C}{C_o} \times 100 \tag{13}$$

Here, C_o and C were defined earlier. Uptake of dye to was measured effects of contents of SMA. The dye removal capacity, the amount of dyes sorbed onto unit dry mass of the gel was calculated for uptake of dye within the hydrogel in 2.00×10^{-3} mol JGB in L of aqueous solutions, and presented in Table VI. Also, Ads% of the hydrogel systems have been calculated, and presented in Table VI, too. Table VI presents that the dye removal capacity of AAm/SMA hydrogels and AAm/SMA/PEG semi IPN's (1.28×10^{-4}–6.21×10^{-4} mol/g) and adsorption percentage of them (20–90%) are increased with together. The dye removal capacity and adsorption percentage of AAm/SMA hydrogels and AAm/SMA/PEG semi IPN's gradually increased with the increase of content of SMA in hydrogels and semi IPNs.

Partitioning of dissolved constituents between an aqueous phase and adsorbents in waters and sediments has commonly been described by an empirical partition coefficient that simply relates the total concentration of a dissolved species to the total concentration of the adsorbed species.[36,37]

$$K_d = \frac{C_b}{C} \tag{14}$$

Here, K_d is empirical partition coefficient at equilibrium. C_b and C were defined earlier. Partition coefficients of JGB between dye solution and hydrogels were calculated, and are shown in Table VI. In Table VI, K_d values of AAm/SMA hydrogels is 0.25–8.96, but K_d values of AAm/SMA/PEG semi IPNs is 0.25–3.21 with the incorporation of PEG groups into the hydrogels. Here, K_d values of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs (having 40 mg and more than this SMA content) are higher than 1.0. So, it can be said that synthesized crosslinked AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs (having 40 mg and more than this SMA content) could be used as potential water adsorbent.[36,37]

The ionic charge content in the polymeric structure is important. SMA contains ionic units (—COONa). The swelling degrees of the hydrogels increase due to increasing of the hydrophilic units on hydrogel structure (Fig. 1). Therefore, AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs have many ionic groups that can increase interaction between the cationic dye molecules and anionic groups of hydrogels. The results of swelling studies

TABLE VI
Some Adsorption Parameters of AAm/SMA Hydrogels and AAm/SMA/PEG (Containing 0.5 g PEG) Semi IPNs in Aqueous Solutions of JGB

SMA/mg	10	20	30	40	50	60	70	80
Dye removal capacity, $q \times 10^4$ (mol/g)								
AAm/SMA	1.28	2.04	3.16	4.20	5.21	5.15	6.21	6.05
AAm/SMA/PEG	1.49	2.56	3.74	3.87	3.66	4.74	4.45	5.02
Adsorption percentage, Ads%								
AAm/SMA	20	36	47	70	81	84	86	90
AAm/SMA/PEG	20	27	45	54	54	66	68	76
Partition coefficient, K_d								
AAm/SMA	0.25	0.55	0.88	2.36	4.16	5.38	6.28	8.96
AAm/SMA/PEG	0.25	0.37	0.83	1.17	1.16	1.98	2.11	3.21

TABLE VII
PEG Effect on Some Adsorption Parameters of AAm/SMA/PEG Semi IPNs with Various Contents of PEG (Containing 60 mg SMA) in Aqueous Solutions of JGB

PEG/g	0	0.25	0.50	0.75	1.00
Dye removal capacity, $q \times 10^4$ (mol/g)	5.15	5.64	4.74	5.51	5.61
Adsorption percentage, Ads%	84	87	66	75	76
Partition coefficient, K_d	5.38	6.79	1.98	3.07	3.21

are parallel character to the results of sorption studies. Both of them, it can be seen that swelling or sorption capability of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs are increased with increasing SMA content in copolymeric structure. The most important effect is hydrophilicity of copolymeric gels. Hydrophilicity of AAm/SMA and AAm/SMA/PEG copolymers becomes greater than that of AAm, when addition of SMA to the copolymeric structure.

PEG effect on the sorption of JGB

For investigation of the effect of mass/content of PEG on the sorption properties of AAm/SMA/PEG semi IPNs, some sorption parameters such as dye removal capacity, adsorption percentage, and partition coefficient of AAm/SMA/PEG semi IPN systems containing 60 mg SMA are tabulated in Table VII.

It was shown that a decreasing of adsorption percentage (84–76%) and partition coefficient (5.38–3.21) of AAm/SMA/PEG semi IPN systems when PEG has been added to the hydrogel systems. Incorporation of PEG into the copolymer network leads to lower values of adsorption percentage and partition coefficient of AAm/SMA/PEG semi IPN systems. Here, K_d values of AAm/SMA/PEG semi IPNs (5.38–3.21) are higher than 1.0. So, it can be said that synthesized crosslinked AAm/SMA/PEG semi IPNs (having 60 mg SMA and 0.25–1.0 g PEG content) could be used as potential water adsorbent.[36,37] On the other hand, it can be said that there is no important chancing of the dye removal capacity of AAm/SMA/PEG semi IPN systems when PEG has been added to the hydrogel systems (4.74×10^{-4}–5.61×10^{-4} mol/g).

Here, it was said that PEG chains was placed in the crosslinked polymeric systems, in stead of crosslinked AAm and SMA molecules, it was seen that decreasing of the adsorption percentage, because of decreasing of hydrophilic character at crosslinked polymeric systems. In addition of this phenomenon, the PEG chains are located in the free space of crosslinked polymer networks; JGB sorption is prevented by the PEG chains. This is also caused of partition decreasing of the adsorption percentage.

CONCLUSION

Incorporation of hydrophilic group containing chemicals such as SMA and a polymer such as PEG in AAm hydrogels can be obtained successively by free radical solution polymerization method. Multifunctional crosslinker such as PEGDMA used at the polymerization process. AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs showed high water absorbency. The equilibrium percentage swelling ranges are 660–2260% for AAm/SMA hydrogels and 580–1980% for AAm/SMA/PEG semi IPNs. It was seen that swelling of AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs increased with the increasing of content of SMA. But, it was seen that a decreasing of values of S_{eq}% from 2000% to 1490% when the adding of PEG for containing of 60 mg of SMA.

To determine the sorption kinetics of JGB into AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs, binding characterization parameters have been investigated. To get the best values for the binding parameters from the experimental data, the linearization methods such as Klotz, Scatchard, and Langmuir linearization methods have been used. For equilibrium sorption studies, dye removal capacity, adsorption percentage and partition coefficient of AAm/SMA hydrogels and AAm/SMA/PEG semi IPN systems, have been investigated.

Consequently, AAm/SMA hydrogels and AAm/SMA/PEG semi IPNs developed in this study may serve as a potential device for water and dye sorbent. The utilization of these types of materials, in pharmaceuticals, agriculture, biotechnology, environment, separation, purification, and immobilization makes hydrogels more popular.

References

1. Chu, B.; Hsiao, B. S. J Polym Sci Part B: Polym Phys 2009, 47, 2431.
2. Güçlü, G.; Al, E.; Emik, S.; İyim, T. B.; Özgümüş, S.; Özyürek, M. Polym Bull 2010, 65.333.
3. Li, S. Bioresource Technology 2010, 101, 2197.
4. Karadağ, E.; Kirişti, T.; Kundakci, S.; Üzüm, Ö. B. J Appl Polym Sci 2010, 117, 1787.
5. Uğuzdoğan, E.; Denkbaş, E. B.; Kabasakal, O. S. J Hazard Mater 2010, 177, 119.
6. Wang, Y.; Zeng, L.; Ren, X.; Song, H.; Wang, A. J Environ Sci 2010, 22, 7.

7. Güven, O.; Şen, M.; Karadağ, E.; Saraydin, D. Radiat Phys Chem 1999, 56, 381.
8. Karadağ, E.; Kundakci, S.; Üzüm, Ö. B. Polym Plast Technol Eng 2009, 48, 1217.
9. Özay, Ö.; Ekici, S.; Baran, Y.; Aktaş, N.; Şahiner, N. Water Res 2009, 43, 4403.
10. Bekiari, V.; Sotiropoulou, M.; Bokias, G.; Lianos, P. Colloids Surf A: Physicochem Eng Aspects 2008, 312, 214.
11. Karadağ, E.; Üzüm, Ö. B.; Kundakci, S.; Saraydin, D. J Appl Polym Sci 2007, 104, 200.
12. Kök Yetimoğlu, E.; Kahraman, M. V.; Ercan, Ö.; Akdemir, Z. S.; Kayaman Apohan, N. React Funct Polym 2007, 67, 451.
13. Crini, G. Prog Polym Sci 2005, 30, 38.
14. Crini, G. Bioresource Technology 2006, 97, 1061.
15. Karadağ, E.; Üzüm, Ö. B. Polym Bull 2005, 53, 387.
16. Karadağ, E.; Üzüm, Ö. B.; Saraydin, D. Eur Polym J 2002, 38, 2133.
17. Üzüm, Ö. B.; Karadağ, E. J Appl Polym Sci 2006, 101, 405.
18. Murthy, P. S. K.; Mohan, Y. M.; Sreeramulu, J.; Raju, K. M. React Funct Polym 2006, 66, 1482.
19. Mohan, Y. M.; Dickson, J. P.; Geckeler, K. E. Polym Int 2007, 56, 175.
20. Kosmala, J. D.; Henthorn, D. B.; Brannon-Peppas, L. Biomaterials 2000, 21, 2019.
21. Chakrabarty, D. Polym Gels Networks 1998, 6, 191.
22. Serra, L.; Domenech, J.; Peppas, N. A. Eur J Pharm Biopharm 2006, 63, 11.
23. Şahiner, N.; Godbey, W. T.; McPherson, G. L.; John, V. T. Colloid Polym Sci 2006, 284, 1121.
24. Krsko, P.; Libera, M. Mater Today 2005, 8, 36.
25. Martinez-Ruvalcaba, A.; Sanchez-Diaz, J. C.; Becerra, F.; Cruz-Barba, L. E. Express Polym Lett 2009, 3, 25.
26. Mohan, Y. M.; Murthy, P. S. K.; Raju, K. M. J Appl Polym Sci 2006, 101, 3202.
27. Lee, S. J.; Kim, S. S.; Lee, Y. M. Carbohydr Polym 2000, 41, 197.
28. Saraydin, D.; Karadağ, E.; Işikver, Y.; Şahiner, N.; Güven, O. J Macromol Sci 2004, A41, 421.
29. Kim, S. J.; Park, S. J.; Kim, S. I. React Funct Polym 2003, 55, 61.
30. Karadağ, E.; Saraydin, D.; Aydin, F. Turk J Chem 1998, 22, 227.
31. Peppas, N. A.; Franson, N. M. J Polym Sci Polym Phys Ed 1983, 21, 983.
32. Çaykara, T.; Kiper, S.; Demirel, G. Eur Polym J 2006, 42, 348.
33. Dengre, R.; Bajpai, M.; Bajpai, S. K. J Appl Polym Sci 2000, 76, 1706.
34. Molyneux, P. Water-Soluble Synthetic Polymers. Properties and Behavior; CRC Press: Boca Raton, FL, 1984.
35. Molyneux, P.; Vekavakayanondha, S. J Chem Soc Faraday Trans L 1986, 82, 291.
36. Schwarte, L. M.; Peppas, N. A. Polymer 1998, 39, 6057.
37. Şahiner, N.; Saraydin, D.; Karadağ, E.; Güven, O. Polym Bull 1998, 41, 371.