Synthesis and Characterization of Polyamphoteric Hydrogel Membrane Based on Chitosan

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ABSTRACT: Polyamphoteric hydrogel membranes were synthesized by graft copolymerization of *N*-isopropylacrylamide (NIPAm) and 2-acrylamido-2-methyl propane sulfonic acid (AMPS) onto chitosan (CS). The incorporation of poly(NIPAm) (PNIPAm) and poly(AMPS) (PAMPS) into CS was confirmed by FTIR spectroscopy. The swelling behavior of membranes as a function of pH, temperature, and ionic strength was studied. Permeability of solutes through these membranes was investigated at different temperatures. The results showed the dual sensitivity of membranes toward pH and temperature. The formation of the polyelectrolyte complex between CS and PAMPS showed influence on the lower critical solution temperature of PNIPAm. The permeabilities of solutes through these membranes were strongly dependent on the size of solutes, solution temperature, and hydrophilicity of the membranes. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1454–1461, 2004

Key words: polyamphoteric membranes; polyelectrolyte complex; hydrogel; thermosensitive polymer

INTRODUCTION

Polyamphoteric hydrogel membranes are attracting increasing attention lately in the area of biomedical and biochemical separations because of their good biocompatibility and low fouling characteristics. These membranes have both positive and negative charges, and therefore, the permeability of solutes through them can be controlled by pH.[1] In a pH and thermoreversible hydrogel membrane, the mesh size of the membrane can be controlled by both pH and temperature. Transition from the swollen state to the collapsed state or *vice versa* in the membrane at a certain temperatures and pHs influences the permeation characteristics of the membrane.[2] The permeation of solutes through the charged membranes can be size selective as well as through solute/polymer interactions. However, which one predominates depends on the type of membrane and the solutes to be separated.[3]

Poly(*N*-isopropylacrylamide) (PNIPAm) is a widely studied thermoreversible hydrogel, which exhibits a lower critical solution temperature (LCST) at around 33°C in an aqueous solution.[4] Below LCST, the gel is in the swollen state, and above LCST, it dehydrates into a collapsed state. Therefore, because of their interesting volume transition properties, thermoreversible polymers have shown a large number of promising applications in biomedical fields. Hydrophilic or hydrophobic modifications of thermoreversible polymer disturbs the critical balance of the hydrophilic/hydrophobic interactions and changes the phase-transition behavior.[5,6] To retain the temperature-induced swelling transition of the membrane over a broad and useful pH range, the polyelectrolyte complexation phenomenon was used.[7]

Chitosan (CS) is a poly[β(1→4)-2-amido-2-deoxy-D-glucopyranose] and can be obtained by the *N*-deacetylation of chitin, poly[β(1→4)-2-acetamido-2-deoxy-D-glucopyranose], which is produced by biosynthesis. It is a nontoxic and easily bioadsorbable biopolymer with excellent gel-forming properties at low pH values. Below pH 6.5, chitosan in solution carries a high-positive charge density. Because of its vast number of —NH_3^+ groups, it readily forms film on biopolymers such as bone, hair, and skin, which are composed of negatively charged mucopolysaccharides and proteins. Temperature- and pH-sensitive interpenetrating network (IPN), semi-IPN hydrogel systems based on chitosan and PNIPAm have already been reported.[8–11] Yao et al.[12] reported on the semi-IPN hydrogel based on crosslinked chitosan with glutaraldehyde polyether network. They investigated the pH sensitivity, swelling, and release kinetics and the structural changes of the gel in different pH solutions. The graft copolymerization of vinyl monomers onto chitosan was reported earlier. For example, chitosan-*g*-PNIPAm polymers were reported with the advantage of their dual sensitivity toward both temperature and

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TABLE I
Stoichiometry for the Preparation of Hydrogel Membranes

Membrane	Chitosan solution (1%) (mL)	NIPAm (g)	AMPS (g)	KPS (g)	Bis-Am (g)	TEMED (μL)
CS-PNIPAm	8.0	0.3125	0.0	0.04	0.0468	40
CS-PNIPAm-PAMPS-5	8.0	0.3125	0.015	0.04	0.0468	40
CS-PNIPAm-PAMPS-10	8.0	0.3125	0.0312	0.04	0.0468	40

pH.[11] However, the effective pH range where the swelling behavior changes is very narrow and is only between 4 and 6. Furthermore, under strong acidic conditions, the graft copolymer tends to become water-soluble, which limits the usage in the wider pH range. Najjar et al.[13] reported on the grafted material based on chitosan and 2-acrylamido-2-methyl propane sulfonic acid (AMPS). The emphasis was, however, made on the optimum reaction conditions to get maximum grafting onto chitosan. Although the system can exhibit amphoteric nature at low pH values, their detailed characterizations have not been reported. Poly(AMPS) (PAMPS), bearing sulfonic acid groups, belongs to a class of polyelectrolytes that has a high degree of ionization. Stoilova et al.[14] investigated the polyelectrolyte complex formation between chitosan and PAMPS.

In this article, we report on the synthesis and characterization of polyamphoteric membrane based on grafting of NIPAm and AMPS monomers onto chitosan. The swelling behavior of these membranes as a function of pH, temperature, and ionic strength was studied. Permeability of two ionic drugs through these membranes is investigated. Advantages of making terpolymer of chitosan, PNIPAm, and PAMPS is that, at low pH, the terpolymer will have both positive and negative charges on the polymer chain and can exhibit interesting swelling behavior and permeating characteristics. Furthermore, because PAMPS is hydrophilic in nature, it can reduce the tendency of fouling of membranes during the separation process.

EXPERIMENTAL

Materials

Chitosan (85% deacetylated) was procured from Sigma–Aldrich (St. Louis, MO). *N*-isopropylacrylamide (NIPAm) and AMPS monomers were procured from Aldrich Chemicals (Milwaukee, WI) and Lubrizol (USA), respectively. Potassium per sulfate (KPS) and *N*,*N*′-methylene bisacrylamide (Bis-A) were purchased from Loba Chemicals (India) and S.D. Fine Chemicals Ltd. (India), respectively. *N*,*N*,*N*′,*N*′-tetramethylethylene diamine (TEMED) was purchased from Aldrich Chemicals. Theophylline and ciprofloxacin hydrochloride were obtained from Aldrich Chemicals and Iotras Pharma (India), respectively.

The molecular weight of chitosan was determined from intrinsic viscosity, [η], measurements in a buffer solvent system (0.3*M* acetic acid and 0.2*M* sodium acetate) at 25°C by using the Mark–Houwink–Sakurada equation (with Mark–Houwink constants, $K = 7.4 \times 10^{-4}$ dlg^{-1}, $\alpha = 0.76$).[15] The molecular weight was determined to be 260,000 g/mol.

Synthesis of chitosan hydrogel membrane

Chitosan hydrogel membranes were prepared by simultaneous graft copolymerization of AMPS and NIPAm monomers onto chitosan at 30°C by using potassium persulfate (KPS) as an initiator and TEMED as an accelerator. Chitosan solution was prepared in 1.0% acetic acid solution and the monomers, initiator, accelerator, and crosslinker (Bis-A) were dissolved in the chitosan solution. The stoichiometry of the reactions is given in Table I. In the two terpolymer hydrogel membranes, the concentrations of AMPS were 5.0 and 10.0 wt % on the basis of the weight of the NIPAm monomer. Nitrogen was purged through this solution to remove the oxygen, which can act as a free-radical scavenger. This solution was poured into a petri dish to cast membranes. The gelation took place in 5–10 min depending on the concentration of the accelerator. These hydrogel membranes were air dried for 8 days at room temperature to facilitate the easy removal of membranes from the petri dish. Further, these hydrogel membranes were soaked in acetone, water, and acidic buffers to remove the unreacted monomers if any. The thicknesses of dry membranes were found to be in the range of 40–50 μm.

Characterization

Fourier transform infrared analysis

Fourier transform infrared analysis was done by using a Perkin–Elmer FTIR spectrometer of model (16 PC) at resolution of 4 cm^{-1}.

Swelling ratios at different pHs, ionic strengths, and temperatures

Buffers were made from McIlvain buffer (0.1*M* citric acid and 0.2*M* Na_2HPO_4) from 2.6 to 7.0 pH. The buffers were made at ionic strength (*I*) corresponding

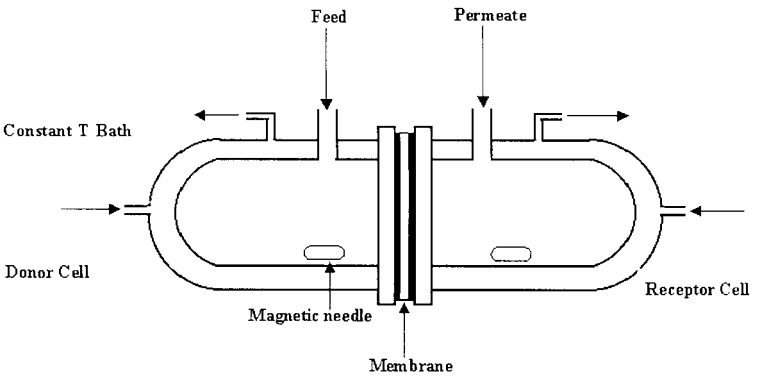

Figure 1 Schematics of the two-chamber (donor and receptor) diffusion cell for the permeation study.

to 0.5 and 0.02*M* by diluting with distilled water of standard buffer. *I* was calculated from the equation,

$$I = \frac{1}{2}\sum C_i Z_i^2 \quad (1)$$

where C_i is the molar concentration and Z_i is the valency of various ionic species.

The dried preweighed membranes were kept in corresponding pH, ionic strength solutions in a constant temperature bath for different temperatures in the range of 20–50°C for 24 h and reweighed after wiping the surface gently.

The swelling ratio (q) of membranes were calculated by using the following equation,

$$q = \frac{W_2}{W_1} \quad (2)$$

where W_2 and W_1 are wet and dry weights of the membrane, respectively.

Permeation studies

Permeation experiments were carried out at different temperatures and pHs by using a two-chamber (donor and receptor) diffusion cell with a chamber volume of 70 cm^3 (Fig. 1). Preconditioned membranes were mounted between two halves of the donor and receptor cell, which were further clamped together and sealed tightly with the rubber packing. The effective membrane area in the cell was 1.76 cm^2. The solution was at the donor side of the cell and the receptor was having only the buffer. A fixed volume (1.0 mL) of the sample was taken out at various time intervals from the receptor cell and the solute concentration was measured by using a UV spectrophotometer at appropriate wavelengths. After taking out samples from the receptor cell each time, the same amount of fresh buffer solution was added to the receptor cell to maintain the constant volume at the receptor cell. Two drugs chosen for the permeation studies were theophylline (M_w = 180) and ciprofloxacin hydrochloride (M_w = 365). The concentrations of these solutes were determined by UV spectrophotometer at wavelengths of 271 and 277 nm, respectively. The initial concentration of theophylline and ciprofloxacin hydrochloride in the donor cell was 0.02 mg/mL.

RESULTS AND DISCUSSION

Graft copolymerization

Chitosan has both reactive amino and hydroxyl groups that can be used to chemically alter its properties under mild reaction conditions. Chitosan and its derivatives have become useful polysaccharides in the biomedical area because of their numerous and interesting biological properties such as biocompatibility, biodegradability, and nontoxic properties. Chitosan, in particular, exhibits pH responsive behavior as a weak polybase due to the large quantities of amino groups on its chain. The modification of chitosan through grafting has become increasingly important. A large number of vinyl monomers were grafted by using initiators such as ceric ammonium nitrate (CAN), persulfates, and Fenton's reagent.[16–20] In our system, the grafting of NIPAm and AMPS monomers onto chitosan was done by using KPS as a redox initiator. The redox initiator generates a free radical on the chitosan backbone and the vinyl monomers polymerize on the backbone. The copolymerization of these monomers onto chitosan can lead to the grafted pendant PNIPAm and PAMPS chains. This could be attributed to the fact that the reactivity ratios r_1 and r_2 of NIPAm and AMPS monomers are reported to be 2.4 $\pm$ 0.8 and 0.03 $\pm$ 0.02, respectively,[21] and because $r_1 \gg r_2$, the NIPAm monomer has a strong affinity to enter into the growing PNIPAm chain. Therefore, the grafted chain will have a large number of NIPAm units. Furthermore, we observe that the LCST of the grafted copolymer has not changed significantly,

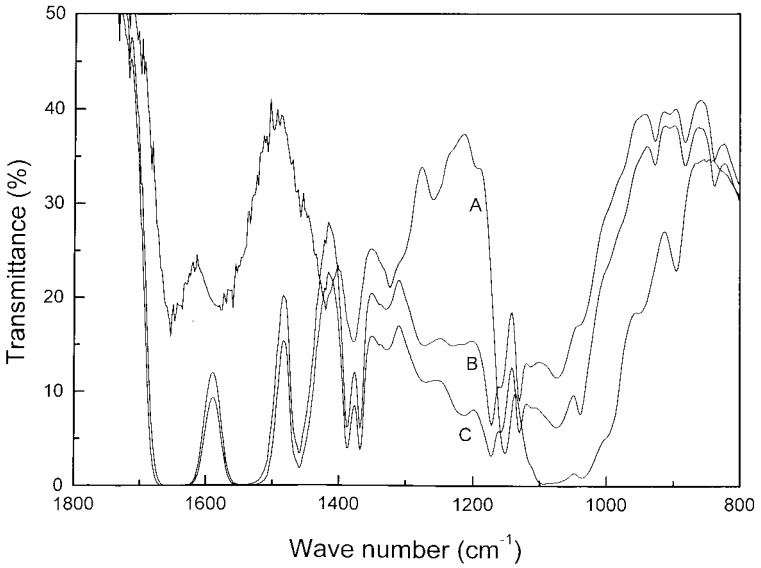

Figure 2 FTIR spectra of chitosan (A), CS-PNIPAm (B), and CS-PNIPAm-PAMPS-5 (C) films in the range of 800-1800 cm^{-1}.

which clearly indicates that the AMPS units are not incorporated in the PNIPAm growing chain. We have used the crosslinking agent, Bis-Am, in the polymerization to enhance the stability of the membranes in the aqueous medium. This can lead to some formation of semi-IPN in the terpolymer. However, the structural evidence for the semi-IPN is beyond the scope of this work.

Proof of grafting by FTIR spectroscopy

Incorporation of NIPA and AMPS onto chitosan was confirmed by FTIR spectroscopy. It can be seen from Figure 2 that CS membrane shows peaks at 900, 1154, and 1560 cm^{-1}. The characteristic broad —OH peak of chitosan observed at 3450 cm^{-1} is not shown in the figure. In the CS-PNIPAm membrane, apart from the chitosan bands, there are new bands at 1368 and 1653 cm^{-1}, which are attributed to the isopropyl groups and —CONH of PNIPAm. While in the case of terpolymer CS-PNIPAm-PAMPS-5 membrane, there exists an additional peak at 1040 cm^{-1}, which corresponds to S═O stretching frequency of PAMPS. Modified chitosan membranes also show two broad peaks between 1600 and 1700 and 1500 and 1600 cm^{-1}, which are due to the inter-, intra-, nonbonded carbonyl, and —NH groups, respectively. The deacetylated chitosan (85% deacetylation) has —NHCOCH$_3$ groups that show peak between 1600 and 1700 and 1500 and 1600 cm^{-1}. With the addition of NIPA and AMPS to chitosan, a number of amide groups increase, which results in inter/intramolecular H-bonding, hence, resulting in broadening of the peaks.

pH dependent swelling ratios

We show in Figure 3 the pH-dependent equilibrium swelling ratios of three hydrogel membranes with the different contents of PAMPS at 30°C. The addition of PAMPS onto CS-PNIPAm polymer introduces a negative charge on the chain and makes the polymer system amphoteric in nature.

Chitosan is a cationic polyelectrolyte with pK_a value of 6.5, and below this pH, it is positively charged, whereas PAMPS is an anionic polyelectrolyte with pK_a value of 2.86.[22] Therefore, above the pH 2.86, PAMPS is in the ionized form. The presence of both the ions on the polymer chain makes the swelling properties interesting in this system. It can be seen from the figure that for CS-PNIPAm polymer (0% AMPS) the swelling ratios are higher at lower pH because of the electrostatic repulsion between the positive charges as a result of ionization of chitosan at lower acidic pH. Upon increasing the pH, there is a decrease in the electrostatic repulsion due to the re-

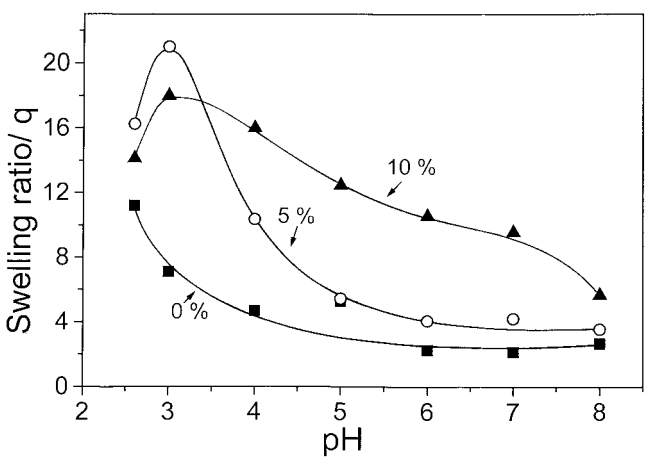

Figure 3 Influence of pH on the swelling ratio of CS-PNIPAm-PAMPS hydrogel membranes with the different contents of PAMPS at 30°C and ionic strength of I = 0.5M.

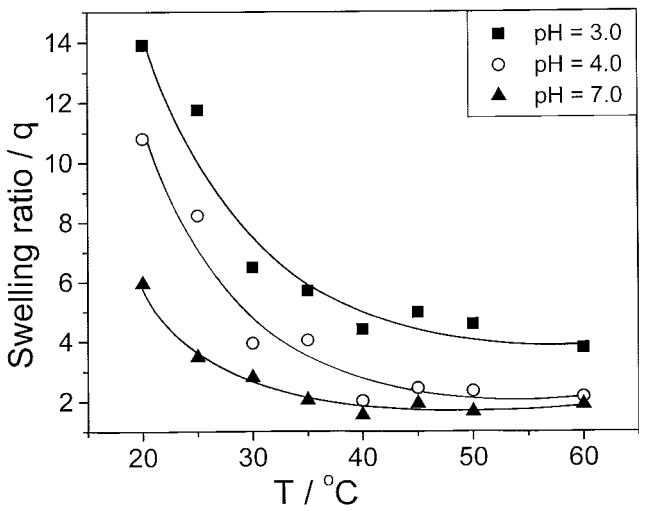

Figure 4 Temperature-dependent swelling ratios of CS-PNIPAm membranes at three different pH values.

versal of NH_3^+ to NH_2, which causes the decrease in swelling.

It can also be readily seen from the figure that addition of PAMPS to CS-PNIPAm polymer increases the hydrophilicity of the system and increases the swelling ratios in the whole pH range studied. It is interesting to note that as the pH increases from 1 to 2.8, the swelling ratio of CS-PNIPAm-PAMPS-5 and CS-PNIPAm-PAMPS-10 increases, showing a maximum at pH 3, and starts to decrease thereafter. This decrease in swelling ratio is due to the electrostatic attraction between the positive and negative charges present in the chains. The electrostatic attraction reduces the coil dimensions and subsequently decreases the swelling ratios. Furthermore, at higher pH, the ionic strength effects start to establish the shielding of electrostatic repulsions and reduce the swelling ratios further.

Temperature-dependent swelling ratios

Temperature-dependent swelling of all the membranes were performed at three different pH values (pH = 3, 4, 7). We show in Figure 4 the equilibrium swelling ratios of CS-PNIPAm membrane as a function of temperature at three different pH values, 3, 4, 7. As expected, the swelling ratios are high at low pH, which is due to the electrostatic charge repulsion of the protonated amine groups in the chitosan. Furthermore, swelling ratios decrease as the temperature is increased. This is due to the presence of PNIPAm chains in the membrane, which is strongly thermosensitive in nature. It is well established that below the LCST (32°C), the PNIPAm chains are hydrophilic in nature and are in the expanded state of conformation. There is extensive hydrogen bonding (H-bonding) between the polymer and water, which contributes to the high swelling ratios. However, upon increasing the temperature, the H-bonding between the polymer and water decreases significantly and there is a large increase in the intermolecular hydrophobic interactions. As a result, the PNIPAm chains undergo coil-to-globule transition, which reduces the swelling ratios.[23]

It is important to note here that, at all the pH values, the swelling ratios decrease continuously without showing any discontinuous volume transitions. The incorporation of PAMPS into the CS-PNIPAm system, however, increases the hydrophilicity of the membrane and in turn increases the swelling ratios. We show in Figure 5 the temperature-dependent equilibrium swelling ratios of the above-mentioned membranes at pH 3.0. It can be seen that the swelling ratios are high at temperatures below 35°C and are still higher especially in the presence of higher incorporation of PAMPS. Furthermore, there is a distinct discontinuous volume transition close to the LCST of PNIPAm. The discontinuous volume transition becomes more predominant at higher content of PAMPS in the system. This discontinuous volume transition is very important in designing hydrogel membranes for the controlled drug delivery systems and offers an on–off switch mechanism to facilitate the release of active drugs from membranes.

The observed discontinuous volume transition can be recoursed to the fact that, as it has been shown in the past, polyacrylamide (Pam) gels in acetone/H_2O mixtures do not show discontinuous transition.[24] However, upon hydrolysis of the —$CONH_2$ groups in the PAm into PAA-salt begin to show distinct discontinuous transition. This is due to the increase in hydrophilicity of the gel by incorporating ionic charges into the gel. The mode of volume transition depends very much on the presence of charge on the polymer

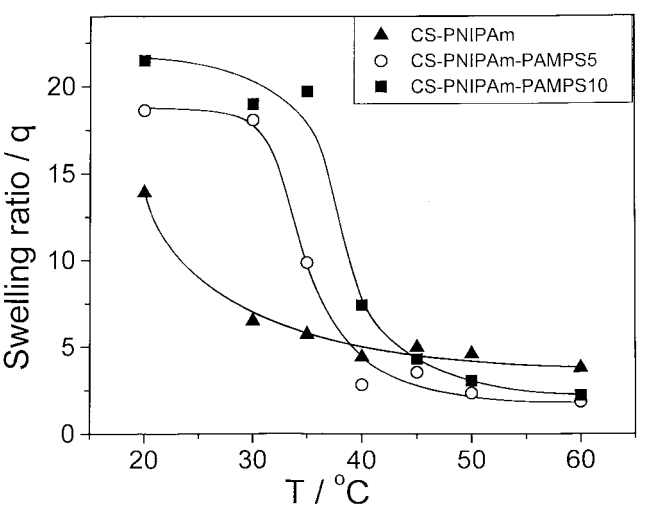

Figure 5 Temperature-dependent swelling ratios of CS-PNIPAm-PAMPS membranes at pH = 3.0 and at two different PAMPS contents.

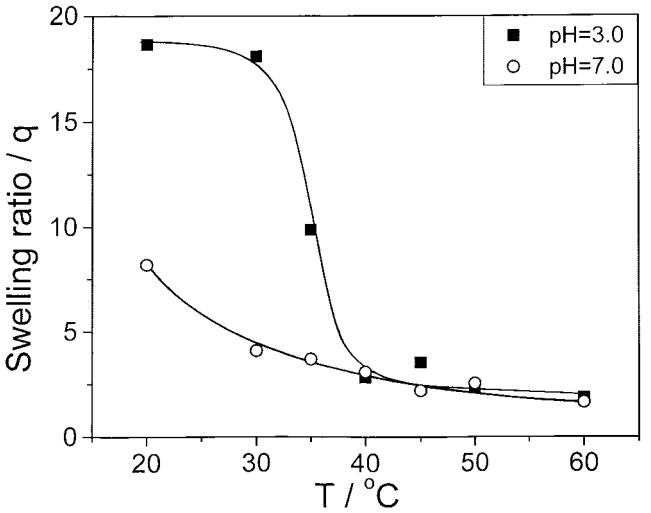

Figure 6 Effect of temperature on the swelling behavior of CS-PNIPAM-PAMPS-5 membrane at two pH values.

chain. Therefore, our observation of discontinuous transition is in line with the earlier finding that the incorporation of PAMPS into CS-PNIPAm gel increases the hydrophilicity of the whole system by addition of charges on the polymer chain, which in turn gives rise to discontinuous volume transition. The incorporation of PAMPS into CS-PNIPAm gel causes addition of opposite charges to CS-PNIPAm membrane at a lower pH of 3.0. So, at this pH, CS-PNIPAm-PAMPS membrane forms a polyelectrolyte complex between positive and negative charges, which results in a discontinuous volume transition. Therefore, we show that, by addition of PAMPS into CS-PNIPAm system, one can get discontinuous transition as a function of temperature. Furthermore, we show in Figure 6 the data of swelling ratios versus temperature for CS-PNIPAm-PAMPS-5 at pH 3 and 7. It can be readily seen that the discontinuous transition is more pronounced at pH 3 and becomes continuous at pH 7. The continuous transition at pH 7 is due to the chitosan becoming neutral at this pH. In addition to this, there is a possibility of intrachain H-bonding between chitosan and PNIPAm that would lead to an increase in hydrophobicity of the membrane and a decrease the interactions with water. Similar observations were made by Huglin et al.[25] in the case of poly(NIPAm-*co*-AA) hydrogels at low pH.

Influence of pH and ionic strength on the swelling

As mentioned earlier, CS-PNIPAm-PAMPS is an interesting system which exhibits both +ve and −ve charges on the polymeric chains at certain pH conditions. The amphoteric nature of the system can give rise to interchain complexations, which can lead to coiled conformation of the chains. This conformation in turn decreases the swelling ratios. We show in Figure 7 the swelling ratios of CS-PNIPAm-PAMPS-10 as a function of pH at two different ionic strengths. At low ionic strength, the swelling ratio keeps on increasing with pH. At low pH, both chitosan and PAMPS are in the ionized state. The polyelectrolyte complexation between the opposite charges can create an interor intrachain crosslinking (physical), thus reducing the swelling ratios. However, at high pH, the positive charge on the chitosan is neutralized and the complexation breaks, resulting in the reduction of physical crosslinking. This leads to the enhanced swelling ratios.

On the contrary, at high ionic strength and low pH, the ionic groups screen the charges on the membrane and prevent the formation of interchain complexation. Thus, the physical crosslinking is reduced, resulting in high swelling ratios. However, upon increasing the pH, the charge neutralization of chitosan reduces the electrostatic repulsions in the chains and it is further reduced by the excess ionic groups, which screens the electrostatic interactions. Consequently, the swelling ratios decrease.

Permeation of solutes

The permeation of solutes through hydrogel membranes depends on properties such as hydrophilic–hydrophobic balance, degree of crosslinking and effective mesh-size, nature of functional groups, and charges on the membrane. As per the Fick's law of diffusion, the permeability of the solute can be given by the equation,

$$\frac{P}{\delta} = \frac{-V}{2At} \ln \frac{\Delta C_t}{C_0} \tag{3}$$

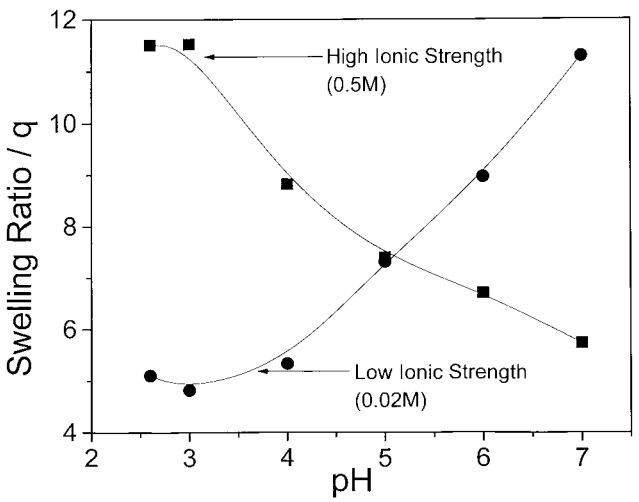

Figure 7 Influence of ionic strength (*I*) on the pH-dependent swelling ratios of CS-PNIPAm-PAMPS-10 membrane.

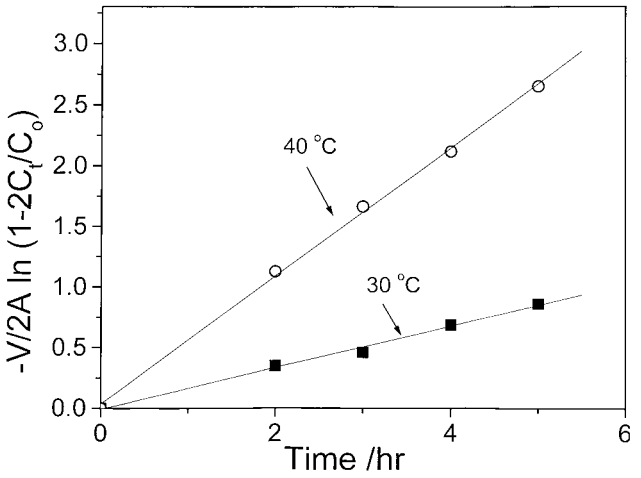

Figure 8 Permeation of theophylline through CS-PNIPAm-PAMPS-5 membrane at two temperatures and at the constant pH = 4.0.

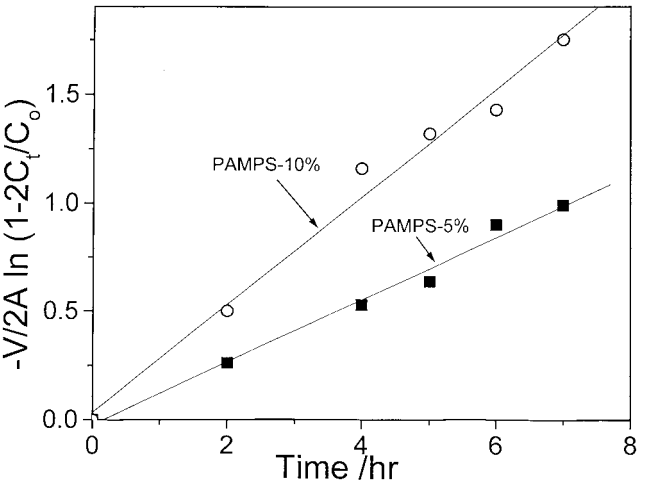

Figure 9 Influence of the hydrophilicity of the CS-PNIPAm-PAMPS membrane on the permeation of theophylline at constant pH (4.0) and temperature (30°C).

where C_i is the solute concentration in the receptor cell; C_0 is the initial solute concentration in the donor cell; V is the volume of each half cell; A is the effective permeation area; P is the permeability coefficient; t is the time; and δ is the thickness of the membrane.

The above equation can be rewritten as

$$\ln\left(1-2\frac{C_t}{C_0}\right) = \frac{-2A}{V}Pt \tag{4}$$

To determine the permeability coefficient, P, a plot of $-V/2A \ln(1 - 2C_t/C_0)$ against t was constructed and linear fitting was performed. The slope of the linear portion of the graph yields a permeability coefficient.

We show in Figure 8 the permeabilities of theophylline in CS-PNIPAm-PAMPS-5 membrane at two different temperatures, one below (30°C) and one above (40°C) the LCST of PNIPAm. It can be readily seen that the slope is larger at the higher temperature (40°C), which indicates the higher permeability for theophylline at higher temperature compared to the one at lower temperature. This observation is in line with the report made by Kubota et al.,[26] where they reported the theophylline release from PAA-*g*-oligo(*N*-isopropyl acrylamide) gel at higher temperature. This can be attributed to the fact that the PNIPAm chains in the hydrogel membrane undergo coil-globule transition at higher temperature and are present in the collapsed state. As a result, the hydrogel network opens up the channels for enhanced permeation of solutes. At lower temperature, however, the PNIPAm chains are in the expanded state, which fills the channels and subsequently reduces the permeation rates. This phenomenon can be effectively used to design hydrogel membranes for specific end applications.

In Figure 9, we show the results of theophylline permeability in two membranes with a different hydrophilic polymer content. The membranes CS-PNIPAm-PAMPS-5 and CS-PNIPAm-PAMPS-10 contain 5.0 and 10.0% hydrophilic polymer (PAMPS), respectively. As can be seen from the figure, the permeability of theophylline is more in the CS-PNIPAm-PAMPS-10 membrane. This is due to the increase in the hydrophilicity of the membrane, which enhances the solubility of theophylline in the membrane, resulting in the enhanced permeation.

The influence of the size of solutes on the permeation characteristics of the membrane CS-PNIPAm-PAMPS-5 is shown in Figure 10. Two solutes, theophylline and ciprofloxacin, of different molecular weights were used for the permeation studies. The

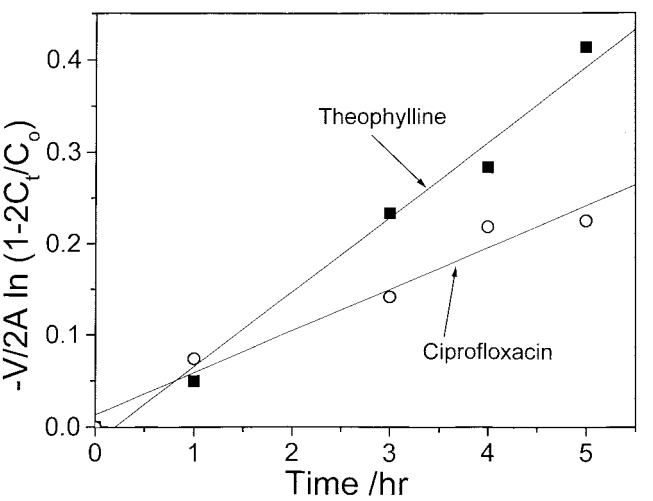

Figure 10 Effect of solute size on the permeation of CS-PNIPAm-PAMPS-5 membrane at constant pH (4.0) and temperature (30°C).

results clearly show that as the size of the solute increases the rate of permeation decreases. To study the selective separation of the biological mixtures through these membranes, extensive experiments have to be performed, which will be the focus of a future study.

CONCLUSION

In conclusion, we have demonstrated that the combination of chitosan, PNIPAm, and PAMPS gives a polyamphoteric hydrogel membrane with good mechanical strength and good handling characteristics. The swelling behavior of membranes was very much influenced by pH, temperature, and ionic strengths of the external medium. The addition of PAMPS to CS-PNIPAm polymer increased the hydrophilicity of the system and the swelling ratios. Furthermore, PAMPS induced a discontinuous swelling transition to the hydrogel membrane that can have potential in stimuli-sensitive separations using membranes. Permeability of solutes through these membranes was investigated at different temperatures. The results showed the dual sensitivity of membranes toward pH and temperature. The formation of polyelectrolyte complex between chitosan and PAMPS showed influence on the lower critical solution temperature of PNIPAm. The permeabilities of solutes through these membranes were strongly dependent on the size of solutes, solution temperature, and hydrophilicity of the membranes.

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