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Poly(ethylene glycol)-Containing Cationic Hydrogels with Lipophilic Character

Sujan Dutta, Debabrata Dey, Dibakar Dhara
Department of Chemistry, Indian institute of Technology Kharagpur, West Bengal 721302, India
Correspondence to: D. Dhara (E-mail: dibakar@chem.iitkgp.ernet.in)

ABSTRACT: Not much effort has been focused towards the development of hydrogels that swell in nonpolar solvents. We have synthesized a new set of polyelectrolyte hydrogels and demonstrated their ability to absorb a less-polar or nonpolar organic solvent, as well as their ability to resist gel-collapse in a predominantly nonpolar medium. The hydrogels were prepared by free radical polymerization of different molar ratios of poly(ethylene glycol) methyl ether acrylate and (3-(methacryloylamino)propyl)-trimethyl ammonium chloride as comonomers in an aqueous medium. Their swelling behavior in organic solvents was studied by varying the dielectric constant of the swelling medium including mixed-solvent systems. Besides a high degree of swelling (up to 200 times) in polar solvents, some of the hydrogels also exhibited moderate swelling (up to 15 times) in less-polar organic solvents. Hydrogels samples with high cationic content showed drastic change in swelling extent in some of the mixed-solvent systems. It was also interesting to note that the retention of significant swelling in dimethyl sulphoxide–toluene mixture with even 90% toluene content for some compositions. These polyelectrolyte hydrogels with improved lipophilicity opens up greater opportunities for the development of even superior soft materials through proper structural optimizations that would successfully function for a wider range of solvents. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39873.

KEYWORDS: gels; hydrophilic polymers; swelling

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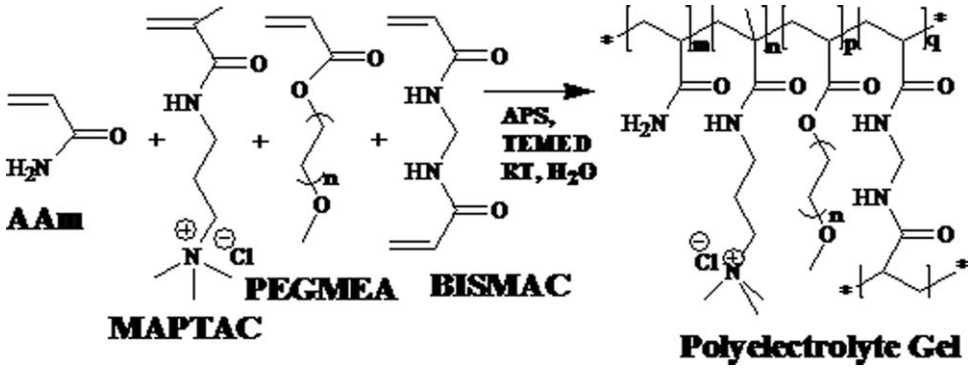
INTRODUCTION

Gels are three-dimensional polymeric structures cross-linked by physical and/or chemical bonding. Hydrogels are gels that are formed in aqueous medium and are capable of absorbing a large amount of water or biological fluids because of the presence of hydrophilic group, e.g. amino, hydroxyl, and carboxyl groups in the polymeric chain.[1,2] The main applications of gels are in absorbing pads, disposable diapers, gel actuators, water blocking tapes, membrane separation, in agriculture,[3] removal of heavy metals,[4–6] horticulture, matrix for electrophoresis,[7] as controlled drug delivery systems,[8–10] protein adsorption,[11–13] tissue engineering,[14,15] etc.

Polyelectrolyte hydrogels have charged polymeric networks. Polyelectrolyte hydrogels can swell many times in water with respect to their dry weight. However, the swelling ability of a polyelectrolyte hydrogel gets reduced drastically in solvents of low polarity. This is because of suppression of dissociation of the ionic groups or formation of tight ion-pairs between two oppositely charged ions that effectively make the polyelectrolyte gels nonionic. Hence, preparation of a gel that swells in low polarity as well high polarity solvents is a challenging task. Recently Sada et al.[16–19] reported for the first time a new class of lipophilic polyelectrolyte gels that swell in moderately polar solvents. However, these gels did not show swelling in highly polar solvents. Hence making hydrogels that swell reasonably well in both polar solvent like water as well as in organic solvents of low polarity is a challenging task.

Tanaka et al.[20–22] discovered discontinuous changes in the volume of a polyelectrolyte gel induced by compositional changes of the solvent. Extensive research has been carried out to study this effect using various polyelectrolyte gels in water and also in mixtures of water and highly polar solvents, e.g. DMF, dimethyl sulphoxide (DMSO), acetone, and alcohols.[23–31] The general tendency of gels is that they swell in the polar solvents and collapse when contacted with the low-polarity polar ones. The volumes of the gels drastically decrease in low-polarity solvents because of collapsing of the polymer network resulting from aggregation of the ionic groups. Thus the phenomenon of discontinuous swelling and collapsing of polyelectrolyte gels in low-polarity or nonpolar organic solvents have been rarely investigated.[32–34] Such limitations have also restricted the range of applications for these gels, e.g. designing of stimuli-responsive materials necessary for the development of actuators in nonaqueous media has remained a challenge.[35]

In the present work we have demonstrated the synthesis and lipophilicity of a new series of polyelectrolyte hydrogels



Scheme 1. Synthesis of polyelectrolyte hydrogels from AAm, PEGMEA, and MAPTAC.

consisting of different molar ratios of poly(ethylene glycol)methyl ether acrylate (PEGMEA) and (3-(methacryloylamino)-propyl)-trimethyl ammonium chloride comonomers. PEGs are known to have unique solubility features as they are soluble in various polar as well as nonpolar solvents. Moreover, PEG-based gels find an important place in biomedical applications owing to their nontoxicity, hydrophilicity, and good biocompatibility.[36–40] By taking advantage of these special features of PEG, and keeping in mind the environmental benignity of aqueous systems, we have focused our efforts towards preparation of PEG-based cationic hydrogels of varied compositions and investigated their swelling behaviors in water as well as organic solvents of different polarities ranging from hexane ($\varepsilon = 1.9$) to dimethyl sulphoxide (DMSO; $\varepsilon = 46$). This is a relatively new concept wherein we have attempted to develop soft material with superior combination of properties using a simple, low-cost, and environment-friendly synthetic method, which would widen their potential for industrial applications.

MATERIALS AND METHODS

Materials

Acrylamide (AAm), PEGMEA (MW 480), (3-(methacryloylamino)propyl)-trimethyl ammonium chloride (MAPTAC; 50 wt % solution in water), ammonium persulphate (APS), N,N,N',N'-tetramethyleneediamine (TEMED), N,N′-methylenebisacrylamide (BISMAC) were procured locally and used as received. Millipore water was used for the synthesis of gels and swelling experiments.

Synthesis of Hydrogels

The synthesis of the hydrogels is shown in Scheme 1. The gels were prepared by free-radical cross-linking polymerization of AAm, PEGMEA, and MAPTAC with BISMAC as cross-linking agent. The mole ratio of AAm to the total of MAPTAC and PEGMEA were fixed at 40/60, whereas MAPTAC/PEGMEA ratio was varied. The cross-linker ratio (mole ratio of cross-linker BISMAC to the total monomer) was fixed at 1/20. A predetermined amount of AAm, MAPTAC, PEGMEA, and BISMAC were dissolved in 50 mL millipore water, and stirred to form a solution. 1 mol % of each of APS and TEMED were added as redox initiator in the solution. The solution was gently stirred and poured between two silicon oil-coated glass plates separated by teflon gasket (4 mm thickness).[41] The polymerization was continued for 24 h at room temperature. Upon the completion of polymerization, the plates were separated and the produced gels were cut into pieces and immersed in millipore water to remove the unreacted monomers. For example, in order to synthesize M18-P42-A40 gel (containing 18 mol % MAPTAC, 42 mol % PEGMEA, and 40 mol % AAm) 0.286 g MAPTAC, 0.725 g PEGMEA, 0.1 g AAm, and 0.029 g BISMAC were dissolved in 5 mL water and purged with nitrogen for 10 minutes (Scheme 1). Then 0.86 mL of APS solution (0.01 g/mL in water) and 0.44 mL of TEMED solution (0.01 mL/mL in water) were added to the monomer solution as initiator. The final monomer concentration was maintained ~10% (w/v) in all the cases in order to eliminate the effect of monomer concentration on the extent of swelling. Thereafter the product gels were dried at room temperature in air for 2 days. Finally the gels were dried for one week in a vacuum oven at 55°C till a constant weight was reached. Table I shows the composition of different synthesized gels. FTIR spectra of the dried hydrogels were recorded using a FT-IR spectrometer. The samples were prepared by grinding the solid material with KBr and the samples were analyzed in the range of 400–4000 cm^{-1} with a Perkin-Elmer 1000 instrument.

Table I. Compositions of Hydrogels Prepared for Swelling Studies

	Mol %			
Sample code[a]	AAm	PEGMEA	MAPTAC	BISMAC
M0-P60-A40	40.0	60.0	0.0	5.0
M6-P54-A40	40.0	54.0	6.0	5.0
M18-P42-A40	40.0	42.0	18.0	5.0
M30-P30-A40	40.0	30.0	30.0	5.0
M36-P24-A40	40.0	24.0	36.0	5.0

[a] In sample code, M, P, and A stand for MAPTAC, PEGMEA, and acrylamide monomer; the number that follows the letter is the mol % of the particular monomer in the hydrogel.

Swelling Studies in Different Solvents

The dried gels were placed in aqueous media and in solvents of different polarities at room temperature in properly wrapped containers to avoid any solvent evaporation. The swollen gels were found to reach a constant weight after 3–4 days and were then removed from the solvents followed by the removal of excess solvent on the gel surface by blotting with filter paper.

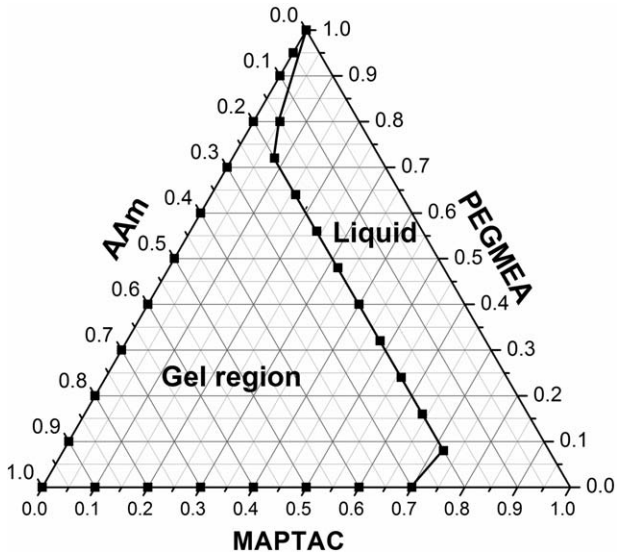


Figure 1. Phase diagram of PEGMEA–MAPTAC–AAm system with 5.0 mol % cross-linker in water at 25°C. The mol % of the three monomers were varied to find out the composition range where gel formation takes place.

The average values of three measurements were taken for each gel, and the equilibrium swelling ratio (ESR) of each gel was reported from the following relation:

$$\mathrm{ESR} = \frac{(m_e - m_0)}{m_0}$$

where m_e is the weight of swollen gel at equilibrium and m_0 is the weight of the dry gel. Similarly, ESRs were determined for swelling in salt solutions of different ionic strengths.

RESULT AND DISCUSSION

Synthesis and Characterization of Hydrogels

In this work we have synthesized hydrogels of varied compositions using PEGMEA containing pendant PEG chains, and a cationic comonomer MAPTAC. As our target was to synthesize gels that can swell in both polar as well as nonpolar solvents, it was imperative to use two different types of monomers having contrasting polarity for making the copolymer. As we wanted to synthesize the gels in aqueous medium for its obvious benefits, it was not possible to synthesize the gels using hydrophobic monomers because of solubility issues. Hence, the use of water soluble monomers was necessary. We chose PEG-based monomer as PEGs are known to be soluble in various polar as well as nonpolar solvents. Our initial choice was a combination of a PEG-acrylate monomer and a cationic monomer as the latter is known to produce highly swelling gels. However, with only these two monomers, we were unable to synthesize rigid gels, which could be handled properly for conducting the swelling studies. Hence, AAm was used as the third monomer to achieve rigid gels in aqueous medium.

In order to establish the correlation between the compositions for which rigid hydrogel formation was possible, a phase diagram (Figure 1) was constructed with the three monomers—MAPTAC, PEGMEA, and AAm, keeping the cross-linker concentration (BISMAC) fixed at 5 mol %. We have tried lower mol % of cross-linkers also. However, in the compositions containing significant amount of MAPTAC, we needed atleast approx. 3–4 mol % cross-linkers (depending on the

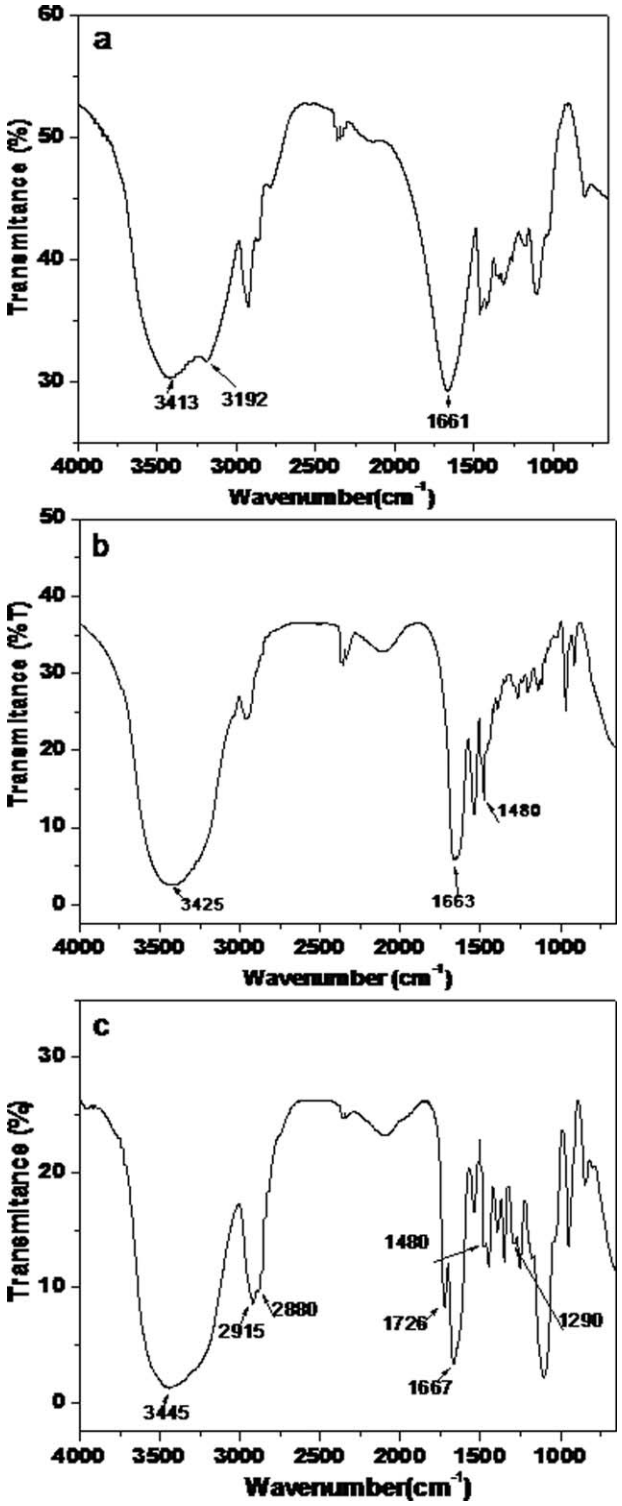


Figure 2. FTIR spectra of (a) AAm hydrogel, (b) MAPTAC–AAm hydrogel (mole ratio 60 : 40), (c) PEGMEA–MAPTAC–AAm hydrogel (sample code M18-P42-A40, Table I).

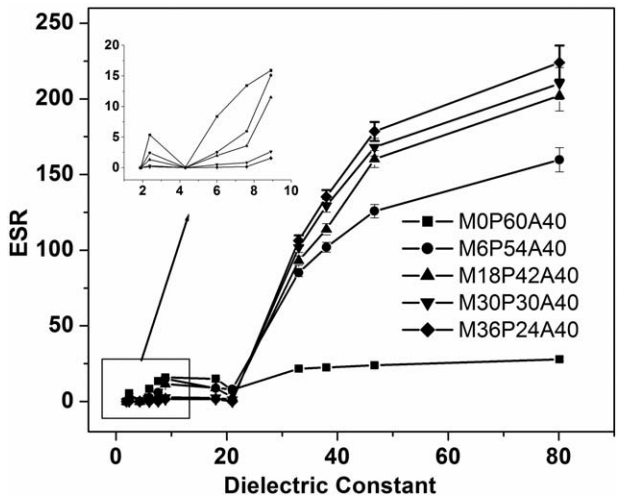


Figure 3. ESR of synthesized hydrogels in organic solvents of different dielectric constant.

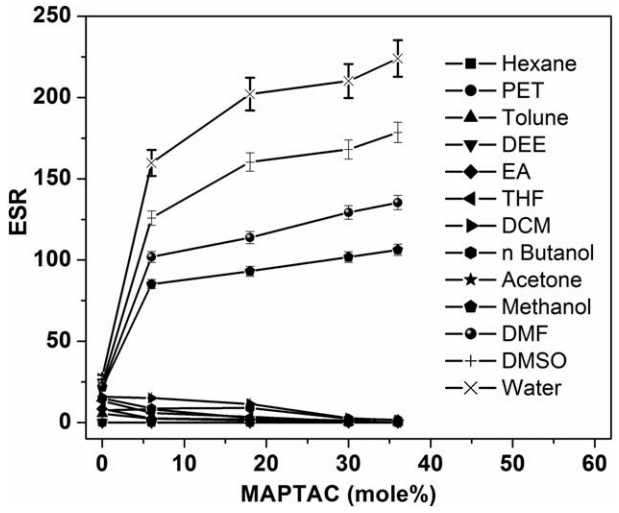


Figure 4. Variation of ESR with amount of MAPTAC (mol %) in the hydrogel compositions in different solvents.

composition) to form hydrogel. So to make sure that the amount of cross-linker do not play any role in determining the gel formation ability of the three monomers, we have used slightly excess (5 mol %) cross-linker for all the compositions. The phase diagram revealed the compositions for which gel formation was possible in our copolymer system. For the present study, we fixed 40 mol % of AAm for the syntheses to ensure the gel formation using various combinations of PEGMEA/MAPTAC monomer ratios.

The synthesized hydrogels were characterized by FTIR spectroscopy. Figure 2 represents the FTIR spectra of three types of hydrogels—only AAm, MAPTAC–AAm, and PEGMEA–MAPTAC–AAm hydrogels. The IR spectra of polyacrylamide hydrogels [Figure 2(a)] showed a characteristic peak at 3413 cm^{-1} because of N-H stretching and a absorption peak at 1661 cm^{-1} because of C=O carbonyl group of AAm unit. The peak at 1480 cm^{-1} in Figure 2(b) relates to a characteristic C-N stretching for the positively charged nitrogen containing groups, which confirm the incorporation of MAPTAC in AAm–MAPTAC hydrogel. The additional peak at 1726 cm^{-1} in Figure 2(c) is because of the C=O absorption peak of PEGMEA in AAm–MAPTAC–PEGMEA. The peaks at 1290 and 1257 cm^{-1} correspond to the stretching of –C–C–O of PEGMEA unit. A characteristic band with very high intensity in 1100 cm^{-1} is related to stretching vibration of the C-O bond for PEGMEA unit. The peaks at 1537 cm^{-1} was because of N-H bending of monosubstituted amide of MAPTAC unit. Thus, the FTIR spectra confirmed the incorporation of MAPTAC and PEGMEA monomers into the polymer structure in the appropriate hydrogels.

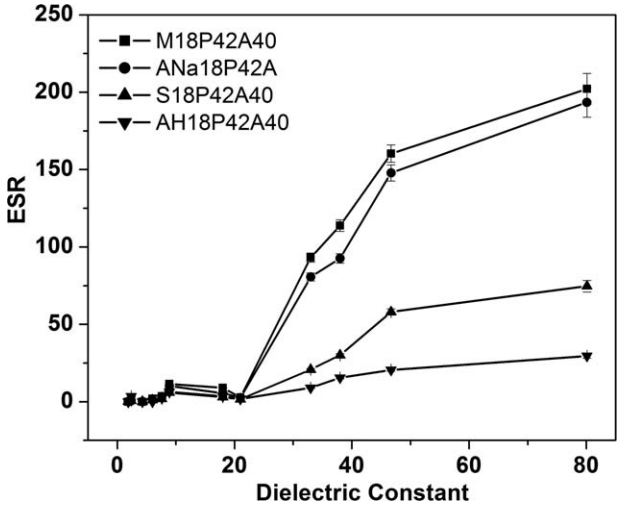


Figure 5. Variation of ESR in different solvents for hydrogels containing equal amount (18.0 mol %) of different ionic monomers; **M,** MAPTAC; **AH,** 2-Acrylamido-2-methylpropane sulfonic acid; **ANa,** 2-Acrylamido-2-methylpropane sulfonic acid sodium salt; **S,** Styrene sulfonic acid sodium salt.

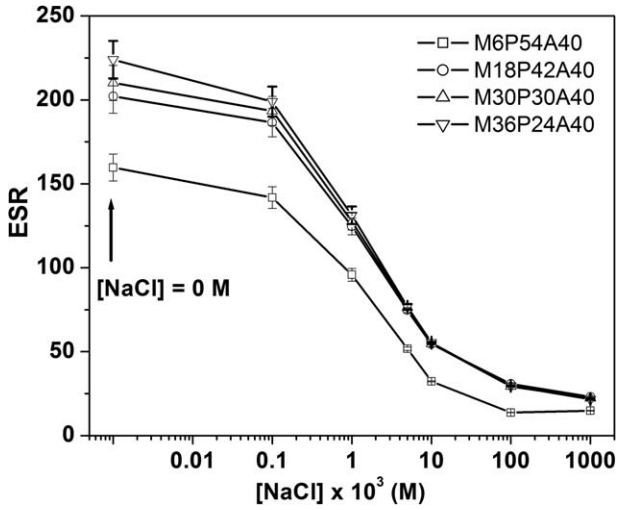


Figure 6. Effect of NaCl concentration on the swelling of MAPTAC containing hydrogels.

Swelling Behavior in Different Solvents

Effect of Dielectric Constant. The swelling behavior of the gels containing various quantities of MAPTAC in solvents with

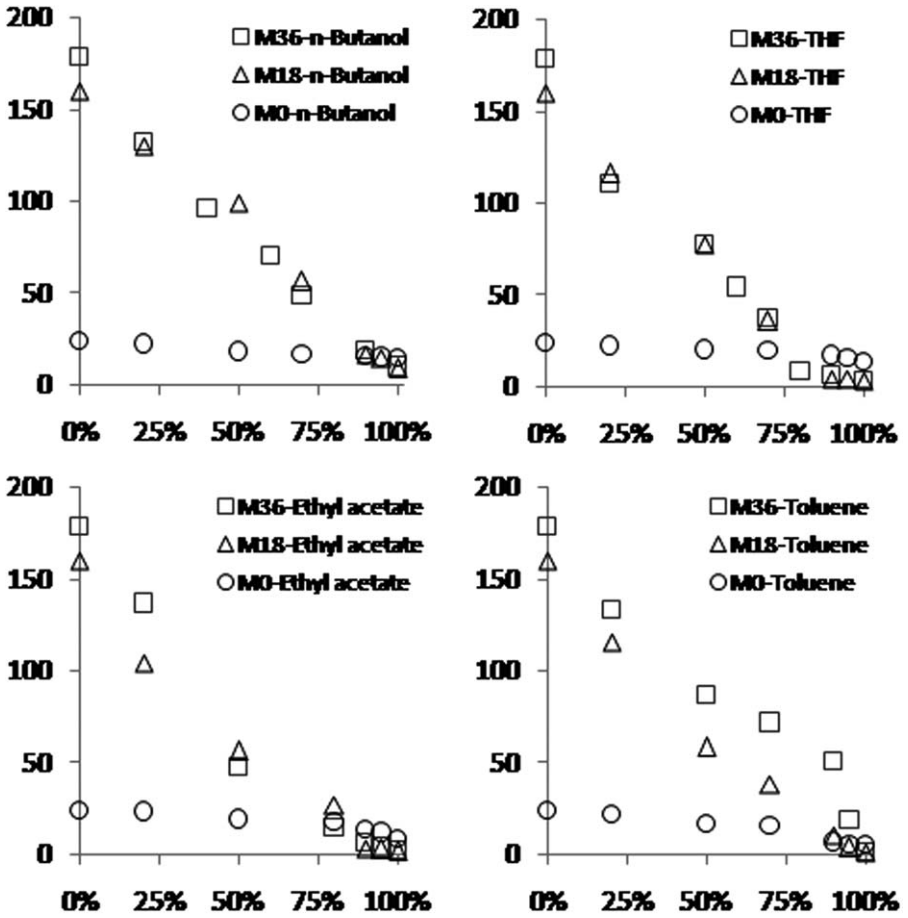


Figure 7. Plot of ESR for hydrogels in various solvent mixtures. In all the plots *Y* axis is ESR, and *X* axis is the % (v/v) of organic solvent (as mentioned in the labels) added in DMSO. Three series are for hydrogels containing different amount of MAPTAC—M0 (0 mol %), M18 (18 mol %), and M36 (36 mol %).

various polarities from hexane ($\varepsilon = 1.9$) to water ($\varepsilon = 81$) were studied and the data are presented in Figure 3. It is seen that for a given composition of a gel, increase in solvent polarity results in increase in the ESR. This is because of a higher extent of dissociation of the cationic groups when the polyelectrolyte gel comes in contact with a highly polar solvent, leading to increased osmotic pressure and increased repulsion between the polymer chains. Whereas in case of nonpolar solvents, the polymer ions and counter ions remain close to each other, thus resulting in lower extent of swelling. It may be observed from the inset of Figure 3 that some gel compositions showed moderate extent of swelling (ESR value as much as 15) even in organic solvents with low polarity like dichloromethane ($\varepsilon = 8.6$), tetrahydrofuran (THF) ($\varepsilon = 7.6$). This extent of swelling in organic solvents for hydrogels has been rarely observed before. Presence of PEG chains may be responsible for this observed swelling ability in organic solvents. The swelling of all the gels in two particular solvents, viz. diethyl ether ($\varepsilon = 4.3$) and acetone ($\varepsilon = 21.0$) was significantly low compare to other solvents, especially when compared to solvents having lower polarity than these two.

Effect of Cationic Charge on Swelling Ratio. Figure 4 shows that swelling ratio as a function of cationic charge is present in the gels. It may be recalled that in the studied compositions, the AAm molar concentration was kept constant and the molar ratios of PEGMEA and MAPTAC were varied such that any increase in the MAPTAC concentration would result in a decrease in the concentration of PEGMEA in the gel. In fact, it is possible to divide the swelling behavior of the hydrogels in two distinct parts—solvents with $\varepsilon \leq 21$ and solvents with $\varepsilon > 21$. In case of the polar solvents ($\varepsilon > 21$), the swelling ratio increases with the increase in cationic monomer content. It is evident that in highly polar solvent the swelling properties of the polyelectrolyte gels are governed by the presence of the cationic monomer MAPTAC, while in the case of solvents with low dielectric constant solvents ($\varepsilon \leq 21$) the swelling ratio decreases with the increase in the concentration of MAPTAC.

In fact, a comparative swelling study using some other ionic monomers (18 mol %), viz. 2-acrylamido-2-methylpropane sulfonic acid (AMPSH), 4-styrenesulfonic acid sodium salt (SSANa), and 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPSNa) revealed (Figure 5) that MAPTAC containing cationic polyelectrolyte gels exhibited the highest swelling among all the hydrogels studied. With bulkier organic counter ion in the MAPTAC containing polyelectrolyte hydrogel, the ionic groups remain more dissociated than other ionic

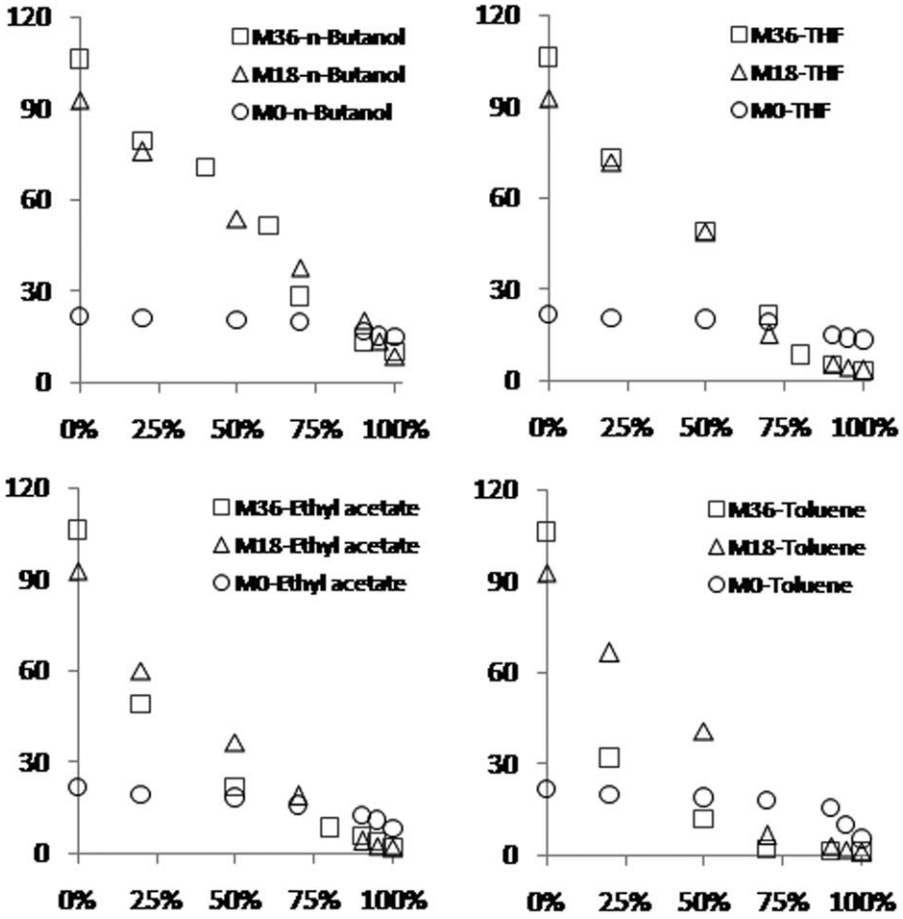


Figure 8. Plot of ESR for hydrogels in various solvent mixtures. In all the plots *Y* axis is ESR, and *X* axis is the % (v/v) of organic solvent (as mentioned in the labels) added in methanol. Three series are for hydrogels containing different amount of MAPTAC—M0 (0 mol %), M18 (18 mol %), and M36 (36 mol %).

gels even in organic solvent with moderate dielectric constant. AMPSNa containg gel showed greater swelling in water than SSANa containing gel because of more hydrophilic nature of the AMPSNa monomer, which in turn showed greater swelling than AMPSH containing gel.

Effect of NaCl Content on Swelling Behaviors of MAPTAC Containing Polyelectrolyte Gels. The degree of swelling of different MAPTAC containing cationic polyelectrolyte hydrogels was also studied as a function of NaCl concentration as shown in Figure 6. For a particular gel with the increase in concentration of NaCl, the swelling is found to be decreased. The gels with high MAPTAC content shows high swelling behavior at low concentration of NaCl solution but after 0.005*M* concentration it is almost same for the gel MAPTAC containing 18, 30, and 36 mol %, although for 6 mol % MAPTAC containing gel shows lower swelling behaviors than the high MPATAC containing gels. This may be explained by the effect of counter ion effect. Initially the gel contains fixed positive charge, thus a large difference in osmotic pressure exists between inside and outside of the gel.[16]

Swelling Behavior in Mixed Solvents

We investigated the swelling and collapsing behavior of the hydrogel sample M36-P24-A40 (containing 36 mol % MAPTAC and 24 mol % PEGMEA) in mixed organic solvents of different compositions in order to test the effect of less-polar or nonpolar solvent. Polar organic solvents like DMSO and methanol were chosen for which the hydrogels showed significant swelling values (∼150 and 100 times of dry weight, respectively). Four different solvents of comparatively less-polarity, viz. toluene, THF, n-butanol, ethyl acetate in which the said hydrogel showed negligible swelling (< 5 times of dry weight) were chosen as the other component in the solvent-mixture. The equilibrium swelling behavior of the hydrogels in various mixed solvents is shown in Figures 7 and 8. As evident from the figures, on addition of a less-polar organic solvent to DMSO or methanol, the swelling ability of the gel is reduced and in few cases, e.g. DMSO-toluene mixture (Figure 7) a discontinuous swelling was observed beyond addition of 90% (v/v) toluene. It is particularly interesting to note that this hydrogel actually existed in swollen state (∼ 50 times of dry weight) even in presence of 90% toluene in the mixture, i.e. to say in a significantly less-polarity medium without undergoing gel-collapse as would otherwise be expected for any hydrogel under such condition. Hence, for a hydrogel that swells significantly in water medium, this kind of observation is very rare. Similarly, in case of DMSO–THF mixture, a discontinuity in swelling was observed around 50% (v/v) THF in the mixture. However, for other mixed solvents the swelling ability decreased steadily (Figure 8) with the increase in the percent of less-polar solvent.

CONCLUSION

A new series of PEG-based polyelectrolyte hydrogels were prepared with the aim of developing a unique class of gels that would exhibit lipophilic character, besides their usual hydrophilicity. The swelling behaviors of these gels were studied in organic solvents of varying dielectric constants as well in aqueous medium. Compared to an appreciable swelling of the prepared hydrogels in water as well as in high-polarity organic solvents, a lower degree of swelling was observed in some of the less-polar solvents. However, such lipophilicity, however small, is quite a significant finding that has been rarely observed in case of hydrogels, and is attributed to the effect of PEG pendant chains present in the gel structure. Few interesting observations were made while conducting swelling studies for hydrogel M36-P24-A40 (containing 36 mol % MAPTAC and 24 mol % PEGMEA).in mixed solvent so as to see the effect of increased concentration of low-polarity, such as its discontinuous swelling beyond 90% (v/v) toluene content in DMSO–toluene mixture. Such discontinuous swelling is also of considerable importance as for the development of stimuli-responsive materials for diverse applications. The retention of swelling capability of the said hydrogel in a predominantly nonpolar medium (90 : 10 v/v toluene/DMSO mixtures) without undergoing any collapse also suggests a reasonably good lipophilicity of the gel. These newly synthesized polyelectrolyte gels can be potentially used as a carrying agent in agricultural, pharmaceutical, and in biomedical applications.

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