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Swelling Behavior of N-t-butylacrylamide Copolymer and Terpolymers

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Copolymers and terpolymers of N-t-butylacrylamide (TBA) with 2-acrylamido-2-methyl propane sulfonic acid (AMPS) and N-hydroxy methyl acrylamide (NHMAAM) were prepared by solution polymerization in a 1:1 (v/v) mixture of methanol and water at 50 °C keeping the TBA content in the feed constant at 60% based on mole ratio. The contents of AMPS or NHMAAM used for the preparation of TBA-AMPS and TBA-NHMAAM copolymers were 40 mole %. Molar percentages of AMPS and NHMAAM monomers in the feed for the preparation of TBA-AMPS-NHMAAM terpolymers were varied as 10:30, 20:20, and 30:10, respectively. The effects of temperature, AMPS and crosslinker contents, and the drying of swollen gels on the swelling behavior of ionic and non-ionic TBA gels were investigated in distilled water between 10–50 °C and in buffer solutions having various pHs (1.9, 3.1, 5.6, 7.1, and 9.8) with constant ionic strength of 0.08 M at 20 °C using both the dry and the swollen forms of gels. The chemical structures and microscopic morphologies of the polymers were investigated by FTIR and SEM, respectively.

Keywords: 2-acrylamido-2-methylpropane sulphonic acid; hydrogels; N-hydroxy methyl acrylamide; N-tert-butylacrylamide; stimuli-sensitive polymers; swelling

INTRODUCTION

Hydrogels are three-dimensional polymer networks that are capable of absorbing large amounts of water. Depending on the nature of the pendant groups along the polymer chains, hydrogels have the ability to respond to external stimuli such as temperature, pH, ionic strength, specific chemical compound, and electrical or magnetic fields. While pH-sensitive ones among these stimulus-sensitive polymers are used in controlled drug delivery applications, temperature-sensitive ones find uses in some separation and concentration processes[1].

The factors affecting the swelling ratio of these polymers depend on the properties of polymers (ionic charge, ionization degree and ionizable group content, pKa value of ionizable group; crosslinking degree; hydrophilicity or hydrophobicity degree of the polymer) and of swelling medium (pH, ionic content, ionic charge and valence state of counter ion)[2].

It is known that the copolymers and terpolymers prepared from N-t-butylacrylamide (TBA), acrylamide (AAM) and sodium salts of 2-acrylamido-2-methyl propane sulfonic acid (Na-AMPS) are temperature sensitive[3,4]. The swollen gels prepared from N-isopropyl acrylamide (NIPAM), sodium acrylate (SA), and TBA using benzoyl peroxide initiator and tetraethylene glycol crosslinker (in 0.1 mole %) in a mixture of dioxan and water released 96% of the adsorbed water at 40 °C as shown previously.[5] It was also observed that equilibrium swelling values and phase transition temperatures of hydrogels decrease with the increase in

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TBA content from 10 to 40%.[5] The water absorption percentages of poly (N-t-butylacrylamide) (PTBA) and poly(2-acrylamido-2-methyl propane sulfonic acid) (PAMPS) polymers prepared from TBA and/or AMPS using azobisisobutyronitrile (AIBN) initiator in methanol at 60 °C are found to be 12 and 210, respectively.[6] Save et al[7] prepared linear PTBA and poly-(acrylamide) (PAAM) homopolymers and poly(TBA-co-AAM) copolymers at 50 °C using ammonium persulfate (APS) as the initiator. Among these polymers, PTBA and the copolymers with the TBA-AAM contents of 80:20 and 70:30%, respectively, did not dissolve in water. While poly(TBA-co-AAM) copolymers with TBA-AAM contents in the molar percentages of 30:70 and 20:80, respectively, and PAAM did not exhibit any phase transition behavior, the copolymers containing 60:40, 50:50, and 40:60 mol% of TBA-AAM, respectively, display phase transition at 17, 27, and 37 °C, respectively.

Zhu et al[8] investigated the effects of the chemical composition on the phase separations of the aqueous solutions of homo- and copolymers prepared from N-substituted acrylamides such as N-tert-butylacrylamide (TBA), N-ethylacrylamide(EA), N,N-dimethylacrylamide (DMA), N,N-diethylacrylamide (DEA). From their experimental lower critical solution temperature (LCST) determination by DSC method, hypothetical LCST values of PTBA and poly(dimethylacrylamide) (PDMA) homopolymers were estimated as -5 °C and >200 °C, respectively. It is known that PDMA is water-soluble while PTBA is insoluble in water. They showed that the copolymers of TBA, which is the most hydrophobic co-monomer among the N-substituted acrylamides with hydrophilic co-monomers of DMA and EA, possess LCST values, which vary depending on the hydrophilicity-hydrophobicity of the final polymer. Keenan et al[9] used the thermo-responsive copolymer films prepared from varying ratios of N-isopropyl acrylamide (NIPAM) to TBA in the delivery of an antimitotic agent to vascular smooth muscle cells. They found that the extent of colchicines release at 37 °C was inversely proportional to the amount of TBA in the copolymer films. Bae et al[10] studied the phase transition of submicron-sized copolymer particles prepared from NIPAM and TBA. They observed that when TBA content exceeds 60 wt%, the phase transition does not occur. In addition, when the amount of TBA is adjusted to a certain level, the copolymer gels lose their reversible characteristic. Karlsson et al[11] investigated the use of poly(TBA-co-AMPS) copolymers as proton conductor and concluded that the increase in the swelling values of the polymers gave increase to the proton conductivity above the melting point of water. In addition, if the amount of water in the samples can be kept low enough to prevent crystallization at temperatures above -20 °C, the proton conductivity might not decrease drastically at low temperatures. Charreyre et al[12] prepared poly(TBA-co-N-octadecylacrylamide (ODAM)) copolymers by reversible addition-fragmentation chain transfer process and found that a well controlled polymerization (polydispersity index (PDI) below 1.3 for number average molecular weight (M_n) until 30.000 g/mol) over a wide range of conversion (until 70%) was performed.

In this work, the copolymers and terpolymers of TBA with AMPS and N-hydroxy methyl acrylamide (NHMAAM) were prepared. To determine the effects of initial monomer composition, co-monomer nature, and cross-linker content on the swelling behavior of polymers, the equilibrium swelling values in water at different temperatures (10–50 °C) and in buffer solutions with different pHs having constant ionic strength (0.08 M) at 20 °C were determined.

EXPERIMENTAL

Materials

TBA was purchased from Acros Organics (New Jersey, USA). AMPS and the cross-linker N, N′-methylenebisacrylamide (NMBA) were of Merck-Schuchardt (Hohenbrunn, Germany) product. The initiator ammonium persulfate (APS) and the accelerator N, N, N′, N′-tetramehylethylenediamine (TEMED) were provided by Riedel-de Haen (Seelze, Germany) and Serva Electrophoresis GmbH (Heidelberg, Germany), respectively. Potassium diphosphate, potassium hydrogen phthalate, sodium hydrogen carbonate, sodium chloride, potassium hydroxide, and hydrochloric acid solution were used for the preparation of buffer solutions and all were of Merck product (Hohenbrunn, Germany). Distilled water was used for the preparation of the hydrogels and buffer solutions, and for the swelling experiments.

Synthesis of Hydrogels

Poly(TBA-co-AMPS) (TBAx-40A), poly(TBA-co-NHMAAM) (TBAx-40N), and poly(TBA-co-AMPS-co-NHMAAM) (TBAx-yA-zN) copolymers and terpolymers were prepared by solution polymerization in a 1:1 (v/v) mixture of methanol and water at 50 °C using ammonium persulfate (APS) as initiator and N,N,N′, N′-tetramehylethylene diamine (TEMED) as accelerator in the presence of N,N′-methylene bis acrylamide (NMBA) as cross-linker. The feed compositions were presented in Table 1, and the structures of the polymers were given in the equations 1–3 in Scheme 1.

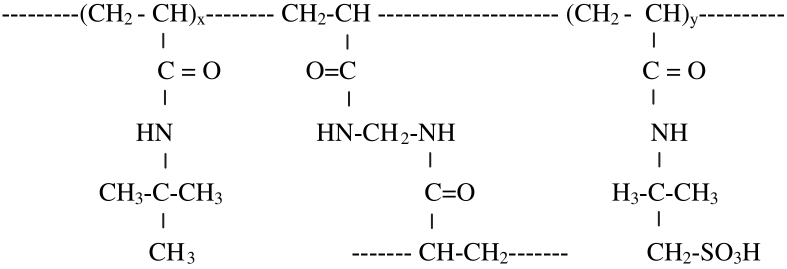
In the preparation of all polymers, TBA content in initial monomer composition was kept at 60-mol %. Molar feed composition of AMPS and NHMAAM used for the preparation of terpolymers were in the percentages of 30:10, 20:20, and 10:30, respectively. Initial total monomer concentration was 1 M. APS in the feed was 1.0 mol % of total monomers. TEMED content was equal to APS amount in weight. Cross-linking agent of NMBA was adjusted to 1.0, 3.0, and 5.0 mol % of total monomers. In the preparation of TBA-AMPS copolymers, NMBA was also added as the total monomers of 7- and 10-mol %.

Polymerization reactions were performed in the tubes with inner diameters of 1.3 cm and lengths of 15 cm. After nitrogen was bubbled through the monomer solution in the mixture of methanol-water for 15 minutes to remove the dissolved oxygen that would act as an inhibitor for the reaction, APS and TEMED were added, respectively. Then, the tubes were sealed and immersed in a water bath at 50 °C (±0.01 °C) and held there for 24 h. At the end of reaction period, the tubes were broken carefully without destroying the hydrogel. The resulting cylindrical hydrogel was cut into discs of 0.6–0.8 cm in length and placed in distilled water for 3 days; the water was

Table 1.
The feed compositions and appearances of TBA gels.

Hydrogel*	TBA (% mol)	AMPS (% mol)	NHMAAM (% mol)	NMBA (% mol)	Appearance
TBA3-40N	60	0	40	3	Opaque
TBA3-10A-30N	60	10	30	3	Semi-transparent
TBA3-20A-20N	60	20	20	3	Transparent
TBA3-30A-10N	60	30	10	3	Transparent
TBA3-40A	60	40	0	3	Transparent
TBA5-40N	60	0	40	5	Opaque
TBA5-10A-30N	60	10	30	5	Semi-transparent
TBA5-20A-20N	60	20	20	5	Transparent
TBA5-30A-10N	60	30	10	5	Transparent
TBA5-40A	60	40	0	5	Transparent

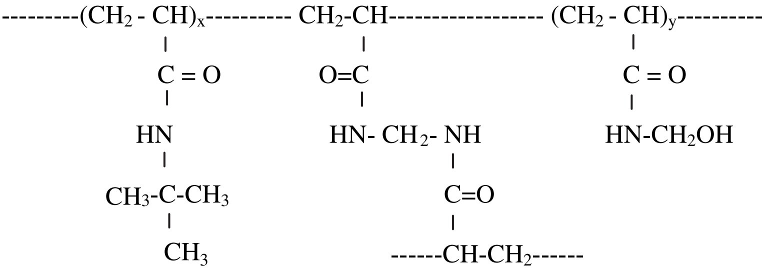
* : A, N, and x (x = 3 or 5) in the polymer codes represents the AMPS, NHMAAM, and NMBA contents in mol %, respectively.



$$\begin{array}{cccc}
\text{---------}(CH_2-CH)_x\text{--------} & CH_2\text{-}CH\text{--------------------} & & (CH_2-CH)_y\text{----------}\\
| & | & & |\\
C=O & O=C & & C=O\\
| & | & & |\\
HN & HN\text{-}CH_2\text{-}NH & & NH\\
| & & | & |\\
CH_3\text{-}C\text{-}CH_3 & & C=O & H_3\text{-}C\text{-}CH_3\\
| & & | & |\\
CH_3 & & \text{-------}CH\text{-}CH_2\text{-------} & CH_2\text{-}SO_3H
\end{array}$$

(1)

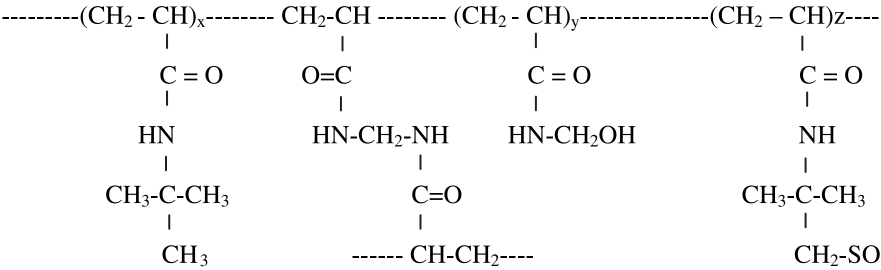
NMBA-crosslinked poly(N-tert-butylacrylamide-co-2-acrylamido-2- methylpropane sulfonic acid).



$$\begin{array}{cccc}
\text{---------}(CH_2-CH)_x\text{----------} & CH_2\text{-}CH\text{-----------------} & & (CH_2-CH)_y\text{----------}\\
| & | & & |\\
C=O & O=C & & C=O\\
| & | & & |\\
HN & HN\text{-}CH_2\text{-}NH & & HN\text{-}CH_2OH\\
| & & | & \\
CH_3\text{-}C\text{-}CH_3 & & C=O & \\
| & & | & \\
CH_3 & & \text{------}CH\text{-}CH_2\text{------} &
\end{array}$$

(2)

NMBA-crosslinked poly(N-tert-butylacrylamide-co-N-hydroxymethyl acrylamide).



$$\begin{array}{ccccc}
\text{---------}(CH_2-CH)_x\text{--------} & CH_2\text{-}CH\text{--------} & & (CH_2-CH)_y\text{---------------} & (CH_2-CH)z\text{--------}\\
| & | & & | & |\\
C=O & O=C & & C=O & C=O\\
| & | & & | & |\\
HN & HN\text{-}CH_2\text{-}NH & & HN\text{-}CH_2OH & NH\\
| & & | & & |\\
CH_3\text{-}C\text{-}CH_3 & & C=O & & CH_3\text{-}C\text{-}CH_3\\
| & & | & & |\\
CH_3 & & \text{------}CH\text{-}CH_2\text{----} & & CH_2\text{-}SO_3H
\end{array}$$

(3)

NMBA-crosslinked poly(N-tert-butylacrylamide-co-N-hydroxymethyl acrylamide-co-2-acrylamido-2- methylpropane sulfonic acid).

Scheme 1.
The structures of NMBA-crosslinked TBA copolymers and terpolymers.

changed every 12 h to remove any unreacted materials, and the sol fraction of the polymer. The resulting ‘‘swollen’’ discs were dried at first in air for 2 days and then in a vacuum oven at 40 °C until their weight remained constant in order to obtain ‘‘dry’’ gels.

Characterization of Hydrogels

FTIR Measurements

The FTIR spectra of dry gels were obtained by Digilab, Excalibur-FTS 3000 MX model instrument. The resolution of FTIR was

4 cm^{-1}, 4 scans added. The dry gel powder was thoroughly ground with potassium bromide (KBr) (IR grade, Merck-Germany) at a ratio of 1:200 and pressed into a pellet and the spectrum was then recorded.

Macroscopic Observation

The morphologies of the hydrogel samples were observed using a scanning electron microscope (JSM 5600 Series, Jeol). Before SEM investigation, the hydrogels were dried by a vacuum freeze-dryer (Armfield SB4) (−45 °C, 38.10^{-3} mmHg). The surfaces of the freeze-dried hydrogels were sputter-coated with gold and observed with a magnification of 500x.

Swelling Studies

Effect of temperature on the swelling in distilled water

Equilibrium swelling values of both swollen and dry gels in distilled water were determined at 10, 20, 30, 40, and 50 °C. A given weight of dry or swollen gel was placed in distilled water at a certain temperature and allowed to swell for 24 h. After swelling, the gel samples were taken out of distilled water, blotted with a piece of filter paper to remove excess water from the sample, and weighed. Then, these swollen gels were dried in air for 2 days followed by drying under vacuum at 40 °C until constant weight was reached. Equilibrium swelling values of the polymers were determined by the equation given below, Equilibrium Swelling Value (ESV) (g H_2O/g polymer) = $(W_{swollen} - W_{dry}) / W_{dry}$

where $W_{swollen}$ and W_{dry} are the weights of swollen and dry gels, respectively.

Effect of AMPS Content on the Swelling in Buffer Solutions with Various pH's

In order to investigate the effect of ionic monomer of AMPS content on the swelling of gels, the dry and swollen gels were placed in different buffer solutions[13] with the pH of 1.9 (HCl-KCl buffer), 3.1 (KHphthalate-HCl), 5.6 (KHphthalate-NaOH), 7.1 (KH_2PO_4-NaOH), and 9.8 ($NaHCO_3$-NaOH) at room temperature, and held there for 24 h. The ionic strength of each buffer solution was kept constant as 0.08 M by NaCl addition if necessary. After swelling, the samples were taken out of the buffer solutions, and their equilibrium swelling values were calculated using the equation given above.

Result and discussion

The feed compositions of poly(TBA-co-AMPS), poly(TBA-co-NHMAAM), and poly(TBA-co-AMPS-co-NHMAAM) gels and the appearance of the reaction mixture for each gel after polymerization were given in Table 1. During the polymerization experiments, it was observed that poly(TBA-co-AMPS) gels are completely transparent. However, poly(TBA-co-NHMAAM) gels are opaque in appearance and white-colored. It was also observed that the transparency of the terpolymers increases with the increase in AMPS content of polymer.

FT-IR Studies

The FT-IR spectra of TBA1-40A, TBA1-40N, and TBA1-20A-20N were given in Figure 1. All the three spectra display the characteristic absorption bands at 1657/1660/1665 cm^{-1} (ν C–O, amide I), at 1551/1545/1550 cm^{-1} (N–H bending, amide II), at about 1185 cm^{-1} (ν C–N, amide III), and the bands assigned to the tertiary butyl groups ($C–(CH_3)_3$) at 1395/1368/1223, 1394/1366/1225, and 1393/1367/1225 cm^{-1} [3,14-17]. The absorption bands at 1457 cm^{-1} in all spectra are attributed to C–H bending in $–C(CH_3)_3$ and $–CH_2$- groups[18]. The bands at 1223/1040 and 1225/1040 cm^{-1} in the spectrums of TBA1-40A and TBA1-20A-20N are attributed to $–SO_3^-$ groups (asymmetric and symmetric stretching of S–O bonds).[6,19–21] The broad and less intense band at 1036 cm^{-1} in the spectrum of TBA1-40N in comparison to the band at the same wave number in other two spectra may provide an evidence of crosslinking

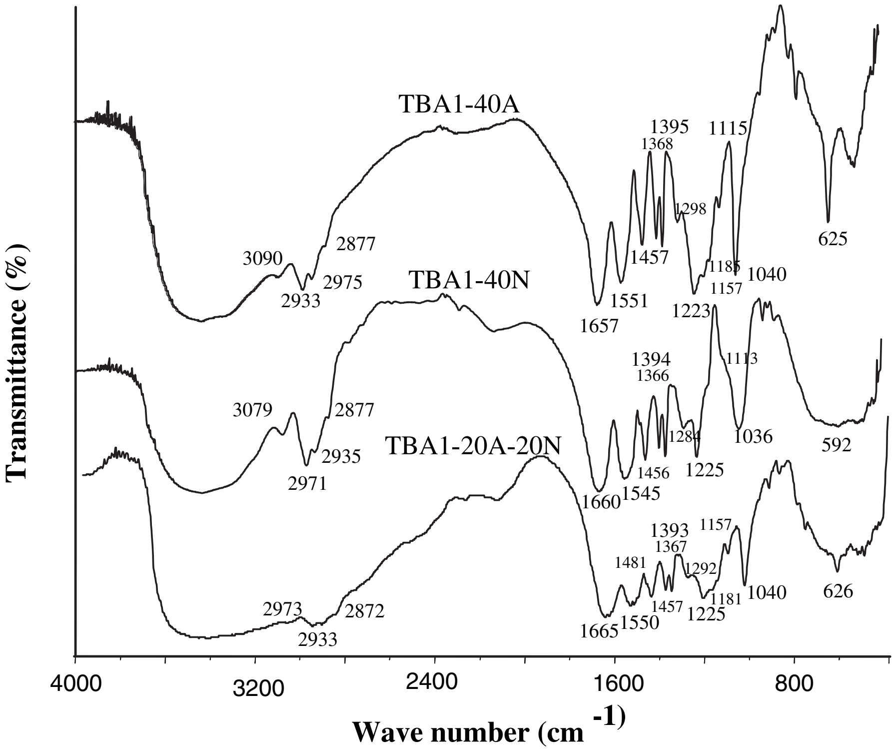


Figure 1.
FTIR spectra of TBA copolymers and terpolymers.

reaction between two N-methylol groups or N-methylol and N–H groups[22] since the intensity of band at ~1040 cm^{-1} in the spectrum of NHMAAm (not given) are apparently higher than those at ~1456 and 1225 cm^{-1}(http://www.sigmaaldrich.com). The absorption region between 2870 and 3000 cm^{-1} corresponds to C–H stretching vibrations of $-CH_3$ and $-CH_2$- groups.[18,23] The broad band above 3000 cm^{-1} is assigned to the stretching of O–H and N–H bonds.[24–29]

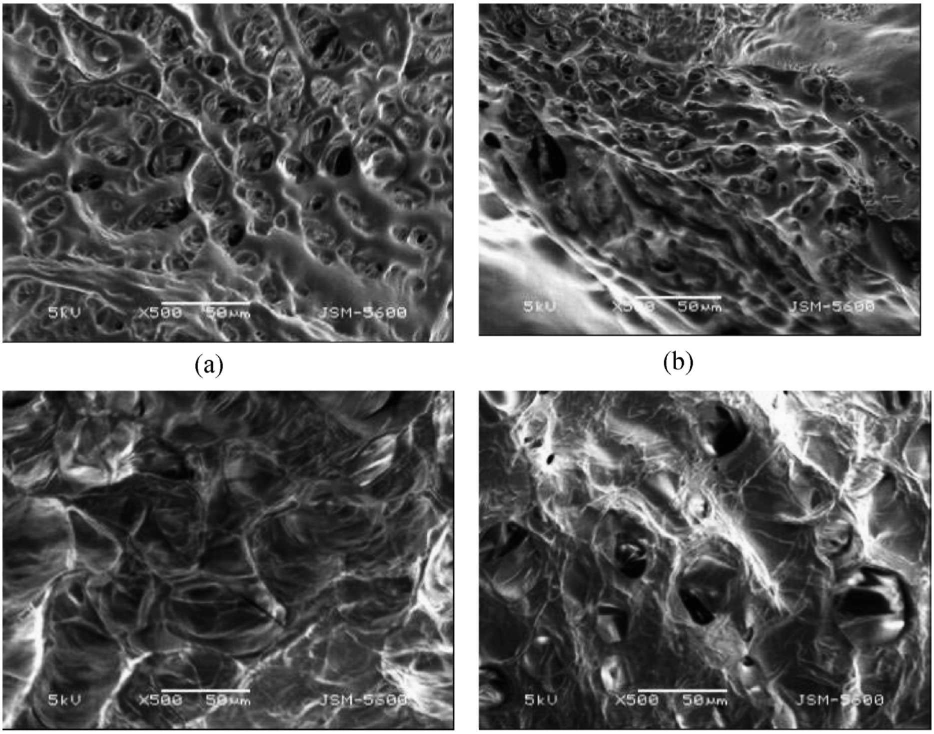
SEM Studies

The structural morphology of polymers was studied by scanning electron microscopy. Swollen gels were frozen in liquid nitrogen and then freeze dried before morphological investigation by SEM. A few representative micrographs for the investigation of interior matrix structure of TBA gels are given in Figure 2.a–d.

TBA-AMPS copolymers have a porous structure with a relatively uniform pore size distribution. Their pore sizes decrease with the increase in crosslinker (NMBA) content from 3 to 7 mol % (Figure 2.a–b). The incorporation of NHMAAM into the TBA-AMPS copolymer structure leads to the formation of a relatively nonporous and bulky structure (Figure 2.c–d).

The Effect of AMPS Content on the Swelling in Buffer Solutions with Various pH's

The equilibrium swelling values (ESV's) of dry and swollen TBA gels containing 3% NMBA in buffer solutions at room temperature are given in Figure 3 and Figure 4, respectively. The relationship between the ESV and AMPS content depending on pH of swelling solution were determined in buffer solutions with constant ionic strength



(a) (b)

(c) (d)

Figure 2.
SEM micrographs of TBA gels: (a) TBA3-40A, (b) TBA7-40A, (c) TBA3-10A-30N, (d) TBA5-20A-20N.

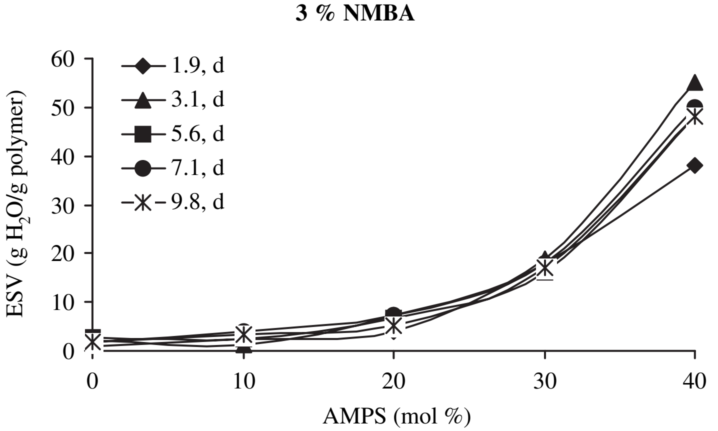


Figure 3.
The variation of equilibrium swelling values of dry TBA3 copolymers and terpolymers in buffer solutions with pH range of 1.9–9.8 (I = 0.8M) at 20 °C with AMPS content (d in legends represent the dry form of the gels).

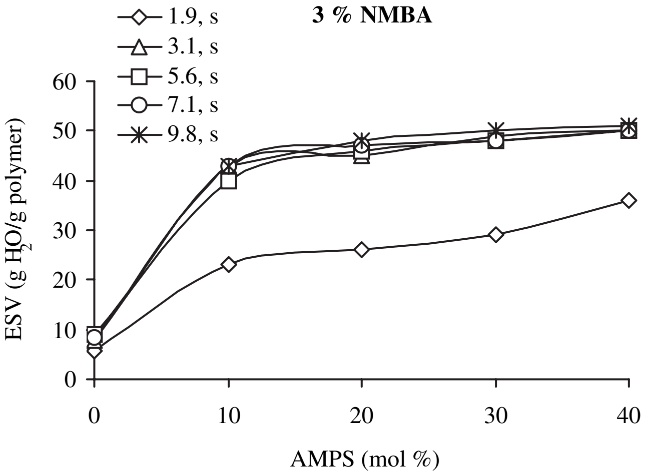


Figure 4.
The variation of equilibrium swelling values of swollen TBA3 copolymers and terpolymers in buffer solutions with pH range of 1.9–9.8 (I = 0.8M) at 20 °C with AMPS content (s in legends represent the swollen form of the gels).

(I = 0.08 M) between solution pH of 1.9 and 9.8.

Swelling values of a non-ionic network are determined by two forces:

1. The elastic retraction response of the network;
2. The free energy of mixing of the network chains with the solvent.

In case of an ionic network, a third factor (ionic swelling pressure or osmotic pressure) resulting from the ionization of ionic groups of polymer also plays role on the swelling values in addition to those given above for non-ionic gels.

The ESV's of dry gels with 3% NMBA (the copolymers of TBA3-40N and TBA3-40A, and the terpolymer of TBA3-yA-zN) in the buffer solutions with the pH of 1.9–9.8 at 20 °C increase with the increase in AMPS content of polymer (Figure 3). Among the dry TBA3 gels, TBA3-40A gels have maximum ESV's in buffer solutions with various pH values due to the presence of strongly ionizable AMPS monomer. ESV's of both dry TBA3 copolymers, TBA3-40N and TBA3-40A, and dry TBA3-yA-zN terpolymers do not depend on the pH of swelling solution as shown in Figure 3 except that of TBA3-40A in the solution with pH of 1.9. Crosslinked copolymer of TBA and NHMAAM (TBAx-40N) are non-ionic in nature. AMPS monomer in TBA-AMPS copolymer and TBA-AMPS-NHMAAM terpolymers is a strong polyelectrolyte and ionizes easily. The lower ESV values of dry TBA3-40A gel in the solution with pH of 1.9 in comparison to those in the solution with higher pH values may be attributed to less ionization of –SO_3H groups in AMPS due to high acidity of solution. While the ESV's of swollen TBA3-40N and TBA3-yA-zN gels in the buffer solutions with pH range of 1.9–9.8 (Figure 4) are apparently higher than those of dry ones (Figure 3), the dry and the swollen TBA3-40A gels have nearly the same ESV's in the buffer solutions at the same pH range. In case of swollen TBA gels, AMPS introduction to the polymer even at 10% increased the ESV's of swollen gels rapidly approximately to maximum values, and further increases in AMPS content of polymer led to slight increases in ESV's for all pH values. Although the ESV's of dry TBA3 gels are nearly the same for all pH values (except that of dry TBA3-40A in buffer solution with pH of 1.9), the ESV's of swollen TBA3 gels in the solution with pH of 1.9 are apparently lower than those in the rest of buffer solutions. These lower ESV's of swollen TBA3 gels in the solution with pH of 1.9 may be attributed to the less ionization of polymer due to high acidity of swelling solution.

The decrease in ESV of NHMAAM-containing dry TBAx-40N and TBAx-yA-zN gels can probably be attributed to the increase in cross-linking by a condensation reaction between –$HNCH_2OH$ (N-methylol) groups with the release of water during the drying of swollen gels. Therefore, the drying of swollen TBA3-40A copolymer did not change its ESV's since a post-crosslinking reaction during the drying did not occur due to absence of –$HNCH_2OH$ groups in that copolymer. A similar decrease in swelling values due to cross-linking by the condensation of N-methylol groups was observed in the poly (acrylic acid-co-acrylamide) copolymers.[22] In addition, Klimchuk et al[30] observed that freeze-drying of cationic acrylamide-N-alkylacrylamide copolymers made the dry sample water-insoluble, probably due to the formation of methylene crosslinks.

The variations in ESV's of the dry and the swollen TBA gels with 5% NMBA in buffer solutions at 20 °C as a function of AMPS content are given in Figures 5 and 6, respectively. Similar to the TBA3 gels, the ESV's of both types (dry and swollen) of TBA5 gels increase with the increase in AMPS content and the ESV's of swollen AMPS-containing TBA5 gels in the swelling solution with pH of 1.9 are considerably lower than those in the rest of solutions due to protonation of polymers in high acidity solution.

In case of both the dry (Figures 3 and 5) and the swollen (Figures 4 and 6) polymers, the increase in crosslinker content from 3 to 5% decreased the ESV's polymers as can be expected. Similar to TBA3 gels, the ESV's of dry TBA5 gels (except TBA5-40A) in pH range of 1.9–9.8 and swollen TBA5 gels in pH range of 3.1–9.8 do not depend on pH of swelling solution practically.

The effect of Temperature on the Swelling Values

The ESV's of dry and swollen poly(TBA-co-AMPS) (TBAx-40A) copolymer gels with various NMBA contents were given in Figure 7. The ESV's of both the dry and the swollen poly(TBA-co-AMPS) gels with 3 and 5 % NMBA are nearly the same and they remain constant at the temperatures between 10 and 50 °C. It can be concluded that the ESV of both the dry and the

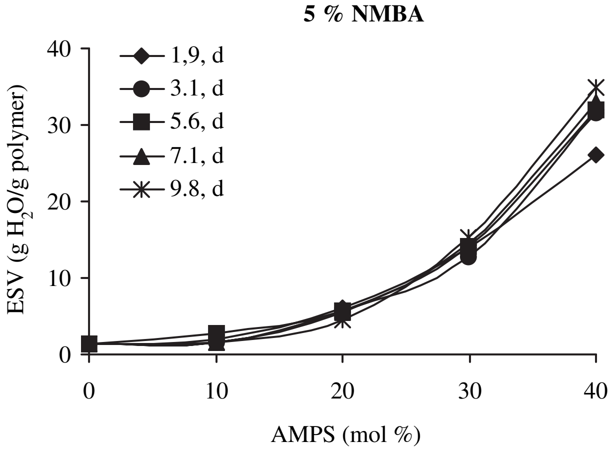


Figure 5.

The variation of equilibrium swelling values of dry TBA5 copolymers and terpolymers in buffer solutions with pH range of 1.9–9.8 (I = 0.8M) at 20 °C with AMPS content (d in legends represent the dry form of the gels).

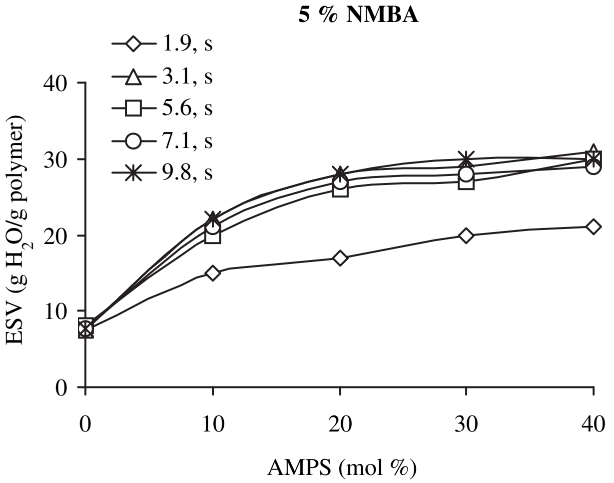


Figure 6.
The variation of equilibrium swelling values of swollen TBA5 copolymers and terpolymers in buffer solutions with pH range of 1.9–9.8 (I = 0.8M) at 20 °C with AMPS content (s in legends represent the swollen form of the gels).

swollen TBA-AMPS copolymer gels decreases with the increase in NMBA content from 3 to 10 mol %.

It is known that PTBA is a temperature sensitive polymer and it displays a phase transition at −5 °C.[8] It is also known that the increase in ionic co-monomer content in thermo/pH-responsive polymer results in at first the decrease and then the lost of stimuli-responsive property similar to the lost of thermo-sensitivity in NIPAM-AA gels due to use of AA content more than 10 mole %.[31] The TBA-AMPS copolymers prepared in our work do not display a phase transition between 10 and 50 °C probably due to high AMPS contents. However, the non-ionic copolymers of TBA with NHMAAm exhibit continuous deswelling with the increase in temperature from 10 to 50 °C (Figure 8).

The ESV's of swollen TBA-NHMAAM copolymers at various temperatures are

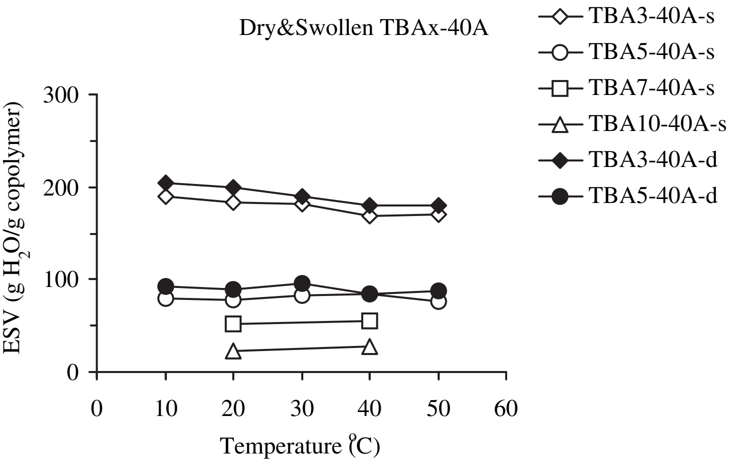


Figure 7.
The variation of equilibrium swelling values of ionic TBA-AMPS copolymers in distilled water with temperature.

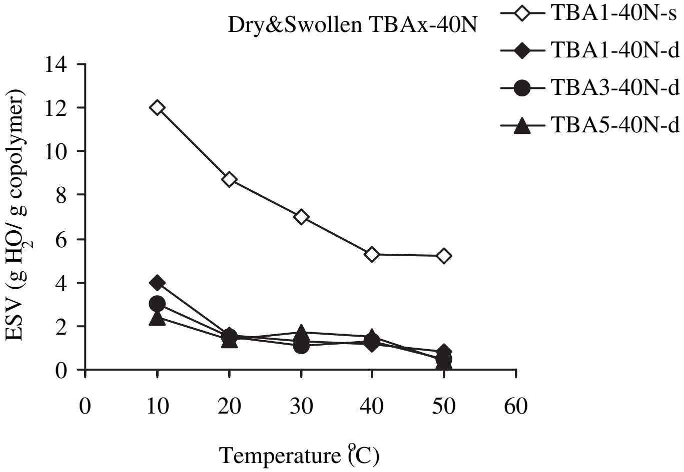


Figure 8.
The variation of equilibrium swelling values of non-ionic TBA-NHMAAM copolymers in distilled water with temperature.

higher than those of identical dry copolymers at the same temperature range like those of dry and the swollen NHMAAM-containing polymers in the buffer solutions with various pH values. The reason exhibiting deswelling with the temperature for this non-ionic copolymer can be attributed to the presence of non-ionic and less hydrophilic NHMAAM co-monomer and its hydrophobic contribution to the phase transition behavior in comparison to AMPS co-monomer.

The variations in ESV of both swollen and dry TBA-AMPS-NHMAAM terpolymers with 3 and 5 mole % NMBA content in distilled water with temperature were given in Figure 9 and 10, respectively. The ESV of both dry terpolymers is considerably lower than those of swollen ones and they do not depend on temperature. The

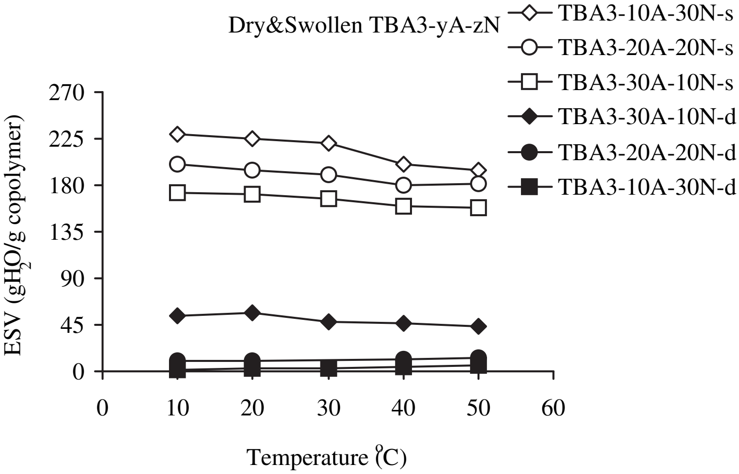


Figure 9.
The variation of equilibrium swelling values of TBA-AMPS-NHMAAm terpolymers with 3% NMBA in distilled water with temperature.

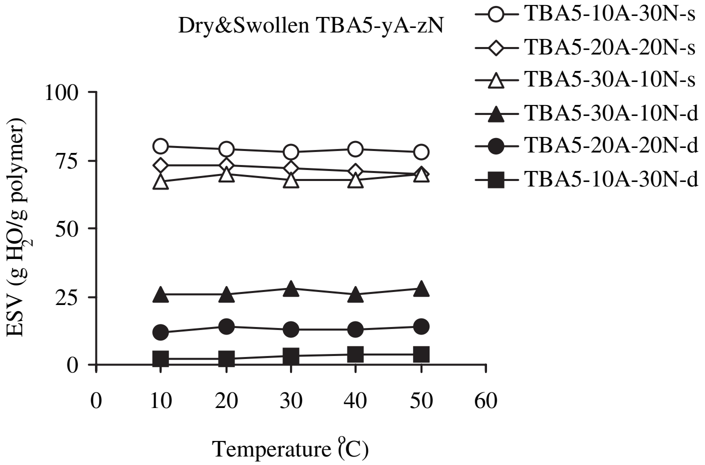


Figure 10.
The variation of equilibrium swelling values of TBA-AMPS-NHMAAm terpolymers with 5% NMBA in distilled water with temperature.

ESV of dry terpolymers decreases with the increase in NHMAAM and NMBA contents due to crosslinking reactions occurring during the polymerization and drying of swollen gels equilibrated in distilled water after polymerization.

An unexpected result was observed from the investigation of swelling and AMPS content relationship of swollen terpolymer gels as it is seen in Figure 9 and 10. Generally, the swelling values in distilled water increase with the increase in ionic monomer content of polymer. In our work, this is valid for the swelling of dry terpolymers in distilled water and the swelling of terpolymers, especially the dry gels, in different buffer solutions. However, in case of swelling of both swollen terpolymers (TBA3-yA-zN and TBA5-yA-zN) in distilled water at different temperatures, the ESV's decrease with the increase in AMPS content in an unexpected manner. This decrease may probably be attributed to the enhanced interaction possibility between highly reactive –CH_2OH and –SO_3H groups acting as physical cross-linking. This swelling versus AMPS content behavior was not observed in dry terpolymers since their cross-linking contents occurred in two steps, polymerization and drying, are apparently higher than those of swollen counterparts and high cross-linking density prevents the expansion of network for the water absorption acting as a dominant factor on the swelling values in comparison to the presence of ionic co-monomer in the network.

CONCLUSION

In this study, poly(TBA-co-AMPS), poly(TBA-co-NHMAAM), poly(TBA-co-AMPS-co-NHMAAM) were prepared and the swelling behavior of both the dry and the swollen gels was investigated in distilled water as a function of temperature, and in buffer solutions with pH range of 1.9–9.8 at 20 °C as a function of AMPS content.

It was determined that while the ESV of both dry and the swollen TBA-AMPS copolymers were nearly the same, an apparent difference was observed between the ESV of dry and swollen TBA-NHMAAM copolymers and TBA-AMPS-NHMAAM terpolymers both in distilled water and in buffer solutions. The decrease in ESV of dry gels in comparison to those of swollen gels results from the formation of cross-linking due to –CH_2OH groups during the drying of swollen gels. Both form of TBA-NHMAAM gels displayed pH-independent behavior in terms of swelling. The swollen gels of TBA-AMPS and TBA-AMPS-NHMAAM and the dry TBA-AMPS gels exhibited the same pH-swelling behavior. Thus, their ESV's were minimal in buffer solution with pH of 1.9, and they increased with the increase in pH to 3.1 and they remained nearly the same with further increase in solution pH to 9.8. In case of dry terpolymers, no change in ESV was observed with the increase in pH range between 1.9 and 9.8 probably due to high cross-linking.

It was observed that the ESV of swollen terpolymers in distilled water slightly decreased with the increase in AMPS content. This decrease results probably from the increasing interaction between the pendant groups of networks in comparison to that between pendant groups and water.

It can be concluded that TBA-NHMAAM copolymers are temperature responsive between 10 and 50 °C, but it is not valid for AMPS-containing copolymers and terpolymers due to their high ionic comonomer contents. Taking the ESV of NHMAAM-containing dry TBA copolymers and terpolymers into consideration, it can also be concluded that NHMAAM can be used as crosslinker.

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