Synthesis and Characterization of New Methacrylate-Type Hydrogels Containing 2-*tert*-Butylamino Ethyl Groups for Sorption Purposes

Nursel Pekel Bayramgil

Department of Chemistry, Hacettepe University, 06800 Beytepe, Ankara, Turkey

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ABSTRACT: Crosslinked poly[2-(*tert*-butylamino)ethyl methacrylate] (PtBAEMA) hydrogels were synthesized by ^{60}Co-γ-radiation-initiated simultaneous polymerization and crosslinking of 2-(*tert*-butylamino)ethyl methacrylate in bulk and in aqueous solutions. The results showed that the gelation percentage decreased with increasing water content. The structural and thermal characterizations of the hydrogels were accomplished with several techniques, including Fourier transform infrared spectroscopy, swelling measurements, thermogravimetry, and differential scanning calorimetry. The effects of time, pH, temperature, and ionic strength on the swelling behavior were also investigated. Swelling equilibrium was attained in 2–3 days. PtBAEMA hydrogels originally swelled to 350% (by volume) in deionized water, but this value reached 3000% around pH 2.0. PtBAEMA hydrogels were reversibly affected by the change in temperature within the temperature range of 4–70°C. The swelling ratios of the gels decreased with increasing ionic strength. As a result, PtBAEMA hydrogels show stimuli-responsive properties depending on the characteristics of the environment, and they are being considered for adoption as some kind of carrying material for separation. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1205–1211, 2008

Key words: hydrogels; irradiation; metal-polymer complexes; phase behavior; stimuli-sensitive polymers

INTRODUCTION

Hydrogels are two-component or multicomponent systems consisting of a three-dimensional network of polymer chains and water that fills the spaces between the macromolecules. Their ability to absorb water is due to the presence of hydrophilic groups such as —OH, —CONH, —$CONH_2$, —NH_2, —COOH, and SO_3H.[1] Hydrogels can be considered to have a physical or chemical nature according to the class of bonds existing between individual polymer chains; physical hydrogels have weak hydrogen bonds or electrostatic interactions, whereas in chemical hydrogels, the chains are crosslinked as a result of covalent bonding between polymer chains. The interchain crosslinks can be obtained either by a reaction with chemical reagents or by means of ionizing radiation.[2,3] The use of ionizing radiation in hydrogel preparation has special advantages: interactions between chains through covalent bonds and polymerization and crosslinking through free radicals in the absence of initiators, crosslinkers, and so forth, which may be harmful and difficult to remove; easy process control; and the possibility of combining hydrogel formation and sterilization in one technological step. All these advantages make irradiation the method of choice in the synthesis of hydrogels, especially for biomedical applications.[4]

Hydrogels may respond uniquely to changes in external environmental conditions such as ionic strength,[5] electromagnetic radiation,[6] pH,[7–10] and temperature.[11–15] These conditions could be introduced individually or in combinations and altered as desired. Other important factors, such as the type of salt used for the preparation of the buffer,[16,17] solvent used as the medium,[18] photoelectric stimulus,[19] and external stress,[20] are also influential on the hydrogel's performance. The swelling behavior of dried hydrogels results from the disentanglement of polymers or hydration of hydrophilic groups caused by the diffusion of water through glassy polymers.[21]

Polyacrylates are frequently used for biomedical purposes, especially as implants. Their rubberlike flexibility when they are hydrated (which minimizes the mechanical damage to surrounding tissues) and their low surface tension (which minimizes cell adsorption and adhesion) are their main advantages for such applications.[22] Acrylic and methacrylic monomers can be tailor-made for specific applications. By a change in the side chain, acrylic and methacrylic polymer polarity can be tuned within almost the entire polarity spectrum, from hydrophilic to hydrophobic. Most acrylic and methacrylic polymers possessing intermediate side-chain polarities

Correspondence to: N. P. Bayramgil (nursel@hacettepe.edu.tr).

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are amphiphilic. As a result, acrylic-type polymers are primarily used in pressure-sensitive adhesives and hydrogels.[23]

Through the synthesis of novel responsive alkyl-branched poly(alkyl methacrylate) polymers, it has been shown that the polymer properties can be controllably altered when this is desired. The top priority for this work was to examine how functional groups could be used to create novel environmentally responsive materials based on branched poly (ethyl methacrylate)s. It is known that poly[2-(*tert*-butylamino)ethyl methacrylate] (PtBAEMA) is a neutral polymer. However, the *tert*-butylamino group alters its character from neutral to cationic even in weakly acidic solutions. Therefore, it can be considered a drug-carrying material because of its conformational alteration. In this work, PtBAEMA hydrogels were synthesized with ionization radiation. The effects of pH, ionic strength, and temperature on the swelling behavior of PtBAEMA hydrogels were studied. The thermal stability and structure of the hydrogels were studied with thermogravimetric and calorimetric analysis and Fourier transform infrared (FTIR) spectroscopy. Stimuli-responsive PtBAEMA hydrogels were subjected to experimentation for metal-ion uptake. Drug release and biomolecule sorption studies are still under consideration. Also, syntheses of some betaine structures based on 2-(*tert*-butylamino)ethyl methacrylate (tBAEMA) will be subjects of further studies.

EXPERIMENTAL

Materials

The tBAEMA monomer was purchased from Aldrich (Steinheim, Germany) and used as received. Phosphate buffers with different pH values in the range of 2–13 were prepared with H_3PO_4, NaH_2PO_4, and Na_2HPO_4 (BDH Co., Ltd., Poole, United Kingdom) to investigate the swelling behavior, and KCl (Merck, Darmstadt, Germany) was used to adjust the ionic strength. All metal salts used for adsorption were purchased from BDH.

Synthesis of the PtBAEMA hydrogels

Aqueous solutions containing different volume fractions of tBAEMA (tBAEMA/water volume ratio = 10.0/0.0, 9.0/1.0, or 8.0/2.0) were placed in poly (vinyl chloride) straws with a 3-mm diameter and irradiated to different doses in air at the ambient temperature in a ^{60}Co Gamma (Isledovatel, Moscow, USSR) irradiator at a fixed dose rate of 1.28 kGy/h. PtBAEMA hydrogels, obtained as long, cylindrical shapes, were cut into pieces 3–4 mm long and were dried in air and in a vacuum oven and weighed. To remove uncrosslinked soluble fractions, hydrogels were extracted with water for 3 days and then dried again to determine the gel fraction:

$$\text{Gel fraction } (\%) = \frac{w_g}{w_0} \times 100 \quad (1)$$

where w_0 is the initial weight of the dry gel and w_g is the weight of the dry gel after water extraction.

Characterization (FTIR and thermal analysis methods)

The dried gel was ground into a powder of a suitable size and was then pressed into pellets with KBr. The spectrum was recorded in a Spectrum One FTIR spectrometer from PerkinElmer Instruments (Waltham, MA) with an average of 10 scans at a 4-cm^{-1} resolution in the range of 4000–400 cm^{-1}.

Thermogravimetric analysis (TGA) of the hydrogels were carried out with a Netzsch STA 409 PC Luxx TGA (Burlington, MA) instrument at a heating rate of 10°C/min under a dynamic N_2 atmosphere (15 mL/min) from room temperature to 600°C. The glass-transition temperature (T_g) was estimated with a Netzsch STA 409 PC Luxx differential scanning calorimetry (DSC) instrument at the same heating rate and with an N_2 flow from 10 to 200°C.

Swelling studies

Swelling studies were conducted on PtBAEMA hydrogels as a function of the time, temperature, pH, and ionic strength of the swelling medium. Dried PtBAEMA hydrogels were accurately weighed and immersed in water for different periods (up to 3 days) at room temperature. After each period, the sample was removed from water, quickly blot-dried, and reweighed. The degree of swelling (%) was calculated as follows:

$$\text{Degree of swelling } (\%) = \frac{w_t - w_0}{w_0} \times 100 \quad (2)$$

where w_0 is the weight of the dried hydrogel and w_t is the weight of the water-immersed and blot-dried hydrogel. Dried hydrogels (w_0) were transferred into water at different temperatures (4–70°C), allowed to reach equilibrium, and reweighed (w_t). The degree of swelling was again calculated with eq. (2). The same procedure was followed to investigate the swelling character of PtBAEMA hydrogels at different pH and ionic strength values.

Adsorption of metal ions

The adsorption trials for divalent and trivalent metal ions were carried out with different pH values to

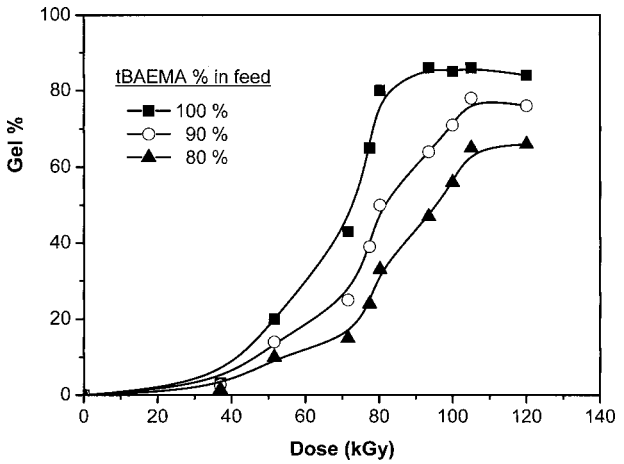

Figure 1 Gel fraction as a function of the absorbed dose for PtBAEMA hydrogels with different initial compositions.

determine the metal-uptake behavior for PtBAEMA hydrogels. The dry hydrogel was put into 100-mL Cu^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Cr^{3+}, and V^{3+} solutions (as chlorides) until the adsorption equilibrium was attained. The adsorption capacity (q_e) of the gel was calculated as follows:

$$q_e = \frac{C_0 - C_e}{w} \times V \tag{3}$$

where C_0 and C_e are the initial and equilibrium concentrations of Me^{n+} ions (ppm), respectively; w is the weight of the dry hydrogel (g); and V is the volume of the Me^{n+} solution (L).

RESULTS AND DISCUSSION

Radiation synthesis of the PtBAEMA hydrogels

tBAEMA monomers with different water contents were irradiated in a ^{60}Co-γ source, and hydrogels were obtained. As it is known, several factors, such as the absorbed dose, dose rate, monomer concentration, amount of the crosslinker, and solvent type, can affect the formation of hydrogels.[24,25] Figure 1 shows curves of the gel fraction versus the absorbed dose for different monomer concentrations. The gel fraction increased with the absorbed dose steeply at the beginning of gelation and leveled off asymptotically to the maximum value (ca. 85% gel) around 100 kGy, regardless of the initial composition. The extent of gelation decreased with increasing water content in the initial mixture during gel preparation. At a fixed irradiation dose of 100 kGy, 85% conversion of the monomer into the polymer was achieved; with increasing water concentrations, the percentage of gelation gradually decreased. Two factors could be effective in causing such a decrease: first, the formation of a gel might decrease with chain scission at high-dose applications in aqueous systems, and second, the probability of combining macroradicals decreases with increasing water content.[26] For further studies on PtBAEMA hydrogels, the composition with a tBAEMA/water volume ratio of 100/0 was selected as the optimum system because of its dimensional stability, geometry, gelation, and swelling properties. Thus, PtBAEMA hydrogels were prepared by the irradiation of solutions with the 100/0 composition at a dose of 100 kGy, which gave the maximum gelation of 85%.

Spectroscopic and thermal characterization of the PtBAEMA hydrogels

The FTIR spectrum of the PtBAEMA hydrogel is shown in Figure 2. The absence of bands at 1670 and 3020–3080 cm^{-1} confirms that the polymerization reaction was accurately achieved. The characteristic bands for the PtBAEMA hydrogels were as follows.

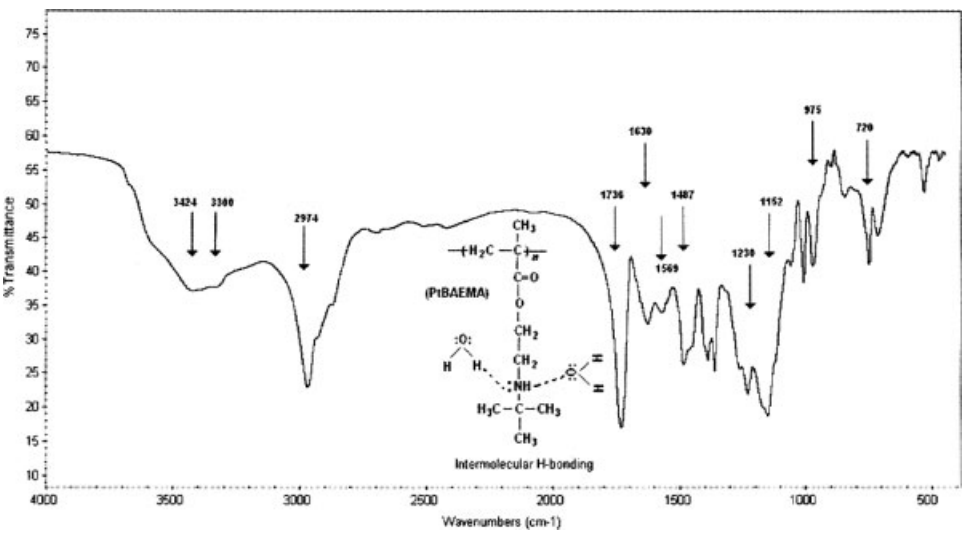

Figure 2 FTIR spectrum of the PtBAEMA hydrogel.

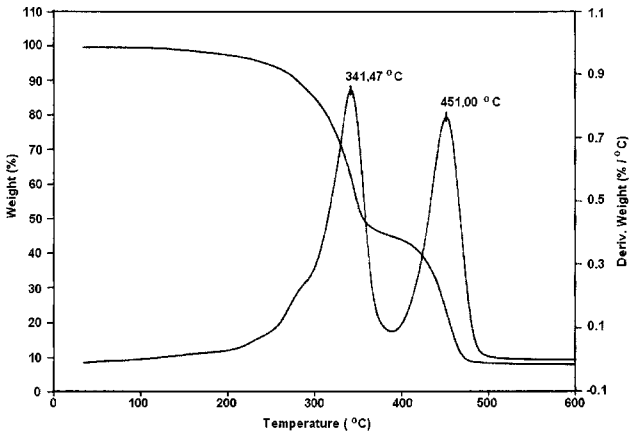

Figure 3 TGA thermogram of the PtBAEMA hydrogel.

The broad band at 3424 cm^{-1} was attributed to associated intermolecular O—H stretching modes for polymeric structures (as shown in the scheme on the spectrum), and the band at 3300 cm^{-1} was assigned to associated N—H stretching for amines. The band at 2974 cm^{-1} was responsible for main-chain asymmetric —CH_2— stretching vibrations. The C=O stretching vibration was located at 1736 cm^{-1}. The characteristic antisymmetric vibration of COO usually appears in the 1550–1610-cm^{-1} region. The band at 1487 cm^{-1} belonged to the C—H deformation mode for symmetric —CH_2— (scissors). Skeletal vibrations that originated from *tert*-butyl groups settled down at 1230 cm^{-1}. This band at the same time was attributed to the C—N stretching mode. Vibrations at 1150 cm^{-1} were responsible for both C—O—C and C—N stretching modes. The band at 720 cm^{-1} was assigned to the O—H deformation (out of plane) and —CH_2— rocking in the main polymer chain. All these bands characterized the PtBAEMA hydrogel well.

Thermal stability studies provide useful information on the selection of materials with the best properties for specific applications. To observe the thermal behavior of the PtBAEMA hydrogels, they were ground into fine pieces, and TGA was performed in an N_2 atmosphere. Figure 3 shows the thermogravimetry (TG) and differential thermogravimetry (DTG) curves for the PtBAEMA hydrogel. It can be interpreted from the TG and DTG data that PtBAEMA shows a two-step mechanism for thermal degradation. The weight loss found in the first major decomposition, which can be observed between 260 and 390°C with a maximum at 341°C, is possibly due to the loss of (*tert*-butylamino)ethyl side chains. The weight loss during the second decomposition stage with a maximum decomposition rate at 451°C corresponds to the total decomposition of the polymer backbone by radical unzipping.

DSC was used to evaluate T_g, at which the polymer starts to present a rubberlike structure. T_g of the PtBAEMA hydrogels was found at 33°C, which is well matched in the literature.[27]

Swelling studies

Crosslinked hydrogels can swell to a considerable extent in many organic solvents and also in water or in a variety of organic or inorganic aqueous solutions. This is particularly important for the charging of a polymer matrix with a drug solution or for biomedical and environmental applications.[26] Hydrogels can be synthesized appropriately to achieve the desired response to a given environmental condition. Parameters such as the polymer composition, degree of crosslinking density, and size and nature of the incorporated drug molecule play important roles in determining the drug release behavior and thus must be considered during the design of swelling-controlled release devices.[28,29] The relationship between the degree of swelling and water content in the initial mixture during PtBAEMA preparation is shown in Figure 4. The degree of swelling for the PtBAEMA hydrogel with a high water content was apparently higher than that for the bulk PtBAEMA hydrogel, which had a higher crosslinking density.

The phase behavior of hydrogels is greatly affected by environmental changes. These external environmental changes could involve the pH, temperature, magnetic field, or ionic strength. The gels may either shrink or swell in response to such environmental changes. The effect of the environmental conditions on a polymer's performance, however, is dependent on the nature of the polymer, which could be ionic or neutral. The swelling-release action in ionic hydrogels is driven by some contributions such as ionic interactions in addition to the thermo-

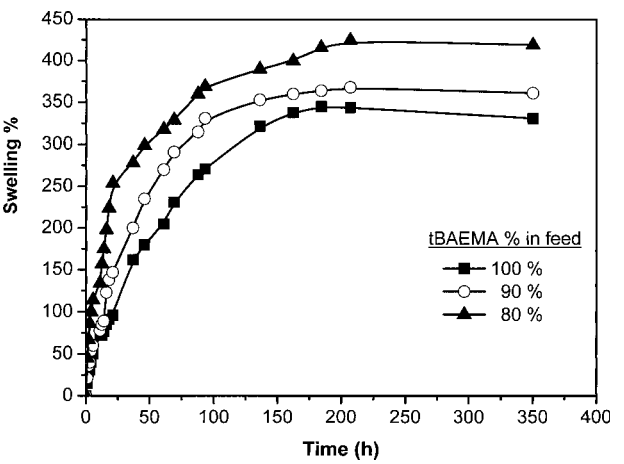

Figure 4 Degree of swelling as a function of the water content for PtBAEMA hydrogels irradiated with a 100-kGy dose.

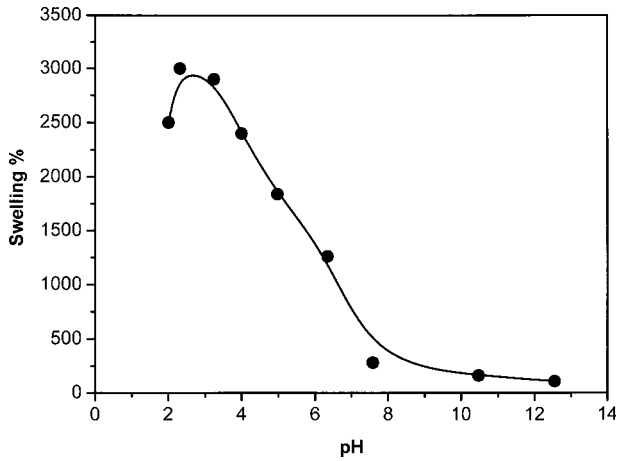

Figure 5 Effect of the pH on the degree of swelling of PtBAEMA hydrogels (ionic strength (I) = 0.02M).

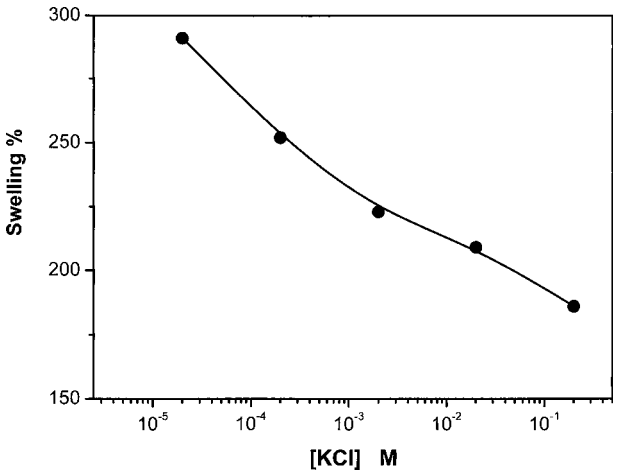

Figure 6 Effect of the ionic strength on the degree of swelling of PtBAEMA hydrogels.

dynamic mixing contribution of the penetrant medium and polymer to the overall free energy, which is coupled with an elastic polymer contribution.[30,31] For most of these polymers, the structural changes are reversible and repeatable upon additional changes in the external environment.

Effect of the pH on swelling

Ionic hydrogels, which could be cationic, containing basic functional groups, or anionic, containing acidic functional groups, have been reported to be very sensitive to changes in the environmental pH.[32,33] To investigate the effect of pH on the swelling degree of PtBAEMA, hydrogels were immersed in phosphate buffer (ionic strength (I) = 0.02M) solutions at different pHs. Figure 5 shows the dependence of the degree of swelling of PtBAEMA on pH. The degree of swelling decreased as the pH values of buffer solutions were increased. This is related to the fact that amine groups of the hydrogel could accept or release protons in response to the changing pH. Consequently, the hydrogels reached a higher degree of swelling at acidic pHs; this resulted from the Coulombic repulsion between newly formed $^{+}NH_2R_2$ groups of the (*tert*-butylamino) side chain.

Effect of the ionic strength on swelling

According to the concept of Donnan equilibrium, an increase in the ionic strength of the swelling agent increases the ionization of a weakly polyelectrolyte system, thus leading to high swelling activity.[30] Anionic gels are normally un-ionized at a pH lower than the gel pK_a, whereas cationic gels display the opposite behavior, and the pH is dependent on pK_b of the gel. For PtBAEMA hydrogels, the dependence of the degree of swelling on the ionic strength is given in Figure 6. The higher the ionic strength was, the lower the degree of swelling was within the concentration range of KCl solutions used in this work. It is well known that the ionic forces depend on the ionic concentration and the proportion of attached ionizable groups in the gels.[34] In a certain buffer medium, when ions in the gels were confronted with ions in the solution, the surrounding solution could hardly penetrate the gels. This was attributed to the difference in osmotic pressures between free ions in the gels and the ions in the outer solution caused by the differences in the ionic strength of the buffers. The osmotic pressures decreased with the increase in the ionic strengths of the media, and this resulted in a decrease in the swelling degrees.

Effect of the temperature on swelling

Changes in the environmental temperature either may enhance the swelling ability of the hydrogel or,

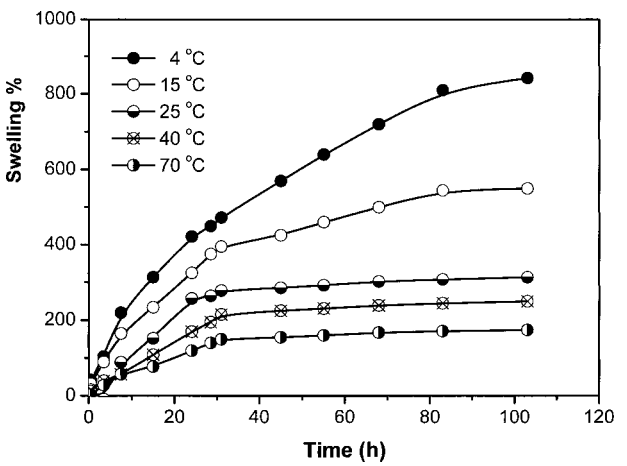

Figure 7 Kinetic swelling curves for the PtBAEMA hydrogel at different temperatures.

TABLE I
Adsorption Values for Each Metal Ion with the PtBAEMA Hydrogel at Different pHs ($[Me^{n+}]_0$ = 1000 ppm, 25°C)

	Adsorption (mg/g)				
	PtBAEMA hydrogel				Distilled water (pH 6.5, nonbuffered system)
Me^{n+} ion	pH 3	pH 4	pH 5	pH 6	
Cu^{2+}	—	22	43	Precipitation	212
Co^{2+}	—	19	26	Precipitation	105
Ni^{2+}	—	17	31	Precipitation	87
Mn^{2+}	—	136	100	Precipitation	548
V^{3+}	32	90	105	Precipitation	283
Cr^{3+}	105	108	123	Precipitation	195

on the contrary, could cause the hydrogel to collapse. The origin of the thermoresponsive behavior lies in the balance of hydrophilicity and hydrophobicity of the hydrogel structure. Gel networks composed of relatively hydrophobic components (e.g., PtBAEMA) shrink at elevated temperatures. These networks are called thermoshrinking networks.[35,36] Thermoshrinking gels undergo reversible swelling and deswelling in response to changes in the environmental temperature. The degree of swelling of the PtBAEMA hydrogels versus time is plotted in Figure 7. The degree of swelling of the PtBAEMA hydrogels decreased with increasing temperature. This occurred because of the coexistence of hydrophilic and hydrophobic groups of PtBAEMA, which had alkyl groups in addition to secondary amine groups.

Adsorption studies

Our first trial with PtBAEMA hydrogels was related to the metal-ion uptake. Our next effort using PtBAEMA hydrogels will be focused on biomedical applications, especially drug delivery and chromatographic separation. Chromatographic separation and purification of biomolecules such as proteins and enzymes require several steps involving methods that select on the basis of the molecular size, electrical charge, hydrophobicity, or biological recognition. One of the most important separation techniques for biomolecules is metal chelate affinity chromatography, which introduces a new possibility for selectively interacting materials on the basis of their affinities for chelated transition-metal ions. The separation is based on differential binding abilities of the proteins or enzymes to interact with chelated metal ions to a solid carrier.[37,38]

In the final part of this work, we introduced some metal ions into the PtBAEMA hydrogels. Chelation of a metal ion by a polymeric ligand is highly dependent on the pH of the medium.[39,40] Because most of the metal ions had a tendency to precipitate at a higher pH, investigations were limited to those pH values at which precipitation was just prevented. The adsorption of metal ions was performed at different pH values with phosphate buffer solutions, and the results are listed in Table I. In highly acidic media (pH 3), no adsorption occurred for most of the ions because of the protonation of the *tert*-butylamino group, which resulted in positively charged pendant groups causing electrostatic repulsion. However, in a weakly acidic solution (pH 4–5), the adsorption of metal ions increased with increasing pH. At even higher pHs, Me^{n+} ions started to precipitate as hydroxides. The highest adsorption values were obtained with distilled water in which no buffer ions probably existed to complex metal ions. Further metal-ion-uptake studies will be carried out with nonbuffered solutions. Each metal ion was more or less adsorbed by the PtBAEMA hydrogels; therefore, we will use all metal ions for chromatographic separations.

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