Synthesis and Characterization of Thermo- and Chemomechanically Responsive Poly(*N*-isopropylacrylamide-*co*-methacrylic acid) Hydrogels

Christopher S. Brazel and Nikolaos A. Peppas*

School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907-1283

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ABSTRACT: Random copolymer hydrogels of methacrylic acid (MAA) and *N*-isopropylacrylamide (NIPAAm) were synthesized by free-radical polymerization in the presence of a cross-linking agent. The gels were characterized for their temperature- and pH-responsive behavior by equilibrium swelling experiments, differential scanning calorimetry, and thermal mechanical analysis. Depending upon composition, the gels showed sharp swelling transitions with small changes in temperature or pH, with initial time-dependent response reaching equilibrium on a time scale of hours.

Introduction

The unique and novel properties of environmentally sensitive polymers have begun to find several applications in new chemical and biological processes. Because these cross-linked polymers exhibit dramatic swelling and collapsing behavior, they have been proposed as devices to facilitate pH-specific membrane separations, promote solvent recovery, improve purification and recovery of pharmaceutical products from solution, serve as temperature-dependent thermal insulation systems, and act as carriers for controlled drug delivery devices. Much research has been done on polymer carriers capable of releasing an active agent at a constant rate over a long period of time (zero-order release).[1] Swelling-controlled release systems have been utilized for responsive release[2] when certain environmental conditions, such as temperature, pH, ionic strength, or glucose level, are changed.

The two polymers studied in this work, poly(*N*-isopropylacrylamide), or PNIPAAm, and poly(methacrylic acid), or PMAA, have characteristic temperature- and pH-sensitivity, respectively. It is important not only that the swelling ratios of these hydrogels change with changes in pH or temperature but that their mesh sizes are reversibly capable of accommodating and preventing solute diffusion. Un-cross-linked PNIPAAm exhibits lower critical solubility temperature (LCST) behavior,[3,4] forming a single phase with water, swelling at low temperatures, and collapsing to form a separate phase above the critical temperature. As the critical temperature of collapse for PNIPAAm is 32 °C, this polymer has potential use for drug delivery to humans as well as in size-selective separation processes involving materials which can be denatured at high temperatures.[5] PNIPAAm has the sharpest swelling transition of the class of thermosensitive alkylacrylamide polymers.[6] This phenomenon has been attributed to a delicate hydrophobic–hydrophilic balance,[7] which changes abruptly across a small temperature range due to a cooperative stabilization. The stable conformations of PNIPAAm in the collapsed and swollen states were shown by Lebedeva et al.[8] using Fourier-transform infrared spectroscopy.

Methacrylic acid polymers exhibit pH-sensitivity, swelling to high degrees in basic solutions and collapsing in acidic solutions. This behavior is due to electrostatic repulsions between the carboxylic acids and ions present in the buffered solution. At high pH values, the pendant carboxylate side chains are repelled by the anions in the solution and expand to minimize charge concentration. Polymers of methacrylic acid have been noted[9–11] to display sharp sensitivity to external pH, with capability of controlling solute permeation due to corresponding changes in swelling behavior. Osada et al.[12] developed a chemomechanical valve from poly(ethylene glycol)-modified PMAA, which was capable of controlling solute penetration with pulses in electric current. Because the heat transfer properties of such swollen and collapsed gels are different, they can act as insulation materials.[13] Finally, such environmentally sensitive hydrogels have been shown to display unique on/off diffusional behavior which responds to changes in physiological conditions.[14–19]

The objective of this work is to determine how random copolymers of temperature- and pH-sensitive moieties would affect the critical swelling transition region and its magnitude and to determine the response time for these hydrogels when exposed to small changes in environmental conditions. A hydrogel which is sensitive to multiple effects, such as temperature and pH, would be able to sense conditions where both phenomena are coupled, such as possibly during the formation of blood clots.[20]

Experimental Section

Hydrogel Synthesis. Free-radical solution polymerization was used to prepare cylindrically shaped cross-linked copolymer samples of NIPAAm and MAA. Prior to the reaction, both monomers were purified of reaction inhibitors; NIPAAm (Eastman Kodak, Rochester, NY) was recrystallized in benzene/hexane, and MAA (Aldrich, Milwaukee, WI) was distilled under vacuum to remove *p*-methoxyphenol. Cross-linked hydrogels were prepared using molar NIPAAm fractions of 0, 0.3, 0.7, 0.8, 0.9, 0.95, and 1.0, with the balance being MAA. In addition, 1 mol % (of total monomers) ethylene glycol dimethacrylate (EGDMA) (Aldrich) was used as a cross-linking agent and 1 wt % 2,2′-azobis(isobutyronitrile) (AIBN) (Aldrich) as the initiator. A 50 vol % solution of the reaction mixture was prepared. Deionized water was used as a solvent for polymerizations with feed monomer composition less than 80 mol % NIPAAm, while a 50/50 mixture of deionized water and methanol was required to dissolve NIPAAm in reactions with NIPAAm feed concentrations of 80 mol % or greater. Nitrogen was bubbled through the monomer/solvent mixture for 5 min to remove oxygen dissolved in the reaction mixture. The

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initiator was added to the mixture, which was then transferred to cylindrical polypropylene vials, sealed and placed in a 50 °C temperature-regulated water bath for 24 h during the reaction.

The resulting hydrogels were recovered and dried at ambient conditions until they were rigid enough to be sliced into thin disks using a diamond-blade rotary saw (Isomet Low Speed Saw, Buehler Ltd., Lake Bluff, IL). Each disk had a thickness of 0.8 mm and a diameter of 14 mm in the dry state. Unreacted monomers, detected in wash solutions by ultraviolet spectrophotometry (Model 559 UV–vis spectrophotometer, Perkin-Elmer, Oak Brook, IL), were extracted from the formed hydrogels until less than 1 ppm monomer was observed in the wash solution. The gel disks were then dried to constant weight at 37 °C in a vacuum oven.

Copolymer Characterization. The compositions of the formed polymers were determined by elemental analysis for nitrogen (Model 240C elemental analyzer, Perkin-Elmer).

Equilibrium and dynamic swelling experiments were performed on the hydrogels to determine the sensitivity of each copolymer to temperature and pH, and to determine the time dependence of the swelling and collapse processes. Equilibrium swelling studies were conducted on the P(NIPAAm-*co*-MAA) hydrogels as functions of environmental pH and temperature. For the temperature swelling studies, gels were swollen in deionized water at various temperatures in the expected range of the LCST phase transition. For the pH-sensitive equilibrium swelling, Sørensen buffer solutions[21] were used to equilibrate the gels at 37 °C and the desired pH. Volume measurements were made by a buoyancy technique[22] and were repeated until each sample had reached equilibrium. Surface water was removed from the gels by blotting with absorbent tissue. All of the hydrogel disks were dried to constant weight under vacuum at 37 °C, the dry volume was measured, and the volume swelling ratio, Q, was calculated as the ratio of the hydrated volume to the dry volume.

Equilibrium swelling, differential scanning calorimetry (DSC), and thermal mechanical analysis (TMA) were used to determine the LCSTs of the hydrogel samples. DSC (Model DSC 2910, TA Instruments, New Castle, DE) experiments were performed on swollen hydrogel specimens of approximately 20 mg by heating them from 15 to 60 °C at 2 °C/min. The onset of the thermogram corresponded to the temperature of collapse.[23] TMA (Model TMA 2940, TA Instruments) experiments were performed on swollen hydrogel pieces of approximately 1 cm diameter and 1.5 cm thickness. The LCST was determined from a sharp drop in sample thickness as the temperature was increased from 15 to 60 °C at 1 °C/min.

In order to determine the response time for the hydrogels upon changes in external temperatures and pH, pulsatile swelling studies using gravimetry were conducted based upon short-time temperature and pH changes. The changes in environmental conditions were small in magnitude but selected so that the critical temperature and pH would be crossed between swelling and shrinking regimes. Prior to swelling pulses, the gels were equilibrated in the swollen state at pH 5.7 and 33 °C for at least 3 days. The weight swelling ratio, q (swollen weight/dry weight), was monitored during shrinking and swelling processes when the P(NIPAAm-*co*-MAA) hydrogel samples were exposed to pH 5.3 and 36 °C for 1 h, and allowed to reswell at the original pH and temperature. The same hydrogel was subjected to the combined temperature and pH change for two pulses, followed by two more pulses, one when the temperature was increased from 33 to 36 °C, without changing the pH, and one at 33 °C where only the pH was changed from 5.7 to 5.3.

Results and Discussion

Copolymer Composition. The copolymer composition is presented in Figure 1 as a function of comonomer feed compositon, as determined by elemental analysis. All of the polymer samples tested were enriched in MAA compared to the comonomer feed composition. From these data, reactivity ratios were calculated using a linearization technique of Peppas and Gehr,[24] which was based upon the technique of Finemann and Ross.[25] The reactivity ratios were determined to be $r_1 = 0.891$ for NIPAAm and $r_2 = 1.128$ for MAA, indicating that MAA is more reactive than NIPAAm. Based on the $Q-e$ scheme values of $Q_1 = 0.98$ and $e_1 = 0.62$ for MAA,[26] the $Q-e$ values of NIPAAm were calculated as $Q_2 = 0.695$ and $e_2 = 0.26$. All data in this work reflect polymer composition as determined by this technique and not the composition of the monomers fed to the reactions.

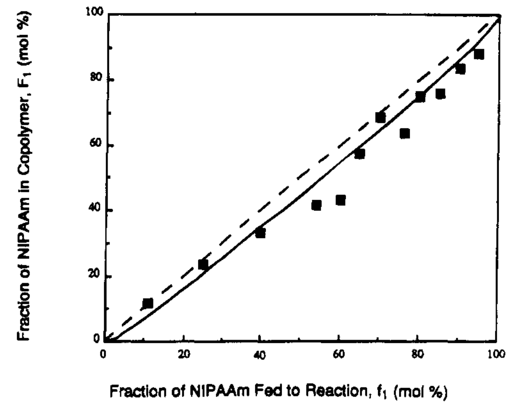

Figure 1. NIPAAm molar fraction in polymer as a function of NIPAAm molar fraction in comonomer feed. The dashed line represents an ideal polymerization, the data points represent compositions of polymers synthesized in this work, and the solid curve is a best fit representing the polymer composition function for NIPAAm/MAA reactions based on reactivity ratios calculated in this work.

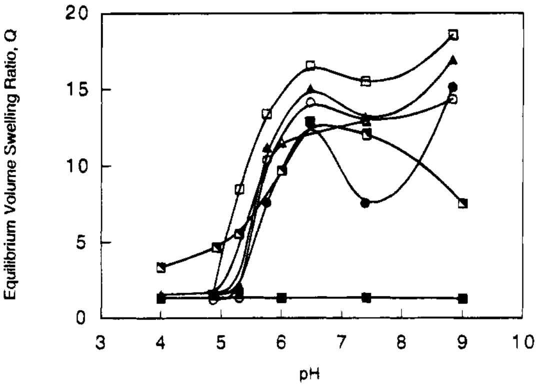

Figure 2. Equilibrium volume swelling ratio of P(NIPAAm-*co*-MAA) hydrogels in buffered solutions at 37 °C as a function of pH. Hydrogels contained 100% NIPAAm (■), 88% NIPAAm (●), 84% NIPAAm (▲), 75% NIPAAm (□), 69% NIPAAm (O), 27% NIPAAm (△), and 0% NIPAAm (◪). All samples were tested in triplicate. Where not shown, error bars are smaller than the data symbols.

Equilibrium Swelling Experiments. Hydrogels were formed with compositions ranging from 0 to 100% NIPAAm, and the effect of copolymer composition on pH- and temperature-sensitivity was determined by equilibrium swelling behavior. In Figure 2, it is shown that all of the hydrogels synthesized in this work demonstrated a sharp swelling transition as a function of pH even with as little as 12 mol % MAA. The equilibrium swelling ratio increased greatly between pH 5.3 and pH 5.7 for all gels except pure homopolymer PNIPAAm, which displayed no sensitivity to pH. Small swelling ratios were observed due to the temperature of the solutions at 37 °C, above the LCST of PNIPAAm. At high pH values, some of the hydrogels containing large fractions of MAA showed a decrease in swelling ratio. This was attributed to a shielding effect, in which

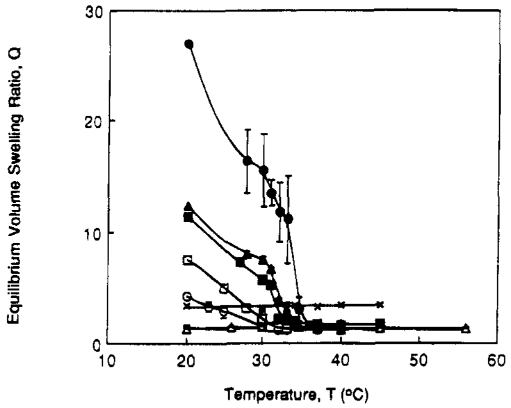

Figure 3. Equilibrium volume swelling ratio of P(NIPAAm-*co*-MAA) hydrogels in deionized water (pH = 6.5) as a function of temperature. Hydrogels contained 100% NIPAAm (■), 88% NIPAAm (●), 84% NIPAAm (▲), 75% NIPAAm (□), 69% NIPAAm (○), 43% NIPAAm (△), 27% NIPAAm (◪), and 0% NIPAAm (×). All samples were tested in triplicate. Where not shown, error bars are smaller than the data symbols.

the high ionic strength of the buffered solution caused fewer acid side groups to become ionized, decreasing the electrostatic repulsion and the swelling ratio.[11]

The temperature-sensitivity of the same copolymer hydrogels is shown in Figure 3. The PMAA hydrogels showed no significant changes in swelling ratio over the temperature range studied but maintained an intermediate level of swelling in water. With increasing amounts of PNIPAAm in the hydrogels, LCST behavior was observed, to a small degree in P(NIPAAm-*co*-MAA) gels containing 69 and 75 mol % NIPAAm and more significantly in gels with more than 75 mol % NIPAAm. The pure PNIPAAm hydrogel displayed a sharp change in swelling behavior at 32 °C, very similar to the hydrogel with 84 mol % NIPAAm. The P(NIPAAm-*co*-MAA) hydrogel with 88 mol % NIPAAm, however, had a significant transition at approximately 34.5 °C. The increase in LCST between the 0 and 12 mol % MAA-containing P(NIPAAm-*co*-MAA) hydrogels was due to the presence of a hydrophilic comonomer MAA, which increased the LCST of PNIPAAm gels by stabilizing the conformation of the macromolecular chains in their solvated state. However, with larger amounts of MAA in the hydrogels, the LCST decreased as noted with samples containing more than 31 mol % MAA, where temperature-sensitivity was not seen over the range of temperatures studied.

The Flory–Rehner theory[27] was used to determine the polymer mesh size from swelling data, by first determining the molecular weight of polymer chains between consecutive crosslinks, $\bar{M}_c$, and then calculating mesh size, ξ, by relating this molecular weight to the appropriate end-to-end distance of the polymer chains. The value of $\bar{M}_c$ was determined by eq 1, as modified by Peppas and Merrill[28] to account for polymer networks formed in the presence of a swelling agent:

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{(\bar{v}/V_1)[\ln(1 - v_{2,s}) + v_{2,s} + \chi_1 {v_{2,s}}^2]}{v_{2,4}\left[\left(\frac{v_{2,s}}{v_{2,r}}\right)^{1/3} - \frac{1}{2}\left(\frac{v_{2,s}}{v_{2,4}}\right)\right]} \quad (1)$$

Here, $\bar{M}_n$ is the number-average molecular weight of the un-cross-linked chains (assumed to be 100 000 for this system), $\bar{v}$ is the specific volume of the dry polymer, determined experimentally, V_1 is the molar volume of water (18 cm^3/mol), $v_{2,s}$ is the polymer fraction in the swollen gel, which is the reciprocal of the volume swelling ratio, and $v_{2,r}$ is the polymer fraction in the relaxed state. Assuming complete reaction and negligible volume change upon reaction, the value of $v_{2,r}$ was equal to the volume fraction of comonomers in the feed, which was 0.5 for all polymers used in this work. The Flory polymer–solvent interaction parameter, χ_1, for PMAA was determined by Mikos and Peppas,[29] whereas that of PNIPAAm was presented by Bae et al.[30] as a function of temperature. In ionic hydrogels such as the ones studied here, the validity of eq 1 is questioned due to the variation of the χ_1 value with degree of ionization. Thus the values of $\bar{M}_c$ determined from this analysis were based on analysis of swelling data in the nonionized state of the MAA moiety of the hydrogel.

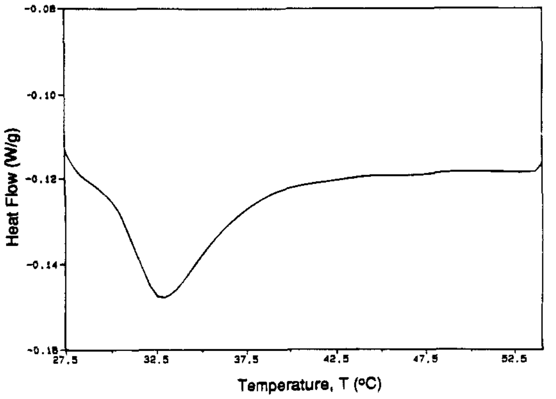

Figure 4. Differential scanning calorimetry thermogram of cross-linked P(NIPAAm), swollen in deionized water, at a temperature ramp rate of 2 °C/min.

The mesh size of a polymer network was then given by Peppas and Barr-Howell:[31]

$$\xi = \alpha r_0 = Q^{1/3}\left[2C_n\left(\frac{\bar{M}_c}{M_r}\right)\right]^{1/2} l \quad (2)$$

where α is the linear elongation ratio, which is equal to the cube root of the volume swelling ratio, r_0 is the unperturbed end-to-end distance of the polymer chains between cross-links, C_n is the characteristic ratio for the polymer (obtained as the molar average of the C_n values of the two homopolymers), and M_r is the effective molecular weight of the repeating unit, which was determined by a weighted average of the two monomer molecular weights, based on the copolymer composition. The l term represents the carbon–carbon bond length of 1.54 Å. Clearly, values of the mesh size determined here were affected by the swelling ratio of the hydrogel studies, as expressed by the term $Q^{1/3}$ of eq 2, where Q is the volume swelling ratio.

Thermal Analysis. LCSTs were also determined by thermal analysis. Figure 4 shows a typical DSC thermogram for an NIPAAm-containing hydrogel. As the phase transition occurred within the gel, the temperature and heat of phase separation could be determined along with the corresponding entropy changes ($\Delta H = T\Delta S$ for $\Delta G = 0$ at phase separation[23]). This value was at approximately 32 °C for PNIPAAm. The thermomechanical analyzer was also capable of discerning the temperature transition of the gel, by sensing significant dimensional changes as the swollen sample collapsed at a specific temperature. The sharp drop in sample thickness shown in Figure 5 occurred at the LCST.

Pulsatile Swelling Experiments. The behavior of 88 mol % NIPAAm-containing P(NIPAAm-*co*-MAA)

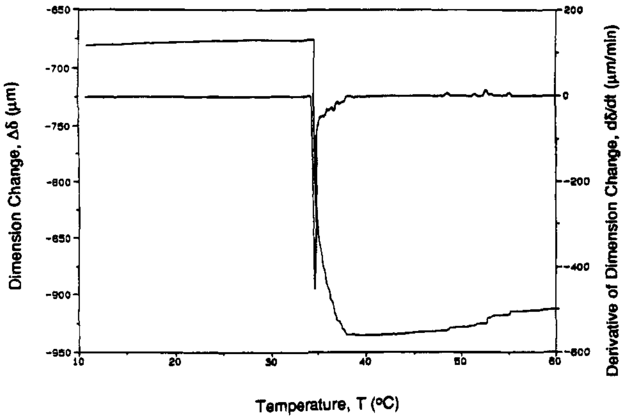

Figure 5. Thermal mechanical analysis of cross-linked P(NIPAAm-*co*-MAA) containing 88 mol % NIPAAm, swollen in deionized water, at a temperature ramp rate of 1 °C/min.

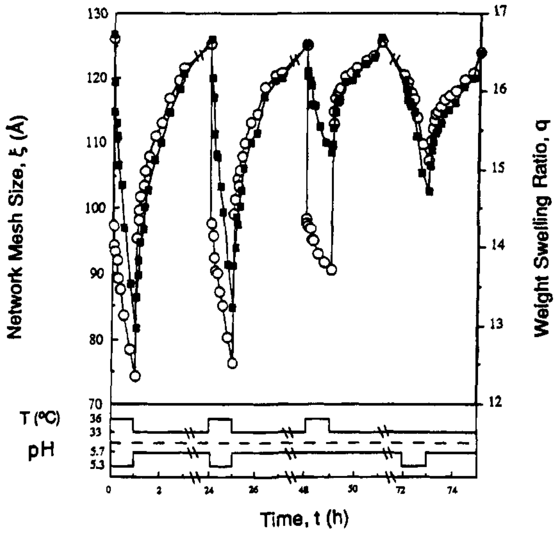

Figure 6. Network mesh size (○) and weight swelling ratio (■) of a cross-linked P(NIPAAm-*co*-MAA) hydrogel sample containing 88% NIPAAm, placed successively in buffered solutions of pH 5.3 at 36 °C and pH 5.7 at 33 °C and equilibrated at pH 5.3 and 36 °C for approximately 1 h and pH 5.7 and 33 °C for several hours. The last two peaks indicate changes in only one of the swelling parameters, temperature or pH. The hydrogel sample was equilibrated at pH 5.3 and 33 °C prior to the experiment.

hydrogels undergoing pulses in temperature and pH environment is shown in Figure 6. The temperature and pH changes were designed to be small but occurred across the critical temperature and pH values as determined from the equilibrium swelling experiments. As a result of decreasing pH and increasing temperature, the networks began to collapse; after 1 h at those conditions, the gels were returned to their original environment. At this point, the hydrogel had not reached an equilibrium state, but the main part of the collapse occurred in the first 30 min.[32] This procedure was repeated once to ensure that the behavior was repeatable. The third and fourth cycles shown in Figure 6 represent the effects of changing only temperature and only pH, respectively. In the first two pulses, the weight swelling ratio responded quickly when the gel was exposed to a temperature increase from 33 to 36 °C and pH change from 5.7 to 5.3. The individual temperature- and pH-change cycles show that the overall effect seen when both factors were changed was produced by a combination of the temperature and pH effects. For this particular P(NIPAAm-*co*-MAA) gel (containing 88 mol % NIPAAm), the temperature and pH effects were nearly equally responsible for the time-dependent swelling behavior.

The mesh size of the network, as determined by eqs 1 and 2, was also followed during these cycles. The mesh size is representative of the space available in the network available for diffusion. In the swollen state, the mesh size was approximately 125 Å, but it dropped rapidly to approximately 80 Å after 1 h of exposure to the higher temperature and lower pH. The change in mesh size was much smaller for changes in only one environmental condition, as seen in the final two pulses in Figure 5. Mesh sizes calculated for the hydrogels in this study ranged from less than 10 to 401 Å depending upon polymer composition and environmental conditions.

Conclusions

The hydrogels synthesized in this work were shown to display both temperature- and pH-sensitivity, with sharp transition regions as functions of environmental conditions and polymer composition. The mesh size of the hydrogels changed greatly between the collapsed and swollen states, and this change would be beneficial in applications such as size-selective permeation or controlled drug delivery.

The polymer composition not only determined the swelling characteristics of the gels due to pH or temperature but also influenced the lower critical solubility temperature (LCST) of the hydrogel. As the MAA content in the hydrogel samples was increased, the LCST increased compared with the PNIPAAm LCST, because the hydrogel was able to maintain its hydrated state at higher temperatures with the addition of the hydrophilic group. However, as the amount of NIPAAm in the hydrogel was decreased to 75% and lower, the LCST dropped below the value for pure PNIPAAm (32 °C) and the sharp transition in swelling behavior disappeared. The properties of these environmentally sensitive materials show promise in a variety of applications, particularly in areas which undergo only minute changes in temperature or pH, triggering the hydrogel to expand or contract to change its diffusional characteristics rapidly.

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References and Notes

(1) Baker, R. W. *Controlled Release of Biologically Active Agents*; John Wiley and Sons: New York, 1987.
(2) Hoffman, A. (*Am. Chem. Soc., Div. Polym. Chem.*) **1991**, *31*, 289.
(3) Heskins, M.; Guillet, J. E. *J. Macromol. Sci., Chem.* **1968**, *A2*, 1441.
(4) Chiklis, C. K.; Grasshoff, J. M. *J. Polym. Sci., Part A-2* **1970**, *8*, 1617.
(5) Frietas, R. F. S.; Cussler, E. L. *Chem. Eng. Sci.* **1987**, *42*, 97.
(6) Ito, S. *Kobunshi Ronbunshu* **1989**, *46*, 437.
(7) Prange, M. M.; Hooper, H. H.; Prausnitz, J. M. *AIChE J.* **1989**, *35*, 803.
(8) Lebedeva, T. L.; Malchugova, O. I.; Valuev, L. I.; Plate, N. A. *J. Polym. Sci.* **1992**, *34*, 794.
(9) Weiss, A. M.; Adler, K. P.; Grodzinsky, A. J.; Yarmush, M. L. *J. Membr. Sci.* **1991**, *58*, 153.
(10) Seno, M.; Len, M. L.; Iwamoto, K. *Colloid Polym. Sci.* **1991**, *269*, 873.
(11) Klier, J.; Scranton, A. B.; Peppas, N. A. *Macromolecules* **1990**, *23*, 4944.
(12) Osada, Y.; Gong, J. P.; Sawahata, K. *J. Macromol. Sci.,Chem.* **1991**, *A28*, 1189.

(13) Chahroudi, D. *Proceedings of the 33rd Annual Technical Conference of the Society of Vacuum Coaters*; Society of Vacuum Coaters: Washington, DC, 1990; p 212.

(14) Kim, Y.-H.; Bae, Y. H.; Kim, S. W. *J. Controlled Release* **1994**, *28*, 143.

(15) Gutowska, A.; Bae, Y. H.; Feijen, J.; Kim, S. W. *J. Controlled Release* **1992**, *22*, 95.

(16) Mukae, K.; Bae, Y. H.; Okano, T.; Kim, S. W. *Polym. J.* **1990**, *22*, 250.

(17) Yoshida, R.; Sakai, K.; Okano, T.; Sakurai, Y. *Ind. Eng. Chem. Res.* **1992**, *31*, 2339.

(18) Yoshida, R.; Sakai, K.; Okano, T.; Sakurai, Y. *J. Biomater. Sci., Polym. Ed.* **1992**, *3*, 243.

(19) Dong, L.-C.; Hoffman, A. S. *J. Controlled Release* **1991**, *15*, 141.

(20) Lewis, A. E.; *Principles of Hematology*; Appleton: New York, 1970; p 36.

(21) The following Sørensen pH-buffered solutions were used: pH = 4.0, citric acid/phosphate, I = 0.289 M; pH = 4.86, citric acid/phosphate, I = 0.070 M; pH = 5.26, phosphate, I = 0.071 M; pH = 5.73, phosphate, I = 0.081 M; pH = 6.0, phosphate, I = 0.081 M; pH = 6.46, phosphate, I = 0.078 M; pH = 7.38, phosphate, I = 0.176 M; pH = 8.83, sodium borate/HCl, I = 0.267 M; and pH = 9.0, sodium borate/HCl, I = 0.267 M.

(22) Peppas, N. A.; Moynihan, H. J.; Lucht, L. M. *J. Biomed. Mater. Res.* **1985**, *19*, 397.

(23) Feil; H.; Bae, Y. H.; Feijen, J.; Kim, S. W. *Macromolecules* **1993**, *26*, 2496.

(24) Peppas, N. A.; Gehr, T. W. *J. Appl. Polym. Sci.* **1979**, *24*, 2159.

(25) Finemann, M.; Ross, S. D., Jr. *J. Polym. Sci.* **1950**, *5*, 259.

(26) Odian, G. *Principles of Polymerization*; Wiley-Interscience: New York, 1993.

(27) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

(28) Peppas, N. A.; Merrill, E. W. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 441.

(29) Mikos, A. G.; Peppas, N. A. *Biomaterials* **1988**, *9*, 419.

(30) Bae, Y. H.; Okano, T.; Kim, S. W. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 923.

(31) Peppas, N. A.; Barr-Howell, B. D. In *Hydrogels in Medicine and Pharmacy*; Peppas, N. A., Ed.; CRC Press, Inc.: Boca Raton, FL, 1987; Vol. 1, pp 27–56.

(32) Brazel, C. S.; Peppas, N. A. In *Biomaterials for Drug and Cell Delivery*; Mikos, A. G., Murphy, R. M., Bernstein, H., Peppas, N. A., Eds.; Materials Research Society: Pittsburgh, PA, 1994; pp 211–216.

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