

Kinetics and Thermodynamics of the Water Sorption of 2-Hydroxyethyl Methacrylate/Styrene Copolymer Hydrogels

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ABSTRACT: A series of polymer hydrogels based on 2-hydroxyethyl methacrylate and styrene were synthesized by bulk polymerization. The kinetic and thermodynamic swelling properties of these hydrogels were studied. The swelling mechanism of the hydrogels followed Fickian behavior. The diffusion coefficients, initial swelling rate, and maximum water uptake all decreased with the styrene content increasing because of the hydrophobicity of styrene. The swelling process was exothermic from 278 to 315 K, and the greater the styrene content was, the lower the enthalpy of mixing was in magnitude. The poly-

mer-water interaction parameter, reflecting thermodynamic interactions, increased with increasing styrene content in the polymers. The negative values and trend of the actual partial molar enthalpy and entropy of dilution could be explained by the structuring of water through enhanced hydrogen bonding and hydrophobic interactions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3018–3023, 2008

Key words: hydrogels; swelling; kinetics; thermodynamics

INTRODUCTION

Hydrogels are polymers in a three-dimensional network arrangement that can absorb and retain water. In the polymer network, hydrophilic groups or domains are present that are hydrated in an aqueous environment, thereby creating the hydrogel structure.¹ Within the wide range of polymer hydrogels, linear and crosslinked homopolymers and copolymers based on 2-hydroxyethyl methacrylate (HEMA) are some of the most studied systems because of their widespread applications in many fields such as drug delivery systems, artificial muscles, and contact or intraocular lenses. HEMA can be polymerized to obtain a hard and glassy material by bulk polymerization, but when swollen in water, it turns into a soft and flexible rubber,² the mechanical strength of which is higher than that of hydrogels prepared through solution polymerization.³ In addition, other modifications have been performed to improve the mechanical properties of HEMA hydrogels. For example, HEMA-based hydrogels have been strengthened by copolymerization with hydrophobic monomers⁴ or with rigid cyclic monomers,^{5,6} the introduction of interpenetrating networks,^{7–9} and fiber or nanoparticle reinforcement.^{2,10} Hydrogels based on HEMA copolymerized with styrene (St), methyl methacrylate, *N*-vinyl-2-

pyrrolidone, 4-*t*-butyl-2-hydroxycyclohexyl methacrylate, *cis*-1,2-bis(2,3-epoxybutanoyloxy)-3,5-cyclohexadine, *n*-butyl methacrylate, cyclohexyl methacrylate, triethylene glycol dimethacrylate, and poly(ethylene glycol) methacrylate have been prepared and studied.^{4–6,11–14} Recently, we introduced a macromonomer epoxy methacrylate (EMA) with a rigid bisphenol A structure for copolymerization with HEMA, obtaining HEMA/EMA copolymer hydrogels with high strength.^{15–17}

As a hydrophobic monomer with a rigid phenyl ring, St has been used for copolymerization with hydrophilic HEMA to prepare hydrogels of high strength.^{4,18} As for the copolymerization of HEMA and St, some studies have been carried out. Schnoobrood et al.¹⁹ investigated the free-radical copolymerization of HEMA with St in bulk and in emulsion, determining the monomer reactivity ratios of HEMA and St, which were 0.49 and 0.27, respectively, in bulk copolymerization. The free-radical copolymerizations of HEMA with St in *N,N'*-dimethylformamide (DMF) solution and in toluene were also researched, and the reactivity ratios for HEMA and St were 0.54 and 0.45 in DMF and 1.65 and 0.50 in toluene, respectively.²⁰ Manuel et al.²¹ also researched the free-radical copolymerization of HEMA with St in a DMF solution, determining the monomer reactivity ratios of HEMA and St to be 0.527 and 0.411, respectively, in that system. However, all these studies were focused only on the copolymerization dynamics between HEMA and St and not aimed at their copolymer hydrogels. Previ-

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ously, we synthesized HEMA/St copolymer hydrogels by bulk copolymerization, studying their swelling and tensile properties and network parameters.¹⁸ As for HEMA/St copolymer hydrogels, studies on the swelling kinetics and thermodynamics have never been published. In this article, we focus on the swelling kinetics and thermodynamics of HEMA/St copolymer hydrogels, exploring the relationship between the swelling properties and copolymer structures.

EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate (HEMA) was supplied by the Tianjin Research Institute of Chemical Reagents (Tianjin, China); St was supplied by Tianjin Chemical Reagents First Plant (Tianjin, China). Benzoyl peroxide (BPO) and *N,N*-dimethylaniline (DMA) were used as an oxidizer and reducer, respectively, and were obtained from Beijing Chemical Reagents Co. (Beijing, China). All materials were used as received without further purification.

Preparation of the polymers

Mixtures of HEMA and St were made gravimetrically, 0.10 wt % BPO with respect to the monomers was added, nitrogen was bubbled for 20 min, and then the same amount of DMA as BPO was added. The solution was poured into a 2-mm-deep Teflon mold and sealed immediately. The whole process was carried out in the protection of an N₂ atmosphere. Then, the mold was placed in an oven at 30°C for 12 h. The xerogels were obtained after being removed from the molds. The weight ratios of HEMA to St were adjusted to 100/0, 90/10, 80/20, 70/30, and 60/40; these samples were named PHEMA, HEMA90/St10, HEMA80/St20, HEMA70/St30, and HEMA60/St40, respectively.

Because bulk polymerization was adopted in this research, the entanglements between polymer chains were enough to act as crosslinks and maintain the gel shapes, so no crosslinkers were used in the synthesis.

Swelling behaviors

Sheet samples (ca. 1.0 cm × 1.0 cm) were cut from each xerogel and then were swollen in deionized water for about 2 weeks, with daily water exchanges, and this allowed swelling to equilibrium. Sheet hydrogel samples were dried *in vacuo* at 80°C for about 24 h to obtain extracted xerogels, which were weighed (m_d). Here the mass ratio of the extracted xerogel to the original xerogel could yield

the gel fraction, which indirectly reflected the copolymerization yield. In this study, gel fractions of all samples were over 98 wt %, reflecting the higher yield ratio of copolymerization between HEMA and St.

To study the swelling kinetics of the xerogels, each extracted sheet xerogel was immersed in deionized water at 30°C. At given times, the sheets were removed from water, blotted with filter paper to eliminate excess water, and weighed (m_t). The water uptake (S) was calculated with eq. (1). When time is infinite, swelling will reach equilibrium, and the equilibrium water uptake is denoted as S_{eq} :

$$S = \frac{m_t - m_d}{m_d} \quad (1)$$

For the swelling thermodynamic studies of the hydrogels, swollen sheet hydrogels were immersed in deionized water at different temperatures and kept there long enough to reach swelling equilibrium. In this state, the volume fraction of the polymer in the hydrogel (ϕ_2) at different temperatures was calculated as follows:

$$\phi_2 = \frac{m_d/\rho_d}{m_d/\rho_d + (m_e - m_d)/\rho_{H_2O}} \quad (2)$$

where m_e is the mass of sheet hydrogels swollen at equilibrium and ρ_d and ρ_{H_2O} are the densities of the xerogels and water, respectively.

RESULTS AND DISCUSSION

Swelling kinetics

For the series of hydrogels with various HEMA/St ratios, the influence of the St content on S at a special time was studied at 30°C. As shown in Figure 1,

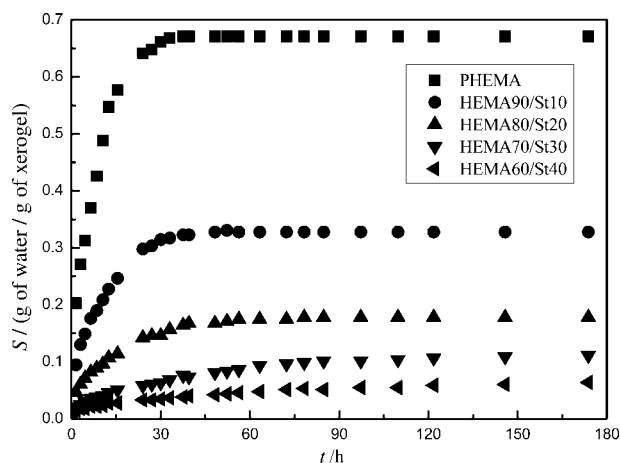


Figure 1 Relationship between S and time t for polymer gels with different St contents.

TABLE I
Values of k , n , D , r_0 , and S_∞ for Polymer Hydrogels

Sample	k	n	D (10^{-3} mm ² /h)	r_0 (h ⁻¹)	S_∞ (g of water/g of xerogel)
PHEMA	0.254	0.420	31.626	0.2386	0.690
HEMA90/St10	0.250	0.400	8.335	0.0847	0.341
HEMA80/St20	0.227	0.384	8.265	0.0264	0.189
HEMA70/St30	0.151	0.392	3.672	0.0060	0.123
HEMA60/St40	0.140	0.379	3.530	0.0032	0.072

with an increase in the hydrophobic St content in the copolymer, S of the hydrogels decreased, and the time to reach equilibrium became longer. For example, it took only about 35 h to reach swelling equilibrium for PHEMA but over 100 h for HEMA60/St40. This phenomenon resulted from the reduction of the HEMA/St copolymer hydrophilicity with the St content, and so the swelling rate became slow. The swelling kinetics of the xerogels and water diffusion within them are studied in detail.

Initial swelling

During the initial stage of swelling, water molecules invade the xerogel surface and diffuse inside; one of two kinds of dynamic swelling mechanisms arises: one is Fickian diffusion, and the other is non-Fickian diffusion. For $S/S_{eq} \leq 60\%$, S/S_{eq} is as the exponential function of time (F)^{22,23}:

$$F = \frac{S}{S_{eq}} = kt^n \quad (3)$$

where S and S_{eq} are the water uptakes at time t and equilibrium, k is a constant related to the structure of the network, and n is a number indicative of the type of diffusion. $n = 0.5$ corresponds to Fickian diffusion, meaning that the rate of water penetration is operative, whereas $0.5 < n \leq 1.0$ indicates non-Fickian diffusion, meaning that the polymer chain relaxation rate is comparable to or much less than the penetrant velocity.²⁴

According to eq. (3), plots of $\ln F$ against $\ln t$ yield straight lines, and the values of k and n can be calculated from the intercepts and slopes of the lines. Based on such lines (not illustrated), the values of k and n were obtained and are listed in Table I. They both generally decreased with an increase in the St content because of the hydrophobicity of St. For the researched samples, the PHEMA homopolymer had the highest k and n values (shown in Table I), which indicated the most relaxed polymer network and the quickest water sorption among the samples, whereas the more St was introduced into the copolymer, the more compact and more hydrophobic the copolymer

networks became, and this reduced the k and n values.

As for n values, cases of n close to 0.5 or over 0.5 have appeared in most published reports about hydrogel swelling, and fewer articles have reported the case of $n < 0.5$.^{25–28} In fact, Fickian diffusion is indicative of the water penetration rate in the gels being less than the polymer chain relaxation rate, and $n = 0.5$ means a perfect Fickian process.²⁴ However, when the water penetration rate is much less than the polymer chain relaxation rate, it is possible for n to be lower than 0.5. In a report²⁵ about hydrogels including St, n reached a value as low as 0.18, and this case was still regarded as Fickian diffusion; it was called less Fickian behavior. For the hydrogels studied in this article, the values of n in Table I are all lower than 0.5, being similar to some of poly(acrylamide-*co*-styrene)/poly(vinyl alcohol) interpenetrating network hydrogels studied by Bajpai et al.²⁵ With the St content increasing in gels, the mobility of the polymer chains decreased; at the same time, the affinity between the water molecules and polymer became much less, and this resulted in a slow rate of water molecule diffusion into the gel; therefore, n values decreased. According to the aforementioned report,²⁵ the swelling of PHEMA and HEMA/St polymers could be considered to follow Fickian behavior or specifically less Fickian behavior.

Then, the diffusion coefficient of water molecules in hydrogels (D) can also be discussed; it can be determined by many methods, one of which is the short-time approximation method, which is mostly in common use. This method is used only for the first 60% of the swelling, during which period the thickness of the polymers basically remains constant. D can be calculated as follows²⁹:

$$F = \frac{S}{S_{eq}} = \frac{4}{d} \sqrt{\frac{Dt}{\pi}} \quad (4)$$

where d is the thickness of the xerogel.

On the basis of the linear relationship between F and $t^{1/2}$, the values of D were calculated from the slopes of these lines, and they are also listed in Table I. The greater the St content was in the polymer, the less hydrophilic the polymer became, and the larger

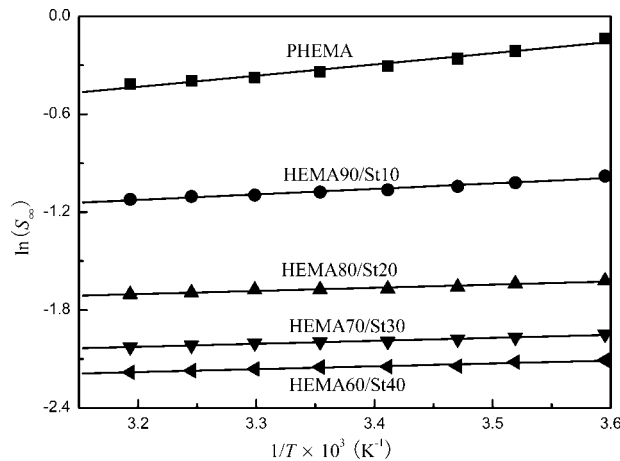


Figure 2 Temperature (T) dependence of S_{eq} for various polymers.

the resistance was that water molecules encountered; this led to the reduction of the D values.

Extensive swelling

For extensive swelling of hydrogels, the swelling rate of hydrogels often obeys second-order kinetics, and the swelling rate can be described as follows³⁰:

$$\frac{dS}{dt} = k_S(S_\infty - S)^2 \quad (5)$$

where S_∞ is the maximum water uptake and k_S is the kinetic rate constant of swelling. After definite integration by the application of the initial conditions $S = 0$ at $t = 0$ and $S = S$ at $t = t$, eq. (5) becomes eq. (6):

$$\frac{t}{S} = A + Bt \quad (6)$$

where $A = 1/k_S S_\infty^2 = 1/(dS/dt)_0$ is the reciprocal of the initial swelling rate of the hydrogel and $B = 1/S_\infty$ is the inverse of the maximum water uptake.

With the plots of t/S versus t , the values of the initial swelling rate [$r_0 = (dS/dt)_0$] and S_∞ of the hydrogels were calculated from the slopes and intercepts of these lines, and they are also listed in Table I. The values of both r_0 and S_∞ decreased gradually as the hydrophobic St content in the HEMA/St copolymer increased. As shown in Table I, for PHEMA, r_0 was 0.2386 h^{-1} , 2 orders of magnitude higher than that of HEMA60/St40. The S_∞ value of PHEMA was 0.690, but this value decreased by about half for HEMA90/St10 and was even reduced to 1/10 for HEMA60/St40. This occurred because the strong hydrophobicity of St resulted in a significant decrease in the water sorption capacity of the copolymer hydrogels.

Swelling Thermodynamics

Mixing enthalpy

A change in temperature will affect S of hydrogels, and the logarithm of S_{eq} is linear with the reciprocal of the swelling temperature according to the Gibbs-Helmholtz equation³¹:

$$\frac{d \ln(S_{eq})}{d(1/T)} = -\frac{\Delta H_m}{R} \quad (7)$$

where S_{eq} is the equilibrium water uptake at temperature T , ΔH_m is the mixing enthalpy between the polymer and water, and R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$). As shown in Figure 2, the S_{eq} values decreased with the temperature increasing, and the data points are fitted well to the straight lines. ΔH_m of every sample was obtained according to the slopes of the lines (Table II). The negative value of ΔH_m indicates that the swelling process of the polymers was exothermic in the range of 278–315 K. The values of ΔH_m were dependent on the polymer composition; that is, the absolute value of ΔH_m decreased with the St content increasing because of its hydrophobicity.

Polymer–water interaction parameter (χ)

In hydrogels, thermodynamic interaction is reflected by χ , which indicates the change in the interaction energy when the polymer and solvent are mixed together. In polymer–water systems, the higher the value of χ is, the weaker the interaction is between the polymer and water, and the stronger the interaction is between the hydrophobic groups or between the polymer chains. According to the literature,³² the value of χ can be calculated as follows:

$$\chi = -\frac{\ln(1 - \phi_2) + \phi_2 + v_e V_1 (\phi_2^{1/3} - 2\phi_2 f^{-1})}{\phi_2^2} \quad (8)$$

where v_e is the effective crosslink density in the hydrogel; V_1 is the molar volume of water ($18.00 \text{ cm}^3/\text{mol}$); and f is the functionality of the crosslinker, which equals 2 because no additional crosslinker was used in this study.

TABLE II
Values of ΔH_m for Various Polymers

Sample	ΔH_m (kJ/mol)
PHEMA	-5.72
HEMA90/St10	-2.81
HEMA80/St20	-1.61
HEMA70/St30	-1.52
HEMA60/St40	-1.47

The values of ϕ_2 for hydrogels at different temperatures were calculated according to eq. (2). With the temperature increasing, ϕ_2 values also increased (not shown in the text). Because of the hydrophobicity of St, the greater the St content was in the hydrogel, the larger the ϕ_2 value was, and the less the extent of the increase was with the temperature.

v_e is another parameter necessary for calculating the value of χ . The values of v_e could be considered constant over the temperature range because of the small increase in ϕ_2 with T .³³ The v_e values were published in our previous article,¹⁸ and they were found to be 0.23, 0.55, 16.26, 27.75, and 30.95 mmol/cm³ for PHEMA, HEMA90/St10, HEMA80/St20, HEMA70/St30, and HEMA60/St40, respectively. With the values of ϕ_2 and v_e , χ values were obtained according to eq. (8), and they are shown in Figure 3. The values of χ rose with the temperature, and the greater the St content was, the larger the χ value was. The relationship between χ and T (K) could be fitted well to polynomials of the second degree^{32,33} [eq. (9)]. The plots and coefficients are shown in Figure 3 and Table III, respectively:

$$\chi = a_0 + a_1T + a_2T^2 \quad (9)$$

The total interaction parameter χ is composed of enthalpic (χ_H) and entropic (χ_S) contributions,^{32,34} which can be obtained with the following equations.

$$\chi_H = -T(d\chi/dT) = -T(a_1 + 2a_2T) \quad (10)$$

$$\chi_S = \chi + T(d\chi/dT) = \chi + T(a_1 + 2a_2T) \quad (11)$$

According to the values of χ_H and χ_S at various temperatures, the actual partial molar enthalpy of dilution ($\Delta\bar{H}_1$) and partial molar entropy of dilution ($\Delta\bar{S}_1$) at different temperatures can be obtained with eqs. (12) and (13)³²⁻³⁴:

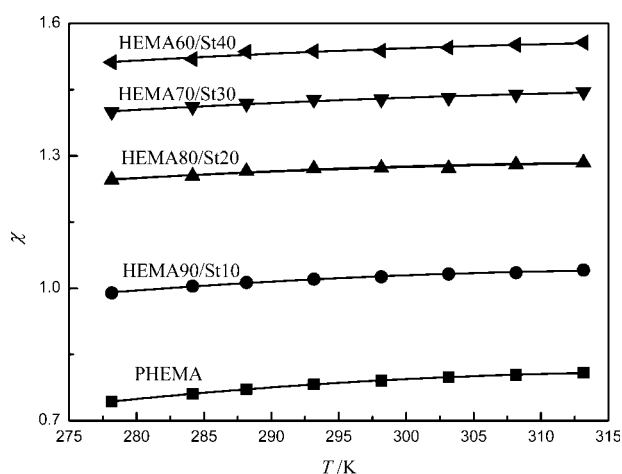


Figure 3 Variations of χ with the temperature (T) for hydrogels.

TABLE III
Coefficients in the Polynomial of χ as a Function of Temperature for Hydrogels

Sample	a_0	$a_1 \times 10^2$ (K ⁻¹)	$a_2 \times 10^5$ (K ⁻²)
PHEMA	-2.96	2.35	-3.66
HEMA90/St10	-1.85	1.81	-2.82
HEMA80/St20	-1.08	1.48	-2.32
HEMA70/St30	-0.30	1.05	-1.57
HEMA60/St40	0.27	0.73	-1.01

$$\Delta\bar{H}_1 = RT\phi_2^2\chi_H \quad (12)$$

$$\Delta\bar{S}_1 = R\phi_2(0.5 - \chi_S) \quad (13)$$

With PHEMA and HEMA60/St40 as examples, the values of $\Delta\bar{H}_1$ and $\Delta\bar{S}_1$ were calculated, and they are illustrated in Figure 4. The values were negative, and their absolute values increased with the temperature. It has been reported³⁵ that the decrease in entropy, that is, $\Delta\bar{S}_1 < 0$, might be ascribable to the structuring of water, which is known to become more pronounced upon the solvation of hydrophobic groups, resulting in hydrogen bonding and hydrophobic interaction enhancement. At the same time, the increase in water structuring resulted in reduced enthalpy, that is, $\Delta\bar{H}_1 < 0$, via enhanced hydrogen bonding.³⁴ For PHEMA and HEMA60/St40, the absolute values of $\Delta\bar{H}_1$ and $\Delta\bar{S}_1$ increased with temperature, and this meant that the fraction of structured water increased with decreasing total water content at elevated temperatures. This phenomenon was more obvious for PHEMA than for HEMA60/St40 because of the greater hydrophilicity of PHEMA.

CONCLUSIONS

Five polymers based on HEMA and St were synthesized by bulk polymerization and swollen in water

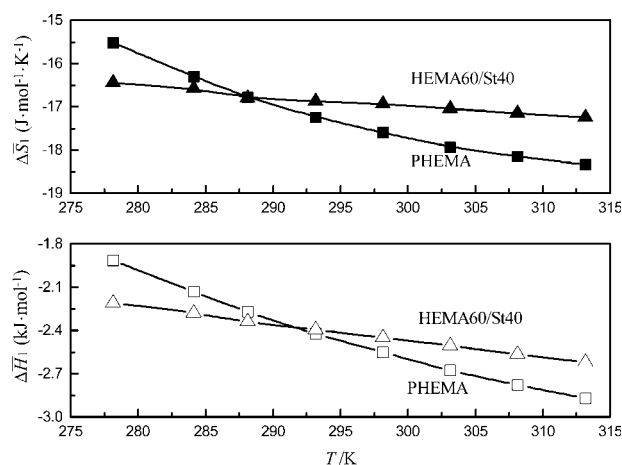


Figure 4 Values of $\Delta\bar{H}_1$ and $\Delta\bar{S}_1$ versus the temperature (T) for PHEMA and HEMA60/St40 hydrogels.

to obtain hydrogels. The swelling properties of these hydrogels were studied.

The initial swelling of the synthesized hydrogels followed Fickian behavior or specifically less Fickian behavior. Because of the hydrophobicity of St, D , r_0 , and S_∞ were all reduced with the St content increasing.

For the synthesized polymer hydrogels, the increase in temperature led to the reduction of S_{eq} in the range of 278–315 K, and this showed that their swelling process was exothermic in this temperature range. The greater the St content was, the lower ΔH_m was in magnitude.

The value of χ reflected the thermodynamic interaction between the polymers and water. The greater the St content was in the polymers, the larger the χ value was. $\Delta \bar{H}_1$ and $\Delta \bar{S}_1$ were determined. They were both negative, and their absolute values increased with the temperature; this meant that there was structuring of water in the researched hydrogels via improved hydrogen bonding and hydrophobic interactions, and the fraction of structured water increased with decreasing total water content at elevated temperatures. Furthermore, this phenomenon was more obvious for PHEMA than for HEMA60/St40 because of the greater hydrophilicity of PHEMA.

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