

Water Vapor Sorption of Stereoregular Poly(2-Hydroxyethyl Methacrylate) and Poly(2,3-Dihydroxypropyl Methacrylate)

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Abstract: Hydrophilic three-dimensional methacrylate polymer networks(hydrogels) were prepared from 2-hydroxyethyl methacrylate and 2,3-dihydroxypropyl methacrylate. Highly isotactic poly(2-hydroxyethyl methacrylate) and highly syndiotactic poly(2-hydroxyethyl methacrylate) were also studied. The sorption of water vapor in the different tactic polymers was measured as a function of water activity. The results were interpreted in terms of Anderson's modified B.E.T. theory and the Hailwood-Horrobin theory of sorption. The former fitting to the experimental isotherms is up to 0.7 equilibrium relative humidity, while the solution theory of Hailwood-Horrobin gives a somewhat better fit to most of the experimental isotherms over the entire range of equilibrium relative humidity. Water vapor sorption by the methacrylate polymers is affected by tacticity and the number of hydrophilic sites in molecules. The amount of water vapor sorbed by isotactic poly(2-hydroxyethyl methacrylate) was found to be greater than that by syndiotactic poly(2-hydroxyethyl methacrylate). Theoretical water sorption models and analysis of the data suggest that isotactic poly(2-hydroxyethyl methacrylate) exists in a surface configuration and structure which provides a larger number of water binding sites in the syndio- or hetero-tactic polymers. Poly(dihydroxypropyl methacrylate) water sorption data and analysis is consistent with its higher hydrophilicity due to the presence of 2-hydroxyl group per repeat unit. These data are also consistent with thermal analysis studies of bound water in fully hydrated systems.

INTRODUCTION

Some crosslinked hydrophilic polymers have been considered as biomaterials for medical

uses^{1,2}. Many of the useful properties of these polymers seem related to their sorption and swelling capacity for water. These polymers become soft hydrogels by the sorption of liquid

water. Synthetic hydrogels have been extensively discussed in the literature².

Sorption of water vapor by polymers has been studied by several methods. Dole and Faller³ reported systematic studies on the water sorption of synthetic linear polymers over a wide vapor pressure range. McLaren et al.⁴ investigated the sorption of water by proteins and polymers. Puffr et al.⁵ studied the mechanism of water sorption in polyamides. They proposed a model that amide groups and carbonyl groups in the regions accessible to water are the sorption centers.

The sorption of water at high relative vapor pressure is not so well understood. Bull and Breese⁶ have suggested that the amount of water bound at high humidity depends on the number of hydrophilic groups present in the protein. Infrared absorption studies of the hydration water in collagen⁷ and globular protein^{8,9} indicates that the peptide bonds are possible sites for water sorption, particularly at high relative vapor pressures. Some other studies have been reported for the effects of chemical modification of specific side chain groups on water uptake by the fibrous protein keratin¹⁰⁻¹², collagen¹³, and silk fibroin¹³.

Recently, Khaw et al.¹⁴ investigated the thermodynamics of water sorption in radiation-grafted hydrogels. Svetlik and Pouchly¹⁵ have studied the sorption isotherms in hydrophilic polymers. They discussed the isotherms from the viewpoints of the Zimm clustering function and Flory-Huggins interaction parameters.

The work presented in this paper is concerned with the study of water vapor sorption in hydrophilic stereoregular poly(2-hydroxyethyl methacrylate) systems, as a function of tacticity and crosslinkers, and in hydrophilic poly(2,3-dihydroxypropyl methacrylate). Some interaction parameters and bonding constants

have been evaluated on the basis of experimental isotherm data and discussed in terms of the modified B.E.T. theory¹⁶ and the Hailwood-Horrobin theory¹⁷.

EXPERIMENTAL

Preparation of Samples

2-Hydroxyethyl methacrylate(HEMA) monomer was supplied by Hydro-Med Sciences, Inc., New Brunswick, New Jersey. The crosslinkers used were ethylene glycol dimethacrylate(EGDMA), tetraethylene glycol dimethacrylate(TEGDMA), and hexamethylene diisocyanate(HMDIC), purchased from Monomer-Polymer Laboratories, Philadelphia, Pennsylvania. Highly isotactic and syndiotactic poly(HEMA) were synthesized by free radical polymerization as previously described¹⁸. The tacticity of the synthesized polymers were measured by ¹³C-NMR¹⁹. Poly(2,3-dihydroxypropyl methacrylate) was prepared from hydrolyzed glyceryl methacrylate using benzoyl peroxide as initiator.

The samples used for the experiments were:

- 1) 40% heterotactic and 60% syndiotactic poly(HEMA);
- 2) Poly(HEMA) containing 1 mole % EGDMA crosslinker;
- 3) Poly(HEMA) containing 1 mole % TEGDMA crosslinker;
- 4) Poly(HEMA) containing 1 mole % HMDIC crosslinker;
- 5) 80% isotactic, 14% heterotactic and 6% syndiotactic poly(HEMA);
- 6) Poly(2,3-dihydroxypropyl methacrylate), abbreviated poly(DHPMA).

Samples 1, 2, and 3 were prepared by polymerization between plane parallel glass plates. The polymerization was initiated with azobis(methyl isobutyrate) at 60°C. Samples 4, 5,

and 6 were prepared by solvent casting from a methanol solution. The size of film samples was in 10mm width, 10mm length, and 1mm thickness. The polymers were extracted for seven days with distilled water at room temperature. The conductivity of distilled water used in this study was less than $1.14 \times 10^{-10} / \Omega \text{cm}$. The samples were dried to constant weight in a vacuum desiccator before measuring the water vapor sorption.

Apparatus and Measurements

Sorption isotherms were measured with a gravimetric sorption apparatus using a Cahn RM-2 electrobalance, recording thermistor, X-Y recorder and humidity meter. The sorption chamber was of height 14cm \times width 11cm \times length 27cm. The inside of the sorption chamber was coated with Teflon and was completely isolated from the outside. Standard drying of samples in the chamber was carried out for 48 hours under phosphorous pentoxide as a drying agent. All instruments used were recalibrated for each run.

The graded series of humidities used were obtained by equilibrating the chamber atmosphere with the following pure saturated aqueous salt solutions²⁰: LiCl (12.4%), MgCl₂·6H₂O (31.8%), K₂CO₃·2H₂O (43%), NaNO₂ (61.3%), NaCl (74.4%), ZnSO₄·7H₂O (90.0%) and K₂SO₄ (96.2%). The figures in parentheses refer to the percent relative humidity established over each solution at $25 \pm 1^\circ \text{C}$. All humidities were rechecked with a calibrated humidity meter. The system was considered to be in equilibrium after humidity readings had stabilized and had remained constant for two consecutive days. Desorption measurements were carried out at the same conditions. All measurements were carried out at $25 \pm 1^\circ \text{C}$.

RESULTS and DISCUSSION

Figures 1, 2, 3 and 4 show the water sorption isotherms as a function of water activity for the systems of 40% heterotactic and 60% syndiotactic poly(HEMA); 1 mole % EGDMA-poly(HEMA); 1 mole % TEGDMA-poly(HEMA); 1 mole % HMDIC-poly(HEMA), respectively. In Figures 1 to 4, N and a represent moles of sorbed water per mole of monomer unit and the activity of water (equilibrium relative humidity), respectively. The sorption of water vapor in the low water activity region (0-0.5) is almost the same in each of the three systems, but are different in the high water activity region (0.5-1.0). Figure 5 shows the sorption isotherm of water vapor as a function of water activity for the system of 80% isotactic, 14% heterotactic and 6% syndiotactic poly(HEMA). Figure 6 shows the sorption isotherm of water vapor as a function

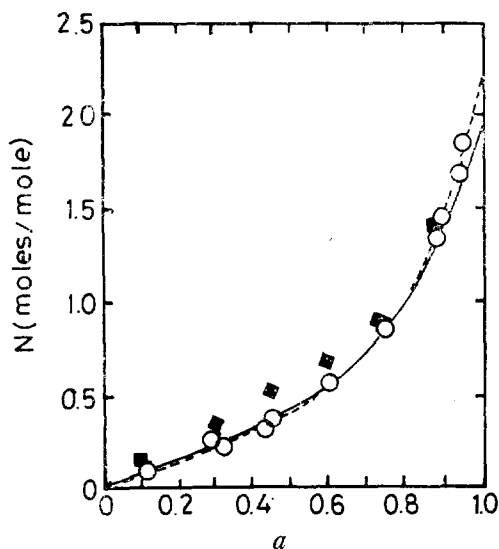


Fig. 1. Sorption Isotherms for Water Vapor in a Sample of 60% Syndiotactic and 40% Heterotactic p(HEMA) at 25°C . a = Activity of Water, N = Amount of Water Sorbed/Monomer Unit of Polymer (Mole/Mole). \circ = Sorption; \blacksquare = Desorption; - - - Modified B.E.T. Theory; Hailwood-Horrobin Theory.

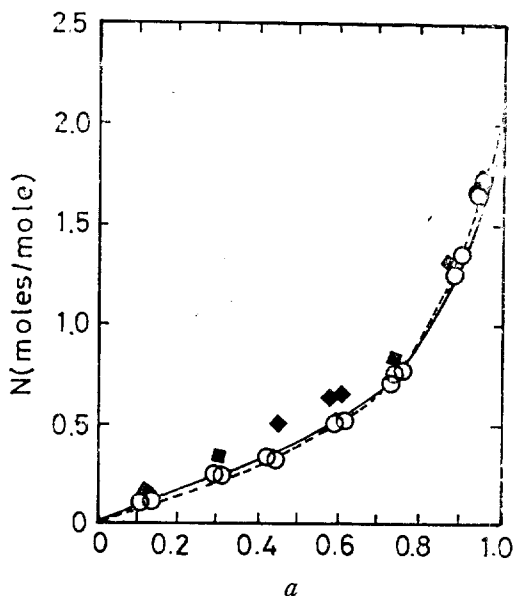


Fig. 2. Sorption Isotherms for Water Vapor in a Sample of 1 mole % EGDMA-p(HEMA) at 25°C. a =Activity of Water, N =Amount of Water Sorbed/Monomer Unit of Polymer(Mole/Mole). \circ =Sorption; \blacksquare =Desorption; — Modified B.E.T. Theory;Hailwood-Horrobin Theory.

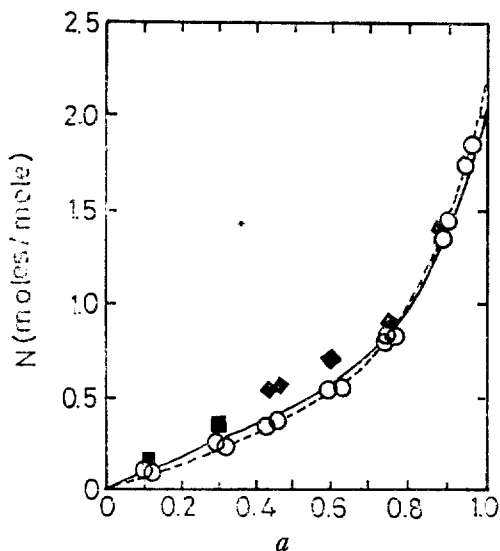


Fig. 3. Sorption Isotherms for Water Vapor in Sample of 1 mole % TEGDMA-p(HEMA) at 25°C. a =Activity of Water; N =Amount of Water Sorbed/Monomer Unit of Polymer(Mole/Mole). \circ =Sorption; \blacksquare =Desorption; — Modified B.E.T. Theory;Hailwood-Horrobin Theory.

of water activity for the poly(DHPMA) system.

Comparing the latter system (Fig.5) with the former systems (Figs.1 to 4), the amount of water sorbed by the isotactic polymer is slightly greater than by the syndiotactic polymers at maximum water activity. This fact shows that the different structure and conformations in these polymers have a significant effect on hydrophilicity as measured by water sorption. The greater amounts of water sorbed are probably due to more hydrogen bonding between water molecules and side chain hydroxyl groups on the polymer surface. The structure of isotactic poly(HEMA) has been discussed by Russell et al.²¹.

All those systems show hysteresis phenomena between sorption and desorption. Hysteresis is commonly observed in gel systems²². Only the initial sorption data were used for the isotherm analysis which follow.

Interpretation in Terms of Modified B.E.T. Theory

Water vapor sorptions have been frequently described by the Brunauer-Emmett-Teller(B.E.T) equations²³ for multilayer adsorption. While the EET equation provides an excellent method of estimating surface area, however, it usually holds only for relative pressures of 0.05 to 0.40. In almost every case, the amount adsorbed at relative pressures higher than 0.40 is less than that predicted by the simple B.E.T. equation. This discrepancy has been explained in three ways: (a) by assuming the heat of adsorption in the second layer to be less than the heat of liquefaction of the adsorbate, (b) by assuming that the structure of the adsorbent is such that it will permit adsorption to only a finite number of layers, and (c) by considering the effect of capillary condensation.

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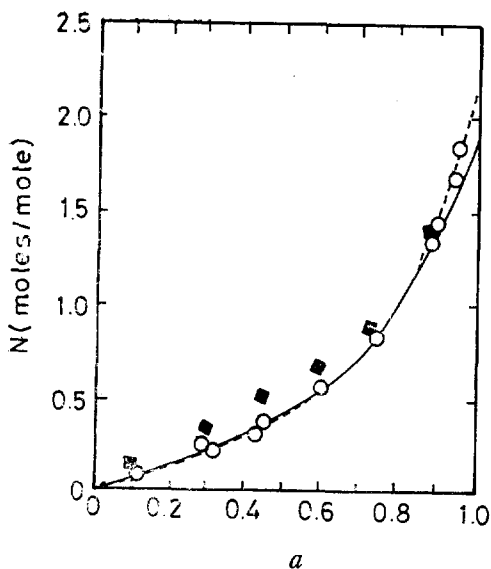


Fig. 4. Sorption Isotherms for Water Vapor in Sample of 1 mole % HMDIC-p(HEMA) at 25°C. a = Activity of Water; N = Amount of Water Sorbed/Monomer Unit of Polymer (Mole/Mole). \circ = Sorption; \blacksquare = Desorption. — Modified B.E.T. Theory; Hailwood-Horrobin Theory.

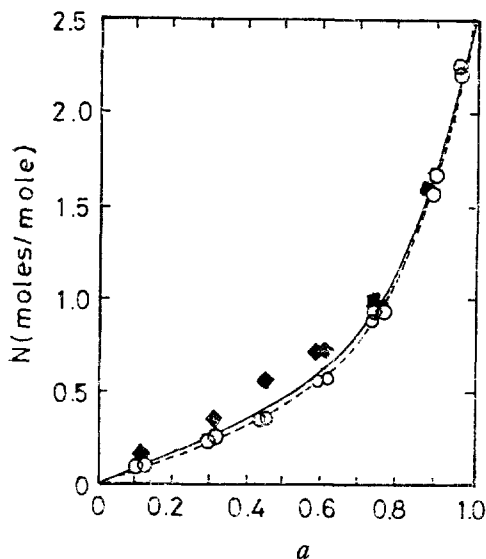


Fig. 5. Sorption Isotherms for Water Vapor in Sample of 80% Isotactic; 14% Heterotactic and 6% Syndiotactic p(HEMA) at 25°C. a = Activity of Water, N = Amount of Water Sorbed/Monomer Unit of Polymer (Mole/Mole). \circ = Sorption; \blacksquare = Desorption; — Modified B.E.T. Theory; Hailwood-Horrobin Theory.

Considering the heat of liquefaction problem, the Anderson-BET equation¹⁶ is

$$\frac{N_i}{M_m} = \frac{c k a}{(1 - k a)[1 + (c - 1)k a]} \quad (1)$$

where N_i is the amount sorbed per unit of polymer, M_m is the concentration of sorption sites required for a monomolecular layer, a is the activity of water, c is a term related to the binding of a water molecule directly to the site to the indirect binding of water molecules, and k is the ratio of the affinity of indirect bonding to that of condensation into liquid water. Equation (1) reduces to the BET equation if $k=1$.

The parameters c , k , and M_m can be evaluated from the sorption data by linearizing equation (1) as

$$\frac{a}{N_i(1 - k a)} = \frac{1}{c k M_m} + \frac{(c - 1)a}{c M_m} \quad (2)$$

The best fit values of the parameters were computed and are listed in Table 1. Equation (2) with these sets of parameters fits well at equilibrium relative humidities less than 0.7, but the plots deviate from the experimental values at equilibrium relative humidities greater than 0.7. The parameter c includes both the net heat of adsorption and the net entropy of adsorption. The constant c increases considerably from poly(DHPMA) to poly(HEMA). This increment reflects the transition from the convex to the S-shaped sorption isotherm. It seems that the higher hydrophilicity of poly(DHPMA) is reflected in its stronger affinity towards weakly bound water, but not in a higher sorption ability of the strongly bonding sites. Among these systems, the most hydrophilic material is poly(DHPMA) which has two hydrophilic hydroxyl groups per repeating unit in the molecule.

Since k is the ratio of the affinity of indi-

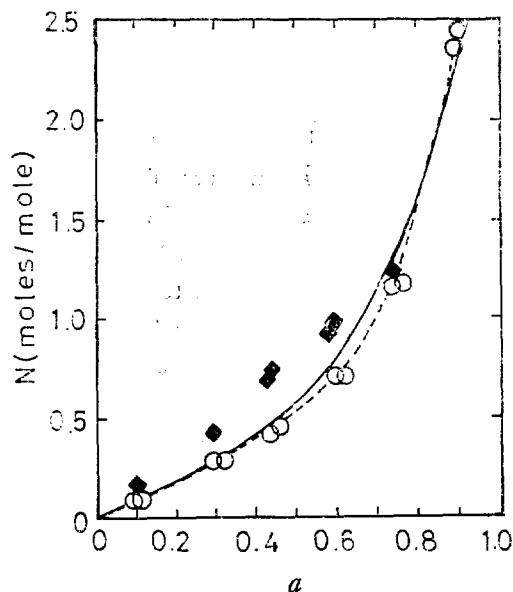


Fig. 6. Sorption Isotherms for Water Vapor in a Sample of Poly(2,3-Dihydroxypropyl Methacrylate) [p(DHPMA)] at 25°C. a = Activity of Water, N = Amount of Water Sorbed/Monomer Unit of Polymer (Mole/Mole). \circ = Sorption; \blacksquare = Desorption; — Modified B.E.T. Theory; Hailwood-Horrobin Theory.

rect bonding to that of the condensation, k smaller than unity reflects the unfavorable interaction of water probably due to the hydrophobic nonpolar parts of the polymer molecules. The values of k for 60% syndiotactic poly(HEMA) systems are slightly lower than those of crosslinked poly(HEMA), 80% isotactic poly(HEMA), and poly(DHPMA) systems; this difference may be due to the greater hydrophobicity of syndiotactic poly(HEMA).

Using M_m , mole of sorbed water per mole of polymer repeat unit, it is possible to calculate the quantities of water bound on the sorption sites of each polymer. The quantities obtained are given in Table 1. The value of $M_m = 0.49$ mole found for poly(DHPMA) roughly corresponds to one mole water sorbed per two moles of monomer unit. A similar result

Table 1. Parameters Evaluated from Anderson's Modified B.E.T. Theory for Water Vapor Sorption of Hydrophilic Methacrylate Polymers

No.	Polymer	c	k	M_m (g/g)	M_m (mole(m ² /g) /mole)	$[A]$
1.	p(HEMA)(60% s, 40% h)	5.01	0.84	0.0402	0.29	199
2.	p(HEMA)-(1 mole % EGDMA)	4.90	0.86	0.0427	0.31	211
3.	p(HEMA)-(1 mole % TEGDMA)	4.72	0.86	0.0436	0.32	216
4.	p(HEMA)-(1 mole % HMDIC)	4.70	0.86	0.0440	0.32	218
5.	p(HEMA) (80% i, 14% h, 6% s)	2.74	0.88	0.0512	0.37	253
6.	p(DHPMA)	1.70	0.92	0.0551	0.49	273

*s=syndiotactic
h=heterotactic
i=isotactic

was found from studies of the effect of water on the low-temperature relaxation spectrum of various glycol methacrylate polymers²⁴. The same stoichiometry was suggested for water sorption in polyamides at low water activity⁵.

The values of M_m obtained for poly(HEMA) and its crosslinked systems are about 0.3 mole/mole while the value for isotactic poly(HEMA) is nearly 0.4.

The effective surface contact area, A , between water and the polymer in the system can be obtained by using the following expression^{25,26}:

$$[A] = \frac{ANM_m}{M_{H_2O}} \times 10^{-4} \quad (3)$$

where A is the area occupied by an adsorbate molecule (taken as $14.8 \times 10^{-20} \text{m}^2$ for water)²⁴, N is Avogadro number, and M_{H_2O} is the molecular weight of water. The calculated effective surface contact area of the polymers is listed in Table 1. Referring to Table 1, one notes that the accessible surface area for water binding in the isotactic poly(HEMA) is greater than that of the syndiotactic poly(HEMA).

This fact can be explained in terms of the configuration of hydroxyl groups in the polymer.

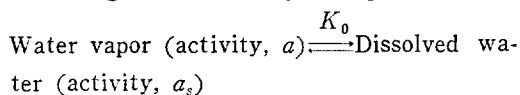
Isotactic poly(HEMA) probably exists in a helical conformation²¹, suggesting that the hydroxyl groups are on the outer surface of the helix. However, some of the hydroxyls in syndiotactic poly(HEMA) are somewhat buried, i.e. the polar side-chains of the polymer may interdisperse into the structure of the molecule. The helical isotactic chains probably have no intrachain hydrogen bonds linking the ester side chains, while the syndiotactic chains probably have intrachain hydrogen bonds between pendant hydroxyl groups. The different stereochemical conformation of the hydroxyl groups may give a different effective surface contact area of sorption sites.

The poly(DHPMA) shows a large effective surface area (273m²/g). This can be explained in terms of its structure, which has two hydroxyl groups in the monomer.

Interpretation in Terms of the Hailwood-Horrobin Theory

The Hailwood-Horrobin theory¹⁷ has been used extensively for textile and polymer materials. This theory considers sorbed water to exist as an ideal solution of three species, i.e., dissolved water, hydrated water to polymer, and polymer components. This solution model produces a measure of hydrated water, condensed water, and the accessibility of sites for sorption.

Assuming the following two processes^{26,27},



and

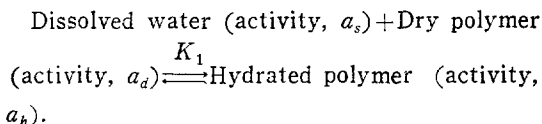


Table 2. Parameters Evaluated from the Hailwood-Horrobin Theory for Water Vapor Sorption of Hydrophilic Methacrylate Polymers

No.	Polymer	K_0	K_1	M_w (g)	M_T (mole / layer)	n (mole / layers)
1.	p(HEMA) (60% s, 40% H)	0.672	3.91	74.40	1.75	6.0
2.	p(HEMA)-(1 mole % EGDMA)	0.669	3.89	70.78	1.85	6.0
3.	p(HEMA)-(1 mole % TEGDMA)	0.632	3.80	62.70	2.10	6.5
4.	p(HEMA)-(1 mole % HMDIC)	0.630	3.79	62.68	2.10	6.5
5.	p(HEMA) (80% i, 14% h, 6% s)	0.611	3.59	59.17	2.20	6.0
6.	p(DHPMA)	0.570	2.38	41.28	3.88	8.0

The Hailwood-Horrobin theory¹⁷ gives

$$\frac{mM_w}{18.02} = \frac{K_0 a}{1 - K_0 a} + \frac{K_0 K_1 a}{1 + K_0 K_1 a} \quad (4)$$

where m is the fractional moisture content, M_w is the molecular weight of polymer per mole of hydrated water, and K_1 is an equilibrium constant in terms of bound water fractions in the polymers. K_0 is an equilibrium constant related to the different degrees of hydrophilicity of the polymers. Equation (4) can be algebraically transformed to the parabolic relationship

$$\frac{a}{m} = \frac{M_w}{18.02} \left[\frac{1}{K_0(K_1+1)} + \frac{(K_1-1)}{(K_1+1)} a - \frac{K_0 K_1}{K_1+1} a^2 \right] \quad (5)$$

Utilizing the sorption isotherm data, equation (5) was best fitted empirically and the constants K_0 and K_1 were evaluated (Table 2).

The modified B.E.T. theory predicted a good fit to most of the experimental isotherms up to 0.7 equilibrium relative humidity. However, a somewhat better fit was found with the solution theory of Hailwood-Horrobin over the entire range of equilibrium relative humidities, resulting in the parameters listed in Table 2.

These parameters provide some interesting comparisons. The values of K_1 are greater than those of K_0 for all systems. This indicates that there are significant interactions between the polymer and the water molecules.

The K_0 values for the hydrogel materials studied range from a low value for poly(DHPMA) of 0.570 to a high value of 0.672 for 60% syndiotactic poly(HEMA). These give us some information on the different hydrophilicities of the molecules. K_0 is decreased with increasing dissolved water, thus decreased K_0 suggests increasing polymer hydrophilicity. Strong polar interactions between the polymers and water molecules might be expected. The values of K_1 give us the fraction of binding water in the gels. Thus, smaller value of K_1 indicates larger degrees of hydration.

The molecular weight of the polymer per mole of hydrated water, M_w , and the mole ratio of total water per monomer unit, M_T , are also listed in Table 2. The data are in good agreement with the mole ratio of bound water per monomer unit obtained from differential scanning calorimetry (DSC) measurements²⁸ of fully equilibrated polymers. These results are also in good agreement with the effective surface area obtained from the modified B.E.T. theory. The trend in polymer hydrophilicity is in line with the trends for bound water and the effective molecular contact area of the polymers. The average number of molecular layers of water sorbed up to the gel-saturation point can be calculated by dividing the water content at the gel saturation point (M_T) by the water content corresponding

to the formation of a complete monomolecular adsorbed layer (M_m). These values are given in Table 2, and are approximately 6 for the poly(HEMA) systems and 8 for the poly(DHPMA) system. Note that the value for isotactic poly(HEMA) is only 6 in spite of higher M_T value, suggesting that the surface configuration of this molecule has a higher effective density of water binding sites than the other poly(HEMA) forms studied.

The hysteresis phenomena may be explained by the irreversibility in the binding of water molecules with the gel networks. The sorption-desorption isotherms of water vapor in the poly(HEMA) samples containing crosslinkers such as EGDMA, TEGDMA, and HMDIC are quite similar to syndiotactic poly(HEMA) system. However, the sorption-desorption isotherms for isotactic poly(HEMA) and poly(DHPMA) systems are slightly different from the syndiotactic poly(HEMA) isotherms. The large "hysteresis loop" in the dehydration-sorption data indicates that changes in the framework have occurred during dehydration resulting in a decrease in the ability to take up water vapor. For water vapor sorbed by gel, it has been considered that desorption hysteresis occurs because a certain number of interchain bonds in the polymers are not reformed in the same manner upon sorption.

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