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pH-Dependent Equilibrium Swelling Properties of Hydrophobic Polyelectrolyte Copolymer Gels

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ABSTRACT: The aqueous equilibrium swelling properties of a series of lightly cross-linked polyelectrolyte copolymers based on *n*-alkyl methacrylate esters (*n*-AMA) of various chain lengths and (dimethylamino)ethyl methacrylate (DMA) have been measured as a function of pH at 25 °C and constant ionic strength. Swelling is highly pH dependent, with water contents ranging from less than 10% (w/w) at high pH to greater than 90% at low pH. The extent of the transition from the collapsed hydrophobic state to the hydrophilic state and the pH interval over which it occurs depend on the comonomer composition. Increasing the proportion of *n*-AMA to DMA generally reduces the extent of the transition and shifts it to lower pH. Increasing the length of the *n*-AMA side chain (at constant comonomer ratio) causes a reduction in the extent of the transition, with a less systematic effect on the transition pH. The specific ionic composition of the solution, at a given pH and ionic strength, affects the extent of swelling. The ionic strength dependence of the equilibrium swelling has also been found to be affected by the ion valencies of the buffer system, as predicted by the Donnan equilibrium theory.

Introduction

It has long been known that a cross-linked polymer gel bearing weakly acidic and/or weakly basic pendant groups will imbibe solvent to an extent that depends on the pH and the ionic composition of the solution bathing the gel. When the gel is relatively solvophilic and contains acidic pendant groups, the swelling increases as solution pH increases.[1,2] Similarly, a weakly basic solvophilic gel expands smoothly as the solvent pH decreases.[3,4]

In recent years, considerable attention has been drawn to systems in which the polyelectrolyte gel and the solvent do not interact favorably. In such cases the polyelectrolyte gel remains in a collapsed state until the external solvent reaches a critical pH, at which point the gel abruptly increases its equilibrium swelling.[5] A plot of gel weight or volume versus pH can exhibit abrupt changes. These transitions in gel volume can also be induced by varying the ionic composition,[6] temperature,[7,9,10] or solvent composition.[5,10,11] This has stimulated research on the feasibility of such gels as artificial muscles and/or switches,[5] as components in chemical separation systems,[1,8] and as physiologically sensitive drug delivery devices.[3,4,9]

In the present study, the equilibrium swelling properties of a class of lightly cross-linked, hydrophobic, tertiary-amine-containing copolymer gels in aqueous solutions of various pH and ionic strengths were studied. The copolymers consisted of *n*-alkyl methacrylate esters (*n*-AMA) and (dimethylamino)ethyl methacrylate (DMA) Copolymer characteristics were varied by altering the *n*-alkyl side chain length of the *n*-AMA comonomer and by varying the ratio of *n*-AMA to DMA.

Experimental Section

Materials. Methyl methacrylate (MMA), ethyl methacrylate (EMA), *n*-propyl methacrylate (PMA), *n*-butyl methacrylate

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Table I
Compositions of the Various Comonomer Solutions Prepared[a]

comonomers	comonomer ratio, mol %	MMA, g	EMA, g	PMA, g	BMA, g	HMA, g	DMA, g
MMA/DMA	70/30	11.99					8.03
MMA/DMA	78/22	13.97					6.14
MMA/DMA	86/14	16.03					4.01
MMA/DMA	93/7	26.04					3.27
EMA/DMA	70/30		13.74				8.03
PMA/DMA	70/30			15.44			8.04
BMA/DMA	70/30				17.02		8.02
BMA/DMA	77/23				19.85		6.60
BMA/DMA	86/14				22.77		4.00
HMA/DMA	70/30					14.33	5.67

[a] Solutions also contained 0.5% (w/w) AIBN and 0.1% (w/w) DVB based on monomer weights listed below.

(BMA), *n*-hexyl methacrylate (HMA), (dimethylamino)ethyl methacrylate (DMA) (Polysciences, Inc.), and divinyl benzene (DVB) (Pfaltz and Bauer, Inc.) were each vacuum distilled in the presence of the polymerization inhibitor 1,3,5-trimethyl-2,4,6-tris[3,5-di-*tert*-butyl-4-hydroxybenzyl]benzene (Ethyl Co.) prior to use in copolymer preparation. The initiator, 2,2′-azobis(isobutyronitrile) (AIBN) (Polysciences, Inc.), was recrystallized from water/ethanol before use. Water used in the swelling studies was double distilled and deionized. Methanol (Fisher Scientific, ACS grade), sodium dihydrogen phosphate and NaCl (Mallinckrodt, Inc., analytical reagent grade), citric acid (Fisher Scientific, analytical reagent grade), dichlorodimethylsilane (Aldrich, 99%), and toluene (Eastman, scintillation grade) were all used as received.

Copolymer Preparation. Each cross-linked copolymer gel was prepared by a free radical bulk copolymerization between two silanized glass plates (13 cm × 13 cm). A Teflon spacer (0.32 mm thick) was inserted between the plates near each of the edges to provide a uniform internal cavity for the monomer solution and the assembly was held together from the outside by metal clamps. Silanization was accomplished by immersing the plates in a solution of dichlorodimethylsilane (2% v/v) in toluene for 2 min. The plates were then air dried and used directly in copolymer preparation.

Each comonomer solution consisted of an *n*-alkyl ester of methacrylic acid (*n*-AMA) and DMA in a known molar ratio in addition to AIBN (0.5% w/w) and the tetrafunctional crosslinking reagent divinyl benzene (0.1 w/w). Table I lists the compositions by weight of the various comonomer solutions prepared. Comonomer solutions were each degassed by stirring under light vacuum for 5 min and then were injected into the cavity between the glass plates from a glass syringe fitted with a 24-gauge needle. The assembly was then incubated in a vertical position under an argon atmosphere at 60 °C for 18 h to facilitate complete polymerization. The solid copolymer slab was separated from the glass plates with a razor blade and cut into 9.5-mm-diameter circular disks by using a punch. All disks were washed in methanol for several days and then in methanol/water (50/50 v/v) overnight. Disks were then dried, first at room temperature for 24 h and then at 50 °C in vacuo for an additional 24 h. The resulting disk thicknesses varied from 0.27 to 0.32 mm as measured with a micrometer. The compositions of the various copolymers were checked by elemental analysis (C, H, N) which indicated that complete polymerization of the monomer feed solution had occurred in each case.

Determination of Copolymer Glass Temperatures. Glass temperatures of the copolymer samples in the dry state were determined by using a Du Pont Model 910 Differential Scanning Calorimeter equipped with a Model 1090 programmer. A linear heating rate of 15 °C/min was used over the range −50 to 150 °C for each sample. The sample cell was maintained under high-purity argon purge. Data reported correspond to inflection temperatures computed from each scan by using the Du Pont DSC analysis program version 3.0.

Equilibrium Swelling Studies. Copolymer disks in triplicate were immersed in either 0.01 M citric acid buffer or 0.01 M phosphate buffer at 25 °C. The total ionic strength (I) of each buffer was adjusted to a desired level with a calculated amount of NaCl. For the ionic strength studies, a 0.01 M citrate/NaCl buffer at pH 4.0 was used for the three copolymers studied. In the case of the 70/30 MMA/DMA copolymer, both a 0.01 M citrate/NaCl buffer and a simple HCl/NaCl solution were employed at pH 4.0 for the purposes of comparison. Periodically, the disks were withdrawn from the buffer solution and weighed after removal of excess surface water by light blotting with a laboratory tissue. The disk weights were individually monitored in this way until they reached a constant value. This typically required from several hours to 3 weeks depending on the copolymer composition and pH. The equilibrium water fraction (EWF) for a copolymer sample was expressed as (grams of water)/(grams of swollen copolymer) and is calculated as EWF = $(W_s - W_d)/W_s$ where W_s and W_d are the fully swollen and dry disk weights, respectively. Excellent reproducibility in the equilibrium swelling values was obtained for each set of triplicate samples with a relative standard error of 1% or less.

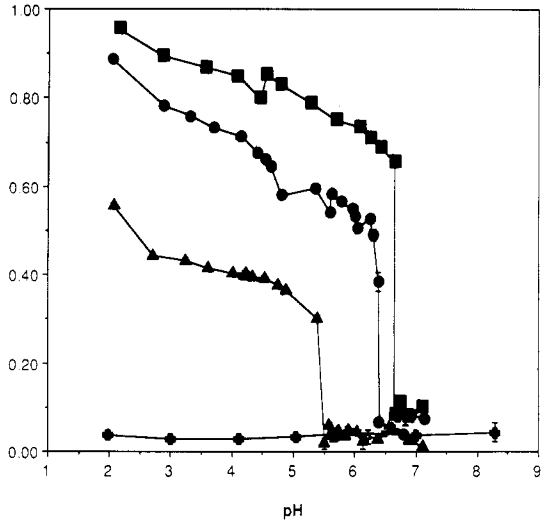

Figure 1. Swelling isotherms for the MMA/DMA copolymers of various comonomer composition measured as a function of pH at 25 °C and a total ionic strength of 0.1 M. (■) 70/30 mol %; (●) 78/22 mol %; (▲) 86/14 mol %; (+) 93/7 mol %.

Results

Figures 1 and 2 show the equilibrium swelling behavior for four MMA/DMA copolymer gels (93/7, 86/14, 78/22, and 70/30 mol %) and three BMA/DMA copolymer gels (86/14, 77/23), and 70/30 mol %), respectively, measured as a function of pH at 25 °C and a total ionic strength of 0.1 M. Citrate buffer was used at and below pH 7, and phosphate buffer was used above pH 7. Each symbol in these figures represents the mean of three samples and the corresponding standard deviations are, in general, smaller than the symbols shown. From these data, it is apparent that all gels are compact and hydrophobic at pH values greater than 6.6 regardless of monomer composition, containing 10% (w/w) water or less at equilibrium. At lower pH values, a point is reached where the equilibrium water

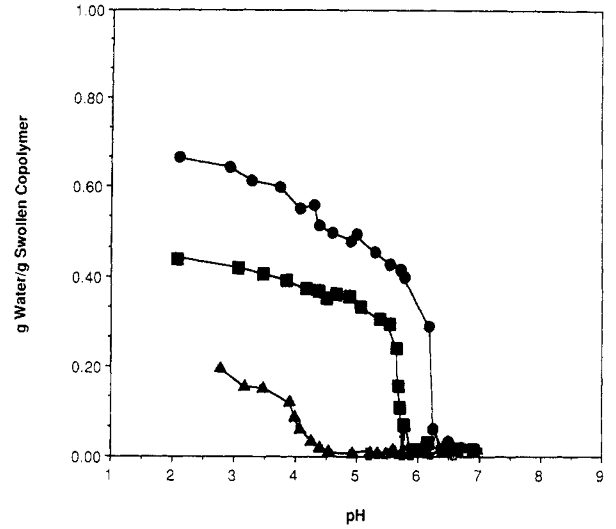

Figure 2. Swelling isotherms for the BMA/DMA copolymers of various comonomer compositions measured as a function of pH at 25 °C and a total ionic strength of 0.1 M. (●) 70/30 mol %; (■) 77/23 mol %; (▲) 86/14 mol %.

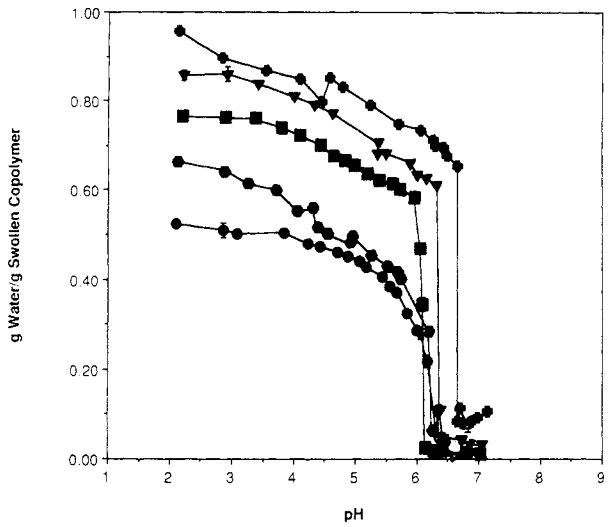

Figure 3. Swelling isotherms for a series of *n*-AMA/DMA copolymers of various side chain lengths measured as a function of pH at 25 °C and a total ionic strength of 0.1 M. Each copolymer contained 30 mol % DMA. (+) MMA/DMA; (▼) EMA/DMA; (■) PMA/DMA; (●) BMA/DMA; (●) HMA/DMA.

Table II
Measured Glass Temperatures (T_g) for Some of the *n*-AMA/DMA Copolymers Prepared

copolymer	comp, mol %	T_g, °C	copolymer	comp, mol %	T_g, °C
MMA/DMA	86/14	114.4	PMA/DMA	70/30	51.6
MMA/DMA	78/22	108.5	BMA/DMA	86/14	34.7
MMA/DMA	70/30	90.8	BMA/DMA	77/23	31.7
EMA/DMA	70/30	67.9	BMA/DMA	70/30	31.1

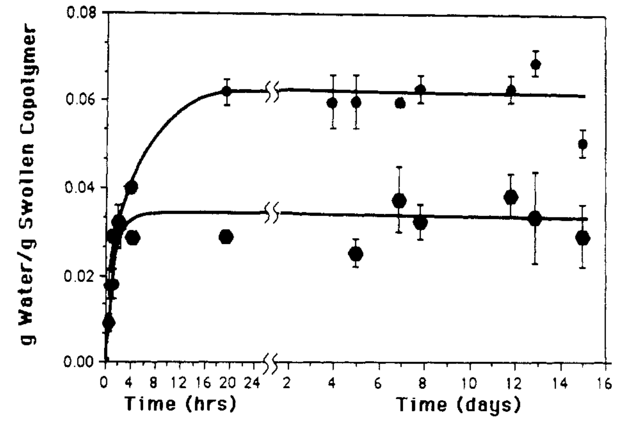

Figure 4. Swelling kinetic curves for copolymer gels in pH 7.0, 0.01 M citrate buffer with ionic strength adjusted to 0.1 M with NaCl. Temperature is 25 °C. (●) 70/30 mol % MMA/DMA; (◆) 70/30 mol % EMA/DMA. Curves are included only to guide the eye.

content abruptly increases, sometimes discontinuously, giving rise to highly swollen gels. At still lower pH values, the water content continues to increase but at a more gradual rate. For example, the 70/30 MMA/DMA gel has an equilibrium water content below 10% in the pH range 6.6–7.2. With a small decrease in pH at 6.6, a discontinuous jump to about 70% water is observed. The water content further increases to values in excess of 90% as the pH is reduced to 2.0. Swelling transitions are also observed for the 78/22 and 86/14 MMA/DMA gels and the 70/30, 77/23, and 86/14 BMA/DMA gels but not for the 93/7 MMA/DMA gel, which remained compact at all pH values tested.

The copolymer composition impacts significantly on the equilibrium swelling behavior of the MMA/DMA and BMA/DMA gels as is evident in Figures 1 and 2, respectively. As the proportion of *n*-AMA monomer to DMA monomer increases, two effects are observed: (1) the pH of the swelling transition shifts to lower pH and (2) the extent of the swelling transition is decreased. Changing the MMA/DMA proportion from 70/30 to 86/14 shifts the transition pH from 6.5 to 4.8, and the equilibrium water content in the low pH range changes from 90 to 40%. Also, the transition for the 70/30 gel appears to be discontinuous while the transitions for other comonomer ratios are continuous.

The influence of the *n*-alkyl ester side-chain length on the pH-dependent equilibrium swelling properties (at 25 °C and 0.1 M ionic strength) is shown in Figure 3 for a homologous series of *n*-AMA/DMA copolymer gels each containing 30 mol % DMA. The *n*-AMA monomers include the methyl, ethyl, propyl, butyl, and hexyl esters of methacrylic acid. Here again, each point represents the mean of three samples. All gels in this series show a swelling transition. The extent of the transition and the pH at which it occurs are affected by the pendant chain length. As the side chain length increases from C_1 to C_6, the water content at low pH (2–3) decreases from 90% for the methyl to about 50% for the hexyl copolymer. The width of the pH interval of the swelling transition broadens with increasing side chain length and shifts progressively to lower pH for the methyl, ethyl, and propyl esters. The latter trend does not, however, continue for the butyl and hexyl copolymers.

Glass temperatures (T_g) for the various *n*-AMA/DMA copolymers are listed in Table II as determined by differential scanning calorimetry. It is clear from these results that the MMA/DMA, EMA/DMA, and PMA/DMA copolymers all have T_g's well above ambient temperature and thus exist in the glassy state when dry. The T_g's for the BMA/DMA copolymers are quite close to ambient temperature. Increasing *n*-alkyl side chain length at a fixed comonomer ratio serves to decrease the T_g as exhibited by the MMA/DMA, PMA/DMA, and BMA/DMA copolymers at 70/30 mol %.

The question of whether the low water contents observed at pH values above the swelling transition reflect true equilibria or are determined by slow sorption kinetics was considered. Figure 4 shows representative swelling kinetics for MMA/DMA (70/30) and EMA/DMA (70/30)

Table III
Effect of Buffer Type on the Equilibrium Swelling of the 70/30 MMA/DMA Gel at 25 °C and a Total Strength of 0.1 M[a]

	equilibrium water content, (g of water)/(g of swollen gel)	
pH	0.01 M citrate	0.01 M phosphate
5.84	0.749 (0.0012)	0.866 (0.0007)
6.02	0.736 (0)	0.859 (0)
6.42	0.694 (0.0040)	0.826 (0.0007)
6.64	0.656 (0.0046)	0.771 (0.0014)

[a] Results in parentheses represent standard deviation.

gels in pH 7.0, $I = 0.1$ M citrate buffer. Water sorption appears to be complete after 1 day, with regain remaining constant up to 13 days. There appears to be no evidence for a slow secondary phase of sorption, at least over this time scale.

The effect of buffer type on the equilibrium swelling of the 70/30 MMA/DMA copolymer is shown in Table III for the pH interval 5.8–6.6. Swelling in both 0.01 M phosphate and 0.01 M citrate buffers at several pH values was determined at 25 °C. The total ionic strength for each buffer was adjusted to 0.1 M with a calculated amount of NaCl. Equilibrium swelling for the MMA/DMA copolymer was higher for the phosphate buffered samples than for the citrate samples for any pH in this interval. Thus, pH and ionic strength are not sufficient to determine equilibrium swelling for these gels. The identity of buffer ions plays a detectable but secondary role.

The influence of total external ionic strength for a fixed buffer system is shown in Figure 5a. The equilibrium water contents of the 70/30 MMA/DMA and PMA/DMA copolymers and the 77/23 BMA/DMA copolymer were measured as a function of the external ionic strength in a 0.01 M citrate buffer at pH 4.0. A fixed ionic strength of the buffer was achieved by addition of NaCl. The copolymers were chosen to test the ionic strength effect over a wide range of hydration values. An initial increase in equilibrium water content is observed as the ionic strength is increased to 0.05 M for all three copolymers. Increasing the ionic strength further up to 2.0 M causes a smooth reduction in the water content, though the effect is small at ionic strengths greater than 1.0 M. The ionic strength effect is greater for the methyl copolymers than for the butyl copolymer. Figure 5b shows the ionic strength dependent swelling properties of the 70/30 MMA/DMA copolymer in citrate/NaCl and HCl/NaCl buffer systems at pH 4.0. In the high ionic strength region (<0.10 M), the extent of swelling is quite similar in the two buffers. At lower ionic strengths, however, the swelling behavior is markedly dissimilar. Swelling in the citrate system reaches a maximum around 0.05 M and decreases with a further decrease in ionic strength, while that in the HCl/NaCl buffer continues to increase over the same interval in ionic strength.

Discussion

Swelling equilibria of polyelectrolyte networks are determined by a balance of three primary forces: (1) the free energy of mixing of the network chains with solvent, (2) the net osmotic pressure within the network resulting from the mobile counterions surrounding the fixed charged groups (ion osmotic pressure), and (3) the elastic retractile response of the network (network swelling pressure).[5,12,13] The methacrylate copolymers studied here are inherently hydrophobic, being composed primarily of residues with n-alkyl ester side chains. This hydrophobic character dominates the overall swelling behavior in water at pH values near and above neutrality. The unfavorable interaction between the network chains and water in this pH range forces the networks to prefer a collapsed conformation with the resulting exclusion of water.

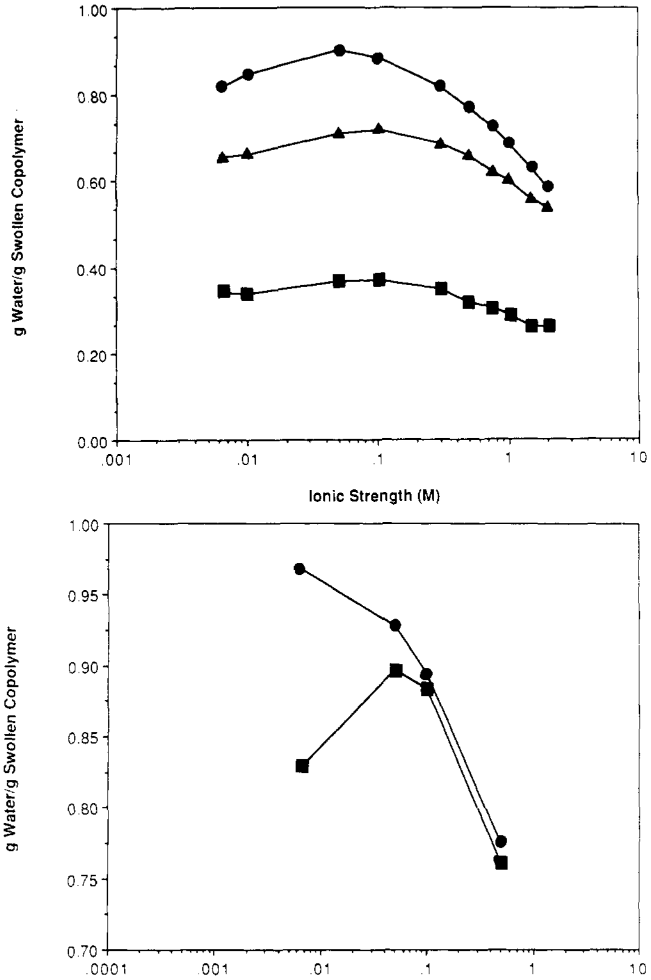

Figure 5. (a, Top) Effect of total ionic strength on the equilibrium swelling of the 70/30 mol % MMA/DMA copolymer (●), 70/30 mol % PMA/DMA copolymer (▲), and 77/23 mol BMA/DMA copolymer (■) measured in a 0.1 M citrate buffer at pH 4.0 and 25 °C. This ionic strength was adjusted to the desired value by the addition of a calculated amount of NaCl. (b, Bottom) Effect of total ionic strength on the equilibrium swelling of the 70/30 mol % MMA/DMA copolymer in either an HCl/NaCl buffer (●) or a 0.01 M citrate/NaCl buffer (■) at pH 4.0 and 25 °C.

The hydrophobic character of these gels is contrasted with the relatively hydrophilic gels that have been studied by other workers.[1-14] The observed volume changes in the present work are accordingly less extensive than those obtained with lightly ionized hydrogels [e.g., poly(acrylamide-*co*-acrylic acid)[5]].

The external pH has a profound effect on the balance of forces that determine equilibrium swelling in these gels. As the pH is lowered to the acidic region, the tertiary amine side chains of the DMA residues become protonated, thus increasing the charge density on the network. The concomitant increase in mobile counterion content of the network sharply increases the internal osmotic pressure which induces the observed swelling transitions.

Varying the molar ratio of n-AMA to DMA for a constant comonomer system (Figure 1 and 2) or varying the n-alkyl side chain length of n-AMA from C_1 to C_6 while at constant molar DMA content (30 mol %; Figure 3) appears to affect both the extent and the nature of the transition. It should be noted that an increase in n-AMA content or in side chain length has two effects. First, the concentration of ionizable amine groups decreases, lowering the osmotic pressure that can be generated by the counterions. Second, the overall hydrophobicity increases. These effects generally combine to decrease the amount of water imbibed.

The systematic reduction is pH at which the swelling transition occurs as *n*-AMA content increases (Figure 1 and 2) is explained in a similar way. A transition will occur when a particular balance of osmotic and hydrophobic forces is achieved. As network hydrophobicity increases, a greater degree of ionization is required to enable the transition. The concomitant decrease in ionizable group density that occurs as DMA content decreases must be countered by a further increase in degree of ionization, requiring a lower pH. Another factor which may contribute to lowering the transition pH is the decrease in dielectric coefficient as *n*-AMA content increases. This will lower the pK_a of the ionizable groups.

In view of the above observations, it is somewhat puzzling that the transitions observed for the homologous *n*-AMA/DMA series (Figure 3) do not show the same behavior. The downward shift of the transition pH as the *n*-alkyl side chain length increases from C_1 to C_3 is halted and reversed somewhat for C_4 and C_6. Moreover, the sharp transitions observed for the C_1–C_3 derivatives become gradual for C_4 and C_6.

One plausible explanation for our results is that the swelling data for the C_1–C_3 copolymers at high pH do not represent final thermodynamic end points. Since these copolymers are glassy at ambient temperature, it is conceivable that the swelling data actually represent completion of the first stage of a "dual-sorption" process.[15] That is, water is intially sorbed into the "excess volume" of the glassy polymer, but the process of chain relaxation leading to the final swelling equilibrium is incomplete. The sorption kinetic curves of Figure 5 argue against this explanation, however. After 2 days, the slopes of the sorption curves appear to be zero. If a secondary, relaxation-controlled process exists, it must be extremely slow.

Another reason to doubt the existence of a slow second sorption phase stems from the observation that the glass transition temperature is actually highest for MMA and decreases with increasing side chain length. One would expect the MMA/DMA copolymer to be the most rigid and thus sorb the least amount of water at high pH. The opposite is actually observed: swelling at high pH decreases as side chain length increases. Thus hydrophobicity, an equilibrium property, appears to correlate better with the sorption end point than does T_g, which is a kinetic property. We believe therefore that the swelling data represent true equilibria.

A plausible explanation for the broadening of the swelling transition with an increase in *n*-AMA side chain length relates to the effect of side chain length on the "stiffness" of the network copolymer chains. Tanaka et al.[5,16] as well as other authors define the stiffness of a copolymer chain as the ratio of the chain's persistence length to its "effective radius". Assuming the persistence length to be relatively independent of the *n*-alkyl side chain length, and noting that an increasing side chain length implies an increased chain radius, it follows that the chain stiffness decreases with increasing side chain length. Tanaka et al.[5,16] have argued that a minimal stiffness is required for swelling transitions to be discrete.

The buffer effect on swelling (Table III) can be explained by considering the distribution of polyvalent anions in the citrate and phosphate buffer systems. Since the gel has positive fixed charges, the Donnan effect will favor distribution into the gel of polyanions over monoanions. Moreover, fewer polyanions are required to neutralize an equivalent amount of charge on the gel. As the concentration of polyanions in the solution increases, at constant overall ionic strength, these two factors will combine to lessen the concentration of counterions inside the gel, reducing the counterion osmotic pressure and the swelling of the gel. The pK_a's for citrate are 3.15, 4.78, and 6.40, while those for phosphate are 2.15, 7.10, and 12.12. At any pH there will be more di- and trivalent anions in citrate buffer than in phosphate buffer. Thus, at constant ionic strength, phosphate buffer should permit greater swelling than citrate buffer, as was observed.

Donnan equilibrium theory[2,14] can be used to explain the observed nonmonotonic behavior of gel swelling as a function of ionic strength at constant pH (Figure 5).

The theory[14] prescribes that ΔC_{tot}, the difference between the total ion concentration inside and outside the gel, is given by

$$\Delta C_{tot} = \sum(\lambda^{Z_i} - 1)C_i \tag{1}$$

where C_i and Z_i are the concentration and valence, respectively, of the ith ionic species and λ is the root of the equation

$$\sum Z_i C_i \lambda^{Z_i} + \frac{\rho\lambda 10^{-pH}}{K_a + \lambda 10^{-pH}} = 0 \tag{2}$$

In eq 2, pH is the solution pH outside the gel, ρ is the concentration of ionizable amine groups in the gel and K_a is the intrinsic dissociation constant of the protonated amine groups.

In using the above equations, we are assuming that the standard-state chemical potential of each ion is the same inside and outside the gel and that ion activities are equal to their concentrations. The former assumption is most reasonable under conditions of high gel swelling and, accordingly, this analysis is restricted to the regime of extensive swelling. The latter assumption is in general not rigorous but is retained for simplicity.

The parameter ρ may be computed by knowing the specific gravity of the dry gel and EWF, plus the mole fraction of each comonomer. For the dry 70/30 MMA/DMA gel, the specific gravity is approximately 1.1. For such a gel swollen to EWF = 0.83 and 0.90 (see Fig. 5), the values of ρ are approximately 0.4 M and 0.25 M, respectively. The parameter K_a was set to $10^{-7.7}$ in accordance with the literature value.[17] Values of C_i were computed from solution pH and the added buffer and salt concentrations, taking the multiple buffer pK_a values into account.

Results of calculations of the difference, ΔC_{tot}, between total ion concentration inside and outside the gel as a function of ionic strength are shown in Figure 6. Calculations were done at pH 4.0 for 0.01 M citrate buffer with added NaCl (heavy lines), for HCl/NaCl solutions (thin lines), and for two concentrations of ionizable amine groups (0.25 M and 0.4 M) in the gel. The latter concentrations correspond to EWF values between 0.83 and 0.90, as are observed for the 70/30 MMA/DMA gels. Using the above values, the calculations show a maximum in ΔC_{tot}, i.e., in ion swelling pressure, near $I = 0.05$ M for the citrate/NaCl case, which is in accord with the observed maximum in the MMA/DMA swelling shown in Figure 5b. The calculations for the HCl/NaCl systems also show maxima, but the latter are considerably broader than those for citrate. Over the range of ionic strengths considered in the HCl/NaCl experiments, theory predicts a decrease in swelling pressure and experimental results show a decrease

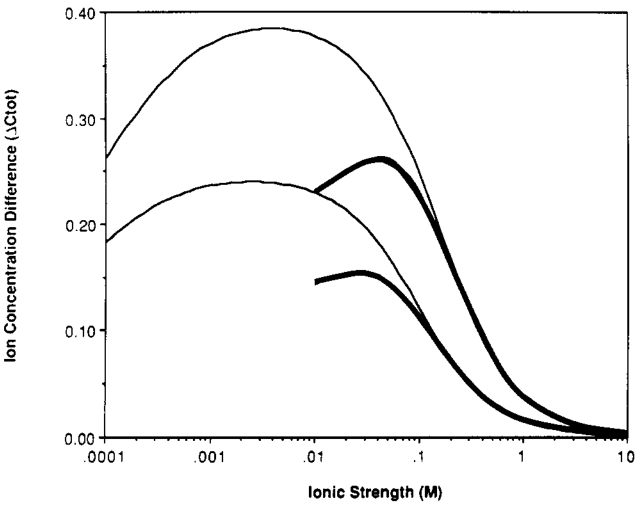

Figure 6. Predictions based on the Donnan equilibrium theory for difference in total free ion concentration inside and outside the gel. Details are given in the text. The pH of the solution outside the gel is fixed at 4.0. Heavy lines: 0.01 M citrate buffer with NaCl added to achieve prescribed ionic strength. Thin lines: HCl/NaCl solutions.

in swelling with increasing ionic strength.

Qualitatively, the nonmonotonic behavior may be explained as follows. At the lowest ionic strength, few amine groups can be protonated since this requires transfer of negative counterions from the solution into the gel. The availability of counterions for the gel is low due to their dilute concentration in the external solution. The limited supply of counterions ultimately limits the extent of gel ionization in the dilute ion regime. As solution ionic strength is increased, more counterions are available permitting greater ionization of the gel and greater swelling. Eventually, the gel ionization will reach a plateau determined by the solution pH. At this point, any increase in solution ionic strength will simply decrease the ion osmotic pressure difference between the gel and solution. The result is a reduction in swelling.[16]

The use of citrate buffer appears from the calculations to sharpen the swelling maximum, reduce its value, and shift it to higher ionic strength compared to that which would occur in a simple HCl/NaCl solution. As noted above, citrate buffer will permit less swelling than phosphate buffer at a given pH and ionic strength, and the same should hold when comparing citrate with HCl/NaCl. In the citrate system at the lowest ionic strength and pH 4.0, many of the counterions in the gel will be divalent. As the ionic strength of the solution is increased by addition of NaCl, stoichiometric equivalents of chloride ions will exchange with the mono and divalent citrate anions in the gel. To the extent that this exchange process occurs, the ion osmotic pressure in the gel will increase and cause greater swelling. Eventually, most of the counterions in the gel will be monovalent and the buffer identity will become inconsequential.

It should be noted that nonmonotonic swelling versus ionic strength curves have been reported for weak acid gels.[14,17] The initial increase in swelling with increasing ionic strength has been attributed in this case to ion exchange between salt cations in the solution and free protons in the gel, which in turn leads to increased ionization of the fixed carboxyl groups through proton mass action.[14] It is interesting to observe that in the absence of added counterions acidic gels can readily ionize whereas basic gels can do so only to the extent that hydroxyl ions are admitted to the gel. Thus, the acidic and basic gels are not symmetric in their swelling properties.

Conclusions

We have demonstrated that an abrupt pH-driven swelling transition can occur in highly hydrophobic polyelectrolyte gels. Characteristic features of the swelling isotherms of these weakly basic gels such as the extent, pH, and type of transition (continuous or discrete) are particularly sensitive to gel composition (both side chain length and copolymer composition). The principal determinant of the swelling equilibrium for any copolymer at any fixed pH is the hydrogen ion concentration with secondary contributions from the solution ionic strength and ion valencies.

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Registry No. (DMA)(MMA)(DVB) (copolymer), 94062-86-9; (DMA)(EMA)(DVB) (copolymer), 115859-45-5; (DMA)(PMA)(DVB) (copolymer), 115859-46-6; (DMA)(BMA)(DVB) (copolymer), 115859-47-7; (DMA)(HMA)(DVB) (copolymer), 115859-48-8; sodium dihydrogen phosphate, 7558-80-7; citric acid, 77-92-9; water, 7732-18-5.

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