Photonic Crystal Chemical Sensors: pH and Ionic Strength

Kangtaek Lee[†] and Sanford A. Asher*

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Received June 6, 2000

Abstract: Diffraction from a photonic crystal material composed of a hydrolyzed polymerized crystalline colloidal array (PCCA) can be used to sense pH and ionic strength. The PCCA is a polyacrylamide hydrogel which embeds a polystyrene crystalline colloidal array (CCA). The diffracted wavelength of the PCCA changes as the PCCA volume changes due to the alterations in the CCA lattice constant. We examine the pH and ionic strength dependence of the hydrolyzed PCCA volume by monitoring the Bragg diffracted wavelength. We also develop a zero free parameter quantitative model to describe the pH and ionic strength dependence of the hydrogel volume.

A major challenge to the fields of chemistry, physics, and materials science over the next decade is to utilize the increased potential richness of nano- and mesoscale materials, compared to small molecules, to create smart materials that can be used to fabricate complex and sophisticated devices. One especially useful class of materials results from the self-assembly of colloidal particles (Figure 1) to form crystalline colloidal arrays (CCA),[1,2] which can then be polymerized to form polymerized CCA (PCCA).[3] The CCA self-assembly results from electrostatic repulsion between monodisperse, highly charged colloidal particles, which forms a soft fluid material where the particles occur in a face-centered cubic or body-centered cubic array.[1,2] These CCA can form large single crystals which intensely Bragg diffract visible light.[1,2] Polymerizing an acrylamide hydrogel network around the CCA forms a highly unusual, soft material[4] that possesses all the rich volume-phase transition phenomenology of polymer gels.[5] It also contains a periodic lattice whose Bragg diffraction sensitively reports on the hydrogel volume.[4]

These CCA and PCCA are examples of photonic crystal materials, which hold the promise to serve numerous applications in optics and physics.[6] Our group demonstrated the first CCA photonic crystal application in 1984, where we fabricated large CCA single crystals for use as optical filters for spectroscopic instrumentation.[2] More recently, we demonstrated the use of PCCA for nanosecond optical switching and optical limiting[7] and demonstrated that these materials could be used for chemical sensing applications.[4] We attached, for example, crown ethers to the PCCA hydrogel to selectively bind Pb^{2+} ions. The binding of Pb^{2+} cations to the crown ether−hydrogel formed a new class of soft materials known as ionic gels.

This immobilization of cations localizes their counterions, which results in a Donnan potential, which creates an osmotic pressure, which swells the hydrogel in proportion to the Pb^{2+} bound. This results in Bragg diffraction shifts that sense the concentration of Pb^{2+} in solution, for example. These photonic crystal sensing materials have the potential utility to sense any analyte, provided recognition elements can be synthesized and attached to the hydrogel to couple analyte binding to hydrogel volume-phase transitions.

Even though hydrogels play a central role in chemistry, biology, and medicine, a fundamental understanding of their volume-phase transitions is incomplete, despite years of extensive theoretical and experimental investigations.[5,8−16] This is especially unfortunate since workers such as Tanaka and others have demonstrated an increasingly rich volume-phase transition phenomenology of hydrogels which potentially can be used for artificial muscles, actuators, etc.[5,8,9]

One major hurdle faced by previous investigations was the difficulty of measuring volume changes and the requirement for macroscopic hydrogels to have sufficient measurement precision. Thus, perturbations of the hydrogel environment required long incubation times for diffusion to reach equilibrium.

* To whom correspondence is to be addressed: (phone) 412-624-8570; (fax) 412-624-0588; (e-mail) asher+@pitt.edu.

[†] Present address: Department of Chemical Engineering, Inje University, 607 Obangdong, Kimhae, Kyongnam, 621-749, Korea.

(1) Krieger, I. M.; O'Neill, F. M.; *J. Am. Chem. Soc.* **1968**, *90*, 3114−3120. Hiltner, P. A.; Krieger, I. M.; *J. Phys. Chem.* **1969**, *73*, 2386−2389.

(2) Carlson, R. J.; Asher, S. A. *Appl. Spectrosc.* **1984**, *38*, 297−304. Flaugh, P. L.; O'Donnell, S. E.; Asher, S. A. *Appl. Spectrosc.* **1984**, *38*, 847−849. Asher, S. A. U.S. Patent 4,627,689, 1986.

(3) Asher, S. A.; Holtz, J. H.; Liu, L.; Wu, Z.; *J. Am. Chem. Soc.* **1994**, *116*, 4997−4998. Asher, S. A. U.S. Patent 5,281,370, 1994.

(4) Holtz, J. H.; Asher, S. A.; *Nature* **1997**, *389*, 829−832. Holtz, J. H.; Holtz, J. S. W.; Munro, C. H.; Asher, S. A. *Anal. Chem.* **1998**, *70*, 780−791. Asher, S. A.; Holtz, J. H. U.S. Patent 5,854,078, 1998.

(5) Tanaka, T. *Sci. Am.* **1981**, 244, 124−138. in *Structure & Dynamics of Biopolymers*; Nicolini, C., Ed.; NATO ASI Ser. E; NATO: Dordrecht, 1986; pp 237−257 and references therein.

(6) Joannopoulos, J. D.; Meade, R. D.; Winn, J. N. *Photonic Crystals: Molding the Flow of Light*; Princeton University Press: Princeton, NJ, 1995.

(7) Pan, G.; Kesavamoorthy, R.; Asher, S. A. *Phys. Rev. Lett.* **1997**, *78*, 3860−3863.

(8) Annaka, M.; Tanaka, T. *Nature* **1992**, *355*, 430−432. Mafe, S.; Manzanares, J. A.; English, A. E.; Tanaka, T. *Phys. Rev. Lett.* **1997**, *79*, 3086−3089.

(9) English, A. E.; Tanaka, T.; Edelman, E. R. *J. Chem. Phys.* **1997**, *107*, 1645−1654. English, A. E.; Tanaka, T.; Edelman, E. R. *Polymer* **1998**, *39*, 5893−5897.

(10) Dusek, K.; Patterson, D. *J. Polym. Sci.* **1968**, *A-26*, 1209−1216. Dusek, K. *J. Polym. Sci.: Symp.* **1973**, *42*, 701−712. Hasa, J.; Ilavsky, M.; Dusek, K. *J. Polym. Sci.: Polym. Phys. Ed.* **1975**, *13*, 253−262.

(11) Konak, C.; Bansil, R. *Polymer* **1989**, *30*, 677−680.

(12) Marchetti, M.; Prager, S.; Cussler, E. L. *Macromolecules* **1990**, *23*, 1760−1765. Marchetti, M.; Prager, S.; Cussler, E. L. **1990**, *23*, 3445−3450.

(13) Baker, J. P.; Hong, L. H.; Blanch, H. W.; Prausnitz, J. M. *Macromolecules* **1994**, *27*, 1446−1454.

(14) Kudaibergenov, S. E.; Sigitov, V. B. *Langmuir* **1999**, *15*, 4230−4235.

(15) Ilavsky, M. *Macromolecules* **1982**, *15*, 782−788.

(16) Janas, V. F.; Rodriguez, F.; Cohen, C. *Macromolecules* **1980**, *13*, 977−983.

10.1021/ja002017n CCC: $19.00
Published on Web 09/13/2000

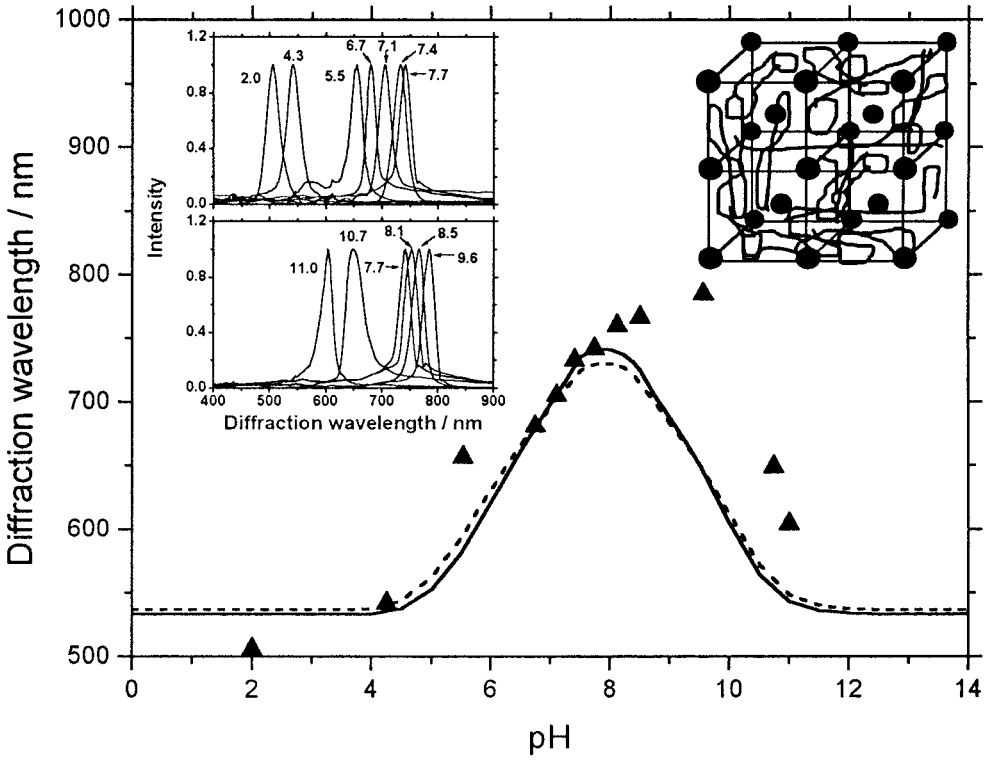

Figure 1. Inset, upper right: a PCCA where the colloidal particles occur in a cubic array embedded within an acrylamide hydrogel. The pH dependence of the hydrolyzed PCCA diffraction wavelength (see the inset on the upper left) is shown by the triangles. The solid line was calculated from the affine model and the broken line from the phantom model.

In the work here, we use Bragg diffraction from carboxylated PCCA hydrogels to monitor their volume-phase transitions in response to pH and ionic strength changes. This work follows the previous studies by Tanaka and others, which clearly demonstrated the pH and ionic strength dependence of the ionic gel volumes.[5,8,9] We also measured the Young's modulus of the hydrogel from the PCCA Bragg diffraction to determine the elastic restoring forces.[12,17] We describe here a detailed hydrogel volume-phase model which accurately models swelling with no adjustable parameters. Finally, the results demonstrate that our carboxylated PCCA photonic crystals are excellent pH and ionic strength sensors.

Experimental Section

The PCCA was prepared by dissolving 5 wt % acrylamide, 0.5 wt % *N*,*N*′-methylenebisacrylamide, and 20 μL of diethoxyacetophenone in a liquid CCA solution (~8 wt % colloids) prepared from 100-nm-diameter highly charged (sulfonated) monodisperse polystyrene colloids. This mixture was injected between two quartz plates separated by a 125-μm-thick Parafilm spacer and was photopolymerized with 365-nm illumination. The PCCA was removed from between the quartz plates and washed with water, and the amide groups in the PCCA were partially hydrolyzed by a 3-min treatment with 1 N sodium hydroxide containing 10 wt % *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED; Sigma). The PCCA was then extensively washed with deionized water. Diffraction spectra were measured by using a reflectance fiber-optic probe coupled to a SI 400 (Spectral Instruments, Inc.) UV−visible spectrophotometer.

The experimental stochastic error in the diffraction measurements derives from ~10-min fluctuations in the sample diffraction, which appears to mainly result from IPCCA flexing associated with the solution movement. We expect a < 2-nm standard deviation in the wavelength maximum measurement.

Results and Discussion

We used Braggs law to relate the diffracted wavelength to the lattice spacing and to the hydrogel volume. The use of the simple Braggs law relationship should lead to insignificant error.[25]

Figure 1 shows the pH dependence of the hydrolyzed PCCA diffraction. At normal incidence, the hydrolyzed PCCA in deionized water at pH 6.7 diffracts 681-nm light. As the pH increases from neutrality, the diffraction monotonically red shifts until pH 9.6, whereupon it blue shifts with further pH increases; by pH 11, the diffraction blue shifts to 604 nm. The diffraction monotonically blue shifts as the pH decreases from pH 6.7 until 506-nm light is diffracted at pH 2.0. The diffraction peaks remain symmetric and relatively narrow for all pH values, which indicates preservation of ordering of the CCA as the gel volume changes.

The pH dependence of diffraction shown in Figure 1 results from the ionic gel response to changes in protonation and ionic strength. When the PCCA is hydrolyzed, some amide groups hydrolyze to carboxyl groups, which ionize as determined by their pK_a and solution pH. Ionization of these covalently attached carboxyl groups immobilizes counterions inside the gel. This results in an osmotic pressure, which swells the gel against its restoring elastic constant.[18] Thus, an increased pH increases the ionization; the gel swells and the diffraction red shifts. Since ionization is complete by pH 9, further pH increases only increase ionic strength. This decreases the osmotic pressure and shrinks the gel. This maximum in hydrogel volume, which occurs near pH 8.5, has also been observed for other ionic gels.[8,14]

The ionic strength dependence of diffraction was studied by using pH 6.7 and 8.5 solutions containing 1 mM NaCl. These solutions have ionic strengths essentially identical to that of the pH 11 solution titrated using a minimum amount of NaOH. Figure 2 shows that the increased ionic strength shrinks the hydrolyzed PCCA and blue shifts the diffraction to a value close to that from the pH 11 solution.

For nonionic gels, the hydrogel volume is determined by only the free energy of mixing of the polymer and the solvent, ΔG_M, and the counterbalancing free energy associated with network elasticity, ΔG_E.

(17) Mark, J. E.; Erman, B. *Rubberlike Elasticity, A Molecular Primer*; John Wiley & Sons: New York, 1988; pp 29−52.

(18) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; pp 432−594.

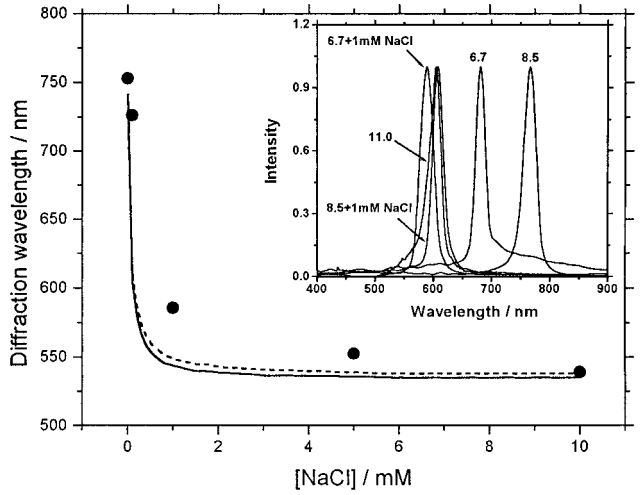

Figure 2. Inset, upper right: ionic strength dependence of the hydrolyzed PCCA diffraction spectra at three different pHs. The ionic strength dependence of the hydrolyzed PCCA diffraction wavelength is shown by the circles (at a constant pH of 8.1). The solid line was calculated from the affine model and the broken line from the phantom model.

Thus, the total free energy, ΔG_T is[18]

$$\Delta G_T = \Delta G_M + \Delta G_E \tag{1}$$

where

$$\Delta G_M = k_B T[n \ln(1-\phi) + n\chi\phi] \tag{2}$$

where k_B, T, n, χ, and ϕ are the Boltzmann constant, the temperature, the number of solvent molecules in the gel, the Flory−Huggins polymer/solvent interaction parameter, and the polymer volume fraction in the swollen network, respectively.

The elastic free energy has been modeled using both affine and phantom network models.[17−19] In the phantom model, cross-links freely fluctuate and are unaffected by neighboring chains, while in the affine model, cross-links are assumed to be embedded in the network. The elastic free energy change is[17−19]

$$\Delta G_E = \frac{3k_B T\nu_e}{2V_m}\left[\left(\frac{V}{V_m}\right)^{2/3} - 1 - \frac{1}{3}\ln\left(\frac{V}{V_m}\right)\right] \quad \text{affine model}$$

$$= \frac{3k_B T\nu_e}{4V_m}\left[\left(\frac{V}{V_m}\right)^{2/3} - 1\right] \quad \text{phantom model} \tag{3}$$

where ν_e is the effective number of the cross-linked chains in the network; V_m and V are the volumes of the prepared gel (before washing) and the swollen gels, respectively. A critical assumption used here is that the hydrogel polymerization occurred under conditions where the cross-linked chain length distribution is in its statistically most probable configurations such that the gel is not under any stress ($\Delta G_E = 0$).

We determined the hydrogel cross-link density (ν_e/V_m) from the hydrogel stress−strain relationships.[20] The $\nu_e/V_m = 1.46 \times 10^{-3}$ M for the affine model and 2.92×10^{-3} M for the phantom model. This indicates only a 2.25 (affine) or 4.5% (phantom) cross-linking efficiency.

The change in volume upon immersion of the prepared PCCA into water induces mixing and elastic free energy changes; the extent of swelling is determined through the equalization of the water chemical potential to that of bulk water. The osmotic pressure is defined as

$$\Pi = \frac{-(\mu_{H_2O} - \mu^0_{H_2O})}{V_{H_2O}} = \frac{-(\partial\Delta G/\partial n)}{V_{H_2O}} \tag{5}$$

where V_{H_2O} is the molar volume of water.

The expressions for osmotic pressure arising from mixing and network elasticity are[18]

$$\frac{\Pi_M}{RT} = -\frac{1}{V_{H_2O}}\left[\ln\left[1 - \left(\frac{\lambda_0}{\lambda}\right)^3\right] + \left(\frac{\lambda_0}{\lambda}\right)^3 + \chi\left(\frac{\lambda_0}{\lambda}\right)^6\right] \tag{6}$$

$$\frac{\Pi_E}{RT} = -\frac{\nu_e}{V_m}\left[\left(\frac{\lambda_m}{\lambda}\right) - \frac{1}{2}\left(\frac{\lambda_m}{\lambda}\right)^3\right] \quad \text{affine model}$$

$$= -\frac{\nu_e}{2V_m}\left(\frac{\lambda_m}{\lambda}\right) \quad \text{phantom model} \tag{7}$$

where we made use of the fact that $\phi = (V_0/V) = (\lambda_0/\lambda)^3$. V_0 is the dry polymer volume and the λ_0 and λ are the diffracted wavelengths for dry and swollen gels, respectively. The λ_0 was calculated to be 178 nm from the polymer volume fraction at preparation ($\phi_m = (\lambda_0/\lambda_m)^3$, polymer density, 1.302 g/cm^3).

At equilibrium, the total osmotic pressure (Π_T), which is the sum of osmotic pressures from mixing (Π_M) and network elasticity (Π_E), must be zero:[18]

$$\Pi_T = \Pi_M + \Pi_E = 0$$

$$\frac{\Pi_M}{RT} = -\frac{\Pi_E}{RT} \tag{8}$$

Thus, using eqs 6 and 7, we determined that the Flory−Huggins interaction parameter, $\chi = 0.503$ for the affine model (0.493 for the phantom model), which is somewhat higher than previously measured values for pure polyacrylamide gels (0.48−0.49),[15,16] presumably due to the presence of the hydrophobic polystyrene colloids.

After hydrolysis, we observe a pH-dependent swelling of the PCCA arising from an osmotic pressure (Π_{Ion}) due to the difference in mobile ion concentration inside and outside the gel.[18] Thus, total osmotic pressure becomes

$$\Pi_T = \Pi_M + \Pi_E + \Pi_{ion} \tag{9}$$

Since the sum of cation and anion electrolyte stoichiometries inside the gel, $\nu = 2$ and $z_- = 1$:

$$\frac{\Pi_{ion}}{RT} = \frac{iC_p}{z_-} - \nu(C_s^* - C_s) = -2C_s^*\eta \tag{10}$$

where i is the degree of carboxyl ionization multiplied by its charge, C_p is the carboxyl concentration, C_s and C_s* are the mobile ion concentrations within and outside the gel, K_a is the carboxyl dissociation constant, C_T is the total concentration of carboxyl groups inside the PCCA, and $\eta = (C_s^* - C_s)/C_s^*$.

(19) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720−5729.

(20) We used a stress−strain method similar to the previous studies[12,17] to determine the cross-link density. The stress, τ is related to the linear strain α as

$$\tau = \frac{\nu_e}{V_m}RT(\alpha - \alpha^{-2}) \quad \text{affine model}$$

$$= \frac{\nu_e}{2V_m}RT(\alpha - \alpha^{-2}) \quad \text{phantom model} \tag{4}$$

where R is the ideal gas constant. We determined $\alpha = \lambda/\lambda_m$ from the diffraction wavelength shift due to loading of an unhydrolyzed PCCA film with weights. The ratio $\tau/(\alpha - \alpha^{-2})$ is used to determine ν_e/V_m.

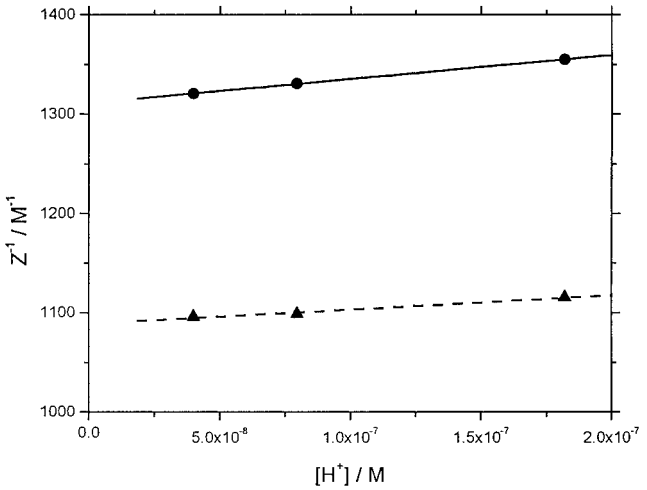

Figure 3. Plot of pH dependence of Z^{-1}. The circles represent the affine model and the triangles the phantom model. See text for details.

At equilibrium, the total osmotic pressure (Π_T) must be zero. Thus,[21]

$$\frac{\Pi_{ion}}{RT} = -\frac{1}{RT}(\Pi_M + \Pi_E) = Z = \frac{K_a C_T}{K_a + [H^+]} - 2C_s^*\eta \qquad (12)$$

We can determine K_a and C_T from the pH dependence of the PCCA swelling.[22] The value of K_a is ~3-fold smaller than that of acetic acid in water ($K_a = 1.76 \times 10^{-5}$ M), due to the decreased acidity expected for sterically hindered carboxylic acids.[23]

(21) Z is defined as

$$Z = -\frac{(\Pi_M + \Pi_E)}{RT}$$

$$= \frac{1}{V_{H_2O}}\left[\ln\left[1 - \left(\frac{\lambda_0}{\lambda}\right)^3\right] + \left(\frac{\lambda_0}{\lambda}\right)^3 + \chi\left(\frac{\lambda_0}{\lambda}\right)^6\right] + \frac{\nu_e}{V_m}\left[\left(\frac{\lambda_m}{\lambda}\right) - \frac{1}{2}\left(\frac{\lambda_m}{\lambda}\right)^3\right]$$

affine model

$$= \frac{1}{V_{H_2O}}\left[\ln\left[1 - \left(\frac{\lambda_0}{\lambda}\right)^3\right] + \left(\frac{\lambda_0}{\lambda}\right)^3 + \chi\left(\frac{\lambda_0}{\lambda}\right)^6\right] + \frac{\nu_e}{V_m}\left(\frac{\lambda_m}{\lambda}\right)$$

phantom model (11)

(22) We can determine K_a and C_T by analyzing the swelling data between pH 6.5 and 7.5. In this pH range, the last term of eq 12 is negligible (~10^{-7}). Taking the inverse of both sides

$$\frac{[H^+]}{K_a C_T} + \frac{1}{C_T} = Z^{-1} \qquad (13)$$

Z is calculated from the measured λ of the hydrolyzed gel and λ_m of the unhydrolyzed gel. A plot of Z^{-1} vs [H$^+$] gives a slope of $1/K_aC_T$ and intercept of $1/C_T$. Figure 3 shows the plot of Z^{-1} vs [H$^+$] between pH 6.5 and 8.5 for our hydrolyzed PCCA. From the slopes and intercepts, we calculated C_T and K_a (Table 1). The value of C_T indicates only ~0.1% hydrolysis of the PCCA amides.

(23) Hammond, G. S.; Hogle, D. H. *J. Am. Chem. Soc.* **1955**, *77*, 338−340.

Table 1. Total Concentration of the Carboxylic Acid Groups (C_T) and the Carboxylic Acid Dissociation Constant (K_a) in the Hydrolyzed PCCA, Calculated from the Slopes and Intercepts in Figure 3

fit params and calcd values	model	
	affine	phantom
slope (M^{-2})	2.41×10^8	1.41×10^8
intercept (M^{-1})	1311.6	1089.3
K_a (M)	5.4×10^{-6}	7.7×10^{-6}
C_T (M)	7.6×10^{-4}	9.2×10^{-4}

Using the parameters calculated above, we can determine η,[24] which allows us to model the pH dependence of the PCCA volume changes and concomitant diffraction wavelength shifts. Figure 1 compares the measured and calculated diffraction wavelength shifts for both the affine and phantom models. These models fit the measured diffracted wavelength shifts reasonably well and predict the observed diffracted wavelength maximum near pH ~8. Note that the affine and phantom models give similar results. The observed discrepancy, where the midpoint of the observed swelling peak occurs at pH 9, probably results from a pH-dependent pK_a or an increased pK_a for buried carboxyl groups. In Figure 2, we also tested our model when the electrolyte concentration was varied at constant pH of 8.1. Figure 2 shows that our model can successfully describe the ionic strength response of the hydrolyzed PCCA.

Thus, we have developed a model that can predict the pH and ionic strength dependence of hydrogel swelling as well as the concomitant diffraction changes. This will be helpful for the design of these types of materials for optimal sensing of pH and ionic strengths. The pH sensors can be optimized for different spectral regions by choosing species which ionize in particular pH regimes. We can optimize these materials for ionic strength sensing by using species whose ionization show no pH dependence. One of the more useful aspects of these materials is that they can be fabricated to be very small. In principle. it is possible to detect diffraction from ~1 μm^3 volumes. These sensors could be placed within cells, for example, to dynamically study pH and ionic strengths.

We have demonstrated a new pH and ionic strength sensor which utilizes a photonic crystal material known as a hydrolyzed PCCA. We have also extended Flory's classical ionic polymer swelling model[18] in order to develop a zero parameter model for the PCCA hydrogel volume response. This model allows us to predict the pH and ionic strength dependence of hydrogel PCCA diffraction.

Acknowledgment. We thank the National Science Foundation, the Office of Naval Research (Grant N00014-94-1-0592), and the Department of Energy (Grant DE-FG07-98ER62708) for financial support.

JA002017N

(24) We calculate η from 18

$$(1 - \eta)^2 + Y(1 - \eta) - 1 = 0 \qquad (14)$$

where

$$Y = \frac{K_a C_T}{C_s^*(K_a + [H^+])}$$

(25) Rundquist, P. A.; Photinos, P.; Jagannathan, S.; Asher, S. A. *J. Chem. Phys.* **1989**, *91* (8), 4932−4941.