Novel Model Networks of Poly(acrylic acid): Synthesis and Characterization

Adi Shefer,[†] Alan J. Grodzinsky,*[,†] Kevin L. Prime,[‡] and Jean-Pierre Busnel[§]

Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138, and Laboratoire de Chimie et Physicochimie Macromoleculaire, Unité associee au CNRS, Université du Maine, 72017 Le-Mans Cedex, France

Received November 2, 1992; Revised Manuscript Received May 28, 1993

ABSTRACT: Model polyelectrolyte networks having controllable and independently known structural characteristics were prepared from different molecular weights of α,ω-amino-terminated poly(acrylic acid), by cross-linking them with a trifunctional isocyanate coupling agent. The density of cross-links, average molecular weight between cross-links, and the functionality of the cross-link points of these networks have been characterized. The swelling behavior of these novel networks was studied as a function of bath pH and ionic strength and the results were interpreted in term of structure–property relationships of the polymeric compounds. The maximum hydration was achieved at values of pH greater than 7. Hydration was linearly dependent upon the average molecular weight between cross-links, $\bar{M}_c$. The hydration relative to this maximum value, $H_{rel} = H/H_{max}$, was a function of pH but not of $\bar{M}_c$. The relative hydration, H_{rel}, and fraction of carboxyl groups ionized, α, were similar functions of the pH of the equilibrating solution. In previous studies, on randomly cross-linked polyelectrolyte networks, $\bar{M}_c$ could not be directly characterized by experimental measurements and has been inferred using theoretical models. In this study, we have directly related the network structural parameters, which were imposed by the synthetic route used and confirmed experimentally, to the macroscopic swelling behavior observed without invoking any theoretical models.

Introduction

Polyelectrolyte networks, a subclass of hydrogels, capable of swelling in contact with water,[1] have received significant attention in recent years due to their exceptional promise to biomedical[2–5] and biotechnological[6,7] applications. The initial work on charged polymers and gels was performed by Katchalsky and co-workers.[8,9] Tanaka and collaborators described the behavior of ionic and natural gels and made additional contributions to theory.[1,10–12] A number of research groups have studied the swelling and mechanical properties of polyelectrolyte networks in recent years.[13–15] In all of these cases, the networks were formed by the free-radical copolymerization of two vinyl-derived monomers, one of which contained an additional polymerizable double bond. This process is random: the cross-links are introduced between chain segments in an indiscriminate, essentially uncontrolled manner.[16–20] As a result, there is no independent knowledge of the crucially important average molecular weight between cross-links, $\bar{M}_c$, and the distribution about this average. Furthermore it is impossible to vary the cross-link functionality, since the joining of a pair of segments from two chains will almost invariably give a junction of functionality four. Characterization and interpretation of structure–property relationships of these materials was therefore exceedingly difficult. Thus, an obvious solution to the problem would be the preparation of "model" polyelectrolyte networks, i.e., polyelectrolyte networks having controllable and independently known structural characteristics. The preparation of such networks is essential to elucidate structure–property relationships in these polymeric systems.

Model networks of well-defined structure have been employed widely in studies of the structure–property relations of elastomers[21–40] and in tests of physical theories of the properties of cross-linked materials.[41–43] The end-linking reaction is a well-known synthetic route to "model" networks—networks that provide access to the molecular and structural characteristics of the elastic chain.[1,2] In end-linking one starts from an end-functional polymer chain of known molecular weight which is reacted stoichiometrically with multifunctional molecules of known functionality. This type of process is basically a cross-linking polycondensation reaction; upon reaction, the chains of the end-functional polymer become the elasticity effective network chains. The network thus obtained is well defined. Model networks are particularly useful to study structure–property relationships; not only is the number of elastic chains and their molecular weight equal to the number of polymer molecules inserted but also the functionality of the cross-link points is given by the functionality of the cross-linking agent used.[21,22] Thus, end-linked networks provide the structural information necessary to determine structure–property relationships in a particularly straightforward way.

Model end-linked networks based on neutral polymers have been prepared and studied thoroughly. Model end-linked polydimethylsiloxane networks have been prepared and studied extensively by Mark and co-workers.[19,20,23–33] Polyurethane model networks were prepared by the end-linking of hydroxyl-terminated chains with multifunctional isocyanate agents.[34–38] Similarly, model polyisobutylene and polystyrene networks were also prepared.[39,40] Although polyelectrolyte networks are of both practical and theoretical interest, their structure–property relationships have not been completely established, and no corresponding end-linked networks of polyelectrolyte chains have been reported.

The objective of this work was to prepare model end-linked poly(acrylic acid) networks, study their swelling behavior and relate it to network structure. We accomplished this goal by end-linking α,ω-poly(acrylic acid)–bis(4-aminophenyl sulfide) (pAA–bAPS)[45] with the tri-

* To whom correspondence should be addressed.
† Massachusetts Institute of Technology.
‡ Harvard University.
§ Université du Maine.

0024-9297/93/2226-5009$04.00/0

isocyanato cross-linking agent, tris(4-isocyanatophenyl)methane (TPIM). Poly(acrylic acid) has chain units of simple structure; networks formed from it could provide useful models for the behaviors and properties of more complex synthetic and biological networks.

Experimental Section

Materials. α,ω-Poly(*tert*-butyl acrylate)-bis(4-aminophenyl sulfide) (pTBA-APS) was prepared by techniques we have described elsewhere.[45] Dimethyl sulfoxide (DMSO, anhydrous, analytical grade, Aldrich) was used immediately after opening the bottle without further treatment. Hexane (Aldrich) and hexadecyltrichlorosilane (Petrarch) were used as received. Tris-(4-isocyanatophenyl)methane (Desmodur R-E) was the kind gift of Miles Polysar and was used in the form received, which was a 27 wt % solution in ethyl acetate. The number-average functionality of the cross-linker was determined by the manufacturer to be 3.01.

Preparation of Glassware for Cross-Linking. Vials and molds in which cross-linking reactions were to be performed were first made hydrophobic by treatment with hexadecyltrichlorosilane. The glassware was dried in an oven at 120 °C prior to treatment. The glassware was removed from the oven and placed hot into a solution of hexadecyltrichlorosilane (1 wt %) and mineral oil. After 30 min, the glassware was removed from the solution, rinsed several times with hexane, and then immersed in a hexane bath. This hexane bath was immersed in turn in an ultrasonic water bath for 15 min. The treated glassware was then removed from the hexane, allowed to dry, and placed in the oven for another 30 min to allow the silane film to condense fully. The glassware could then be stored at room temperature in the laboratory ambient without becoming significantly moistened by contact with the air.

Network Formation. pAA-bAPS was freeze-dried in a hydrophobic vial for 24 h prior to cross-linking. Fresh DMSO (2 g/g of polymer) and a catalytic amount of pyridine were added to the vial under nitrogen; the polymer dissolved. TPIM (0.67 mol/mol of polymer) was added to the vial under nitrogen. This stoichiometry provided one isocyanate group for each amino group on the polymer chains. The solution was swirled to mix the reagents thoroughly and then allowed to stand at room temperature. Gelation was observed within 30 min. The reaction was allowed to proceed for 48 h in order to ensure complete conversion. Membranes were formed using the same method, except that two hydrophobic glass plates separated by a 1-mm Teflon ring were used to contain the reaction mixture. After the reaction was complete, the plates were separated using a razor blade and the membranes were removed from the glass plates by swelling them in deionized water.

We verified the complete consumption of the cross-linker by infrared spectroscopy. Isocyanates absorb strongly at 2300 cm^{-1}; after cross-linking, the membranes did not absorb in that region of the spectrum. The infrared spectra were obtained by transmission through a thin film of the neat membrane using a Nicolet 205 FT-IR spectrometer.

Solid-state NMR spectra of the membranes were obtained by cross-polarized magic-angle spinning in a Chemagnetics CMC200A spectrometer with a 7-mm probe spinning at ≈3 kHz. The densities of the membranes were determined by measuring the rejected volume of cyclohexane by a known weight of the dry membrane.

Equilibrium Swelling of the Membranes. Each membrane was swollen in 50-mM KCl for approximately 1 week and then cut while wet into 2-cm disks. Each disk of gel was placed in a bath at a specified pH and ionic strength and allowed to equilibrate, which took about 2 weeks. The disks were then removed from the baths, blotted with tissue paper to remove all surface fluid, and weighed (the swollen weight). The samples were then washed in deionized water for 2 days to remove salts, dried under vacuum, and weighed again (the dry weight).

Membrane Titration Curves. The concentration of carboxylic groups in the membrane was determined as a function of pH by titration. The experimental procedure has been described elsewhere.[46] In order to minimize buffering by CO_2, the titration was carried out under an atmosphere of nitrogen that had been passed through a concentrated, aqueous solution of NaOH. Titration was performed in a degassed solution of KCl (50 mM, 100.0 mL). The membrane (0.5 g) was suspended in the KCl solution, and the pH of the solution was raised to 12 using a measured volume of a standard solution of KOH. The membrane was then broken into small fragments. The titration was performed by the addition of aliquots of 1.0 M HCl. The pH of the solution was monitored with an Orion Ross electrode. The measurements were taken after stirring was stopped and the reading from the pH electrode was stable.

Results and Discussion

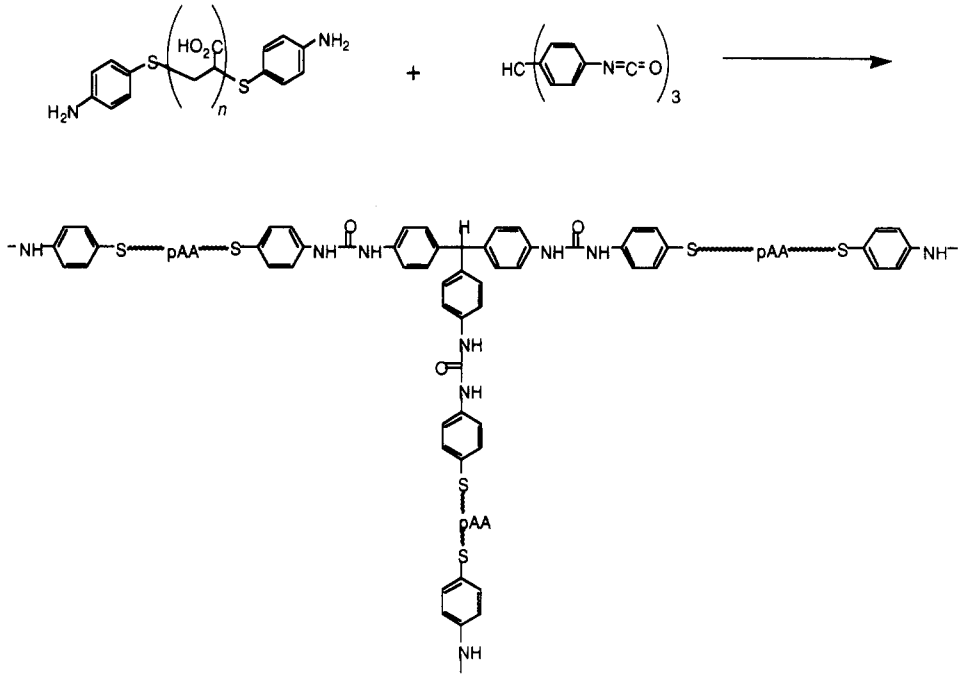
Structure of the Cross-Linked Networks. The synthesis of well defined model polyelectrolyte networks by the end-linking reaction requires a polyelectrolyte fitted quantitatively at the chain end with a known function that can be reacted selectively by a multifunctional cross-linker. Direct telomerization of polyelectrolytes by free-radical reaction is often not straightforward due to their high chain propagation rate and termination mechanism.[44]

Our approach[45] to the synthesis of terminally functionalized poly(acrylic acid) involved the telomerization of the protected monomer, *tert*-butyl acrylate, followed by the removal of the protecting group from the resulting polymer. Free-radical telomerization of *tert*-butyl acrylate was carried out in bulk, with α,α'-azobis(isobutyronitrile) (AIBN), in the presence of the functional "iniferter" (*ini*tiator trans*fer ter*minator agent), bis(4-aminophenyl)-disulfide. The molecular weights of the polymers were determined by size-exclusion chromatography (SEC) measurements, and the number of amino groups per chain was determined by end-group analysis. The poly(*tert*-butyl acrylate) was then hydrolyzed quantitatively to poly-(acrylic acid) under acidic conditions. The complete removal of the *tert*-butyl groups was confirmed by ^1H- and ^{13}C-NMR spectroscopy. Poly(acrylic acid) of controlled molecular weight having amino groups at both ends of the chain was obtained.[45]

Amines react with isocyanates to form ureas.[21] Scheme I presents the reaction of pAA-bAPS with TIPM that we used to cross-link the networks. The spectroscopic evidence is consistent with the occurrence of this reaction. Figure 1 shows that the solid-state ^{13}C-NMR spectra of the end-linked networks contained, in addition to peaks derived from poly(acrylic acid), peaks at 130–140 ppm corresponding to aromatic carbons, which could have arisen from the chain termini, the cross-linker, or—most likely—both. We expected that the isocyanate cross-linking groups would react so rapidly with the amino termini of pAA-bAPS that cross-linking would occur exclusively at the chain termini and not at any weakly nucleophilic carboxylate groups present. No spectroscopic technique available to us could quantify the relative numbers of the desired ureas and undesired carbamates, so direct evidence is lacking. However, we believe that the swelling data presented below provide convincing evidence that cross-linking occurred predominantly, if not exclusively, at the chain termini. We shall return to that question when those data are presented.

Swelling of the Networks. That the pH and ionic strength of contacting solutions have a profound effect on the swelling of polyelectrolyte networks has been known for some time.[8-14] Kuhn and co-workers[47] showed that the pH of the surrounding solution controlled the degree of ionization of cross-linked gels of poly(methacrylic acid) and of poly(acrylic acid). One of our laboratories has studied extensively the chemically and electrically controlled swelling of membranes formed from the copolymerization of methacrylic acid and ethylene glycol dimeth-

Scheme I. Cross-linking of pAA–APS with Tris(4-isocyanatophenyl)methane



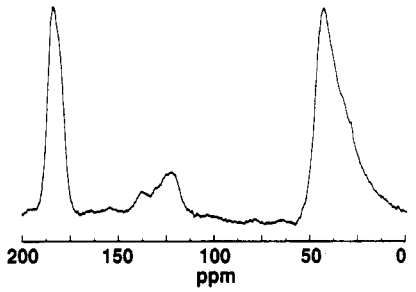


Figure 1. Solid-state CP/MAS ^{13}C-NMR spectrum of the end-linked poly(acrylic acid) network revealing the presence of aromatic carbons in the APS and TIPM residues. The peaks between 100 and 150 ppm corresponded to aromatic carbons. The peaks between 25 and 50 ppm and between 175 and 200 ppm corresponded to the poly(acrylic acid) chain.

acrylate.[6,48,49] Changes in the pH of the contacting solution affect swelling by changing the interchain electrostatic repulsion:[50] networks with more charge per chain swell more than those with less charge per chain. Changes in the ionic strength affect the Debye shielding of the charged group:[50] higher ionic strengths lead to more screening, less interchain repulsion, and less swelling than lower ionic strengths.

The swelling of hydrogels is normally reported in terms of hydration, H, defined as the ratio of fluid volume, V_w, to the solid volume of the network, V_m:[3,6,7]

$$H = V_w/\bar{V}_m \tag{1}$$

Thus, the total volume, V, can be written as

$$V = V_w + V_m = (1 + H)V_m \tag{2}$$

The value of H can be related to the wet and dry weights of the membrane by

$$H = \frac{W_t - W_d}{W_d}\left(\frac{\rho_m}{\rho_w}\right) \tag{3}$$

where W_t is the total (wet) weight, W_d is the dry weight of the membrane, ρ_m is the density of the network, and ρ_w is the density of the fluid. We measured $\rho_m = 1.255$ g/cm^3, and ρ_w for water is 1.00 g/cm^3.

Effect of pH on Swelling. We measured the wet and dry weights of different membranes that had been equilibrated with aqueous solutions of different pH values. Each solution had the same ionic strength. The pH of the surrounding solution had a pronounced effect upon the swelling of the network. The swelling was reversible and without hysteresis: the size of a membrane was determined by the pH, and not the past history of the membrane.

Figure 2 presents the equilibrium hydration of the different networks as a function of the pH of the surrounding solution. Two or three different membrane disks from each type of membrane (2-cm disks of 1-mm thickness) were equilibrated at each value of pH. Each data point in Figure 2 represents the mean of these values. The variation in hydration between disks that were equilibrated at the same pH value was less than 10%.

The hydration of these membranes increased dramatically between approximately pH 3 and 7 and remained almost constant above pH 7. The curves had the general shape of a titration curve, suggesting that the hydration was driven principally by the fraction of polymer-bound carboxylic acids that were deprotonated.

The maximum value of H, H_{max}, was a linear function of the molecular weight of the telomer used to prepare the network or, equivalently, of $\bar{M}_c$ (Figure 3). Had the chains been cross-linked to any significant extent between carboxyl groups, rather than at the chain termini, then the distribution of molecular weights between cross-links would have been random and unrelated to the molecular weight of the telomer. We therefore consider the data in Figure 3 to provide further substantial evidence that the chains were almost exclusively end-linked, as we suggested above.

The degree of hydration relative to the maximum value was almost independent of the molecular weight of the precursor telomer: relative hydration appeared to depend only upon the pH of the solution (Figure 4). Thus, the value of H/H_{max} for a given membrane increased by almost exactly an order of magnitude between pH 3 and pH 7, regardless of the molecular weight of the polymer.

Because the hydration data in Figures 2 and 4 had the general shape of titration curves, we decided to see how closely related the hydration was to the fraction of carboxyl

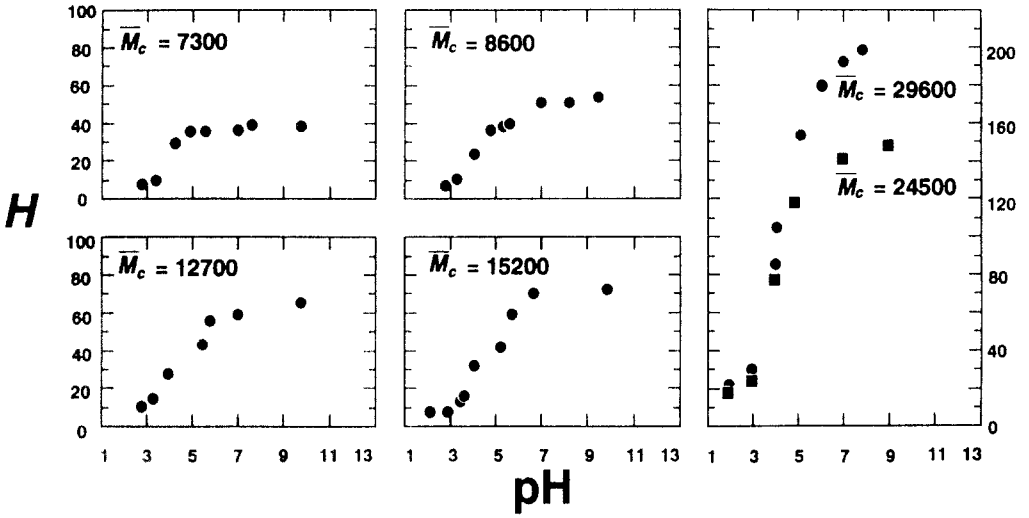


Figure 2. Strong dependence of hydration of poly(acrylic acid) membranes by aqueous solutions upon both the pH and the value of $\bar{M}_c$ for the membrane. The equilibrium hydration, H, defined as the ratio of the volume of water to the volume of membrane, is shown as a function of the pH of the contacting solution for membranes with different values of $\bar{M}_c$. The membranes were immersed in the contacting solutions for 2 weeks in order to reach an equilibrium hydration. The contacting solutions contained 50 mM KCl.

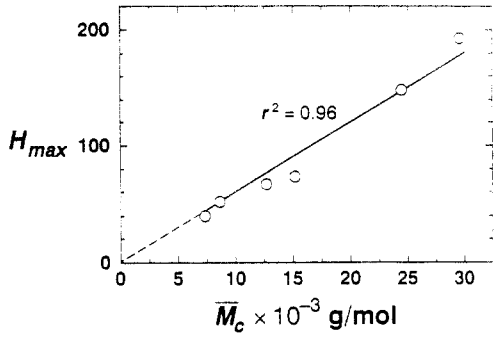


Figure 3. Maximum equilibrium hydration, H_{max}, of a membrane as a linear function of the value of $\bar{M}_c$ for the membrane. The line represents a least-squares fit to the function $H_{max} = m\bar{M}_c$. The zero intercept was imposed because negative values of H_{max} are not physically realistic. There was no significant difference in the quality of fits to the functions $H_{max} = m\bar{M}_c$ and $H_{max} = m\bar{M}_c + b$.

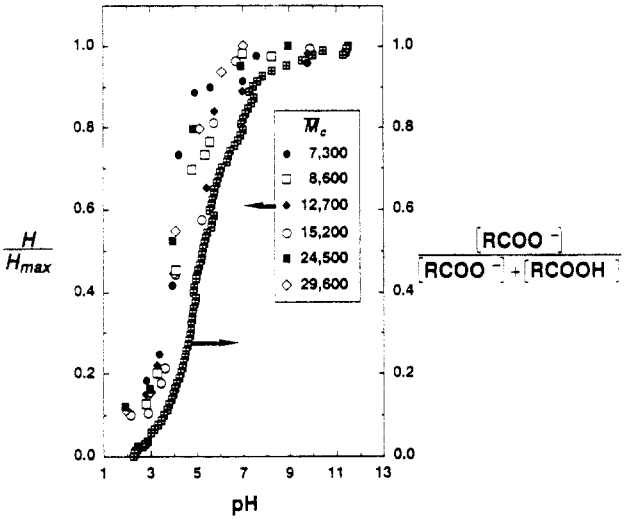


Figure 4. Relative hydration of a membrane, H/H_{max} as a function of pH but not of $\bar{M}_c$. The value of H/H_{max} increased by a factor of 10 between pH 2 and pH 12. Values of H/H_{max} as a function of pH are compared with values of α obtained by titration of the membranes. The two curves were nearly identical, demonstrating that the degree of hydration is strongly influenced by the state of ionization of the polymer chains.

groups that were ionized, α. We titrated the membranes using the procedure given in the Experimental Section and used that data to calculate the value of α as a function of pH. The equations permit the calculation of an absolute number of charges per unit of membrane. In this case, we have set $\alpha = 1$ to the number of charges obtained at pH = 11.5, which corresponded to approximately 14 mmol/dry g of membrane. This number almost certainly represented complete deprotonation of the carboxyl groups in the polymer.

The results of the titration are presented in Figure 4. The degree of ionization was essentially independent of the molecular weight of the telomer chains; one representative curve corresponding to data from the $\bar{M}_c = 8600$ membrane is presented. The degree of ionization was clearly very closely related to the relative hydration, although not perfectly. The relative hydration reached its half-maximum value in the pH range 4–5, while the degree of ionization reached its half-maximum value closer to pH 5. Nevertheless, the variation in the two properties was nearly parallel, suggesting that changes in the swelling of the polymer were almost entirely the result of changes in the number of charges born by each polymer chain.

Previous studies of the swelling of randomly cross-linked polyelectrolyte networks have shown the effect of fixed charge density on the swelling behavior of these networks.[6,7,10-14,48,49] Relationships between the swelling behavior and the network structural parameters had to be inferred using theoretical models.[3,13,14,16,49] In contrast, in this study the molecular parameters of these networks were imposed by the synthetic route used and confirmed experimentally. An important observation that has not previously been reported is the linear relationship between the maximum hydration and the molecular weight of the chains between the cross-link points. Further theoretical work is needed to better understand this observation and to relate the network structural parameters to the macroscopic swelling behavior of charged polymeric networks.

Effect of Ionic Strength upon Swelling. The ionic strength of the surrounding bath also plays an important role in determining the swelling of a polyelectrolyte network.[19,20,29] Dissolved ions modify both the Debye length within the membrane and the Donnan equilibrium between the membrane and the bath.[17,29] We examined the effect upon hydration of changes in the ionic strength at constant pH for three networks with different lengths between cross-links. The equilibrations were carried out at pH 7, so the observed values of H were equal to H_{max}.

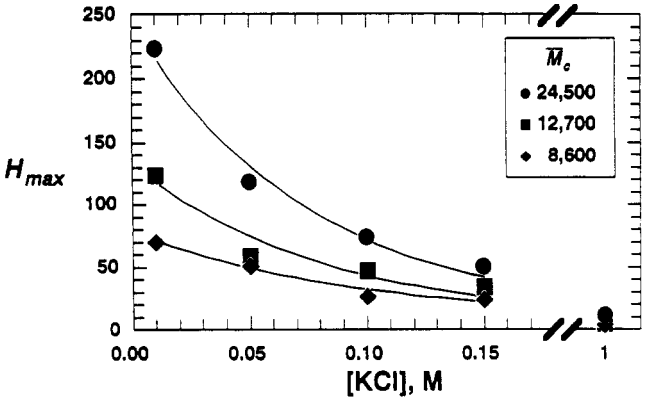


Figure 5. Hydration of a poly(acrylic acid) membrane decreasing exponentially with the ionic strength of the contacting solution at ionic strengths less than 0.30 ([KCl] = 0.15). The value of H is plotted as a function of [KCl] in the bath. The equilibration occurred at pH 7; the observed values of H were therefore equal to H_{max}. The curves represent least-squares fits to the equation $H - H_{min} = k_1 \exp(-k_2[KCl])$, where H_{min} was the hydration at 1 M KCl and k_2 had the values of 13.8 (circles), 12.1 (squares), and 9.8 (diamonds).

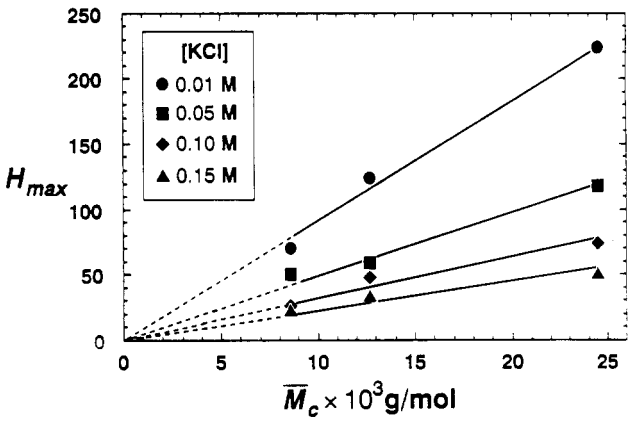


Figure 6. Maximum hydration of poly(acrylic acid) membranes as a linear function of $\bar{M}_c$. The slope of the line depended upon the ionic strength of the solution. The value of H_{max} is plotted as a function of $\bar{M}_c$ for membranes equilibrated at different ionic strengths. The lines represent least-squares fits to the equation $H = m\bar{M}_c$. Constraining the fits to pass through the origin did not significantly change the value of r^2 for the fit, but did reflect physical constraints on the system.

The data are presented in Figures 5 and 6. In Figure 5, the value of H_{max} is plotted as a function of the concentration of KCl in solution for networks with three different values of $\bar{M}_c$. In Figure 6, the value of H_{max} is plotted as a function of $\bar{M}_c$ for the four different concentrations of KCl used in the study.

Figure 5 shows that the swelling due to electrostatic effects decreased exponentially as the ionic strength increased, for concentrations of KCl less than 0.2 M. At high ionic strengths, polyelectrolyte membranes behave essentially as neutral membranes. We therefore took the swelling at [KCl] = 1.0 M as the lower limit of hydration, H_{min}, corresponding to no electrostatic swelling. We then fit the data to the equation $H - H_{min} = k_1 \exp(-k_2)$, where k_1 and k_2 were adjustable parameters. The data fit these curves well ($r^2 > 0.95$), as seen in Figure 5. Tanaka and co-workers[9,18-20] observed similar effects with random polyelectrolyte membranes but much lower bath salt concentrations. The ionic strengths that we examined were not sufficiently low to observe the leveling of hydration those authors reported.

We observed previously that the maximum hydration of a network was a linear function of the value of $\bar{M}_c$ for the network (Figure 3). The data in Figure 6 confirm this observation for four different ionic strengths. In each case, the relation of hydration to molecular weight fits quite well to a line through the origin. We therefore conclude that the effect of molecular weight between cross-links upon hydration is a general one for these systems.

Conclusions

We have prepared new model polyelectrolyte networks from α,ω-amino-terminated poly(acrylic acids) of different molecular weights. One reason that these compounds are of such interest is that progress in theoretical modeling of the behavior of polyelectrolyte networks has been hampered by the lack of synthetic approaches to well defined networks. We believe that the networks presented here can help to close this gap. These networks are useful models for the study of structure–property relationships and the development of theoretical treatments of this important class of polyelectrolyte compounds. The principal structure–property relationships that we have observed for these poly(acrylic acid) networks are summarized below.

1. The maximum hydration of a network was a linear function of the molecular weight of the chains between cross-link points. We do not know of any previous report of such a relationship, which could be explored in this study using the model networks prepared by direct measurements of the networks structural parameters without invoking any theoretical models.
2. The hydration relative to the maximum hydration was a function of pH, but not of the molecular weight between cross-links.
3. The relative hydration and the degree of ionization of the carboxyl groups in the network were similar functions of pH, strongly suggesting that the degree of ionization is a principal factor in determining the hydration of the network.
4. At moderate ionic strengths, the hydration of the membrane decreased exponentially with increases in the ionic strength. The exponential coefficient was, within our ability to determine, not dependent upon the molecular weight between cross-links.

Acknowledgment. We gratefully acknowledge Prof. George Whitesides for helpful discussions and the use of lab space. We thank Watson Lees for assistance with the NMR spectroscopy and Tom Quinn for the use of his computer program to calculate the charge density of the network from the titration data. This work was supported by the National Science Foundation (NSF) under the Engineering Research Center Initiative by a grant to the Massachusetts Institute of Technology Biotechnology Process Engineering Center (cooperative agreement CDR-88-03014). The Bruker NMR spectrometer was provided to Chemical Laboratories of Harvard University through a grant from the NSF (CHE-8410774).

References and Notes

(1) Tanaka, T. *Scient. Am.* **1981**, *244*, 110.
(2) Peppas, N. A. *Hydrogels in Medicine and Pharmacy*; CRC: Boca Raton, FL, 1987.
(3) Peppas, N. A.; Moyniham, H. J.; Lucht, L. M. *J. Biomed. Mater. Res.* **1985**, *19*, 411.
(4) Langer, R. *Chem. Eng. Commun.* **1980**, *6*, 1.
(5) De Moor, C. P.; Doh, L.; Siegel, R. A. *Biomaterials* **1991**, *12*, 836.
(6) Grimshaw, P. E.; Nussbaum, J. H.; Grodzinsky, A. J.; Yarmush, M. L. *J. Chem. Phys.* **1990**, *93*, 446.
(7) Weiss, A. M.; Grodzinsky, A. J.; Yarmush, M. L. *Recent Advances in Separation Techniques-III*; AIChE Symposium Series 82; AIChE: New York, 1986; p 85.

(8) Katchalsky, A.; Lifson, S.; Eisenberg, H. *J. Polym. Sci.* **1951**, *7*, 571.
(9) Katchalsky, A. *Pure Appl. Chem.* **1971**, *26*, 327.
(10) Tanaka, T.; Fillmore, D.; Sun, S. T.; Nishio, I.; Swislow, G.; Shah, A. *Phys. Rev. Lett.* **1980**, *45*, 1636.
(11) Ricka, S.; Tanaka, T. *Macromolecules* **1984**, *17*, 2916.
(12) Amiya, T.; Tanaka, T. *Macromolecules* **1987**, *20*, 1162.
(13) Dusek, K.; Janacek, J. *J. Appl. Polym. Sci.* **1975**, *19*, 3061.
(14) Hasa, J.; Ilavsky, M. J. *Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 263.
(15) Schosseler, F.; Ilmain, F.; Candau, S. J. *Macromolecules* **1991**, *24*, 225.
(16) Flory, P. J. *Principle of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.
(17) Treloar, L. R. G. *The Physics of Rubber Elasticity*, 3rd ed.; Clareendon: Oxford, U.K., 1975.
(18) Dusek, K.; Prins, W. *Adv. Polym. Sci.* **1969**, *6*, 1.
(19) Mark, J. E. *Makromol. Chem. Suppl.* **1979**, *2*, 87.
(20) Mark, J. E.; Sullivan, J. L. *J. Chem. Phys.* **1977**, *66*, 1006.
(21) Rempp, P.; Merrill, E. W. *Polymer Synthesis*; Huthig & Wepf: Basel, 1986; pp 224–227.
(22) Dusek, K. In *Telechelic Polymers: Synthesis and Application*; Gothal, E. J., Ed.; CRC: Boca Raton, FL, 1989; pp 289–360.
(23) Valles, E. M.; Macosko, C. W. *Rubber Chem. Technol.* **1976**, *49*, 1232.
(24) Valles, E. M.; Macosko, C. W. In *Chemistry and Properties of Cross-Linked Polymers*; Labana, S. S., Ed.; Academic Press: New York, 1977.
(25) Valles, E. M.; Macosko, C. W. *Macromolecules* **1979**, *12*, 673.
(26) Meyers, K. O.; Bye, M. L.; Merrill, E. W. *Macromolecules* **1980**, *13*, 1045.
(27) Gottlieb, M.; Macosko, C. W.; Benjamin, G. S.; Meyers, K. O.; Merrill, E. W. *Macromolecules* **1981**, *14*, 1039.
(28) Mark, J. E. *Pure Appl. Chem.* **1981**, *53*, 1495.
(29) Falender, J. R.; Yeh, G. S. Y.; Mark, J. E. *Chem. Phys.* **1979**, *70*, 5324. Falender, J. R.; Yeh, G. S. Y.; Mark, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 7353. Falender, J. R.; Yeh, G. S. Y.; Mark, J. E. *Macromolecules* **1979**, *12*, 1207.
(30) Llorente, M. A.; Mark, J. E. *Macromolecules* **1980**, *13*, 681.
(31) Llorente, M. A.; Mark, J. E. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 181.
(32) Llorente, M. A.; Mark, J. E. *Rubber Chem. Technol.* **1980**, *53*, 988.
(33) Mark, J. E. *Makromol. Chem. Suppl.* **1979**, *2*, 87.
(34) Mark, J. E.; Sung, P.-H. *Eur. Polym. J.* **1980**, *16*, 1223.
(35) Sung, P.-H.; Mark, J. E. *Polym. J.* **1980**, *12*, 835.
(36) Sung, P.-H.; Mark, J. E. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 507.
(37) Mark, J. E. *Rubber Chem. Technol.* **1981**, *54*, 000.
(38) Busnel, J. P.; Durand, D.; Bruneau, C. M. *Eur. Polym. J.* **1984**, *20*, 589.
(39) Sung, P.-H.; Pan, S.-J.; Mark, J. E.; Chang, V. S. C.; Lackey, J. E.; Kennedy, J. P. *Plym. Bull.* **1983**, *9*, 375.
(40) Chaumont, P.; Beinert, G.; Herz, J.; Rempp, P. *Eur. Polym. J.* **1979**, *15*, 259.
(41) Macosko, C. W.; Miller, D. R. *Macromolecules* **1976**, *9*, 199.
(42) Miller, D. R.; Macosko, C. W. *Macromolecules* **1978**, *11*, 656.
(43) Miller, D. R.; Valles, E. M.; Macosko, C. W. *Polym. Eng. Sci.* **1979**, *19*, 272.
(44) Shefer, A.; Grodzinsky, A. J.; Prime, K. L.; Busnel, J. P. Unpublished data.
(45) Shefer, A.; Grodzinsky, A. J.; Prime, K. L.; Busnel, J. P. *Macromolecules* **1993**, *26*, 2240.
(46) Nussbaum, J. H. Ph.D. Thesis, MIT EECS, 1986.
(47) Khun, W.; Hargityay, B.; Katchalsky, A.; Eisenberg, H. *Nature* **1950**, *165*, 514.
(48) Grimshaw, P. E.; Grodzinsky, A. J.; Yarmush, M. L.; Yarmush, D. M. *Chem. Eng. Sci.* **1989**, *44*, 827.
(49) Weiss, A. M.; Adler, K. P.; Grodzinsky, A. J. *J. Membr. Sci.* **1991**, *82*, 85.
(50) Oosawa, F. *Polyelectrolytes*; Marcel Dekker: New York, 1971.