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Analysis of the Complexation/Decomplexation Phenomena in Graft Copolymer Networks

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ABSTRACT: Graft copolymer networks of poly(methacrylic acid-*g*-ethylene glycol) exhibiting pH-dependent swelling behavior due to the formation of interpolymer complexes were prepared by free radical solution polymerization of methacrylic acid and poly(ethylene glycol) monomethacrylate. Dynamic swelling studies established the swelling/deswelling process due to hydrogen bonding. Additionally, the effects of copolymer composition, graft chain molecular weight, and environmental pH on network structure were studied. The average network correlation length changed significantly due to changes in environmental pH. The largest changes in network structure were observed in gels containing nearly equimolar amounts of methacrylic acid and ethylene glycol and the longest molecular weight poly(ethylene glycol) grafts. Water diffusion coefficients, determined through dynamic swelling analysis, varied by 2 orders of magnitude between the uncomplexed and complexed states.

Introduction

Polymer complexes are insoluble, macromolecular structures formed by the non-covalent association of polymers with the affinity for one another. The complexes form due to association of repeating units on different chains (interpolymer complexes) or on separate regions of the same chain (intrapolymer complexes). Polymer complexes can be classified as stereocomplexes,[1,2] polyelectrolyte complexes,[1−6] and hydrogen bonded complexes.[1,2,7−17]

Interpolymer complexation during association of macromolecular chains with the affinity for one another can be described as a reversible interaction of repeating units on two polymer chains.

$$P_1 + P_2 \underset{k_{-c}}{\overset{k_c}{\Leftrightarrow}} C \qquad (1)$$

Interpolymer complexes stabilized by hydrogen bonds form between electron-donating protons and groups containing regions of high electron density, typically ethers, alcohols, or pyrrolidones. These complexes are cooperative in nature. Thus, the length of the interacting chains significantly affects complex stability.[1,2,9−11,18] Additionally, complexation is stabilized by the polymer composition and structure, as well as hydrophobic interactions.

Complex stability is dependent on many environmental factors such as temperature, the nature of the solvent, pH, or ionic strength. In hydrogen bonded complexes, the interactions are between polyacids, typically polycarboxylic acids such as poly(methacrylic acid) (PMAA) or poly(acrylic acid) (PAA), and neutral electron donating polymers such as poly(ethylene glycol) (PEG) or poly(*N*-vinyl-2-pyrrolidone). These complexes form when the pH is sufficiently low to allow for substantial protonation of the acid groups.[1,2,7−17] Accordingly, complex stability is strongly dependent on the environmental pH and ionic strength. Complex formation is typically enhanced by decreases in environmental temperature.[1,2]

In three-dimensional networks, the formation of interpolymer complexes can dramatically affect the effective network structure. Copolymer networks of poly(methacrylic acid) grafted with poly(ethylene glycol) (henceforth designated as P(MAA-*g*-EG)) exhibit reversible, pH-dependent swelling behavior due to the formation of interpolymer complexes between protonated pendant acid groups and the etheric groups on the graft chains.[14−17] In acidic media, the complexes form due to protonation of the pendant groups; thus, the gel is unable to imbibe much fluid. However, in neutral or basic media, the complexes dissociate due to ionization of the pendant groups, and the gels swell to a high degree. These gels have been found to respond rapidly to changes in the external pH and ionic strength. Due to complexation, these networks collapse at rates up to 8 times faster than the corresponding rates of swelling.[15] Additionally, solute permeation is severely hindered in complexed networks.[14,16,17] Because of their nature, these systems have been identified for use in a wide variety of applications including ultrafiltration membranes, sensing devices, and drug delivery systems.[12−17]

The formation of interpolymer complexes in copolymer networks significantly alters the network structure. Complex formation in copolymer systems can be affected by many parameters such as the size and concentration of the interacting polymer chains as well as the nature of the environmental fluid. In this work we analyze the effects of solution pH, graft chain molecular weight, and copolymer composition on the P(MAA-*g*-EG) network structure.

Experimental Section

Hydrogel Synthesis. P(MAA-*g*-EG) hydrogels were prepared by free radical solution polymerization of methacrylic acid (MAA, Aldrich Chemical Co., Milwaukee, WI) and methoxy-terminated poly(ethylene glycol) monomethacrylate (PEGMA, Polysciences Inc., Warrington, PA) with PEG of molecular weight 200, 400, and 1000. The MAA was vacuum distilled at 54 °C/25 mmHg to remove the inhibitor, methoxyethylhydroquinone. PEGMA was used as received. The monomers were mixed in ratios ranging from 1:1 to 4:1 MAA/EG repeating units.

The solutions were diluted to 50% by weight of the total monomers with a 1:1 by weight mixture of ethanol and water. Tetraethylene glycol dimethacrylate (TEGDMA, Polysciences Inc., Warrington, PA) was added as the cross-linking agent in

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the amount of 0.75% moles of total monomers. Nitrogen was bubbled through the well mixed solution for 30 min to remove dissolved oxygen. The redox initiator pair, sodium metabisulfite and ammonium persulfate (Mallinckrodt Chemical Inc., Paris, KY), was added in the amount of 2% total monomer in a nitrogen atmosphere. The mixture was poured between flat plates to form films of 0.9 mm thickness. The monomer films were sealed under nitrogen and allowed to react for 24 h at 37 °C. The polymers were then cut into the desired shapes and rinsed in deionized water for 7 days to remove unreacted monomer and the sol fraction. For the swelling experiments, polymer disks were cut so that the aspect ratio, the ratio of the gel radius to gel half-thickness, was greater than 10.

Swelling Studies. Following the rinsing, polymer disks were dried to a constant weight and volume under vacuum at 37 °C. The dry volumes were calculated by using a buoyancy technique.[18] Dry disks of each type were placed in 100 mL of dimethylglutaric acid (DMGA) buffers ranging in pH from 3.2 to 7.6. The ionic strength of each solution was adjusted to 0.1 M by the addition of NaCl. The dynamic weight swelling ratio, q, was calculated as the ratio of the swollen polymer weight to the dry polymer weight.

To detemine the equilibrium swelling characteristics, the polymer remained in buffer solution and was weighed every 24 h until the volume remained constant (±5%) for 48 h. The buffer solution was changed daily. The equilibrium volume swelling ratio, Q, was determined as the ratio of the swollen polymer volume to the dry polymer volume. The polymer volume fraction in the swollen state, $v_{2,s}$, was calculated as the inverse of the volume swelling ratio.

Characterization of Network Structure. In order to characterize the network structure, rubber elasticity experiments were performed by using an automated tensile testing system (Instron Model 4301, Park Ridge, IL). Materials were swollen to equilbrium in DMGA buffers (I = 0.1 M) ranging in pH from 3.2 to 7.4. Swollen samples were cut into strips of width 0.6 mm. The grips of the Instron were submerged in 37 °C buffer solution to allow the samples to remain swollen during the experiment. The samples were elongated at 2 mm/min until the hydrogel reached a maximum elongation of 10%. The stress−strain behavior of the swollen networks was observed.

Results and Discussion

Conformational Changes in P(MAA-*g*-EG) Networks. Complexing hydrogels have the ability to respond to changes in their external environment. Macroscopic changes in the network structure can be attributed to changes in the polymer correlation length, ξ, or in the end-to-end distance of the polymer chains between junction points. The distinction is made here between junction points and classical covalently cross-linked structures, because in complexing hydrogels the hydrogen bonding forms regions of quasi-permanent nature which act as additional physical cross-links or junctions. In our complexing P(MAA-*g*-EG) hydrogels, complexation resulted in the formation of temporary physical cross-links due to hydrogen bonding between the PEG grafts and the PMAA pendant groups. These physical cross-links were reversible in nature and dependent on the pH of the environment. Thus, the degree of cross-linking and the effective molecular weight between cross-links of these systems, M_e, decreased due to interpolymer complexation in these gels. Additionally, the correlation length or mesh size, ξ, was reduced dramatically as more temporary, physical cross-links were introduced into the system as a result of complex formation (Figure 1).

Swelling Studies. Equilibrium and dynamic swelling studies were performed in order to characterize the conformational transitions of the network structures based on macroscopic properties. Interpolymer complexation in polymer networks results in a reduction in the correlation length or distance between junction points due to the macromolecular association of the polymer chains. Therefore, materials which are highly complexed are unable to imbibe as much water as uncomplexed materials. The macroscopic swelling behavior of the copolymer networks was analyzed to investigate the critical parameters for complexation. The effects of parameters such as copolymer composition, PEG graft chain molecular weight, and solvent pH on the conformational states of the networks were investigated.

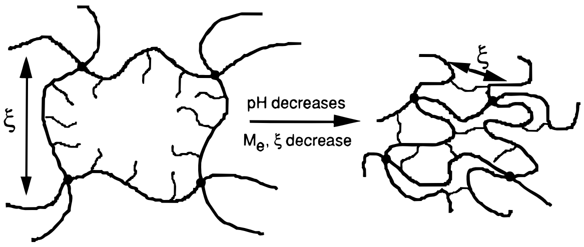

Figure 1. Effect of complexation on the correlation length, ξ, and the effective molecular weight between cross-links, M_e, in graft copolymer networks with permanent, chemical cross-links (●).

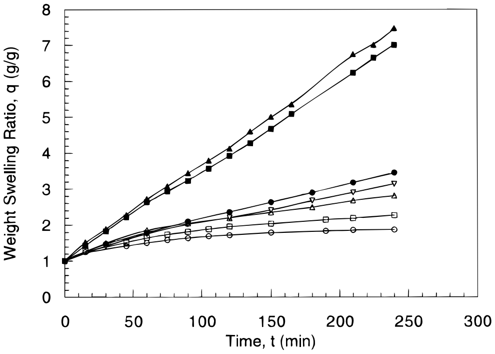

Figure 2. Weight swelling ratio of initially dry, cross-linked P(MAA-*g*-EG) samples (with MAA:EG ratio of 1:1 and PEG graft chains of molecular weight 1000) swollen in buffer solutions of varying pH values (3.5 (○), 4.2 (□), 4.6 (△), 5.2 (▽), 5.6 (●), 6.4 (■), and 6.8 (▲)) at 37 °C (at constant ionic strength, I = 0.1 M) plotted as a function of swelling time.

Dynamic Swelling. The ability of a polymer network to absorb water is significantly hindered by the presence of cross-links as well as physical obstructions such as entanglements, crystallites, or polymer complexes.[19−21] Thus, in the complexed state the rate of water uptake was reduced dramatically, as indicated by the data in Figure 2. These data represent water uptake of initially dry networks. For the case of polymers in solutions of pH greater than 5.6, the rate of water uptake was significantly faster than for polymers in lower pH media. This was due to the complexation/decomplexation of P(MAA-*g*-EG) hydrogels. In higher pH media (pH greater than 5.6), complexation did not occur as the pendant acid groups are ionized. In these cases, the gels swelled rapidly due to a large swelling force generated due to electrostatic repulsions between the ionized acid groups. In media of pH less than 4.6, the swelling of the polymer samples was governed by the formation of interpolymer complexes. The formation of additional physical cross-links acted to hinder diffusion through the gels. For these cases, the gels swelled at significantly lower rates than the noncomplexing gels. In buffer solutions of pH between 4.6 and 5.6, the transition region, the swelling of the

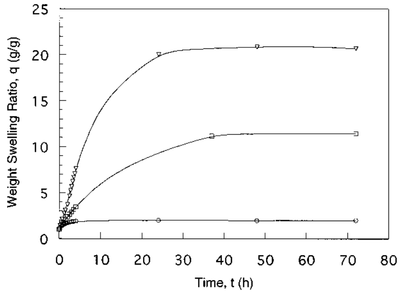

Figure 3. Weight swelling ratio of initially dry, cross-linked P(MAA-*g*-EG) samples (with MAA:EG ratio of 1:1 and PEG graft chains of molecular weight 1000) swollen in buffer solutions of varying pH values (3.5 (○), 5.6 (□), and 7.4 (△)) at 37 °C (at constant ionic strength, $I = 0.1$ M) plotted as a function of swelling time.

samples was due to ionic interactions as well as interpolymer complexation. In these solutions, the gels were partially ionized and some complexes formed. These samples swelled at an intermediate rate due to ionization and the presence of the physical cross-links.

The full water uptake for three swelling samples in different pH buffers is shown in Figure 3. These three pH values represent the uncomplexed state (pH = 7.4), the transition region (pH = 5.6), and the complexed state (pH = 3.5). For all three regions, the rate of water uptake followed a Fickian dependence for the entire swelling curves. Additionally, the degree to which the polymers swelled increased with decreasing complexation.

Due to the one-dimensional transport characteristics of the system, the water transport into dry P(MAA-*g*-EG) samples can be expressed by the classical diffusion equation for planar geometries.[22]

$$\frac{\partial C_1}{\partial t} = D_{1,2}\frac{\partial^2 C_1}{\partial x^2} \tag{2}$$

In this expression, $D_{1,2}$ represents the diffusion coefficient of water through the swelliong samples. The solution to eq 2, for the assumption of constant boundaries, can be written as[22]

$$\frac{M_t}{M_\infty} = 1 - \left[\sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\left(\frac{-D_{1,2}(2n+1)^2\pi^2}{2\delta^2}t\right)\right] \tag{3}$$

where δ is the half-thickness of the sample. The full swelling data for each polymer sample were analyzed by eq 3 in order to calculate the complexation dependent diffusion coefficients (Figure 4). For the complexed state (pH less than 4.6), the water diffusion coefficient was significantly reduced as the presence of complexes impeded the ability of the water to diffuse in the network. In these polymers, the diffusion coefficient was on the order of 10^{-6}. As the pH was raised to the range 4.6–5.6, some of the complexes dissociated as the pendant acid groups were ionized. The water diffusion coefficient in the transition region increased by an order of magnitude from the complexed state to 10^{-5} due to the presence of fewer hindrances to diffusion. In solutions above pH = 5.6, all of the complexes were completely dissociated and the network was transformed into a highly swollen network as the backbone chains were in an extended conformation due to electrostatic repulsions between the ionized pendant groups. In this pH region, the diffusion coefficient of the water was calculated to be 2 orders of magnitude greater than those calculated for the complexed gels (10^{-4}). These values were nearly equal to the self-diffusion coefficient of water.

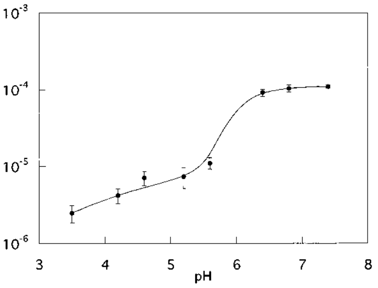

Figure 4. Water diffusion coefficients in P(MAA-*g*-EG) samples (with MAA:EG ratio of 1:1 and PEG graft chains of molecular weight 1000) swollen in buffer solutions at 37 °C (at constant ionic strength, $I = 0.1$ M) plotted as a function of the swelling solution pH.

Equilibrium Swelling. Interpolymer complexes stabilized between polyacids and neutral, electron donating polymers are thermodynamically favorable structures in acidic media.[1,2] The complexes are cooperative in nature and stabilized by an entropic effect.[1,2,23] Accordingly, the formation of complexes will be dependent on the concentration of the individual repeating units and length of the interacting polymer chains. Because of the cooperative nature, complexation was increased in hydrogels containing nearly equimolar amounts of MAA/EG and high PEG graft chain molecular weight. Increased amounts of complexation resulted in the formation of a more highly cross-linked gel. Accordingly, gels exhibiting the highest degrees of complexation swelled to the lowest degree.

In equilibrium swollen complexation networks, the degree of network swelling is dependent on the number of chemical and physical cross-links present in the system. In P(MAA-*g*-EG) networks, the equilbrium swelling ratio was affected by the solution pH, copolymer composition, and PEG molecular weight. For the case of equimolar amounts of MAA and EG at low pH values, the degree of complexation was high and the polymer volume fraction in the swollen state, $v_{2,s}$, was almost 0.70. However, as the pH of the swelling solution increased above pH = 4.6, the complexes began to dissociate and the backbone chains extended, resulting in a significant decrease in the equilibrium polymer volume fraction in the gel. The highly swollen, uncomplexed gels contained less than 5% polymer as more water was incorporated into the structure (Figure 5). Significantly, the gels containing the larger graft chains exhibited the largest change in swelling behavior over the range of pH studied.

The effect of copolymer composition on the swelling of P(MAA-*g*-EG) hydrogels is shown in Figure 5a. In regions of low pH, lower than pH = 4.6, all of the P(MAA-*g*-EG) hydrogels contained some degree of interpolymer complexes stabilized by hydrogen between protonated pendant acid groups and the ether groups of the PEG graft chains. Gels containing equimolar amounts of MAA/EG exhibited the lowest degree of swelling at low pH increased complexation. As the amount of MAA in the gels was increased, the gels swelled to a higher degree due to the presence of fewer interpolymer complexes. For solutions of pH greater than 4.6, all of the gels swelled to a higher degree due to dissociation of the complexes as the pendant groups ionized.

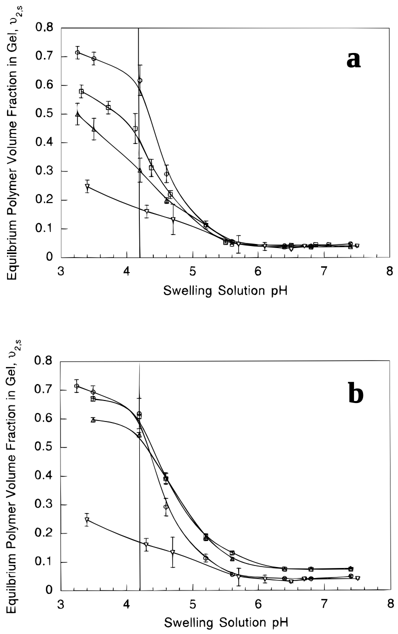

Figure 5. Equilibrium polymer volume fraction in P(MAA-*g*-EG) hydrogels swollen in buffer solutions (at constant ionic strength, $I = 0.1$ M) at 37 °C plotted as a function of the swelling solution pH for gels (a) with PEG graft chains of molecular weight 1000 containing varying ratios of EG/MAA (1 (○), 3/7 (□), and 1/4 (△)) and (b) with EG/MAA ratio of 1 containing PEG grafts chains of varying molecular weight (1000 (○), 400 (□), and 200 (△)) (The value for pure PMAA is denoted by (▽)).

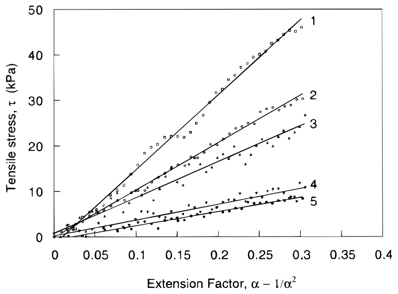

Figure 6. Tensile stress at short deformations for P(MAA-*g*-EG) hydrogels (with EG/MAA ratio of 1 and PEG graft chains of molecular weight 1000) swollen in buffer solutions (at constant ionic strength, $I = 0.1$ M) of varying pH (1, pH = 3.5; 2, pH = 4.2; 3, pH = 4.6; 4, pH = 5.6; 5, pH = 6.8) at 37 °C plotted as a function of the extension factor.

The equilbrium swelling of P(MAA-*g*-EG) was dependent also on the PEG graft chain molecular weight (Figure 5b). At low pH (less than pH = 4.6), all of the PEG- containing gels were in the complexed state. However, the degree of swelling was lowest in gels containing the longer PEG grafts (molecular weight 1000). Because of the longer graft chains, complexation was enhanced resulting in a lower degree of swelling in these gels. In solutions of pH greater than 4.6, the swelling of all of the gels increased significantly due to complex dissociation. Gels containing the longer PEG grafts (molecular weight 1000) swelled to the highest degree in the uncomplexed state. For these materials, the gel contained over 95% water in the highly swollen state. For gels containing a 1/1 ratio of MAA/EG, the number of MAA repeating units between graft chains was approximately equal to the length of the PEG graft chains. Therefore, gels containing the longer PEG graft chains had the largest blocks of ionizable groups between grafts. In these gels, the swelling force due to ionic repulsions was greatest, thus, these materials swelled to the highest degree.

Table 1. Maximum Degree of Complexation in P(MAA-*g*-EG) Hydrogels Swollen in Buffer Solutions of pH = 3.5 (with Constant Ionic Strength, $I = 0.1$ M) at 37 °C

EG/MAA in hydrogel	PEG graft chain molec wt	max degree of complexation, $\beta_{\max}$
1	1000	0.62
1	400	0.56
1	200	0.46
0.43	1000	0.37
0.25	1000	0.21

The degree of complexation in these materials can be expressed in terms of the parameter β, defined as the number of bound graft chain repeating units divided by the total number of backbone chains in the material. Because complexation occurs between two individual repeating units, β, as defined, can take values between 0 and 1, inclusive. However, the maximum value for the degree of complexation can be no greater than the ratio of EG/MAA units in the copolymer.

In order to compare the molecular level degree of complexation to the macroscopic swelling of complexation gels, the degree of complexation, β, was calculated from the polymer volume fractions in the swollen state.

$$\beta = \frac{\upsilon_{2,s} - \upsilon_{2,s}}{1 - \nu_{2,s}} \tag{4}$$

In this expression, $\upsilon_{2,s}$ is the polymer volume fraction for the complexing copolymers of interest and $\upsilon'_{2,s}$ is the polymer volume fraction for gels containing infinitely small graft polymer chains (when no complexation can occur). Therefore, the value of $\upsilon'_{2,s}$ can be estimated as the polymer volume fraction of swollen PMAA networks.

The degree of complexation was calculated for P(MAA-*g*-EG) hydrogels from the equilibrium swelling data (Figure 5). The maximum degree of complexation for all the gels examined occurred at pH = 3.5, because gels swollen at this pH contained the lowest fraction of ionized acid groups. The maximum degree of complexation is given in Table 1. These data show the dependence of complexation on the coplymer composition and the molecular weight of the PEG graft chains. Gels containing an equimolar ratio of MAA/EG contained the greatest amount of interpolymer complexes due to the cooperative nature of the interactions as well as the stoichiometric ratio of the associating units. Additionally, gels containing the PEG graft chains of molecular weight 1000 exhibited the highest degree of complexation.

Small Deformation Analysis. In order to characterize the effects of complexation on the structure of the true crosslinked network as a function of the solution pH, copolymer composition, and PEG graft chain molecular weight, rubber elasticity experiments were performed. The stress–strain behavior at short deformations for P(MAA-*g*-EG) hydrogels is shown as a function of the swelling solution pH in Figure 6. In these experiments, the tensile stress, τ, was calculated from the experiments as the force per cross sectional area of the unstretched, unswollen polymer sample. The elongation, α, was calculated as the length at any time divided by the initial length of the polymer sample. The slope of the individual curves is proportional to the tensile modulus of the swollen network, which is a representation of the physical strength of the materials.

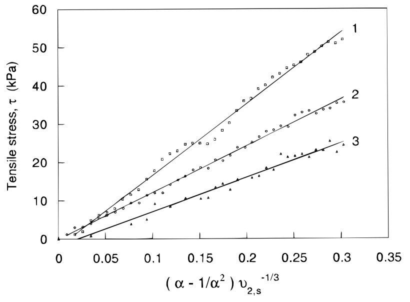

Figure 7. Tensile stress at short deformations for P(MAA-*g*-EG) hydrogels (with EG/MAA ratio of 1 and PEG graft chains of molecular weight 1000) swollen in buffer solutions (at constant ionic strength, $I = 0.1$ M) of varying pH (1, pH = 3.5; 2, pH = 4.6; 3, pH = 6.8) at 37 °C plotted as a function of the extension factor normalized to account for the swelling of the gel.

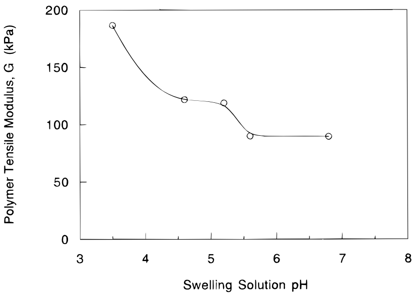

Figure 8. Polymer modulus at short deformations for P(MAA-*g*-EG) hydrogels (with EG/MAA ratio of 1 and PEG graft chains of molecular weight 1000) swollen in buffer solutions (at constant ionic strength, $I = 0.1$ M) at 37 °C plotted as a function of the swelling solution pH.

The gels swollen in the lower pH solutions (pH = 3.5) had the largest slope of the materials studied. The high strength of the materials was due to the relatively low degree of swelling caused by the formation of physical cross-links due to interpolymer complexation in the networks. As the solution pH was increased, the modulus decreased as the gels became weaker due to increased swelling.

Based on the theory of rubber elasticity, the tensile modulus, G, is related to degree of swelling by the following expression:[24,25]

$$\frac{\tau}{\alpha - 1/\alpha^2} = G v_{2,s}^{\ -1/3} \tag{5}$$

where τ is the tensile stress and α is the polymer elongation. The stress–strain behavior of the P(MAA-*g*-EG) hydrogels normalized to account for the differences in the swelling behavior is shown in Figure 7. In this figure, three distinct regions are represented, a region of highly complexed gels (region 1) containing large amounts of physical cross-links (pH = 3.5), a region of moderately complexed gels (region 2) containing some physical cross-links and ionized pendant acid groups (pH = 4.6), and a region of highly swollen gels (region 3) containing ionized pendant acid groups (pH = 6.8). By removing the effects of the network swelling, the relative amounts of physical cross-links in the gels were compared. The modulus was then calculated for each pH value (Figure 8).

The three clear conformations of the gel are shown in this figure. For pH = 3.5, the modulus was high due to the large amounts of complexation occurring in the gel. These complexes served as physical cross-links providing the gel with additional mechanical strength.

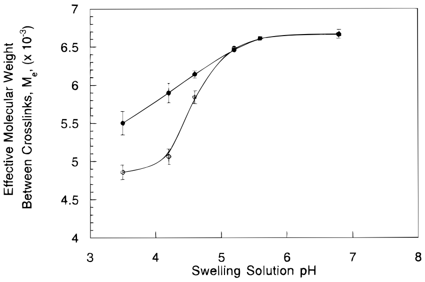

Figure 9. Effective molecular weight between cross-links in P(MAA-*g*-EG) hydrogels (with PEG graft chains of molecular weight 1000) containing varying ratios of EG/MAA (1:1 (○) and 4:1 (●)) swollen in buffer solutions (at constant ionic strength, $I = 0.1$ M) at 37 °C plotted as a function of the swelling solution pH.

In the intermediate pH solutions (pH = 4.6 and 5.2), some complexes were present along with ionized pendant acid groups. However, gels swollen in pH = 6.8 solutions were sgnificantly weaker as the physical cross-links due to complexation were not present. The modulus for these materials was 90 kPa, a 50% reduction from gels in the complexed state.

Using rubber elasticity theory, we were able to calculate the effective molecular weight between cross-links and the correlation length for gels exhibiting different degrees of complexation. For networks cross-linked in the presence of a solvent, eq 5 becomes[26]

$$\frac{\tau}{\alpha - 1/\alpha^2} = RT\rho_{2,r}\left(\frac{1}{M_e} - \frac{2}{M_n}\right)\left(\frac{v_{2,s}}{v_{2,r}}\right)^{1/3} \tag{6}$$

In this expression, $\rho_{2,r}$ represents the density of the polymer in the relaxed state, immediately after cross-linking but prior to swelling and $v_{2,r}$ is the polymer volume fraction in the relaxed state. The number-average molecular weight of polymer chains if no cross-links were introduced, M_n, was determined by calculating the length of a linear polymer chain prepared by radical polymerization.[27]

$$M_n = aM_o v = \frac{aM_o k_p[M]}{2(fk_t k_d[I])^{1/2}} \tag{7}$$

In this expression, [M] (5.1×10^{-3} mol/cm^3) is the monomer concentration, [I] (1.7×10^{-5} mol/cm^3) is the initiator concentrations, f (0.5)[28] is the initiator efficiency, k_d (0.0165 s^{-1})[28] is the rate constant for initiator dissociation, k_p (670 L/mol s)[28] is the rate constant for chain propagation, k_t (2.1×10^{-6} L/mol s)[28] is the rate constants for chain termination, M_o is the molecular weight of the monomeric repeating units, and a (1.33)[27] is a constant related to the method of termination. The number average molecular weight of the linear chains was calculated by using these values as 11 550.

From eq 6, the effective molecular weight between cross-links was determined for the swollen P(MAA-*g*-EG) networks (Figure 9). For both copolymer compositions, the effective molecular weight between cross-links changed dramatically from the low pH solutions to the high pH soluions. For all of the gels swollen in solutions of pH greater than 5.6, no physical cross-links were present due to complete ionization of the pendant acid groups and the effective molecular weight between cross-links was approximately equal to 6700. The molecular weight between cross-links did not vary with pH, copolymer composition, or graft chain molecular

Table 2. Cross-Linking Ratio, *X*, of P(MAA-*g*-EG) Hydrogels (Containing PEG Grafts of Molecular Weight 1000) as Calculated from Small Deformation Analysis for the Complexed and Uncomplexed States at 37 °C

EG/MAA in hydrogel	cross-linking ratio, *X*		
	nominal	complexed gel	uncomplexed gel
1	0.75	0.89	0.65
0.25	0.75	0.78	0.65

weight in these solutions. For all of the PEG containing gels, however, the molecular weight between cross-links was reduced as the pH was decreased below 5.6 due to interpolymer complexation. For the case of the copolymers containing equimolar amounts of EG/MAA, the gel had an effective molecular weight between cross-links of only ~4800 in the lower pH solutions. Gels containing increased amounts of MAA (EG/MAA = 0.25) had a larger effective molecular weight between cross-links of 5500 in the lower pH solutions. Additionally, the transition between the uncomplexed and complexed states was sharper for the gels containing equimolar amounts of EG/MAA due to cooperative stabilization of complexation.

For all of the gels studied, the nominal cross-linking ratio, *X*, defined as the moles of cross-linking agent divided by the total moles of monomer, was 0.75. The cross-linking density can be calculated for gels in both the uncomplexed and complexes states by[29]

$$X = M_o/2M_e \tag{8}$$

Values for the cross-linking ratio are given in Table 2. In solutions of high pH where no complexation could occur, all of the materials contained the same degree of cross-linking, which was only the permanent, chemical cross-links introduced into the system. However, gels in the complexed state contained both physical and chemical cross-links. For the materials containing equimolar amounts of EG and MAA, the cross-linking ratio increased by 25% from the uncomplexed to complexed states. This was due to the presence of significant amounts of interpolymer complexation in these networks resulting in the formation of physical cross-links. In complexed gels containing EG/MAA = 0.25, the cross-linking ratio increased by 20% from the uncomplexed state due to complexation.

The effective molecular weight between cross-links was also used to compare the network structure in the complexed and the uncomplexed states. The network correlation length or mesh size, ξ, was calculated as the end to end distance of the swollen polymer chains between junction points.[29]

$$\xi = \left(\frac{2C_n M_e}{M_o}\right)^{1/2} l v_{2,s}^{-1/3} \tag{9}$$

In this equation, C_n (14.6 for PMAA)[28] is the polymer characteristic ratio and *l* is the carbon−carbon bond length.

The average network mesh size or correlation length was dramatically affected by the pH of the swelling solution (Figure 10). In low pH solutions in which complexation will occur, the network mesh sizes for P(MAA-*g*-EG) hydrogels were as low as 70 Å. However, as the pH was increased the physical cross-links dissociated and the polymer chains elongated resulting in a significant increase in the network mesh size to almost 210 Å.

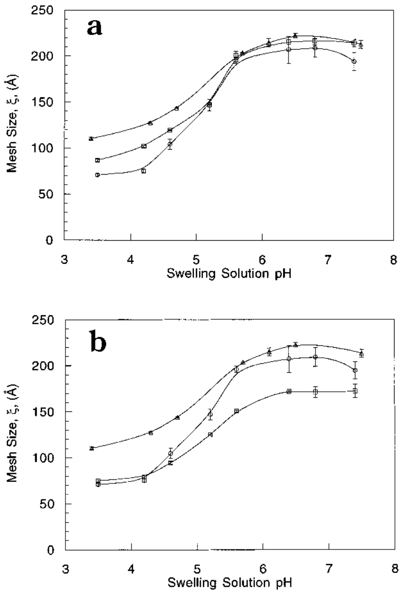

Figure 10. Network mesh size in P(MAA-*g*-EG) hydrogels swollen in buffer solutions (at constant ionic strength, *I* = 0.1 M) at 37 °C plotted as a function of the swelling solution pH for gels (a) with PEG graft chains of molecular weight 1000 containing varying ratios of EG/MAA (1 (○) and 1/4 (□)) and (b) with EG/MAA ratio of 1 containing PEG grafts chains of varying molecular weight (1000 (○) and 200 (□)). The data for PMAA hydrogels are represented by △.

Table 3. Ratio of Network Correlation Lengths for P(MAA-*g*-EG) Hydrogels Swollen to Equilibrium at 37 °C in the Uncomplexed State (ξ_{unc}) at pH = 6.8 and the Complexed State (ξ_{com}) at pH = 3.5 (with *I* = 0.1 M)

hydrogel composition	PEG graft chain molec wt	ξ_{unc}/ξ_{com}
EG/MAA = 1	1000	2.96 ± 0.19
EG/MAA = 1	400	2.38 ± 0.15
EG/MAA = 1	200	2.28 ± 0.16
EG/MAA = 0.25	1000	2.50 ± 0.10
MAA		1.92 ± 0.10

All complexing systems exhibited a marked change in their structure between the acidic environment (complexed) and the higher pH regions (uncomplexed). However, to evaluate a particular membrane for use in an application where this complexation/decomplexation mechanism is to be exploited, the ratio of the mesh size between the two states is important (Table 3). For gels containing a ratio EG/MAA of 1 and PEG graft chains of molecular weight 1000, the greatest amount of complexation occurred and the network mesh size changed by 296% from the complexed state to the uncomplexed. As more MAA was incorporated into the system, the ratio of the network mesh size decreased to lesser amounts of physical cross-links being present in the materials in the acidic media. Also, as the length of the PEG graft chain was decreased, the change in the correlation length between the two states decreased. This was due to the reduced ionic swelling forces generated in these gels in the high pH solutions.

The complexation phenomena allow for a more dramatic change in the network structure than a pH-sensitive network such as PMAA, in which no complexation occurs. In PMAA hydrogels, the change in network mesh size was only affected by the polymer/solution interactions. In high pH solutions, the acid groups in PMAA ionized and the mechanism for swelling was the same as in the P(MAA-*g*-EG) hydrogels. In low pH solutions, the compatibility of the PMAA chains with the swelling fluid was low and the chains were in a coiled conformation. As a result, the gels swelled to a relatively low degree and the mesh size was 110 Å. However, in the complexation gels at low pH, the change in correlation length between the high pH and low pH solutions was twice that seen in purely ionic networks as complexation resulted in increased amounts of cross-links in the system, which actually reduced the distance between junction points.

Conclusions

The formation of complexes due to macromolecular associations in polymer networks has a significant effect on the structure and properties of the material. The effects of complexation on the network structure and macroscopic swelling properties were observed in P(MAA-*g*-EG) gels. In acidic media, complexes formed in these networks. The diffusion coefficient and the amount of fluid that the gels could imbibe in the complexed state were significantly reduced due to the presence of additional physical cross-links. The degree to which complexation occurred varied with the copolymer composition and the molecular weight of the PEG chains grafted to the polymer backbone. Additionally, the presence of complexes in these gels provided mechanical stability and reduced the available area for diffusion in the networks.

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