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Molecular analysis of interpolymer complexation in graft copolymer networks

A.M. Lowman[1], N.A. Peppas*

Polymer Science and Engineering Laboratories, School of Chemical Engineering, Purdue University, West Lafayette, IN 47907-1283, USA

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Abstract

Interpolymer complexation is associated with the formation of hydrogen bonds between pendent and/or grafted groups of a single polymer or copolymers. The degree of complexation can be described theoretically in terms of complexation/decomplexation equilibrium characteristics. Graft copolymer networks of poly(methacrylic acid-g-ethylene glycol) were prepared by free radical solution polymerization of methacrylic acid and poly(ethylene glycol) monomethacrylate. The ensuing gels exhibited drastic network structural changes in response to environmental pH changes due to the formation/dissociation of interpolymer complexes. The molecular level degree of complexation was determined as a function of copolymer composition, PEG graft chain molecular weight and environmental pH. The largest degrees of complexation were observed in gels containing nearly equimolar amounts of the monomeric units and the longest molecular weight poly(ethylene glycol) grafts. These trends were predicted by the equilibrium complexation theory and were in good agreement with the experimental data.

Keywords: Complexation; Poly(ethylene glycol); Graft copolymers

1. Introduction

Interpolymer complexation is the non-covalent association between groups on different polymer chains. These macromolecular complexes form under conditions in which the polymers are thermodynamically compatible. Polymer complexes form due to van der Waals interactions, polyelectrolyte association and hydrogen bonding [1–7].

Polymer complexation is a thermodynamically favorable event [1–5]. Complex formation is promoted by a negative free energy of association between repeating units. This association is also promoted by an exothermic reaction of the functional groups or by a large positive entropy change upon complex formation [2,5]. These complexes are also reversible in nature [1–7].

Interpolymer complexes are stabilized by the cooperative nature of their bonds. In general, the formation of individual complexes decreases the conformational entropies of the interacting chains. However, the rupture of an individual complex does not increase the system energy, as no additional translation degrees of freedom are created. As a result, the cooperative stabilization of the complexes is an entropic effect. Due to the cooperative nature of the bonds, there exists a critical chain length for complexation in polymer solutions [8].

Interpolymer complexes stabilized by hydrogen bonds form between electron deficient groups such as polyacids and groups containing regions of high electron density, typically ethers, alcohols or pyrrolidones. These complexes generally form in aqueous media within a narrow range of solvent composition, pH and ionic strength. Additionally, complexation is stabilized by the cooperative nature of the bonds as well as hydrophobic interactions.

Some examples of polymer systems which form complexes due to hydrogen bonding include: poly(acrylic acid) and polyacrylamide [9], poly(acrylic acid) and poly-(vinyl alcohol) [10–14], poly(acrylic acid) and poly(ethylene glycol) [1,8,15–19], poly(methacrylic acid) and poly-(ethylene glycol) [8,15,16,20–36], and poly(methacrylic acid) and poly(vinyl pyrollidone) [37–39]. Complexes formed between poly(methacrylic acid) and poly(vinyl pyrrolidone) are the most stable of the hydrogen bonded complexes [2,4–6,37–39]. This stabilization was attributed to the strong intermolecular affinity between the polymer chains. Additionally, complexes containing poly-(methacrylic

* Corresponding author. Tel. +1-765-494-7944; fax: +1-765-494-4080.
E-mail address: peppas@ecn.purdue.edu (N.A. Peppas)
[1] Current address: Chemical Engineering Department, Drexel University, Philadelphia, PA 19104, USA.

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acid) are more stable than complexes involving poly(acrylic acid) due to hydrophobic stabilization of the hydrogen bonds by the α-methyl group [2,4–6,15,16]. The complexes containing poly(methacrylic acid) were found to occur over a wider pH range than complexes containing poly(acrylic acid).

In three-dimensional polymer networks, complexation can significantly affect the network structure. As a result, the swelling behavior, mechanical properties and solute transport characteristics will vary dramatically between complexed and uncomplexed networks [8,11,24,25,30–36]. Because of this behavior, complexing polymer gels have the ability to function in a wide variety of applications. These include applications such as desalination and ultrafiltration membranes [21], chemo-mechanical systems [8,18,21,23] and mechanical sensors. Additionally, these gels could be advantageous in biomedical applications such as biosensors, dialysis membranes, peptide stabilizers [4,36,40], molecular imprinting [41] and drug delivery devices [13,26,31,33–36].

In our research, we have concentrated on a fundamental understanding of the molecular level complexation phenomena and conditions under which the complexes form. We have previously determined that complex formation in copolymer networks can be affected by many parameters including the size and concentration of the interacting polymer chains, and the nature of the environmental fluid [34]. In this work, we present methods for determining the molecular level complexation in crosslinked copolymer gels of poly(methacrylic acid) grafted with poly(ethylene glycol), i.e. poly(methacrylic acid-g-ethylene glycol), henceforth designated as P(MAA-g-EG). Additionally, a molecular level analysis was performed to gain insight into the relative degrees of complexation in the network structure.

2. Experimental

2.1. Polymer synthesis

Hydrogels of P(MAA-g-EG) 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.

MAA was vacuum distilled at 54°C/25 mmHg to remove the inhibitor, methoxyethyl hydroquinone. 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 crosslinking agent in the amount of 0.75% moles of total monomers. Nitrogen was bubbled through the well mixed solution for 30 min to remove dissolved oxygen, a free radical scavenger, which would act as an inhibitor.

Dimethoxy propyl acetophenone (Sigma Chemical Company, St. Louis, MO) was added in the amount of 1% weight of the monomers in a nitrogen atmosphere. The reaction mixture was poured between flat plates to form films of 0.9 mm thickness. The monomer films were sealed under nitrogen and exposed to UV light (Ultracure 100, Efos Inc., Buffalo, NY) at 1 mW/cm^2 at 365 nm and allowed to react for 30 min at 37°C.

Following the polymerization, polymer disks were cut into the desired shapes and the weight of the polymer was measured in air and in heptane, a non-solvent for the material. The polymer volume was determined by the buoyancy technique [42]. The gels were rinsed in deionized water for 7 days to remove unreacted monomer, initiator and the sol fraction. They subsequently were dried under vacuum at 37°C. The volume of the dry polymer samples was determined as previously described. The polymer volume fraction was calculated in the so-called relaxed state, i.e. immediately after crosslinking but prior to swelling or deswelling [42].

2.2. Small deformation analysis

In order to characterize the network structure, rubber elasticity experiments were performed using an automated tensile testing system (Instron model 4301, Park Ridge, IL). The grips of the apparatus were submerged in a water bath ($T = 37$°C) to ensure that the samples remained swollen during the experiments.

The copolymers were swollen to equilibrium in dimethyl glutaric acid buffer solutions (ionic strength constant, $I = 0.1$ M) ranging in pH from 3.2 to 7.4. Swollen samples were cut into dumbells using an ASTM die to yield specimens of length, l_0, of 25 mm and width, w, of 2 mm. The sample thickness, 2δ, was dependent on the pH of the swelling agent. The samples were positioned in the grips and allowed to equilibrate for 15 min. 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.

3. Results and discussion

The gels were prepared by crosslinking the monomers under conditions in which complexation would not occur. The MAA provided the materials with an ionizable backbone whereas the addition of the PEGMA provided the materials with the tethered PEG chains anchored to the ionic backbone. Using this technique we were able to carefully engineer materials with specific molecular compositions and graft chain molecular weights.

The degree of complexation in complexing graft copolymer networks may be expressed in terms of the parameter β, defined as the number repeating units of the graft chain

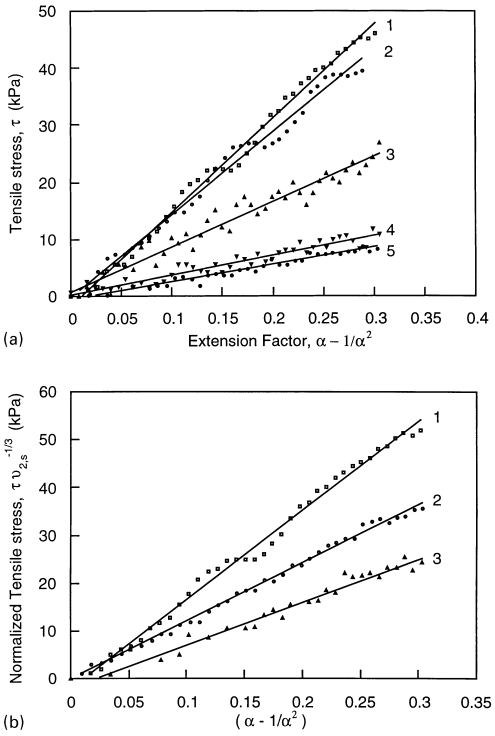

Fig. 1. Tensile stress, τ, at short deformations of P(MAA-g-EG) hydrogels (with EG/MAA ratio of 1 and PEG graft chains of molecular weight 1000) swollen in buffer solutions ($I = 0.1$ M) of varying pH (a) (1. pH = 3.5, 2. pH = 4.2, 3. pH = 4.6, 4. pH = 5.6, 5. pH = 6.8) at 37°C plotted as a function of the extension factor, $\alpha - \alpha^{-2}$ and (b) (1.pH = 3.5, 2. pH = 4.6, 3. pH = 6.8) at 37°C plotted as a function of the extension factor, $\alpha - \alpha^{-2}$, normalized to account for the swelling of the gel.

participating in the complexes, $n_{b,g}$, divided by the total number of backbone units in the material, n'_m.

$$\beta = \frac{n_{b,g}}{n'_m}. \tag{1}$$

In these gels, the number of backbone units in the materials is defined as the number of methacrylic acid (MAA) repeating units and the number of graft chain units is defined as the number of ethylene glycol (EG) repeating units. Because complexation occurs between two individual repeating units, β can take values between 0 and 1. However, the maximum value for the degree of complexation cannot be greater than the ratio of EG/MAA units in the copolymer.

3.1. Analysis of effective crosslinking upon complexation

The effects of the solution pH, copolymer composition and PEG graft chain molecular weight on the structure of crosslinked network were analyzed using rubber elasticity theory. First, the tensile stress, τ, was calculated as the force, F, per unstretched, swollen polymer area, $2w\delta$.

$$\tau = \frac{F}{2w\delta}. \tag{2}$$

The elongation, α, was also calculated as

$$\alpha = \frac{l(t)}{l_0} \tag{3}$$

where $l(t)$ is the length at different deformations and l_0 initial swollen length.

Studies were performed at pH values of 3.5, 4.2, 4.6, 5.6 and 6.8. As indicated in previous studies [33], gels tested at low pH values were expected to be in the complexed (and syneresed) state. Application of small deformation, rubber elasticity theory to the swelling of the hydrogel [43,44] were done using the following equation:

$$\frac{\tau}{\alpha - \alpha^{-2}} = G\upsilon_{2,s}^{-1/3}. \tag{4}$$

Here, G is the tensile modulus and $\upsilon_{2,s}$ is the equilibrium polymer volume fraction in the gel.

Fig. 1 shows the typical data of small deformation of the gels tested at 37°C and plotted according to Eq. (4). Indeed, the slopes of the curves of Fig. 1(a) decreased as the pH decreased. The increased modulus of the gel was due the presence of additional physical crosslinks resulting from interpolymer complexation in the networks. These in turn would lead to a significant decrease of the equilibrium polymer volume fraction in the gel. On the other side, as the complexes dissociated and the gels swelled, the modulus decreased significantly.

To uncouple the effects of gel swelling and complex formation on the elastic properties of the hydrogels, the tensile stress was normalized with respect to the polymer volume fraction, $\upsilon_{2,s}^{1/3}$. The normalized data were plotted in Fig. 1(b). Three distinct regimes of small deformation behavior can be distinguished. A regime of highly complexed gels containing a large number of physical crosslinks appears at pH = 3.5 as indicated by curve 1. A regime of moderately swollen gels containing some physical crosslinks and ionized pendant acid groups at pH = 4.6 is indicated by curve 2. Finally, a regime of highly swollen gels containing just the chemical crosslinks but virtually no additional physical crosslinks due to complexation appears at pH = 6.8 (curve 3). These data offer evidence for the existence of additional physical crosslinks due to complexation.

Such data can be used to determine the average molecular weight between effective crosslinks, M_e, and the correlation length of gels exhibiting different degrees of complexation. For example, networks crosslinked in the presence of a solvent can be analyzed [33,45] using the following equation:

$$\frac{\tau}{\alpha - \alpha^{-2}} = \mathrm{RT}\rho_{2,r}\left(\frac{1}{M_e} - \frac{2}{\bar{M}_n n}\right)\frac{\upsilon_{2,s}^{1/3}}{\upsilon_{2,r}}. \tag{5}$$

In this expression, $\rho_{2,r}$ is the density of the gel in the relaxed state, i.e. immediately after crosslinking but prior to swelling, and $\upsilon_{2,r}$ is the polymer volume fraction in the relaxed state. The term, $\bar{M}_n$, is the number average molecular weight of the linear polymer chains of the copolymer if no

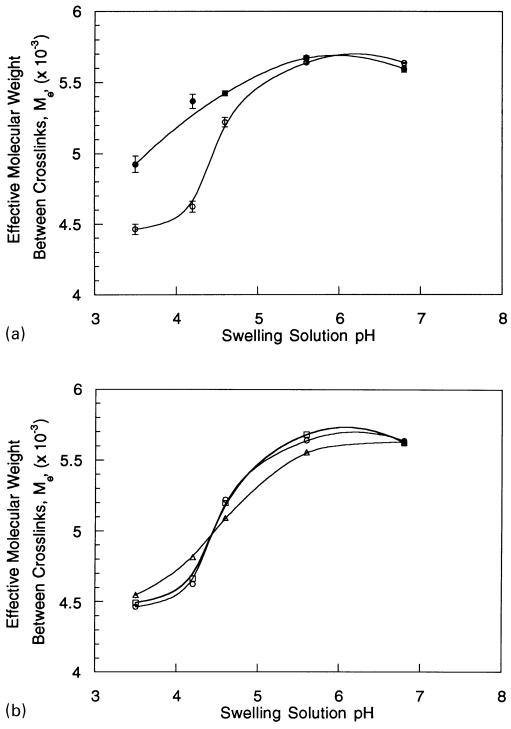

Fig. 2. Average molecular weight between effective crosslinks, M_e, of P(MAA-g-EG) hydrogels swollen in buffer solutions ($I = 0.1$ M) at 37°C plotted as a function of the swelling solution pH for gels (a) with PEG graft chains of molecular weight 1000 and varying ratios of MAA/EG (1:1 (○) and 4:1 (●)) and; (b) with an EG/MAA ratio of 1 and graft PEG chains of molecular weight 1000 (○), 400 (□) and 200 (△).

crosslinks are introduced. It was determined by calculating the kinetic chain length of a linear polymer chain prepared by the same type of free radical polymerization [46]. For the conditions used here, $\bar{M}_n$was calculated [25] as 11,550.

Using Eq. (5), the average molecular weight between crosslinks was determined for P(MAA-g-EG) networks containing a 1:1 MAA/EG molar ratio and swollen at various pH values. As shown in Fig. 2, the effective molecular weight between crosslinks increased significantly from the low pH solutions to the high pH solutions. In solutions of pH greater than 5.6, no physical crosslinks were present in the gels due to complete ionization of the pendant acid groups and the effective molecular weight between crosslinks was approximately equal to 5700. The molecular weight between crosslinks did not vary significantly with pH, copolymer composition or graft chain molecular weight under these conditions. For all of the PEG-containing gels, however, the molecular weight between crosslinks was reduced extensively as the pH was decreased below 5.6 due the presence of increased amounts of intermolecular crosslinking.

Based on these data, we were able to effectively calculate the total number of crosslinks, both chemical and physical. The total number of crosslinks in the gel at any time, n_{tot}, was equal to the number of temporary, physical crosslinks due to interpolymer complexation, n_{phys}, and the number of permanent, chemical crosslinks in the system, n_{chem}, which were introduced during the polymerization reaction,

$$n_{tot} = n_{chem} + n_{phys}. \tag{6}$$

The total degree of crosslinking in the system was due to contributions from chemical crosslinks and the interpolymer complexes. The degree of chemical crosslinking in the system was calculated from the reaction feed ratio and confirmed by experiment in solutions in which no complexation occurred.

The degree of complexation is equal to the number of bound graft polymer (EG) units divided by the total number of backbone chain (MAA) repeating units in the gel. Based on changes in the number of crosslinks and the effective molecular weight between crosslinks from the complexed state and the uncomplexed state, the total number of pendant chain units participating in the polymer complexes was calculated.

The effective molecular weight between crosslinks, M_e, is equal to the number of monomeric repeating units between crosslinks, x, times the molecular weight of the repeating unit, M_0. In interpolymer complexing P(MAA-g-EG) hydrogels, the number of monomeric repeating units between crosslinking points depended on the degree of complexation in the gels. Therefore, the degree of complexation was calculated from the effective molecular weight between crosslinks in the following manner.

For the case of the gels in which no complexes occur, the effective molecular weight between crosslinks, $M_{e,unc}$, was equal to:

$$M_{e,unc} = \frac{n'_m}{N} M_0. \tag{7}$$

Here, n'_m is the total number of backbone units in the gel and N is the total number of chains. For gels in the complexed state, the effective molecular weight between crosslinks was equal to:

$$M_{e,com} = \frac{n_{u,m}}{N} M_0. \tag{8}$$

Here, $N_{u,m}$ is the number of unbound pendant acid groups.

Because complexation in these gel occurs between a 1:1 ratio of repeating units, the number of bound graft chain repeating units, $n_{b,g}$, is equal to the number of bound backbone units, $n_{b,m}$. By subtracting Eq. (7) from Eq. (8) and rearranging, the total number of graft chain units participating in complexes is equal to

$$n_{b,g} = n_{b,m} = n'_m - n_{u,m} = \frac{N}{M_0}(M_{e,unc} - M_{e,com}). \tag{9}$$

Upon combination of these equations, the degree of complexation can be calculated directly from the molecular weight between crosslinks as

$$\beta = \frac{M_{e,unc} - M_{e,com}}{M_{e,unc}} = 1 - \frac{M_{e,com}}{M_{e,unc}}. \tag{10}$$

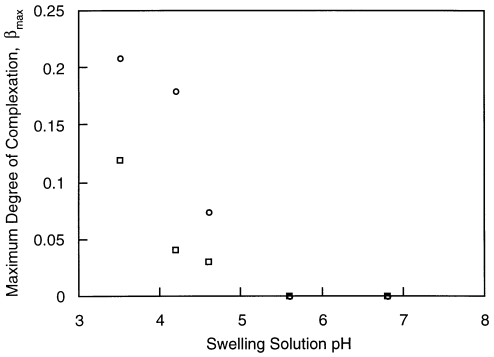

Fig. 3. Maximum degree of complexation, β_{max}, calculated from tensile experiments plotted as a function of the swelling solution pH for P(MAA-g-EG) hydrogels containing graft PEG chains of molecular weight 1000 and varying mole fractions of MAA ((○) 0.5 and (□) 0.8) swollen in buffer solutions (at constant ionic strength, $I = 0.1$ M) at 37°C.

Using this equation, the equilibrium degree of complexation was calculated as a function of swelling solution pH, copolymer composition and graft PEG chain molecular weight. The copolymer composition had a dramatic effect on the degree of complexation in the networks (Fig. 3). For the gels containing equimolar ratios of MAA/EG, the degree of complexation was 0.21 in the solution of lowest pH. Complexation occurred in these materials in solutions of pH = 4.6 or less. For the case of gels containing increased amounts of MAA (MAA/EG = 4), the degree of complexation was significantly lower in solutions of pH = 4.6 or less. In solutions of pH = 3.5 in which the largest amount of complexation occurred, the degree of complexation in the gels was around 0.12.

The effects of graft PEG chain molecular weight on complexation are shown in Fig. 4. All of the data were for gels containing equimolar amounts of MAA/EG. In solutions of pH 3.5, the degree of complexation ranged from 0.21 for gels containing the longest PEG grafts (molecular weight 1000) to 0.19 for gels containing the shortest PEG grafts (molecular weight 200). At pH = 4.2, the difference in complexation for gels containing graft PEG chains of differing molecular weight was the largest. Under these conditions, the maximum degree of complexation occurred in the gels containing the longest PEG grafts. However, in solutions of higher pH (pH = 4.6), the degree of complexation was highest in gels containing the shortest PEG grafts. In solutions of pH = 4.6, significant ionization occurred in the gels. Due to the ionization, a swelling force developed and the complexes dissociated. In gels containing the shortest PEG grafts, the swelling force was the smallest due to the fact that the blocks of ionizable units between PEG grafts were the shortest. In these gels, fewer complexes were dissociated due to swelling.

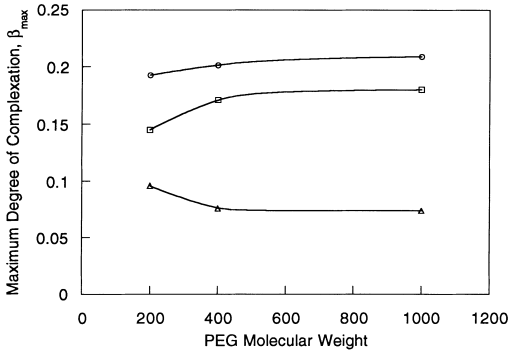

Fig. 4. Maximum degree of complexation, β_{max}, calculated from tensile experiments plotted as a function of graft PEG molecular weight for P(MAA-g-EG) hydrogels containing MAA/EG ratios of 1 swollen in buffer solutions (at constant ionic strength, $I = 0.1$ M) of varying pH ((○) 3.5, (□) 4.2 and (△) 4.6 at 37°C.

3.2. Theoretical description of complexation

Experimental studies have provided information on the macroscopic behavior of interacting polymer systems. Additionally, previous researchers have developed expressions to describe complexation in solutions of copolymers [2,6]. In this work, we have developed an equilibrium complexation theory to describe complexation based on the copolymer parameters and characteristics of the environmental fluid.

Interpolymer complexation can be described as a reversible association between two repeating units. In the case of complexing systems of anionic and neutral polymers, a complex is only formed between an unionized backbone group, m^*, and a neutral group on the graft chains, g:

$$g + m \underset{k_{-c}}{\overset{k_c}{\Leftrightarrow}} c. \tag{11}$$

Complexation can be described by a first-order reaction mechanism such that the rate of complex formation is equal to the rate of change of the number of bound graft chain units, $n_{b,g}$.

$$\frac{\partial n_{b,g}}{\partial t} = k_c n_g n_m - k_{-c} n_c. \tag{12}$$

In this expression, n_m is the number of unionized backbone groups not involved in the complexes and n_c is the number of complexes formed. By writing a balance on each species and exploiting the fact that the number of complexes is equal to the number of bound graft chain mers, Eq. (12) becomes

$$\frac{\partial n_{b,g}}{\partial t} = k_c n'_g n^*_m - (n'_g + n^*_m) n_{b,g} + n^2_{b,g}) - k_{-c} n_{b,g}. \tag{13}$$

Here, n^*_m is the total number of unionized backbone groups and n^*_g is the total number of grafted chain repeating units in the system.

This expression can be simplified further by using of definition of the degree of complexation, β, and the degree of ionization, α. The degree of complexation is the total number of bound oligomer units, $n_{b,g}$, divided by the total number of backbone units in the system, n'_m. The degree of ionization, α, is described using the Henderson–Hasselbach

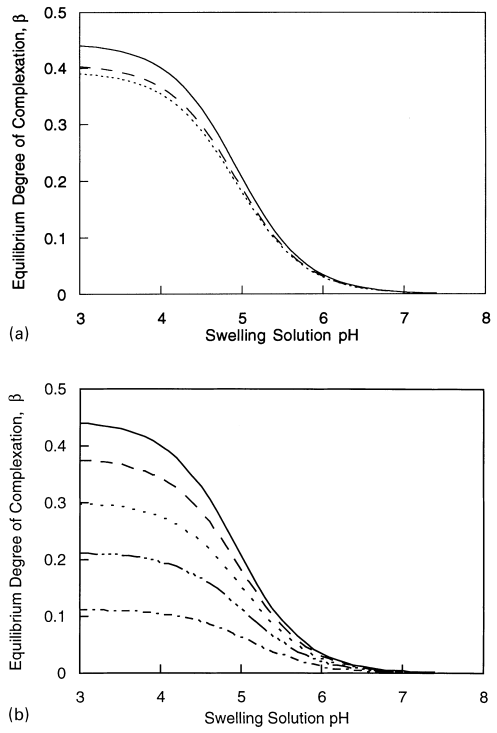

Fig. 5. Equilibrium degree of complexation as a function of pH at 37°C for copolymers of P(MAA-g-EG) (a) with $r = 1$ and PEG grafts of molecular weight (—) 1000, (— —) 400, and (- - -) 200 and; (b) with PEG grafts of molecular weight 1000 and r of (—) 1, (— —) 0.8, (- - -) 0.6, (– - – –) 0.4 and (– – –) 0.2.

equation and is equal to the fraction of unionized acid group

$$\alpha = \frac{n_m^*}{n_m'} = \frac{10^{-\mathrm{pH}}}{10^{-\mathrm{pH}} + K_a}. \tag{14}$$

Applying these definitions, the rate of change in the degree of complexation can be written as

$$\frac{\partial \beta}{\partial t} = k_c[n_g'\alpha - (n_g' + n_m'\alpha)\beta + \beta^2 n_m'] - k_{-c}\beta. \tag{15}$$

At equilibrium, the degree of complexation is constant

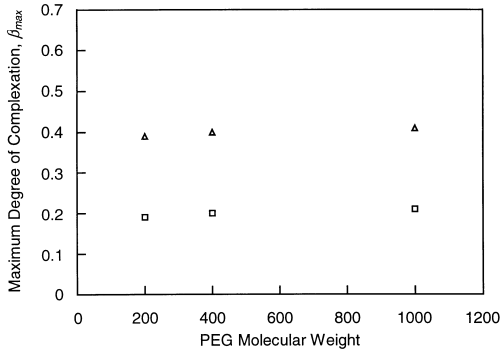

Fig. 6. Maximum degree of complexation, β_{max}, calculated from (□) tensile testing and (△) complexation theory plotted as a function of graft PEG molecular weight for P(MAA-g-EG) hydrogels containing MAA/EG ratios of 1 swollen in buffer solutions (at constant ionic strength, $I = 0.1$ M) at 37°C.

and the equation for the equilibrium degree of complexation becomes a quadratic expression.

$$\beta^2 - (r + \alpha + C)\beta + \alpha r = 0. \tag{16}$$

In this expression, r is ratio of the number of graft chain repeating units and the number of backbone repeating units, n_g', divided by the total number of matrix units in the system, n', and C is the inverse reaction rate constant normalized to the total number of complexes which can form. The normalized reaction constant is written [2] as

$$C = \exp^{(\nu \Delta G^0/\mathrm{RT})}. \tag{17}$$

In this expression, ΔG^0 is the specific free energy of complexation and v is the length of the graft molecular weight chain. By solving the equation and subjecting the expression to the constraints, at $r = 0$, $\beta = 0$, the equilibrium degree of complexation can be calculated as

$$\beta = \frac{1}{2}\left(r + \alpha + \exp^{(\nu \Delta G^0/\mathrm{RT})}\right) - \left(r + \alpha + \exp^{(\nu \Delta G^0/\mathrm{RT})}\right)^2 - \alpha r^{1/2}. \tag{18}$$

Interpolymer complexes are stabilized by the cooperative nature of their bonds. Thus, complexation is enhanced as the length of the interacting polymer chains is increased. The dependence of the degree of complexation on the graft chain length, ν, is shown in Fig. 5(a) for P(MAA-g-EG) hydrogels with $r = 1$. Gels containing PEG grafts of molecular weight 1000 exhibit a maximum degree of complexation of 0.44 at low pH, while gels containing grafts of molecular weight 200 have a maximum value of $\beta = 0.39$. Eq. (18) was developed based on the earlier theories of Kabanov [2] for interpolymer complexation between linear homopolymers. More recently, we [6] determined that complexation was not as dependent on chain length in graft copolymer systems. Using this analysis, the graft PEG chain length dependence was more significant than what was experimentally observed using mechanical testing.

The composition of the polymer gel also affects the degree of complexation. As defined, β can take a maximum value of r for $r < 1$ and 1 for $r \geq 1$. The theoretical degree of complexation is shown in Fig. 5(b) as a function of copolymer composition for P(MAA-g-EG) hydrogels containing graft PEG chains of molecular weight 1000. The theory predicts a significant change in the degree of complexation with changing copolymer composition. The maximum degree of complexation occurs in gels containing equimolar amounts of MAA/EG. For $r = 1$, the maximum degree of complexation is 0.44, while for $r = 0.20$, the maximum value of β is only 0.10. Additionally, as the amount of EG in the system is increased, the maximum degree of complexation will not increase above 0.44. This is evidence that the number of ionizable MAA sites were controlling the total amount of complexation. Thus, the conformation of the

Table 1
Maximum degree of complexation, β_{max}, in P(MAA-g-EG) hydrogels swollen at 37°C in buffer solutions of pH = 3.5 and constant ionic strength, $I = 0.1$ M

Molar ratio of EG/MAA	Graft chain molecular weight	β_{max} from small deformation testing	β_{max} from theoretical calculations
1	1000	0.21	0.44
1	400	0.20	0.40
1	200	0.19	0.39
0.25	1000	0.12	0.11

PMAA backbone chain was vital for complexation in the P(MAA-g-EG) gels.

3.3. Comparison of theoretical and experimental data

The degree of complexation was determined for P(MAA-g-EG) hydrogels as a function of swelling solution pH, graft PEG chain molecular weight and copolymer composition using swelling studies, tensile experiments and a complexation theory. The maximum degree of complexation observed using all of the methods occurred at the lowest pH value studied (pH = 3.5). Under these conditions, the greatest fraction of pendant units was protonated allowing for substantial complexation.

The maximum degree of complexation is shown in Fig. 6 experimentally and theoretically as a function of the graft PEG chain molecular weight for gels containing equimolar amounts of MAA/EG and in Table 1 for all of the gels examined. The values of the degree of complexation determined from the tensile experiments were lower than those calculated using equilibrium complexation theory. The values from tensile experiments are deemed to be more accurate.

The degree of complexation predicted by the complexation theory was higher than the actual value. The theoretical value was higher due to the fact that the model was for an ideal gel assuming that complexation could occur between any two complimentary units. In real systems, complexation is hindered by the presence of chemical and physical crosslinks. Therefore, the theoretical value was higher than the actual value. However, the theory and experiment are in good agreement with the weak dependence of complexation on PEG graft chain molecular weight and the strong decrease in complexation with increasing amounts of MAA in the gel.

4. Conclusions

The change in the network structure in response to interpolymer complexation was examined using tensile experiments. These data were analyzed using rubber elasticity theory. The degree of crosslinking and effective molecular weight between crosslinks were calculated for gels swollen in solutions of pH ranging from 3.5 to 7.4. Because of complexation, the degree of chemical and physical crosslinking in the gels was increased by up to 25% under conditions in which complexation occurred. Additionally, the effective molecular weight between crosslinks was decreased by up to 20% between the uncomplexed and complexed states.

The molecular level degree of complexation was experimentally determined. The degree to which complexation occurred was strongly dependent on the environmental pH, copolymer composition and the PEG graft chain molecular weight. The largest amounts of complexation were observed in gels containing nearly equimolar amounts of the monomeric units and the longest molecular weight poly(ethylene glycol) grafts.

Additionally, a complexation model was developed to describe the mechanism of complexation. These data were compared to the experimental values. The theoretical model and experimental data were in good agreement with the dependence of complexation on the polymer parameters and the swelling solution pH.

Acknowledgements

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