Self-Associating Networks of Poly(methacrylic acid-*g*-ethylene glycol)

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ABSTRACT: Poly(methacrylic acid-*g*-ethylene glycol) networks were prepared by the copolymerization of methacrylic acid and poly(ethylene glycol) methacrylate in the presence of a tetraethylene glycol dimethacrylate cross-linking agent. Their swelling characteristics depended on swelling solution pH, swelling temperature, copolymer composition, and network structure. In aqueous swelling solutions at acidic pH, copolymer networks swelled to a much lower extent than homopolymer networks. This behavior was attributed to complex formation between poly(ethylene glycol) and poly(methacrylic acid) segments. Nuclear Overhauser enhancement measurements revealed that graft copolymers formed complexes under a wider range of concentrations and poly(ethylene glycol) molecular weights than the two ungrafted homopolymers. This enhancement in complexation was attributed to elimination of the unfavorable translational free energy change of complexation by covalent attachment of the complexing species.

Introduction

Polymer networks that exhibit swelling transitions in response to changes in solvent pH, temperature, or composition have been considered as candidate materials for controlled release, separations, control of enzyme–substrate reactions, and sensor applications. Hoffman and collaborators[1,2] devised a hydrogel system based on poly(isopropylacrylamide) that undergoes thermally reversible swelling and deswelling, allowing control of dye, vitamin, and myoglobin release. Similar gels were used to control reactions of asparagine with immobilized enzymes, by controlling substrate diffusivity via swelling changes. Temperature- and pH-sensitive gels were also used by Cussler and collaborators[3,4] to concentrate proteins by absorbing the water of protein solutions and excluding the protein macromolecules from the network.

Similarly, hydrogel membranes, which undergo dimensional changes and permeability modification due to variations in pH, have been suggested for controlled solute release. Bioresponsive membranes for insulin delivery have been developed by Horbett et al.[5] and Ishihara and Matsui.[6,7] According to the method of Horbett et al., the enzyme glucose oxidase was immobilized in a pH-responsive poly(hydroxyethyl methacrylate-*co*-(diethylamino)ethyl methacrylate) membrane. In the presence of glucose, this enzyme produced gluconic acid, which lowered the membrane pH, protonating the amino moieties and inducing membrane swelling. Enzymatic systems of this type can also be used to form biological sensors.[8] A potentiometric, amperometric, or mechanical sensor coated with an enzyme-containing hydrogel can be used to detect products of an enzyme–substrate reaction.

The most common temperature-sensitive networks are made from hydrophobically associating homopolymers including poly(isopropylacrylamide) or copolymers containing hydrophobic substituents. Networks containing ionizable functional groups exhibit pH sensitivity. Amine substitution results in swelling in acidic pH solution due to formation of the ammonium polyelectrolyte. Similarly, carboxylic acid substituents form ionized salts at basic pH resulting in increased network swelling.

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Complex formation between complementary polymers may also result in precipitation of polymers from solution and changes in network swelling.[9-13] Polymers that form complexes may associate due to van der Waals interactions, ionic bonds, hydrogen bonds, coordination interactions, or salt bridges formed by polyvalent metal ions.[9-13]

In solution, polymer complexation is often cooperative in nature,[9-11] resulting in a significant increase of complex stability with polymer chain length. Complexation of large chains involves a smaller translational entropy loss per interacting site than binding of small chains. Consequently, a critical molecular weight may exist, below which complexation does not occur.[9-11]

Complexes of poly(methacrylic acid) [PMAA] with poly(ethylene glycol) [PEG] have been studied in blends and in solutions by using techniques such as viscometry, sedimentation, potentiometric titration,[9-11] and, more recently, fluorescence spectroscopy.[14-17] When PMAA is formed by free-radical polymerization, complexes with PEG appear to form in a 1:1 repeating unit molar ratio in water at acidic pH. They are formed by hydrogen bonds between a polymeric Lewis acid such as PMAA, and a Lewis base such as PEG, and are stabilized by hydrophobic interactions. In solution, a critical PEG molecular weight around 2000 has been reported,[9-11] below which complexes will not form. In water, these complexes are broken by neutralization of the PMAA with base or by addition of alcohols, which disrupt hydrophobic interaction. Due to the hydrophobic stabilization, PMAA/PEG complexes also get stronger with temperature.

Complexes of PEG with PMAA membranes have been studied over the past 15 years.[11] Addition of PEG to a PMAA membrane causes the latter to contract sharply. The contraction occurs in water and is promoted by an increase in temperature and low solvent pH values. In these systems, a critical PEG molecular weight for complexation has been identified at approximately 600. Below this molecular weight, network contraction was not detected.

Similarly, membranes made of interpenetrating networks (IPN) of poly(acrylic acid) (PAA) and PEG have been studied.[18,19] These membranes exhibited similar contraction behavior to the PMAA membranes discussed above. Whereas PMAA-containing networks contracted with increase in temperature, PAA containing networks swelled to a greater extent. This effect was attributed to

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the greater role of hydrophobic interactions in stabilization of PMAA complexes than PAA complexes.

Here, we present results on the synthesis and swelling of environmentally sensitive poly(methacrylic acid-*g*-ethylene glycol) networks. These polymers have two complex-forming constituents covalently linked to one another, and swelling is largely regulated by control of complexation. The dependence of network swelling on solvent pH, temperature, and composition as well as on network structure is examined. In addition, the unique complex-forming properties of the graft copolymers in dilute solution are examined by using the time-dependent nuclear Overhauser effect and are compared to the properties of homopolymer mixtures.

Experimental Section

Monomer Synthesis. Poly(methacrylic acid-*g*-ethylene glycol) networks, henceforth referred to as P(MAA-*g*-EG), were synthesized by copolymerization of poly(ethylene glycol) methacrylate (PEGMA, Polysciences, Warrington, PA) with methacrylic acid (MAA) in the presence of a tetraethylene glycol dimethacrylate (TEGDMA) cross-linking agent. All monomers were purified and characterized prior to use.

PEGMA monomers including hydroxyethoxyethyl methacrylate [HEEMA] and related species were synthesized by esterification of methacryloyl chloride with PEG of the required molecular weight. To 50 mL of a 20 wt % solution of dried PEG in dry dichloromethane was added 50 mL of dry dichloromethane containing methacryloyl chloride and triethylamine in a 3:7 molar ratio to the PEG. The reaction mixture was cooled in an ice water bath, the reactants were added dropwise, and the reaction was allowed to proceed for 3 h followed by 15 h at room temperature. The reaction mixture was subsequently cooled in an ice water bath and filtered to remove the ammonium hydrochloride. The solution was washed with dilute HCl followed by distilled water and dilute sodium carbonate solution. The solvent was then evaporated, and the monomer was dissolved to 4 times its volume in water. The aqueous solution was extracted three times with heptane. The amount of heptane used was 25 vol % of the aqueous solution. The extraction was followed by an identical extraction with cyclohexane. These extractions were conducted to remove the dimethacrylate impurities. The monomer was then extracted with a 25:75 (v/v) mixture of hexane/dichloromethane. The organic phase was dried over anhydrous sodium sulfate, filtered, and evaporated. A small amount of hydroquinone inhibitor was added to the monomer before storage. Just before use, the inhibitor was removed using a "dehibit" column (Polysciences, Warrington, PA). Commercially obtained monomers were stirred with 15 wt % anhydrous sodium carbonate followed by extraction as described above.

Monomer Characterization. The PEGMA macromonomers were characterized by using ^{1}H NMR spectroscopy and HPLC. ^{1}H NMR spectra were obtained in D_2O by using a 200-MHz Fourier transform spectrometer (NTC-200, Nicolet, Minneapolis, MN) at 21 °C. The ratios of ethylene and ester to vinyl intensities were used to determine the degree of esterification and the pendant chain molecular weight. Monomer purity was determined by HPLC by using a column packed with 5-μm C-18 reversed-phase packing (Alltech Associates, Inc., Deerfield, IL), and concentrations were measured by using a UV detector (Waters Associates, Milford, MA) at 254 nm. The MAA and dimethacrylate impurities were identified by their distinct retention times and quantified. A 60:40 (v/v) methanol/water solution under isocratic conditions was used as the eluant.

Polymer Synthesis. The copolymer networks were synthesized by the free-radical copolymerization of methacrylic acid with PEGMA in the presence of TEGMA present at 2 wt % of the total monomers. The monomer mixture was diluted with a 50:50 (w/w) mixture of ethanol/water to a final monomer concentration of 40 wt %. Polymerization took place in sealed polyethylene vials under nitrogen at 37 °C for 24 h and was initiated by using 0.025 wt % ammonium persulfate and sodium bisulfite based on monomer weight. The un-cross-linked polymers were prepared by a similar solution polymerization using 10 wt % monomer without TEGDMA. The gels were purified by washing them with distilled water for 2 weeks, and the un-cross-linked polymers were reprecipitated in acetone or hexane, followed by dialysis against distilled water at pH = 3.

Table I
Molecular Weights of PEGMA Monomers

monomer	pendant chain mol wt	monomer	pendant chain mol wt
PEGMA 100	88.0	PEGMA 400	393.9
PEGMA 200	214.1	PEGMA 1000	1071.0

Polymer Characterization. The copolymer networks were dried in vacuo and crushed into microparticles. They were then neutralized with an aqueous solution of NaOD in D_2O. The final solvent content was 85–90 wt %. The swollen gels were analyzed by using ^{13}C NMR spectroscopy with an inverse-gated pulse sequence with sufficient relaxation delay for quantitative measurement. Principally, the carbonyl and carboxylate peaks were studied. Soluble copolymers were characterized by using ^{1}H NMR spectroscopy in a manner identical with that used for monomer characterization.

Equilibrium Swelling. The washed gels were equilibrated in acidic aqueous solutions of the appropriate pH by changing the solution twice daily for 2 weeks. Equilibrium swelling in basic solutions was accomplished by preequilibrating the gels in a pH = 11 solution for 2 days followed by equilibration in the basic aqueous solution of the desired pH. Subsequently, the gels were allowed to equilibrate at the desired temperature ±1 °C in a water bath for 2 weeks in sealed containers. Swelling in salt and alcohol solutions was done under air. Swelling in HCl and NaOH solutions between pH 5.5 and 8.5 was done under a nitrogen atmosphere by using decarboxylated water in sealed pressure bottles. After swelling, the gel weights were determined in air, the gels were dried to constant weight in vacuo, and the dried gels were weighed to determine the solvent weight fraction.

Nuclear Overhauser Effect Measurements. Proton nuclear Overhauser enhancement (NOE) measurements were conducted on graft copolymer and homopolymer solutions in D_2O, in D_2O with NaOD, and in D_2O/MeOD mixtures. The NOE values were obtained by using an interleaved difference spectrum. The pulse sequence consisted of a presaturation of the desired proton, a 2-ms equilibration delay, acquisition of the free induction decay (FID), and, finally, a relaxation delay. Presaturation times ranged from 25 μs to 3 s.

The pulse sequence with saturation of the desired proton was repeated eight times, and the accumulated FID was stored. This was followed by acquisition of 8 FID with irradiation "off resonance". This procedure was repeated until 160–360 acquisitions were obtained. The FID were Fourier transformed and the on and off resonance spectra subtracted. The integrated intensity of the observed peak in the difference spectrum was divided by the intensity of the peak in the "off resonance" spectrum to obtain the NOE. Time-dependent NOEs were obtained by varying the irradiation times, and all irradiations were done by using identical power settings, polymer concentrations, and NMR parameters.

Results and Discussion

Characterization. NMR characterization of the monomers showed that an effective purification had been achieved. No MAA or solvent peaks were detected in the monomers. HPLC results indicated MAA and dimethacrylate concentrations lower than 0.5 mol % in all PEGMA monomers considered here. PEGMA pendant chain molecular weights as determined by NMR are indicated in Table I.

The P(MAA-*g*-EG) networks consisted of PMAA backbone chains with pendant PEG chains; the PMAA chains were cross-linked by TEGDMA monomer units. All networks were clear and homogeneous in appearance, both after polymerization and after equilibrium swelling.

The P(MAA-*g*-EG) networks were analyzed by ^{13}C NMR spectroscopy. The carbonyl/carboxyl regions of the spectra

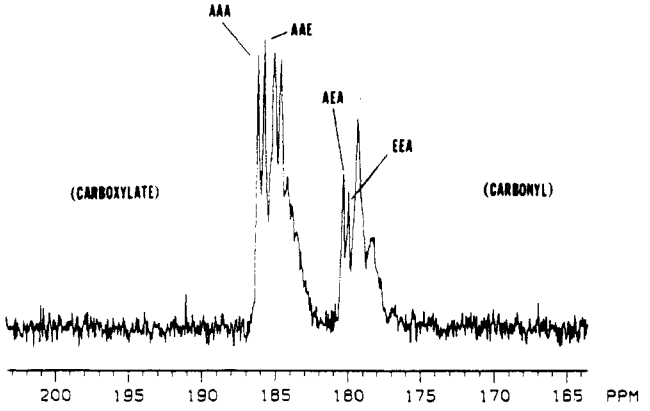

Figure 1. Carbonyl/carboxyl portion of the ^{13}C NMR spectrum of a P(MAA-*g*-EG) network with a PEG $\bar{M}_n$ of 200 showing functional groups and structure. The spectrum was obtained in deuterium oxide.

were used to obtain the approximate network compositions. In all cases, the carboxylate fractions determined by NMR spectroscopy were within 3 mol % of those predicted by monomer stoichiometry. In addition, extracted sol fractions were lower than 4.5 wt % of the polymer.

Qualitative information about the monomer sequence distribution (MSD) and copolymer stereochemistry was obtained from the ^{13}C spectrum. The carbonyl and carboxylate peaks shown in Figure 1 were split into three large subpeaks corresponding to syndiotactic, heterotactic, and isotactic triads in the order of decreasing chemical shift.[20] These peaks were, in turn, split into smaller peaks arising from triads in the monomer sequence distribution (MSD).

For the network whose spectrum is illustrated in Figure 1, the AAA (all acid triad) and AAE (an acid surrounded by an acid and an ester) triads were expected to be equal in intensity based on monomer concentration in the initial reaction mixture if the monomers reacted in a random manner. Although the peaks arising from the MSD could not be quantitatively integrated due to peak overlap, the AAA and AAE peaks were nearly equal in amplitude, suggesting that the copolymerization was random in nature. Significant block copolymerization would have resulted in an AAA peak, which would be much larger than the AAE peak. The primary splitting also was predominantly syndiotactic and heterotactic in the nature of the copolymer.

Equilibrium Swelling Studies. The effect of pH on the equilibrium solvent weight fraction of P(MAA-*g*-EG) networks in distilled water and in 0.1 M aqueous sodium chloride solutions at 37 °C is shown in Figure 2. Changes in pH resulted in swelling transitions from approximately 32 wt % (w_1 = 0.32 water) at acidic conditions to over 99.5 wt % at basic conditions. This corresponds to a change of equilibrium weight swelling ratios, q, from 1.47 (at pH = 3.0) to 200 (at pH = 8.0). Similar pH-dependent swelling transitions were observed in all P(MAA-*g*-EG) networks considered. The corresponding transitions in identically prepared pure PMAA gels were from 90 wt % (w_1 = 0.90) water at acidic conditions to over 99.5 wt % at basic conditions; this corresponds to a change of swelling ratios from 10 (at pH = 3.0) to 200 (at pH = 8.0). Pure PEGMA networks did not exhibit a pH-dependent swelling transition.

A series of copolymer gels ranging in composition from pure PEGMA networks to pure PMAA networks were synthesized and swollen in acidic and basic aqueous solutions and in methanol. Figure 3 shows the equilibrium solvent weight fractions of the copolymer networks at pH = 4 in water. Although homopolymer network swelling was high, typically near 90 wt % water (swelling ratio of

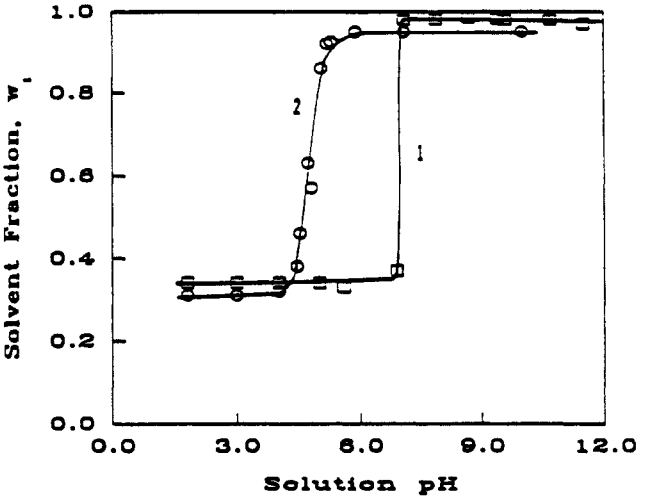

Figure 2. Equilibrium solvent weight fraction, w_1, in P(MAA-*g*-EG) gels versus swelling pH. Gels were prepared with a PEG of $\bar{M}_n$ = 200 and EG:MAA = 60:40. Swelling was in distilled water (curve 1) or in a 0.1 M NaCl solution (curve 2) at 37 °C.

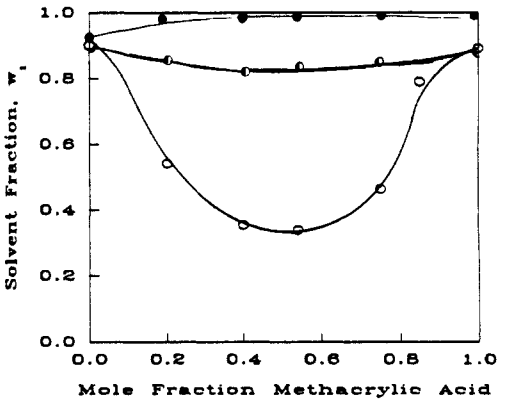

Figure 3. Equilibrium solvent weight fraction, w_1, in P(MAA-*g*-EG) gels versus MAA mole fraction. Gels were prepared with a PEG $\bar{M}_n$ = 200. Swelling was in distilled water at pH = 4.0 and 37 °C.

q = 10), copolymer swelling was sharply lower, exhibiting a minimum (w_1 = 0.36, q = 1.56) near the 1:1 ethylene oxide/methacrylic acid repeating unit molar ratio.

When these gels were placed in a basic solvent at pH of 9.0 (Figure 3), the equilibrium solvent weight fraction was high and increased with MAA content. Similarly, in methanol, all of the copolymer networks exhibited nearly equal equilibrium solvent weight fractions regardless of the MAA mole fraction. Similar behavior was observed with all PEG molecular weights considered, including hydroxyethoxyethyl methacrylate (HEEMA). When 2-hydroxyethyl methacrylate (HEMA) was used, the equilibrium solvent weight fraction in the homopolymer gel was low (about 40 wt %) and a pronounced minimum in swelling was not observed.

The minima in equilibrium swelling ratios for copolymers with composition in the vicinity of a 1:1 EO/MAA molar ratio may be attributed to formation of hydrogen-bonded hydrophobically stabilized complexes. The stoichiometry seen here is consistent with complex stoichiometry in solutions as determined by previous investigators. Neutralization of the gels in base resulted in high equilibrium swelling ratios. The absence of swelling ratio minima at basic pH confirms the absence of specific polymer/polymer interactions involving the sodium methacrylate form of PMAA. Furthermore, the increase in equilibrium solvent weight fraction with MAA content at basic pH may be attributed to the increasingly ionic nature

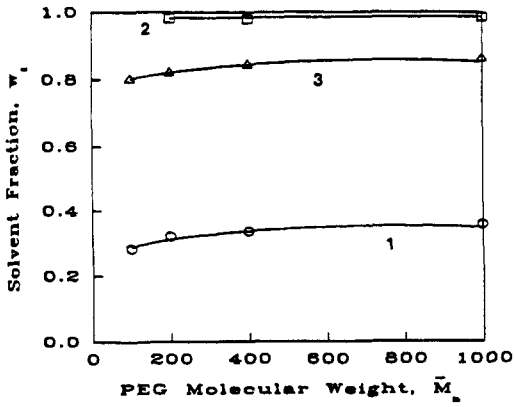

Figure 4. Equilibrium solvent weight fraction, w_1, in P(MAA-*g*-EG) gels versus PEG pendant chain molecular weight. Gels were prepared with EG:MAA = 60:40. Swelling was in distilled water at pH = 4.0 (curve 1), distilled water at pH = 9.0 (curve 2), and methanol (curve 3) at 37 °C.

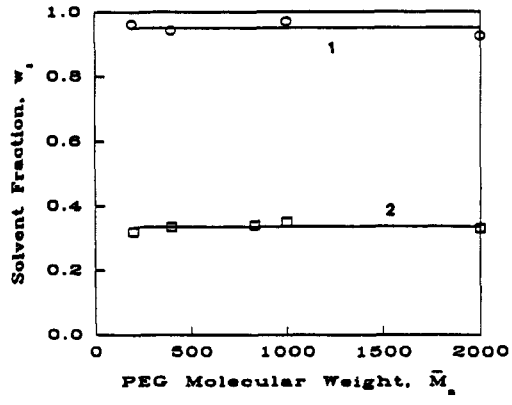

Figure 5. Equilibrium solvent weight fraction, w_1, in P(MAA-*g*-EG) and a PMAA gel/PEG mixture versus pendant chain molecular weight. Gels were prepared in bulk with EG:MAA = 60:40. Swelling in distilled water with mixture (curve 1) and copolymer gel (curve 2) at 37 °C.

of the polymers.

Alcohols are known to disrupt hydrophobic interactions in complexes of PEG and PMAA.[9-11] When the P(MAA-*g*-EG) networks are swollen in methanol, no swelling ratio minima were observed, indicating that the minima observed in aqueous media were due to specific interactions between the PEG and PMAA segments and suggesting that hydrophobic interactions play a role in the complex formation.

The equilibrium solvent weight fraction and swelling transitions were little affected by the PEG molecular weight (Figures 4 and 5). The results of these figures showed that complexes form at lower molecular weights in graft copolymers than observed in solution[9-11] or in PMAA membranes exposed to PEG solutions.[18,19] In addition, the swelling of PMAA gels polymerized in the presence of PEG and then washed as described earlier exhibited uniform weight swelling ratios of approximately 90 wt %, indicating that covalent attachment of the complexing species is necessary for effective permanent complexation.

The swelling of graft copolymer networks was also temperature-dependent as shown in Figure 6. The equilibrium solvent weight fractions of homopolymer networks were high and little affected by temperature, while those of nearly stoichiometric networks were low and largely independent of temperature. Swelling of networks of intermediate composition, containing nonstoichiometric ratios of MAA to EO repeating units, was sensitive to

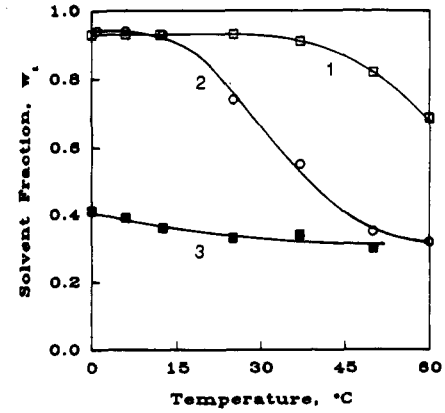

Figure 6. Equilibrium solvent weight fraction, w_1, in P(MAA-*g*-EG) gels versus temperature. Gels were prepared with a PEG $\bar{M}_n$ = 200. Swelling was in distilled water at pH = 4.0 with EG:MAA = 100:0 (curve 1), 80:20 (curve 2), and 45:55 (curve 3) at 37 °C.

temperature and decreased substantially with increases in temperature.

The reduction in equilibrium solvent weight fraction with increasing temperature may be attributed to an increased complex strength due to hydrophobic interactions between complexing polymers and/or from secondary hydrophobic aggregation of the complexed chains. Gels with nearly equivalent monomer molar ratios probably contain a high fraction of monomer units involved in complexes. Nonstoichiometric gels, on the other hand, may contain both complexed and uncomplexed PEG sequences. At low temperatures, the "free" monomer units impart a hydrophilic nature to the network, balancing the hydrophobic nature of the complexes and resulting in high network swelling. When the temperature is raised, however, hydrophobic interactions between complexes, within complexes, or between complexes and free PEG sequences may result in a reduction in solvent weight fraction. Since homopolymer networks exhibit a much smaller change in swelling with temperature, interactions between like polymers probably contribute little to deswelling of the copolymer networks.

NOE Measurements. The presence of a proton–proton nuclear Overhauser enhancement (NOE) in the NMR spectrum of a two-spin system is indicative of interproton distances of 5 Å or less.[21,22] Relative NOE magnitudes and NOE growth rates may be used to calculate interproton distances, and this kind of analysis will be presented in future papers for the system P(MAA-*g*-EG) polymers. In general, though, NOE evolution rates increase as interproton distances decrease. When molecular complexes are considered, increasing intermolecular (or intersegmental) NOE growth rates may also arise from an increasing fraction of molecules bound to one another.

The intermolecular NOE values of the PEG ethylene protons in PEG/PMAA solutions in D_2O are shown in Figure 7 as functions of PEG molecular weight. Here, the α-methyl protons of PMAA were irradiated and NOE values of the PEG ethylene protons were observed.

Under acidic conditions a negative NOE developed. This indicates that PEG and PMAA molecules were bound with interproton distances of 5 Å or less. When the PMAA was neutralized with NaOD or the experiment was conducted in deuterated methanol, no NOE was detected as shown in Figure 8, indicating an absence of binding under these "complex-breaking" conditions.

The NOE enhancements of the PEG ethylene protons were all negative. This effect is explained in terms of the

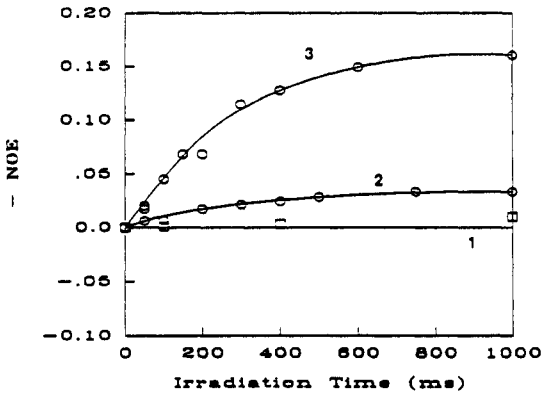

Figure 7. Nuclear Overhauser enhancement (NOE) of PEG ethylene protons in a solution of PEG and PMAA versus irradiation time. Proton enhancements are reported for systems prepared with a PEG of $\bar{M}_n$ = 200 (curve 1), 100 (curve 2), and 1500 (curve 3). The PEG concentration was 0.01 wt %, PMAA concentration was 0.09 wt %, solvent was D_2O, and temperature was 21 °C.

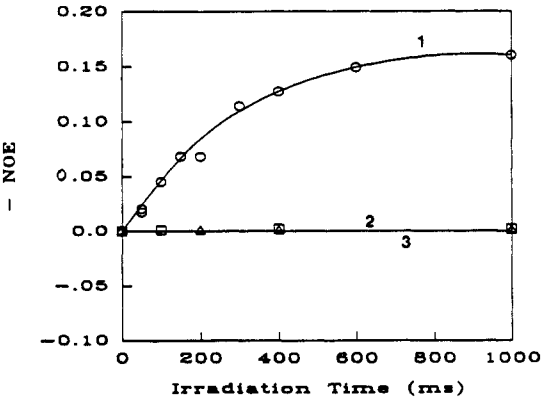

Figure 8. Nuclear Overhauser enhancement (NOE) of PEG ethylene protons in a solvent of PEG and PMAA versus irradiation time. Proton enhancements are reported in D_2O (curve 1), NaOD solution (curve 2), and MeOD (curve 3). The PEG $\bar{M}_n$ was 1500, PEG concentration was 0.01 wt %, PMAA concentration was 0.09 wt %, and temperature was 21 °C.

influence of molecular weight on rotational correlation time, τ_c, of the complex. At high molecular weights, the macromolecular rotation is slow and τ_c is long. Above 5000 molecular weight in a 200-MHz NMR experiment, this typically leads to an increased contribution of the zero quantum transitions to the spin–lattice relaxation process, resulting in negative NOE.[21,22] Consequently, the negative sign of the NOE reflects the long rotational correlation times of PEG in the PEG/PMAA complex.

Furthermore, the NOE growth rates under complex-promoting conditions increased with PEG molecular weight and decreased with dilution. This indicates that the fraction of PEG involved in complexes increases as the PEG molecular weight increases, a result that is consistent with solution-phase results obtained by previous investigators.[9-12] No transferred NOE was detected in the complex-breaking solvent methanol as shown in Figure 8.

The NOE in graft copolymers was substantially greater than that in homopolymer mixtures, under acidic conditions. No NOE was detected in graft copolymers under basic conditions and in methanol, indicating effective disruption of complexes under these conditions. Figure 9 shows the α-methyl/ethylene NOE in very dilute graft copolymer solutions compared to NOE of homopolymer solutions of identical composition and dilution at 400-ms irradiation time. The low PEG concentration in solution is used so that (a) all of the PEG molecules have potential binding sites and (b) hydrophobic agglomerates

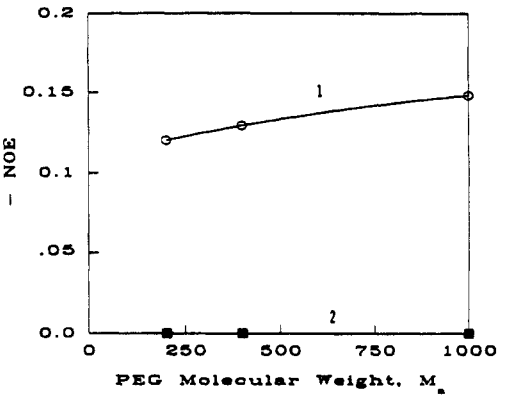

Figure 9. Nuclear Overhauser enhancement (NOE) of PEG ethylene protons versus PEG molecular weight, $\bar{M}_n$, at 400-ms irradiation time. Proton enhancements of graft copolymers (curve 1) and polymer mixtures (curve 2). PEG concentration is 0.001 wt %, PMAA concentration is 0.009 wt %, solvent is D_2O, and temperature is 21 °C.

are prevented from forming in dilute solution. At the dilutions considered, no complexation was detected in the mixture of homopolymers.

Under these conditions, all of the graft copolymers showed substantial transferred NOE and, therefore, complexation, regardless of PEG molecular weight. This testifies to the enhancement of complexation, which arises from covalent grafting. A physical manifestation of this enhanced complexation is the propensity of the graft copolymers to precipitate at PEG molecular weights and concentrations where homopolymer mixtures form homogeneous solutions.

The enhanced complex-forming ability of graft copolymer may be explained by considering the effect of grafting on the free energy of binding. In order for a PEG oligomer to bind with PMAA, the PEG must first lose its translational degrees of freedom. This unfavorable contribution to the binding free energy is compensated for by contact free energy changes.

When PEG is grafted to PMAA, complexation is no longer accompanied by a loss in translational degrees of freedom. Consequently, the net complexation free energy change becomes more favorable and complexation takes place at a larger range of PEG molecular weights and dilutions than complexation in homopolymer mixtures. A semiquantitative model describing graft-promoted complexation is described elsewhere.[23]

The binding free energy of an oligomer (PEG) and a polymer (PMAA) can be separated into two components. Specific interactions between PEG and PMAA including hydrogen bonds and hydrophobic interactions give rise to a negative component of the binding free energy and result in complexation. However, the complexation process is also accompanied by changes in the translational and rotational degrees of freedom of both PEG and PMAA. These changes give rise to an unfavorable (positive) component of the binding free energy. The translational free energy change, in particular, depends on the concentration of the polymers in solution. As the polymers become more concentrated, the probability of polymer/polymer interactions increases (the magnitude of the translational free energy change is reduced) and complexation becomes more favorable. If the polymers are covalently attached to one another, the probability of polymer/polymer interactions increases since the local concentration of the complexing species is increased, and complexation becomes much more favorable.

Conclusions

Graft copolymers of poly(methacrylic acid) and poly(ethylene glycol) form complexes under a wider range of poly(ethylene glycol) molecular weights and concentrations than mixtures of homopolymers. The copolymers may be cross-linked into networks, and the complex formation may be used to regulate swelling in response to a wide range of environmental conditions.

Similar environmentally sensitive networks may ultimately be used for controlled release, separations, or sensor applications. In addition, the graft-promoted complexation may take place with a wide variety of polymer pairs other than PMAA and PEG.

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