Complexation of Poly(acrylic acid) and Poly(methacrylic acid) with Pyrene-End-Labeled Poly(ethylene glycol). pH and Fluorescence Measurements

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ABSTRACT: The pH behavior of pyrene-end-labeled poly(ethylene glycol) (PEG) complexed with either poly(acrylic acid) (PAA) or poly(methacrylic acid) (PMAA) has been examined. The effect of pH on the ratio of pyrene excimer to monomer fluorescence emission, I_D/I_M, is reported. Both the intramolecular and intermolecular I_D/I_M in PAA–PEG and PMAA–PEG systems are affected by changes in pH. A maximum in the PMAA intermolecular I_D/I_M as a function of the ratio of PMAA–PEG concentrations is shown to be caused by the collapse of the PMAA coils. It was found that the hydrophobic pyrene fluorescent labels interact with the hydrophobic α-methyl groups of PMAA, causing enhanced complexation. The pyrenes interact in the ground state and participate in preformed excimers. A qualitative model is presented that summarizes the interactions that occur in the PMAA–PEG and PAA–PEG systems. This model explains the observed red-shifted monomer excitation and absorption spectra, blue-shifted excimer excitation spectra, increases in monomer lifetimes, the absence of excimer rise times, a rapid initial decrease in intramolecular I_D/I_M, and a rapid initial increase in intermolecular I_D/I_M in PMAA–PEG solutions. Since there are no hydrophobic regions in the analogous PAA–PEG systems, none of the non-hydrogen-bonding phenomena are observed. All of these hydrophobically driven phenomena can be eliminated by destroying the consolidated hydrophobic regions in PMAA systems. This has been experimentally accomplished by the addition of methanol and by the ionization of the carboxy groups in PMAA. We also demonstrate the usefulness of $K_0/K_{co\text{-}op}$, the ratio of the initial complexation equilibrium constant to the equilibrium constant when 50% of the hydrogen bonding sites are complexed. This parameter describes the interaction between specific types of complementary complexing units and is related to the chemical nature of the interacting polymers. It is independent of molecular weight and concentration.

Introduction

A sizable body of literature has resulted from investigations of complexation reactions between synthetic polymers.[1-6] Some of the goals of past research have been to describe the nature of the interaction forces (hydrogen bonding, ionic, hydrophobic), to determine structural effects (molecular weight, stoichiometry, chemical composition), and to study the effect of reaction conditions (temperature, pH, solvent). This work has resulted in excellent descriptions of many of the specific properties of complexation systems. However, due to the diverse character of these interactions, there has been less of an effort to link these specific observations into an overall picture of what happens when two complementary polymers are placed in solution. Recently, however, Iliopoulos[7] has provided a first step toward a better overall picture by developing a semiquantitative model that describes complexation.

Our previous work focused on providing qualitative molecular level details of the environment of pyrene-labeled chain ends of poly(ethylene glycol) (PEG) that interact with poly(acrylic acid) (PAA) or poly(methacrylic acid) (PMAA) in water.[8-10] This allowed stationary fluorescence measurements to be used to monitor the fraction of the pyrene probes in an overlapping excimer configuration. By judicious selection of overall concentration and tagging levels, the ratios of pyrene excimer to pyrene monomer emission intensities, I_D/I_M, for both intramolecular and intermolecular interactions of the labeled PEG were determined. Also, we recently used this probe to examine the effect on complexation when NaOH was used to neutralize the polyacid.[11] These investigations have demonstrated the effectiveness of the excimer fluorescence technique as a local probe of complexation.

Figure 1 shows our previous results for the normalized intramolecular and intermolecular I_D/I_M ratios for pyrene-end-tagged PEG upon the addition of PMAA or PAA.[8,9] In general, the intramolecular I_D/I_M decreases and the intermolecular I_D/I_M increases as polyacid is added to the system. These effects are more dramatic for the PMAA–PEG system than for the PAA–PEG system. That is, the PMAA data show a much stronger initial dependence on molar ratio, where molar ratio is defined as the concentration of polyacid monomeric repeat units divided by the concentration of PEG monomeric repeat units. In order to better quantify this difference, we compare the normalized initial slopes. For the intramolecular I_D/I_M data, these values are −0.4 for PAA and −9.5 for PMAA. These calculations show that during the initial stages of complexation, the intramolecular PEG excimer in the PMAA–PEG system is over 20 times more sensitive to additional polyacid than that in the PAA–PEG system.

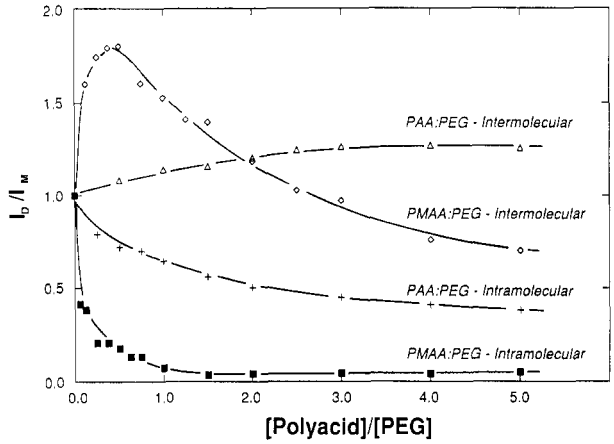

Figure 1. Normalized I_D/I_M versus molar ratio: (△) PAA–PEG, intermolecular; (◇) PMAA–PEG, intermolecular; (+) PAA–PEG, intramolecular; (■) PMAA–PEG, intramolecular.

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Similarly, the normalized initial slope for the intermolecular data is 0.65 for the PAA, whereas it is 6.1 for the PMAA. The intermolecular excimer is initially over 9 times more sensitive to the addition of polyacid in the PMAA solution, as compared to the PAA solution. Additionally, the intermolecular PMAA–PEG data of Figure 1 show a maximum at a molar ratio of about $^1/_2$. This maximum was qualitatively explained as being due to the complex becoming more compact as more PMAA was added, thus destabilizing the intermolecular excimers.[9]

The large differences in initial slope and the PMAA–PEG maximum at a molar ratio of $^1/_2$ prompted us to extend our investigation of complexation in PAA–PEG and PMAA–PEG systems. One objective of this study is to gain a better understanding of the complexation processes between these polymers. To do this, our primary approach is the examination of the pH behavior of these systems. pH measurements were chosen since they allow calculation of quantitative parameters, such as the complexation equilibrium constant and the degree of complexation, that describe the complexation process. Since we have developed a large body of observations from our previous fluorescence studies,[8-11] we wished to make direct comparisons of the pH measurements performed in this paper with this earlier spectroscopic work. For this reason, we followed the identical experimental protocol that was used earlier. This affords a direct comparison between our fluorescence results and the more traditional pH method of monitoring complexation.

A second objective of this study is to combine the results from the fluorescence and pH experiments into one coherent model that describes the interactions between the complexing polymers in greater detail. It will become apparent that the system used for the previous fluorescence work is quite complex, with variations in stoichiometry and in degree of dissociation. Nevertheless, the addition of pH results permits a consistent picture to emerge that unifies all of the fluorescence data. Moreover, quantitative estimates of complexation parameters are shown to agree with existing literature.

Experimental Section

Materials. Poly(methacrylic acid) (PMAA) and poly(acrylic acid) (PAA) are described in more detail elsewhere.[8,9] The PMAA was obtained from BDH Chemicals Ltd. (Poole, England), and the PAA was obtained from Polysciences Inc. (Warrington, PA). Both materials were purified by dialysis against water by using a pressurized stirred cell and then freeze-dried. The viscosity-average molecular weights were 9500 for PMAA and 1850 for PAA. Narrow distribution (polydispersity < 1.10) poly(ethylene glycol) (PEG) of molecular weight 9200 was obtained from Polysciences Inc. None of the polymers were found to contain any fluorescent impurities and so were used without any further purification.

Solution Preparation. Solutions of PEG were made by dissolving the appropriate amount of PEG to achieve the desired final concentration in glass-distilled deionized water. Solutions of PAA and PMAA that were 100 times more concentrated than their corresponding PEG solutions were similarly prepared. This polyacid–PEG concentration ratio was selected in order to minimize the effect of dilution upon the addition of polyacid to PEG. The composition of the complex was described by the molar ratio of the two repeating units, [polyacid]–[PEG], because the complex is known to be formed between a carboxylic acid group and the ether oxygen of PEG.[1,2] To prepare a sample, 4 mL of PEG was placed in a quartz tube and the polyacid solution was added to the PEG with a microsyringe. A sample was newly prepared for each data acquisition. A water bath was used to keep the temperature of the solutions at 303 K.

pH Measurements. The pH of PEG solutions was measured upon addition of either PMAA or PAA by using a Beckman Φ44 pH meter calibrated to within ±0.02 with pH buffer standards. For blank pH measurements in which no complexation can occur, distilled, deionized water was used in place of the PEG solution. All pH experiments were done at 303 K, with the temperature being controlled by a water bath.

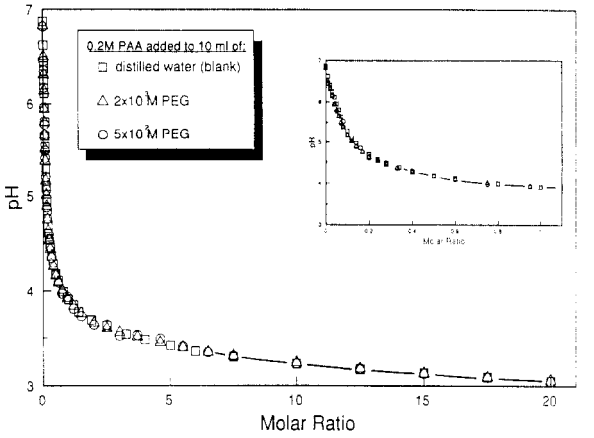

Figure 2. Change in pH upon addition of PAA to distilled water (□), 2×10^{-3} M PEG (△), and 5×10^{-2} M PEG (○).

Results

1. pH of PAA–PEG Solutions. Figure 2 shows the change in pH of a 10-mL solution of 2×10^{-3} M PEG when 2×10^{-1} M PAA is added. Note the monotonic drop in pH as the polyacid is added. This decrease in pH is solely due to the intrinsic acidity of the polyacid. No buffering of the solution was done in order to completely reproduce the conditions of our previous fluorescence work.[8,9] Most of the pH decrease occurs between molar ratios of 0 and 1, as shown in the inset. This range over which the pH changes is significant in that PAA and PEG form a 1:1 complex.[2] This means that most of the complexation in this system will occur between molar ratios of 0 and 1. PAA was also added to 10 mL of distilled water, and the pH was monitored. This "blank" run was used to determine whether complexation was detectable by using the pH method. An "equivalent molar ratio" equal to the molar ratio that would have existed in the system if the 10 mL of water had been replaced with 10 mL of 2×10^{-3} M PEG was used for the x axis in the "blank" data in Figure 2. This was necessary since the concept of molar ratio, as defined above, is meaningless when referring to the PAA–H_2O system. If complexation occurs between PAA and PEG, the pH of the solution containing PAA–PEG should be higher than that of the PAA–H_2O solution at a given molar ratio, since some of the acidic hydrogen atoms in the PAA will be participating in complexation hydrogen bonds rather than being free in solution. Figure 2 clearly indicates that there is no pH difference between the PAA–PEG system and the PAA–H_2O system.

Also shown in Figure 2 is the change in pH of the same PAA–PEG combination as above, except for an increase in the concentration of PEG. The PEG concentration was increased with the expectation that if there were more total hydrogen bonds in the system, there would be more of a detectable difference between the PAA–PEG solution and the blank. However, even though the concentration was increased by a factor of 25, once again there was no difference between the PAA–PEG mixture and the PAA–H_2O solution, as Figure 2 demonstrates. The results of these two experiments indicate that either PAA and PEG do not complex under these conditions or complexation is not detectable for PAA–PEG using pH measurements. In light of our previous results,[8] we feel that the latter conclusion is the correct one.

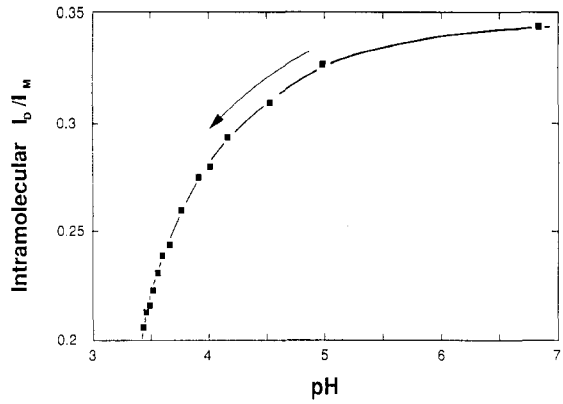

Figure 3. Change in intramolecular I_D/I_M with pH upon the addition of PAA to 2×10^{-3} M PEG. The arrow indicates the direction in which the experiments were conducted.

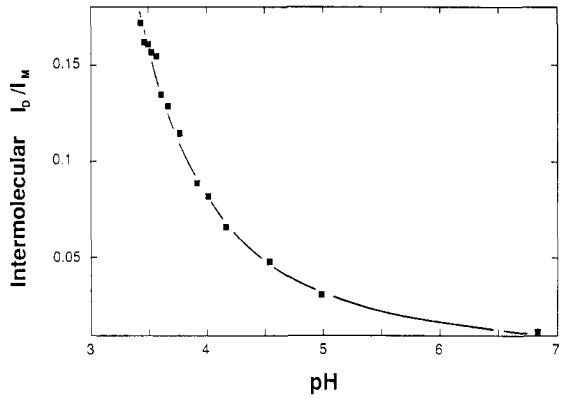

Figure 4. Change in intermolecular I_D/I_M with pH upon the addition of PAA to 2×10^{-3} M PEG.

This is not necessarily surprising since the molecular weight of the PAA is low. Most other studies[12] of PAA–PEG complexation used much higher molecular weights, usually 2–3 orders of magnitude greater. This confirms our previous conclusion[8] of the enhanced sensitivity of our fluorescence technique, which is able to detect complexation in the low molecular weight PAA–PEG system.

2. Comparison of PAA–PEG Fluorescence and pH Results. Since the fluorescence measurements conducted earlier[8] showed complexation of PAA–PEG under identical conditions as above ([PEG] = 2×10^{-3} M, 303 K), these earlier fluorescence results are plotted against the pH results of the present study. The intramolecular I_D/I_M data as a function of pH are given in Figure 3. It is important to remember that in all of these experiments the polyacid was added to the PEG solution. This is equivalent to movement from high pH to low pH (i.e., right to left as indicated by the arrow in Figure 3). As the pH of the system decreases, the intramolecular I_D/I_M of the end-tagged PEG monotonically decreases. Another important feature, which will be discussed below, is that the second derivative of the data is negative, producing a curve that is concave downward.

Figure 4 is the analogous plot for intermolecular I_D/I_M in PAA–PEG. Note that the opposite trends are observed. Specifically, I_D/I_M increases with decreasing pH and the curve has upward concavity.

3. pH of PMAA–PEG Solutions. The same set of experiments conducted on PAA–PEG were also done on PMAA–PEG. The change in pH of 10 mL of 1×10^{-3} M PEG upon the addition of 1×10^{-1} M PMAA is shown in Figure 5. A blank run was also done to determine whether complexation could be monitored under these conditions.

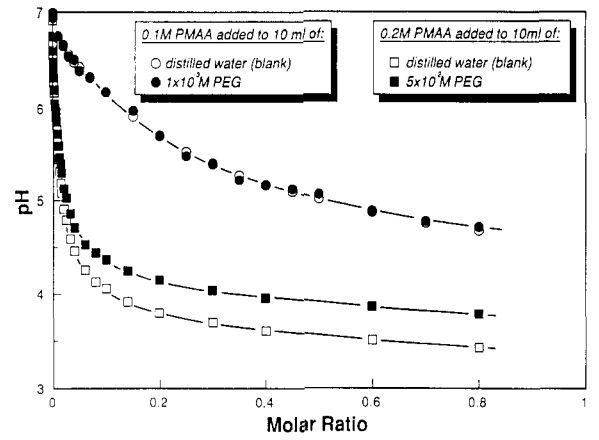

Figure 5. Change in pH with molar ratio: (●) 0.1 M PMAA added to 10 mL of 1×10^{-3} M PEG solution, (○) 0.1 M PMAA added to water blank, (■) 0.2 M PMAA added to 10 mL of 5×10^{-2} M PEG solution, and (□) 0.2 M PMAA added to water blank.

As in the case of PAA–PEG, no difference between the PMAA–PEG data and the PMAA–H_2O data was observed.

As was done for PAA–PEG, the PEG concentration was increased and the experiment was repeated. It was not until the PEG concentration reached 5×10^{-2} M that complexation was first detectable with pH. These results are also presented in Figure 5, along with the PMAA–H_2O pH "blank" data. There is a clear difference between the two sets of data, indicating complexation has been detected. This measurable difference allows quantitative parameters that describe the complexation process, such as degree of linkage, to be calculated. In order to derive the equations for these parameters, one must start from the equilibrium expressions governing these systems.

The equilibrium expression that describes polyacid dissociation is

$$\underset{\text{polyacid}}{-COOH} \overset{K}{\leftrightarrow} \underset{\text{dissociated polyacid}}{-COO^-} + H^+ \quad (1)$$

In general

$$K = [COO^-][H^+]/[COOH] \quad (2)$$

where $[COO^-]$ = carboxylate ion concentration, $[H^+]$ = hydrogen ion concentration, and [COOH] = concentration of undissociated, uncomplexed polyacid monomer units.

For the case in which there is no PEG present, i.e., the "blank" system, the solution equilibrium is described only by eq 1. The following expressions then apply

$$[PMMA]_{total} = [COOH] + [COO^-] \quad (3)$$

$$[COO^-] = [H^+]_{blank} \quad (4)$$

where $[PMAA]_{total}$ = total concentration of PMAA monomer units and $[H^+]_{blank}$ = hydrogen ion concentration with no PEG present (i.e., no complexation). Substituting eqs 3 and 4 into eq 2 yields K_{blank}, the equilibrium dissociation constant for the blank system:

$$K_{blank} = \frac{[H^+]_{blank}^2}{[PMAA]_{total} - [H^+]_{blank}} \quad (5)$$

For the case in which PEG is present, both eq 1 and the following equilibrium expression are needed to describe the interactions:

$$\underset{\text{polyacid}}{-COOH} + \underset{\text{PEG}}{-OCH_2CH_2-} \overset{K_c}{\leftrightarrow} \underset{\text{complexation hydrogen bond}}{-COOH\text{-}OCH_2CH_2-} \quad (6)$$

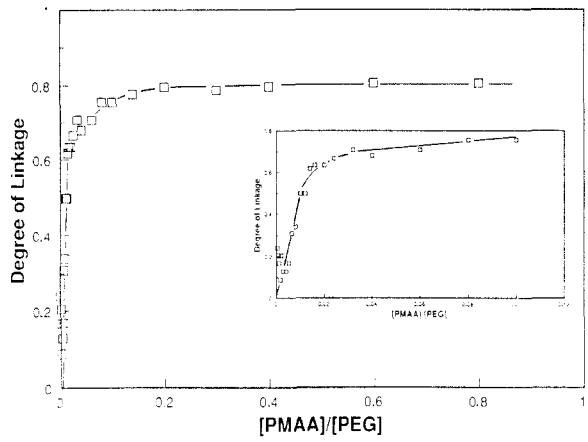

Figure 6. Degree of linkage versus molar ratio for the PMAA–PEG system.

The following relations are then valid

$$[\text{PMAA}]_{\text{total}} = [\text{COOH}] + [\text{COO}^-] + [\text{PMAA–PEG}] \quad (7)$$

$$[\text{COO}^-] = [\text{H}^+]_{\text{PEG}} \quad (8)$$

where [PMAA–PEG] = concentration of complexation hydrogen bonds and $[\text{H}^+]_{\text{PEG}}$ = hydrogen ion concentration in the presence of PEG (i.e., with complexation). Substituting eqs 7 and 8 into eq 2 yields K_{PEG}, the equilibrium dissociation constant for the complexation system:

$$K_{\text{PEG}} = \frac{[\text{H}^+]_{\text{PEG}}^2}{[\text{PMAA}]_{\text{total}} - [\text{H}^+]_{\text{PEG}} - [\text{PMAA–PEG}]} \quad (9)$$

We now make the assumption that the equilibrium dissociation constant does not significantly change between systems with and without PEG.[13] This assumption should be reasonably valid if the pH difference between the two systems is not too great, as is the case for our data of Figure 5 (ΔpH < 0.5). We can then equate eqs 5 and 9.

$$K_{\text{blank}} \sim K_{\text{PEG}} \quad (10)$$

$$\frac{[\text{H}^+]_{\text{blank}}^2}{[\text{PMAA}]_{\text{total}} - [\text{H}^+]_{\text{blank}}} = \frac{[\text{H}^+]_{\text{PEG}}^2}{[\text{PMAA}]_{\text{total}} - [\text{H}^+]_{\text{PEG}} - [\text{PMAA–PEG}]} \quad (11)$$

Dividing both sides of eq 11 by $[\text{PMAA}]_{\text{total}}$ gives

$$\frac{[\text{H}^+]_{\text{blank}}^2}{1 - \frac{[\text{H}^+]_{\text{blank}}}{[\text{PMAA}]_{\text{total}}}} = \frac{[\text{H}^+]_{\text{PEG}}^2}{1 - \frac{[\text{H}^+]_{\text{PEG}}}{[\text{PMAA}]_{\text{total}}} - \theta} \quad (12)$$

where the degree of linkage, θ, is defined as the fraction of possible hydrogen bond sites that are actually participating in a hydrogen bond

$$\theta = \frac{[\text{PMAA–PEG}]}{[\text{PMAA}]_{\text{total}}} \quad (13)$$

Rearranging eq 12 and solving for θ gives

$$\theta = \left(1 - \frac{[\text{H}^+]_{\text{PEG}}}{[\text{PMAA}]_{\text{total}}}\right) - \left(1 - \frac{[\text{H}^+]_{\text{blank}}}{[\text{PMAA}]_{\text{total}}}\right)\frac{[\text{H}^+]_{\text{PEG}}^2}{[\text{H}^+]_{\text{blank}}^2} \quad (14)$$

The degree of linkage as a function of molar ratio for the data showing complexation in Figure 5 is presented in Figure 6. There is a rapid rise in hydrogen bond formation up to a molar ratio of 0.1. It then levels off at a degree of complexation of about 0.81. This means that at molar ratios above 0.1, about 80% of available hydrogen bonding sites are participating in complexation hydrogen bonds.

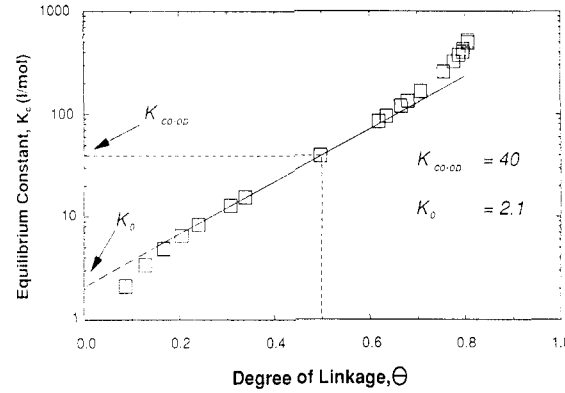

Figure 7. Change in equilibrium constant, K_c, with degree of linkage, θ, for the PMAA–PEG system.

The equilibrium constant, K_c, for the complexation reaction given in eq 6 can also be calculated as

$$K_c = \frac{[\text{PMAA–PEG}]}{[\text{COOH}][\text{PEG}]} \quad (15)$$

where [PEG] is the concentration of uncomplexed PEG monomer units. Substituting for known quantities in eq 15 gives

$$K_c = \frac{\theta}{[\text{PMAA}]_{\text{total}}(1-\theta)^2} \quad (16)$$

where the parameters are defined as above.

A plot of ln K_c as a function of θ allows the calculation of parameters that give an indication of the cooperative nature of the complexation process. Figure 7 reveals a linear region betwseen θ = 0.2 and 0.7 in the plot of ln K_c versus θ. Extrapolating to θ = 0 gives K_0, the apparent equilibrium constant for the first interacting site of PMAA binding to PEG in the absence of any other interactions between the sites.[12] For this system K_0 was found to be 2.1.

Another parameter that can be obtained from Figure 7 is $K_{\text{co-op}}$, the equilibrium constant for forming a complexation hydrogen bond adjacent to a site already participating in a complexation hydrogen bond.[12] As indicated in Figure 7, $K_{\text{co-op}}$ for this system is 40. Both K_0 and $K_{\text{co-op}}$ are useful in describing the complexation process and will be considered in more detail in the Discussion.

4. Comparison of PMAA–PEG Fluorescence and pH Results. As was done above for the PAA data, the fluorescence results previously obtained for the PMAA–PEG system were cross-plotted against pH. This is shown in Figure 8 for intramolecular I_D/I_M. As the pH of the system is decreased, the intramolecular I_D/I_M monotonically decreases. The curve has an upward concavity in contrast to the analogous plot for PAA data shown in Figure 3.

The behavior of the intermolecular I_D/I_M for the PMAA–PEG system as a function of pH is given in Figure 9. As the pH decreases, I_D/I_M initially increases. However, at a pH of about 6 the data start to level off and eventually pass through a maximum at a pH of 5. The data then decrease monotonically with decreasing pH. This behavior is very different from the PAA–PEG data in Figure 4.

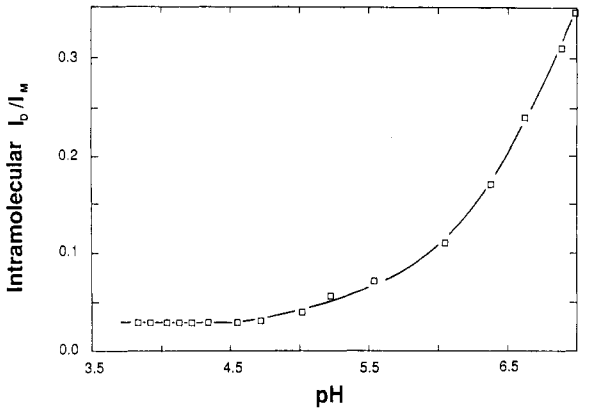

Figure 8. Change in intramolecular I_D/I_M with pH upon the addition of PMAA to 1×10^{-3} M PEG.

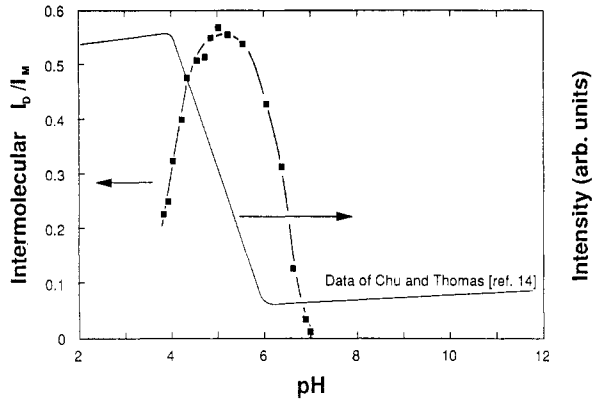

Figure 9. Change in intermolecular I_D/I_M with pH upon the addition of PMAA. Data from Chu and Thomas[14] for the dependence of isolated PMAA coil size on pH are superimposed on the I_D/I_M data.

Discussion

1. Fluorescence and pH Results. The fluorescence and pH results presented above, coupled with previous experiments by other investigators, enable us to gain a better understanding of the overall molecular processes occurring in a complexation reaction. In order to help organize subsequent discussion, we begin by proposing a physical model that describes the interactions that occur when a polyacid is added to a solution of pyrene-end-labeled PEG. We will then show how the pH data support this model. A substantial amount of previous data, such as monomer excitation, degree of neutralization, monomer and excimer lifetimes, solvent composition, monomer and excimer peak position, and monomer absorption, will also be shown to be in agreement with the model.

The initial state of the system is one in which pyrene-end-labeled PEG chains are in aqueous solution at a known concentration. There will be a fraction of the pyrene probes participating in intramolecular and intermolecular excimers.[16] In the case of PAA–PEG complexation, as PAA is added the solution pH drops and PEG chains start to form hydrogen bonds with the added PAA, resulting in a lowering of the free PEG chain concentration. This complexation process continues smoothly until there is an excess of PAA.

In the case of PMAA–PEG complexation, the same two phenomena, initial complexation and a drop in pH, occur. However, the hydrophobic nature of PMAA due to the methyl side group causes additional complications. A hydrophobic interaction is defined as the effect of attraction between nonpolar molecules determined by the behavior of the free energy of the system composed of water plus solvated molecules.[17] This effect has been observed experimentally in many different types of systems[14,16,18] and has been successfully modeled.[17,19,20] Hydrophobic clustering of the PMAA molecules will form regions of greater hydrophobicity than the surrounding environment. This will have a significant effect on the hydrophobic pyrene probe molecules covalently attached to the PEG chain ends, as will be discussed in greater detail below.

A second complication in the PMAA–PEG system, which is related to the hydrophobic nature of PMAA, is that PMAA undergoes a rather sharp coil contraction as the pH is lowered. Chu and co-workers[14] used PMAA with pyrene probes covalently attached at random points along the chain. At high pH the pyrenes produced a small amount of fluorescence, indicating that the pyrenes were in a water-rich environment. This led to the conclusion that the PMAA chains were uncoiled. Conversely, at low pH there was a strong pyrene emission showing that the PMAA chains were tightly coiled and the pyrenes were in a hydrophobic environment. This abrupt change in chain conformation is due to the fact that at high pH a significant fraction of the carboxy groups are ionized. The tendency to maximize the separation between the ionic charges thus produces an expanded chain. As the pH is lowered, the carboxy groups are protonated and the chain relaxes into a more compact structure. They also showed that, as the pH was lowered, it became more difficult for fluorescence quenching molecules to reach the pyrenes. A sharp transition in quenching ability with pH was found, further confirming the collapse of PMAA with decreasing pH. By tagging the PMAA on the chain ends and then monitoring the change in pyrene fluorescence, they were also able to obtain some configurational information about the PMAA collapse. Their results indicate that the transition from extended to compact coil is via a "winding" process, with the chain ends proceeding first. This type of collapse mechanism would seem to still be possible with a ladderlike complex[2] such as the PMAA–PEG used in this study.

The parameters under our experimental control in this study are the segmental ratio of component polymers (molar ratio), the hydrophobic nature of the polyacid (PAA vs PMAA), and the total polymer concentration. The interaction of these parameters will govern the observed behavior of the system.

It is beneficial to examine the PAA–PEG data initially. Since PAA does not have the methyl side group found in PMAA, there will be significantly fewer hydrophobic effects due to PAA. Therefore, the only dominant interactions that can occur are due to hydrogen bonds between PEG and PAA (i.e., complexation bonds). Note from Figures 2 and 3 that, as PAA is added to the PEG solution, the pH drops and intramolecular I_D/I_M also drops. This agrees with the idea that, as a complex forms, free PEG molecules are complexed and the PEG molecule becomes less mobile.[8] Therefore, the chain ends are less likely to encounter each other and the intramolecular I_D/I_M decreases. The corresponding data for PMAA, Figures 5 and 9, also show a decrease in intramolecular I_D/I_M as the acid is added, indicating the same phenomenon outlined above is occurring. However, the drop in intramolecular I_D/I_M is much more drastic initially (i.e., at high pH) in the PMAA case. This rapid initial drop results in the upward concavity of Figure 8 as compared with the corresponding data for PAA in Figure 3.

This difference between PMAA and PAA is linked to the difference in hydrophobicity of the two polymers. When the first PMAA is added to the PEG solution, two events

occur simultaneously. Not only do hydrogen bonds form between the acid and PEG but some pyrenes on the end-tagged PEG are hydrophobically attracted to the hydrophobic PMAA. This combination of effects results in a much more rapid decrease in intramolecular I_D/I_M for the PMAA system than for the PAA system, where only complexation hydrogen bonds cause a reduction in the number of free end-tagged PEG chains in solution. Therefore, the picture of complexation in the PMAA system as seen from the PEG intramolecular I_D/I_M is one of intramolecular excimers being destroyed by complexation with PMAA *and* hydrophobic attraction to PMAA.

This scenario can also be used to explain the intermolecular I_D/I_M data in Figure 9. In the PAA system, intermolecular I_D/I_M increases with added PAA because more complexes are forming and the local pyrene concentration is increasing. Thus, intermolecular excimer emission increases as pH decreases. The PMAA system initially follows the same general behavior: intermolecular I_D/I_M increases with added acid. However, two distinct differences are found in the PMAA system. The first is that the initial increase in intermolecular I_D/I_M with added acid (i.e., at high pH) is much greater for the PMAA system than for the PAA system. The second is that a maximum occurs in the PMAA intermolecular I_D/I_M plot.

The reason for the difference in initial I_D/I_M increases is exactly the same as that for the intramolecular I_D/I_M data presented above. For the PMAA system, not only is there an increase in local pyrene concentration due to complexation but also there is a contribution to that increase from the hydrophobic attraction of pyrene groups to the hydrophobic regions in the PMAA complex. This implies that the pyrenes that are "hydrophobically aggregating" are still mobile enough, or are located correct distances apart, to form excimers. However, they most likely are somewhat confined and exist in a preformed state. If more PMAA is added, those hydrophobic regions will most likely increase in local density, and thus the steric constraint on the intermolecular excimers resulting from loss of pyrene mobility will continue to increase. If this trend continues, eventually the excimers could become so destabilized that the excimer configuration is destroyed, causing I_D/I_M intermolecular to decrease. This would produce the observed maximum mentioned above. Further evidence for preformed excimers and their subsequent destabilization is given below.

As discussed above, the main reason for the destabilization of the intermolecular excimers, however, is the fact that the PMAA chain undergoes a conformational change from an extended structure to a compact coil as the pH drops from 6 to 4.[14] The fluorescence data of Chu et al. demonstrating this chain contraction are plotted along with our fluorescence data in Figure 9.

This basic expansion/contraction scenario with decreasing pH holds true, in general, for any polyacid. In the case of PAA, however, the transition is gradual. The unique feature of PMAA is the sharpness of the transition. This is most likely due to the attractive hydrophobic forces, which work in opposition to the repulsive ionic forces. Thus, when a sufficient number of carboxy groups are protonated in PMAA, the hydrophobic forces become dominant and the chain rapidly collapses. In the case of our PMAA–PEG complexes, this contraction destabilizes the intermolecular excimers and produces the maximum in the I_D/I_M data of Figure 1.

Additional data previously published[10,11,15] lend support to the model presented above. Specifically, monomer excitation spectra of 100% tagged PEG show an initial red shift of about 3 nm with increasing molar ratio in the PMAA system, indicating the existence of ground-state interactions.[15] This dramatic shift was not observed in the PAA system. These observations are in agreement with the idea that in the PMAA system the pyrenes are hydrophobically aggregating, causing some of them to exist in a preformed excimer state. In a system with 1% of the PEG chains tagged, no shift in the monomer excitation spectrum was observed. This is not surprising since in a 1% tagged system the probes are only able to form intramolecular excimers, and thus no ground-state interactions should be detected.

The results from the partial neutralization of the PMAA–PEG hydrogen bonds[11] can also be explained in terms of this model. When the carboxy groups of the PMAA were 30% ionized by the addition of NaOH, no monomer excitation shift was observed in either the 100% or 1% tagged systems. This indicates that the neutralization of some of the complexation bonds effectively breaks up the PMAA hydrophobic regions by forcing the PMAA chains into a more extended conformation. This extension is driven, in part, by ionic repulsion between ionized chain segments. Without these consolidated hydrophobic regions, there is no hydrophobically enhanced pyrene aggregation and no ground-state interactions are observed. The same arguments can be used to explain the analogous 2.5-nm red shifts in the pyrene absorption spectra.[11]

Similarly, excimer excitation spectra blue shifts are explained by this model. Earlier work showed that, as PMAA was added, the maximum in the excimer excitation spectrum shifted by 10 nm to shorter wavelengths.[11] This is evidence of increasing excimer destabilization with increasing complexation with PMAA. In the PAA–PEG system, a similar excimer peak shift was not found.

When the PMAA was 30% neutralized, no excimer peak shift was observed. This is further evidence that when PMAA is neutralized, it assumes a more extended conformation. This results in the dispersal of the hydrophobic regions, the elimination of hydrophobically driven pyrene aggregation, and the corresponding reduction in excimer destabilization.

These phenomena are also reflected in the intermolecular I_D/I_M data.[11] At 30% neutralization, the PMAA intermolecular I_D/I_M increases monotonically and does not pass through a maximum as the unneutralized solutions do. Qualitatively, the data look very similar to those for PAA shown in Figure 1.

The effects of changes in local environment due to differing solvent conditions are also explained by the above model. For example, the hydrophobic regions in the PMAA–PEG system can be dispersed by the addition of methanol.[10] This process is similar to the dispersal of hydrophobic regions due to polyacid neutralization presented above. As methanol is added, the excimer excitation peak blue shift is eliminated.[10] Similarly, the maximum in the intermolecular I_D/I_M data disappears. Again, the I_D/I_M versus molar ratio curve looks qualitatively similar to the PAA curve in Figure 1.

The ground-state interactions mentioned above can also be monitored via fluorescence lifetime measurements. The monomer lifetime for a PMAA–PEG system was found to increase from 20 to 110 ns upon the addition of PMAA.[10] This is another indication of ground-state interactions due to pyrenes hydrophobically aggregating. In a similar PAA system, the monomer lifetime only increased from 20 to 27ns. Moreover, the excimer lifetime also increased in the PMAA–PEG system. An additional important fact is that no excimer rise time was measured. This indicates that

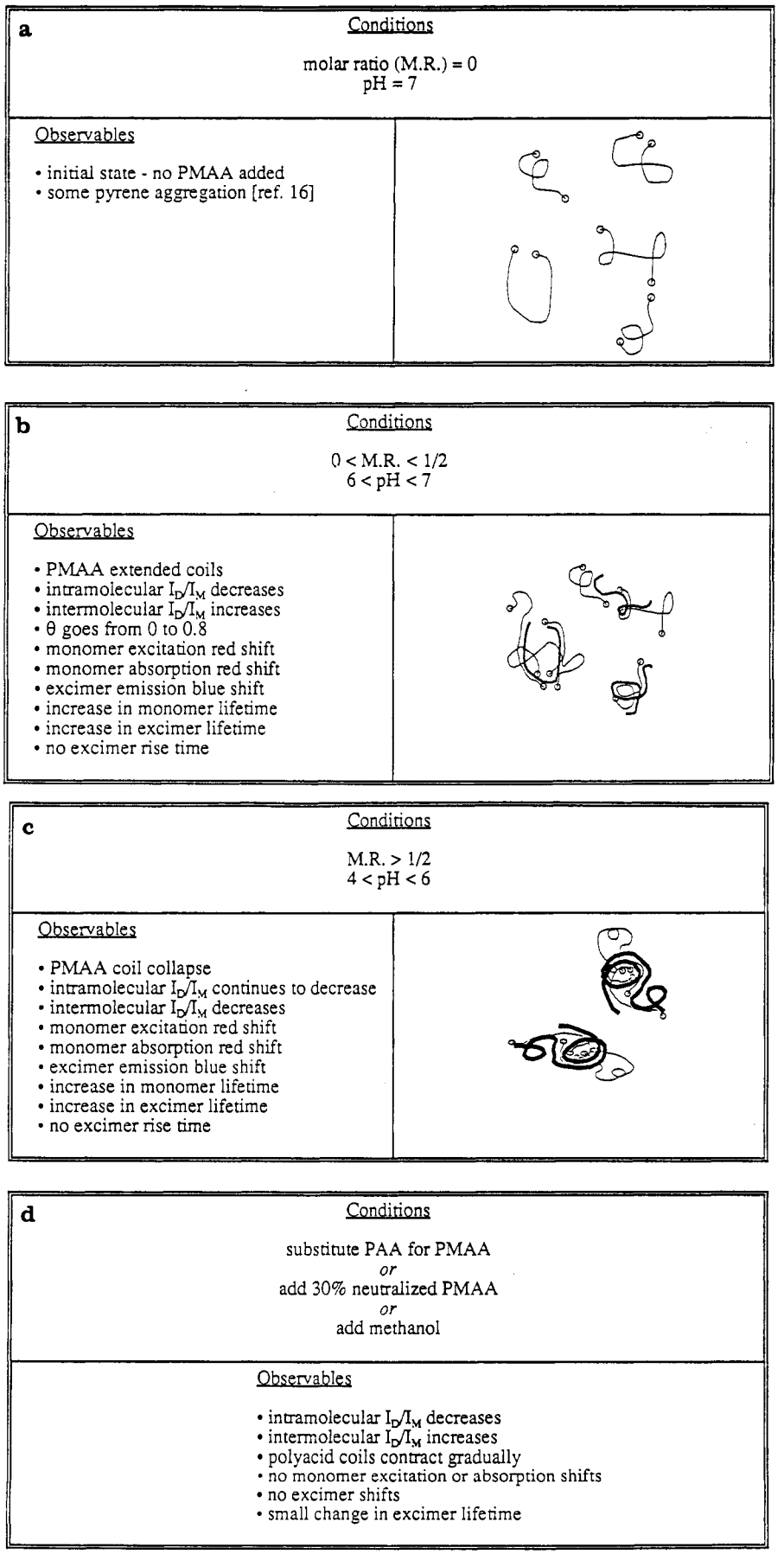

Figure 10. Schematic diagram summarizing the observables for (a) pyrene-end-tagged PEG solution, (b) PMAA–PEG solution with a molar ratio (M.R.) between 0 and $^1/_2$, (c) PMAA–PEG solution with a M.R. greater than $^1/_2$, and (d) PAA–PEG system or neutralized PMAA–PEG system or PMAA–PEG system with methanol.

the excimers exist in a preformed state, as is predicted by the model given above. These differences between PMAA and PAA lifetime data were eliminated with the addition of methanol. This fact is consistent with the concept that

methanol eliminates the hydrophobic interactions in the system.

A summary of these processes is presented in Figure 10 in the form of a schematic diagram.

2. Complexation Parameters. It is useful to examine in more detail the complexation parameters for PMAA–PEG calculated above. The plateau value of 0.8 for θ found in Figure 6 is consistent with the results of Tsuchida et al.[12] for PMAA–PEG complexation. They observed a θ of 0.83 for a unit molar ratio of PMAA (MW = 66 000) and PEG (MW = 7500) at 303 K and noted that θ was insensitive to the PMAA–PEG molecular weight ratio for PEG molecular weights above about 3000. They did not, however, report the dependence of θ on molar ratio. The agreement of these values indicates the relative insensitivity of θ to the PMAA–PEG molecular weight ratio, since our ratio was 8.5 times lower.

The general shape of the θ vs K plot in Figure 7 also agrees with that of Tsuchida et al.[12] The increase in K with θ implies that the complexation reaction is a cooperative process. That is, K is enhanced by a higher degree of complexation. Quantitatively, the curve in Figure 7 is shifted down from that determined by Tsuchida. This is manifested in a K_0 of 2.1 compared to the value of 14.5 obtained by Tsuchida. Likewise, our value of 40 for $K_{co\text{-}op}$ is less than their $K_{co\text{-}op}$ value of 347. The difference between the two systems, as mentioned above, is the PMAA–PEG molecular weight ratio.

Since K_0 is the extrapolated equilibrium constant for the first hydrogen bond, a lower K_0 value for a lower PMAA–PEG molecular weight ratio means that the driving force to form the first bond, and hence to start the cooperative complexation process, is not as great in our system. This is in agreement with the general finding that, as the molecular weight of the component polymers decreases, the complexation interaction is not as strong. Tsuchida points out that a lower K_0 means it is more difficult to start the complexation process, but once started longer runs of unbroken bond sequences will be found.[12]

Similarly, this effect is seen in the $K_{co\text{-}op}$ data. $K_{co\text{-}op}$ describes the equilibrium situation for forming a hydrogen bond on a site next to a site already participating in a bond. A larger $K_{co\text{-}op}$ value will result in longer uninterrupted sequences of hydrogen bonds. The ratio of $K_0/K_{co\text{-}op}$, therefore, should be less dependent on molecular weight ratio and more indicative of the specific interacting monomer groups. Our $K_0/K_{co\text{-}op}$ is 0.05 compared to a value of 0.04 determined by Tsuchida. This good agreement supports the hypothesis that $K_0/K_{co\text{-}op}$ is a parameter that describes the basic interaction between two complementary hydrogen-bonding monomer units.

Summary

We conclude by summarizing the interactions that occur in the PMAA–PEG and PAA–PEG systems. As the polyacid is added, complexation occurs and is stabilized by the hydrogen bonds between the polyacid and the PEG chains. Additionally, in the PMAA system, some pyrenes covalently attached to the ends of PEG chains are attracted to hydrophobic regions. These regions are created by the interaction between the α-methyl group of PMAA and water. The pyrenes interact in the ground state and participate in preformed excimers. This phenomenon manifests itself in red-shifted monomer excitation and absorption spectra, blue-shifted excimer excitation spectra, increases in monomer lifetimes, the absence of excimer rise times, a rapid initial decrease in intramolecular I_D/I_M, and a rapid initial increase in intermolecular I_D/I_M. Since there are no hydrophobic regions in the analogous PAA–PEG systems, none of the non-hydrogen-bonding phenomena are observed. In fact, all of these observations can be eliminated by destroying the consolidated hydrophobic regions in PMAA systems. This has been experimentally accomplished by the addition of methanol and by the ionization of the carboxy groups in PMAA.

We also demonstrated the usefulness of $K_0/K_{co\text{-}op}$ as a parameter describing the interaction between specific types of complementary complexing units. This parameter appears to be related to the chemical nature of the interacting polymers and is independent of molecular weight and concentration.

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