Complexation between Poly(methacrylic acid) and Poly(vinylpyrrolidone)

SHOUXIN LIU,[1] YU FANG,[1,2] DAODAO HU,[1] GAILING GAO,[1] JIANBIAO MA[2]

[1] Department of Chemistry, Shaanxi Normal University, Xi'an 710062, People's Republic of China

[2] State Key Lab of Polymer Materials for Adsorption and Separation, Nankai University, Tianjin 300072, People's Republic of China

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ABSTRACT: The complexation between poly(methacrylic acid) (PMAA) and poly(vinylpyrrolidone) (PVP) in aqueous phase was studied by various fluorescence techniques, including fluorescence anisotropy measurements, fluorescence probe studies, and nonradiation energy transfer. It was demonstrated that the complexation of PMAA with PVP occurs within a pH range of 1 to 5 and along with complexation, the conformation of PMAA changed from a hypercoiled to a loosely coiled form. The complex ratio between the two polymers is 2:1 (PMAA/PVP, in monomer unit). Salt effect studies showed that the complexation occurred due to formation of hydrogen bonds between the two polymers. Based on these conclusions and the "connected cluster model" for PMAA at low pH, a "ladder with connected cluster" model was proposed for the structure of PMAA/PVP complex formed at low pH. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 620–627, 2001

Key words: poly(methacrylic acid); poly(vinylpyrrolidone); complexation; conformation; fluorescence

INTRODUCTION

Poly(vinylpyrrolidone) (PVP) is a typical neutral water soluble polymer. It has found increasing use in a variety of applications range from, for example, additives in medicine to adhesives in a variety of products.[1] Among other properties, PVP is a kind of polymer surfactants. It has a good solubility in water, methanol, ethanol, chloroform, and dichloromethane.[1, 2] The PVP films formed by casting and spinning are colorless and transparent. However, the film is brittle when the humidity of the environment is low. To improve the quality of the film, a typical practice is to add some plasticizers, which interact with the polymer. Several reports have discussed the interaction of PVP with other polymers,[3–9] surfactant,[10,11] and adsorbents.[12–15] The solution properties of PVP and the effect of additives on the properties have been studied by viscosity, light scattering, and calorimetry techniques.[16–19]

PVP forms stable complexes with polyacids. For example, Iliopoulos and co-workers[20] studied the complexation of poly(acrylic acid) (PAA) at varying degrees of ionization with PVP. Bimendina et al.[21] introduced nonionic maleic anhydride into PAA and studied the complexation between the copolymer and PVP. Furthermore, Bimendina et al.[22] also studied complexation of poly(methacrylic acid-co-methacrylate) containing 63.6–76.8mol% of the acid monomer residues with PVP, but this system could only be investi-

Correspondence to: Y. Fang (yfang@snnu.edu.cn)

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gated in water containing 30% ethanol. In most of the cases, the interaction of PVP with polyacids in aqueous phase forms polymer complexes, which may result in solid–liquid phase separation or liquid–liquid phase separation.

Unlike other polyacids, poly(methacrylic acid) (PMAA) behaves differently. It adopts hypercoiled conformation at low pH because of the hydrophobic interactions introduced by the methyl groups in the polymer. However, on addition of base to the solution, the carboxyl groups ionize and acquire negative charges. The increase in Coulombic repulsive forces results in a non-uniform, sudden conformational transition from the hypercoiled to the expanded form. This conformational change is reversible.[23, 24] It is expected that the smart behavior of PMAA may be introduced into a PMAA/PVP polymer blend, and the blend may form the basis of the preparation of new kinds of films and hydrogels. In view of this possibility, we investigated the interactions between PVP and PMAA.

In continuation of the studies of polymer interactions,[25–27] in this paper, we used various fluorescence techniques to study the complexation of the two polymers and the effects of complexation on the hypercoiled conformation of PMAA.

EXPERIMENTAL

Materials

Acenaphthylene (ACE, 85%; Aldrich) was purified by triple recrystallization from ethanol followed by sublimation. Pyrene (Py, 96%; Aldrich) was purified by recrystallization from ethanol and then extraction with ethanol in a Soxhlet's extractor. Perylene (Pe, gold label; Aldrich) and 8-anilino-naphthalenesulfonic acid (ANS; Aldrich) were used directly without further purification. ACE-labeled PMAA (PMAA/ACE) was prepared by free radical copolymerization using AIBN as initiator in benzene. The content of ACE in the starting formulation is 0.7 mol % [ACE/(ACE + MAA), in mole unit]. The sample was thoroughly degassed, sealed under high vacuum ($\sim 10^{-4}$ Torr), and polymerized at 60 °C. Polymerization was terminated at <10% conversion. The polymer was purified by multiple dissolution (×5) in methanol followed by precipitation into diethyl ether. The same method was employed to prepare ACE-labeled PVP and unlabeled PMAA and PVP.

The contents of ACE in PMAA/ACE and PVP/ACE, measured by ultraviolet (UV) spectroscopy (Pye Unicam SP-400UV/VIS spectrometer), were 0.4 and 0.5 mol %, respectively. The number average molecular weights of PMAA, PMAA/ACE, PVP, and PVP/ACE are 5.8×10^5, 2.7×10^5, 5.5×10^4, and 4.0×10^4 g/mol, respectively.

Water used throughout this work was purified by deionization and double distillation.

Sample Preparation

Polymer solutions were prepared from their stock solutions. The concentrations of the stock solutions for PMAA, PMAA/ACE, PVP, and PVP/ACE are all 0.1 wt %. It is to be noted that the pH of the stock solution of the polyacid was ~10, whereas that of PVP was ~7.

For the experiments involving dissolution of organic probe molecules into the water-soluble polymer solutions, the probe, Py, was initially dissolved in diethyl ether to obtain a stock solution of known concentration ($\sim 10^{-3}$mol L^{-1}). This solution was diluted to 10^{-5} mol L^{-1} just before use. One milliliter of the probe solution (10^{-5}mol L^{-1}) was injected into a 10 mL volumetric flask. The ether was evaporated at room temperature. Subsequently, a polymer solution of known pH (10^{-3} wt %) was added to the flask. To ensure solubilization and equilibration, the polymer/probe solution was sonicated for 20 min, and then left at room temperature for >12 h. Similar procedures were followed when Pe was used a probe, but the final concentration of the probe was 10^{-5}mol L^{-1}.

For the energy transfer experiment, ANS was initially dissolved in methanol to obtain a stock solution of known concentration ($\sim 6 \times 10^{-4}$ mol L^{-1}). To determine the influence of complexation on the energy transfer efficiency from ACE to ANS, 500 μL of ANS stock solution was added to 3 mL of the PVP/ACE, PMAA/ACE, and PMAA/ACE–PVP solutions at a given pH, and the fluorescence emission spectrum for each system was measured.

For complexation measurements, all samples of different PVP-to-PMAA/ACE ratios (0.01:1; 0.02:1; 0.06:1; 0.1:1; 0.16:1; 0.2:1; 0.4:1; 0.6:1; 0.8:1; 1:1; 1.6:1; 2:1; 3:1, and 4:1) were prepared in a similar manner. The method is described by using the example of the preparation of a solution containing 2.8×10^{-6} mol % PMAA/ACE and 2.8×10^{-6} mol % PVP (in residue unit, pH = 3). To make this solution, 0.1 mL of PMAA/ACE stock

solution (2.8×10^{-4} mol %) and 0.1 mL of PVP stock solution (2.8×10^{-4} mol %) were added to a 10 mL volumetric flask with shaking. The mixture was diluted to ~9 mL and its pH was adjusted to 3.0 using 0.1 M HCl and 0.1 M NaOH solutions. The solution obtained in this manner was diluted to 10 mL with water.

Analytical Methods

All fluorescence measurements were conducted on a Perkin-Elmer LS-50B Luminescence Spectrometer. The advantage of fluorescence technique is that information about the behavior of the polymer at the molecular level can be obtained, as opposed to the bulk properties determined by nonspectroscopic techniques. Furthermore, it can be imagined that the segmental mobility of the polymer in the complexation state, particularly that of the segments existing in direct contact with another polymer chain would be lower than that in the bulk solution. Therefore, comparison of the segmental motions of polymers in the complexation state with that in the bulk solution should allow reasonably detailed conclusions to be drawn regarding the interactions between polymers in the complexation state. Like the fluorescence polarization measurement, the fluorescence anisotropy measurement is a direct measure of the segmental mobility of polymers. In the determining process, a plane polarized light is used as a light source, and the fluorophore labeled on the polymer chain is excited to its excited state. If the label has no movement within its excited state lifetime, the emission from the label will be fully polarized. However, the emission from such kinds of labels is partially or fully depolarized because of segmental motions of the polymer. In the present study, ACE was chosen as label because it has no motion independent of the polymer chain on which it was attached. The rate of depolarization of a label can be determined by examination of the intensities of fluorescence emitted in planes parallel, I_{vv}, and perpendicular, I_{vh}, to that of vertically polarized excitation. In the steady-state measurement, the anisotropy, r, is a measure of the extent to which fluorescence polarization is retained within the excited state lifetime and is constructed according to equation 1:[28]

$$r = \frac{I_{vv} - GI_{vh}}{I_{vv} + 2GI_{vh}} \quad (1)$$

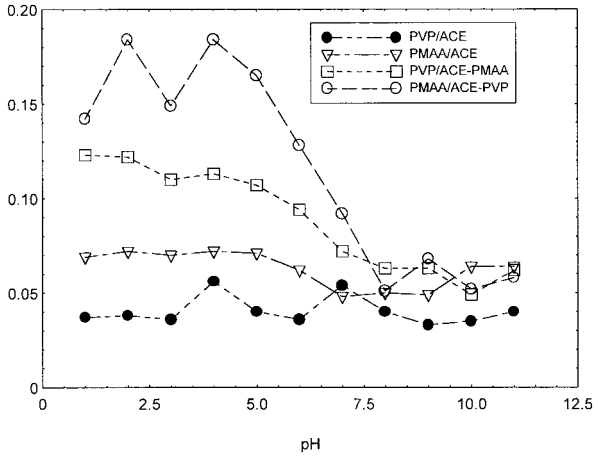


Figure 1 Plots of fluorescence anisotropy (r) versus pH in PMAA/ACE, PVP/ACE, PMAA/ACE–PVP, and PVP/ACE–PMAA aqueous solution (2.8×10^{-6} mol %, in residue unit, for either PMAA/ACE, PVP/ACE, PMAA, or PVP).

where G is the instrumental correction factor and is defined by eq, 2,

$$G = I_{hh}/I_{hv} \quad (2)$$

where I_{hh} and I_{hv} are the fluorescence intensities emitted in planes parallel and perpendicular to that of horizontally polarized excitation, respectively. By employing the polarization accessory and software of the machine, the parameters G and r can be determined automatically. However, as a normal practice, the r values are recorded >80 times for a given sample at a given condition. The data shown in the results are average values. It is clear that the r value is determined by both the nature of the label and the segmental mobility of the polymer. For a given fluorophore, a larger r value corresponds to a lower segmental mobility of a polymer, and *vice verse*.

RESULTS AND DISCUSSION

Fluorescence Anisotropy Studies

Considering the fact that complexation will reduce the flexibility of polymer chain, our approach to the determination of the complexation between PMAA/ACE and PVP is to focus on the segmental mobility of PMAA/ACE. Fluorescence anisotropy of PMAA/ACE was measured as a function of pH. The results, shown in Figure 1, indicate a transition in the r values between pH 5 and 7 for PMAA/

ACE, which corresponds to the conformational transition of the polymer from hypercoiled to extended coil structure.[23, 24] It is easy to understand that the low segmental mobility of the polymer at low pH is likely to be a consequence of stereoscopic restrictions. In contrast, at high pH, the segmental mobility of the polymer should be fast and, therefore, the *r* value should be smaller. For PVP/ACE, however, the anisotropy value (with reference to Figure 1) is significantly lower than that of PMAA/ACE at pH values <7. Furthermore, the *r* value of PVP/ACE is almost pH independent, indicating that the polymer may adopt relatively open coil conformation within the wide pH range studied. For the system with PMAA/ACE and PVP, the *r* value at pH <7 is much greater than that of the corresponding system with no second polymer. Clearly, the increase in *r* value may be attributed to the complexation of PMAA/ACE with PVP. The *r* value of the complexation system at pH >7.5 is no different (within the experimental error) than that for the system without PVP, indicating that there is no complexation between the two polymers. The finding that the complexation between PMAA and PVP occurs at pH <7 was further confirmed by the anisotropy measurement of the system of PVP/ACE in the presence of blank polymer PMAA. This finding is not difficult to understand because at pH >7, PMAA exists as polyanions. The negatively charged structure is unfavorable for H-bonding formation between the two polymers and, hence, unfavorable for the complexation.

Results for the complex systems of different PVP-to-PMAA ratios (in residue unit) at pH 3.0 are shown in Figure 2. The *r* value for PMAA/ACE in the complex system increases from ~0.10 in the absence of PVP to ~0.165 in the presence of PVP (PVP-to-PMAA/ACE ratio is ~1:2). Beyond the 1:2 ratio, the *r* value does not change very much with further increases in PVP concentration, obviously because of complexation between PMAA/ACE and PVP. When the ratio of PVP to PMAA/ACE is low, the anisotropy data are dominated by the contribution of the free PMAA/ACE. As the concentration of PVP is progressively increased, the segmental mobility of the PMAA/ACE is hindered because of complexing with PVP. The *r* value reaches a maximum at a ratio of 1:2 (PVP–PMAA/ACE), indicating that the polymer chain experiences greatest restraint due to complexation. The result may be understood by considering that PVP is a typical H-bond acceptor[22] and PMAA is a H-bond donor because of the carbonyl group in the lactone ring and the carboxyl group in MAA. Each residue unit in PVP or in PMAA has only one functional group. Therefore, it is expected that the ideal complexation would be complete at the stoichiometric ratio, if all of the interaction sites were equally accessible and participated in the complexation. However, at pH 3, the carboxyl groups on the PMAA chain are partially ionized and, therefore, only some of the residue units of the polymer have the ability to take part in the complexation. In other words, some segments of PMAA/ACE chain would exist as loops or tails in the PVP–PMAA/ACE complex. The 1:2 complexation ratio can be also understood from another viewpoint. It is well known that PMAA adopts hypercoiled conformation at pH <5–7; therefore, most of the segments of the PMAA chain will be buried within the coil and some may appear on the coil surface as loops or tails. On addition of PVP, it is these segments on the coil surface that have the priority to complex with PVP. Thus, the anisotropy of the ACE-labeled PMAA increases dramatically with increasing PVP concentration at the very early stage. Clearly, there is a balance between the complexation and the hydrophobic interaction within PMAA that makes the polymer adopt a compact coil structure. From the fact that the complexation occurs most effectively at a ratio of ~1:2 (PVP–PMAA/ACE), it may be inferred that the compact coil conformation of PMAA/ACE would be partially altered due to complexation between the two polymers. To further confirm the tentative conclusions just described, some probe solubilization experiments were conducted.

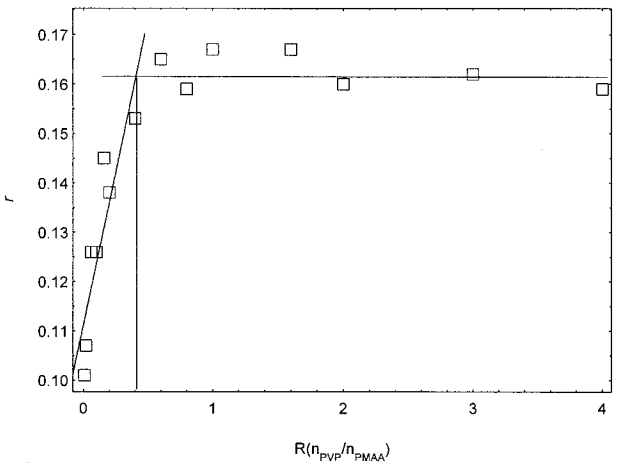


Figure 2 Plots of fluorescence anisotropy (*r*) versus the ratio of PVP to PMAA/ACE in aqueous solution at pH 3.0.

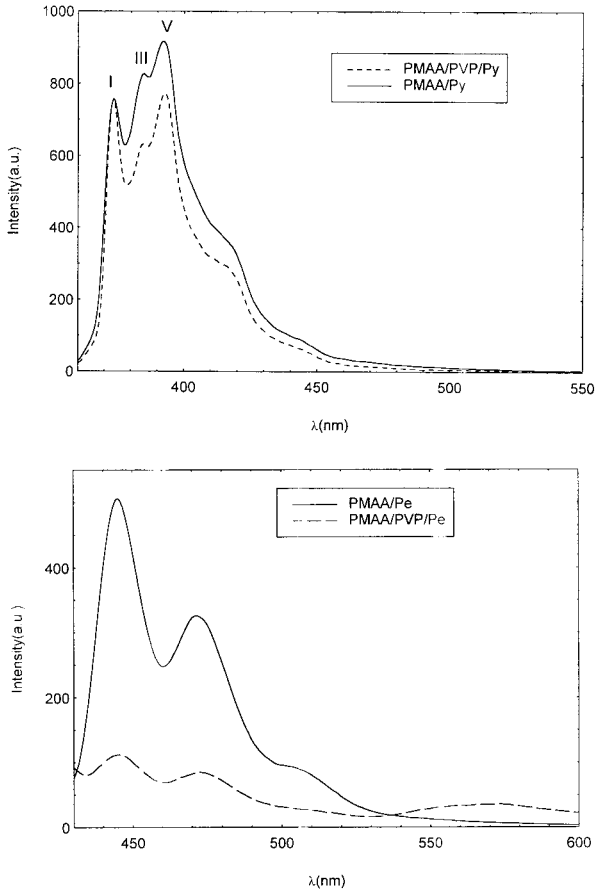


Figure 3 (a) Fluorescence emission spectra of Pyrene (10^{-6} mol L^{-1}) dispersed in PMAA (2.8×10^{-5} mol L^{-1}, in residue unit) and in PMAA/PVP (1:1, 2.8×10^{-5}mol L^{-1}, in residue unit) aqueous solution at pH 3.0. (b)Fluorescence emission spectra of perylene (10^{-5} mol L^{-1}) dispersed in PMAA (2.8×10^{-5} mol L^{-1}, in residue unit) and in PMAA/PVP (1:1, 2.8×10^{-5} mol L^{-1}, in residue unit) aqueous solution at pH 3.0.

Probe Studies

It is to be expected that the tightly coiled conformation of PMAA might favor solubilization of organic guests into its hydrophobic microdomains. Therefore, fluorescence probe studies should be useful in investigating the effects of complexation on the conformational behavior of PMAA. The probes used in the current study were Py and Pe. Py was used because the fine structure of its fluorescence emission spectrum is highly sensitive to the changes in the polarity of its microenvironment.[29, 30] The larger values of I_3/I_1 indicate a more hydrophobic environment (see Figure 3). This property has been widely used to monitor the conformational behavior of water-soluble polymers in aqueous phase.[31]

The effect of complexation on the fine structures of the fluorescence emission spectra of Py solubilized in PMAA and PMAA/PVP (1:1, in residue unit) solution, respectively, at pH 3 and at a polymer concentration of 2.8×10^{-5}mol % and probe concentration of 10^{-6} mol L^{-1} is depicted in Figure 3(a). Complexation between PMAA and PVP was accompanied, as expected, by a conformational change as proved by the decrease in the hydrophobicity of the environment of the probe. This result is because the ratio I_3/I_1 of the probe decreased from ~1.1 for PMAA to ~0.7 for PMAA/PVP.

The effect of complexation on the PMAA conformation at pH 3 was also probed using Pe as another probe. The result is shown in Figure 3(b). Obviously, complex formation is accompanied by a decrease in the solubilizing ability of the polymer. Unlike Py, Pe is almost insoluble in water.[32] Therefore, a decrease in the solubilizing capacity of the PMAA/PVP for Pe is an indication of decrease in the number of hydrophobic microdomains or reduction of the domain size. The tentative result about the conformational change of PMAA on complexation is in support of the result from anisotropy measurements. Furthermore, the decrease in the solubilizing ability of PMAA for hydrophobic molecules is direct evidence for the broken or partially broken of hydrophobic microdomains in PMAA solution at low pH. The alteration to the PMAA conformation may be attributed to the complexation between the two polymers.

Further evidence about the complexation between PMAA and PVP is afforded by energy transfer studies.

Energy Transfer Studies

Because the excitation spectrum of ANS is well over lapped by the emission spectrum of ACE, nonradiation energy transfer (NRET) from ACE to ANS should be possible, provided the donor and acceptor are brought sufficiently close. NRET is widely used in biochemistry and polymer science because the efficiency of NRET occurs independently of the linker joining the donor and acceptor and depends only on the donor–acceptor distance.[28] Hence, any process bringing the donor and acceptor into close proximity, including association interactions between polymers, will result in energy transfer. ANS is frequently used to label proteins noncovalently.[33] It is weakly fluorescent in water but it fluoresces strongly when

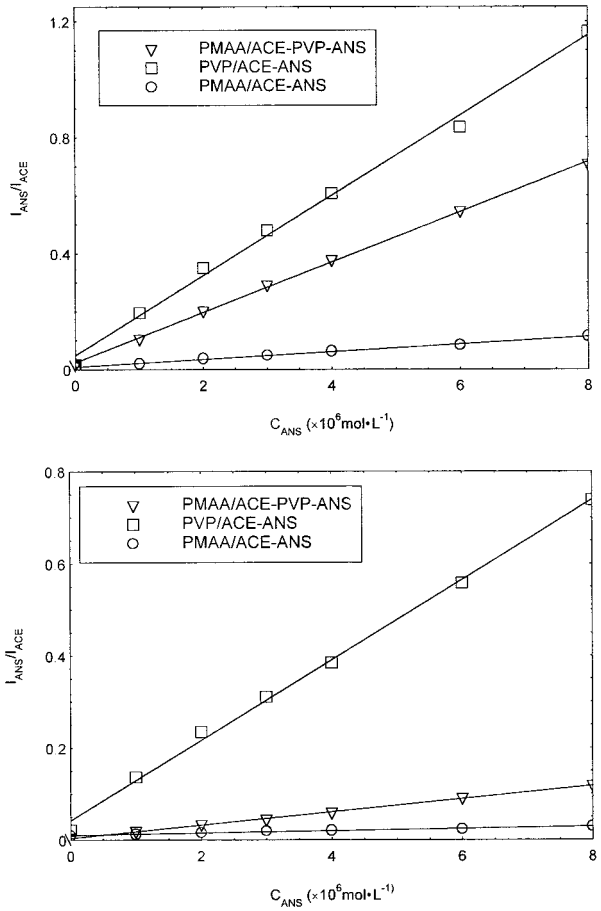


Figure 4 (a) Plots of the ratio of ANS fluorescence intensity to ACE fluorescence intensity to ANS concentration in PMAA/ACE–ANS, PVP/ACE–ANS, and PMAA/ACE–PVP–ANS aqueous solution at pH 3.0 (2.8×10^{-5} mol L^{-1}, in residue unit, for either PMAA/ACE, PVP/ACE, or PVP). (b)Plots of ratio of ANS fluorescence intensity to ACE fluorescence intensity against ANS concentration in PMAA/ACE–ANS, PVP/ACE–ANS, and PMAA/ACE–PVP-ANS aqueous solution at pH 9.0 (2.8×10^{-5}mol L^{-1}, in residue unit, for either PMAA/ACE, PVP/ACE, or PVP).

bound to proteins or membranes. Considering that PVP is frequently used as a synthetic polymeric model for proteins, it might be possible to use ANS as a nonconvalent label for PVP. Via the label, the interaction between PVP and PMAA may be studied. The emission spectra of PVP/ACE excited at 290 nm as the sample is titrated with ANS are shown in Figure 4(a). In the absence of PVP/ACE, the emission from the ANS dissolved in water was insignificant (not shown). It may be noted that the ACE emission from PVP/ACE is quenched on addition of ANS and that the ANS emission increases as the ACE emission decreases. The efficient NRET from PVP/ACE to ANS (I_{ANS}/I_{ACE}) clearly indicates the association between the polymer and ANS. For the PMAA/ACE system, the NRET efficiency (I_{ANS}/I_{ACE}) does not vary very much with increasing ANS-to-ACE ratio, showing that there is little association between the two components. Based on these findings, it may be possible to look at the interaction between PMAA and PVP via NRET from ACE to ANS. The ANS titration result for the system of PMAA/ACE-PVP, in which the polymer concentration was maintained at 2.8×10^{-5} mol L^{-1}(in monomer unit) and the pH was adjusted to 3, is depicted in Figure 4(a). Clearly, unlike the PMAA/ACE–ANS system, the NRET efficiency (I_{ANS}/I_{ACE}) from ACE labeled on PMAA to ANS increased dramatically with the introduction of PVP. This result may only be understood by assuming that there is a strong association (complexation) between PMAA and PVP. A similar experiment was conducted at pH 9, and the results are shown in Figure 4(b). Clearly, introduction of PVP does not enhance the NRET efficiency from PMAA/ACE to ANS, a strong evidence to support the conclusion from fluorescence anisotropy and probe studies.

Nature of Complexation

To gain further understanding of the nature of the complexation between PMAA and PVP, an experiment was undertaken to study the effect of NaCl on the interaction. The fluorescence anisot-

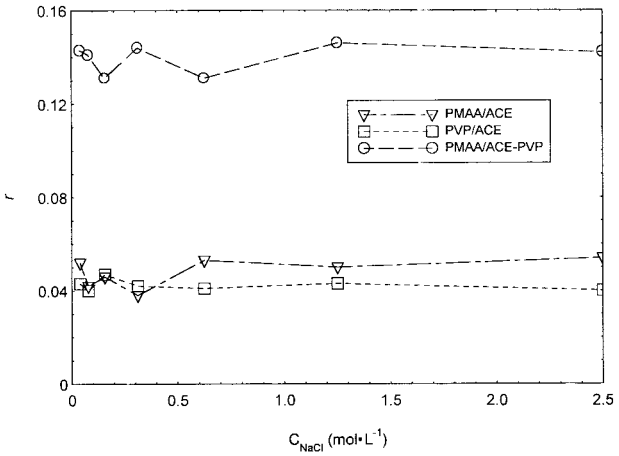
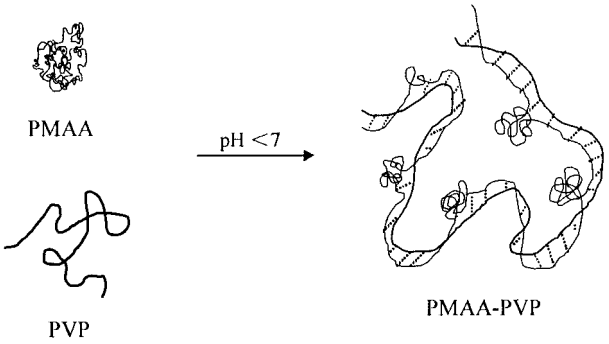


Figure 5 Plots of fluorescence anisotropy (r) bersus NaCl concentration in PMAA/ACE, PVP/ACE, PMAA/ACE–PVP aqueous solution at pH 3.0 (2.8×10^{-5} mol L^{-1}, in residue unit, for either PMAA/ACE, PVP/ACE, or PVP).



Scheme 1 Diagram of the model for the structure of PMAA/PVP.

ropy data of PMAA/ACE, PVP/ACE, and PMAA/ACE–PVP at pH 3 as a function of NaCl concentration is depicted in Figure 5. Inspection of the figure reveals that the anisotropy data of the three systems do not change very much with increasing NaCl concentration. Furthermore, the anisotropy data for PMAA/ACE–PVP system are significantly greater than those for either PMAA/ACE or PVP/ACE. Therefore, the nature of the complexation between PMAA/ACE and PVP may be not electrostatic attraction, which was commonly found in other polyelectrolyte complexation systems,[25–27] but most likely formation of hydrogen bonds.

Considering the "connected cluster model" for PMAA at low pH[34] and the experimental results already described, it might be reasonable to propose a "ladder with connected cluster model" for the structure of the PMAA/PVP complex (see Scheme 1). In the model, it was supposed that the two polymer chains would be connected by hydrogen bonding, and the clusters existing along the ladder would be the remains of the partially broken clusters originally existing within the compact PMAA coils. With this model, it should not be difficult to explain all the results just described..

CONCLUSIONS

Fluorescence studies show that interpolymer complexation between PMAA and PVP is both pH and molar ratio dependent, and a major conformational change occurs when PMAA is mixed with PVP in aqueous phase at pH of <5. The conformational change of PMAA from the hypercoiled to the loose coiled form is evidenced by the decrease in the hydrophobic microdomain size or domain number. At pH 3, the complexation occurs most efficiently at a molar ratio of ~1:2 (PVP/PMAA, in residue unit), suggesting that only some of the segments of PMAA have taken part in the complexation. Introduction of NaCl has little effect on complexation between PMAA and PVP, showing the nonCoulombic nature of the complexation. Based on these conclusions and the "connected cluster model" for PMAA at low pH, a "ladder with connected cluster" model was proposed for the structure of PMAA/PVP complex formed at low pH.

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