Effect of the Degree of Ionization of Poly(methacrylic acid) on the Complex Formed with Pyrene End-Labeled Poly(ethylene glycol)

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ABSTRACT: Pyrene chromophores labeled at both chain ends of poly(ethylene glycol) (PEG) are utilized to determine the effect of dissociated carboxylic acid groups on hydrogen bonding with poly(methacrylic acid) (PMAA). When nonionized PMAA is added to a PEG solution, PEG chains interact with PMAA very efficiently. This strong interaction causes a rapid increase in intermolecular excimer formation and in ground-state interactions. There is also an abrupt decrease in intramolecular excimer formation. The loss of carboxy structures upon ionization of PMAA causes intermolecular excimer formation to be suppressed because there are fewer PEG chains in the vicinity of PMAA coils. Simultaneously, the extent of the decrease in intramolecular excimer formation upon complexation is diminished with increasing ionization. It appears that this latter observation is due to a less effective suppression of intramolecular chain mobility in the partially dissociated system.

Introduction

In our previous papers complexation between poly(acrylic acid) (PAA)[1] or poly(methacrylic acid) (PMAA)[2] and poly(ethylene glycol) (PEG) was examined in aqueous solution. Pyrene groups were attached to both chain ends of PEG, and pyrene excimer fluorescence was used to probe the complexation. The excimer to monomer intensity ratio, I_D/I_M, was measured under two conditions to distinguish intramolecular and intermolecular excimer formation. The first consisted of the poly(carboxylic acid) and a mixture of 1% labeled PEG and 99% unlabeled PEG; the second consisted of the poly(carboxylic acid) and 100% end-labeled PEG. A decrease in the intramolecular contribution to I_D/I_M was attributed to a suppression of the end-to-end cyclization rate in the labeled PEG. This decrease was much larger for PMAA than for PAA. On the other hand, there was an initial increase in intermolecular excimer formation upon addition of the poly(carboxylic acid). In the PAA system this was followed by rather constant values of I_D/I_M for stoichiometric excess of PAA. By contrast, in the PMAA system further addition of PMAA caused a dramatic suppression of intermolecular excimer formation, counteracting the initial increase.

The contrasting behavior of intramolecular and intermolecular excimer formation for PMAA compared to PAA seems to be related to the greater hydrophobicity of PMAA, which causes a more compact and rigid structure to be formed for PMAA. The compactness of the PMAA probably causes the larger decrease in intramolecular excimer formation than observed for PAA. At the same time there is a blue shift of the excimer peak position in the PMAA–PEG system, suggesting that excimer destabilization is occurring. The hydrophobic effect became less significant upon addition of methanol; for the 40 wt % methanol–60 wt % water mixture the fluorescence behavior for PMAA was very similar to that for PAA in pure water.

These earlier studies have demonstrated that fluorescence techniques can be more sensitive to complex formation than conventional methods such as viscometry, potentiometry, and turbidimetry.[1] For example, Ikawa et al. reported that they did not observe any change in viscometric data when the PEG molecular weight was less than 1760 for the PMAA–PEG complex or 8800 for the PAA–PEG complex.[3] It is worth mentioning that our pyrene end-labeled PEG probe appears to be more sensitive to complexation than other fluorescent probes.[4] Chen and Morawetz reported the association between PAA randomly labeled with dansyl residues and poly(ethylene oxide) (PEO).[4] They observed an increase in dansyl fluorescence intensity when PAA (MW of PAA = 1.4×10^5, 5.9×10^5) was complexed with PEO of high molecular weight. They suggested that this indicates a more hydrophobic environment around the chromophore. However, they observed only a minor change in fluorescence intensity for the PEO with molecular weight 8000 and no change for the PEO with molecular weight 3400. In our study, the pyrene end labeled PEG probe was sensitive enough to permit detection of the interaction between labeled PEG of molecular weight 4800 and PAA having molecular weight between 1850 and 890K.[1]

In the present investigation we have extended our previous work to examine the effect of ionization of the polymeric proton donor on complexation between PMAA and the pyrene end-labeled PEG. Poly(carboxylic acid) is known to form a hydrogen bonding complex with a proton-accepting polymer, as well as a polyelectrolyte complex with a polycation. In the first case, represented by the PMAA–PEG and PAA–PEG systems, the poly(carboxylic acid) functions as a proton donor so that it is necessary to have a sufficient number of carboxy groups to interact with the proton acceptor. By contrast, in a polyelectrolyte complex, such as with poly(ethylene imine) or poly(vinyl amino acetal),[5,6] the poly(carboxylic acid) is in the form of a polyanion in which the dissociated carboxylate groups become active sites for complexation. This means that the level of dissociation of the carboxy groups will be critical in determining whether a complex is formed. We find that the complexation between PMAA and PEG is inhibited by the ionization of PMAA. Although this result is expected, we demonstrate several new photophysical features of our terminally labeled probe. We also perform pH measurements and show that fluorescence is more sensitive to complexation than pH for very low polymer concentrations.

Experimental Section

Materials. Poly(methacrylic acid) (PMAA) obtained from BDH Chemical Ltd., Poole, England, was described previously.[2] It was purified by dialysis against water using a pressurized stirred cell (Amicon Corporation) and then freeze-dried. The viscosity-average molecular weight of this material was 9500, as measured in methanol at 299 K. Pyrene end labeled poly(ethylene glycol) (PEG*) has also been described in previous papers.[1,2] Here the

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asterisk denotes the fluorescent pyrene label. This sample was synthesized by direct esterification of 1-pyrenebutyric acid with poly(ethylene glycol) of M_w = 9200 and M_w/M_n < 1.10. The tagging percentages were calculated by UV absorption in THF with methyl 1-pyrenebutyrate as the model compound. The product was fully labeled at both chain ends with ±5% accuracy.

Spectroscopy. The UV–visible absorption spectra were measured with a Varian Cary 210 spectrophotometer. The excitation spectra were taken with a SPEX Fluorolog 212 spectrophotometer. The monomer excitation spectrum was monitored at 376 nm and the excimer excitation spectrum was monitored at 500 nm in the scanning excitation range between 300 and 370 nm. The spectrofluorometer used to measure photostationary fluorescence spectra was described previously.[7] The excitation was at 343 nm and a 1-mm slit width was used for both excitation and emission monochromators. The spectra were recorded with a PDP11/23+ computer and corrected for spectral response. I_D/I_M was calculated from areas for an excimer and for a monomer, respectively.[1,2] The polymer concentration of total PEG was 2.0×10^{-3} M and that of PMAA was 2.0×10^{-1} M for fluorescence measurements. The concentration is reported in units of moles of repeating unit per liter, and the composition of the solution is described based on the molar ratio of PMAA to PEG, [PMAA]/[PEG]. The degree of ionization (DI) is calculated by the molar concentration of sodium hydroxide added to the PMAA solution relative to that of the repeating unit of PMAA.

pH Measurements. The pH of 2×10^{-3} M PEG was measured with addition of 2×10^{-1} M PMAA by using a Beckman Φ 44 pH meter. For the blank pH measurement in which no complexation can occur, distilled, deionized water was used in place of the PEG solution. All experiments were done at 303 K with the temperature being controlled by a water bath.

Results

Effect of Ionization on Intramolecular Excimer Formation. The mixture of 1% PEG* (labeled) and 99% PEG (unlabeled) in aqueous solution emits fluorescence from both the locally excited pyrene chromophore (monomer) and also from the excimer. 1-Pyrenebutyric acid was used as a model compound for the monomer entity.[1,2] Since I_D/I_M of the (1% PEG* + 99% PEG) solution was constant regardless of further dilution, it should yield information on the intramolecular excimer formation of pyrene groups attached to the same PEG chain, presumably due to end-to-end cyclization.

It is important to consider the mechanism of excimer formation in aqueous solution in some detail. Cheung et al. have shown that the pyrene excimer of PEG* is formed from a diffusion-controlled cyclization process in nonprotonic solvents.[8] However, we recently observed that I_D/I_M for the aqueous solution of PEG*(9200) was three times greater than the value expected for the diffusion-controlled cyclization process in nonprotonic solvents; moreover, I_D/I_M was 8.4 times greater than for the diffusion controlled process for PEG*(4800).[1] Thus, this effect is strongly enhanced by a decrease of PEG molecular weight. Furthermore, PEG*(4800) showed a large red shift of approximately 3 nm in the excitation spectra monitored at the excimer emission compared to that monitored at the monomer emission. By contrast, PEG*(9200), which is employed in the present work, showed only a very slight red shift of 0.7 nm, as shown in Figure 1. These observations[1,2] and others[9] imply that a hydrophobic attraction exists between the terminal pyrene groups in water resulting in a higher I_D/I_M value than that for the diffusion-controlled cyclization process. However, pyrene aggregation in the ground state is not nearly as significant for PEG*(9200) as that for PEG*(4800).

The intramolecular fluorescence was monitored upon the addition of partially ionized PMAA. When the added PMAA was not ionized, I_D/I_M decreased sharply upon complexation and became constant at a [PMAA]/[PEG] composition ratio of 3/4. In order to isolate the effect on I_D/I_M caused by changing the DI, the data for 0% ionization were subtracted from those for each DI. The results obtained are presented as $\Delta(I_D/I_M)$ in Figure 2. Each curve shows an initial increase upon addition of PMAA, with the more pronounced enhancement occurring for the higher DI. The fluorescence data observed for different DI in this figure may be described by the summation of two monotonic changes: the decrease in I_D/I_M for nonionized PMAA and the increase obtained for each DI in Figure 2. It is clear that the individual PEG* chain gains intramolecular mobility upon suppression of complex formation compared to the PEG* reacted with nonionized PMAA.

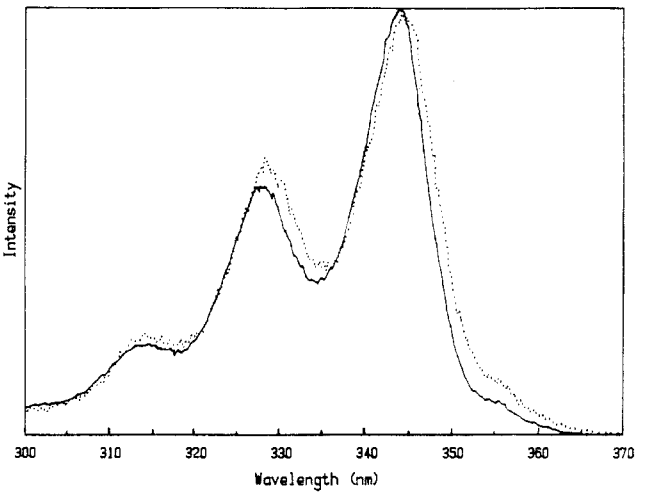

Figure 1. Excitation spectra of 1% PEG*(9200) + 99% PEG-(9200). Total polymer concentration = 2×10^{-3} M. (a) monitored at 376 nm (solid line). (b) monitored at 500 nm (broken line).

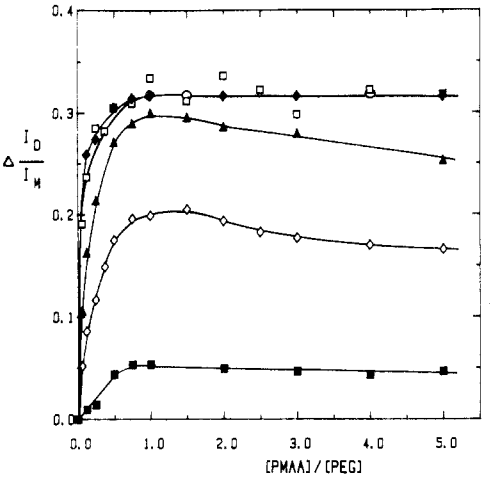

Figure 2. Difference between I_D/I_M values upon addition of PMAA for a sample that is partially ionized and one that is nonionized, i.e., $\Delta(I_D/I_M) = (I_D/I_M)_{DI\%} - (I_D/I_M)_{0\%}$: (a) (■) 10%; (b) (◇) 20%; (c) (▲) 25%; (d) (□) 30%; (e) (◆) 40%; and (f) (○) 50%.

Recently Turro and Arora have described hydrogen bonding, hydrophobic, and Coulombic interactions between PAA containing 1.5 mol % pyrene groups in side chains and complementary polymers including poly(ethylene oxide) (PEO) and poly(1-vinyl-2-pyrrolidinone) (PVP).[10] Both PAA–PEO and PAA–PVP complexes are formed predominantly through hydrogen bond interaction. They observed an increase in I_M/I_D, the monomer-to-excimer intensity ratio, and P, the peak-to-valley ratio for the (0,0) transition in the ^1L_a band of the absorption spectrum, upon complexation of PAA with either PVP or

PEO. Herkstroeter et al. demonstrated earlier that increased interaction of pyrene groups causes broadening of the pyrene absorption spectrum, which leads to a decrease in P.[11] Thus, the work of Turro and Arora indicates that there is a reduction of both the ground- and excited-state interactions of pyrene groups in pyrene-labeled PAA in the presence of proton-accepting polymers. They suggested that this was due to changes in PAA chain conformation as well as in the structure of the interpolymer complexes. Unequivocal explanations were not presented, however. The changes in I_M/I_D and P were more pronounced in PAA–PVP (MW of PVP = 24 000 and 360 000) compared to PAA–PEO (MW of PEO = 5000 and 100 000). They suggested that the more pronounced change for PAA–PVP arises because this system has a stronger complexation due to the additional hydrophobic and Coulombic contributions.[10]

Turro and Arora also reported on the effect of ionization at a 1:1 molar ratio. In the acidic region (pH <4) the association of PAA and PEO was indicated by higher I_M/I_D values for PAA–PEO than those for PAA with $(CH_3O-CH_2)_2$, a monomer model for PEO. In the pH range 6–8 the I_M/I_D values for PAA–PEO were lower than those for PAA–$(CH_3OCH_2)_2$, suggesting that the presence of PEO probably caused PAA to assume a more compact conformation in this pH range. At high pH values (>9), in the presence of PEO, the PAA assumed an expanded form by ionization with as large an I_M/I_D as that found in the PAA–$(CH_3OCH_2)_2$ system.

In a subsequent paper Arora and Turro focused on the interpolymer interactions of PAA arising from Coulombic forces.[12] Two new parameters, P_M and P_E, were used instead of P; here P_M is the peak-to-valley ratio for the (0,0) transition of the ^1L_a band in the excitation spectrum viewed at the monomer emission and P_E is that viewed at the excimer emission. The polymer concentration they employed is in a range such that interaction among pyrene groups in PAA is expected to be solely intramolecular. They used the increase in P_M, which arises due to a narrowing of the vibrational bands in the monomer excitation spectrum, as an indication of reduced intrachain interactions of isolated pyrene groups. The increase in P_E arising from a corresponding narrowing of the excimer excitation spectrum was used as an indication of reduced efficiency of excimer formation. When the pH of the PAA aqueous solution was increased from 4 to 9, an increase in P_M for the excitation spectrum showed that ionization of carboxy groups caused chain expansion. A corresponding decrease in P_E suggested that the excimer is formed from pyrene groups solely in neighboring repeating units in the absence of groups separated by large PAA blocks. Furthermore, they suggested that hydrophobic interactions of pyrene groups present in neighboring positions on the polymer main chain or of those brought closer by coiling of the polymer chain could facilitate and stabilize excimer formation.

In the present study, we followed the approach of Arora and Turro and obtained P_M and P_E values for the (1% PEG* + 99% PEG)–PMAA system. The P_M shown in Figure 3 depends both upon the addition of PMAA and upon the degree of ionization. For DI between 0 and 10%, P_M increased rapidly up to [PMAA]/[PEG] = 1–1.5, becoming constant above that ratio, indicating that intrachain interactions of pyrene groups are reduced upon complexation. This tendency was more pronounced at lower DI. At 20% ionization, P_M decreased initially followed by a gradual increase upon addition of PMAA. At 30% ionization P_M decreased at low [PMAA]/[PEG] and

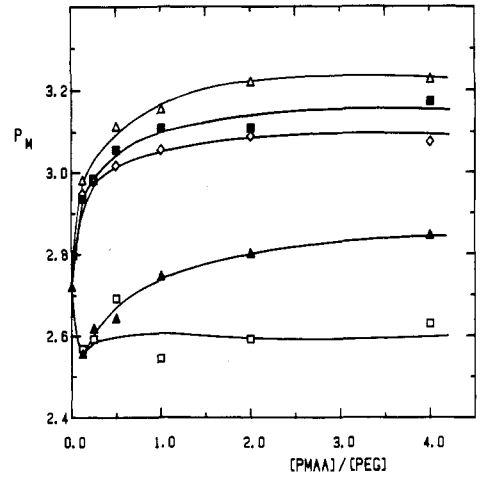

Figure 3. Change in the peak-to-valley ratio for the (0,0) transition of the ^1L_a band in the excitation spectrum viewed at 376 nm, P_M: (a) (△) 0%; (b) (■) 5%; (c) (◇) 10%; (d) (◆) 20%; and (e) (□) 30%.

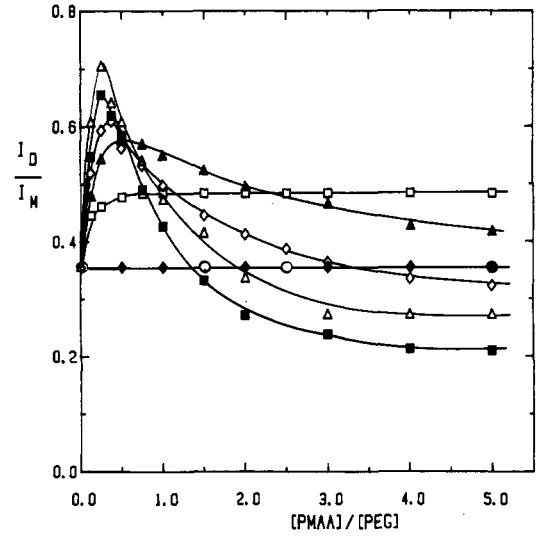

Figure 4. I_D/I_M change of the fully labeled PEG in water upon the addition of PMAA ionized to various degrees. △, 0%. See Figure 2 for other details.

became constant at high [PMAA]/[PEG] ratios. The results for 20 and 30% ionization might indicate an increase in intramolecular interaction of the isolated pyrene groups as the degree of ionization increases.

By contrast, a rapid decrease of P_E, not shown, was observed at every DI even for addition of a very small amount of PMAA. This decrease indicates an increased efficiency of excimer formation between pyrene groups labeled on the same PEG chain, presumably due to an increase in mobility. This observation is consistent with the increase in intramolecular excimer formation with increasing DI as shown in Figure 2.

Effect of Ionization on Intermolecular Excimer Formation. Next, PMAA was added to an aqueous solution of the fully labeled PEG*, changing the DI in the same manner as for the mixture of 1% PEG* and 99% PEG in the previous section. Figure 4 shows the I_D/I_M change for this system. In the nonionized case I_D/I_M increases up to twice its initial value of [PMAA]/[PEG] = $^1/_4$ and then decreases upon further addition of PMAA. The initial increase in I_D/I_M upon complexation is suppressed by ionization of PMAA. At the same time the maximum in I_D/I_M moves to a higher [PMAA]/[PEG] ratio. At 30% ionization the change in I_D/I_M becomes smaller, showing a monotonic increase up to [PMAA]/

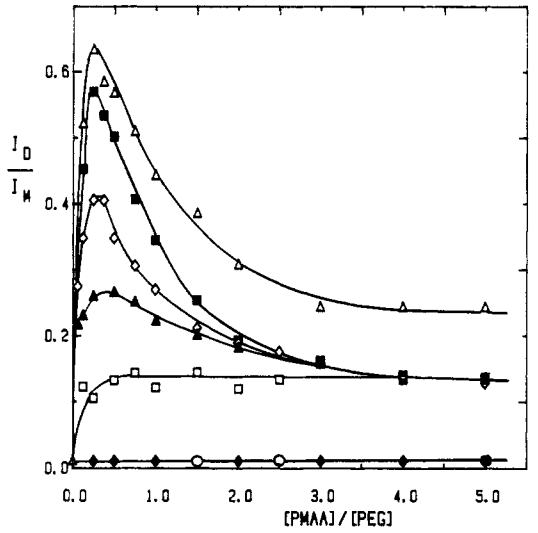

Figure 5. Change in intermolecular excimer formation upon the addition of PMAA ionized to various degrees. △, 0%. See Figure 2 for other details.

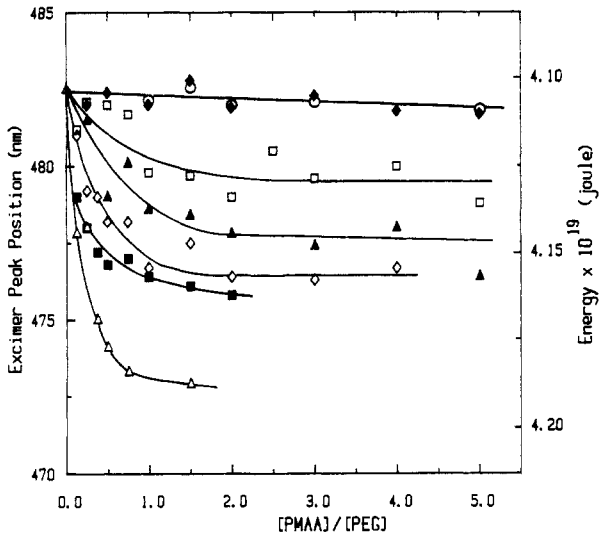

Figure 6. Excimer peak position in the system of PEG* with partially ionized PMAA. △, 0%. See Figure 2 for other details.

[PEG] = 3/4 followed by constant values. Above 40% ionization I_D/I_M was independent of PMAA content.

In Figure 5, the data on intramolecular excimer formation were subtracted from those in Figure 4 in order to get the net contribution due to intermolecular excimer formation, in the same manner used in the previous work.[1,2] The initial maximum in I_D/I_M is reduced in magnitude as the DI increases, with the final values becoming identical for DI = 10% up to 30%. It is apparent that the presence of carboxylate groups in PMAA reduces the local PEG concentration, thereby suppressing excimer formation between pyrene groups on different PEG chains. The high overshoot observed for 0% DI indicates extensive hydrophobic clustering of pyrene groups. As more PMAA is added these pyrene clusters are broken up by the greater number of hydrophobic PMAA molecules. However, this overshoot diminishes upon ionization of PMAA in a similar manner to that observed in PMAA–PEG in a water–methanol mixture.[2]

In Figure 6, the excimer peak position is presented as a function of DI. We focus on the range over which the I_D/I_M increased in Figure 4 for all systems, i.e., [PMAA]/[PEG] = 0–$^1/_4$. Here we observe that the shift of the excimer peak position, corresponding to an increase

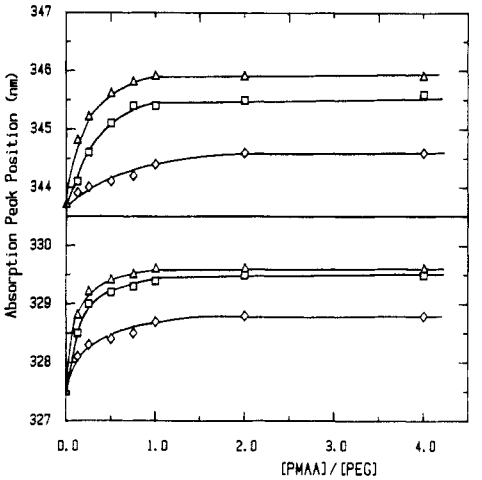

Figure 7. Change in absorption peak position of PEG* upon the addition of partially ionized PMAA: (a) (△), 0%; (b) (□) 20%; and (c) (◇) 30%.

in energy by 261 cm^{-1} at [PMAA]/[PEG] = $^1/_4$ in the case of 0% ionization, became smaller upon ionization of PMAA. Above 40% ionization there was little change in excimer peak position with added PMAA. Thus, the destabilization of excimer formation upon complexation was not as significant upon ionization. This hydrophobic interaction between PMAA and PEG seems to be significantly hindered by the decrease in undissociated carboxy groups and the ionic repulsion between PMAA chain segments. The resultant structure is less rigid and less prone to destabilization of the excimer coplanar sandwich structure. In the region of very low I_D/I_M, such as for 0% or 10% ionization at high [PMAA]/[PEG] ratios, the excimer peak position was not distinct enough to be determined from the envelope of the fluorescence spectra.

We showed in our previous work that UV–visible absorption spectra also provide important information on the ground-state pyrene interactions.[1,2] The absorption spectrum of the ^1L_a band was measured upon addition of partially ionized PMAA, with the absorption peak positions shown in Figure 7. The absorption peaks shift red upon complexation. We earlier attributed the red shift for the nonionized PMAA system to the formation of a ground-state interaction between pyrene groups brought about by complexation. The red shift becomes smaller upon ionization, indicating that the pyrene–pyrene interactions in the ground state are weakened as a result of ionization of the PMAA.

In order to investigate this phenomenon in more detail, we refer to previously measured excitation spectra for 1% and 100% labeled PEG having [PMAA]/[PEG] ratios between $^1/_8$ and 4.[13] No change in monomer excitation spectra with changing stoichiometry occurs for the intramolecular data for either 0% or 30% DI. However, a significant red shift of about 4 nm occurs for the 100% labeled sample as PMAA is added. This indicates the presence of ground-state interactions between pyrene groups in the fully tagged system at 0% DI. A much smaller red shift of the order of 1 nm is observed for the 100% labeled PEG at 30% DI. Thus the pyrene–pyrene interactions in the ground state are facilitated by complexation. This is consistent with the results of I_D/I_M for intermolecular excimer formation observed in Figure 5, where the excimer emission comes from the preformed pyrene–pyrene interactions in the ground state. When the carboxy groups of PMAA are partially ionized, the local concentration of PEG chains in the vicinity of PMAA decreases, causing ground-state interactions between

pyrene groups to be reduced dramatically.

Discussion

Illiopoulos and Audebert have used potentiometry and viscometry to investigate the effect of ionization on complexation for different molecular weights and concentrations in the PAA–PEG system.[14] They observed that the presence of even a low content of carboxylate sites (less than 15%) in the PAA chain was sufficient to destroy complexation. They showed that the complex becomes less compact upon ionization and that the minimal chain length for PAA complexation was seven repeating units. Compared to the PAA–PEG system, the PMAA–PEG complex is much more stable in that there still is interaction between the two polymers even up to 30% ionization. These results are entirely consistent with our earlier studies[1,2] in which hydrogen bonding coupled with strong hydrophobic effects caused PMAA to interact with PEG much more strongly than did PAA.

From an alternate perspective, Tsuchida and Abe have discussed the effect of complexation on the degree of dissociation of poly(carboxylic acid).[6] Potentiometric measurement revealed that dissociation of the poly(carboxylic acid) is suppressed in the presence of PEO. An apparent dissociation constant, pK_a, for PMAA–PEO (MW = 1300) at 50% of ionization was 7.5 and that for PMAA–PEO (MW = 25 000) was 7.9, whereas that for PMAA itself was 7.3.[6] They also found that there is a critical state of dissociation, above which the complex is not formed. Thus, the presence of a certain number of undissociated carboxy groups is necessary for PMAA and PEO to form a stable complex. In such complex formation, dissociated carboxylate groups are influenced by the complexation and extract protons from the solution into the domain of the polymer chains. This critical pH depends mainly on the facility of dissociation of the poly(carboxylic acid), in which the stronger acid shows the higher critical pH. For example, it is about 5.7 for PMAA, 5.2 for an alternating copolymer of styrene and maleic acid (PSMA), and 4.8 for PAA. The pK_a for PMAA is found to be 7.3, for PSMA to be 6.5, and for PAA to be 5.6.[6]

Anufrieva and Gotlib have extensively utilized polarized luminescence to obtain detailed information on micro-Brownian motion in polymer chains.[15] They measured the relaxation time, τ_w, of poly(carboxylic acid) labeled at a low concentration by reaction with 1-(aminocarbonyl)-naphthalene-5-sulfonic acid.[15] The disappearance of the compact structure of PMAA due to ionization of the carboxy groups is revealed by an increase in the intrinsic viscosity of aqueous solutions of PMAA. In addition, there is a considerable decrease in τ_w from ca. 50 to ca. 13 ns, indicating an increase in the PMAA intramolecular mobility. PMAA exhibits greater intramolecular hindrance than PAA and $1/\tau_w$ changes very little at low degrees of ionization of the carboxy groups.

Anufrieva et al. also measured the polarized fluorescence of anthracene-labeled PMAA interacting with PEO and with poly(1,2-dimethoxyethylene) (PDME).[16] They employed the inverse of fluorescence polarization, $1/P$, where $P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$ and $I_\parallel$ and $I_\perp$ are emission intensities detected with parallel and perpendicularly oriented analyzers. In the PMAA–PEO system, $1/P$ increased rapidly for DI between 20 and 40% followed by constant values above that range. In the PMAA–PDME system, $1/P$ was small up to DI = 40% and then increased rapidly for DI between 40 and 60%. The additional nonpolar group in PDME compared to PEO provides stronger hydrophobic interaction, resulting in a more stable complex. The transition took place over a narrow range of DI, which practically coincided with that over which the internal structure of the PMAA was destroyed. This transition range is directly related to the ionization of carboxy groups. The shift of the transition range to higher DI for PMAA–PDME compared to PMAA–PEO implies that stronger interaction between complementary polymers retards the destruction of the complex structure.

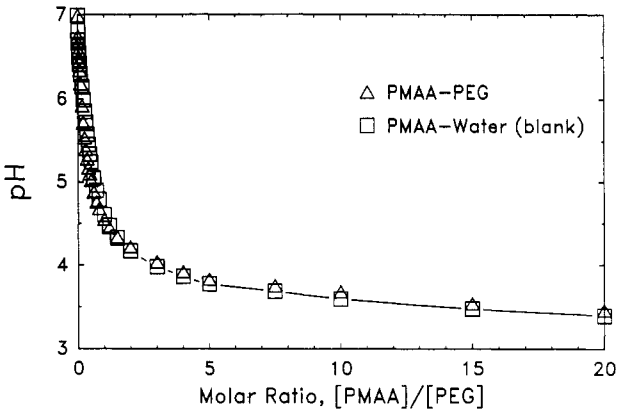

Figure 8. pH as a function of molar ratio for (△) 2×10^{-1} M PMAA added to 2×10^{-3} M PEG and (□) 2×10^{-1} M PMAA added to water blank.

In the present study, an increase in DI from 20 to 30% caused a large change in I_D/I_M for both intramolecular and intermolecular excimer formation. The intramolecular $\Delta I_D/I_M$ increased, as shown in Figure 2, and the intermolecular I_D/I_M decreased, as shown in Figure 5. This range of DI corresponds to that over which the rapid increase in $1/P$ was observed in Anufrieva's study. In addition, her increase in $1/P$, indicating an increase in chain mobility, supports our observation of the decrease in destabilization of excimer formation upon ionization in Figure 6. This is because the coplanar excimer sandwich structure is less subject to the constraints encountered in the rigid and compact structure of the nonionized complex system. Moreover, Anufrieva showed that above DI = 40%, $1/P$ became almost constant, indicating that complexation of the PMAA–PEO system was no longer possible. Our observation that there was no change in the fluorescence spectra in spite of addition of PMAA above 40% ionization is consistent with these results.

Ideally, we would like to relate I_D/I_M quantitatively to some other more established parameter used to measure complexation. With this goal in mind, pH measurements were made on a system identical with the 0% degree of neutralization system monitored previously via fluorescence, i.e., 2×10^{-1} M PMAA added to 2×10^{-3} M PEG, with the exception that unlabeled PEG was used. The pH of a "blank" system consisting of 2×10^{-1} M PMAA added to distilled water was also measured. The basic concept behind the use of pH to measure complexation is that in order for a hydrogen bond to be established in a complex, the carboxylic acid group of the polyacid must be protonated. Thus, if complexation occurs, the pH of that system will be higher relative to that of the blank, since some hydrogen atoms remain bound to the acid groups participating in the hydrogen bonds. This difference in pH allows for the calculation of parameters such as the degree of linkage and the stability constant of the complex.[17]

The pH measurements are shown in Figure 8. In this figure, in order to compare the blank with the PEG system, the "molar ratio" for the blank was determined by calculating what the molar ratio would have been if the blank contained 2×10^{-3} M PEG. This figure shows that, within experimental uncertainty, the data for the PMAA–PEG

system fall on the same curve as the data for the blank. Thus, pH is not sensitive enough to detect complexation in this system. However, complexation was detected via pH measurements in a similar system in which the PEG concentration was increased by a factor of 25.[18] Unfortunately, this large increase in concentration makes it difficult to directly compare with the fluorescence data of the present study.

Since pH measurements were not sensitive enough to detect complexation in any of the same systems used in this neutralization study, a more detailed effort was undertaken to attempt to link the fluorescence results of this and previous work[1,2] to pH measurements of complexation. In that investigation we show that the maximum in I_D/I_M is related to the pH of the complexing system, which in turn can be related to PMAA chain conformation. We found that the maximum in I_D/I_M occurs at a pH of about 5.5, the same pH at which PMAA undergoes an expanded/compact coil transition. This coil transition most likely disturbs the pyrene excimer coplanar sandwich configuration. We also calculated the degree of complexation and stability constants for the PMAA–PEG system at the high concentration. These results will be presented in a subsequent paper.[18]

Summary

The effect of ionization of poly(methacrylic acid) (PMAA) on the complexation with poly(ethylene glycol) (PEG) was investigated by a fluorescence technique employing PEG labeled with pyrene at both chain ends. When nonionized PMAA is added to a PEG solution, PEG chains are bound with PMAA very efficiently. The presence of dissociated carboxylate groups suppresses intermolecular excimer formation because the interaction between PMAA and PEG decreases with loss of carboxy groups, resulting in fewer PEG chains in the vicinity of PMAA. In addition, the decrease in intramolecular excimer formation upon complexation due to the suppression of chain mobility becomes smaller upon ionization. Hydrogen bond interaction between PMAA and PEG was still possible up to 30% ionization but not for 40%. In contrast, the interaction between PAA and PEG is reported to be eliminated for ionization greater than 15%.[14] The results obtained in this study are consistent with Anufrieva's data on the PMAA–PEG system where around 40% ionization the dissociation of carboxy groups decomposes the complex.[16] Excimer formation between pyrene groups serves as a useful tool to monitor both the statistical properties of the isolated probe chain as well as the effective segment density of chromophores. It was also shown that this fluorescence technique is more sensitive than pH measurements for detecting complexation at low concentration.

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Registry No. PMAA, 25087-26-7; polyethylene glycol pyrenebutyric acid diester, 82870-83-5; PMMA–PEG complex, 9043-60-1.

References and Notes

(1) Oyama, H. T.; Tang, W. T.; Frank, C. W. *Macromolecules* **1987**, *20*, 474.
(2) Oyama, H. T.; Tang, W. T.; Frank, C. W. *Macromolecules* **1987**, *20*, 1839.
(3) Ikawa, T.; Abe, K.; Honda, K.; Tsuchida, E. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1505.
(4) Chen, H. L.; Morawetz, H. *Eur. Polym. J.* **1983**, *19*, 923.
(5) Bekturov, E. A.; Bimendina, L. A. *Adv. Polym. Sci.* **1981**, *41*, 99.
(6) Tsuchida, E.; Abe, K. *Adv. Polym. Sci.* **1982**, 45.
(7) Oyama, H. T.; Frank, C. W. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1813.
(8) Cheung, S.; Winnik, M. A.; Redpath, A. E. C. *Makromol. Chem.* **1982**, *183*, 1815.
(9) Char, K.; Frank, C. W.; Gast, A. P.; Tang, W. T. *Macromolecules* **1987**, *20*, 1833.
(10) Turro, N. J.; Arora, K. S. *Polymer* **1986**, *27*, 783.
(11) Herkstroeter, W. G.; Martic, P. A.; Hartman, S. E.; Williams, J. L. R.; Farid, S. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2473.
(12) Arora, K. S.; Turro, N. J. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 243.
(13) Hemker, D. J.; Char, K.; Oyama, H. T.; Gast, A. P.; Frank, C. W. Submitted for publication in *ACS Symposium Series on Water Soluble Polymers*.
(14) Illiopoulos, I.; Audebert, R. *Polym. Bull.* **1985**, *13*, 171.
(15) Anufrieva, E. V.; Gotlib, Yu. Ya. *Adv. Polym. Sci.* **1981**, *40*, 35.
(16) Anufrieva, E. V.; Gotlib, Yu. Ya.; Krakoviak, M. G.; Skorokhodov, S. S. *Vysokomol. Soedin., Ser. A* **1972**, *14*, 1430 (translated in *Polym. Sci. USSR (Engl. Transl.)* **1972**, *14*, 1604).
(17) Tsuchida, E.; Osada, Y.; Ohno, H. *J. Macromol. Sci., Phys.* **1980**, *B17*, 683.
(18) Hemker, D. J.; Oyama, H. T.; Garza, V.; Frank, C. W. Manuscript in preparation.