Effect of the Hydrophobic Interaction in the Poly(methacrylic acid)/Pyrene End-Labeled Poly(ethylene glycol) Complex

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ABSTRACT: Pyrene groups were attached to monodisperse poly(ethylene glycol) (PEG) at both chain ends to allow pyrene excimer fluorescence to be used as a molecular probe of the complexation between PEG and poly(methacrylic acid) (PMAA) in aqueous solution and also in methanol–water mixtures. It was found that PMAA was a stronger proton-donating polymer than poly(acrylic acid) (PAA) and that the addition of PMAA to a PEG aqueous solution caused a larger emission change of labeled PEG than observed for the comparable experiment with PAA. The greatest difference in the behavior of the PMAA–PEG complex compared to that of the PAA–PEG complex was that in the former case, the mobility of PEG chains became restricted so that intermolecular excimer formation was suppressed. Simultaneously, the excimer peak position shifted to higher energies. This phenomenon was first observed much before a stoichiometric ratio had been reached.

Introduction

Intermolecular complexes formed through hydrogen bonding between poly(carboxylic acid) as a proton donor and poly(ethylene glycol) as a proton acceptor have been studied extensively for a number of years. Good reviews by Bekturov and Bimendina[1] and Tsuchida and Abe[2] summarizing the progress are available.

In a previous paper, we utilized fluorescence spectroscopy to study complex formation between poly(acrylic acid) (PAA) and poly(ethylene glycol) (PEG).[3] Since neither component polymer has an intrinsic fluorescent chromophore, pyrene groups were attached to monodisperse PEG at both chain ends to allow pyrene excimer fluorescence to be used as a molecular probe of the complexation. The pyrene tagged PEG was denoted as PEG* where the superscript * indicates a fluorescent marker. It was observed that excimers are formed mostly intramolecularly in 1.0×10^{-3} M PEG* aqueous solution, presumably due to cyclization of the PEG chain. Only a small excimer contribution resulted from intermolecular interaction between chromophores attached to different polymer chains. We did note, however, that the excimer to monomer intensity ratio, I_D/I_M, was higher than that expected for the purely diffusion-controlled intramolecular cyclization process. Moreover, this deviation from diffusion-controlled behavior was reduced for the higher molecular weight PEG*. This was interpretated in terms of some preferential pyrene interactions in the PEG*–water system.

In the present study, the method we used in the previous paper is extended to the poly(methacrylic acid) (PMAA)–PEG* complex system. This approach may be outlined as follows. First, the pyrene aggregation in PEG* aqueous solution that was suggested in the previous work is assumed to have a negligible effect on complexation between PMAA and PEG. This is equivalent to stating that any equilibrium that might exist between aggregated PEG* and free PEG* in aqueous solution is shifted strongly toward the free PEG* such that complexation between PMAA and PEG* is unaffected. Second, a mixture of 1% PEG* (pyrene labeled) and 99% PEG (unlabeled) is examined under the assumption that it permits intramolecular excimer formation to be studied for an individual PEG chain. We confirmed at the outset that the 1% PEG* + 99% PEG mixture did not form any intermolecular excimers. This allows the contribution of intermolecular excimer formation to be elucidated by taking the difference in the results for the fully labeled PEG system (PEG*) and the 1% PEG* + 99% PEG system.

When two different macromolecules approach each other, the molecular interaction energy is affected by several types of secondary binding forces: Coulombic, hydrogen-bonding, van der Waals, charge transfer, and hydrophobic interactions.[2] These factors never act individually in real cases; one factor works with the other cooperatively, or one induces another. We especially focus here on the effects of hydrophobic interaction on complexation, which is enhanced by the presence of the α-methyl group of PMAA. It is essentially different from other forces because this interaction is not caused by a direct cohesive force between molecules, but primarily by the structural rearrangement of water molecules. The hydrophobic interaction occurs when nonpolar (hydrophobic) molecules are dissolved in aqueous medium.[4,5]

Hydrophobic solutes form local regions of "hydrophobic hydration" in which the water molecules are even more ordered and even more highly hydrogen bonded than in the bulk, possibly with a structure similar to that formed in the clathrate hydrates. Since the formation of hydrophobic hydration is entropically very unfavorable, hydrophobic groups in aqueous solution are attracted to one another by the "hydrophobic interaction" (also referred to as the "hydrophobic effect") which thereby allows some of the highly structured water to be released back into the bulk when the two groups come close to another. Since the formation of hydrophobic hydration is exothermic (representing even more efficient hydrogen bonding than in bulk water), then the hydrophobic interaction must be endothermic; i.e., it becomes stronger with a rise in temperature. The potential of mean force between two hydrophobic molecules in water is an oscillating function and has an effective range of several water molecular diameters. At ordinary temperatures the equilibrium separation of two nonpolar molecules is considerably greater than the sum of the van der Waals radii.[6]

The hydrophobic effect of PMAA in water has been investigated in comparison with PAA in many publications.[7] Whereas PAA expands smoothly with increasing density of ionic charges along the polymer chain, the chain dimensions of PMAA undergo little change in the initial stages of ionization. With continuing increase in the charge density, there is an abrupt transition to a highly expanded state within a relatively narrow critical range. Long-range attractive interactions of hydrophobic groups attached to polyions apparently provide a powerful resistance to chain expansion. Anufrieva et al. also reported that the local compact structures formed in uncharged PMAA molecules in aqueous solutions are stabilized by hydrophobic interaction.[8] The cooperative breakdown of these structures

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occurs when the PMAA molecule is ionized or when alcohol is added. They noted that the hydrophilic groups of PMAA screen the hydrophobic groups of different structural segments from contacts with water and with each other. Chu and Thomas observed by a quenching experiment employing pyrene-labeled PMAA and PAA that PAA is more loosely coiled than PMAA in the closed compact form, allowing greater access of the quenchers to the bound pyrene.[9]

In an intermacromolecular complex system, the resulting complex itself becomes more hydrophobic in nature. This is because the main chains of the component polymers shield the hydrophilic groups, i.e., a carboxyl group of PMAA or PAA and an ether group of PEG, away from the water molecules, as observed by Morawetz.[10,11] This phenomenon would be enhanced by the presence of a nonpolar side group. Under such a condition, the contribution from the higher order structure as well as individual hydrophobic groups might be also important.

Even though a significant driving force for complexation in the PMAA–PEG aqueous system is hydrogen bond interaction between a carboxyl group of PMAA and an ether oxygen of PEG, the hydrophobic interaction is reported to stabilize the complexation.[1,2] This can occur by decreasing the critical chain length for complexation below which no complex can be formed due to lack of cooperative interactions or by increasing the critical pH above which the complex is decomposed by dissociation of the poly(carboxylic acid).[2] In the previous paper for the PAA–PEG complex, we considered mainly the significance of the hydrogen bond interaction between component polymers. The same methodology will clarify the influence of hydrophobic interaction on the PMAA–PEG complexation. The results for the PMAA–PEG complex formed in aqueous solution are discussed along with those for complexation in methanol–water mixture and compared to those for the PAA–PEG complex reported in the previous paper.[3]

Experimental Section

1. Materials. Poly(methacrylic acid) (PMAA) samples were obtained from two sources: Polysciences Inc., PA, and BDH Chemicals Ltd., Poole, England. They were purified by dialysis against water using a pressurized stirred cell (Amicon Corp.) and then freeze-dried. The intrinsic viscosity in methanol at 299 K was found to be 10.2 and 25.8 mL/g, respectively. If these values are introduced into the Mark–Houwink–Sakurada equation $[\eta] = KM^a$, where $K = 0.242$ mL/g and $a = 0.51$,[12] the viscosity-average molecular weights of PMAA are calculated to be 1530 and 9500. They were denoted as PMAA(1530) and PMAA(9500).

Poly(acrylic acid) (PAA) samples of three molecular weights were described in a previous paper.[3] They were denoted as PAA(1850), PAA(4600), and PAA(890 K), where the numbers inside the parentheses refer to the viscosity-average molecular weights.

Pyrene end-labeled poly(ethylene glycol) (PEG*) was synthesized by direct esterification between poly(ethylene glycol) and 1-pyrenebutyric acid.[3,13] Two samples of PEG with weight-average molecular weights of 4800 and 9200 having polydispersity less than 1.10 were used for the synthesis. The products were purified by repeated precipitation into anhydrous ether from THF solution. The percentages of tagging were calculated by UV absorption with methyl 1-pyrenebutyrate as the model compound in THF. The results revealed that the products were fully labeled at both ends with ±5% accuracy. These materials were designated as PEG*(4800) and PEG*(9200).

2. Spectroscopy. The UV–visible absorption spectra were measured with a Cary 210 spectrophotometer manufactured by Varian. The excitation spectra were recorded with a SPEX Fluorolog 212 spectrofluorometer. 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 fluorescence emission lifetimes were determined by using a single photon-counting apparatus from Photochemical Research Associates (PRA). Nitrogen gas was used for the flashlamp in order to obtain sufficient intensity. The spectrofluorometer has been described previously.[3,14] The excitation was at 343 nm, corresponding to the ^1L_a band of the pyrene ring. The recorded fluorescence spectra were corrected by the spectral response function using a PDP11/23$^+$ computer. The excimer to monomer intensity ratio, I_D/I_M, was calculated from the areas for an excimer and for a monomer, respectively. In order to get the monomer envelope, 1-pyrenebutyric acid was used as a model compound. The excimer area was then calculated by subtraction of the monomer area from the total area. A water bath was used to keep the temperature of the sample at 303 K. For measurements, the polymer concentration of total PEG was adjusted to 1.0×10^{-3} M and that of PMAA or PAA was 1.0×10^{-1} M. The concentration of the poly(carboxylic acid) was selected to be 100 times greater than that of PEG in order to neglect the effect of dilution upon its addition to PEG. 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].

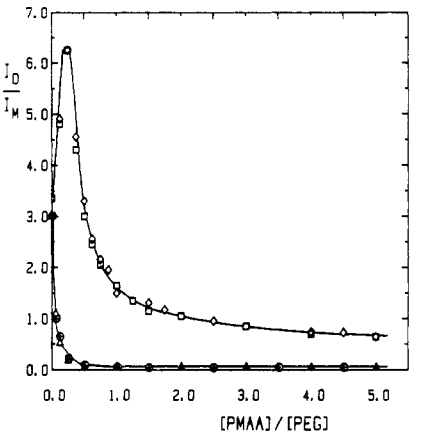

Figure 1. Change in I_D/I_M of PEG*(4800) by the addition of PMAA at 303 K: (a, △) 1×10^{-3} M (1% PEG* + 99% PEG) + 1×10^{-1} M PMAA(9500); (b, ○) 1×10^{-3} M (1% PEG* + 99% PEG) + 1×10^{-1} M PMAA(1530); (c, □) 1×10^{-3} PEG* + 1×10^{-1} M PMAA(9500); and (d, ◇) 1×10^{-3} M PEG* + 1×10^{-1} M PMAA(1530).

Results and Discussion

1. Fluorescence Behavior of the PMAA–PEG* Complex in Water. The fluorescence spectrum of 1.0×10^{-3} M 1% PEG* + 99% PEG aqueous solution measured at 303 K consists of a structured monomer emission from the isolated chromophore resulting from the $^1L_b \rightarrow {}^1A$ transition between 350 and 430 nm and an excimer band centered at 480 nm. The I_D/I_M change of this system upon complexation with PMAA, which is assumed to show the behavior of a PEG* isolated chain, is given in curves a and b of Figures 1 and 2. Addition of PMAA causes a drastic drop of I_D/I_M, with the majority of the change occurring prior to a [PMAA]/[PEG] composition ratio of about $^1/_4$. Above the 1/1 stoichiometric ratio of [PMAA]/[PEG], the excimer emission becomes almost negligible.

On the other hand, the I_D/I_M change of fully tagged PEG at the same polymer concentration shows a completely different behavior as observed in curves c and d of Figures 1 and 2. The initial I_D/I_M value was slightly higher than that for a 1% PEG* + 99% PEG system, due to intermolecular excimer formation. In both cases, I_D/I_M reached a maximum value approximately twice that of the initial value followed by a decrease to below the initial I_D/I_M. Here, the change for PEG*(4800) in Figure 1 was more pronounced than that for PEG*(9200) in Figure 2;

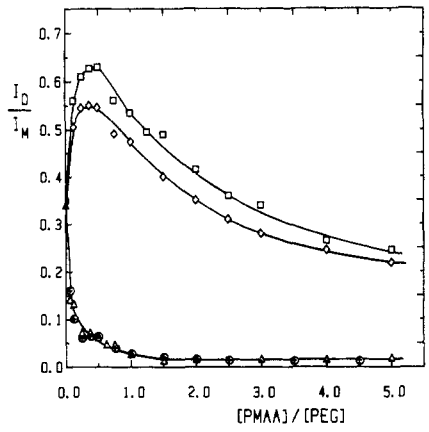

Figure 2. Change in I_D/I_M of PEG*(9200) by the addition of PMAA at 303 K: (a, △) 1×10^{-3} M (1% PEG* + 99% PEG) + 1×10^{-1} M PMAA(9500); (b, ⊗) 1×10^{-3} M (1% PEG* + 99% PEG) + 1×10^{-1} M PMAA(1530); (c, □) 1×10^{-3} M PEG* + 1×10^{-1} M PMAA(9500); and (d, ◇) 1×10^{-3} M PEG* + 1×10^{-1} M PMAA(1530).

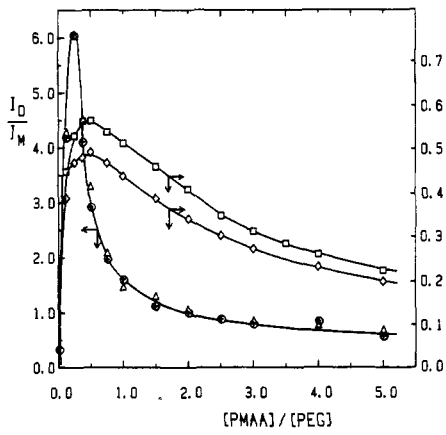

Figure 3. Change in intermolecular excimer formation by the addition of PMAA at 303 K calculated from the data in Figures 1 and 2: (a, △) PEG*(4800) + PMAA(9500); (b, ⊗) PEG*(4800) + PMAA(1530); (c, □) PEG*(9200) + PMAA(9500); and (d, ◇) PEG*(9200) + PMAA(1530).

the former reached a maximum at [PMAA]/[PEG] = $^1/_4$ and the latter at [PMAA]/[PEG] = $^3/_8$.

In order to obtain the net contribution of intermolecular excimer formation to the I_D/I_M ratio of the 1.0×10^{-3} M PEG* aqueous solution, the smoothed I_D/I_M data for a 1% PEG* + 99% PEG system were subtracted from those for the fully tagged PEG system. The results are given in Figure 3. The I_D/I_M of the intermolecular excimer calculated by this method shows a dramatic initial increase until [PMAA]/[PEG] = $^1/_4$ for all systems. However, the subsequent behavior is quite different for the PEG*(4800) compared to PEG*(9200). In the PEG*(4800) system, the maximum is followed by a rapid decrease in I_D/I_M up to [PMAA]/[PEG] of about 2, whereas the PEG*(9200) system showed a much more gradual decrease. Furthermore, whereas the behavior of I_D/I_M was independent of the PMAA molecular weight for the PEG*(4800) system, in the PEG*(9200) system PMAA(9500) showed higher values of I_D/I_M over the whole range compared to PMAA(1530).

In order to elucidate the effect of the α-methyl group of PMAA on the fluorescence behavior, it is of interest to compare data for the PMAA–PEG* complex with those for the PAA–PEG* complex, which were reported in a previous paper.[3] This is done in Figures 4, 5, 8, and 9. Figure 4 shows the I_D/I_M change of the intramolecular excimer in PEG*(4800). Figure 5 contains similar data for

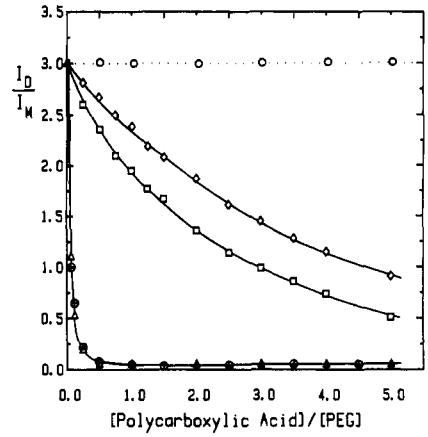

Figure 4. Comparison of intramolecular excimer formation in PMAA–PEG*(4800) and PAA–PEG*(4800) systems at 303 K: (a, ○) PEG* + acetic acid; (b, ◇) PEG* + PAA(1850); (c, □) PEG* + PAA(890 K); (d, △) PEG* + PMAA(9500); and (e, ⊗) PEG* + PMAA(1530).

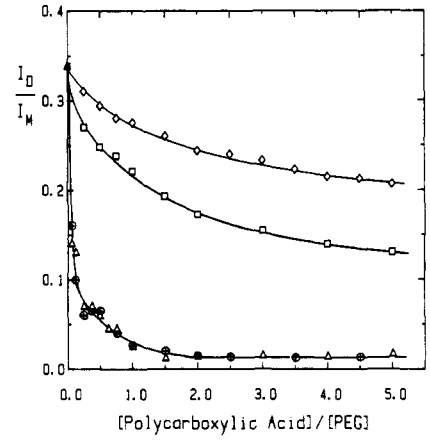

Figure 5. Comparison of intramolecular excimer formation in PMAA–PEG*(9200) and PAA–PEG*(9200) systems at 303 K: (a, ◇) PEG* + PAA(1850); (b, □) PEG* + PAA(890 K); (c, △) PEG* + PMAA(9500); and (d, ⊗) PEG* + PMAA(1530).

PEG*(9200). As both figures show, the addition of PMAA has a much greater effect on reducing intramolecular excimer formation in PEG* than does PAA. Perhaps as a consequence of this enhanced ability of PMAA to suppress intramolecular cyclization of the PEG*, there is no dependence on PMAA molecular weight. On the other hand, the reduced effect of PAA showed a clear molecular weight dependence, with the longer chain of PAA inducing a larger decrease of I_D/I_M. This effect seemed to be more pronounced for PEG*(9200) compared to PEG*(4800).

As discussed in the previous paper,[3] the observed intramolecular I_D/I_M is dependent on the intramolecular mobility of the PEG chain. Thus, the suppression of intramolecular mobility due to PEG complexation with poly(carboxylic acid) would have a direct influence on the cyclization rate of the PEG* chain. This effect may be more predominant for the PMAA–PEG* complex than for the PAA–PEG* complex because of stronger interactions between component polymers arising from the assistance of the PMAA hydrophobicity. It is significant to note that acetic acid did not cause any change over the whole composition range. This means that the driving force toward hydrogen bond interaction between an individual ether and a monocarboxylic acid in water is negligible and that a stable complex can only form by a cooperative interaction of many ether and carboxyl groups.

Lifetime measurements for the isolated PEG* chain also support the proposal that the PEG chain has diminished

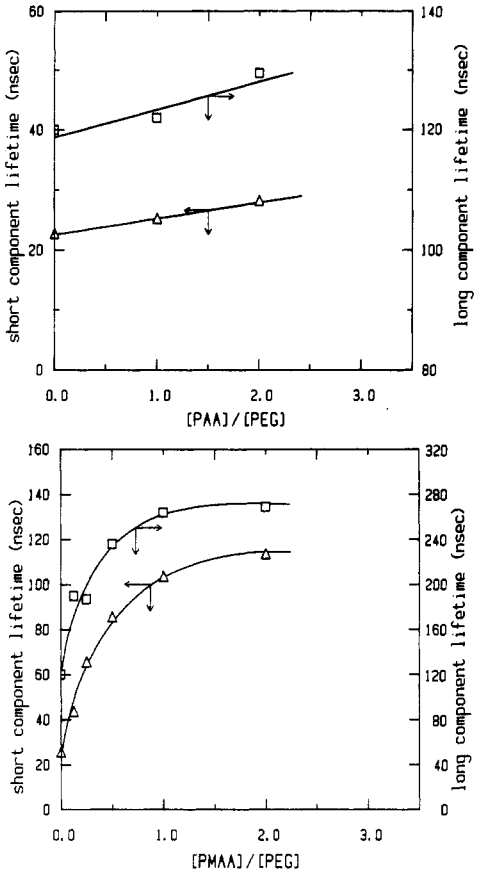

Figure 6. Change in lifetime of monomer emission of PEG*(4800) upon complexation with (a, top) PAA(890 K) and (b, bottom) PMAA(9500).

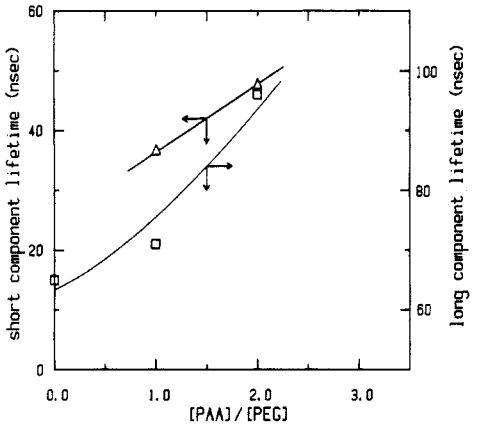

Figure 7. Change in lifetime of intramolecular excimer emission upon complexation in the PAA(890 K)–PEG*(4800) system.

flexibility upon complexation and that PMAA has a larger effect than PAA. Figure 6 shows the monomer emission decay change in the (1% PEG* + 99% PEG)–PMAA and –PAA systems. The transient data were analyzed by a two-exponential fitting. They showed an increase of both lifetime components, with a much larger increase observed for PMAA than PAA. It appears that it is considerably more difficult for the isolated pyrene group to achieve the proper geometrical structure to form an excimer in the PMAA–PEG* complex compared to the PAA–PEG* complex, resulting in the longer lifetimes of monomer emission. This is consistent with the observation in Figure 4 in which the excimer emission of the isolated PEG* chain in the PMAA–PEG system becomes almost negligible for [PMAA]/[PEG] ratios greater than $^1/_2$. By contrast, the PAA–PEG system still shows a considerable amount of

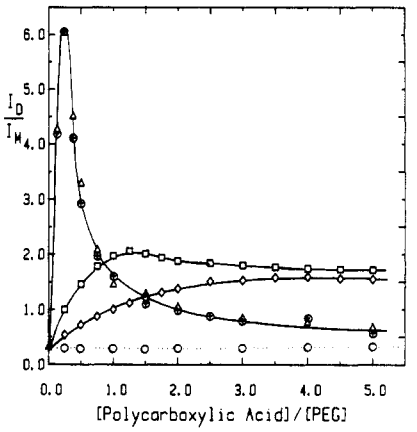

Figure 8. Comparison of intermolecular excimer formation in PMAA–PEG*(4800) and PAA–PEG*(4800) systems at 303 K. The numbers show the same conditions as those in Figure 4.

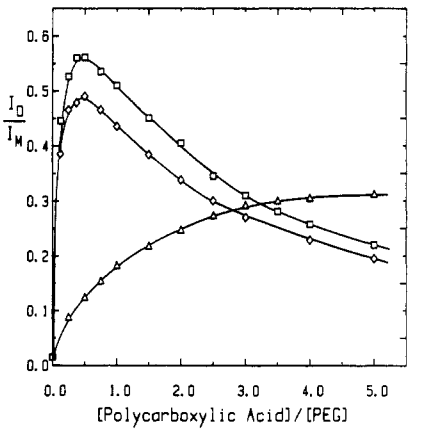

Figure 9. Comparison of intermolecular excimer formation in PMAA–PEG*(9200) and PAA–PEG*(9200) systems at 303 K: (a, △) PEG* + PAA(890 K); (b, □) PEG* + PMAA(9500); and (c, ◇) PEG* + PMAA(1530).

emission from the excimer. Figure 7 gives the excimer lifetime change upon complexation in the PAA–PEG system. The excimer lifetimes also increase upon complexation. In the PMAA–PEG system, the excimer emission was too weak to obtain accurate transient data, as expected from Figure 4.

It is important to note that in all excimer emission decay measurements, the profiles did not show any growing in component on the nanosecond time scale. We must note, however, that the nitrogen gas, which was required in order to get sufficient intensity, leads to a broad excitation pulse having a width of 7 ns at half height. Thus, it is conceivable that a small contribution of a rise component could be missed in the reconvolution fitting process. In spite of this slight caveat, the results strongly suggest that most of the excimer emission in the PEG*(4800) system comes from preformed pyrene–pyrene pairs in the ground state. This point will be discussed further in the third section.

Results for the intermolecular excimer of the PEG*-(4800) systems are presented in Figure 8 and those for PEG*(9200) in Figure 9. An increase of PEG concentration in the vicinity of the poly(carboxylic acid) chains is expected due to complex formation. The subsequent increase in the local pyrene concentration will then lead to an increase in I_D/I_M due to increased contribution from intermolecular excimer. Figures 8 and 9 show that the enhancement of the local pyrene chromophore concentration by addition of proton donor is much greater for PMAA than for PAA at low [proton donor]/[PEG] com-

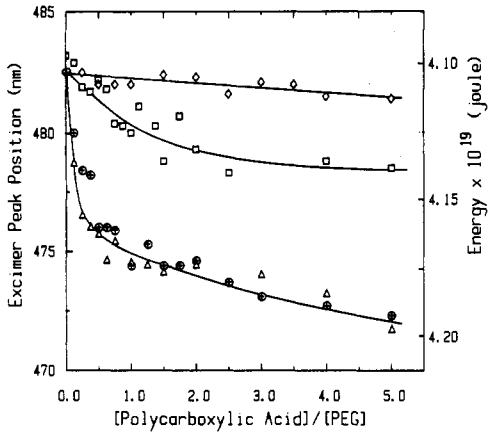

Figure 10. Excimer peak shift of PEG*(4800) with addition of poly(carboxylic acid): (a, ◇) PEG* + PAA(1850); (b, □) PEG* + PAA(890 K); (c, △) PEG* + PMAA(9500); and (d, ⊗) PEG* + PMAA(1530).

position ratios, even in the range where the molecular weight of PMAA is lower than that of PAA. However, the qualitative behavior of the intermolecular PEG* excimer is very different for PMAA–PEG* compared to that for PAA–PEG*. I_D/I_M passes through a maximum much before the stoichiometric composition ratio for the PMAA–PEG* complex, whereas the PAA–PEG* complex showed a monotonic increase followed by relatively constant I_D/I_M values at higher [PAA]/[PEG] compositions. This difference seems to be related to complementary observations on the effect of complexation on the excimer peak position, to be described next.

In general, the excimer peak position determined from the emission envelope tends to shift to a shorter wavelength with a decrease of I_D/I_M. This was especially pronounced just before the excimer peak disappeared in a system such as (1% PEG* + 99% PEG)–PMAA. In such a case, it is difficult to know whether to ascribe that shift to a true blue shift of the excimer emission peak or merely to an apparent shift because of the small contribution from the excimer peak to the emission envelope even though the excimer position is the same. However, the PEG* (fully labeled)–PMAA of both molecular weights showed the shift toward shorter wavelengths even in the region where the I_D/I_M was increasing, i.e., [PMAA]/[PEG] ranging from 0 to $^3/_8$ for PEG*(9200) + PMAA and from 0 to $^1/_4$ for PEG*(4800) + PMAA. We believe that it can be considered as a net blue shift of excimer.

The excimer peak position data for both PMAA and PAA systems are shown in Figure 10, where PEG*(4800) was used for the example because PEG*(9200) has a much weaker excimer intensity resulting in some ambiguity in determination of peak position. For example, the excimer peak position of ca. 482.5 nm in a pure PEG* aqueous solution shifted to 476.5 nm at [PMAA]/[PEG] = $^1/_4$. This blue shift corresponds to an increase in energy of 261 cm^{-1} or 5.16×10^{-21} J. On the other hand, the blue shift was negligible in the PAA(1850)–PEG*(4800) complex and only 0.6 nm, which is equivalent to 26 cm^{-1} or 5.16×10^{-22} J, at the same composition ratio in the PAA(890 K)–PEG*(4800) complex. It appears from the blue shift that an excimer of PEG* becomes less stable upon complex formation with PMAA. This could be explained by the creation of a more compact and rigid structure. This would be especially true for cases involving the assistance of hydrophobic interaction between PMAA and PEG. It presumably results in the distortion and quite possibly the destruction of the expected coplanar sandwich structure for excimer formation between the two chromophores.

The formation of a compact structure upon complexation has been observed previously in viscometric measurements. For example, Antipina applied Einstein's equation for a solution of dense spherical particles to reduced viscosity data and found that the PMAA–PEG complex coils contained ca. 75% water and 25% polymer even though the overall polymer concentration was 0.1 g/dL.[15] The complex is composed of dense coils containing relatively little solvent. Another piece of evidence for chain contraction upon complex formation was beautifully demonstrated by the observation that a PMAA cross-linked network became contracted upon the addition of PEG.[16,17] The PMAA membrane in the presence of PEG in the steeping solution contracted by more than 90% of its original length when heated from 283 to 333 K. Upon a decrease of the temperature, the membrane recovered almost completely its original state. However, this interesting phenomenon was not observed in the PAA–PEG system.

With respect to the intramolecular mobility of chains in the complex, Ohno measured the fluorescence polarization, P, of PMAA labeled with 8-anilino-1-naphthalenesulfonic acid 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.[18] They found that the fluorescence polarization increased as a result of complexation in several hydrogen bonding complexes, including PMAA–PEG. This means that the intramolecular chain mobility in a complex decreases upon complex formation.

Anufrieva et al. also examined the intramolecular mobility of PMAA–PEG and PAA–PEG complexes by using a polarized luminescence technique.[19,20] They observed that the relaxation time, τ_w, of anthracene-containing PMAA and PAA became much longer upon complexation with PEG: from 77 to 290 ns for PMAA and 23 to 50 ns for PAA. This shows not only that the intramolecular mobility of a proton-donating polymer becomes restricted upon complex formation but also that PMAA chains in the PMAA–PEG complex are much less flexible than PAA chains in the PAA–PEG complex. The same phenomenon was also observed in anthracene-labeled PEG, for which τ_w changed from less than 1 to 350 ns in the PMAA–PEG complex. They concluded from this result that the structure of the polymer complex of PMAA–PEG consists of a fairly long continuous linear succession of bonds between monomer units of the complementary polymer chains.

Although less attention has been directed toward the role of hydrophobic influence played by the poly(ether) component compared to that given the poly(carboxylic acid) component, Anufrieva examined the hydrogen bond complex resulting from replacing PEG with poly(1,2-dimethoxyethylene) (PDME).[21] Anthracene-tagged PMAA showed an increase in the relaxation time, τ_w, from 74 to 400 ns upon complexation with PDME, and anthracene-tagged PDME showed an increase in τ_w from 18 to 350 ns upon complexation with PMAA at a 1/1 stoichiometric ratio at 298 K. This also shows that PMAA in the PDME–PMAA complex is less flexible than that in the PEG–PMAA complex because, as noted above, the τ_w of anthracene-tagged PMAA in the PEG–PMAA system is 290 ns.[20] This is again connected with the considerable hydrophobicity of PDME molecules.

To summarize the results so far, the hydrophobicity of PMAA segments arising from the presence of the α-methyl groups creates a more compact and rigid structure upon complexation in aqueous solution than observed for PAA.

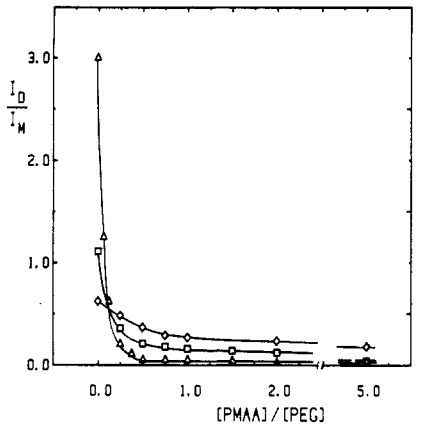

Figure 11. Intramolecular excimer formation of the PMAA-(9500)–PEG*(4800) complex mixtures of methanol and water at 303 K: (a, △) H_2O; (b, □) 20 wt % MeOH + 80 wt % H_2O; and (c, ◇) 40 wt % MeOH + 60 wt % H_2O.

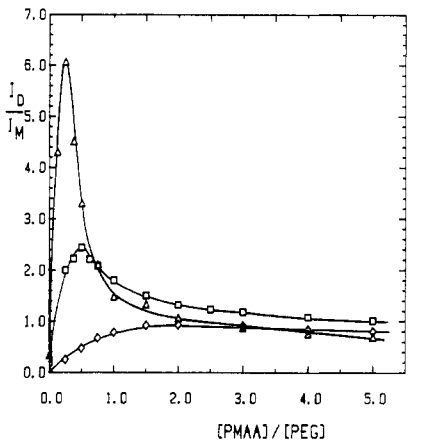

Figure 12. Intermolecular excimer formation of the PMAA-(9500)–PEG*(4800) complex mixtures of methanol and water at 303 K. See Figure 9 for details.

This seems to cause a dramatic decrease in I_D/I_M of intramolecular excimer and a suppression of intermolecular excimer formation counteracting the dramatic initial increase.

2. Complexation in Mixtures of Methanol and Water. It was found above that the fluorescence characteristics of intramolecular and intermolecular excimer formation were quite different in the PMAA–PEG* and the PAA–PEG* complexes, presumably due to the strong hydrophobic interaction in the former system. In order to investigate the hydrophobic interaction further, complex formation between PMAA and PEG was examined in methanol/water mixtures. Because it is a less polar solvent, methanol is expected to disrupt the clathrate structure of water molecules, resulting in a suppression of hydrophobic interaction; the dielectric constant for methanol is reported to be 33.62 and that for water to be 80.37 at 293 K.[22] Figure 11 shows the change in intramolecular I_D/I_M of 1×10^{-3} M (1% PEG*(4800) + 99% PEG(4800)) + 1×10^{-1} M PMAA(9500) upon addition of methanol. The effect of complexation on I_D/I_M becomes smaller upon addition of methanol. A steep initial decrease in I_D/I_M was observed in aqueous solution. However, in the 40 wt % MeOH–60 wt % H_2O solution, the initial I_D/I_M value was much lower, and the final plateau value at large [PMAA]/[PEG] was higher compared to the pure water case.

Intermolecular excimer formation shown in Figure 12 was obtained in the same manner as in Figure 8 and 9, i.e., by subtracting the data in Figure 11 from those for the fully tagged PEG* and PMAA system, not shown. As the methanol content in the solution is increased, the peak value of I_D/I_M decreases and shifts toward a larger [PMAA]/[PEG] composition ratio. It is interesting to note that in the 40 wt % MeOH–60 wt % H_2O solution, the behavior in I_D/I_M is very similar to that of the PEG*-(4800)–PAA(1850) in aqueous solution, as shown in Figure 8. Furthermore, the region of composition where the intramolecular excimer is varying corresponds to that where the intermolecular excimer is also varying. For example, I_D/I_M for the intermolecular excimer increases up to polymer composition ratios of $^1/_4$, $^1/_2$, and $^3/_2$ in water, 20 wt % MeOH, and 40 wt % MeOH, respectively, while I_D/I_M for the intramolecular excimer was suppressed drastically over the polymer composition range just prior to those composition ratios. This might imply that chain opening of the individual PEG chain facilitates intermolecular excimer formation between pyrene groups tagged at the PEG chain ends. Neutralization experiments are being performed to clarify this point.

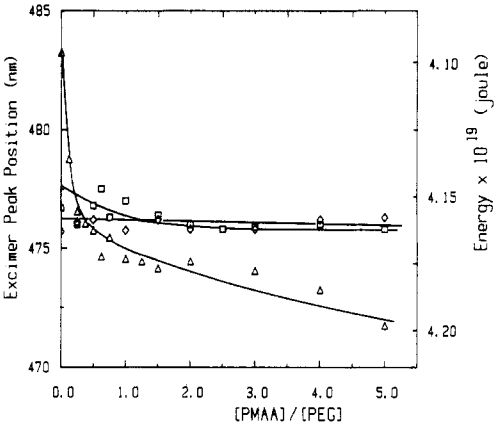

Figure 13. Excimer peak shift of PEG* in the PMAA(9500)–PEG*(4800) system in the methanol–Water mixture. See Figure 9 for details.

Finally, the effect of complexation on the excimer peak position in the methanol–water solution is shown in Figure 13. With increasing methanol content, the initial value of the excimer band position shifts to the blue. Addition of PMAA, which has a strong effect of destabilizing the excimer in pure water, has a reduced influence as the methanol content increases. In the mixture of 40 wt % MeOH and 60 wt % H_2O, the shift upon addition of PMAA is negligible.

In the hydrogen bonding complex replacing PEG with poly(1,2-dimethoxyethylene) (PDME), the effects of hydrophobicity on complexation in the mixture of methanol and water have been reported by Anufrieva.[23] The polarized luminescence method showed that the PDME–PMAA complex is more stable than PEG–PMAA, where the former complex did not decompose up to the addition of 55% w/w methanol content. However, the latter complex decomposes at a concentration as low as 30% w/w methanol. Ikawa et al. have also reported on the complexation of PMAA–PEG in water–methanol mixtures.[24] They found through viscosity measurements that the critical chain length of PEG for complexation below which the complex cannot be formed was affected by the hydrophobic interaction. For example, the critical chain length for the PAA–PEG complex was constant, regardless of the addition of methanol to the solution, although that of the PMAA–PEG complex increased. Thus, the hydrophobic interaction between component polymers stabilizes the complex.

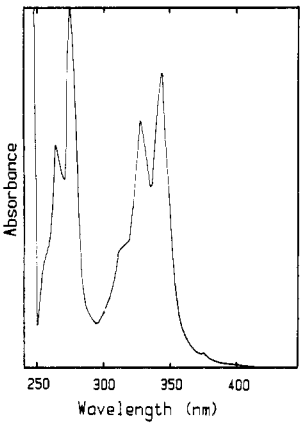

Figure 14. Absorption spectrum of 1×10^{-3} M PEG*(4800) in an aqueous solution.

Papisov studied the complexation of PMAA–PEG and PAA–PEG in water–methanol mixtures by calorimetry, potentiometric titration, and viscosity.[1,2,25] In aqueous medium, the complex formation was characterized by positive enthalpy (0.30 kcal/mol for the PMAA–PEG complex and 0.13 kcal/mol for the PAA/PEG complex) and positive entropy. By contrast, in a methanol–water medium (30 vol % methanol), both the enthalpy and entropy of the process changed signs; ΔH's for the PMAA–PEG and PAA–PEG complexes are −0.17 and −0.18 kcal/mol, respectively. They suggested that this was due to the significant role of hydrophobic interaction in stabilizing the complex in aqueous media. By contrast, in methanol–water mixtures, the main driving force toward complex formation arises from the hydrogen bonds between the components. Therefore, the fluorescence behavior observed in the present study is readily explained by proposing that the addition of methanol decomposes the hydrophobic interaction between PMAA and PEG. At some methanol composition, only hydrogen bond interactions will be significant in the complex formation, leading to results that are similar to those found for PAA and PEG in water where the hydrophobic interaction provides a very minor influence.

3. Effect of Complexation on Absorption and Excitation Spectra. In order to get information on the ground state, UV–visible absorption and excitation spectra were also measured. The UV–visible absorption spectrum of PEG* has peaks between 250 and 400 nm, as shown in Figure 14. As a Jablonski diagram shows, the energy of absorption is higher than that of emission because of internal relaxation of the excited photon to the first excited singlet state. The absorption peaks around 380 nm, between 300 and 360 nm, and between 250 and 300 nm result from transitions from ^1A of the pyrene ring to the ^1L_b band, the ^1L_a band, and the ^1B_b band, respectively.[26] They correspond to excitation to the first, the second, and the third singlet excited states. The first band has a very weak intensity because the corresponding transition is symmetry forbidden. The second and third bands exhibit relatively high extinction coefficients. In fact, the ^1L_b band of pyrene on PEG*(4800) was too small to monitor the effect of complexation. On the other hand, the ^1L_a absorption bands at 327.8 and 343.8 nm were observed to red shift by 1.7–2.5 nm upon complexation, as shown in Figure 15. The pyrene absorption bands showed a much more rapid increase with addition of PMAA compared to addition of PAA. However, the plateau values at high [poly(carboxylic acid)]/[PEG] were either identical or very close. The constant value was obtained at [PMAA]/[PEG] = $^1/_2$–$^3/_4$ in composition and at [PAA]/[PEG] = 2.

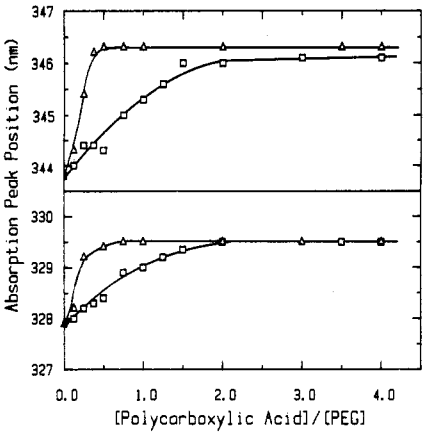

Figure 15. Absorption peak shift of PEG*(4800) upon the addition of poly(carboxylic acid): (a, △) PEG* + PMAA(9500) and (b, □) PEG* + PAA(890 K).

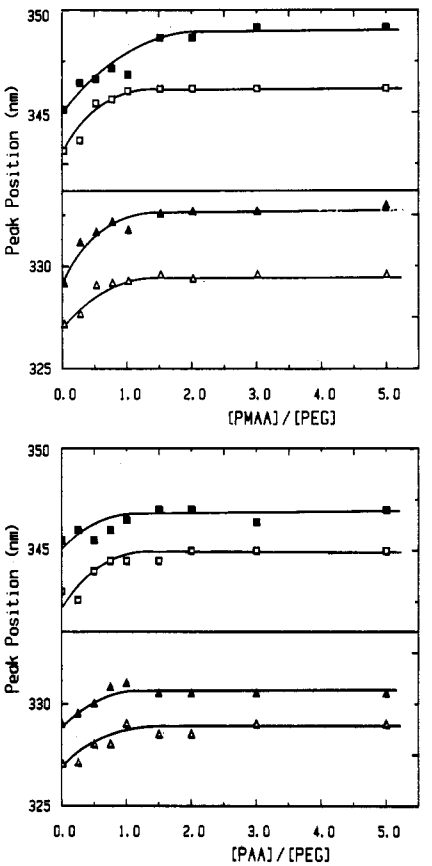

Figure 16. Peak positions of the excitation spectrum of (a, top) PEG*(4800)–PMAA(9500) and (b, bottom) PEG*(4800)–PAA(890 K) systems observed at the monomer emission (open symbols) and at the excimer emission (filled symbols).

In addition, as was discussed regarding the excitation spectra in the previous paper,[3] the shape of the excitation spectrum of the PEG*(4800) aqueous solution monitored at the excimer emission (500 nm) was less structured and was spectrally red shifted by ca. 2.5 nm compared to that monitored at the monomer emission (376 nm). Furthermore, it was noticed in this study that both excitation spectra monitored at the monomer emission and at the excimer emission showed another red shift of about 2.5–3.5 nm as a complex formation occurred. This is shown in Figure 16a for PMAA(9500)–PEG*(4800) and Figure 16b for PAA(890 K)–PEG*(4800).

Avis and Porter investigated pyrene in a solid solution of poly(methyl methacrylate) by changing the pyrene

concentration.[27] They found that the three vibronic bands in the absorption and excitation spectra shift to the red at the higher pyrene concentration. They concluded that there was a ground-state interaction between pyrenes due to long-range dispersion forces (van der Waals forces) forming a pair of molecules close to the excimer configuration. The maximum of the absorption of a 1 mol·dm^{-3} sample was red shifted by 200 cm^{-1} with respect to the dilute standard, which is in reasonable agreement with our observation, being 210 cm^{-1} for the PMAA–PEG system and 189 cm^{-1} for the PAA–PEG system.

More recently, it has been reported that pyrene groups attached to polyelectrolytes (4% and 7% per repeating unit) show not only excited-state interaction but also ground-state interaction in aqueous solution through hydrophobic interaction.[28] This also means that pyrene substituents are hydrophobic enough to be repelled by ionic entities and attracted to hydrophobic centers in water. This ground-state hydrophobic interaction also occurs with other aromatic hydrocarbons such as a substituted anthracene.

In the present study, a portion of the pyrene groups at the PEG* chain ends are attracted to each other as a result of hydrophobic interaction in water. Initially, in the pure PEG* aqueous solution where most excimer is formed intramolecularly, a portion of pyrene groups is already aggregated, presumably in a manner such that the PEG chain forms a cyclized structure. This tendency was more pronounced in the PEG*(4800) than in the PEG*(9200), in which the effect of hydrophobic interaction of pyrene groups on the I_D/I_M was observed to reduce with an increase of PEG molecular weight.[3] This initial aggregation of pyrene groups was also verified by the following observations. First, the excimer excitation spectrum was red shifted and poorly resolved compared to the monomer excitation spectrum.[3] Second, there was no rising time observed in the excimer decay profile on the nanosecond time scale. Third, upon complexation the intramolecular excimer formation is suppressed and the contribution of the intermolecular excimer formation becomes significant in the system. The red shift in the absorption and excitation spectra and I_D/I_M change upon complexation have confirmed that more end-tagged pyrene groups are located closer to each other as a result of PEG* aggregation along the poly(carboxylic acid), presumably through interaction between pyrenes attached to different PEG chains. This formation allows pyrene groups to have some additional interaction in the ground state.

In summary, a portion of the intermolecular excimer formation as well as the intramolecular excimer formation we observed seems to result from the arrangement of pyrene groups which were preformed in the ground state. As such, the excimer is formed almost instantly upon excitation without the requirement of diffusion to form a coplanar sandwich structure. The absorption and excitation spectra also show that in the ground state pyrene groups stay very close in spite of the fact that the system is in the range that the intermolecular excimer is suppressed. This supports our proposal that the decrease in the intermolecular excimer fluorescence is probably due to the distortion and destruction of the coplanar sandwich structure of the pyrene excimer because of the creation of an inflexible and compact chain structure, not due to the dissociation of the PMAA–PEG intermolecular complex.

After completion of this study, we found similar work reported recently by Turro and Arona.[29] They employed PAA containing pyrene groups distributed randomly in the side chains to investigate intermolecular interactions with poly(ethylene oxide) (PEO), poly(1-vinyl-2-pyrrolidinone) (PVP), or poly(vinylamine hydrochloride) (PVAm). They demonstrated that the intensity ratio of monomer to excimer emission could be used to monitor the extent of intermolecular association and polymer displacement reactions for terpolymer systems in aqueous solution. The extent of interactions with three complementary polymers could be ranked in the order of PEO < PVP < PVAm. PEO and PVP form hydrogen bonding complexes with PAA. PVAm works as a polycation to form a complex via Coulombic interaction. This rank was consistent with the nature of secondary forces involved in the association of PAA and the complementary polymers.

Summary

The intramolecular excimer of PEG* decreases upon complexation with poly(carboxylic acid), probably due to a decrease in intramolecular mobility. This effect is more predominant in the PMAA–PEG complex than in the PAA–PEG complex due to the assistance of the hydrophobicity of PMAA. Simultaneously, the addition of poly(carboxylic acid) induces an increase in the local concentration of PEG in the vicinity of poly(carboxylic acid) chain. This was observed as an initial increase of intermolecular excimer formation and as a red shift in the absorption and excitation spectra. The greatest difference in the behavior of the PMAA–PEG compared to that of the PAA–PEG complex is that the PMAA complex forms a more compact structure accompanied by a larger decrease in intramolecular chain mobility with influence of hydrophobicity of PMAA. In addition, intermolecular excimer formation is suppressed, counteracting the dramatic initial increase in intermolecular excimer formation. At the same time, the excimer peak position shifts to higher energies. This phenomenon is first observed much before a stoichiometric ratio is reached. The addition of methanol to an aqueous solution decomposes the hydrophobic interaction in the PMAA–PEG system. Hydrogen bonding is then the major influence governing the complex formation, for which PMAA and PAA behave in a very similar manner as proton donors.

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Registry No. (PEG)(PMAA) (complex), 108617-77-2; (PEG)(PAA) (complex), 106250-10-6.

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Significance of Entropic Factors in Mechanical Deformation of Polymeric Glasses

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ABSTRACT: The formally entropic factors that influence the response of homogeneous polymeric materials to simple states of stress are examined. A very general derivation for the portions of the bulk and shear moduli that are entropic is given. This ratio of the entropic part to the total of the bulk modulus is given by the very simple formula $\Upsilon^* = B_1 - 10\alpha$ for a material that obeys the Tait equation of state in the limit of low pressure. Existing data on such materials are used to compute Υ^* for a number of polymeric glasses. Limitations of this analysis and fruitful directions for improving it are indicated. Entropic factors cannot be generally excluded when considering polymeric glasses.

Solids resist deformation. Their ability to resist is founded in the arrangement and interactions of their component molecules or atoms. From a thermodynamic point of view, their resistance to deformation can be decomposed into energetic and entropic contributions. The understanding and prediction of various moduli and other mechanical properties based on microscopic models is much more accessible when information is available on this most basic thermodynamic decomposition. A clear example can be found in the field of rubber elasticity. Here, the early experimental establishment that entropic factors dominated when a "good" rubber was extended permitted rapid and quite elegant development of a general theory with the assurance that particular details of the intermolecular forces were irrelevant.[1,2] Only the configurational choices available to a chain molecule by virtue of rotations about internal bonds are important in first approximation. Subsequent developments of both academic and practical importance right up through today are encouraged and derive their significance because of our appreciation for the molecular origin of rubber elasticity.

Recently, Theodorou and Suter[3] have reported computer simulations of the molecular origin of mechanical properties of polymeric glasses. In a very general development, they have produced a criterion for assessing the importance of entropic contributions to the bulk and shear moduli, together with a citation of relevant data on poly(methyl methacrylate).[4] In contrast to the classical case of rubber elasticity, they find that entropic effects are negligible in PMMA glass. However, just as in the historical example, this definite information proves to be invaluable for focusing attention on the important features of an initially hopelessly complex problem.

The present contribution rederives and extends the criterion introduced by Theodorou and Suter. Such a labor is clearly desirable in order to facilitate further, rational development of molecular understanding of the mechanical properties of polymeric glasses. Although we accept the conclusion of Theodorou and Suter[3] as regards PMMA, in the accompanying paper we report experimental data that demonstrate that entropic effects are by no means negligible in other polymeric glasses. First, a brief thermodynamic discussion is presented in order to place our results in context. Details of a new derivation of the Theodorou–Suter result (eq 16) are reserved for the appendix. Related expressions for simple states of stress in addition to hydrostatic compression are also deduced. Next, these results are specialized to the particular case of a material obeying the empirical equation of state due to Tait.[5] This equation is often approximately obeyed by amorphous polymeric materials.[6] Finally, we comment on the significance of some existing data and motivate the need for the experiments reported in the accompanying paper.

General Theory

The first law of thermodynamics is most often encapsulated by writing for the differential of the internal energy, U,

$$dU = \delta q + \delta w \tag{1}$$

Here, q denotes heat, w denotes a generalized work done on the system, and δ reminds us that these quantities are path dependent. The heat change for a reversible transformation forms the usual basis for defining the entropy, S,

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