Complex Formation of Syndiotactic Poly(methacrylic acid) with Complementary Polymers through Hydrogen Bonding

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Complex formations between syndiotactic poly(methacrylic acid) (st-PMAA) and poly(N-vinyl pyrrolidone) (PVP), and that between st-PMAA and polyethyleneoxide (PEO) through hydrogen bonding were studied by viscometry and potentiometry. Reduced viscosity (η_{red}) was measured at various mole fraction of PVP or PEO with respect to a constant amount of st-PMAA. Observation shows a sharp minimum at the 1:1 mole ratio of st-PMAA: PVP or st-PMAA: PEO, which shows that the complexation becomes optimal and the complex has a compact structure in this ratio. Variation of pH also supports this conclusion. This is the case of the system of st-PMAA and PVP in water as well as in DMF. Also the complexation is much enhanced when the molecular weight of PVP is high. Meanwhile, the system of st-PMAA and PEO shows a little different behavior, *i.e.*, this system does not form the complex in DMF and does only in water. It is because the interaction st-PMAA with PEO is weaker than that with PVP.

Introduction

Intermacromolecular complexes are formed by secondary binding forces and are divided into four classes according to their nature;[1] hydrogen bonding complexes, polyelectrolyte complexes, stereocomplexes due to van der Waals forces,[2-4] and charge transfer complexes.

Studies on the complex formation between proton-donating polymer and proton-accepting polymer by hydrogen bonds has been carried out using calorimetry, viscometry, turbidimetry, potentiometry, conductometry, and IR spectroscopy.[5-9] Another interest related to this subject is the solvent effect on the complex formation.[10,11] Especially the study of selective complexation has been widely studied,[12,13] which is controlled by many factors such as interaction forces, solvent, ionic strength, temperature, pH, *etc.*

In the previous works, the complex formations between atactic poly(methacrylic acid) (at-PMAA) and polyethyleneoxide (PEO)[5-8] or between at-PMAA and poly(N-vinyl pyrrolidone) (PVP)[9-11] were studied in detail. They showed that the complex is formed at unit mole ratio, *i.e.*, 50% mole fraction of PEO or PVP with respect to a constant amount of at-PMAA.

The complex formation between syndiotactic poly(methacrylic acid)(st-PMAA) and PVP(or PEO) remains unstudied provided the case between st-PMAA and PVP in DMF,[9] and also the effects of molecular weight and solvent on the complexation also are not studied completely.

In our study, the effects of solvent and molecular weight on the formation of complex between st-PMAA and PVP(or PEO) are studied in two different solvents, DMF or H_2O.

Experimental

Materials. Methacrylic acid (MAA) monomer (Tokyo Kasei) was purified by vacuum distillation (63°C, 12 mmHg). Polyethyleneoxide (Mw = 18,500; 100,000), and poly(N-vinyl pyrrolidone)(Mw = 10,000; 40,000; 360,000) were obtained from Tokyo Kasei Co. Syndiotactic poly(methacrylic acid) was synthesized by the following method. Solution of distilled methacrylic acid monomer in dry 2-propanol was sealed in glass vials under vacuum. These samples were polymerized in liquid state at -78°C by irradiating Co γ-ray. Dose rate was 0.2 Mrad/hr.[14,15] N,N-Dimethylformamide(DMF) (Merck) was used without further purification, and three-times distilled water was used.

Characterization of Stereoregularity.[16] The PMAA sample obtained in the above was esterified by using diazomethane, and then IR and NMR analyses of the esterified polymer were performed to determine the stereoregularity(or tacticity) of PMAA. In ^{1}H-NMR analysis, three α-methyl proton peaks are characteristics of stereoregular structures. The chemical shift of α-methyl proton appears at $\delta = 0.86$ for st-PMMA, 1.02 for at-PMMA, and 1.22 for isotactic PMMA (it-PMMA), respectively.[16] According to the NMR analysis of our product of st-PMAA, it was conformed that the latter has 100% syndiotacticity.

Although it is difficult to determine the extent of stereoregularity from the analysis of IR data, it serves as a good method to distinguish st-PMMA from other stereochemical PMMA. The peak at 1060 cm^{-1} of IR spectrum is characteristic for the st-PMMA while it does not appear for the other stereoisomer, we also found this peak in our st-PMAA sample esterified.

Viscometry. Viscometric measurements were performed at 25°C ± 0.05°C. We used an Ubbelohode type viscometer. Measurement of the reduced viscosity was carried out with concentrations, 1×10^{-1} M for PMAA, 5×10^{-2}M for PVP, and 5×10^{-2}M for PEO.

Results and Discussion

Figure 1 shows the change of the reduced viscosity η_{red} (a), and the pH(b) of the system as a function of the unit mole fraction of PVP in the mixture of PVP and st-PMAA in H_2O. η_{red} decreases monotonically with increasing unit mole fraction of PVP untill the latter reaches 50%, and then increases again. The decrease in the viscosity in the range of (0–50%) of PVP seems to be caused by the complex formation between st-PMAA and PVP. The presence of a minimum in η_{red} at 50% PVP is a critical evidence for the 1:1 complex formation between st-PMAA and PVP. In fact, the conformation of the complex has somewhat extened structure when the amount of PVP is small, and becomes more compact as it increases. The minimum η_{red} in corresponds to the most 1:1 compact complex in which all possible sites for proton donating in st-PMAA are bound by the proton-accepting sites in PVP. In the range (50-100%) of PVP, the PVP exists in excess, in a sense that there is no more sites for hydrogen-bonding in st-PMAA. Thus the viscosity increases. The complexation by hydrogen bonding is shown in Figure 2a for the mixture system of st-PMAA and PVP.

When PVP is added to a given amount of st-PMAA, the change of pH of the system is also shown in Figure 1. It noted that the pH increases until the mole fraction of PVP reaches 50% and then remains constant. This observation also supports our explanation that st-PMAA and PVP is stabilized by complexation through hydrogen-bonding. Since the acidic hydrogens in st-PMAA which participate in the formation of hydrogen bonding can not dissociate into free hydrogen ions, the pH increase is as the complexation increases. Once complexation becomes complete, *i.e.*, when the amount of PVP exceeds 50% mole fraction, pH does not change any more irrespective of the excess PVP.

Figure 3 shows that the reduced viscosity of the mixture of st-PMAA and PVP in DMF depends on the molecular weight of PVP. In DMF, the reduced viscosity exhibits similar behavior as in water (see Figure 1), if the molecular weight of PVP lies above 40,000. Another remarkable feature is that when molecular weight of PVP is higher, we can observe sharper minimum in η_{red}. It means that the power of complexation depends on the molecular weight of PVP, *i.e.*, the higher the molecular weight of PVP, the stronger the power of complextion. Thus, we note that when the latter is small (*i.e.* 10,000), no minimum appears.

Figures 4 and 5 show the reduced viscosity of the mixture of st-PMAA and PEO in H_2O and DMF, respectively. As can be seen from Figure 4, the reduced viscosity of (st-PMAA)-PEO mixture shows a minimum point in H_2O solvent. In contrast, there exists no minimum point in DMF, meaning that no complexes is formed in DMF.

From the above-mentioned fact, it may be said that the solvent effect seems to be one of the most important factors controlling the complexation. Before considering the solvent effect, we turn to the problem that st-PMAA and PVP make a complex in DMF (see Figure 3) while st-PMAA and PEO does not in the same solvent (Figure 5). This is due to the fact that in the system of st-PMAA and PVP in DMF, the com-

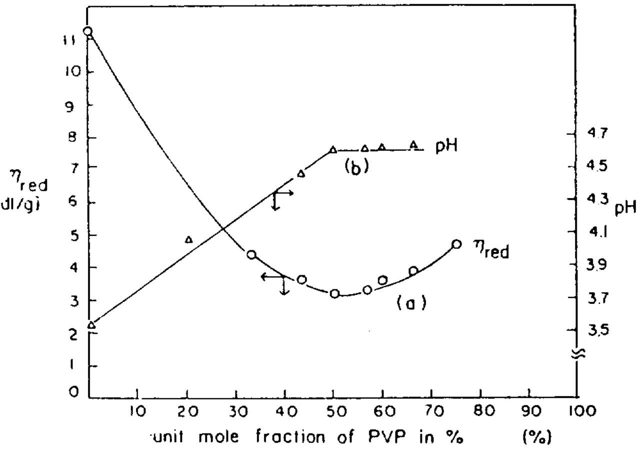

Figure 1. pH and reduced viscosity of (st-PMAA)-PVP mixtures in H_2O vs. unit mole fraction of PVP (in percent). The molecular weight of PVP used is 40,000. (a): reduced viscosity of the system, (b): pH of the complex solution.

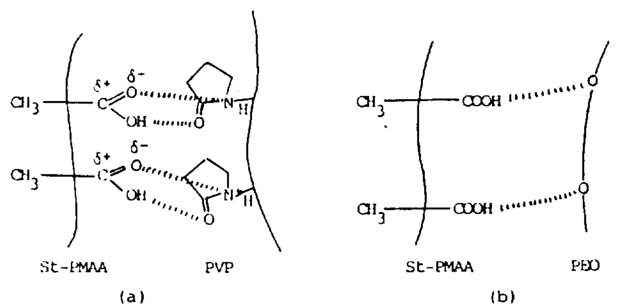

Figure 2. Complex formation of st-PMAA (a) with PVP, and (b) with PEO. In (a), the electrostatic interaction appears besides the hydrogen bonding.

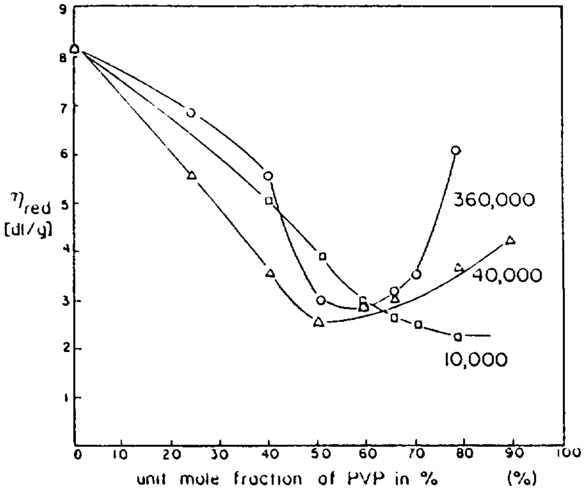

Figure 3. Reduced viscosity of (st-PMAA)-PVP mixtures in DMF vs. unit mole fraction of PVP in percent. Open circle, triangle, and square correspond to the PVP Mw=360,000, 40,000, and 10,000, respectively.

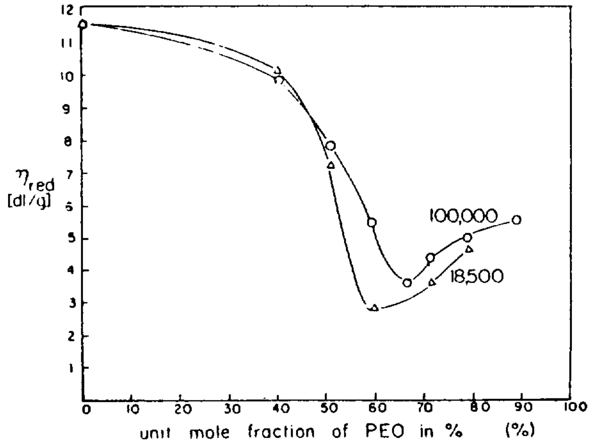

Figure 4. Reduced viscosity of (st-PMAA)-PEO mixtures in H_2O vs. unit mole fraction of PEO in percent. Open circle = reduced viscosity when the molecular weight of PEO is 100,000; triangle = reduced viscosity when the molecular weight of PEO is 18,500.

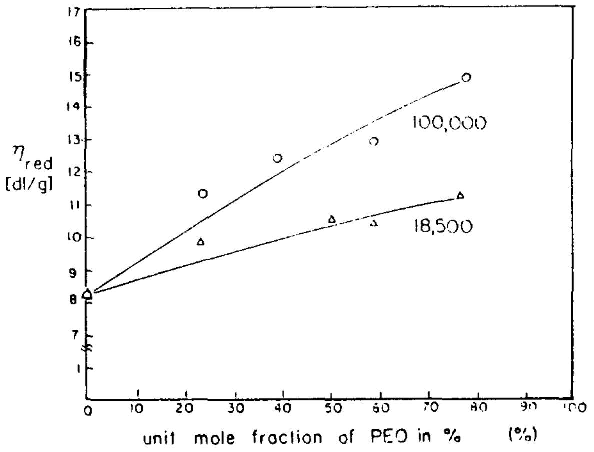

Figure 5. Reduced viscosity of (st-PMAA)-PEO complex in DMF vs. unit mole fraction of PEO in percent. Open circle and triangle have the same meaning as in Figure 4. See the caption in Figure 4.

plex formation occurs via hydrogen bonding as well as an electrostatic interaction (see Figure 2a) whereas in the system of st-PMAA and PEO in DMF, only the hydrogen bond action appears (Figure 2b) which is too weak to form a complex, thus causing no complex formation (see Figure 5).

Next we compare the system of PMAA + PEO in water (Figure 4) and that in DMF (Figure 5). One notices immediately that the former makes the complexation while the latter does not. The reason is as follows: in the system of PMAA + PEO in water, the water molecule helps the hydrogen bonding between PMAA and PEO, *i.e.*, it takes the role of H^+-carrier from the PMAA to the PEO. In the system of PMAA + PEO in DMF, however, the DMF $[(CH_3)_2N\cdot CHO]$ molecule interrupts the hydrogen bonding since the H^+ from the PMAA is captured by the DMF, thus no complexation occurs (Figure 5).

Conclusion

We have studied the possibility of complex formation between st-PMAA and PEO or PVP. The most important factor for the complexation is hydrogen bonding between proton-donating polymer (st-PMAA) and proton-accepting polymer (PVP or PEO). The measurement of viscosity shows a good evidence for the aforementioned situation. The next important factor affecting the complexation is solvent effect. It was analyzed by the observation that PVP forms compelx in both DMF and water, while PEO does only in water. The results indicate the fact that (1) the ability of PEO to form complex is weaker than that of PVP, and (2) compared with DMF, water greatly enhance the complexation by hydrogen bonding. Another interesting result extracted from the present work is that the degree of complexation depends on the molecular weight of PVP. Further study related to this work will be of great interest. Especially the study on the complexation using the two competing polymers, *i.e.*, PEO and PVP, is expected to show many other interesting effects which are not investigated as yet.

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