Notes

Studies on the Complexes Prepared by Template Polymerization. 1. Effect of Molecular Weight

S. S. AL-ALAWI

Chemistry Department, College of Science, University of Bahrain, P.O. Box 32038, Bahrain

Received June 12, 1990;
Revised Manuscript Received January 8, 1991

Introduction

It is known that macromolecules in solution have a strong tendency to interact with each other to form a super molecular structure through various secondary binding forces, i.e., Columbic forces, hydrogen bonds, van der Waals force, and hydrophobic interactions. There are various factors that affect the degree of complex formation and ability of stabilization, namely, the molecular weight of the reacting chain, concentration, temperature, nature of solvent, pH, and degree of ionization. Sato et al.[1] studied the radical polymerization of maleic acid initiated by potassium persulfate in the presence of poly(vinylpyrrolidone) (PVP) in aqueous solution. They found that the formation of the polymer complex was accelerated by an increase in the reaction temperature, concentration of initiator and monomer, and molecular weight of PVP used. The effect of the structure of a component polymer chain on the interpolymer complexes has been reported.[2] The authors found that the effective ionic sites for complexation are changed significantly by the pH change of the solution. The temperature effect on template polymerization of methacrylic acid in the presence of isotactic poly(methyl methacrylate) (it-PMMA) in DMF and other solvents was studied by Lohmeyer et al.[3] They found that in DMF at -10 °C the distinct kinetic template effect was detected in the polymerization. In the present studies the effect of the molecular weight of PVP on the crystallinity of the complexes was investigated.

Experimental Procedures

Materials. Acrylic Acid (AA). Acrylic acid was obtained from British Drug Houses (BDH Ltd.) and was distilled under vacuum.

Poly(vinylpyrrolidone) (PVP). Commercial PVP of three different molecular weights was supplied by Fluka and was used without any further purification. The molecular weights of the different PVP samples were PVP (K-15) 10 000, PVP (K-30) 44 000, and PVP (K-90) 360 000. Other samples of PVP of two different molecular weights were synthesized in the laboratory. Their molecular weights were measured by the viscometry method. Their molecular weights were as follows: PVP (1) 60 000, PVP (2) 180 000.

***tert*-Butyl Acrylate.** *tert*-Butyl acrylate (purum) was obtained from Fluka. It was purified by vacuum distillation.

Hexane. Hexane (puriss) was obtained from Fluka and was used without any further purification.

1,4-Dioxane. 1,4-Dioxane was obtained from BDH Ltd. Before use it was refluxed with sodium metal for 3 h to remove the peroxide content. The precipitate formed was removed by filtration.

Table I
Comparison of the Solubility of the Isotactic and Atactic Poly(*tert*-butyl acrylate)

solvent	isotactic	atactic
acetone	swells	soluble
chloroform	soluble	soluble
carbon tetrachloride	swells	soluble
monomer	insoluble	soluble
dioxane	insoluble	soluble
toluene	insoluble	soluble
chlorobenzene	soluble	soluble

Potassium Persulfate (K-PS). K-PS AnalaR quantity was obtained from BDH Ltd. It was used directly without any further purification to initiate the polymerization reaction in an aqueous medium.

***n*-Butyllithium.** *n*-Butyllithium (practical) was obtained from Fluka and was used without any further purification to initiate the polymerization reaction in nonaqueous media.

Preparation of Atactic Poly(acrylic acid) (at-PAA). Atactic PAA was prepared in an aqueous medium by using freshly distilled acrylic acid and potassium persulfate as an initiator at 60 °C. The molecular weight of at-PAA was measured by the viscometry method. The result showed that at-PAA had a molecular weight of 10 000.

Preparation of Crystalline Poly(*tert*-butyl acrylate).[4] Highly purified *tert*-butyl acrylate was polymerized in hexane at -70 °C, using *n*-butyllithium as initiator. At the end of the reaction (after 16 h) the amorphous catalyst was removed by extraction. The crystalline poly(tert-butyl acrylate) was found insoluble in monomer form and in most of the solvents that dissolve ordinary amorphous poly(tert-butyl acrylate).

Preparation of Isotactic Poly(acrylic acid) (it-PAA).[5] Isotactic PAA was prepared by hydrolysis of crystalline poly(*tert*-butyl acrylate). At the end of reaction, when conversion to PAA was complete, the mixture was dialyzed against water to remove the solvent and the acid, and the isotactic PAA was freeze-dried.

Preparation of Poly(vinylpyrrolidone) (PVP). *N*-vinylpyrrolidone was polymerized in an aqueous medium by use of a mixture of 30% hydrogen peroxide and concentrated ammonia as initiator at 50 °C. The molecular weight of the prepared PVP was measured by the viscometric technique.

Preparation of Macromolecular Complexes. Macromolecular complexes were prepared by two methods: (a) the mixing method and (b) the polymerization method (template polymerization).

(a) Mixing Method. An aqueous solution of at-PAA was mixed with an aqueous solution of PVP at 60 °C, without initiator. Each experiment was repeated with PVPs of different molecular weight (complexes I). Complexes III were prepared by mixing an aqueous solution of it-PAA with PVP as described for complexes I.

(b) Polymerization Method. Acrylic acid was polymerized in the presence of PVP (template polymer) and potassium persulfate as initiator at 74 °C. Each experiment was repeated using PVPs of different molecular weight (complexes II).

Differential Scanning Calorimetery (DSC). Thermal scanning calorimetry was carried out using a differential scanning calorimeter (DT-30, Shimadzu). The temperature range for this instrument was 0-500 °C. A heating rate of 10 °C/min was used for scanning.

Moisture Regain Measurements. Aliquots of the complexes were dried under vacuum to constant weight and were left in a controlled humidity chamber at 20 °C for 72 h. Finally, the

0024-9297/91/2224-4206$02.50/0

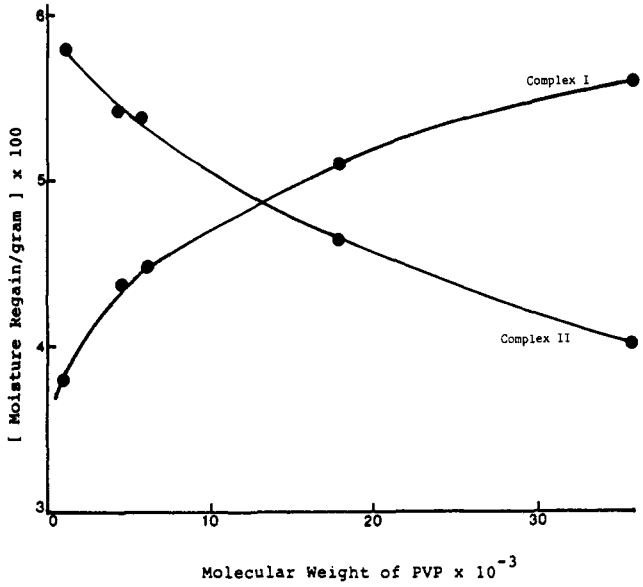

Figure 1.

samples were reweighed and the moisture regain was calculated per gram of sample.

Discussion

In this investigation two types of complexes were prepared. Complexes I were prepared by mixing an aqueous solution of atactic poly(acrylic acid) (MW 10 000) with poly(vinylpyrrolidone)s of different molecular weights in an aqueous medium. Complexes II were prepared by template polymerization of acrylic acid in the presence of PVPs of different molecular weights in an aqueous medium. FT-IR studies showed that the two types of complexes were composed of PAA and PVP.[6] In this study, the effect of molecular weight of PVP on the complexes was investigated. In both types of complexes five different molecular weights of PVP were used. The differential scanning calorimetery (DSC) measurements showed that T_g values for PAA varied from 110 to 120 °C. It was found that the T_gs for the PVPs were independent of molecular weight. The results showed that the T_gs for PVPs for different molecular weights were between 90 and 100 °C, and that was in agreement with the results reported by Faucher,[10] although some authors reported that the T_g of a regular homopolymer generally increases, up to a limiting value, with increasing molecular weight.[11-13] The T_g values for PAA and PVPs were different in comparison with values obtained for all complexes. The results were in agreement with those reported by Sato et al.[1] The authors reported the formation of a complex by template polymerization of maleic acid in the presence of PVP. They found that the T_g values for the complex were substantially different from those of PVP and poly(maleic acid). In this investigation, moisture regain (MR) was chosen to detect the effect of molecular weight of PVP on the crystallinity of the molecules in the complexes. The results showed that the MR for the complexes prepared by mixing an aqueous solution of PAA with an aqueous solution of PVP (complexes I) was increased as the molecular weight of PVP increased (Figure 1).

The opposite results were obtained for the complexes prepared by polymerization of acrylic acid in the presence of PVP (complexes II), where the MR was decreased as the molecular weight of PVP increased (Figure 1). The MR value for the complexes could be related to the number of gaps between the particles and accordingly could be related to the degree of crystallinity of the complexes.

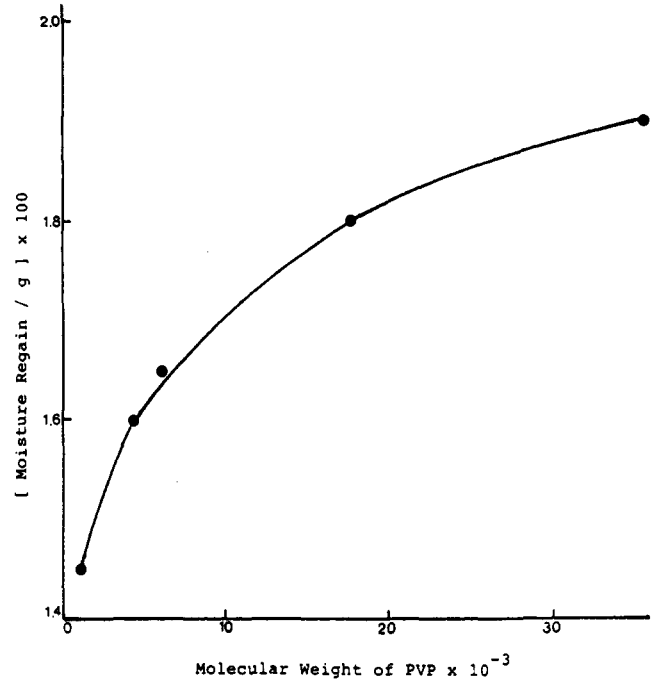

Figure 2.

Therefore, increases in MR in complexes I with increase in the molecular weight of PVP could be due to increasing gaps between the molecules of PVP and PAA as the molecular weight of PVP increased. In the case of complexes II, the increase in MR should be due to a decrease in the gaps between the molecules of PVP and PAA in the complexes as the molecular weight of PVP increased. These results could lead us to the conclusion that there is a difference in crystallinity between the two types of complexes I and II.

Another series of complexes were prepared by mixing an aqueous solution of highly crystalline PAA [isotactic (it-PAA)] with aqueous solutions of PVP of different molecular weight (complexes III). The results showed that the MR of the complexes increased as the molecular weight of PVP increased (Figure 2). The trend of the results was the same for complexes I where the MR increased as the molecular weight of PVP increase. Comparison between Figures 1 and 3 indicates that although the MR of both complexes increased as the molecular weight of PVP increased, there is a detectable difference between the amount of MR for the two types of complexes. As shown in Figures 1 and 2, MR for complexes III were less compared to complexes I, which could indicate that there is a difference in crystallinity between the two series of complexes due to differences in crystallinity of the PAA used in the preparation of the complexes. These results could indicate that, in the preparation of complexes by mixing, the interaction between the polymers occurs randomly, leading to the formation of amorphous complexes even if we use highly crystalline PAA, whereas in the complexes prepared by polymerization, the interactions between the interacting groups are precise and organized and produced complexes with a high degree of crystallinity. In the present study it was decided to measure the T_g values drawn from DSC measurements to give more details on the results taken from the MR in terms of crystallinity of the complexes. It has been reported that the T_g values are related to the crystallinity of the polymer. Some authors reported that crystallinity has little effect on the T_g value,[7] while others found that the T_g increases with increase in crystallinity.[8,9] The opposite results were also reported where the T_g values decrease as the crystallinity

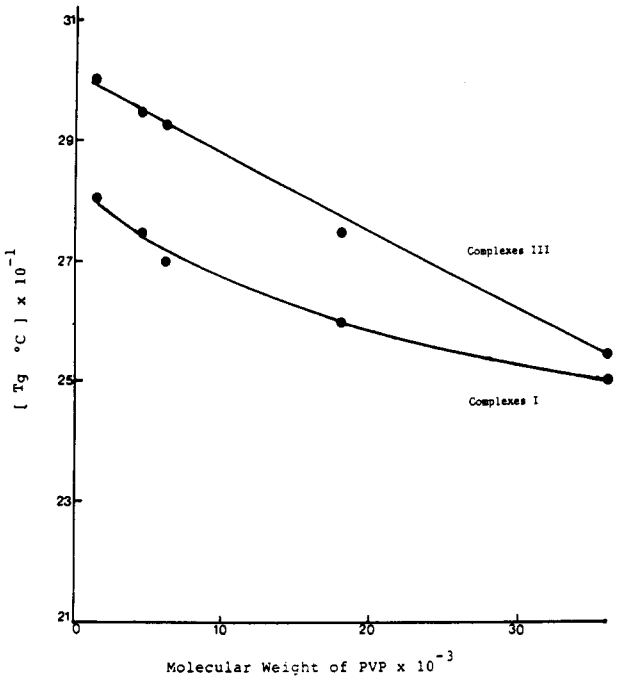

Figure 3.

increases. Figure 3 shows the decrease in T_g values for complexes I and III as the molecular weight of PVP increased.

It is clear that the T_g values for complexes III are higher in comparison with the T_gs for complexes I. This result supports the results obtained from the MR study of the same types of complexes. Opposite results were obtained from the measurement of the T_g values for the complexes III. As Figure 4 shows, the T_g values increased with increase in the molecular weight of PVP.

Comparing the results in Figures 3 and 4, it is clear that complexes II have higher T_g values than complexes I and III for any particular PVP. The T_g results for all the complexes show that there is a difference in T_g shifts for complexes prepared by mixing (complexes I and III) and those prepared by polymerization (complex II). As results show, the shifts for complexes I and III were only 30 and 45 °C, respectively, while for complexes II, the shift was 100 °C. This is a clear indication for the effect of molecular weight of the template polymer on the complexes. This effect could be attributed (a) to the method of preparation, which is different in complexes I and III from those of complexes II, and (b) to the existence of different amounts of grafted polymer, which is higher in complexes II as compared to complexes I and III. This is due to the fact that in the preparation of complexes I and III no

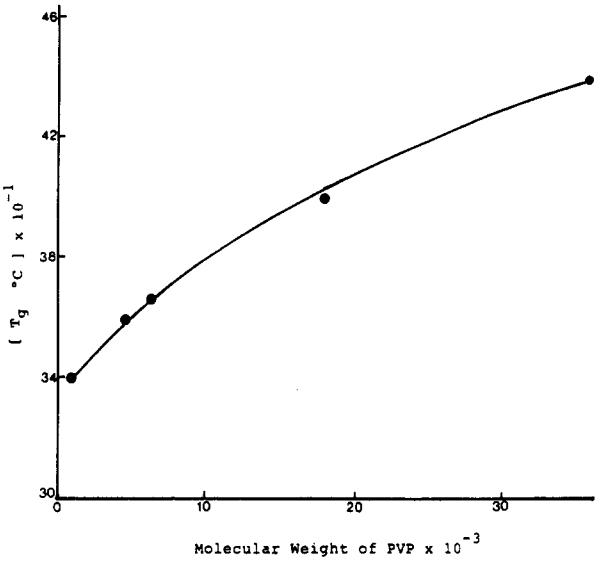

Figure 4.

initiator was used, whereas in complexes II initiator had been used. From the results of T_gs and MR it could be said that the polymers in complexes I and III interact randomly with each other through the interacting group, which leads to the formation of complexes with less crystallinity and which was shown by the amount of moisture that the complexes could adsorb and also by their T_g values. In other cases, the polymers in complexes II interacted with each other in an organized pattern that leads to the formation of complexes with high crystallinity, as shown by the results of the MR and T_g studies.

References and Notes

(1) Sato, T.; Nemoto, K.; Mosi, S.; Otsu, T. *J. Macromol. Sci., Chem.* **1979**, *A13*, 751–766.
(2) Lohmeyer, J.; Tan, Y.; Challa, G. *J. Macromol. Sci., Chem.* **1980**, *A14*, 945–957.
(3) Abe, K.; Tsuchida, E. *Polym. J.* **1977**, *9*, 79–86.
(4) Miller, M. L.; Ranhut, C. E. *J. Polym. Sci.* **1959**, *38*, 63.
(5) Blauer, G.; Kathchalsky, A. *Trans. Faraday Soc.* **1951**, *47*, 1360.
(6) Al-Alawi, S. S.; Saeed, N. A. *Macromolecules* **1990**, *23*, 4474.
(7) Iobst, S. A.; and Manson, J. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1970**, *11*, 765.
(8) Roshchupkin, V. P.; Koherninskii, V. V. *Vysokomol. Soedin., Ser. B* **1971**, *13*, 194.
(9) Faucher, J. A.; Koleski, J. V.; Santee, E. R.; Stratta, J. J.; Wilson, C. W. *J. Appl. Phys.* **1966**, *37*, 3962.
(10) Faucher, J. A. *J. Polym. Sci., Part B: Polym. Lett.* **1965**, *3*, 143.
(11) Shan, M. C.; Eisenberg, A. *Rubber Chem. Technol.* **1970**, *43*, 95.
(12) Pezzin, G.; Filio-Grandi, F.; Sanmartin, P. *Eur. Polym. J.* **1970**, *6*, 1053.
(13) Smekhon, F. M.; Nepomnyashchii, A. T.; Sanzharonskii, Yakubonich, S. V. *Polym. Sci., USSR (Engl. Transl.)* **1971**, *13*, 2362.

Registry No. AA·PVP, 53608-09-6; H_2O, 7732-18-5; poly(*tert*-butyl acrylate) (homopolymer), 25232-27-3.