Preparation and Separation of Complexes Prepared by Template Polymerization

Saeed Al-Alawi* and N. A. Saeed

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

Received July 3, 1989; Revised Manuscript Received February 2, 1990

ABSTRACT: Acrylic acid (AA) was polymerized in the presence of poly(vinylpyrrolidone) (PVP) as a template polymer in an aqueous medium. The result was a complex of poly(acrylic acid) (PAA) and PVP. Comparison of the FTIR spectrum of the complex with that prepared by mixing of PAA and PVP indicates that the complex is composed of PAA and PVP. The separation of the complex was achieved by methylation, indicating that the polymers were interacting through hydrogen bonding. The low yield of separation indicates the existence of some grafted complex. When the complex was prepared by using PVP of different molecular weights, the yield of separation changed. The degree of the separation decreased as the molecular weight of PVP increased.

Introduction

The hydrogen bonding is the most important and common type of bonding that is responsible for interaction between polymers. An example exists in the polycondensation of dimethyl tartarate (DMT) with hexamethylenediamine (HMD) in the presence of various polymer templates such as poly(vinylpyrrolidone) (PVP), poly(vinylpyridine) (PVPy), polysaccharides, and poly(vinyl alcohol) (Ogata et al.).[1] The authors suggested that the interaction of DMT and HMD with the template was due to hydrogen bonding. Complex formation of PAA and PEO has been reported by Ferguson and Shah.[2,3] They suggested that the stability of this complex is due to the formation of hydrogen bonds between monomeric units in the macromolecules of the polyacids and PEO. Sato et al.[4] prepared a complex by polymerizing maleic acid (MA) in the presence of PVP. Their results indicated that hydrogen bonding was responsible for the interaction of the two polymers. They achieved the separation of the complex by using diazomethane to break the hydrogen bonds. Lohmeyer et al.[5] reported the preparation of a complex by polymerizing methacrylic acid (M-acid) in the presence of poly(methacrylic acid) in DMF. They achieved the separation by means of selective extraction by alternatively treating a finely powdered sample with boiling acetone to extract PMMA and boiling methanol to extract PM acid.

Govzdetskii et al.[6] have investigated the polymerization of 4-vinylpyridine in the presence of polyphosphate macromolecules. They performed the separation by boiling the complex for several hours in very dilute hydrochloric acid.

Experimental Section

An FTIR Mattson-Polaris spectrometer with icon software was used for all IR measurements.

Materials. Poly(vinylpyrrolidone) (PVP). Commercial PVP was supplied by Fluka and was used without any purification. Four different molecular weights of PVP were used (360 000, 80 000, 44 000, and 10 000).

Acrylic Acid and Methyl Acrylate (AA and MA). Both monomers were supplied by BDH and used after distillation under reduced pressure.

Poly(methyl acrylate) (PMA). PMA was synthesized in the laboratory by bulk polymerization at 60 °C using AIBN as initiator.

Poly(acrylic acid) (PAA). PAA was synthesized in the laboratory by radical polymerization at 60 °C using potassium persulfate as initiator. The molecular weight of the prepared PAA was measured by the viscosity method, and it was found to be 9500.

Preparation of Complexes. Acrylic acid was polymerized in the presence of poly(vinylpyrrolidone) (PVP) in an aqueous medium at 74 °C using potassium persulfate as initiator. The formation of the complex was completed in about 20 min (complex I). The suspended complex was precipitated by addition of several drops of 3 M HCl. The physical state of the complex was soft and elastic, and it remained in the same state while it was in water. However, it became hard when it was allowed to dry. A differential scanning calorimetry (DSC) measurement for the complex shows that at 450 °C a change in phase was occurring. The complex was not soluble in any solvent tried (acetone, chloroform, DMF, DMSO, methanol, and ethanol). Therefore, for the IR measurement, a thin film was prepared by placing a small piece of the fresh and soft complex between two cast acrylic sheets under pressure. It was noted that the film under pressure was first semitransparent, but after drying in a vacuum oven for about 4–5 h, it became completely transparent. Four samples of complex of different molecular weights were prepared (360 000, 80 000, 44 000, and 10 000).

Another complex was prepared by mixing ready-made aqueous solutions of PAA and PVP (mol wt 10 000) at 60 °C (complex II). The physical state of this complex was exactly the same as that of complex I in terms of solubility in water and other solvents. DSC measurement shows only 10° difference in comparison with complex I. The same technique was used for the preparation of the sample for IR measurement.

Separation Technique. About 0.7 g of the polymer complex was dispersed in benzene. An excess of freshly prepared diazomethane in ether was added to this solution. The reaction mixture was allowed to stand for about 36 h at room temperature. Completion of the reaction was indicated by decolorization of the initial yellow solution and cessation of the liberation of nitrogen gas. The separated PAA was in the form of poly(methyl acrylate) (PMA), which was soluble in the benzene solution. The polymer was obtained by evaporation of the solvent. The unseparated complex plus insoluble PVP was washed with methanol to dissolve the separated PVP.

Results and Discussion

The complex of PVP and PAA was prepared by polymerization of acrylic acid (AA) in the presence of PVP in an aqueous medium. Previous results by Ferguson and Shah[2,3] indicated that the molar ratio of PAA to PVP was 1:1. Their calculation was based on the determination of the nitrogen content. On the basis of the structures of the PAA and PVP, it seems that hydrogen bonding can occur between the hydroxyl group of the PAA and the carbonyl group of PVP.

0024-9297/90/2223-4474$02.50/0

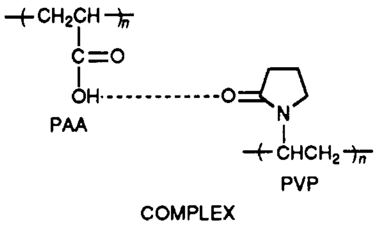
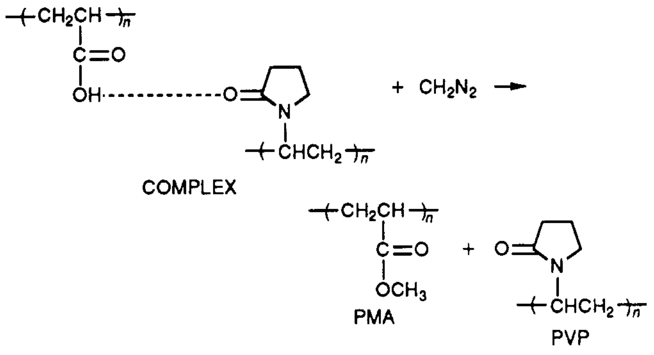


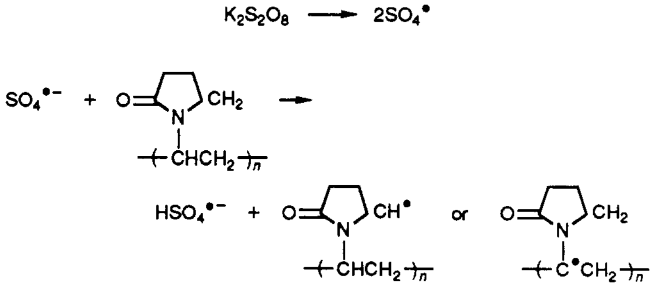
Figure 1 shows the comparison between the FTIR spectra of the complex prepared by template polymerization (complex I) and that prepared by mixing ready-made aqueous solutions of PAA and PVP (complex II). The figure shows similarity between two spectra, which indicates that the complex I is composed of two polymers.

The methylation technique was used for separation of the complexes. In this process, PAA was recovered from the solvent in the form of poly(methyl acrylate) (PMA) and the PVP was found to be unchanged.



A sample of poly(methyl acrylate) was prepared by bulk polymerization for comparison with the PMA isolated from the complex (Figure 2). Also the comparison was made between the PVP before the interaction and after separation (Figure 3).

In this investigation the results showed that nearly 50% of the complex was separated. To be certain of complete separation, the unseparated complex was subjected, after drying, to methylation once more. After completion of the reaction and evaporation of benzene, it was found that neither PMA nor PVP was isolated. The low yield of the products might be attributed to either the formation of dimers, trimers, and oligomers on the template polymer or to the grafting of the newly formed polymer on the matrix polymer. The grafting might result from (a) a transfer reaction between the growing PAA radical and the PVP molecules followed by initiation or (b) direct reaction between an initiator radical and the PVP molecules.



Complex II, which was prepared by mixing of aqueous solutions of PAA and PVP, was separated by the same technique. The result showed that approximately 90–95% of the complex was separated into its components.

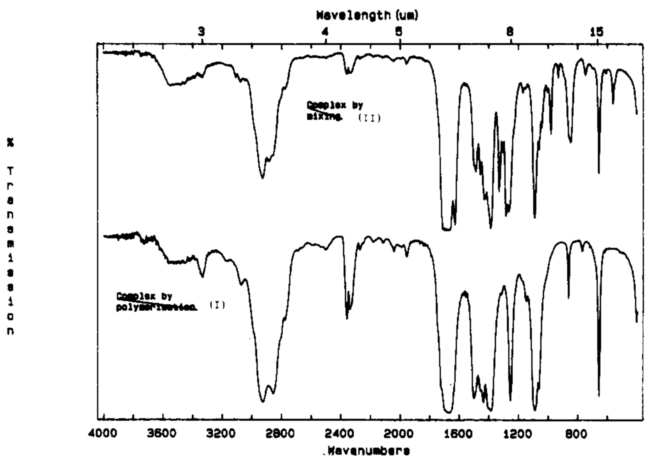


Figure 1. Comparison between the FTIR spectra of the complex by mixing (complex I) and the complex by polymerization (complex II).

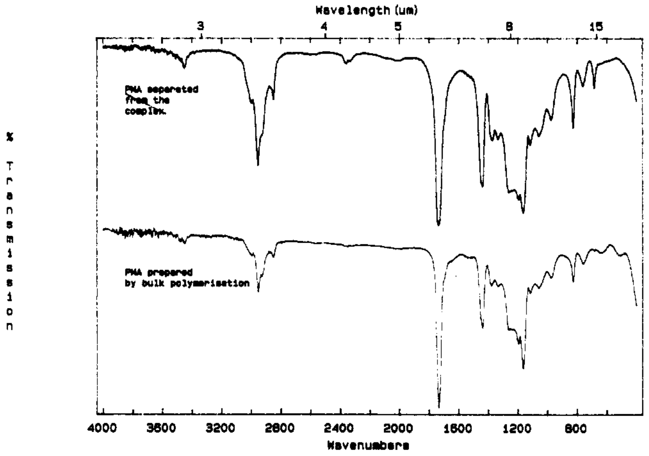


Figure 2. Comparison between the FTIR spectrum of PMA prepared by bulk polymerization and that separated from the complex.

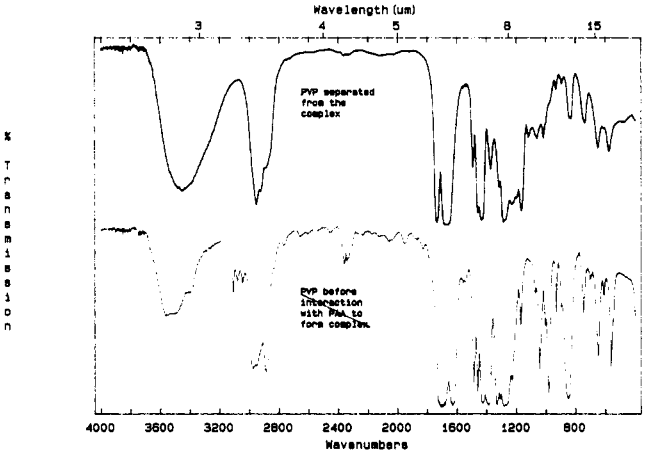


Figure 3. Comparison between the FTIR spectrum of PVP separated from the complex and that before the interaction.

The high yield of this process could be due to the absence of grafting because there was no initiation.

Comparing the separation yield of complex I with that of complex II could lead us to attribute the existence of grafted polymer in complex I to initiation in the polymerization system.

Sato et al.[4] in their investigation reported the polymerization of maleic acid in the presence of PVP. They separated the complex by the methylation technique. They found that only 50–60% of the poly(maleic acid) was

Table I
Relation between the Yield of Separated Complex and the Molecular Weight of PVP

PVP mol wt	mass of unseparated complex, g	separated complex, %
360 000	0.15	21.5
80 000	0.21	30.0
44 000	0.30	43.0
10 000	0.36	51.4

separated as its methyl ester. They also attributed the low yield to the grafting of the monomer onto PVP.

In this study, the effect of the molecular weight of the matrix polymer on the product yield was also investigated. It was found that increasing the molecular weight of the matrix polymer increased the amount of grafting complex; i.e., the yield of separated complex was decreased as the molecular weight of the PVP increased (Table I). It is suggested that increasing the molecular weight of the matrix polymer increases the probability of the formation of the grafted complex. This might be due to the viscosity effect in the reaction medium. It is well-known that the viscosity of the polymer solution increases with the increasing molecular weight of the polymer.

References and Notes

(1) Ogata, N.; Sanui, K.; Nakamura, H.; Kuwahara, *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 939.

(2) Ferguson, J.; Shah, S. A. O. *Eur. Polym. J.* **1968**, *4*, 343.

(3) Ferguson, J.; Shah, S. A. O. *Eur. Polym. J.* **1968**, *4*, 611.

(4) Sato, T.; Nemoto, K.; Mori, S.; Otsu, T. *J. Macromol. Sci. Chem.* **1978**, *A13* (6), 751.

(5) Lohmeyer, J. H. G. H.; Tan, Y. Y.; Challa, G. *J. Macromol. Sci. Chem.* **1980**, *A14* (6), 945.

(6) Govzdetskii, A. N.; Kim, V. O.; Smeianyuk, V. I.; Kabanov, V. A. *Vysokomol. Soedin.* **1971**, *A13* (13), 2409–2416.