Effects of Hydrophobic Unit and Its Distribution on Solution Properties of Vinyl Pyrrolidone and Vinyl Acetate Copolymer

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ABSTRACT: A series of vinyl pyrrolidone and vinyl acetate copolymers with different monomer ratios and homogeneity in backbone distribution were synthesized and their solution properties studied. In water, the phase diagram curve is concave, with the lower critical solution temperature, due to the cooperation of hydrophobic and hydrophilic hydration. In order to make a substantially homogeneous copolymer, a new method to determine the monomer mole fraction is suggested. When the vinyl pyrrolidone to vinyl acetate mole ratio in the copolymer is close to unity, sequence distribution plays an important part in solution behavior. The more homogeneous the structure, the better the solubility in water, and the higher the cloud point. This is attributed to the balance between hydrophobic and hydrophilic forces in solution. Copolymerization kinetic analysis on monomer conversions and turbidity measurement on poly(vinylpyrrolidone/vinyl acetate) solutions give consistent results to confirm this interpretation. © 19991999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 345–352, 1999

Key words: hydrophobic unit; vinyl pyrrolidone; vinyl acetate

INTRODUCTION

Behavior of nonionic polymers containing both hydrophobic and hydrophilic groups in water has been the subject of many investigations.[1–9] The interest stems from the need to understand the role which water plays in the stability and interaction of both synthetic and biological macromolecules. However, few, if any, studies have been performed to elucidate the effects of backbone homogeneity regarding hydrophobic and hydrophilic units distribution on the conformation and solubility of macromolecules in aqueous solution. The properties of copolymers depend not only on the nature of the comonomers and the overall compositions, but also on the distribution of monomer units along the chain. Vinyl acetate (VA), a hydrophobic compound, and its homopolymer, Poly(vinyl acetate) (PVA), are water insoluble,[10] while vinyl pyrrolidone (VP) which contains polar, hydrophilic lactam ring, and its homopolymer, poly(vinyl pyrrolidone) (PVP), are completely water soluble at all temperatures.[1,11] Therefore, the VA and VP copolymer (PVP/VA) is a model to assess the impact of each monomer as a function of polymer solution behavior. The chemical formulas of these compounds are shown in Figure 1. The range of VP/VA mole ratios in these copolymers available for this study is broad, covering from 16/84 to 62/38. The copolymers can be synthesized in different ways resulting in different homogeneity of backbone monomer distribution. This gives us a unique opportunity to study the effect of varying VP to VA ratios and monomer unit distribution on solution properties, which is the subject of this paper.

It was found that the solubility of PVP/VA in water is first decided by the overall composition. When VP is the major component, i.e., VP is greater than 60 mol %, the copolymer may more likely, but not necessarily (still depending on the homogeneity), be soluble in water. When VA is the major component, the copolymer will be insoluble in water, no matter how homogeneously the

Figure 1 Monomers and copolymer.

monomers are distributed. In this study, we have focused on the copolymer with VP to VA mole ratio close to unity and described the novel properties of PVP/VA aqueous and alcoholic solutions as functions of temperature and concentration, and the relation between the monomer sequence distribution in the copolymer backbone and the cloud point of PVP/VA aqueous solutions.

EXPERIMENTAL

Materials

PVP/VA copolymers with different monomer ratios and different homogeneity in their backbone were prepared through free radical copolymerization in alcohol solution followed by solvent exchange to obtain aqueous solution and freeze drying to obtain the final product in powder form. The method of PVP/VA synthesis was described in detail in the United States Patents.[12–14] Molecular weights were determined by gel permeation chromatography (GPC) measurement.

VP and VA Measurement

For the purpose of reaction kinetics studies, samples were taken during the copolymerization process and the residual VP and VA monomer levels were measured by gas chromatography with a Hewlett Packard DB-1 column.

Turbidity Measurement

The turbidity of PVP/VA copolymer aqueous and alcoholic solutions was measured at various temperatures, ranging from $-15°C$ to $80°C$, and polymer concentrations, ranging from 0% to 50%, by using a HACH Ratio Turbidimeter, with the nephelometric turbidity unit (NTU). When the reading was higher than 20, solution haze was observed visually and it was judged as phase separation.

Viscosity Measurement

The viscosity of the polymer solution was determined at 25°C with a 0.63 mm Ubbelohde dilution viscometer. The kinetic energy and shear rate were found to be negligible. The concentration of the polymer solution was 1 g per deciliter.

RESULTS AND DISCUSSION

1. Phase Diagrams and LCST

The temperature-composition phase diagram of the PVP/VA copolymer (sample 1) and water system was determined by turbidity measurement on copolymer aqueous solutions at different temperatures and different polymer concentrations (cloud point method), and is presented in Figure 2. The VP to VA mole ratio in sample 1 is 53/47 and its molecular weight is 22,900 (weight average). The curve shows the solubility as a function of temperature for this particular sample in water. Below the curve, the two-component system is a single phase in all proportions. The region above the curve is the two-phase region. The

Figure 2 Phase diagram of PVP/VA–water system. Sample 1. Monomer mole ratio = 53/47.

Figure 3 Phase diagram of PVP/VA–2-propanol system. Sample 2. Monomer mole ratio = 29/71.

curve is sometimes referred to as the cloud-point curve because, typically on heating from the one-phase region, the solution becomes cloudy as droplets of the second phase form. This concave curve gives a lower critical solution temperature (LCST) of 68°C with the critical concentration of 4% (weight fraction), which is the lowest temperature at which two phases can coexist in the PVP/VA-water system.

The temperature composition phase diagram of the PVP/VA copolymer (sample 2) and isopropanol system is presented in Figure 3. The VP and VA mole ratio in sample 2 is 29/71 and its molecular weight is 13,300 (weight average). The curve is convex giving an upper critical solution temperature of 6°C with the critical concentration of 5% (weight fraction), which is the highest temperature at which two phases can coexist in the PVP/VA-isopropanol system.

Lower critical solution temperatures are sometimes found in systems that have strong specific intermolecular interactions between polymer and solvent.[16] For PVP/VA aqueous solutions, the concave phase diagram and LCST probably can be attributed to the cooperation of hydrophilic and hydrophobic hydration.[1,2] In PVP/VA aqueous solutions there are two types of hydration:

1) Hydrophilic hydration: Interaction through hydrogen bond formation between water molecules and the oxygen and nitrogen atoms in the polar amide linkage. Although the hydrogen bonding is very strong, its strength is affected by the movement of molecules, which is a function of temperature.

2) Hydrophobic hydration: The dispersion interaction of water with the nonpolar methylene groups, which is connected with structural organization of water molecules and the formation of

"microscopic icebergs," as nicknamed by Frank and Evans,[15] who first clearly elucidated the effect of dissolved molecules and ions on the structure of water. Similar to hydrophilic hydration, hydrophobic hydration also is a function of temperature.

When PVP/VA and water are mixed at a temperature below the LCST, heat is released ($\Delta H_{mix} < 0$) owing to the preferentially favorable attraction. Both the water and polymer molecules have less kinetic energy and the hydrogen bonds, formed through the hydrophilic hydration, are stable. At the same time, the hydrophobic hydration stabilizes the water and the solution structure. Therefore the copolymer is soluble in water. When the temperature is raised, the molecular motion is increased, breaking the hydrogen bonds and the hydrophobic hydration, consequently the water "icebergs" disappear and the solution structure is destabilized. Thus ΔH_{mix} increases with increasing temperature and phase separation eventually takes place. Therefore PVP/VA has a better solubility in water at lower temperature.

In alcoholic solution, the degree of hydrogen bonding between the alcohol molecules and amide linkages on the polymer chains is much less, compared with the aqueous system. Similar to the binary system of lower molecular weight compounds, at a temperature below the upper critical solution temperature, the cohesive force among the macromolecules causes the polymer chains to aggregate and separate from the solvent.[16] Only at higher temperature, the thermal motion of the polymer chains make them overcome the cohesive force and separate into the solution to become a homogeneous phase. Therefore in alcohol PVP/VA has a better solubility at higher temperature.

Recently A. A. Tager, et al.[1,2] reported that when hydrophilic hydration was predominate, such as with the copolymer of vinyl caprolactam (VCL) and VP (80 mol %), the solutions were homogeneous at all temperatures up to the boiling point, whereas when both hydrophobic and hydrophilic hydration exist, such as with aqueous solution of poly(vinyl caprolactam), there is lower critical solution temperature. In other words, the LCST in the polymer-water system is caused by hydrophobic hydration. Our results on PVP/VA copolymer aqueous solutions are consistent with this observation and conclusion.

Most polymers contain both hydrophilic and hydrophobic moieties. Therefore the existence of only hydrophobic or only hydrophilic hydration is very unusual. The important factor is which hydration type is predominant in the aqueous solu-

tion. It was estimated[17] that in the PVP homopolymer aqueous solution, each molecule strongly bonds (through hydrophilic hydration) 3 molecules of water, and loosely bonds (through hydrophobic hydration) 10 molecules of water. Compared with PVP, PVP/VA has more hydrophobic (methylene and ester) groups and less hydrophilic (amide) groups. Obviously, in PVP/VA aqueous solutions the ratio of hydrophobic to hydrophilic hydration should be much higher than that in PVP aqueous solution. Therefore, in PVP/VA aqueous solutions the hydrophobic hydration should predominate. Although when VP is the major component, PVP/VA is soluble in water within a certain temperature range, water is only a poor solvent of PVP/VA. When heated, phase separation occurs at the lower critical solution temperature.

Relative viscosities of PVP/VA sample 1, measured in alcohol and water separately, turned out to be: solvent : ethanol and water, and relative viscosity (1 g/deciliter, 25°C): 1.21 and 1.17, respectively.

The higher relative viscosity in alcohol indicates ethanol is a better solvent for PVP/VA macromolecules, in which the polymer chains are more expanded, whereas in water, the polymer molecules were more compact therefore water is a poorer solvent. This is consistent with our above discussion.

2. Effect of Homogeneity in Backbone Monomer Distribution on the Solution Property

In free radical copolymerization, the monomer reactivity ratios for VP and VA are 3.3 and 0.20, respectively. Because of these widely differing reactivity ratios, the copolymer formed initially will contain a higher percentage of the more reactive VP monomer than the copolymer formed at the end of reaction.[18] The sequence distribution in PVP/VA macromolecular chains will affect the copolymer solution behavior. PVP/VA obtained from high conversion through nonuniform method, which will be described below, has heterogeneous microstructure and is less soluble in water. Ideally, it is preferred to make a copolymer in which VP and VA units incorporated are in proportion to their relative concentrations giving near perfect regularity along the chain. When this substantially homogeneous copolymer is added into water, solvation of the VA units is facilitated by neighboring VP units pulling them into water.

During copolymerization at high conversion from two monomers having quite different reac-

tivity ratios, in order to avoid making a product with very broad copolymer composition distribution range, it is common to supplement the faster reacting monomer, either continuously or portion wise, during the reaction. This strategy has been demonstrated for the extreme case of vinyl chloride ($r_1 = 0.02$) and acrylonitrile ($r_2 = 3.2$) copolymerization.[18] But this method is not good enough to generate substantially homogeneous copolymers. We intended to explore a more elaborated method to precisely determine the monomer ratios in the initial charge and later feeding, for a particular copolymer with a specific composition.

Flory developed the copolymerization equation as follows[19]:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{1}$$

where F_1 is the mole fraction of monomer 1 in the copolymer; r_1 and r_2 are the reactivity ratios for monomer 1 and monomer 2, respectively; f_1 and f_2 are the mole fraction of unreacted monomer 1 and monomer 2, respectively, in the reactor.

This equation gives the instantaneous copolymer composition (F_1 and F_2), if the compositions of unreacted monomers in the reactor (f_1 and f_2) and monomer reactivity ratios (r_1 and r_2) are known. It is necessary to distinguish between the instantaneous copolymer composition (F_1 and F_2), which is the composition of chains formed at any moment during a copolymerization process, and the cumulative copolymer composition, which is the accumulation of the copolymer composition formed throughout the whole course of the copolymerization. Similarly, it is necessary to distinguish between the instantaneous monomer composition (f_1 and f_2) and the overall comonomer composition. Obviously for a copolymerization occurring in a closed system to a higher conversion, the cumulative copolymer composition should be equal to the overall monomer composition. In order to obtain a homogeneous product, it is desirable to maintain the instantaneous copolymer composition (F_1 and F_2) to be 1) stable during the copolymerization process and 2) equal to the predecided, cumulative copolymer composition. To achieve this instantaneous copolymer composition, we need a method to decide the instantaneous monomer composition (f_1 and f_2).

Starting from eq. (1) and the equivalent equation for F_2, after derivation, we can obtain the following equation:

Figure 4   PVP/VA copolymerization kinetic analysis. Sample 3. Monomer mole ratio = 53/47.

Figure 5   PVP/VA copolymerization kinetic analysis. Sample 4. Monomer mole ratio = 53/47.

$$\left(\frac{f_1}{f_2}\right) = \frac{(F_1 - F_2) + [(F_2 - F_1)^2 + 4F_1F_2r_1r_2]^{1/2}}{2F_2r_1} \quad (2)$$

Also from the definition of mole fraction we have

$$f_1 + f_2 = 1 \quad (3)$$

By using eqs. (2) and (3) we can decide the initial monomer composition (f_1 and f_2) to make the initial copolymer having the instantaneous composition of F_1 and F_2. Therefore, the initial monomer concentration is established based on the monomer reactivity ratios (r_1, r_2) and F_1 and F_2. As the reaction progresses, monomers should be supplemented continuously based on their consumption ratios to maintain the instantaneous monomer composition to be constant at f_1 and f_2, therefore, the instantaneous copolymer composition can be maintained constant at F_1 and F_2, and equal to the cumulative copolymer composition.

During the reaction, each monomer and solvent should be added into the reactor separately. Therefore, each monomer feeding rate can be adjusted independently to keep the monomer conversion ratio constant, and the solvent feeding rate can be adjusted independently, according to the monomer feeding rates.

The above method of predicting the instantaneous monomer composition based on monomer reactivity ratios and copolymer composition was tested in the PVP/VA synthesis. For the purpose of this study, we chose a PVP/VA in which the VP/VA mole ratio 53/47. A well organized distribution of VP and VA units in the macromolecule chain should maximize the copolymer's aqueous

solution solubility. Calculations from eqs. (2) and (3) indicated that the monomer mole ratio in the initial monomer charge of VP to VA should be 0.41. After the reaction initiation, the mole ratio of monomers in feeding should be 1.13. Obviously, because the reactivity ratio of a monomer is a function of many factors, such as temperature, solvent, monomer concentration, monomer ratio, microenvironment, etc, values of f_1 and f_2 calculated from eqs. (3) and (4) are subject to adjustment based on experimental results.

It was found that the monomer feeding method during reaction determined the homogeneity in PVP/VA backbone, which further established the sample solubility in water and the cloud point. Figures 4–7 present the kinetic analysis during PVP/VA copolymerization process of samples 3–6, in which the monomer and solvent addition methods were different. All these samples had the same VP/VA mole ratio, 53/47, and similar molecular weights, in the range of 22,900 to 26,000

Figure 6   PVP/VA copolymerization kinetic analysis. Sample 5. Monomer mole ratio = 53/47.

Figure 7 PVP/VA copolymerization kinetic analysis. Sample 6. Monomer mole ratio = 53/47.

(weight averages). The copolymerization for all samples was carried out to high conversion (>99% for both VP and VA monomers). The concentrations of unreacted VP and VA monomers in the reactor during copolymerization were measured by gas chromatography to determine the % conversion. The closer the VP and VA monomer conversion curves, the more homogeneous the copolymer microstructure.

Let us examine the conversion graph for each sample:

Sample 3: This sample was prepared by a simple semi-batch procedure. All VA monomer, all 2-propanol solvent and about two thirds of VP monomer were added before the reaction was started. The remaining VP was added portion-wise during the reaction. As shown in Figure 4, the VP and VA conversion curves are far apart during the major part of the process, indicating the very heterogeneous microstructure in copolymer.

Sample 4: The initial charge was only 20% of the total reactants and the rest was added continuously during reaction. The VP to VA mole ratios in initial charge and later feed were identical, 0.97. After 3.5 h VP and VA feeding, the VA addition was completed and the rest VP was continuously fed in 1 h. The comonomer/polymer concentration was maintained constant. Due to adopting continuous feeding, monomer conversion curves shown in Figure 5 come closer, compared with sample 3 in Figure 4. But because the monomer ratios in initial charge and feed were not determined based on eqs. (2) and (3), the conversion curves are still separated.

Sample 5: This was similar to sample 4 except that the VP and VA mole ratio in the initial charge and feed were 0.41 and 1.23, respectively, determined based on eqs. (2) and (3). As shown in

Figure 6, the monomer conversion curves are very close during the major portion of reaction, which proves the validity of eqs. (2) and (3) of determining the correct monomer ratio in generating a copolymer with a desired composition. Figure 6 also indicates that initially VA was still consumed faster than VP and the VP and VA addition ratio should be adjusted accordingly.

Sample 6: This was similar to sample 5 except that the VP to VA mol ratios in the initial charge and feed were 0.48 and 1.26, respectively, determined based on eqs. (2) and (3) and the experimental results of sample 5 as well. In Figure 7, the VP and VA conversion curves almost coincide for the major portion of the reaction, indicating a substantially homogeneous copolymer was generated by carefully controlled the monomer feedings. The rates of VP and VA transferring into the copolymer chains were almost the same.

The homogeneity in backbone monomer distribution of samples 3 to 6 were demonstrated by their solubility in water and the cloud points. Figure 8 presents the turbidity measurements of 10% aqueous solutions of samples 3 to 6, by using HACH Ratio Turbidimeter, over the temperature range from ambient temperature to 80°C. At the same temperature, the lower HACH number means the sample has a better solubility in water and the solution has a higher cloud point.

Sample 3 had very poor solubility in water. Its solution was very hazy at room temperature with HACH reading higher than 200 ntu, indicating its cloud point is below room temperature, which is consistent with the large spread in VP and VA conversion curves as shown in Figure 4, and its resultant heterogeneous microstructure. Samples 4 to 6 had increasingly better solubility. Their solutions were clear (HACH reading below 20) at room temperature, and turned hazy at much higher temperatures. Especially for Sample 6, the cloud point was higher than 80°C. Turbidity measurement at higher temperature was impossible due the limit of experimental conditions. The trend of turbidity for solutions of Samples 3–6 appearing in Figure 8 shows excellent agreement with the trend of the approach of VP and VA curves for samples 3–6 appearing in Figures 4–7.

Because all the copolymer samples had identical VP/VA ratios and similar molecular weights, the difference of their solubility in water can only result from the differences in their microstructure homogeneity (the monomer unit distribution). The more homogeneous the PVP/VA copolymer, the better the solubility in water. The above results indicated that, even when the VP to VA mole

Figure 8 Turbidity of PVP/VA aqueous solutions. Samples 3–6. Monomer mole ratio = 53/47.

(a)   **(b)**

Figure 10 Conformation of PVP/VA in aqueous solution. (a) VA blocks form hydrophobic aggregation. (b) Random coil conformation.

ratio is close to unity, the copolymer can still be water soluble and have a cloud point much higher than room temperature. In this copolymer the monomer distribution must be homogeneous in the backbone, obtained by a control of the monomer feeding schedule.

The affect of copolymer backbone homogeneity on its solubility in water can be attributed to the balance between the hydrophobic and hydrophilic forces existing in the copolymer aqueous solution, which has been the subject of many investigations.[1–9] If the monomer feed method is not designed very well, due to the low reactivity ratio of VA, large VA blocks will be formed in the later portion of reaction, as shown in the schematic diagram given in Figure 9(a). In water these VA blocks may aggregate and form a hydrophobic domain, and its conformation is showed in Figure 10(a). Therefore, the copolymer precipitates out, phase separation happens, and solution appears cloudy. In contrast, if the monomer feed method is decided based on the reactivity ratios as shown in eqs. (2) and (3) and the VP and VA conversion rates are very close during the entire reaction process, the microstructure will be homogeneous,

VA units are uniformly separated by VP units, i.e., no large VA blocks will be formed, as shown in the schematic diagram given in Figure 9(b). Consequently in water there is no hydrophobic aggregation, the polymer chains exist as random coils and remain in solution, and the conformation is showed in Figure 10(b).

Li[3] reported that binding of the fluorescent probe, 1-anilinonaphthalene-8-sulfonate (ANS), to a PVP/VA sample with the VP mole fraction of 0.55 caused a strong enhancement of fluorescent intensity, compared with that of PVP and ANS complex. While the intensity of other PVP/VA samples, with the VP molar fractions of 0.84, 0.74, 0.70, decreased as the VP content decreased, and was lower than that of PVP and ANS complex. Also in the solution containing PVP/VA sample with VP mole fraction of 0.55 the emission λ_{max} exhibited a further blue shift, while the other PVP/VA solutions exhibited the same blue shift of PVP/ANS. These effects were attributed to the formation of hydrophobic domains in the PVP/VA solution when the VP and VA amounts in

Figure 9 Schematic diagram of PVP/VA chain. (a): Substantially heterogeneous structure, VA blocks formed. (b): Substantially homogeneous structure, no VA block formed.

the composition were close to equal. PVP/VA with high VA composition, prepared by Li through a traditional procedure, probably contains VA blocks, as we have shown in Figure 9(a), and forms hydrophobic domains in aqueous solution, as we showed in Figure 10(a). Therefore, Li's observation and conclusion are consistent with our above discussion.

Esumi et al.[4] reported their results of surface tension measurements on PVP/VA aqueous solutions, in which the copolymer compositions (mol VP/VA) were 92 : 8, 87 : 13, 66 : 34, and 20 : 80. Esumi et al. found that when the content of VA in PVP/VA increased, the surface tension was reduced significantly. However, their data showed that the surface tension of an aqueous solution of the PVP/VA sample with a VP/VA ratio of 66 : 34 was lower than that with a ratio of 20 : 80 in the entire measurement range, which did not follow the trend indicated by the authors. Similar abnormal phenomena for PVP/VA with a VP/VA ratio of 66 : 34 were also found in the decrease of surface tension in copolymer-surfactant systems and in the shifts of maximum fluorescence wavelength in copolymer solutions and in copolymer-surfactant systems. We believe the total content of vinyl acetate in the copolymer, as K. Esumi mentioned, has an affect on the PVP/VA aqueous solution behavior and on the interaction between the copolymer and surfactants. In addition, the lack of the VA homogeneity is, based on our study, another important factor. Details of sample preparation by K. Esumi et al. were not reported in their paper. The results would suggest that all VP and VA monomers were added before copolymerization was started and heterogeneous copolymer was formed. When the VP/VA ratio in PVP/VA become closer to unity, it is possible to have VA blocks in the copolymer chain, which may form hydrophobic aggregation in solution. Along with this special feature in the copolymer microstructure, its solution, including the surface tension, will behave abnormally. This composition deserves more attention.

Recently, GPC-Fourie Transform infrared spectroscopy, and GPC-nuclear magnetic resonance techniques were employed to investigate the homogeneity of the VP and VA copolymer, i.e., the sequence distribution, over the entire molecular weight distribution. The microstructure analysis results indicated that with the new copolymerization strategy, product with more constant composition was generated, which is consistent with the conclusion in this paper, as indicated by better water solubility discussed above. A paper to discuss the compositional analysis methods and results with GPC-Fourie Transform infrared spectroscopy and GPC-nuclear magnetic resonance measurement on PVP/VA copolymer will be submitted soon.

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