Synthesis, Characterization, and Solution Properties of Hydrophobically Modified Poly(vinyl alcohol)

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Received 5 January 1998; accepted 5 May 1998

ABSTRACT: A series of hydrophobically modified water-soluble poly(vinyl alcohol) (PVA) polymers was prepared by grafting urethanized PVA with varying fractions of fatty acid chlorides of various chain lengths. The objective of the synthesis was to prepare polymers that can be applied to enhanced oil recovery. The solution viscosity was investigated as a function of polymer concentration, temperature, shear rate, and salinity. Furthermore, the surface and decane-water interfacial tensions were investigated with respect to polymer and salt concentrations. Micelle formation was probed by measuring pyrene fluorescence as a function of polymer concentration. The solution viscosity was enhanced by the hydrophobic modification, compared with the unmodified PVA as a result of hydrophobic association. The viscosity of a 3% polymer solution decreased with increasing salt concentration from 0.0 to 6.0 wt %, above which some polymer precipitated from the solution. The solution viscosity decreased with both temperature and shear rate. Pyrene fluorescence measurements showed that hydrophobic micelles formed above a polymer concentration of 0.5%. The micelle formation was relatively insensitive to salt concentration. The surface tension decreased sharply with increasing polymer concentration to reach a minimum at a polymer concentration of 0.15% and then increased gradually up to a polymer concentration of 3%. Interfacial tension with *n*-decane showed a continuous decrease with polymer concentration. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2499–2506, 1998

Key words: hydrophobic association; fluorescence probe; micellar polymers; viscosity; interfacial tension

INTRODUCTION

Hydrophobically associating water-soluble polymers have attracted appreciable interest in recent years due to their potential commercial applications in the manufacture of cosmetics, paints, detergents, drug delivery systems, and drag reduction fluids. These polymers are composed of a water-soluble polymer containing a small fraction of hydrophobic moieties.¹⁻⁹ Above a certain polymer concentration, the hydrophobic groups from the same molecule and from different molecules tend to associate in aqueous solutions to minimize exposure to the hydrophilic medium. This association leads to formation of large intermolecular aggregates that behave as a single molecular species, resulting in substantial thickening equivalent to that observed of much higher molecular weight homopolymers.^{3,4} The physical links between the associated molecules break under increased shear. Consequently, irreversible mechanical degradation characteristic of high molecular weight polymers in high shear applications can be avoided.⁴ Furthermore, the presence of hydrophobic moieties in the polymer chain imparts desirable surface and interfacial activities

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Journal of Applied Polymer Science, Vol. 70, 2499–2506 (1998) © 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/122499-08

to the polymer.^{5,6} The combination of thickening and surface activity properties makes hydrophobically associating polymers ideal for application to enhanced oil recovery.

Preparation of associative water-soluble polymers can be conducted either by chemical modification of a reactive water-soluble polymer or by copolymerization of an appropriate combination of hydrophilic and hydrophobic monomers.⁶ The former synthesis route has been applied to cellulose derivatives; poly(oxyethylene); and polyacrylic, acrylic, and methacrylic ester copolymers. The latter route has been applied to copolymerizing acrylamide and maleic anhydride with different hydrophobic moities.^{8,9}

One of the commonly used water-soluble polymers is poly(vinyl alcohol) (PVA) that can be hydrophobically modified by garafting of long chain hydrophobic moities to form a comb copolymer.⁶ PVA contains hydroxyl functional groups, which can react with acid chlorides of long chain fatty acids to form ester linkages. Some reactions of fatty acid chlorides with PVA have been investigated,^{10,11} with the objective of producing materials that can be used in surface coatings and as substrates for photographic systems.⁶

Hydrophobically modified PVA exhibits enhanced viscofication properties, because the hydrophobic chains grafted to different molecules tend to associate in aqueous solutions to minimize exposure to the hydrophilic medium. This intermolecular association leads to the formation of molecular aggregates with large hydrodynamic volumes causing the observed increase in solution viscosity. Furthermore, as a result of the amphiphilic nature of the polymer caused by the presence of hydrophilic and hydrophobic domains, the polymer exhibits high surface and interfacial activities. In this study, the solution properties of hydrophobically modified PVA were investigated as part of a continuing program for the study of associative polymers as viscofiers and surface active agents in enhanced oil recovery applications. PVA was hydrophobically modified by chemical modification with long chain fatty acid chlorides. Prior to hydrophobic modification, PVA was partly urethanized by reaction with urea, because it has been established that urethanized PVA is more stable and more soluble in polar solvents, such as water, dimethylformamide (DMF), and dimethylsulfoxide (DMSO) than pure PVA.¹² The hydrophobe content of the associative copolymer was varied by changing the percentage of hydrophobic modifiers. The objective of the synthesis

process was to design polymers with both enhanced viscofication and improved interfacial activities. Solubilities of the resulting comb copolymers in water were determined. Viscosities of the soluble copolymers were then investigated under different conditions of polymer concentration, temperature, shear rate, and salt concentration. Interfacial properties of the copolymer solutions with air and an organic oil (*n*-decane) were also studied as functions of copolymer and salt concentrations. The nature of the hydrophobic domains and the onset of hydrophobic association were probed by measuring the variation of pyrene fluorescence with increasing polymer concentration in the aqueous medium.⁷

EXPERIMENTAL

Materials

PVA polymer with a degree of polymerization of 1,600 and a molecular weight of 72,000 was used as received from Fluka Chemie AG. Decanoic acid chloride, docosanoic acid chloride, and stearic acid chloride were also obtained from Fluka Chemie AG and were used as received. Urea, DMF, and DMSO were obtained from Fluka Chemie AG.

Instruments

Fluorescence measurements were conducted using a Shimadzu RF-5000 spectrofluorometer. Viscosity was measured using a Brookfield digital DV2PLUS viscometer. Surface and interfacial tensions (IFT) were measured using a KRUSS K12 process tensiometer.

Synthesis of Copolymers

PVA was first partly urethanized by adding 13.5 g of urea to a solution of 10 g of 97.5% hydrolyzed PVA in 50 mL of distilled DMF. The mixture was placed in a round-bottomed flask equipped with a thermometer, a magnetic stirrer, and a condenser. The reaction mixture was maintained at a temperature of 150°C under an atmosphere of nitrogen to prevent oxygen-free radicals from degrading the polymer. The reaction mixture was homogeneous within a few minutes from the start of the reaction, and the reaction was left to proceed, accompanied with evolution of ammonia for 2.5 h. The resulting polymer was then precipitated in methanol, filtered, and washed with liberal excess of methanol to remove any residual

Sample	Hydrophobe Content	Solubility
PVA1	C18 (1 mol %), C10 (1 mol %)	Insoluble (2-day stirring)
PVA2	C18 (0.75 mol %), C10 (0.5 mol %)	Insoluble (2-day stirring), cloudy, low viscosity
PVA3	C18 (0.75 mol %), C10 (0.5 mol %)	Insoluble (2-day stirring), foamy, slightly viscous
PVA4	C18 (0.5 mol %), C10 (0.5 mol %)	Soluble (2-day stirring), highly viscous
PVA5	C18 (0.5 mol %), C10 (0.25 mol %)	Soluble (2-day stirring), viscous

Table I Water Solubility of Various Hydrophobically Modified PVAs (3 wt % Polymer in Solution)

impurities from the polymer. The polymer was then dried under vacuum at 70°C until a constant weight was obtained.

The hydrophobic modification step was conducted by dissolving 4 g of the urethanized polymer in 40 mL of distilled DMF at 140°C. The mixture was gently stirred until a homogeneous solution was obtained. Solutions with various concentrations and compositions of the fatty acid chlorides in DMF were added dropwise to the reaction mixture with vigorous stirring. The reaction was conducted under an atmosphere of nitrogen to prevent polymer degradation by oxygen-free radicals. After 2 min of reaction time, the reaction mixture was cooled and the resulting polymer was precipitated into methanol, filtered, and then dried at 70°C under vacuum. Different fractions of the hydrophobic chains were incorporated by varying the fractions and types of the fatty acid chlorides added to the reaction mixture. The fractions and types of fatty acid chlorides used in the hydrophobic modification are shown in Table I.

Measurement of Viscosity

Solution viscosities of the copolymers were investigated with respect to polymer concentration, temperature, shear rate, and salinity. Concentrated stock solutions of the copolymers were prepared 72 h prior to viscosity measurement. The dissolution process lasted for 1-2 days. Final solutions were obtained by dilution of the stock solution to the desired concentration. Saline solutions were prepared by dissolving solid NaCl in the dilute polymer solution and stirring gently for 2 h. Viscosities were then measured using the digital Brookfield rotational viscometer with UL adapter accessories or an SC4-18 spindle accessory, whichever was appropriate at shear rates ranging from 0.79 to 7.92 s^{-1} . The temperature of measurement ranged from 30 to 70°C.

Measurement of Surface Tension (ST) and Interfacial Tension (IFT)

Similar to the viscosity measurements, solutions of various polymer concentrations were prepared

by diluting concentrated stock solutions of the copolymers. Solid NaCl was dissolved in the dilute solutions by gentle stirring for 2 h. The airliquid STs of the copolymer solutions were determined using the plate method. All measurements were performed at 25°C. The polymer concentration ranged from 0.0 to 3.0 wt %. Effect of salinity was investigated by measuring the ST of a 1.0 wt % polymer solution with salt concentrations ranging from 1 to 6 wt %.

The IFTs between *n*-decane and copolymer solutions were determined using the ring method. The IFT was measured as a function of polymer concentration in the range from 0.0 to 3.0 wt %. The effect of salt on IFT was investigated for a 0.5% polymer solution, with salt concentration ranging from 1.0 to 6.0 wt %. All of the ST and IFT measurements were conducted at 25°C.

Probe Studies of Host Sites

The nature of the hydrophobic sites and the onset of association in aqueous polymer solutions were probed using pyrene. The utility of pyrene as a fluorescent probe in the study of organized assemblies has been demonstrated.^{13–17} Variation of the ratio of the third (I₃) to the first (I₁) pyrene fluorescence peaks in hydrophobically modified polymer solutions is indicative of the nature of the pyrene environment in solution.⁷ A more hydrophobic environment is indicated by a higher (I₃/I₁) peak ratio.

A saturated aqueous solution of pyrene was first prepared followed by dissolution of solid polymer to form a solution with the desired copolymer concentration. Fluorescence measurements were then conducted for copolymer concentrations ranging from 0.01 to 0.5 wt %.

RESULTS AND DISCUSSION

Solution properties of hydrophobically modified PVA copolymers were studied under different conditions of copolymer and salt concentrations,



Figure 1 Variation of viscosity with shear rate for unmodified PVA and PVA4 solutions at 25°C.

temperature, and shear rate. The compositions and water solubilities of different combinations of fatty acid chlorides with PVA are shown in Table I. It can be seen that only two samples were soluble in water and showed enhancement in viscosity. The foam formation indicates a high surface activity of the polymer. These solubility results indicate that a delicate balance is required between the number and size of hydrophobic segments and size of the hydrophilic backbone polymer to both maintain solubility and obtain hydrophobic association in solution. An excess in the percentage and size of the hydrophobic side chains results in a decrease in solubility (samples 1 and 2), whereas a reduction beyond a certain limit results in loss of associative behavior. Because PVA4 (containing 0.5% C_{18} and 0.5% $\mathrm{C}_{10})$ and PVA5 (containing 0.5% $\mathrm{C_{18}}$ and 0.25% $\mathrm{C_{10}})$ were the only samples displaying high solubilities and promising properties, all of the subsequent detailed studies were conducted using these two samples.

Figure 1 shows the change in viscosity of polymer solution as a function of shear rate for unmodified PVA in comparison with the hydrophobically modified PVA (sample PVA4). The modified PVA shows a much higher viscosity, compared with the unmodified polymer over the whole shear rate range, indicating that hydrophobic association is in effect at the PVA4 concentration used. Figure 2 shows the change in viscosity of PVA4 as a function of polymer concentration at two different shear rates. The change in viscosity shows a gradual increase at low concentrations, followed by a sharper increase at a polymer concentration of 2.5%. This phenomenon indicates the presence of a critical polymer concentration above which appreciable aggregation takes effect in the solution. This behavior is expected because at low polymer concentrations, the hydrophobic chains have little chance of interacting with one another and as a result form intramolecular aggregates with a small hydrodynamic radius. At higher polymer concentrations, intermolecular interactions dominate and aggregates with larger hydrodynamic volumes are formed leading to the observed increase in viscosity.¹⁸⁻²² To probe the onset of hydrophobic association in solution, fluorescence of pyrene in solution was measured as a function of concentration of the modified PVA. Figure 3 shows the ratio of the third (I_3) to the first (I_1) fluorescence peaks of pyrene in the copolymer solution. It can be seen that the peak ratio (I_3/I_1) reaches the hydrophobic limit at a copolymer concentration of 0.5 wt %. Shown in the same graph is the ratio of the two fluorescence peaks in the presence of 5.0 wt % salt. No significant change is observed in the fluorescence behavior of pyrene in the presence of salt, compared with the



Figure 2 Variation of the viscosity of PVA4 solution with polymer concentration at 25°C.



Figure 3 Variation of I_3/I_1 fluorescence peak ratio with PVA4 concentration in the presence and absence of NaCl.

unsalted solution, indicating that salt does not interfere strongly with the hydrophobic association process at low polymer concentrations. This type of behavior is typical of nonionic polymers, where the absence of charges on the polymer chain minimizes interactions with the salt ions. It can also be observed that the onset of hydrophobic association observed by pyrene fluorescence takes place at a much lower polymer concentration than the critical aggregation concentration observed in the viscosity measurements. The difference between the two critical concentrations results from the fact that the fluorescence measurement is conducted on a static solution in which hydrophobic aggregation can take place with no disturbance caused by the shear forces. On the other hand, the viscosity measurements are conducted under dynamic conditions where the shear forces interrupt formation of large aggregates, except at very high concentrations where the rate of formation of aggregates exceeds the rate of their degradation by shear forces.

Figures 4 and 5 depict the change in solution viscosity for polymers PVA4 and PVA5 as a function of shear rate for a polymer concentration of 2% and different salt concentrations. The viscosity of the polymer solution decreases from 2,800 cp at a shear rate of 0.79 s^{-1} to 2,100 cp at a shear rate of 16 s⁻¹ in the absence of salt. Adding 4 wt % salt reduces the total viscosity; however, the



Figure 4 Variation of PVA4 solution viscosity with shear rate at 25°C.

rate of change of viscosity with shear rate remains unchanged. Increasing the salt concentration to 6% results in some polymer precipitation and a subsequent drop in viscosity. The viscofication caused by the hydrophobically modified polymer results from the formation of large molecular aggregates characterized by high apparent molec-



Figure 5 Variation of 2 wt % PVA5 solution viscosity with shear rate.



Figure 6 Variation of viscosity with NaCl concentration for 3% PVA4 solutions at different shear rates.

ular weight and thus high viscosity. Under high shear conditions, the hydrophobic aggregates can be disrupted by the shear forces, which tend to disentangle and align the molecules resulting in a decrease in the size of the aggregates and, consequently, the measured viscosity. However, under low shear conditions, intermolecular association can reform, restoring the large aggregate size and hence the high viscosity. By comparing viscosity values from Figures 4 and 5, it can be observed that PVA4 shows a higher solution viscosity than PVA5, which indicates that the incorporation of a larger fraction of hydrophobic moities enhances association in solution.

Figures 6 and 7 show the effect of NaCl concentration on the viscosity of 3 wt % solutions of PVA4 and PVA5 at low and high shear rates. The viscosity decreased with increasing salt concentration from 0% to 5% for both shear rates. The solution tolerated up to 5% salt concentration, beyond which the polymer started precipitating. The decrease in viscosity with salt concentration is not typical of nonionic polymers similar to the one under investigation. However, the presence of salt ions might be decreasing the amount of water molecules available to dissolve the polymer, causing individual polymer molecules to coil on themselves and thus reducing the chances of intermolecular hydrophobic association. The smaller size of the polymer coils results in the observed decrease in viscosity.



Figure 7 Variation of viscosity with NaCl concentration for a 3 wt % PVA5 solution at two shear rates.

Figure 8 depicts the effect of polymer concentration on the air-water ST. The ST shows a sharp decrease up to a polymer concentration of 0.20 wt %, then it levels off. The initial sharp decrease in ST results from the migration of the hydrophobic moities to the air-water interface to minimize exposure to the hydrophilic medium.



Figure 8 Variation of ST with PVA4 concentration in the absence and presence of 5 wt % NaCl.



Figure 9 Variation of IFT with polymer concentration for PVA4 at 25°C (0 wt % NaCl).

When the interface is saturated with polymer molecules, the ST reaches a constant value. The influence of salt on ST is also shown in Figure 8. Compared with the unsalted solution, it can be observed that the salt shifts the minimum in ST to a lower polymer concentration (from 0.2 to 0.1 wt %) and lowers the ST at the minimum from 50 to 45 mN m⁻¹. The increased hydrophobicity of the medium induced by presence of salt ions causes more of the hydrophobic side chains to migrate from solution to the interface at lower polymer concentration resulting in the observed shift and decrease in ST.

A similar behavior to the ST is displayed by the n-decane-water IFT. Figure 9 shows the IFT of the copolymer solution with n-decane as a function of polymer concentration. The lower IFT compared with ST values is a result of the greater hydrophobicity of n-decane, compared with air. Consequently, the concentration of hydrophobic chains at the oil-water interface is higher at lower polymer concentrations, compared with the air-water interface.

The change in IFT of a 0.5 wt % polymer solution with salt concentration is shown in Figure 10. The IFT decreases with increasing salt concentration and reaches a constant level at a salt concentration of 1 wt %. The slight decrease in IFT with salt concentration might be a result of the higher concentration of hydrophobic chains at

the interface as a result of the greater hydrophobicity of the salt solution induced by NaCl ions. The drop in IFT observed at 5 wt % salt concentration is a result of partial precipitation of some polymer from solution.

CONCLUSIONS

A series of associative hydrophobically modified PVA comb copolymers have been prepared by esterification of urethanized PVA with different combinations and ratios of long chain fatty acid chlorides with the objective of producing copolymers with high solution viscosities and high surface and interfacial activities. The main objective of the synthesis was to maintain the delicate balance between hydrophilic groups and hydrophobic moities in such a way to preserve water solubility and promote hydrophobic association. Two combinations of hydrophobically modified urethanized PVA were characterized by this balance and, as a result, were characterized with high solubilities and good thickening and interfacial properties, comparable with those required in enhanced oil recovery applications at a low concentration. The first combination contained $0.5\%~C_{18}$ and $0.5\%~C_{10}$ (PVA4), whereas the other contained 0.5% C_{18} and 0.25% C_{10} (PVA5). PVA4 had better thickening properties compared with PVA5, indicating that the incorporation of a larger



Figure 10 Variation of IFT of 0.5 wt % PVA4 solution with salt concentration.

fraction of hydrophobic moities enhances association in solution as long as solubility could be maintained. The polymer solutions were found to be salttolerant up to a salt concentrations of 6 wt %. The viscosities of the solutions were lowered by the addition of salt. The decrease in solution viscosity in the presence of salt is attributed to the contraction of polymer as a result of the reduction in the number of water molecules available for dissolving the polymer. The contraction of polymer chains leads to entrapment of hydrophobic chains, which in turn causes a reduction in hydrophobic association. When probed by pyrene fluorescence, the hydrophobic association was determined to start at a relatively low polymer concentration of ~ 0.5 wt %. The onset of association was not significantly influenced by the presence of salt, which indicates that the effect of salt on hydrophobic association is not significant at low polymer concentrations. The polymer solution showed a typical shear thinning behavior at low shear rates with the viscosity reaching a constant asymptotic value at high shear rates. This behavior is advantageous in enhanced oil recovery applications where injecting the polymer at high shear in the injection well bore reduces power consumption. The polymer solution viscosity increased as the solution moved away from the well bore. As the solution penetrates more deeply into the formation, higher temperatures reduce solution viscosities. The polymer showed greatly enhanced interfacial properties with air and *n*-decane. The surface and interfacial activities were relatively insensitive to salt concentration.

The polymer reduced air-water and oil-water IFTs appreciably at very low polymer concentration. IFT is lower than ST because of the more favored hydrophobic environment of n-decane, compared with air.

The facilities provided by King Fahd University of Petroleum and Minerals are gratefully appreciated.

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