Polymer Bulletin 18, 385–389 (1987)

Polymer Bulletin

Synthesis of poly(vinyl alcohol-co-vinyl gallate) by the chemical modification of poly(vinyl alcohol)

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Summary

Poly(vinyl alcohol-co-vinyl gallate) was successfully synthesized utilizing an esterification reaction in which poly(vinyl alcohol) was transesterified with methyl gallate under alkaline conditions. Aqueous solutions of this copolymer exhibited a sharp critical micelle concentration value, indicating that surface activity is exhibited by the copolymer. Most aqueous solutions of this copolymer possess a black coloring, which indicates that the gallate group is complexing with metal ions present in solution.

Introduction

In the past, there has been a significant amount of work concentrating on modifications of poly(vinyl alcohol). Most of these studies have dealt with either preparing graft copolymers or varying the degree of hydrolysis. This study deals with the modification of poly(vinyl alcohol) via a transesterification reaction. Poly(vinyl alcohol) was reacted with methyl gallate-(methyl-3,4,5-trihydroxybenzoate) utilizing potassium tert-butoxide as a base catalyst[1]. This reaction can be successfully carried out, but the following critical conditions must be utilized: i) dilute solutions, ii) careful control of reaction temperature, and iii) anhydrous conditions.

Experimental

Commercial grade poly(vinyl alcohol) of M_n = 25,000 was purified by dissolving it at 90°C in distilled water, and reprecipitating in acetone. The polymer was dried at room temperature under vacuum. A dilute solution (less than 6.5% by weight) of purified poly(vinyl alcohol) and dimethyl sulfoxide was prepared by heating to 80°C in a round bottom flask which was equipped with a hot plate and a magnetic stirrer. The solution was purged with dry nitrogen for approximately 5 minutes, and the temperature of the solution was lowered to 75°C. After the addition of potassium tert-butoxide (0.4% by weight) the reaction mixture was again stirred for 5 minutes, then methyl gallate was added with stirring and the temperature was maintained between 75° - 78°C. The reaction was carried out for a variable length of time, ranging from 20 min to 4 hours, in order to obtain different amounts of substitution. After the required period of time, the reaction was quenched, and the

polymer was precipitated by pouring the reaction solution into a beaker containing acetone, in an approximate volume ratio of one part reaction solution to ten parts acetone. The crude polymer precipitate was filtered and washed with small amounts of methanol to remove any by-products. The polymer was dried at room temperature under vacuum for 12 hours.

The production and solubility of the by-products were tested by running the reaction under the same reaction conditions except, in the absence of poly(vinyl alcohol). This reaction solution was quenched in acetone and washed with methanol which dissolved the precipitate.

Critical micelle concentrations (CMC) were determined for the copolymers prepared in this study and for poly(vinyl alcohol) utilizing the Rosano Surface Tensiometer.

The structure of the purified copolymer was verified by both infrared and ultraviolet spectroscopy.

Results and Discussion

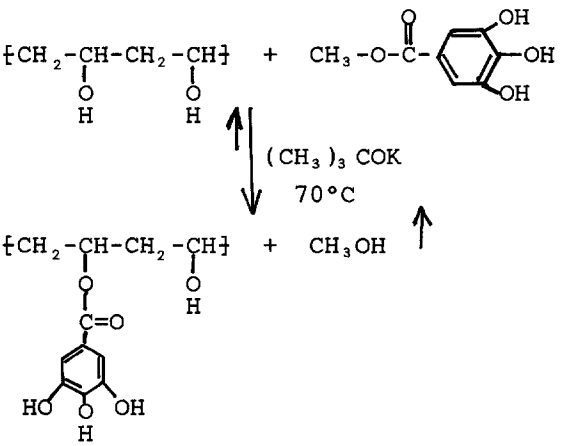
Although the utilization of poly(vinyl alcohol) as a surface active material has been of interest for a long time, in some applications, its effectiveness has not always met the requirements. For example, in applications where poly(vinyl alcohol) is used as a stabilizing agent for poly(vinyl acetate) latices, instability often results. Since the modification of poly(vinyl alcohol) for improved properties has received interest both industrially and academically, the synthesis of custom designed materials has gained importance for many applications such as the previously mentioned case.

The study reported here deals with the synthesis of a vinyl alcohol - vinyl gallate copolymer. The purpose of this research was to prepare a surfactant which would exhibit some unique characteristics possessed by the gallate group. One such characteristic is the ability of the gallate group to function as a metal chelating agent in which it complexes with metal ions in solution[2,3,4] . This capability may offer some distinct advantages in stabilizing a latex and in improving the properties of a film resulting from the application of that latex. Experimental results show that this surface active copolymer cannot be used in emulsion polymerization, but it can be beneficial as surfactant or co-surfactant for the preparation of a polymer colloid. When using the latter approach, the results indicate that film forming properties are enhanced for polystyrene latices. The films were continuous and they possessed stronger bonds to metal substrates than latices without the copolymer.

The inhibition observed during the emulsion polymerization in the presence of this copolymer-surfactant, could be explained by the observation made by Kurland[5]. He claims that substituted phenols such as p-methoxyphenol and similar materials act as inhibitors in the presence of oxygen. In order to circumvent this problem, the emulsion polymerization system was purged with dry nitrogen, but the polymerization was still unsuccessful. The reason for this failure was not ascertained. The possibilities include complexation between

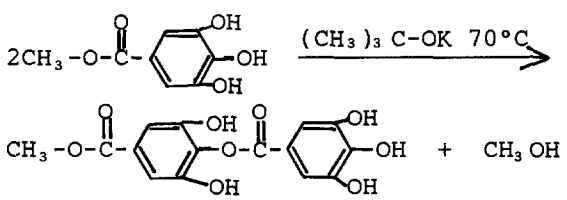
the gallate group and the initiator causing inhibition.

Experimentally, the transesterification reaction proceeds according to the following equation:[1]



As indicated by the above equation, this reaction is at equilibrium. In order to push the equilibrium far to the right, one of the products must be removed. The methanol by-product is the easiest to remove, and this can be accomplished by running the reaction above 65.5°C, its boiling point.

There are obviously some possible side reactions which could have a detrimental effect on the yield. One of the major side reactions is a transesterification reaction between the hydroxyl groups on the benzene ring and the ester group. This occurs according to the following equation:



Even though this reaction occurs, the substitution onto poly (vinyl alcohol) occurs more readily due to the following reasons: i) The aromatic hydroxyl groups are less nucleophilic than the hydroxyl groups on the polymer, ii) The hydroxyl groups on the benzene ring will complex with the potassium ion in solution thereby, rendering these groups less reactive. However, only a careful purification technique will ensure a pure product. In the case where reaction time was less than one-half hour, acetone had precipitated only the polymer and not the by-product. For longer reaction times, it was necessary to wash the precipitated polymer with methanol to insure a pure product.

The percent yield was considerably lower than one would expect. The values were generally less than 55%. This

observation is probably due to side reactions and loss during purification procedure.

Critical micelle concentrtions (CMC) were determined for poly(vinyl alcohol) and the new copolymer. Table I shows the results, where it can be seen that both the homopolymer and copolymers exhibit a CMC. The CMC values will differ depending on the reaction time or the extent of substitution. The higher the extent of substitution, the higher the CMC. These results seem reasonable because the CMC should be expected to increase with increasing water solubility, and the water solubility is increased with increasing gallate functionality.

Table I

Cricical Micelle Concentrations

Surfactant	CMC
PVA (mw. 25,000)	0.36
Copolymer I*	0.40
Copolymer II**	1.40

* Reacted for 20 minutes

**Reacted for 3 hours

Infrared and ultrviolet spectroscopies were used to verify the structure of the prepared copolymer. In the case of infrared spectroscopy, the spectrum of the vinyl alcohol-vinyl gallate copolymer as shown in Figure 1 exhibited an absorption at 1580 cm^{-1} which is due to the carbon-carbon double bond ring stretch. There was also an increase in the absorption due to the carbonyl group at 1710 cm^{-1}.

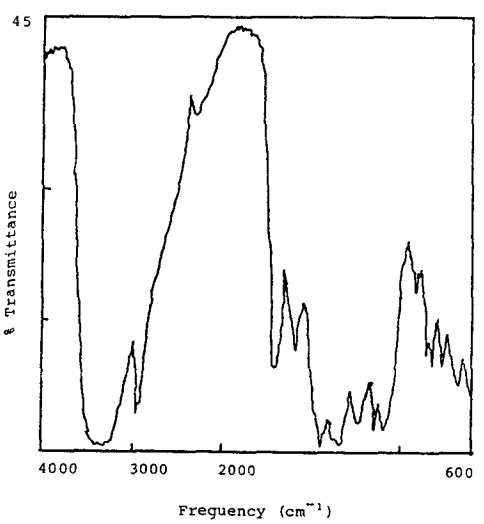


Figure 1. IR Spectrum of Vinyl alcohol-Vinyl Gallate Copolymer

In the case of ultraviolet spectroscopy, the spectrum of the vinyl alcohol-vinyl gallate copolymers as shown in Figure 2 exhibited a maximum at approximately 270 nm which is due to the gallate functionality.

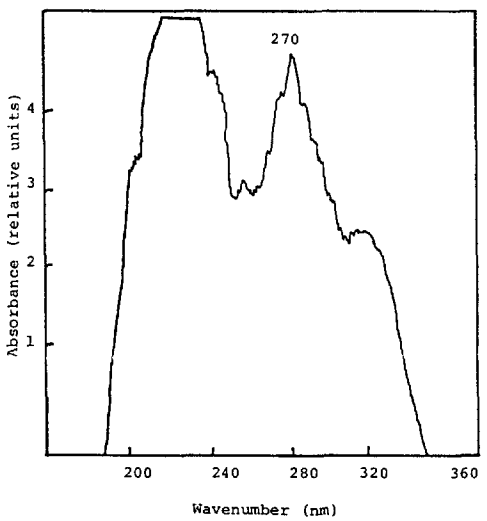


Figure 2. UV Spectrum of Vinyl Alcohol-Vinyl Gallate Copolymer

One unique aspect is that the color of the purified copolymer had a dark brown to black color as did the reaction solution. This coloration is the result of the gallate group complexing with the metal ions and removing these ions from solution upon coagulation of the copolymer[2].

Conclusion

The results of this study can be summarized as follows: Transesterification reactions utilizing base catalysis were used to successfully synthesize poly(vinyl alcohol-co-vinyl gallate). As the extent of substitution increases, the water solubility and the CMC increases also. IR and UV spectroscopies provide evidence that this product was obtained.

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Accepted August 24, 1987 K