

## Synthesis and characterization of hydrophobically modified poly(vinyl alcohol)

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### Summary

Two different routes for the preparation of hydrophobically modified poly(vinyl alcohol), PVA are reported. The first method involves the formation of the polymeric alcoholate. An alkylhalide and propanesultone are coupled with the polymer in two subsequent steps of the Williamson ether synthesis. The product is a hydrophobically modified polymer with anionic functionality. The other method proceeds via a 1,4 addition of acrylamide and the Hoffman degradation of the amide to an amine. In the next step, the amine is alkylated with an alkylhalide. The polymers are characterised by quantitative <sup>1</sup>HNMR spectroscopy and titration.

### Introduction

In recent years there has been a growing interest in the use of hydrophobically modified water-soluble polymers or associative thickeners (1,2) for different industrial applications. Above a certain concentration in aqueous solutions of the polymer, the hydrophobic moieties start to interact in order to minimise their exposure to water. The molecules associate and create physical links between the polymer chains. The viscosity of such a solution may show several tenfold increases when compared to the corresponding solution of the unmodified polymer. When a solution of a hydrophobically modified polymer is subject to shear forces, the physical links are disrupted and a shear thinning behaviour is observed. These links reform when the shear is removed and the zero shear viscosity is regained. Very high molecular weight polymers such as polyacrylamide commonly used in enhanced oil recovery operations, may undergo mechanical degradation when being exposed to the high shear forces that are encountered during injection into the reservoirs. The zero shear viscosity may not be regained (3). The polymer solution is also subject to other strenuous conditions such as high salinity, elevated temperatures and high pressure. The polymer solution should keep its properties after several years in such environments.

One approach to solve these problems is to manufacture a hydrophobically modified polymer of relatively low molecular weight, which also has a good chemical stability. There are several different water-soluble polymers that can be used as a starting material for the manufacture of a hydrophobically modified water-soluble polymer; polyacrylamide, poly(ethylene glycol), cellulose ethers and poly(vinyl alcohol). PVA is a polymer with good chemical stability and it has an abundance of hydroxyl groups that are relatively easily modified by different synthetic methods.

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There may however be a problem with the water solubility of the hydrophobically modified PVA (4), and further modification may be necessary in order to improve the water solubility of the polymer.

Two of the most common reactions of the hydroxyl groups are esterification and etherification. Esterification of PVA with acid chlorides (5) is an established method and esterification of PVA with fatty acids has recently been reported (4). To improve the water solubility of the modified PVA, it was urethanised with urea. The ester bond is however easily hydrolysed and chemical modification with ether linkages may be a better approach. The ether bond is much more stable than the ester bond. One method that involves the formation of the dimethylsulfinyl anion by sodium hydride in DMSO has previously been reported (6). In that case, the alcoholate of PVA is prepared prior to addition of the reagents. Epoxies are also reported to be used in the etherification of PVA (7).

The carbonyl group in aldehydes or ketones may be coupled to PVA via the acetal (8) or ketal (9) functionality. The aldehyde may even be prepared *in situ* by the Kornblum reaction (10). The hydroxyl functionality of PVA also reacts with isocyanates (11) to produce carbamic esters. Other routes to produce hydrophobically modified PVA are by copolymerisation methods (12).

The aim of this study is to establish simple methods to prepare hydrophobically modified PVA, where the hydrophobic groups are linked to the polymer backbone via an ether bond. Two different approaches are studied:

1. The Williamson ether synthesis, in which the alcoholate of PVA reacts with both an alkylhalide and propane sultone. The latter reagent is used to introduce sulfonic acid functionality to the polymer. This is done to recapture water solubility of the polymer after a large number of hydrophobic groups are added to the polymer chain. The coupling between PVA and propane sultone has previously been studied (13), but then different synthetic conditions were used. We believe that this is the first time the synthetic conditions using the solvent *N*-methyl-2-pyrrolidone (NMP) and the base potassium *tert*-butoxylate are reported. The are two main advantages by this method. Potassium *tert*-butoxylate is not as strong as sodium hydride, it is easier to handle and the reaction proceeds without an intermediate anion such as the dimethylsulfinyl anion. The second advantage is the use of NMP instead of DMSO. DMSO may under certain conditions oxidise the hydroxyl functionality (14).
2. The 1,4 conjugate addition (Michael addition) with acrylamide, followed by the Hoffman degradation to an amine. The amine then undergoes a nucleophilic substitution with an alkylhalide. The hydrophobe are linked to the polymer backbone via both an ether linkage and an amine linkage. Both reactions are well studied and the first step has been employed to PVA before using acrylamide (15) and acrylonitril (16). We believe this is the first time this method has been used to synthesise hydrophobically modified PVA. The first step is performed in water. The second step is done in NMP and anhydrous conditions are not required.

## Experimental

### Materials

PVA (TCI-EP,  $M_n = 77000$ ) was further hydrolysed in 0.1 M NaOH (aq) using reflux under nitrogen for 3 hours, dialysed against water and freeze dried. *N*-methyl-2-

pyrrolidone, NMP (Fluka, >99%) was distilled under vacuum from  $\text{CaH}_2$ . Acrylamide (Fluka, 99%), 1,3 propanesultone (Fluka, 98%), potassium *tert*-butoxylate (Fluka, 97%), 1-brom hexadecane (Fluka, 98%) and bromine (Fluka, 99%) were used as received. Potassium carbonate was dried at 150°C overnight. The glass equipment was dried for at least 24 hours at 150°C prior to use. The water was distilled twice.

#### *Hydrophobically modified PVA via the Williamson ether synthesis.*

PVA was dissolved in NMP (4 wt%) at 130-150°C and cooled down to 50°C. The reaction mixture was stirred vigorously and kept under nitrogen throughout the whole process. Propane sultone was added followed by dropwise addition of a solution of the base, potassium *tert*-butoxylate in NMP. The relative low reaction temperature and the dropwise addition of the base are important to avoid discolouring of the polymer. The molar ratio of base to sultone was 1:1. The addition was completed after 1½ hour. Then after 30 minutes, 1-brom hexadecane is added and more of the base is added dropwise. The reaction time in the second step was 3 hours and the molar ratio of the base to the alkylhalide was 1:1. The reaction mixture was then allowed to stand for another ½ hour before the polymer was precipitated with a 1:1 mixture of acetone-hexane and filtered off. The product was redissolved in water and dialysed, first against 0.1 mM HCl, and then against water. Freeze-drying isolated the polymer. Water insoluble polymer was washed several times with acetone and dried under vacuum. The reaction was also tried up to a fourfold increase in the total reaction time in one or both steps.

#### *Hydrophobically modified PVA via Michael addition of acrylamide*

PVA was dissolved in carbonate buffer (pH = 10) to give a 6 wt% solution. Acrylamide was added and the reaction was allowed to proceed at room temperature for 2.5 - 70 hours before a solution of  $\text{Br}_2$  in 6 M NaOH (aq) was added dropwise (molar ratio acrylamide- $\text{Br}_2$ -NaOH 3:4:20). After heating to 70°C, the mixture was allowed to stand at least 30 min before the excess bromine was destroyed with methanoic acid. The aminoethylated polymer was dialysed, first against 0.1 mM HCl, and then against water. Freeze-drying isolated the polymer. Large quantities of the polymer were first precipitated with a 5:1 mixture of acetone-ethanoic acid, and then redissolved in water prior to dialysis. The aminoethylated PVA was dissolved in NMP (4 wt%) under nitrogen and cooled down to 50°C. A large excess of dry potassium carbonate was slurred into the solution and 1-brom hexadecane was added. After 5 hours, the polymer is precipitated with a 1:1 mixture of acetone-hexane, filtered off, redissolved in water, dialysed several times against water and finally freeze-dried.

#### *Characterisation*

The amount of sulfonic acid or amino hydrochloride on the polymer chains was determined by titration with 0.02 M NaOH (aq) using phenolphthalein as indicator. Elemental analysis of one sample of the aminoethylated PVA was employed in order to verify the results obtained by titration.

The amount of hydrophobic groups on the polymer chain was determined by quantitative  $^1\text{H}$ NMR spectroscopy (17). The spectra were recorded at 25°C on a Bruker Advance DPX 300 spectrometer equipped with a 5 mm QMP probe, using about 1 wt%

solution in DMSO- $d_6$  and 10 s delay time. The area under the peak assigned to the methene protons ( $\text{CH}_2$ ,  $\delta \approx 1.2$  ppm) and the methyl protons ( $\text{CH}_3$ ,  $\delta \approx 0.9$  ppm) on the alkyl substituent was compared to that for the methine ( $\text{CH}$ ,  $\delta \approx 3.9$  ppm) protons on the polymer backbone.

IR spectra were recorded on a Nicolet Magna IR 550 spectrometer using KBr tablets.

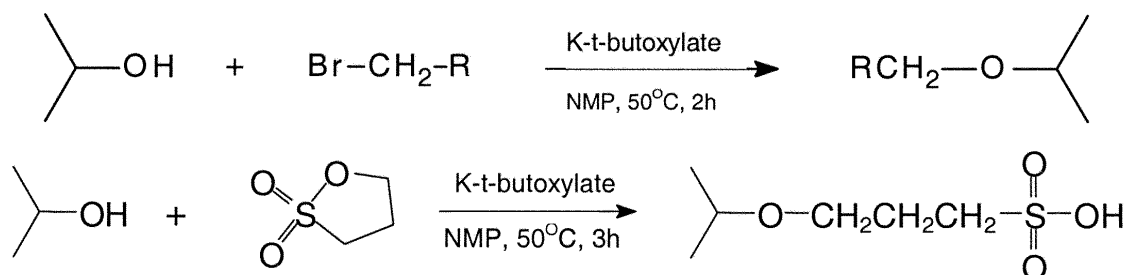


Figure 1. The reaction scheme for the Williamson ether syntheses,  $R = \text{C}_{15}\text{H}_{31}$

Table 1: Assignment of the peaks from the  $^1\text{H}$ NMR spectrum in Figure 2.

Multiplicity	$\delta$ (ppm)	From
triplet	4.2/4.45/4.65	hydroxyl protons, the ratio 1:2:1 indicates an atactic polymer
broad	3.8	methine(CH) protons from the polymer backbone
singlet	3.3	water
five	2.5	DMSO
broad	1.4	methene ( $\text{CH}_2$ ) protons from the polymer backbone
singlet	1.2	24 of the methene protons from the alkyl side chain
triplet	0.9	methyl protons from the alkyl side chain

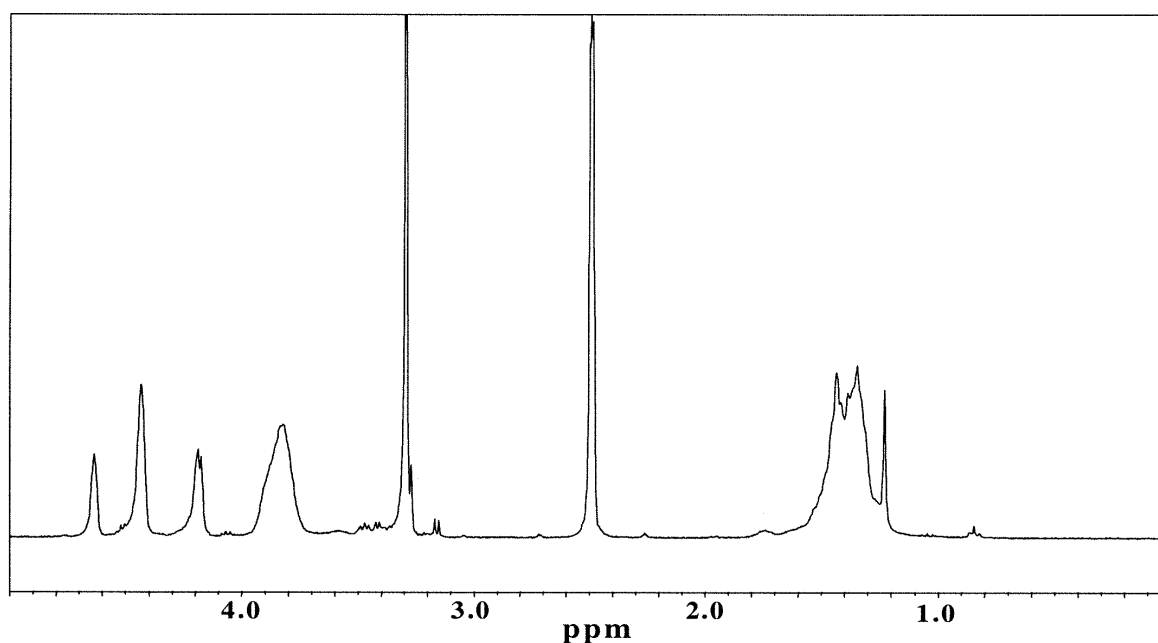


Figure 2. The 300 MHz  $^1\text{H}$ NMR spectrum of hydrophobically modified PVA prepared by the Williamson ether synthesis.

## Results and Discussion

### *Hydrophobically modified PVA via the Williamson ether synthesis.*

The reaction scheme for the preparation of sulfopropylated and hexadecylated PVA can be written as a sequence of two steps of the Williamson ether syntheses. This is displayed in figure 1.

The IR spectrum of the modified PVA has two peaks, at  $1038\text{ cm}^{-1}$  and  $1387\text{ cm}^{-1}$  that is assigned to the sulfonic acid group  $-\text{SO}_3\text{H}$ . The IR spectrum also shows a large increase of the absorbance in the  $\text{CH}_2$  region, at about  $2900\text{ cm}^{-1}$ . Figure 2 shows the 300 MHz  $^1\text{H}$ NMR spectrum of a sample containing the modified PVA in  $\text{DMSO-d}_6$ . The assignment of the peaks is given in table 1. Extracting the area under the peak at  $\delta \approx 1.2\text{ ppm}$  is not straightforward and the error was estimated to be about  $\pm 10\%$ . This peak contains 24 of the methene protons on alkyl substituent. The signals from the two methene groups closest to the ether bond are going to show up at higher frequency.

The maximum degree of substitution tried in this study was 20% for the alkylation and 10% for the sulfopropylation. The experimental degree of substitution is plotted against the theoretical value in figure 3. The error bars indicate the error in each single determination of the degree of substitution. The average yield for the alkylation is about 50% and the average yield for the sulfopropylation is about 30%. The yield did not improve with longer reaction times. The two steps of the reaction were also carried out in the reversed order with no detectable change in the yield. The main reason for the low yield is probably the relative low concentration of polymer in NMP. Competing reactions, such as elimination is going to be more pronounced when the concentration of the substrate is low.

### *Preparation of amino PVA via the Michael addition of acrylamide*

The Michael addition of acrylamide and the subsequent Hoffman degradation to the amine is outlined in Figure 4. The yield of this two step reaction, calculated from the amount of added acrylamide, is in the range of 6-9%. This low yield may be explained by the lowering of the nucleophilicity of the hydroxyl groups in the presence of water due to hydrogen bonding. The maximum degree of substitution tried was 60%; the experimental result was 5%. The yield is independent of the reaction time in the range of 2.5 - 70 hours. These findings indicate that the first step has reached equilibrium in the time range studied. The IR spectrum of the aminoethylated polymer did not show any signs of the carboxylate anion or amide, indicating that the second step the Hoffman degradation is almost complete. The amount of amino hydrochloride on the polymer determined by titration was verified by elemental analysis.

The alkylation of the amine with 1-brom hexadecane proceeded to about 100% conversion, calculated from the amount of added alkylhalide. Quantitative  $^1\text{H}$ NMR-spectroscopy was used in the determination (peak at  $\delta \approx 1.2\text{ ppm}$ ) of the amount of alkyl substituted on the amino functionalised polymer.

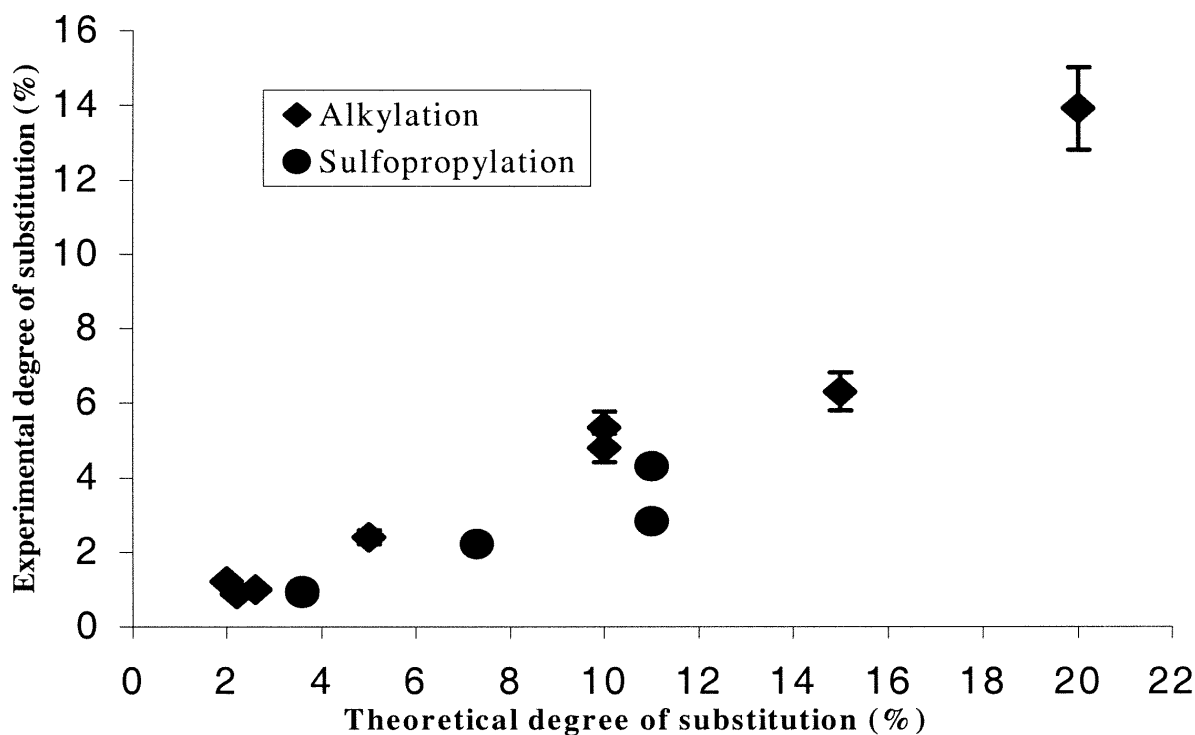


Figure 3. Experimental degree of substitution vs. theoretical value for modification of PVA by the Williamson ether synthesis.

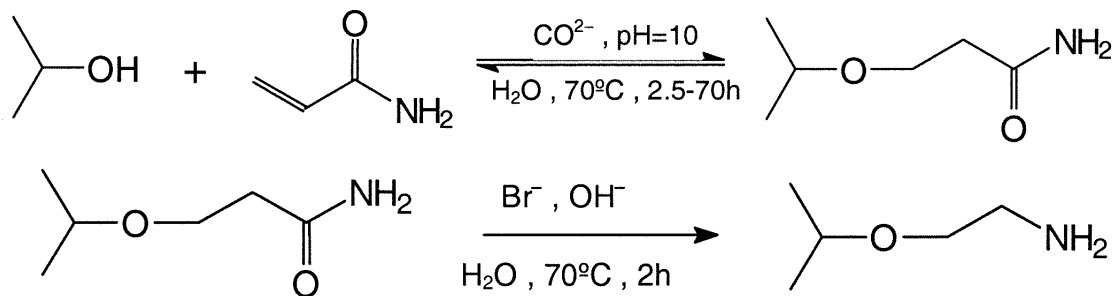


Figure 4. The reaction scheme for the Michael addition of acrylamide and the subsequent Hoffman degradation

## Conclusion

Two different methods for the preparation of hydrophobically modified PVA have been examined. They give either an anionic polymer containing sulfonic acid or an amino functionalised polymer. The degree of substitution may be predicted from the composition of the reaction mixture.

Further work will be undertaken in our laboratory to study the viscoelastic and dynamic behaviour of aqueous solutions of the modified polymers.

## Acknowledgement

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