Synthesis and Hydrolysis of β -Cyanoethyl Ether of Poly(vinyl alcohol)

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ABSTRACT: Poly(vinyl alcohol) (PVA) was cyanoethylated by reaction with acrylonitrile in the presence of sodium hydroxide and quaternary ammonium halide. Quaternary ammonium halide, acting as a phase transfer catalyst, increases the degree of substitution (DS) of PVA. The DS also increased with increasing acrylonitrile concentration. Cyanoethylation of PVA up to 98% can be achieved under optimum conditions. The hydrolysis of β -cyanoethyl ether of PVA (CN–PVA) was studied. The rate of hydrolysis was affected by the sodium hydroxide concentration and the reaction temperature. The rheological properties of aqueous solution of hydrolysis product of CN–PVA were determined at different temperatures, and the flow activation energy was calculated. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2771–2777, 1999

Key words: cyanoethylation; hydrolysis; rheology

INTRODUCTION

Poly(vinyl alcohol) (PVA) has found widespread industrial applications since its commercial introduction in the 1930s. It is a water-soluble and biodegradable polymer with excellent physical properties.¹ The properties of PVA can be modified by attaching substituents, such as acetate, acetal, or cyano groups, to its backbone.^{2–8} Cyanoethylation of PVA with acrylonitrile has received much attention. β -Cyanoethyl ether of PVA (CN-PVA) has a high dielectric constant with low dielectric loss tangent and high breakdown voltage and can be used as a polymer dielectric for electric luminescent screens.^{8–11} Through reaction with hydroxylamine, the nitrile groups in CN-PVA can be converted to amidoxime to bind cupric ions.⁵

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Journal of Applied Polymer Science, Vol. 73, 2771–2777 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/132771-07 To achieve a high degree of cyanoethylation of PVA, a high acrylonitrile-to-PVA ratio of about 8 to 10 is generally required.^{12,13} In this article, we report the cyanoethylation of PVA using quaternary ammonium halides as phase transfer catalysts to achieve a high degree of cyanoethylation. In addition, the hydrolysis of CN–PVA and the rheological properties of the hydrolysis product will be discussed. These are of practical importance for the application of the title polymer.

EXPERIMENTAL

Materials

PVA was a commercial product (BDH Chemicals Ltd.); its weight-average molecular weight was 14,000. PVA was purified by a conventional reprecipitation method using water as solvent and methanol as precipitant. Acrylonitrile was freshly distilled before use. Other chemicals were used as received.



Figure 1 IR spectra of (a) PVA and (b) CN-PVA.

Preparation of CN-PVA

100 mL of an aqueous PVA solution (3 mol [OH] L^{-1}) and 100 mL of 3*M* sodium hydroxide solution were introduced into a 500-mL three-necked, round-bottom flask equipped with a mechanic stirrer. To this, 200 mL acetone and the appropriate amounts of acrylonitrile and quaternary ammonium halide were added successively. The reaction was allowed to proceed for 6 h at 25°C. The upper layer was separated and poured into water. The precipitate was dissolved in acetone and reprecipitated in water to give CN–PVA. In the kinetic study, samples were withdrawn from the reaction mixture at appropriate times to determine the degree of substitution (DS).¹²

Hydrolysis of CN-PVA

1 g of CN–PVA with a degree of substitution of 98% and 15 mL acetone and 60 mL water were introduced into a 100-mL, three-necked, roundbottom flask equipped with a mechanic stirrer. To this, an appropriate amount of sodium hydroxide was added. The reaction was allowed to proceed for 15 h at 75°C. The mixture was then cooled and poured into absolute ethanol. The precipitate was dissolved in water and reprecipitated with absolute ethanol and finally dried in vacuum.

Measurements

The nitrogen content of CN–PVA was determined by the Kjeldahl method. The DS was calculated from the nitrogen content using the following formula:

$$\mathrm{DS} = rac{44 imes \mathrm{N}\,\%}{1400 - 53 imes \mathrm{N}\%}$$

The degree of hydrolysis (DH) of CN–PVA was determined according to a reported method.¹⁴

The rheological properties of the hydrolysis product in aqueous solution were determined using a NDJ-79 model rotary viscometer at various temperatures.¹⁵ Infrared (IR) spectra of the modified products were recorded with a NICOLET FT-20SX spectrophotometer.

RESULTS AND DISCUSSION

Cyanoethylation of PVA

PVA was cyanoethylated by reaction with acrylonitrile in the presence of sodium hydroxide and quaternary ammonium halide according to the following scheme:

$$\begin{array}{c} -(CH_2 - CH)_n - + m CH_2 = CHCN & \xrightarrow{Catalyst} \\ OH & \xrightarrow{OH^-} \\ -(CH_2 - CH)_{n-m} - (CH_2 - CH)_m - \\ & & | \\ OH & OCH_2 CH_2 CH_2 CN \end{array}$$

During the cyanoethylation of PVA, the OH groups were converted to OCH_2CH_2CN groups, as shown by the appearance of the C=N band at

Table I Effect of the Catalyst on the Cyanoethylation Reaction of PVA

Catalyst	TMAC	TEAI	TBAB	DDMEAB	No Catalyst
N%	12.22	12.08	12.85	12.35	$\begin{array}{c} 11.85\\ 66\end{array}$
Degree of substitution (DS)	71	70	79	73	

[NaOH] = 3 mol/L; [PVA]/[AN] = $\frac{1}{4}$; catalyst = 5 mol % of PVA; temperature, 25°C; time, 6 h.



Figure 2 Effect of concentration of TBAB on the DS of PVA. [AN]/[PVA] = 4 : 1; [NaOH] = [PVA] = 3 mol/L; time, 6 h; 25°C.

2249 $\rm cm^{-1}$ and the decrease of OH band at 3250–3365 $\rm cm^{-1}$ in the IR spectrum of CN–PVA (Fig. 1).

The cyanoethylation reaction was carried out under a variety of conditions. Variables included the structure and concentration of quaternary ammonium halide, acrylonitrile concentration, and reaction temperature.

As shown in Table I, the DS of PVA increased in the presence of quaternary ammonium halides, such as tetramethylammonium chloride (TMAC), tetraethylammonium iodie (TEAI), tetrabutylammonium bromide (TBAB), and dodecyldimethylethylammonium bromide (DDMEAB). The largest increase in DS was achieved when TBAB was used. This suggests that quaternary ammonium halide acts as a phase transfer catalyst. Since PVA is hydrophilic and acrylonitrile is hydrophobic, it is difficult for acrylonitrile to diffuse onto the surface of PVA. The addition of quaternary ammonium halide facilitates the diffusion of acrylonitrile onto the surface of PVA and so increases the DS of PVA. The effect of the concentration of TBAB is shown in Figure 2. The DS increases with increasing TBAB concentration initially; but when the concentration of TBAB increases beyond 5%, the DS decreases gradually with further increase in TBAB concentration.

For a constant amount of TBAB at 5 mol %, the effect of the concentration of acrylonitrile on the DS is shown in Figure 3. The DS increases with increasing acrylonitrile concentration and reaches 98% when the mole ratio of [PVA]/[AN] is 1 : 8. This suggests that the concentration of acrylonitrile plays an important role in the cya-



Figure 3 Effect of concentration of acrylonitrile on the DS of PVA: (\bullet) no TBAB; (\blacktriangle) TBAB = 5 mol % of [OH]. [NaOH] = [PVA] = 3 mol/L; time, 6 h; 25°C.

noethylation of PVA. Since the hydroxyl groups are attached to the PVA main chain, reaction of hydroxyl groups with acrylonitrile would depend on the availability of acrylonitrile molecules in their vicinity. With increasing acrylonitrile concentration, more acrylonitrile molecules diffused onto the surface of PVA, thereby promoting the reaction. The effectiveness of TBAB in cyanoethylation is also shown in Figure 3. In the absence of TBAB, a DS of 72% was achieved, while a near 100% conversion was achieved in the presence of TBAB.



Figure 4 Effect of temperature on the DS of PVA. [NaOH] = [PVA] = 3 mol/L; TBAB = 5 mol % of [OH]; [AN]/[PVA] = 4 : 1. Temperature (°C): (\blacklozenge) 25; (\blacktriangle) 30; (\blacklozenge) 35; (\blacksquare) 40.



Figure 5 IR spectra of CN–PVA at (a) 25 (b) 35 and (c) 45° C.

The relationship between the DS of PVA and reaction temperature is shown in Figure 4. It can be seen that the DS of PVA and the reaction rate increase with increasing temperature at first. However, at a temperature above 30°C, the DS decreases. The higher DS of PVA at 30°C than that at 25°C could be associated with increasing mobility of the acrylonitrile molecules, whereas the lower DS at temperature above 30°C is due to the partial conversion of the cyanoethyl groups to carboxyethyl groups under the effect of the alkali. This is supported by the appearance of the absor-



Figure 6 IR spectra of hydrolysis products of CN– PVA. Degree of hydrolysis (DH %): (a) 60; (b) 35; (c) 0.



Figure 7 IR spectra of hydrolysis products of CN–PVA. Degree of hydrolysis (DH %): (a) 60; (b) 75; (c) 89.

bance band of CONH_2 at 1676–1701 cm⁻¹ at 35 and 40°C, as shown in Figure 5.

Hydrolysis of CN-PVA

The IR spectra of the hydrolysis products of CN– PVA are shown in Figures 6 and 7. As the hydrolysis proceeds, the C=N band at 2224 cm⁻¹ disappears gradually. Meanwhile, the carbonyl band of CONH₂ at 1672 cm⁻¹ appears. However, the carbonyl band disappears slowly with the concurrent appearance of the carboxylate bands of COONa at 1570 and 1457 cm⁻¹. This suggests that the hydrolysis of CN–PVA occurs in two steps. The C=N group of CN–PVA was first converted into CONH₂, which was then converted to COONa.

$$\begin{array}{c} -(CH_2 - -CH) -_n & \xrightarrow{NaOH} \\ OCH_2CH_2CN & \xrightarrow{H_2O} \\ -(CH_2 - -CH) -_n & \xrightarrow{NaOH} \\ OCH_2CH_2CONH_2 & \xrightarrow{H_2O} \\ -(CH_2 - -CH) -_n \\ & & \downarrow \\ OCH_2CH_2COONa \end{array}$$

The dependence of the DH on the reaction time and the sodium hydroxide concentration is shown in Figures 8 and 9. The DH increases with in-



Figure 8 Effect of reaction time on the DH of CN– PVA. CN–PVA (1 g; DS = 98%); CH₃COCH₃ (15 mL); H₂O (60 mL); [NaOH] = [CN]; 75°C.

creasing NaOH concentration and reaches a maximum of about 90%. This shows that the C \equiv N groups of CN-PVA cannot be completely converted into COONa under the reaction condition. It is possible that the COONa groups initially incorporated into the polymer chains may hinder the diffusion of OH⁻ groups onto the surface of CN-PVA through electrostatic repulsion.

The effect of reaction temperature on the hydrolysis of CN–PVA is shown in Figure 10. Increasing the reaction temperature from 60 to 75° C causes an increase in the DH and the rate of the hydrolysis of CN–PVA. The analysis of the



Figure 9 Effect of concentration of sodium hydroxide on the DH of CN–PVA. CN–PVA (1 g; DS = 98%); CH_3COCH_3 (15 mL); H_2O (60 mL); Time, 15 h; 75°C.



Figure 10 Effect of reaction temperature on the DH of CN–PVA. CN–PVA (1 g; DS = 98%); CH₃COCH₃ (15 mL); H₂O (60 mL); [NaOH] = [CN]; time: 15 h. Temperature (°C): (\blacktriangle) 75; (\blacksquare) 70; (\spadesuit) 65; (\blacklozenge) 60.

kinetic results in the initial stage of hydrolysis of CN–PVA leads to a plot of log R_p versus 1/T, as shown in Figure 11. From the slope of the plot, the apparent activation energy ΔE_a was calculated to be 72.3 kJ/mol.

Rheology

The rheological properties of the hydrolysis product of CN–PVA in aqueous solution have been determined by a NDJ-79 model rotary viscometer at various temperatures, concentrations, and degrees of hydrolysis. The solutions of the hydrolysis products of CN–PVA show shear thinning and



Figure 11 Plot of $\log R_p$ versus 1/T.



Figure 12 Rheogram of the hydrolysis product solution of CN–PVA as a function of DH, η_a versus $\dot{\gamma}$ at 30°C; solution concentration, 6%. DH (%): (\bigstar) 80; (\bigstar) 75; (\blacksquare) 60; (\spadesuit) 35.

have viscosities that can be described by the following power law equation:

$$\eta_a = \tau/\dot{\gamma} = K\dot{\gamma}^{n-1}; n = d \log \tau/d \log \dot{\gamma}.$$

where η_a is the apparent viscosity, τ is the shear stress, $\dot{\gamma}$ is the shear rate, K is the shearing viscosity coefficient, and n is the power law exponent. Fluids with n value less than 1.0 are shear thinning (non-Newtonian).¹⁶

Rheological test curves measured at 30°C of various solutions are given in Figures 12 and 13. These plots show that the η_a of the solution in-



Figure 13 Rheogram of the hydrolysis product solution of CN–PVA as a function of concentration, η_a versus $\dot{\gamma}$ at 30°C; DH, 75%. Solution concentration (%): (\blacklozenge) 8; (\blacklozenge) 6; (\bigstar) 4.



Figure 14 Plot of log τ versus log $\dot{\gamma}$ (6% aq. solution; DH 75%). Temperature (°C): (\blacktriangle) 27; ($\textcircled{\bullet}$) 30; ($\textcircled{\bullet}$) 35; (\blacksquare) 40.

creases with increasing solution concentration and hydrolysis degree. However, the degree of shear thinning increases as the concentration and hydrolysis degree increase.

The log τ -log $\dot{\gamma}$ curves of the two solutions at various temperatures are shown in Figures 14 and 15. Table II shows that the exponent *n* of a given solution remains constant with increasing temperature but it decreases with increasing concentration at a given temperature. This suggests that as the concentration increases, the solution becomes more shear thinning.

The flow activation energy ΔE_{η} can be determined from the equation $\eta_a = Ae^{\Delta E \eta/RT}$, where η_a is the apparent viscosity and A is a constant. The results are shown in Table III.



Figure 15 Plot of log τ versus log $\dot{\gamma}$ (8% aq. solution; DH 75%). Temperature (°C): (**I**) 27; (**O**) 30; (**O**) 35; (**A**) 40.

As shown in Table III, ΔE_{η} decreases as $\dot{\gamma}$ increases and it is larger than other water-soluble polymer solutions (around 20 kJ/mol). The results show that the viscosity of hydrolysis product of CN–PVA solution decreases with increasing temperature and shear rate. The large value of ΔE_{η} is due to the hydrogen bonds between polymers since the viscosity of the solution is more sensitive to temperature.

CONCLUSIONS

- 1. A high degree of substitution (DS) of cyanoethylation of PVA was achieved by using quaternary ammonium halides as phase transfer catalysts. The effects of various factors, such as the structure of the quaternary ammonium halide, the concentration of the quaternary ammonium halide, the concentration of acrylonitrile, and the reaction temperature were investigated.
- 2. The hydrolysis of CN–PVA in the presence of sodium hydroxide and the effects of various factors on the degree of hydrolysis (DH) were investigated.
- 3. The rheological behavior of the hydrolysis product in aqueous solution has shown to be effective for thickening and these solutions are pseudoplastic fluids (non-Newtonian). The flow activities energy ΔE_{η} decreases as the shear rate increases and is larger than those of other water-soluble polymers. The viscosity of the solution de-

Table IIPower Law Exponent (n) of theHydrolysis Product of CN-PVA^a

Concentration (%)	Temperature (°C)	n
6	27	0.92
6	30	0.93
6	35	0.94
6	40	0.93
8	27	0.88
8	30	0.87
8	35	0.88
8	40	0.87

 $^{\rm a}$ The sample has a DS of 98% and a DH of 75%.

Table III	ΔE_{η} Value of a 6% Aqueous Solution	
of Hydroly	vsis Product of CN-PVA ^a	

$\dot{\gamma} (\mathrm{s}^{-1})$	$\Delta E_{\eta} \; (\rm kJ/mol)$
176	108.8
195	105.4
251	103.9
282	98.9
344	94.3
391	92.8
532	90.1

 $^{\rm a}$ The sample has a DS of 98% and a DH of 75%.

creases with increasing shear rate and temperature and is more sensitive to temperature.

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