

Water-Soluble Poly(vinyl alcohol) Grafted with Propylene Oxide and Epichlorohydrin: Characterization, Mechanical Properties, and Model Reactions

STÉPHANE J. CARLOTTI, OLIVIA GIANI-BEAUNE, FRANÇOIS SCHUÉ

Laboratoire de Chimie Macromoléculaire, UPRESA 5073 CNRS Organisation Moléculaire, Evolution, et Matériaux Fluorés, Université Montpellier II, Place E. Bataillon, 34095 Montpellier, France

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ABSTRACT: Poly(vinyl alcohol) (PVA) prepared by full hydrolysis of poly(vinyl acetate) was etherified with propylene oxide and epichlorohydrin. The reaction was done in water with sulfuric acid or sodium hydroxide. Previously, model reactions were carried out on propan-2-ol, pentan-3-ol, and pentan-2,4-diol in order to make the NMR characterization of grafted PVA easier. The new materials were also characterized by DSC and mechanical tests. A determination of their solubility in cold water was done as well. Generally, the prepared polymers showed excellent solubility in water at 10°C and a very low glass-transition temperature. Consequently, the properties of tension, elongation, elasticity, and resistance were improved. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2868–2874, 2001

Key words: poly(vinyl alcohol); etherification; epoxides; water soluble; mechanical properties

INTRODUCTION

There is still increasing interest in poly(vinyl alcohol) (PVA) and its derivatives for various applications like biomedicine, adhesives, paintings, packaging, and others.

Specific polymers can be obtained by esterification of PVA in water,^{1–4} DMSO,^{5,6} or DMF.^{7–9} However, the chemistry of PVA is also largely concerned with ether formation by nucleophilic substitution or epoxide ring opening. Along the same lines, the preparation of modified PVA was reported by reacting their hydroxyl groups with ethylene oxide,¹⁰ chloroacetic acids,¹¹ or epichlorohydrin (ECH).^{12–14} The solubility in water and mechanical properties were modified according to the nature and extent of grafting. Grafted mono-,

di-, or trichloroacetic acid PVA, prepared in water with sodium hydroxide, showed better flexibility of the corresponding films.¹¹

In the following we report the synthesis and characterization of PVA derivatives grafted with propylene oxide (PO) and ECH. We sought to prepare materials that were soluble in cold water and had a very low glass-transition temperature (T_g) and therefore had different mechanical properties. The polymers were characterized by NMR, DSC, and solubility tests in cold water. The flexibility and resistance properties were also measured. A NMR characterization of the model compounds (propan-2-ol, pentan-3-ol, and pentan-2,4-diol) was necessary to identify the etherified PVA.

EXPERIMENTAL

Materials

The PVA with a molecular weight of 25,000 g/mol and >99 mol % hydrolyzed was obtained by hy-

Correspondence to: O. Giani-Beaune (ogiani@crit.niv-montp2.fr).

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Table I Characteristics of Alcohols Grafted with Propylene Oxide (PO) and Epichlorohydrin (ECH)

Alcohol	Catalyst Type ^a	Epoxide	Yield ^b (%)	Isomer (%)		Grafted Oligomer
				α	β	
Propan-2-ol	Acid	PO	20	35	65	No
	Acid	ECH	26	100	—	No
	Basic	PO	21	100	—	Yes
	Basic	ECH	26	100	—	No
Pentan-3-ol	Acid	PO	13	35	65	No
	Acid	ECH	24	100	—	No
	Basic	PO	26	100	—	Yes
	Basic	ECH	24	100	—	No
Pentan-2,4-diol	Acid	PO	8	30	70	No
				(97 mono + 3 di) ^d		
	Acid	ECH	14	100	—	No
				(91 mono + 9 di) ^d		
	Basic	PO	14	100	—	Yes
				(75 mono + 25 di) ^d		
	Basic	ECH	16	100	—	No
				(81 mono + 19 di) ^d		

^a See the Experimental section.^b Isolated yield.^d mono, diol monosubstituted; di, diol disubstituted.

drolysis of poly(vinyl acetate) (Rhône Poulenc) in methanol with potassium hydroxide. Propan-2-ol, pentan-3-ol, pentan-2,4-diol, PO, and ECH were purchased from Aldrich and used without further purification. Deionized water was used in this study as well.

Etherification of Propan-2-ol, Pentan-3-ol, and Pentan-2,4-diol with PO

Propan-2-ol (12.02 g, 0.2 mol), pentan-3-ol (17.63 g, 0.2 mol), or pentan-2,4-diol (20.83 g, 0.2 mol) were separately charged under nitrogen in three reaction vessels. For the reaction in an acidic medium the PO (11.616 g, 0.2 mol) was added first, which was followed by the slow addition of sulfuric acid (0.814 g, 8.3 mmol). For the reaction in a basic medium we first added NaOH powder (5 wt %) to the alcohol followed by the epoxide. The base was generally dissolved at 80°C in propan-2-ol or pentan-2,4-diol and at 115°C in pentan-3-ol. The etherification reaction was allowed to proceed at 45°C for 24 h. Then the mixture was neutralized and extracted with ethyl ether, and the final products were isolated by distillation and weighed to calculate the yields. They are given in Table I.

Etherification of Propan-2-ol, Pentan-3-ol, and Pentan-2,4-diol with ECH

Propan-2-ol (12.02 g, 0.2 mol), pentan-3-ol (17.63 g, 0.2 mol), and pentan-2,4-diol (20.83 g, 0.2 mol) were reacted separately with ECH (18.506 g, 0.2 mol) at 120°C for 24 h under nitrogen. In acidic conditions the epoxide was added first, followed by the slow addition of sulfuric acid (0.814 g, 8.3 mmol). In basic conditions NaOH powder (10 wt %) was first added to the alcohol followed by the ECH. The base was dissolved at reflux of the alcohols. The mixture was then neutralized and extracted with ethyl ether, and the final products were isolated by distillation and weighed to calculate the yields. They are given in Table I.

Etherification of PVA with PO

The PVA was dissolved in water (10 wt % solution) by heating to 60–80°C. An acidic or basic medium was used. In both cases the PVA (5 g, 0.114 mol, based on —CH₂—CHOH— as the repeat unit) was dissolved in 50 mL of water. Then NaOH powder (0.5 g, 10 wt %) or a sulfuric acid solution 2*N* (7.3 mmol) was added to the PVA solution followed by the slow addition of an excess of PO (9.57–15.95 mL, 0.137–0.228 mol). The etherification process was carried out by stirring

and heating the reaction mixture at 60°C for 24 h. Then the basic medium was neutralized by an acidic solution or the acidic medium by an aqueous sodium carbonate solution (10%). The reaction solution was precipitated in acetone (10-fold volume) and dried under a vacuum at 30°C for 24 h. Varied conversion percentages to ether (grafting percentage of the polymer) were obtained.

Etherification of PVA with ECH

A similar experimental process was used to synthesize PVA grafted with ECH. The PVA (5 g, 0.114 mmol) was dissolved in 50 mL of water at 60–80°C. The NaOH powder (1.591 g, 39.8 mmol) or H₂SO₄ solution 2*N* (7.3 mmol) was added to the polymer solution. Then ECH (17.83 mL, 0.228 mol) was added dropwise. Twenty-four hours later the mixture was neutralized and precipitated in acetone (10-fold volume). The final product was dried under a vacuum at 30°C for 24 h. Varied grafting percentages were obtained according to the rate of addition of ECH in the reaction mixture.

Characterization

Four hundred megahertz ¹H- and 100.6 MHz ¹³C-NMR spectra were obtained at 25°C with a Bruker DRX400 spectrometer using polymer solutions in D₂O and tetramethyl silane as internal standards.

Solubility tests in water were carried out by putting a piece of film (polymer, 35–40 μm thickness) in a flask filled with water at 10°C. The solution was stirred in that flask. The solubility or nonsolubility of the film in water was observed as well. A time of disintegration and a time of dissolution were noticed for some cases.

Calorimetric studies were carried out on a differential scanning calorimeter (Mettler DSC 30, low temperature probe) in sealed aluminum pans. The *T_g* values were determined with a heating rate of 10°C/min after storage of the samples at 50% relative humidity and 20°C for 48 h. Two runs were carried out. The first *T_g* obtained corresponded to a material containing water and the second one to a material without water.

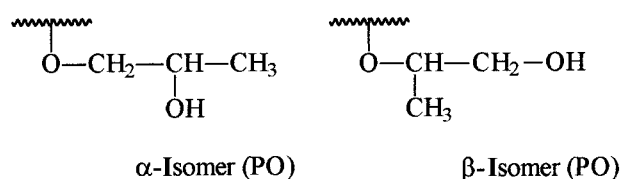
Mechanical measurements were determined on films (35–40 μm thickness) stored at 50% relative humidity and 20°C. The tensile measurements were made on an Instron model 1011, and the tear resistance properties were measured on

an Elmendorf tearing tester (Thwing–Albert instrument).

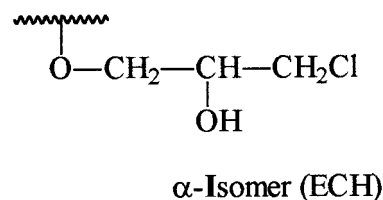
RESULTS AND DISCUSSION

Etherification of Propan-2-ol, Pentan-3-ol, and Pentan-2,4-diol with PO and ECH

The preliminary work was to characterize different ethers formed by separate reactions of propan-2-ol, pentan-3-ol, and pentan-2,4-diol in acid and basic conditions with PO and ECH. Table I summarizes the characteristics of these ethers. The very low yields (8–26%) can be explained by the low reactivity of the alcohol due to the secondary nature and by the relative steric hindrance. Some side products, like hydrated epoxides, and especially unreacted reagents were observed. The purpose of this work was not to get high yield reactions but to observe the nature of the products synthesized in the same conditions as the reactions with PVA. These side products do not influence the precipitated material properties. Whatever alcohol was reacted with PO in an acidic medium, a mixture of α- and β-isomers at around 35 and 65%, respectively, were obtained.



In basic conditions only the α-isomer (PO) was formed. Nevertheless, the experimental conditions allowed an oligomerization of the grafted PO (maximum number of PO units, ≈9). In the presence of ECH only the α-isomer (ECH) was synthesized in acid or basic conditions. That was explained by the presence of the chlorine atom. The carbon in the γ position was more electropositive than the carbon in the α (due to the mesomeric effect of Cl). However, no oligomerization was observed.



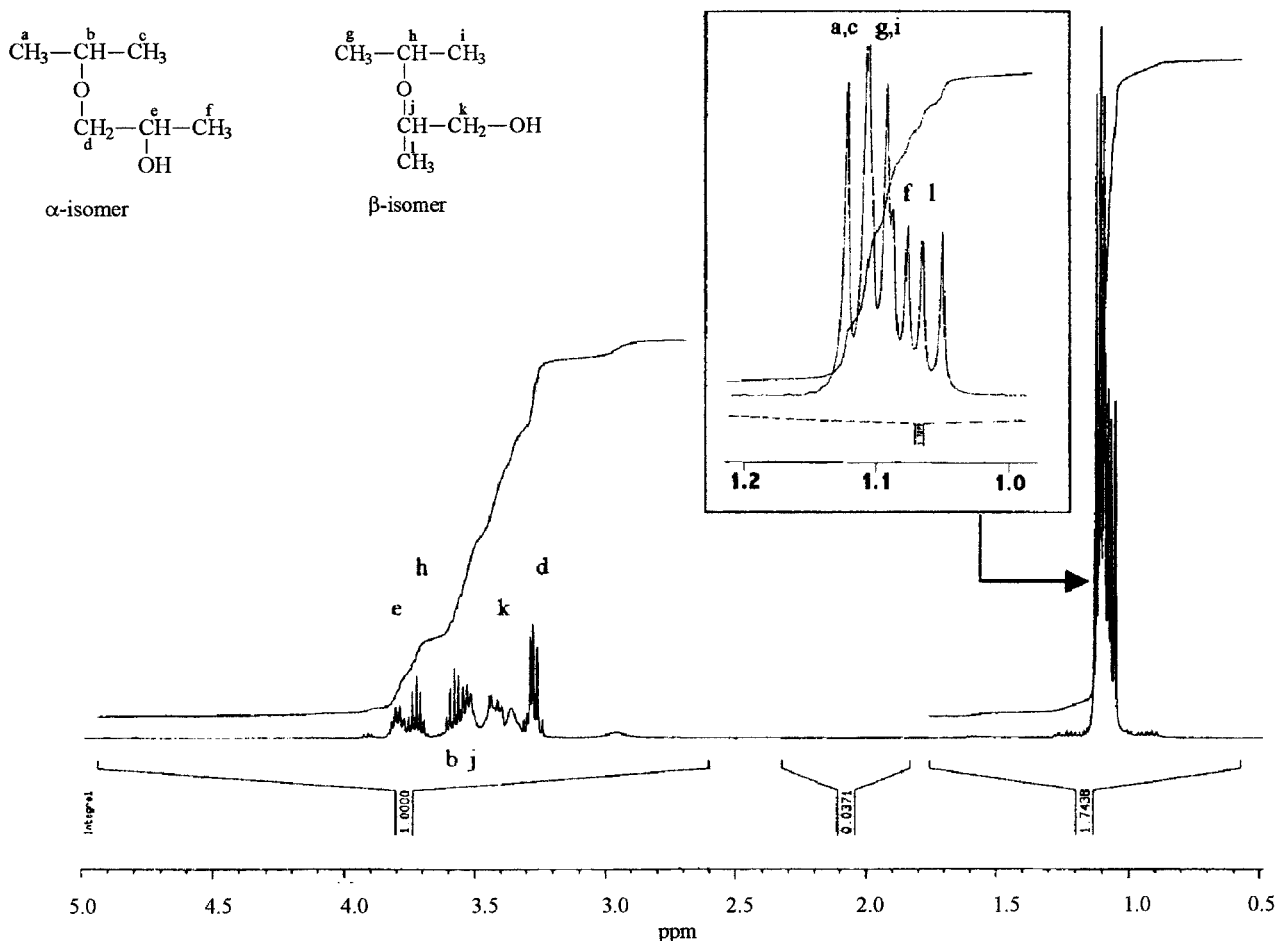


Figure 1 The $^1\text{H-NMR}$ (400 MHz, 20°C , CD_3COCD_3) spectrum of a mixture of 1-isopropoxypropan-2-ol (α -isomer) and 2-isopropoxypropanol (β -isomer).

The mechanisms of such reactions were described starting in the 1950s.^{15–20}

The interest in pentan-2,4-diol lay in the presence of two secondary alcohols spaced by a methylene group. Despite their closeness, some disubstituted products were obtained (3–25%). We expected the same percentages for the PVA.

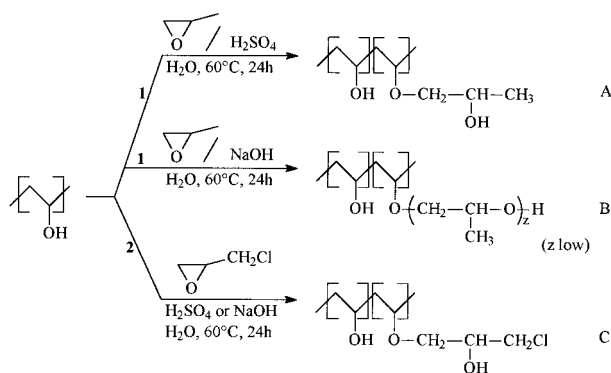
The nature of these ethers was verified by ^1H - and ^{13}C -NMR, GC, and elementary analysis. For instance, Figure 1 shows a proton NMR spectrum of an isomeric mixture of 1-isopropoxypropan-2-ol (α -isomer) and 2-isopropoxypropanol (β -isomer). These compounds were synthesized from the reaction of propan-2-ol and PO with sulfuric acid. Methyl groups were clearly visible at around 1.10 ppm. The doublet at 1.05 ppm and another one at 1.08 ppm emphasized the presence of the two isomers. The exact assignment came from the NMR study of other compounds like the 1-isopropoxypropan-2-ol (α -isomer) synthesized in basic

conditions. The ^{13}C -NMR analysis showed a single peak at 17.5 ppm for the methyl group of grafted PO (β -isomer) and another single one at 19.5 ppm corresponding to the $-\text{CH}_3$ of the α -isomer.

An accurate characterization of each ether synthesized allowed us to imagine the potential structures of grafted PVA with PO or ECH in acid or basic conditions.

Chemical Modification of PVA with PO and ECH

The previous model reactions showed the formation of two isomers (α and β) and one isomer (α) for PO and ECH grafts, respectively, in the presence of an acid. With a base both epoxides led to a graft (α -isomer) that was oligomerized or not (between 1 and 9 units). The acidic and basic media seemed to provide the interesting fact, which was the difference in the structure of the grafts.



Scheme 1 The etherification reaction of PVA with propylene oxide (1) and epichlorohydrin (2).

Fully hydrolyzed PVA was etherified with epoxides, PO, and ECH in water and in the presence of sulfuric acid or sodium hydroxide (Scheme 1). The ¹H- and ¹³C-NMR analysis of these new materials and their comparison with the model compounds or literature²¹ spectra allowed us to draw conclusions about their structures. The modification of PVA with PO in acid conditions led only to the α-isomer graft [Scheme 1(A)]. This observation can be explained by the steric hindrance of PVA macromolecular chains. The nucleophilic attack occurs preferentially on the less hindered carbon of PO, not on the more stable one. The same reaction with NaOH led to oligomerized PO grafts [Scheme 1(B)], but the exact degree of polymerization (very low) was very difficult to figure out. The modification of PVA with ECH was in agreement with the model reaction. The acid and basic conditions both led to a 3-chloro-2-hydroxypropoxy graft [Scheme 1(C)].

Various grafting percentages were obtained, depending on the concentration of PVA in water,

the temperature, the reaction time, the epoxide to PVA ratio, and the quantity or nature of the catalyst. Four PVA grafted POs are reported in Table II. The grafting percentages, which were calculated by ¹H-NMR (integration heights of the grafts compared to the PVA ones), varied from 10 to 23%. All the materials presented in this table were also characterized by a solubility test in water at 10°C and by DSC (*T_g* determination). In DSC the first run corresponded to a material with some humidity traces. The water and graft both acted like a plasticizer in the macromolecular chains. As a result, the *T_g* can be very low, for example, -5°C for PVA-PO-4 synthesized in the presence of NaOH and grafted with 23% PO. This temperature corresponded to a decrease of 44°C. The *T_g* obtained after the second run resulted from a polymer free of water. The *T_g* value was between 50 and 66°C. The most interesting results (basic conditions) seemed to be due to the relative length of the PO grafts (fairly low) and not necessarily to a high grafting percentage. All these materials were soluble in water at 10°C. The unmodified PVA was soluble in water at 20°C when the PVA was a piece of film (35–40 μm thickness) or around 60–80°C for the precipitated polymer.

Two samples were mechanically analyzed at room temperature. The PVA-PO-2 was synthesized in the presence of sulfuric acid and PVA-PO-4 was prepared with NaOH (Table III). Very poor tensile, elastic, elongation, and resistance properties were obtained for PVA-PO-2 because of a *T_g* (first run) close to the ambient temperature (*T_g* = 20°C). However, a solubility test in water at 10°C showed a rapid dissolution time that was only equal to 4 s. On the other hand, the tensile

Table II Etherification of PVA with Propylene Oxide: Characterization by NMR, DSC, and Solubility Analysis

Sample	Medium	Grafting (%)	<i>T_g</i> (°C)		Solubility in Water at 10°C ^c
			1st Run ^a	2nd Run ^b	
Nonmodified PVA		0	39	82	No (20°C)
PVA-PO-1	Acid	15	11	66	Yes
PVA-PO-2	Acid	10	20	66	Yes
PVA-PO-3	Basic	13	6	50	Yes
PVA-PO-4	Basic	23	-5	58	Yes

^a Some water present in the polymer.

^b No water present in the polymer.

^c Solubility measurements carried out with a film of polymer (35–40 μm thickness).

Table III Mechanical and Solubility Properties of PVA Grafted with Propylene Oxide

	PVA-PO-2	PVA-PO-4
Tensile strength at break (kg/cm ²)	4.7	148
Young's modulus (kg/cm ²)	Not determined	128
Elongation at break (%)	0	170
Elmendorf tear resistance (kg/mm)	0	4.7
Solubility in water at 10°C ^a		
Disintegration time (s)	0	10
Dissolution time (s)	4	33

^a Solubility measurements carried out with a film of polymer (35–40 μm thickness).

strength at break, Young's modulus, elongation at break, and the Elmendorf tear resistance of PVA-PO-4 were consequently improved and could be of interest in a packaging use, for instance. Generally those values were close to 0 for an unmodified PVA.

The disintegration time in water at 10°C did not exceed 10 s, and no more than 32 s were necessary for a complete dissolution.

A similar study was carried out for PVA grafted ECH. Another parameter, the rate of addition of the epoxide, was used for the reaction. Rates were chosen between 25 and 70 μL/min. The slower the addition of ECH was, the higher the grafting percentage was. Moreover, the limit of grafting was achieved at 15% when acid conditions were used and it was achieved at 27% in the presence of the base. Therefore, the results gathered in Table IV come from the best conditions, the reactions with NaOH. The higher the grafting percentage was, the lower the glass-transition temperature (DSC) was. The best result was ob-

tained for PVA-ECH-5 with a grafting percentage of 27%. The corresponding T_g values were –36°C for the first run (some water was present in the polymer) and only 2°C for the second run (no water was present). Very low T_g values were achieved. Moreover, a material with at least 15% graft was soluble in water at 10°C.

The mechanical properties of two PVAs modified with ECH were determined (Table V). The tension, elasticity, elongation, and resistance of these new materials (PVA-ECH-2 and PVA-ECH-3) were much improved compared to PVA-PO-4. The most significant increases were obtained for PVA-ECH-3 with an Elmendorf tear resistance of 12.2 kg/mm and an elongation at break of 244%.

CONCLUSIONS

Etherifications of fully hydrolyzed PVA were carried out first with PO and then with ECH. The

Table IV Etherification of PVA with Epichlorohydrin: Characterization by NMR, DSC, and Solubility Analysis

Sample	Grafting (%)	T_g (°C)		Solubility in Water at 10°C
		1st Run ^a	2nd Run ^b	
Nonmodified PVA	0	39	82	No (20°C)
PVA-ECH-1	9	29	48	No (70°C)
PVA-ECH-2	12	27	37	No (85°C)
PVA-ECH-3	15	–25	18	Yes
PVA-ECH-4	23	–26	21	Yes
PVA-ECH-5	27	–36	2	Yes

^a Some water present in the polymer.

^b No water present in the polymer.

^c Solubility measurements carried out with a film of polymer (35–40 μm thickness).

Table V Mechanical Properties of PVA Grafted with Epichlorohydrin (ECH)

	PVA-ECH-2	PVA-ECH-3
Tensile strength at break (kg/cm ²)	163	152
Young's modulus (kg/cm ²)	158	113
Elongation at break (%)	209	244
Elmendorf tear resistance (kg/mm)	8.5	12.2

prepared polymers were soluble in cold water (10°C) and exhibited very low glass-transition temperatures. The mechanical properties such as the tension, elongation, elasticity, and tear resistance were improved compared to an unmodified PVA. A minimum of grafting was necessary to reach the desirable characteristics. Poly(propylene oxide) oligomers grafted onto the PVA backbone showed higher mechanical properties than grafted single monomer units. Thus, it turned out with ECH that the higher the grafting percentage was, the lower the T_g was.

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