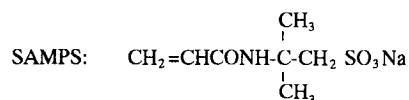


Functional modification of poly(vinyl alcohol) by copolymerization: II. Modification with a sulfonate monomer

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A functional monomer containing the sodium sulfonate group, sodium 2-acrylamide-2-methylpropane sulfonate (SAMPS), the chemical formula being shown below, has been found useful for the production of modified poly(vinyl alcohol) containing the sodium sulfonate group, $-\text{SO}_3\text{Na}$, in the molecular chain by solution copolymerization with vinyl acetate and alcoholysis. The poly(vinyl alcohol)s modified with a sodium sulfonate group show strong hydrophilic properties, which permits poly(vinyl alcohol)s of much lower degree of hydrolysis less than 80 mol% to dissolve in water. In contrast to the poly(vinyl alcohol) modified with carboxylic monomers, reported in the preceding paper, the solubility of the poly(vinyl alcohol) modified with a sodium sulfonate group is less sensitive to pH or to the presence of inorganic salts.



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(Keywords: poly(vinyl alcohol); copolymerization; sulfonic monomer)

INTRODUCTION

Modification of poly(vinyl alcohol) (PVAL) with carboxylate groups has widely been discussed in the preceding paper¹, where various modified PVALs have been synthesized from copolymerization of vinyl acetate (VAc) and various carboxylic monomers, followed by alcoholysis of the resulting modified poly(vinyl acetate)s (PVACs).

One of the typical effects of introducing ionic groups like carboxylate into the PVAL chain has been demonstrated by the fact that a new group of partially hydrolysed PVALs or poly(vinyl acetate-co-vinyl alcohol)s (PVAC-VALs)², of much lower degrees of hydrolysis (DH), even less than 80 mol% have been able to be used as water soluble polymers. Such effective results must be given by the hydrophilic property of carboxylate group. On the other hand, much complexity has been observed due to the fact that the polymer chain contains two chemical groups which are reactive with each other, hydroxyl and carboxyl.

Modification of PVAL and PVAC-VAL with another anionic group, sulfonic acid, $-\text{SO}_3\text{H}$, or its salts, $-\text{SO}_3\text{M}$, can also be expected to give a useful water-soluble polymer³, because sulfonic acid shows stronger acidity than carboxylic acid and also because the group is unreactive to hydroxyl group. Concerning the modified PVAL containing sulfuric acid sodium salt group, $-\text{OSO}_3\text{Na}$, the preparation by the polymer reaction of PVAL with chlorosulfonic acid has been investigated^{4,5}. This polymer, however, has the disadvantage of hydrolytic decomposition in aqueous solution. As methods of

modification with more stable sulfonic or sulfonate groups by copolymerization with VAc, sodium allyl sulfonate, sodium methallyl sulfonate or sodium vinyl sulfonate can be candidates for modifier-comonomers. Among these, the latter two comonomers have difficulties such as stability or solubility in copolymerization. The first comonomer, sodium allyl sulfonate, can be copolymerized with VAc and modified PVALs containing sulfonate groups can be obtained, as reported in literature^{6,7}. This modification, however, also shows some inconveniences in the fact that the copolymerization rate with VAc decreases remarkably and that it is difficult to obtain polymers of higher degrees of polymerization. As another different modification, the polymer reaction between PVAL and sodium benzaldehydesulfonate has been investigated⁸.

In this work, a new effective method of modifying PVALs with sulfonate group has been reported: copolymerization of VAc and sodium 2-acrylamide-2-methylpropane sulfonate (SAMPS), followed by alcoholysis⁹.

EXPERIMENTAL

Materials

The monomer for modification, SAMPS ($M_w = 229.3$), was supplied by Nitto Chemical Industry Co., Tokyo. Its purity was over 99% by the analysis of ¹H nuclear magnetic resonance (n.m.r.). The VAc used was a commercial product from Kuraray Co.

Syntheses

Copolymerization. Copolymerizations of VAc and

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Table 1 Synthesis of poly(vinyl alcohol)s modified with sodium 2-acrylamide-2-methylpropane sulfonate (SAMPS) by copolymerization and alcoholysis

No.	Theoretical mole fraction of SAMPS in copolymer (mol%)	Feed in copolymerization (part)				Reaction time (min)	Extent of conversion of VAc (%)	Modified PVAC		Modified PVAL		
		VAc	SAMPS	Methanol	AIBN			SAMPS group (mol%)	SAMPS group (mol%)	Degree of hydrolysis (mol%)	Degree of polymerization \bar{P}_v	Viscosity of aqueous solution (4%, 20°C) (cP)
1	None	1000	0/0	250/77	0.30	237	62.8	0	0	99.5	1621	27.0
2	None	1000	0/0	1185/0	13.3	105	73.1	0	0	99.0	788	8.5
3										89.2		8.2
4										71.5		Phase separation
5	0.3	1000	0.6/5.5	1174/14.4	21.8	100	71.5	0.3	0.3	98.5	752	7.5
6										75.7		7.8
7										68.8		7.0 (Cloudy)
8	1	1000	1.7/22.6	1325/70	9.5	255	88.0	1.0	1.0	91.8		8.1
9												
10	1	1000	1.9/17.9	333/46.8	0.58	200	61.8	1.1	1.1	98.7		23.3
11												
12	2	1000	1.3/29.4	250/77	0.30	240	60.2	1.8	1.7	99.0	1603	26.6
13										86.6		22.2
14										70.3		24.3
15	3	1000	1.71/43.5	333/126	0.43	180	58.8	3.0	2.9	98.8		24.1
16	6	1000	13/22	333/64	0.30	40	10.8	6.0	6.2	94.5		25.5

SAMPS were carried out using a glass reactor equipped with a stirrer, a reflux condenser and an apparatus supplying a methanol solution of SAMPS (25 wt%). All the copolymerization reactions were carried out using methanol and 2,2'-azobisisobutyronitrile (AIBN) as solvent and initiator, respectively, at boiling temperatures of the system, 60–62°C under the atmosphere of nitrogen gas. The degree of polymerization was controlled by changing the amount of methanol in the system. The solution system during copolymerization was basically homogeneous, but showed milky or opaque appearance for the cases where the mole fraction of SAMPS in the copolymer was higher, 2–6 mol%. In order to obtain copolymers having homogeneous composition at any degrees of conversion, the 'feeding comonomer method'^{1,10} was adopted, where more reactive SAMPS was continuously added to the reaction system. The balance amount added was determined from the monomer reactivity ratios, r_1 and r_2 , and from the solid content analysed occasionally. The values, $r_1 = 11.60$ and $r_2 = 0.05$ reported in literature¹¹, were used where monomer 1 was SAMPS and monomer 2 was VAc. The other procedures were similar to the method carried out in the preceding paper¹. After the residual VAc was distilled out by introducing methanol gas, clear solutions were obtained even for the cases which had shown milky or opaque appearance in copolymerization. The small amount of the modified PVAC was purified by reprecipitation of the methanol solution in cooled water twice and analysed using ¹H n.m.r. Typical examples of copolymerization are shown in Table 1.

Alcoholysis. Modified PVALs were obtained by alcoholysis reaction of the modified PVACs using sodium hydroxide as a catalyst. The samples having various DH were

obtained by controlling the amount of sodium hydroxide. The method was similar to that reported before¹. Typical examples of modified PVALs obtained are also shown in Table 1.

Structural analysis and characterization. ¹H n.m.r. spectra were obtained with Varian EM-390 at 90 MHz. As solvents and internal standard reagents, CDCl₃ and hexamethyldisiloxane were used for modified PVACs, while D₂O and 3-(trimethylsilyl)propionic acid-*d*₆-sodium salt were used for modified PVALs. Viscosity for aqueous solution of 4 wt% of PVAL was measured using a Brookfield viscometer. Limiting viscosity number, $[\eta](dl/g)$, was measured in aqueous solution of sodium chloride (1 M) using capillary viscometer at 30°C. Viscosity-average degree of polymerization was calculated by the equation $\bar{P}_v = ([\eta] \times 10^4 / 8.33)^{1/0.6212-14}$.

Mixing with inorganic salts in aqueous solution. A qualitative mixing experiment was made in order to evaluate the sensitivity of SAMPS-modified PVAL to inorganic salts, sodium sulfate and aluminum sulfate in aqueous solution. A non-modified PVAL and the PVAL modified with itaconic acid, modification degree of sodium itaconate being 2.0 mol%, were also tested for comparison.

RESULTS AND DISCUSSION

Copolymerization of VAc and SAMPS

The rates of copolymerization for the present cases where the mole fractions of SAMPS in resulting copolymers were 0.3–6.2 mol% are almost as same as the rate of homopolymerization of VAc. The milky or opaque appearance observed in copolymerization is regarded as due to poorer

Table 2 Effects of pH on the solubility in water for non-modified and modified PVALs having lower degrees of hydrolysis, around 70 mol%

	PVAL			Aqueous solution (10 wt%)	
	Δ^a	DH ^b	$\eta_{4\%,20^\circ\text{C}}^c$	Neutral	Acidic (pH 3.0)
Non-modified PVAL	0	71.5	Phase separation	Phase separation	Phase separation
IA-PVAL ^d	2	70.5	25.2	Clear	Phase separation
SAMPS-PVAL ^e	2	70.3	24.3	Clear	Clear

^aMole fraction of modification group^bDegree of hydrolysis^cViscosity of aqueous solution (4%, 20°C)^dIA-PVAL: Modified PVAL with itaconic acid^eSAMPS-PVAL: Modified PVAL with sodium 2-acrylamide-2-methylpropane sulfonate

solubility of SAMPS to VAc and to the mixture of VAc and methanol in copolymerization. The observed mole fractions of SAMPS in purified copolymers are consistent with the target values calculated from the reactivity ratios within experimental errors. Therefore the resulting copolymers are regarded as basically homogeneous in spite of the apparent poorer solubility of SAMPS to the copolymerization system.

Syntheses of modified PVALs

Figure 1 shows the ¹H n.m.r. spectrum of the purified sample of the modified PVAL with SAMPS (SAMPS-PVAL). The mole fraction of SAMPS in the modified PVAL is observed as 6.2 mol%, which agrees well with the observed mole fraction of SAMPS in the modified PVAc before alcoholysis, 6.0 mol%. Therefore the amido linkage in SAMPS units is so stable in the alcoholysis reaction that modified PVALs with sulfonate group can be produced. From the observed degrees of polymerization (Samples 1 and 12, Samples 2 and 5), it has been concluded that copolymerization of VAc with SAMPS results in similar degrees of polymerization to those obtained in homopolymerization of VAc under similar conditions.

Partially hydrolyzed SAMPS-PVALs

Table 1 shows resulting PVALs with various modification degrees, 0–6.2 mol%, and various DH, 68.8–99.0 mol%. It has been observed that the modified PVALs of much lower DH, 68.8 and 70.3 mol% (Sample numbers 7 and 14), are soluble in water while non-modified PVAL with DH of 71.5 mol% loses its solubility in water or shows phase separation. Similar effects of ionic group have already been found for modified PVALs containing sodium carboxylate group or typically for PVALs modified using itaconic acid as a comonomer-modifier¹.

Solubility in water and effects of pH and salts. Table 2 shows the solubility in water for PVALs having lower D.H. around 70 mol% and the effects of pH. The non-modified PVAL with D.H. of 71.5 mol% does not dissolve in water clearly but only disperses in it. The resulting white aqueous dispersion causes phase separation on standing. It has been well known that partially hydrolyzed PVALs or PVAcVALs with lower DH than 80 mol% lose their solubility in water because the precipitation points or cloud points are below room temperature^{15–17}. In the case of the modified PVAL containing 2 mol% of sodium itaconate group and with 70.5 mol% of DH (IA-PVAL), clear aqueous solution is obtained but phase separation occurs under acidic conditions (pH 3.0) by adding 1 N sulfuric acid to the aqueous solution. This phase separation can be explained by the mechanism that carboxyl group reacts with neighboring hydroxyl group to form lactone under the acidic

conditions and consequently loses its ionic property¹. In contrast, the modified PVAL with 2 mol% of SAMPS and with 70.3 mol% of DH (SAMPS-PVAL) dissolves in water clearly both under neutral and acidic conditions. SAMPS group keeps its hydrophilic property enough to make the modified PVAL with lower DH soluble in water even under acidic conditions.

Table 3 illustrates the effects of salts (a) sodium sulfate and (b) aluminum sulfate, on the solubility of highly-hydrolysed PVALs in aqueous solution. The aqueous solution of non-modified PVAL shows phase separation when the aqueous solution of sodium sulfate (1 M) is added with stirring until the concentration is reached to 0.33 M in resulting solution. This phase separation is due to salting-out effects¹⁸. The solution of IA-PVAL also generates precipitation tentatively by adding sodium sulfate, but it dissolves completely with time and results in clear solution under the same amount of sodium sulfate. However, phase separation occurs at a pH of 3.0 by adding 1 N sulfuric acid to the solution. This can also be explained by lactone formation as stated above. SAMPS-PVAL, on the other hand, keeps its solubility in water both under neutral and acidic conditions in the same concentration of sodium sulfate as above. More addition of sodium sulfate makes the modified PVAL precipitate.

The addition of aluminum sulfate into aqueous solution of IA-PVAL causes a remarkable viscosity increase but no apparent change in both the cases of non-modified PVAL and SAMPS-PVAL. Reaction of modified PVALs containing carboxylate group such as IA-PVAL with aluminum salts has been discussed in the preceding paper¹. Sodium sulfonate group in the modified PVALs is also inactive to polyvalent salts like aluminum sulfate.

The inactivity of SAMPS-PVAL to salts and pH concerning its solubility in water is regarded as advantageous because it can keep its stable solubility in the broad range of conditions. Using these characteristics, SAMPS-PVALs have widely been used for applications such as paper sizing¹⁹, textile sizing²⁰, emulsifiers, adhesives and specialty films with highly solubility²¹.

CONCLUSIONS

- (1) SAMPS has been found useful for producing modified PVALs containing sulfonate group in the chain.
- (2) The SAMPS-modified PVALs having much lower DH, even less than 80 mol%, can show good solubility in water. The solubility is kept under acidic conditions. This is in contrast to the modified PVALs with carboxylate group, where solubility is lost by the formation of lactone as the result of reaction with neighboring hydroxyl group.

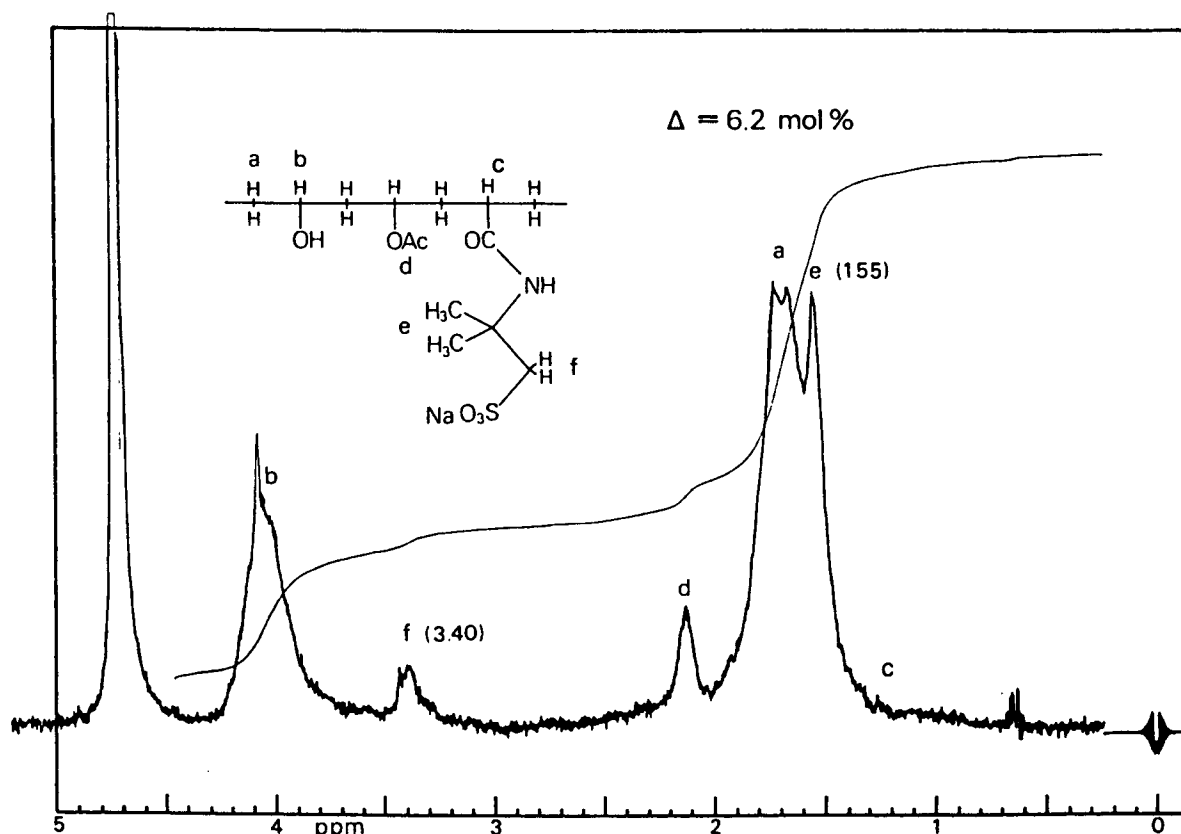


Figure 1 ^1H n.m.r. spectrum of poly(vinyl alcohol) modified with sodium 2-acrylamide-2-methylpropane sulfonate (SAMPS)

Table 3 Effects of salts, sodium sulfate and aluminum sulfate, on the solubility of non-modified and modified PVALs of higher degrees of hydrolysis in aqueous solution

	PVAL			(a) Aqueous solution (PVAL: 10 wt%) including sodium sulfate (0.33 M)		(b) Aqueous solution (PVAL: 10 wt%) including aluminum sulfate (0.18 M)
	Δ^a	DH ^b	η_{sp}^c , 20°C	Neutral	Acidic (pH 3.0)	
Non-modified PVAL	0	98.5	28.3	Phase separation	Phase separation	No change
IA-PVAL ^d	2	97.0	27.3	Clear	Phase separation	Viscosity increase
SAMPS-PVAL ^e	2	99.0	26.6	Clear	Clear	No change

^aMole fraction of modification group

^bDegree of hydrolysis

^cViscosity of aqueous solution (4%, 20°C)

^dIA-PVAL: Modified PVAL with itaconic acid

^eSAMPS-PVAL: Modified PVAL with sodium 2-acrylamide-2-methylpropane sulfonate

(3) The SAMPS-modified PVALs can show better solubility in aqueous solution containing salts like sodium sulfate or sodium aluminate.

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