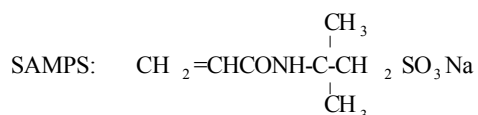


CHAPTER 8**MODIFICATION WITH A SULFONATE MONOMER**

A functional monomer containing 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)s containing 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 the sodium sulfonate group show strong hydrophilic property, 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 sodium sulfonate group is less sensitive to pH or to the presence of inorganic salts.

**8.1 INTRODUCTION**

Modification of poly(vinyl alcohol) (PVAL) with carboxylate groups has widely been discussed in the preceding chapter,¹ 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 typical effects of introducing ionic groups like carboxylate into PVAL chain has been demonstrated by the fact that a new group of partially hydrolyzed PVALs or poly(vinyl acetate-co-vinyl alcohol)s (PVAL-ACs),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 each other, hydroxyl and carboxyl.

Modification of PVAL and PVAL-AC 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 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 comonomer has difficulties such as stability or solubility in copolymerization. The first comonomer, sodium allyl sulfonate, can be copolymerized with VAc and modified PVALs containing sulfonate group 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 investigated.⁸

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 alcoholysis.⁹

8.2 EXPERIMENTAL

8.2.1 *Materials*

The monomer for modification, SAMPS (MW=229.3), was supplied by Nitto Chemical Industry Co., Tokyo. Its purity was over 99% by the analysis of $^1\text{H-NMR}$ VAc used is a commercial product from Kuraray Co.

Table 16 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%	VAc	Feed in copolymerization (part)			AIBN	Reaction time min	Extent of conversion of VAc %	Modified PVAc		Degree of hydrolysis mol%	Modified PVAL Degree of Polymerization P_n
			SAMPS Initial/Additional	Methanol Initial/Additional	SAMPS group mol%				SAMPS group mol%			
1	None	1000	0 / 0	250 / 77	0.30	237	62.8	0	0	99.5	1621	
2												
3	None	1000	0 / 0	1185 / 0	13.3	105	73.1	0	0	89.2	788	
4												
5												
6	0.3	1000	0.6 / 5.5	1174 / 14.4	21.8	100	71.5	0.3	0.3	75.7	752	
7												
8	1	1000	1.7 / 22.6	1325 / 70	9.5	255	88.0	1.0	1.0	91.8	68.8	
9												
10	1	1000	1.9 / 17.9	333 / 46.8	0.58	200	61.8	1.1	1.1	96.7	98.5	
11												
12												
13	2	1000	1.3 / 29.4	250 / 77	0.30	240	60.2	1.8	1.7	86.6	1603	
14												
15	3	1000	1.71 / 43.5	333 / 126	0.43	180	58.8	3.0	2.9	98.8	70.3	
16	6	1000	13 / 22	333 / 64	0.30	40	10.8	6.0	6.2	94.5	98.8	

8.2.2 Syntheses

Copolymerization Copolymerizations of VAc and SAMPS were carried out using a glass reactor equipped with a stirrer, a reflux condenser and an apparatus supplying 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° to 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 copolymer was higher, 2 to 6 mol%. In order to obtain copolymers having homogeneous composition at any degrees of conversion, the "feeding comonomer method"^{10,1} 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 analyzed occasionally. The values, $r_1 = 11.60$ and $r_2 = 0.05$ reported in literature,¹¹ were used where monomer 1= SAMPS and monomer 2=VAc. The other procedures were similar to the method carried out in the preceding paper.¹ 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 analyzed using ¹H-NMR. Typical examples of copolymerization are shown in Table 16.

Alcoholysis Modified PVALs were obtained by alcoholysis reaction of the modified PVAc's 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 before.¹ Typical examples of modified PVALs obtained are also shown in Table 16

8.2.3 Structural Analysis and Characterization

¹H-NMR spectra were obtained with Varian EM-390 at 90MHz. As solvents and internal standard reagents, CDCl₃ and hexamethyldisiloxane were used for modified PVAc's, while D₂O and 3-(trimethylsilyl)propionic acid-d₆-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 (1M) using capillary viscometer at 30°C.

Viscosity-average degree of polymerization was calculated by the equation, $\overline{P}_v = ([\eta] \times 10^4 / 8.33)^{1/0.62}$.¹²⁻¹⁴

8.2.4 *Mixing with Inorganic Salts in Aqueous Solution*

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.

8.3 RESULTS AND DISCUSSION

8.3.1 *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 to 6.2 mol% are almost as same as the rate of homo-polymerization of VAc. Milky or opaque appearance observed in copolymerization is regarded due to poorer 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 basically homogeneous in spite of the apparent poorer solubility of SAMPS to copolymerization system.

8.3.2 *Syntheses of Modified PVALs*

Figure 47 shows the ¹H-NMR 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 homo-polymerization of VAc under similar

conditions.

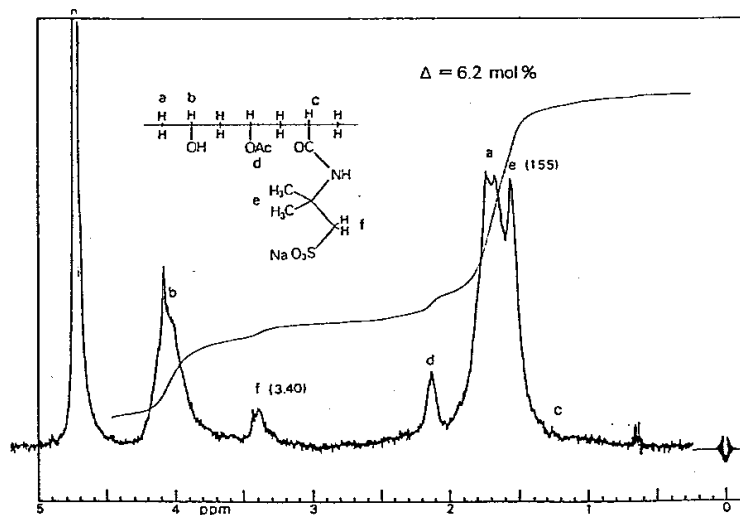


Figure 47 ¹H-NMR spectrum of poly(vinyl alcohol) modified with 2-acrylamide-2-methylpropane sulfonate (SAMPS)

8.3.3 Partially Hydrolyzed SAMPS-PVALs

Table 16 shows resulting PVALs with various modification degrees, 0 to 6.2 mol%, and various DH, 68.8 to 99.0 mol%. It has been observed that the modified PVALs of much lower DH, 68.8 and 70.3 mol% (Sample Nos. 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-modifier.¹

8.3.4 Solubility in Water and Effects of pH and Salts

Table 17 shows the solubility in water for PVALs having lower DH around 70 mol% and the effects of pH. The non-modified PVAL with DH 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

Table 17 Effects of pH on the solubility in water for non-modified and modified PVALs having lower degrees of hydrolysis, around 70 mol%

		Non-modified		
		PVAL	IA-PVAL ^{*1}	SAMPS-PVAL ^{*2}
PVAL	Δ ^{*3}	0	2	2
	DH ^{*4}	71.5	70.5	70.3
	η 4%,20°C ^{*5}	Phase separation	25.2	24.3
Aqueous solution (10 wt%)	Neutral	Phase separation	Clear	Clear
	Acidic (pH 3.0)	Phase separation	Phase separation	Clear

*1 IA-PVAL: Modified PVAL with itaconic acid.

*2 SAMPS-PVAL: Modified PVAL with sodium 2-crylamide-2-methylpropane sulfonate

*3 Mole fraction of modification group.

*4 Degree of hydrolysis.

*5 Viscosity of aqueous solution (4%, 20°C)

PVALs with lower DH than 80 mol% lose their solubility to 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 1N 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 property.¹ 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 18 illustrates the effects of salts, (a) sodium sulfate and (b) aluminum sulfate, on the solubility of highly-hydrolyzed PVALs in aqueous solution. The aqueous solution of non-modified PVAL shows phase separation when the aqueous solution of sodium sulfate (1M) is added with stirring until the concentration is reached to 0.33M in resulting solution. This phase separation is due to salting-out effects.¹⁸ 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 pH of 3.0 by adding 1N sulfuric acid to the solution. This can also be explained by lactone formation 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 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 paper.¹ 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 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 sizing,¹⁹ textile sizing,²⁰ emulsifiers, adhesives and specialty

Table 18 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

		Non-modified	IA-PVAL ^{*1}	SAMPS-PVAL ^{*2}
PVAL	Δ ^{*3}	0	2	2
	D. H. ^{*4}	98.5	97.0	99.0
	η 4%,20°C ^{*5}	28.3	27.3	26.6
	Neutral	Phase separation	Clear	Clear
Aqueous solution (PVAL:10 wt%) including sodium sulfate (0.33M)	Acidic (pH 3.0)	Phase separation	Phase separation	Clear
Aqueous solution (PVAL:10 wt%) including sodium sulfate (0.18M)		No change	Viscosity increase	No change

*1 IA-PVAL: Modified PVAL with itaconic acid.

*2 SAMPS-PVAL: Modified PVAL with sodium 2-crylamide-2-methylpropane sulfonate

*3 Mole fraction of modification group.

*4 Degree of hydrolysis

*5 Viscosity of aqueous solution (4%, 20°C).

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