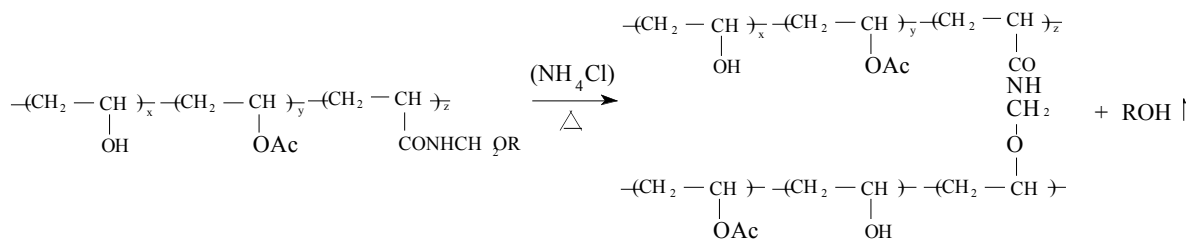


CHAPTER 10

SELF-CROSSLINKABLE PVAL

An investigation has been made on the copolymerization of vinyl acetate with N-(methoxymethyl)-acrylamide, N-(n-butoxymethyl)-acrylamide or N-methylol-acrylamide, and on the alcoholysis of copolymers and crosslinking properties of resulting modified PVALs. The former two comonomers, N-(alkoxymethyl)-acrylamides, have been found useful for producing self-crosslinkable PVALs where timing of crosslinking is controllable: no crosslinks are included in the powder as well as in aqueous solution, and crosslinked materials having high water-resistance can be produced in the dry state as the aid of ammonium chloride. The following crosslinking reaction can be assumed:



From a modified PVAL containing 1.0 mol% of N-(n-butoxymethyl)-acrylamides units, crosslinked film showing high resistance to boiling water, 0.8 % of sol fraction and 2.4 wt/wt of swelling degree, has been obtained. Modification with N-(methoxymethyl)-acrylamide also shows a similar performance. In contrast, N-methylol-acrylamide can not be used for this purpose because crosslinking occurs in alcoholysis. The monomer reactivity ratios for the copolymerization of N-(n-butoxymethyl)-acrylamide (monomer-1) and vinyl acetate (monomer-2) have been determined as $r_1 = 8$ and $r_2 = 0.095$.

10.1 INTRODUCTION

Insolubilization by crosslinking, or increasing water-resistance, is basically significant in the applications of PVAL, such as fiber, film, coating, sizing, adhesive, binder, emulsifier and others.^{1,2} For this purpose, various types of crosslinking agents reacting with hydroxyl group have been proposed,³ for example, urea- and melamine-formaldehyde resins, dialdehydes like glyoxal and glutaraldehyde, and other organic compounds.⁴⁻¹¹ Inorganic salts have also been proposed for this purpose, for example, boron compounds like boric acid, sodium borate, and other compounds containing titanium,¹² zirconium, vanadium¹³ or chromium. Using such crosslinking agents show sometimes difficulties in controlling the viscosity of the aqueous solution of PVAL because crosslinking reaction proceeds in aqueous mixture. In order to improve the controllability, it has been proposed to use modified PVALs with functional groups together with crosslinking agents to react them, for example modified PVAL with carboxylate group and polyamide epichlorohydrine,¹⁴ that with acetoacetyl group and glyoxal,^{15,16} and that with amino group and glyoxal.¹⁷ Instead of using crosslinking agents, modified PVAL containing aldehyde group as crosslinkable units has been synthesized by copolymerization of vinyl acetate (VAc) and allylidene diacetate, followed by alcoholysis.¹⁸⁻²⁰

The present work has been done for the purpose of making new “self-crosslinkable and controllable” PVALs. They are self-crosslinkable as they contain crosslinkable group in the chain. They are so perfectly soluble in water that no crosslinking reaction occurs in aqueous solution, but crosslinked materials having high water-resistance can be produced in the dry state with the aid of a curing agent. By this means, the timing of crosslinking is controllable for the modified PVALs. Such new modified PVALs have been synthesized by copolymerization of VAc and an N-(alkoxymethyl)-acrylamide shown below, followed by alcoholysis:

N-(Methoxymethyl)-acrylamide (MMAM): $\text{CH}_2=\text{CH}\cdot\text{CONH}\cdot\text{CH}_2\text{OCH}_3$

N-(n-Butoxymethyl)-acrylamide (BMAM): $\text{CH}_2=\text{CH}\cdot\text{CONH}\cdot\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

Another modification using N-methylol-acrylamide has also been investigated for comparison but found not useful for this purpose.

N-Methylol-acrylamide (MAM): $\text{CH}_2=\text{CH}\cdot\text{CONH}\cdot\text{CH}_2\text{OH}$

Copolymerization of N-(alkoxymethyl)-acrylamides with various monomers like acrylic monomers and VAc has been well known,²¹⁻²⁴ but the copolymers of vinyl alcohol and N-(alkoxymethyl)-acrylamide has not yet been reported before the present work.²⁵⁻²⁷ The present work has been done as one of the investigations concerning functional modification of PVAL by copolymerization. Modifications with carboxylic,²⁸ sulfate²⁹ or cationic³⁰ monomers have already been reported in the preceding chapters.

10.2 EXPERIMENTAL

10.2.1 *Materials*

N-(Methoxymethyl)-acrylamide (MMAM) was synthesized from acrylamide, formaldehyde and methanol and purified by vacuum distillation, based on the reported method in literature.³¹ It was slightly yellow oil: bp 104°C/2mmHg. N-(n-Butoxymethyl)-acrylamide (BMAM) and N-methylol-acrylamide (MAM) were obtained from Nitto Chemical Industry Co. and Soken Chemical & Engineering Co., respectively, both located in Tokyo, and were used as received. All the reagents were analyzed by ¹H-NMR and the purity was determined as >95%. Vinyl acetate (VAc) and 2,2'-azobisisobutyronitrile (AIBN) were obtained from Kuraray Co. and Wako Pure Chemical Industries, Osaka, respectively.

10.2.2 *Syntheses*

Copolymerization Using a glass reactor equipped with a stirrer, a reflux condenser and an apparatus supplying comonomer solution, copolymerizations were carried out in homogeneous system using methanol and AIBN as solvent and initiator, respectively, at boiling temperatures of the system, 60° to 62°C under an atmosphere of nitrogen gas. All the copolymerization system in this work showed clear appearance. Monomer reactivity ratios in copolymerization of BMAM (monomer-1) and VAc (monomer-2) have been determined as $r_1=8$ and $r_2=0.095$ from the analyses of the copolymers of various compositions synthesized under lower conversions of VAc, less than 5%. The same values were assumed for the copolymerization between MMAM and VAc. In the case of MAM and VAc, $r_1=9.68$ and $r_2=0.074$ have been calculated from Q, e values for the monomers.³² In order to obtain homogeneous composition in copolymerization at any degrees of conversion, the "feeding-comonomer method"^{33,34} was adopted, as shown in Chapter 2. The other procedures during and after copolymerization were basically the same as

the method carried out in the previous papers.²⁸⁻³⁰ Typical examples of copolymerization results are shown in Table 22.

Alcoholysis and Drying Modified PVALs were obtained by alcoholysis reaction of the modified poly(vinyl acetate)s (PVACs) using sodium hydroxide as a catalyst. The samples having various degrees of hydrolysis (DH) were synthesized by controlling the amount of sodium hydroxide. The method was also similar to that reported in the preceding chapters.²⁸⁻³⁰ In the cases of the copolymers modified with MMAM or BMAM, modified PVALs were obtained by the usual procedures. All the powder samples of

Table 22 Copolymerization of vinyl acetate (VAc) with N-(methoxymethyl)-acrylamide (MMAM) or N-(butoxymethyl)-acrylamide (BMAM) or N-methylol-acrylamide (MAM), and the hydrolyzed products of the copolymers (modified PVALs)

		$\Delta_t^{(a)}$	Feed in copolymerization (part in weight)				Reaction Time	Extent of conversion	Modified PVAL		
			VAc	Comonomer	Methanol	AIBN			$\Delta_{obs}^{(b)}$	DH ^(c)	$\eta_{4\%}^{(d)}$
		mol%	Initial/ Additional	Initial/ Additional		min	%	mol%	mol%	cP	
1	MMAM	3	1000	3.2 / 24	251 / 0	1.4	110	62	2.9	98.7	40.5
2										86.7	29.2
3	MMAM	8	1000	12 / 30	252 / 0	0.4	180	23	8.2	97.2	48.5
4	BMAM	8	1000	16 / 38	254 / 0	0.7	120	21	7.9	99.5	Insoluble to H ₂ O (Soluble to DMSO)
5	BMAM	3	1000	4 / 32	251 / 0	1.4	120	63	3.0	97.4	37.7
6	BMAM	2	1000	2.7 / 27	1500 / 0	9	180	74	2.0	98.0	5.5
7										88.1	(Cloudy)
8										83.1	(Cloudy)
9	BMAM	1	1000	1.4 / 11	250 / 0	1.4		67	1.0	98.9	38.0
10							110			87.4	29.8
11										83.4	27.6
12	MAM	3	1000	3 / 22	283 / 22	1.4	115	62	2.8	88.6	Insoluble
13										98.2	Insoluble

(a) Theoretical mole fraction of comonomer units in copolymer

(b) Observed mole fraction of comonomer units

in modified PVAL

(c) Degree of hydrolysis of vinyl acetate units in modified PVAL

(d) Viscosity of

4% aqueous solution at 20°C.

higher DH showed good solubility in water and did not show any generation of gel by crosslinking under the drying conditions at 105°C for 5 to 14 hours, except the PVALs with higher modification degrees. The generation of gel was observed in cases of PVALs modified with around 8 mol% of MMAM or BMAM units, dried at higher temperatures for long time.

There was large difference in the alcoholysis of modified PVAC with MAM. In this case sodium hydroxide was consumed during alcoholysis and the resulting PVAL was insoluble in water or in dimethyl sulfoxide even for the samples before drying.

10.2.3 Crosslinking and Water resistance

Crosslinked film (50 μ m thick) was prepared from modified PVALs in the following manner. The aqueous solution of modified PVAL (9 to 12 wt%) was mixed with the aqueous solution of ammonium chloride at the amount of 2.4 g-solid/100g-solid-PVAL, casted on a rotating drum at 75°C. The film obtained was heat-treated at 150°C for 20 min inside an electric oven equipped with a safeguard against explosion. In the heat-treatment procedure, the odor of alcohol, methanol or butanol depending on the comonomer used, was detected. Another type of crosslinked film was prepared using N/2-sulfuric acid instead of ammonium chloride at the amount of 56 g liquid/100g-solid-PVAL.

Water resistance of the crosslinked film was evaluated by its sol fraction, g_s , and swelling degree, q , after soaking in boiling water in the manner described below. The crosslinked film sample (0.1 to 1 g) was weighed precisely and soaked in boiling water for one hour. After the film sample was filtered off, the concentration of modified PVAL dissolved in the water was determined by an iodine method.³⁵

The iodine solution with deionized water was prepared by mixing 12.7 g of iodine and 25 g of potassium iodide and diluting 1000 ml (Solution-a). Another solution of 1000 ml dissolving 40 g of boric acid was prepared (Solution-b). The mixture of 90 ml of Solution-a and 450 ml of Solution-b was used as the coloration reagent. 10 ml of sample solution was mixed with 10 ml of the coloration reagent. The absorbance was recorded at 20°C in the range from 600 to 700nm. The maximum value of absorbance was determined. Calibration curve was made for each modified PVAL.

The weight of modified PVAL dissolving in water (g_s) was obtained from the observed concentration and the weight of the solution. On the other hand, the weight of the solid part of the original sample (g_o) was determined by the correction of the volatile content of the original sample, usually 1 to 5 wt%. The volatile content was determined from the weight difference between the original sample and the sample dried at 105°C for 24 hours.³⁶ The sol fraction, S , can be defined as $S = g_s/g_o$.

The crosslinked film soaked in boiling water and filtered off was stored in distilled water at 20°C for 24 hours and weighed after removing liquid water on the surface. When g_w is the observed weight of the wet

or swollen film sample, gravimetric swelling degree, q_w , of the crosslinked film can be defined as $q_w = \text{g}_w/\text{g}_o$.

10.2.4 Investigation on Chemical Structure of BMAM Group

Preparation of Samples In order to investigate the chemical behavior of BMAM group in the BMAM-modified PVAL when treated with alkali, acid or ammonium chloride in aqueous solution, the following five samples were prepared.

(A) Control: the aqueous solution (5wt%) of the PVAL modified with 3 mol% of BMAM units was poured into large amount of acetone, the precipitate was ground, purified by washing using a Soxhlet's extractor with methanol for ten hours and dried.

(B) Treatment with alkali: the powder of the modified PVAL (30g) was soaked in the mixture of methanol (1.5 liter) and aqueous sodium hydroxide solution (500g/l, 30 ml) at 40°C for two hours with stirring. The

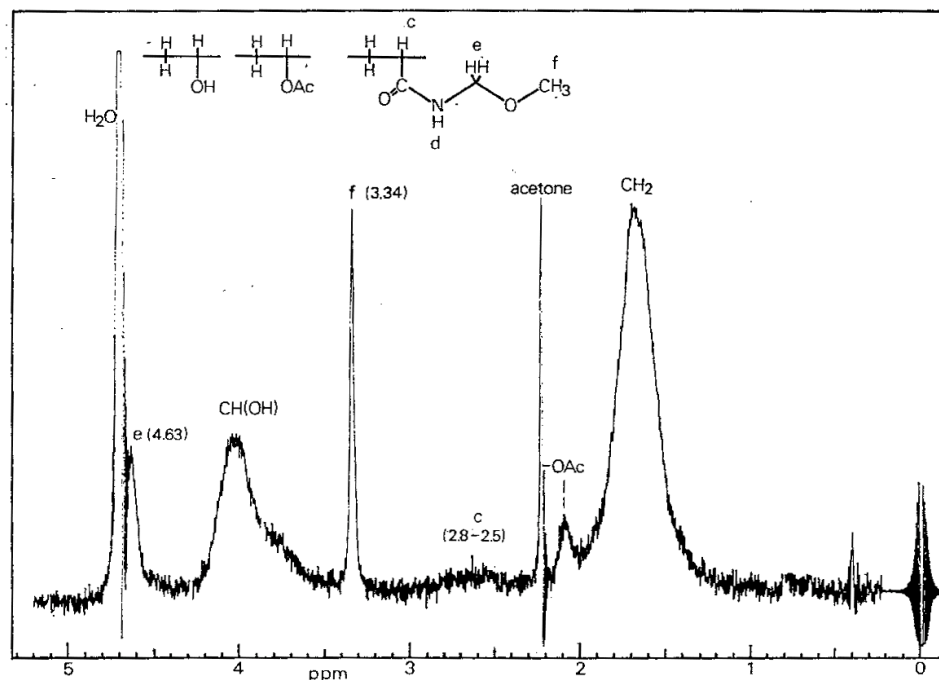


Figure 56 The 90 MHz ¹H NMR spectrum of PVAL modified with 8.2 mol% of N-(methoxymethyl)-acrylamide.

sample was filtered off, soaked in methanol at 40°C with stirring and washed using a Soxhlet's extractor in the same way as above.

(C) Mixing with acid at 40°C: the aqueous N/2-sulfuric solution (13 ml) was added to the modified PVAL aqueous solution (5wt%, 250g) and the mixture (pH 3) was stirred at 40°C for 3.5 hours, followed by the same procedure as the sample A.

(D) Mixing with acid at 80°C: the same with Sample C except for stirring at 80 °C.

(E) Mixing with ammonium chloride: the ammonium chloride (0.6 g) was added to the modified PVAL aqueous solution (5wt%, 250g) and the mixture (pH 6.2) was stirred at 80°C for 3.5 hours, followed by the same procedure as the sample A.

(F) Film (50 μ m) was prepared using a rotating drum at 75°C from the aqueous solution of the mixture of modified PVAL (5wt%, 250g) and ammonium chloride (0.6 g). The film was heat-treated at 150°C for 20 min for crosslinking.

Structural Analysis $^1\text{H-NMR}$. spectra of the modified PVALs were obtained with Varian EM-390 at 90MHz using D_2O and 3-(trimethylsilyl)propionic acid- d_6 -sodium salt as solvent and internal standard, respectively. For the samples insoluble in water owing to their stronger hydrophobicity, dimethyl sulfoxide- d_6 and hexamethyldisiloxane, were used as solvent and internal standard, respectively. IR spectra were obtained with IR-270 spectrometer from Shimadzu Corp. for the film samples of 10 μ m thick. Elementary analysis was carried out using NC-80 from Shimadzu Corp. Conductometric titration was carried out using the CA-6A conductometer from Toa Electronics Ltd. for aqueous solution of modified PVAL. Modified PVAL sample (3g) precisely weighed was dissolved in distilled water (100 ml) by heating. After cooling, N/2-sodium hydroxide aqueous solution (10 ml) was added and the solution was stored for 10 hours in a closed glass vessel. Standard N/10 sulfuric acid solution was used for the titration. From the titration amount between two crooked points observed in the data of conduction, the mole fraction of lactone generated between amido and hydroxyl groups as a side reaction was obtained. The value was corrected by the elimination of the effects of residual acetate group in the modified PVAL, which had been measured by $^1\text{H-NMR}$ or by a chemical method, alkaline re-hydrolysis followed by acid titration.³⁶

10.3 RESULTS AND DISCUSSION

10.3.1 Modified PVAL with MMAM

Copolymerization of VAc and MMAM can be carried out without any problem such as the

reduction of the rate of polymerization. Under the usual conditions of alcoholysis procedures, PVAL modified with 2.9 and 8.2 mol% of MMAM units are obtained and they show good solubility in water (Samples 1 to 3 in Table 22) although the aqueous solution of the partially hydrolyzed product (No. 2), 2.9 mol% of modification degree and 86.7 mol% of DH, shows cloudy appearance at higher temperatures than 70°C. The temperature can be called as “cloud point” which has been observed for usual partially hydrolyzed PVALs or poly(vinyl alcohol-co-vinyl acetate) having lower DH than 80 mol%.³⁷⁻³⁹ Figure 56 shows the ¹H-NMR spectrum of the modified PVAL containing MMAM units of 8.2 mol%. The mole fraction of MMAM units in the modified PVAC and that in the resulting PVAL by hydrolysis were determined as analytically the same, and accordingly MMAM units are kept stable during the alcoholysis process. Consequently the modified PVALs having the following chemical formula are obtained as new water-soluble polymers. Their self-crosslinkable property is discussed later.

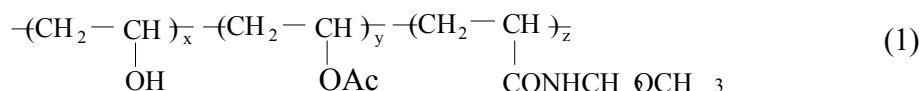


Table 23 The resistance to boiling water for the crosslinked film made from modified PVALs with BMAM or MMAM

No.	Modified PVAL				Curing agent			Resistance to boiling water		
	Comonomer ^(a)	$\Delta_{\text{obs}}^{\text{(b)}}$	D. H. ^(c)	$\eta_{4\%}^{\text{(d)}}$	g/100g-PV	pH ^(e)	Conditions of heat treatment	Sol fraction	Swelling degree at 20°C ^(f)	
	mol%	mol%	mol%	cP	AL		°C / min	%	wt/wt	
1	BMAM	1.0	98.9	38.0	N/2-H ₂ SO ₄	56	2.2	Not Heat-treated	4.7	3.6
2	BMAM	1.0	98.9	38.0	NH ₄ Cl	2.4	6.2	Not Heat-treated	100	—
3	BMAM	1.0	98.9	38.0	NH ₄ Cl	2.4	6.2	150° / 5	0.8	2.4
4	BMAM	2.0	98.0	5.5	NH ₄ Cl	2.4	6.3	150° / 5	1.3	2.7
5	MMAM	1.0	86.1	29.3	N/2-H ₂ SO ₄	56	2.0	150° / 5	0.3	2.6

(a) BMAM: N-(n-butoxymethyl)-acrylamide MMAM: N-(methoxymethyl)-acrylamide

(b) Observed mole fraction of comonomer units in copolymer (c) Degree of hydrolysis of vinyl acetate units in copolymer

(d) Viscosity of 4% aqueous solution at 20°C

(e) pH of the aqueous solution including modified PVAL and curing agent

(f) Gravimetric swelling degree. Soaked in boiling water for one hour, filtered off and stored in distilled water at 20°C for 24 hours.

10.3.2 Modified PVALs with BMAM

In the case using BMAM as a comonomer, copolymerization and alcoholysis can be carried out without any problem in the similar way for using MMAM. Figure 57 - A shows the $^1\text{H-NMR}$ spectrum of the modified PVAL containing 3.0 mol% BMAM units. The modified PVALs having the following chemical formula are thus obtained as new water-soluble polymers.

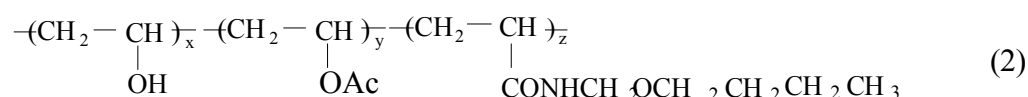


Table 22 shows the samples of modified PVALs with various degrees of BMAM units, 1.0 to 7.9 mol% and with various DH, 83.1 to 99.5 mol%. The modified PVAL with higher mole fraction of BMAM, 7.9 mol% (Sample 4 in Table 22), is insoluble in water but soluble perfectly in dimethyl sulfoxide. The insolubility in water is attributable to the hydrophobic property of butoxymethyl group. The highly-hydrolyzed PVALs modified with 1 to 3 mol% of BMAM units show good solubility in water, while the partially hydrolyzed modified PVAL samples containing 2 mol% of BMAM units, 83.1 and 88.1 mol% of DH, are soluble in water but the solution shows cloudy appearance at room temperature. This can also be regarded as the effects of the hydrophobic property of butoxymethyl group.

Concerning the solubility of modified PVALs in water, MMAM can be more advantageous than BMAM. Even 1 mol% of the degree of modification of BMAM, however, has been found to give PVAL the function of self-crosslinking which can make it highly water resistant, as discussed later. PVALs modified with 1 mol% of BMAM units and having lower DH down to 83.4 mol% shows good solubility in water and no cloud point up to boiling temperature. Therefore, BMAM is also regarded practical as a comonomer giving the present self-crosslinkable PVALs.

It must be significant that the modified PVALs with BMAM or MMAM can be prepared as powder material not including any crosslinking or gel under usual synthetic processes. The relation between drying conditions after alcoholysis process and the solubility of the resulting modified PVALs was carefully observed because heat in drying can make

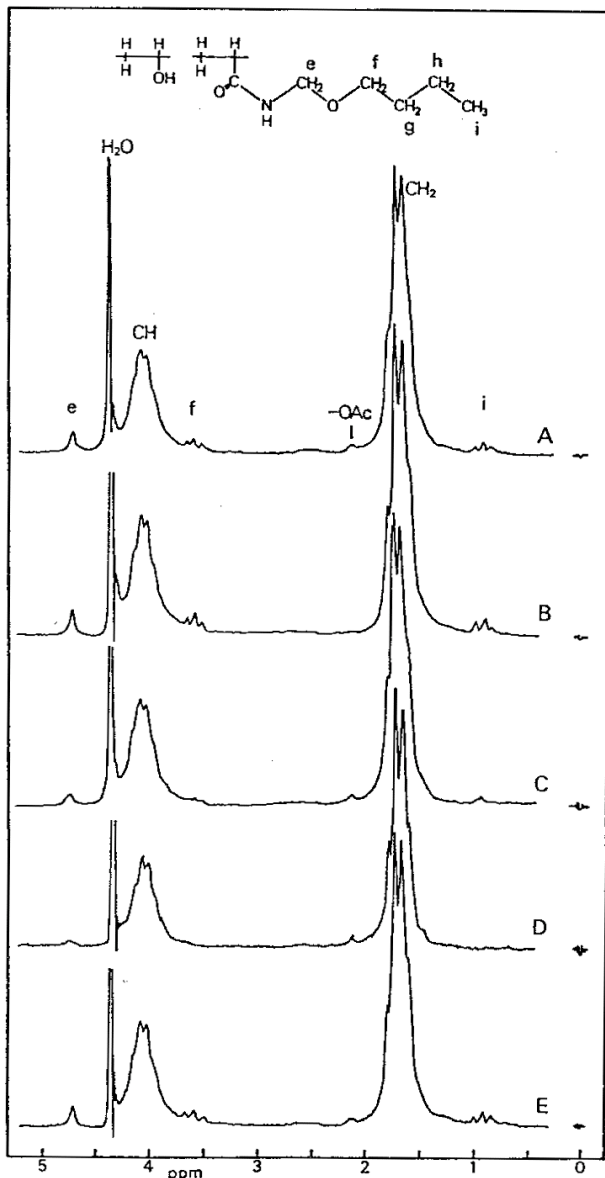


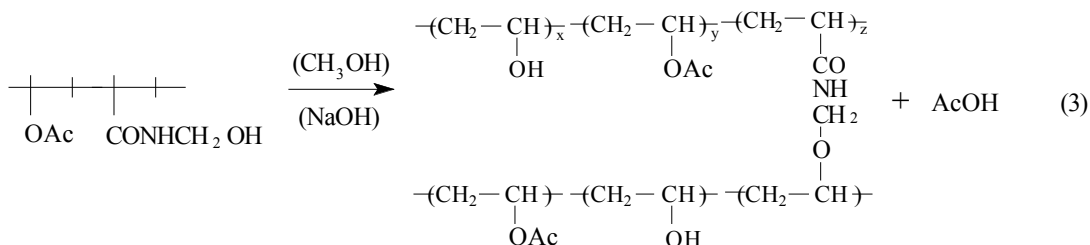
Figure 57 The 90-MHZ $^1\text{H-NMR}$ spectra of poly(vinyl alcohol) modified with 3.0 mol% of N-(butoxymethyl)-acrylamide. The five spectra are for the samples treated under the various conditions shown in Table 3.

- (A) Original,
- (B) Treatment by alkali in methanol,
- (C) Mixing with H_2SO_4 at 40°C (pH 3),
- (D) Mixing with H_2SO_4 at 80°C (pH 3),
- (E) Mixing with NH_4Cl at 80°C (pH 6.2).

crosslinking. The modified PVALs containing MMAM or BMAM units of 1 or 2 mol%, the standard degrees of modification giving sufficient water resistance after crosslinking procedure, showed no gel or insoluble fraction under drying conditions at 105°C for 5 to 14 hours. They also showed little change of viscosity for 4 % aqueous solution independent of drying time. For PVALs modified with higher MMAM units, 8.2 mol%, the generation of gel was observed after drying at 105°C for 5 hours but little gel was observed after drying at 80°C for 5 hours. Therefore, it can be concluded that the powder of perfectly water-soluble PVALs modified with 1 to 2 mol% of MMAM or BMAM units can practically be produced.

10.3.3 Modified PVALs with MAM

The situation has been found quite different in the modification with MAM in contrast to MMAM and BMAM. PVAC modified with 2.8 mol% of MAM units is perfectly soluble in methanol. In the alcoholysis of the modified PVAC, sodium hydroxide as a catalyst is consumed and more amount of sodium hydroxide is required for the completion of reaction. The resulting modified PVALs give insoluble gel or white dispersion when they are dissolved under the usual dissolution procedure in water or in dimethyl sulfoxide (Samples 12 and 13 in Table 22). As the PVAL sample before drying also gives gel in the solvents, crosslinking is regarded to occur during alcoholysis. The following reaction can be assumed in alcoholysis process:



Thus, water soluble PVAL cannot be obtained using MAM as a modification comonomer.

10.3.4 Crosslinking and Water Resistance

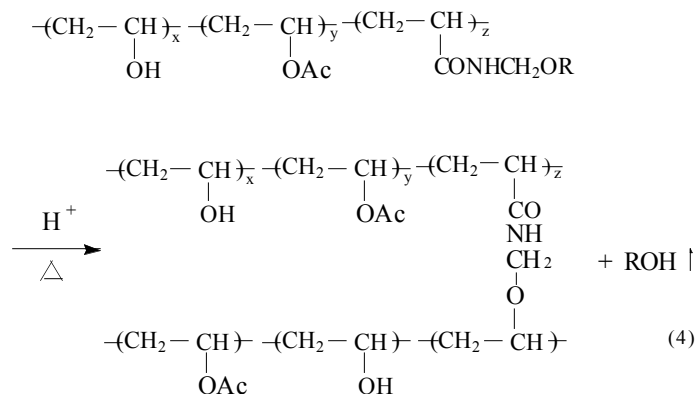
Table 23 shows the water-resistance of the film made from the aqueous solutions of PVALs modified with BMAM or MMAM with the aid of ammonium chloride or sulfuric acid curing agent. Water resistance is evaluated by sol fraction in boiling water and swelling degree at 20°C. The film made by casting on a rotating drum at 75°C from the aqueous solution of the PVAL modified with 1.0 mol% of BMAM units, using sulfuric acid as a curing agent and not heat-treated, (Sample 1) keeps its shape in boiling water. It shows 4.7 % of sol fraction and 3.6 wt/wt of swelling degree. The film from the same modified PVAL using ammonium chloride as a curing agent instead of sulfuric acid and not heat-treated (Sample 2) is perfectly soluble in boiling water. When this film is heat-treated at 150°C for five min (Sample 3), it shows high water resistance, 0.8 % of sol fraction and 2.4 wt/wt of swelling degree. The modified PVAL of lower polymerization degree or lower

viscosity, (Sample 4) shows higher values of sol fraction (1.3%) and swelling degree (2.7 wt/wt). This can be reasonably explained by gel formation theory^{40,41} and by the theory concerning swelling of networks.^{40,42} The comparison of the experiment with the theories will be discussed in Chapter 11.⁴³ The PVAL modified with 1.0 mol% of MMAM units also yields highly water-resistant film (Sample 5) showing 0.3 % of sol fraction and 2.6 wt/wt of swelling degree.

Ammonium chloride can be regarded more advantageous as a curing agent because crosslinking reaction does not occur in aqueous solution of the modified PVAL mixed with the agent. In contrast, when using sulfuric acid as a curing agent, crosslinking reaction occurs in solution and its viscosity increases. In the case of the aqueous solution (10 wt%) of the sample 1 in Table 23, it showed 1410 cP at 20°C just after mixing sulfuric acid and its viscosity increased to 3240 cP after storing for two days at 20°C.

10.3.5 Chemical Behavior of BMAM Group

Insolubilization of PVALs modified with N-(alkoxymethyl)-acrylamide like MAAM and BMAM can be attributable to the crosslinking reaction between the N-(alkoxymethyl) group and hydroxyl group as follows:

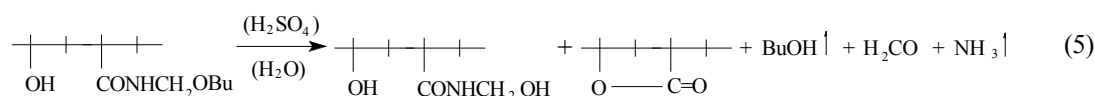


The chemical behavior of BMAM group in modified PVAL treated under various conditions have been investigated using five analytical methods, viscosity, elementary analysis, ¹H-NMR, IR and conductometric titration, as shown in Table 24, Figures 57 and 58.

The starting modified PVAL (Sample A) was obtained from the alcoholysis of modified

PVAC containing 3 mol% of BMAM and 1.7 mol% of residual acetyl groups. Treatment of the modified PVAL with alkali in methanol (Sample B) results in the removal of residual acetate group but little effects for other structure and viscosity. BMAM group shows the resistance to hydrolysis by the alkali treatment.

In Samples, C and D, mixing with H_2SO_4 at 40° and $80^\circ C$, respectively, viscosity increase is observed together with the reduction of butoxy and $-CONHCH_2O-$ groups. In Sample D, all the butoxy groups are liberated as butanol gas; 1.7 mol% of $-CONHCH_2OH$ group and 1.4 mol% of lactone are generated, as shown in *Equation (5)*.



The mixing with ammonium chloride in aqueous solution at $80^\circ C$ (Sample E) causes no change in the structure of BMAM group nor in viscosity. In the crosslinked film made from the aqueous solution of Sample E followed by heat-treatment at $150^\circ C$ for 20 min (Sample F), almost all the amide linkage is not hydrolyzed and makes crosslinking shown in the *Equation (4)* because Sample F shows almost the same value of nitrogen by elementary analysis as Sample A. Small amount of lactone due to the decomposition of amide linkage, however, is regarded to generate as a side reaction because the absorption at 1745 cm^{-1} is observed in the IR spectrum.²⁸ From the intensity analysis, the amount of lactone can be estimated as about 0.2 mol%. The degree of decomposition of amide linkage of BMAM is about 6% in the process of heat-treatment.

10.3.6 Applications of the Self-Crosslinkable PVALs

Using the specific properties of the present “crosslinkable and controllable” modified PVALs, various applications have been proposed such as coating or sizing agent for paper,^{44,45} emulsifier,⁴⁶ fiber⁴⁷ and others.⁴⁸

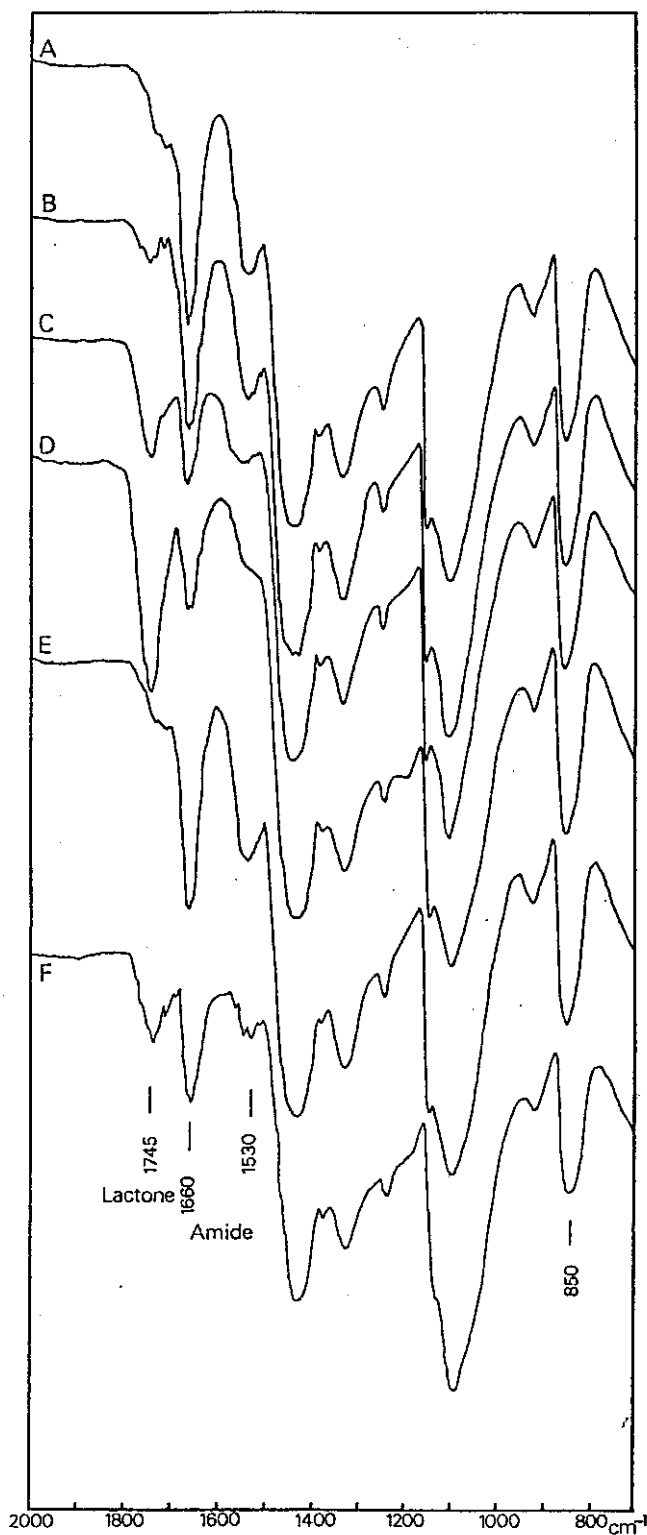


Figure 58 The IR spectra of poly(vinyl alcohol) modified with 3.0 mol% of (butoxymethyl)-acrylamide. The five spectra are for the samples treated under various conditions shown in Table 3.

- Original,
- Treatment by alkali in methanol,
- △ Mixing with H₂SO₄ at 40°C (pH 3),
- ◇ Mixing with H₂SO₄ at 80°C (pH 3),
- Mixing with NH₄Cl at 80°C (pH 6.2),
- Crosslinked film made from the solution of Sample E.

Table 24. The structural analysis of poly(vinyl alcohol) modified with N-(n-butoxymethyl)acrylamide (BMAM) treated under various conditions.

Sample	Treatment	$\eta_{sp}/c^{(a)}$ cP	Elementary analysis			$^1\text{H NMR}$			IR (intensity ratio)			Conductometric titration
			Nitrogen wt%	BMAM units mol%	-OAc mol%	-OBu mol%	-CONHCH ₂ O ⁻ mol%	Lactone I_{1742}/I_{1550}	Amide I_{1669}/I_{1550}	Amide I_{1519}/I_{1550}	Lactone mol%	
A	Original sample	37.7	0.88	3.0	1.7	3.0	3.1	0.0	1.54	0.52	0.0	0.0
B	Treatment with alkali	34.5	0.87	3.0	0.0	3.0	2.9	0.18	0.97	0.45	0.0	0.0
C	Mixing with H ₂ SO ₄ at 40°C (pH3) ^(b)	65.0	0.76	2.6	1.7	1.2	2.1	0.55	0.47	0.25	1.2	1.2
D	Mixing with H ₂ SO ₄ at 80°C (pH3) ^(b)	74.8	0.41	1.4	1.7	0.0	1.7	1.50	0.64	0.10	1.4	1.4
E	Mixing with NH ₄ Cl at 80°C (pH6.2) ^(b)	33.3	0.91	0.91	1.3	3.0	3.2	0.0	1.42	0.50	0.0	0.0
F	Crosslinked film made from Sample E ^(c)	NA ^(d)	0.82	2.8	NA ^(d)	NA	NA	0.38	0.95	0.30	NA	NA

(a) Viscosity of 4% aqueous solution at 20°C.

(b) The samples precipitated in acetone and washed by methanol after the treatment.

(c) The film was heat-treated at 150°C for 20 min.

(d) Not available.

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