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# Functional modification of poly(vinyl alcohol) by copolymerization: IV. Self-crosslinkable poly(vinyl alcohol)s

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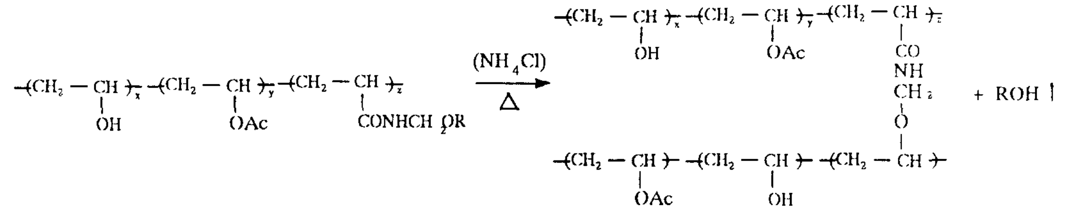
An investigation has been made on the copolymerization of vinyl acetate with *N*-(methoxymethyl)-acrylamide, *N*-(*n*-butoxymethyl)-acrylamide or *N*-methylol-acrylamide, and or the alcoholysis of copolymers and crosslinking properties of the resulting modified poly(vinyl alcohol)s (PVALs). The former 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 or in aqueous solution, and crosslinked materials having high water-resistance can be produced in the dry state with the aid of ammonium chloride. The following crosslinking reaction can be assumed:



From a modified PVAL containing 1.0 mol% of *N*-(*n*-butoxymethyl)-acrylamide units, a crosslinked film showing high resistance to boiling water, 0.8% of the sol fraction and 2.4% (w/w) of the swelling degree, has been obtained. Modification with *N*-(methoxymethyl)-acrylamide also shows a similar performance. In contrast, *N*-methylol-acrylamide cannot 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 $r_2 = 0.095$. © 1997 Elsevier Science Ltd.

**(Keywords: poly(vinyl alcohol); copolymerization; crosslinking)**

## INTRODUCTION

Insolubilization by crosslinking, or increasing water-resistance, is basically significant in the applications of poly(vinyl alcohol) (PVAL), such as fibre, film, coating, sizing, adhesive, binder, emulsifier and others[1,2]. For this purpose, various types of crosslinking agent that react with the 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, vanadium[13] or chromium. Using such crosslinking agents sometimes shows difficulties in controlling the viscosity of the aqueous solution of PVAL because the crosslinking reaction proceeds in the 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 a carboxylate group and polyamide epichlorohydrine[14], that with an acetoacetyl group and glyoxal[15,16], and that with an amino group and glyoxal[17]. Instead of using crosslinking agents, a modified PVAL containing aldehyde groups 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 groups in the chain. They are so perfectly soluble in water that no crosslinking reaction occurs in the aqueous solutions, 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) :

$CH_2{=}CH{-}CONH{-}CH_2OCH_3$

*N* – (*n* – butoxymethyl) – acrylamide (BMAM) :

$CH_2{=}CH{-}CONH{-}CH_2OCH_2CH_2CH_2CH_3$

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**Table 1** Copolymerization of VAc with *N*-(methoxymethyl)-acrylamide (MMAM), *N*-(butoxymethyl)-acrylamide (BMAM) or *N*-methylol-acrylamide (MAM), and the hydrolysed products of the copolymers (modified PVALs)

| | | Feed in coplymerization (part in weight) | | | | | | | Modified PVAL | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\Delta_t$ [a] (mol%) | VAc | Comonomer initial/additional | Methanol initial/additional | AIBN | Reaction time (min) | Extent of conversion of VAc (%) | $\Delta_{obs}$ [b] (mol%) | D.H.[c] (mol%) | $\eta_{4\%}$ [d] (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 $H_2O$(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 VAc units in modified PVAL
[d] Viscosity of 4% aqueous solution at 20°C

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

$$N - \text{methylol} - \text{acrylamide (MAM)}:$$

$$CH_2{=}CH{-}CONH{-}CH_2OH$$

Copolymerization of *N*-(alkoxymethyl)-acrylamides with various monomers, like acrylic monomers and VAc, is well known[21–24], but the copolymers of vinyl alcohol and *N*-(alkoxymethyl)-acrylamide have not yet been reported until now[25–27]. The present work has been done as one of the investigations concerning functional modification of PVAL by copolymerization. Modifications with carboxylic[28], sulfate[29] or cationic[30] monomers have already been reported.

## EXPERIMENTAL

### *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 is a slightly yellow oil: b.p. 104°C/2 mmHg. *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 analysed by $^1H$ n.m.r. and the purity was determined as $> 95\%$. VAc and 2.2′-azobisisobutylonitrile (AIBN) were obtained from Kuraray Co. and Wako Pure Chemical Industries, Osaka, respectively.

### *Syntheses*

*Copolymerization.* Using a glass reactor equipped with a stirrer, a reflux condenser and an apparatus supplying comonomer solution, copolymerizations were carried out in a 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 systems in this work showed a 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 of 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 a homogeneous composition in the copolymerization for any degree of conversion, the ''feeding-comonomer method''[33,34] was adopted. 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 1*.

*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 (D.H.) were synthesized by controlling the amount of sodium hydroxide. The method was also similar to that reported in the previous papers[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 higher D.H. 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 h, 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 a long time.

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

### *Crosslinking and water resistance*

Crosslinked film (50 $\mu$m thick) was prepared from modified PVALs in the following manner. The aqueous solution of modified PVAL (9 to 12 wt%) was mixed with an aqueous solution of ammonium chloride in the amount of 2.4 g-solid/100 g-solid-PVAL, cast 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 odour 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/100 g-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 1 h. After the film sample was filtered off, the concentration of modified PVAL dissolved in the water was determined by the 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 700 nm. The maximum value of absorbance was determined. A 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 $g_0$ 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 h[36]. The sol fraction $S$ can be defined as $S = g_s/g_0$.

The crosslinked film soaked in boiling water and filtered off was stored in distilled water at 20°C for 24 h and weighed after removing liquid water on the surface. When $g_w$ is the observed weight of the wet or swollen film sample, the gravimetric swelling degree $q_g$ of the crosslinked film can be defined as $q_g = g_w/g_0$.

### *Investigation of the chemical structure of the BMAM group*

*Preparation of samples.* In order to investigate the chemical behaviour of the 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 (5 wt%) of the PVAL modified with 3 mol% of BMAM units was poured into a large amount of acetone; the precipitate was ground, purified by washing using a Soxhlet extractor with methanol for 10 h and dried.

(B) Treatment with alkali: the powder of the modified PVAL (30 g) was soaked in a mixture of methanol (1.5 l) and aqueous sodium hydroxide solution (500 g $l^{-1}$, 30 ml) at 40°C for 2 h with stirring. The sample was filtered off, soaked in methanol at 40°C with stirring and washed using a Soxhlet 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 (5 wt%, 250 g) and the mixture (pH 3) was stirred at 40°C for 3.5 h, followed by the same procedure as the sample (A).

(D) Mixing with acid at 80°C: the same as 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 (5 wt%, 250 g) and the mixture (pH 6.2) was stirred at 80°C for 3.5 h, followed by the same procedure as for sample (A).

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

*Structural analysis.* $^1H$ n.m.r. spectra of the modified PVALs were obtained with a Varian EM-390 at 90 MHz 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. I.r. spectra were obtained with an IR-270 spectrometer from Shimadzu Corp. for the film samples of 10 μm thick. Elemental analysis was carried out using an NC-80 from Shimadzu Corp. Conductometric titration was carried out using the CA-6A conductometer from Toa Electronics Ltd. for an aqueous solution of modified PVAL. The modified PVAL sample (3 g, 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 h 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 $^1H$ n.m.r. or by a chemical method: alkaline rehydrolysis followed by acid titration[36].

## RESULTS AND DISCUSSION

### *Modified PVALS 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, PVALs 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 1*) although the aqueous solution of the partially hydrolysed product (No. 2), 2.9 mol% of modification degree and 86.7 mol% D.H., shows a cloudy appearance at temperatures higher than 70°C. This temperature can be called the "cloud point", and has been observed for usual partially hydrolysed PVALs or poly(vinyl alcohol-co-vinyl acetate) having lower D.H. than 80 mol%[37–39]. *Figure 1* shows the $^1H$ n.m.r. spectrum of the

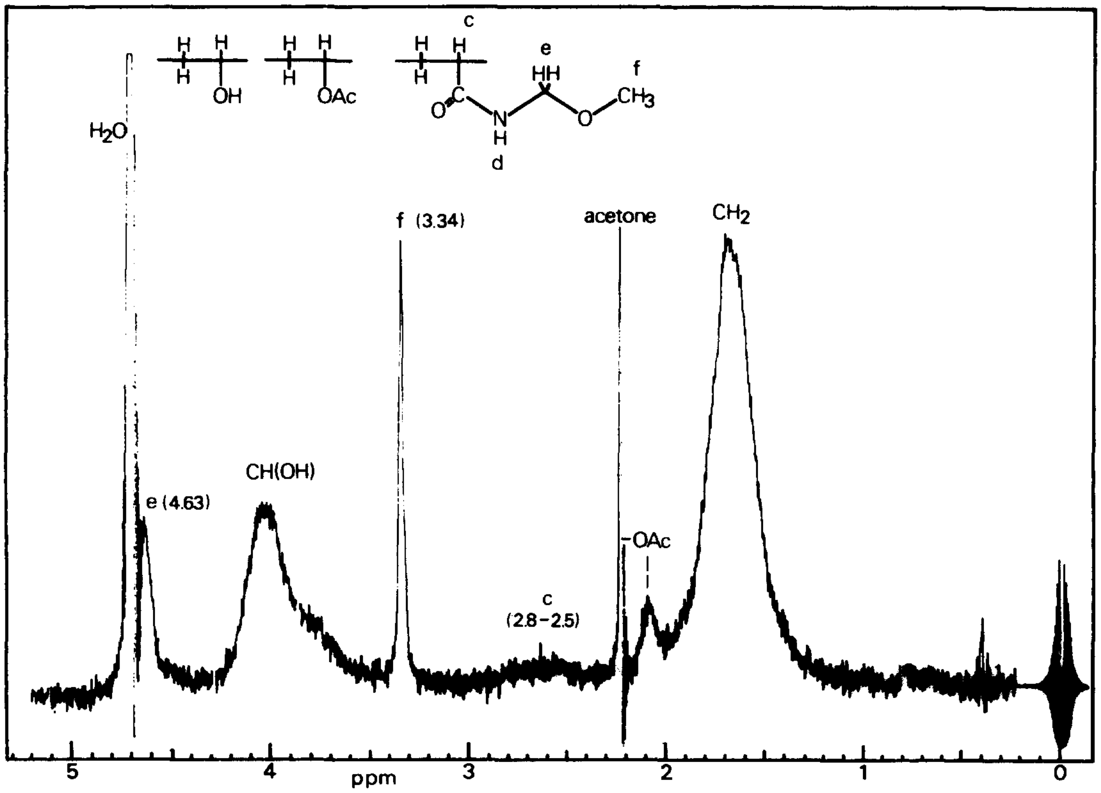
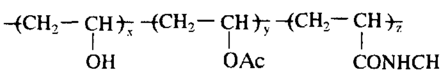


**Figure 1** The 90 MHz $^1H$ n.m.r. spectrum of PVAL modified with 8.2 mol% of *N*-(methoxymethyl)-acrylamide

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 analytically to be the same; hence, the MMAM units remain stable during the alcoholysis process.

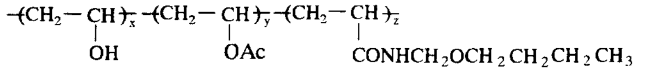
Consequently, the modified PVALs having the following chemical formula are obtained as new water-soluble polymers. Their self-crosslinkable property is discussed later.


(1)

$$-(CH_2-\underset{OH}{CH})_x-(CH_2-\underset{OAc}{CH})_y-(CH_2-\underset{CONHCH_2OCH_3}{CH})_z- \quad (1)$$

*Modified PVALs with BMAM*

In the case when using BMAM as a comonomer, copolymerization and alcoholysis can be carried out without any problem in a similar way to that for MMAM. *Figure 2A* shows the $^1H$ n.m.r. 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.


(2)

$$-(CH_2-\underset{OH}{CH})_x-(CH_2-\underset{OAc}{CH})_y-(CH_2-\underset{CONHCH_2OCH_2CH_2CH_2CH_3}{CH})_z- \quad (2)$$

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

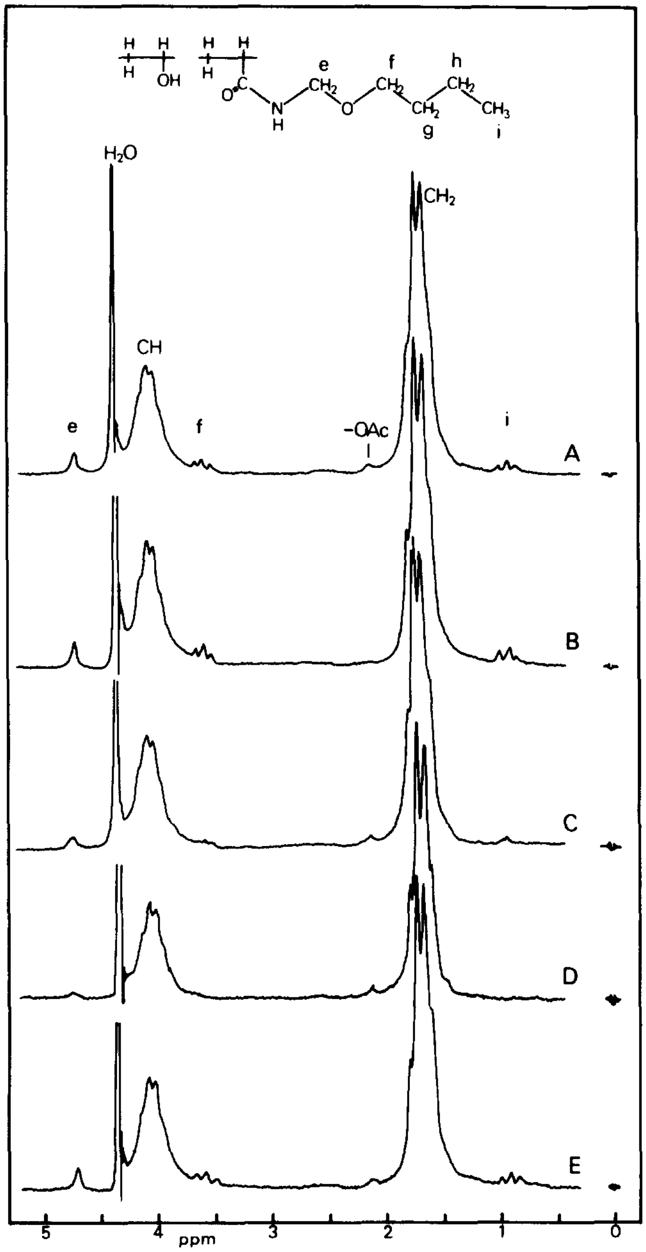


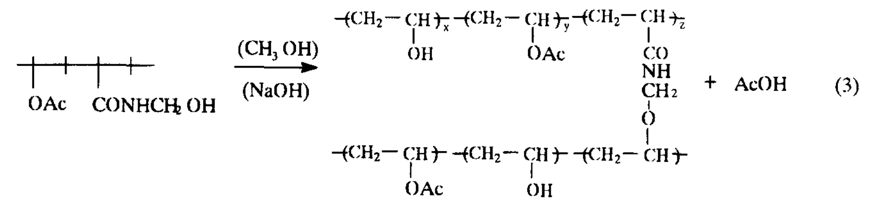
**Figure 2** The 90 MHz $^1H$ n.m.r. spectra of PVAL modified with 3.0 mol% of *N*-(butoxymethyl)-acrylamide. The five spectra are for the samples treated under the various conditions shown in *Table 3*. (A) Original. (B) Treatment by alkali in methanol. (C) Mixing with $H_2SO_4$ at 40°C (pH 3). (D) Mixing with $H_2SO_4$ at 80°C (pH 3). (E) Mixing with $NH_4Cl$ at 80°C (pH 6.2).

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 D.H. down to 83.4 mol% show good solubility in water and no cloud point up to the boiling temperature. Therefore, BMAM is also regarded as a practical comonomer to give 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 the alcoholysis process and the solubility of the resulting modified PVALs was carefully observed because heat in drying can lead to crosslinking. The modified PVALs containing MMAM or BMAM units of 1 or 2 mol%, the standard degrees of modification giving sufficient water resistance after the crosslinking procedure, showed no gel or insoluble fraction under drying conditions at 105°C for 5 to 14 h. They also showed little change of viscosity for 4% aqueous solution independent of the 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 h, but little gel was observed after drying at 80°C for 5 h. 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.

*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 sodium hydroxide is required for completion of the reaction. The resulting modified PVALs give an 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 1*). As even the PVAL sample before drying gives gel in the solvents, crosslinking is regarded to occur during alcoholysis. The following reaction can be assumed in the alcoholysis process:



(3)

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

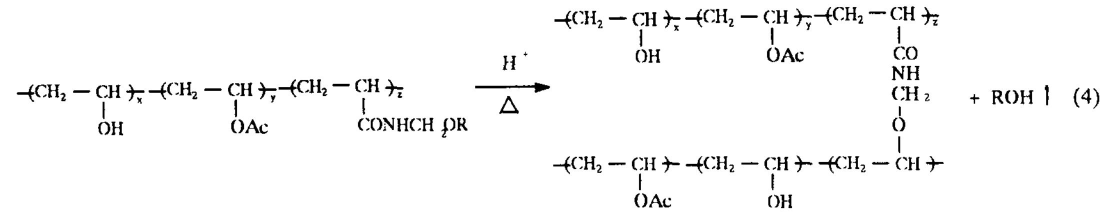
*Crosslinking and water resistance*

*Table 2* 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 agents. Water resistance is evaluated by sol fraction in boiling water and swelling degree. 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% (w/w) 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 5 min (sample 3) it shows high water resistance, 0.8% of sol fraction and 2.4% (w/w) of swelling degree. The modified PVAL of lower polymerization degree or lower viscosity (sample 4) shows slightly higher values of sol fraction (1.3%) and swelling degree (2.7% (w/w)). This can be reasonably explained by gel formation theory[40,41] and the theory concerning swelling of networks[40,42]. The comparison of the experiment with the theories will be discussed in a subsequent paper[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% (w/w) of swelling degree.

Ammonium chloride can be regarded as being more advantageous as a curing agent because the 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 the crosslinking reaction occurs in the solution and its viscosity increases. In the case of the aqueous solution (10 wt%) of the sample 1 in *Table 2*, it showed a viscosity of 1410 cP at 20°C just after mixing sulfuric acid and its viscosity increased to 3240 cP after storing for 2 days at 20°C.

*Chemical behaviour of BMAM group*

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



(4)

The chemical behaviour of the BMAM group in modified PVAL treated under various conditions has been investigated using five analytical methods, viscosity, elementary analysis, $^1H$ n.m.r., i.r. and conductometric titration, as shown in *Table 3*, *Figures 2 and 3*.

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 removal of residual acetate groups but little effects on either structure or viscosity. The BMAM group shows resistance to hydrolysis by the alkali treatment.

**Table 2** The resistance to boiling water for the crosslinked film made from modified PVALs with BMAM and MMAM

| | Modified PVAL | | | | Curing agent | | | | Resistance to boiling water | |
|---|---|---|---|---|---|---|---|---|---|---|
| No. | Comonomer[a] | $\Delta_{obs}$ [b] (mol%) | D.H.[c] (mol%) | $\eta_{4\%}$ [d] (cP) | | g/100 g-/ PVAL | pH[e] | Conditions of heat treatment (°C, min) | Sol fraction (%) | Swelling degree at 20°C[f] (% w/w) |
| 1 | BMAM | 1.0 | 98.9 | 38.0 | N/2 $H_2SO_4$ | 56 | 2.2 | not heat-treated | 4.7 | 3.6 |
| 2 | BMAM | 1.0 | 98.9 | 38.0 | $NH_4Cl$ | 2.4 | 6.2 | not heat-treated | 100 | - |
| 3 | BMAM | 1.0 | 98.9 | 38.0 | $NH_4Cl$ | 2.4 | 6.2 | 150, 5 | 0.8 | 2.4 |
| 4 | BMAM | 2.0 | 98.0 | 5.5 | $NH_4Cl$ | 2.4 | 6.3 | 150, 5 | 1.3 | 2.7 |
| 5 | MMAM | 1.0 | 86.1 | 29.3 | N/2 $H_2SO_4$ | 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 VAc 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 1 h, filtered off and stored in distilled water at 20°C for 24 h

**Table 3** The structural analysis of PVAL modified with *N*-(*n*-butoxymethyl)-acrylamide (BMAM) treated under various conditions

| Sample | Treatment | $\eta_{4\%}$ [a] (cP) | Elemental analysis: Nitrogen (wt%) | Elemental analysis: BMAM units (mol%) | $^1H$ n.m.r.: –OAc (mol%) | $^1H$ n.m.r.: –OBu (mol%) | $^1H$ n.m.r.: –CONHCH$_2$O– (mol%) | I.r. (intensity ratio): Lactone $I_{1745}/I_{850}$ | I.r. (intensity ratio): Amide $I_{1660}/I_{850}$ | I.r. (intensity ratio): Amide $I_{1510}/I_{850}$ | Conductometric titration (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 |
| B | Treatment with alkali | 34.5 | 0.87 | 3.0 | 0.0 | 3.0 | 2.9 | 0.18 | 0.97 | 0.45 | 0.0 |
| C | Mixing with $H_2SO_4$ at 40°C (pH 3)[b] | 65.0 | 0.76 | 2.6 | 1.7 | 1.2 | 2.1 | 0.55 | 0.47 | 0.25 | 1.2 |
| D | Mixing with $H_2SO_4$ 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 |
| E | Mixing with $NH_4Cl$ at 80°C (pH 6.2)[b] | 33.3 | 0.91 | 3.1 | 1.3 | 3.0 | 3.2 | 0.0 | 1.42 | 0.50 | 0.0 |
| F | Crosslinked film made from sample E[c] | NA[c] | 0.82 | 2.8 | NA[d] | NA | NA | 0.38 | 0.95 | 0.30 | 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

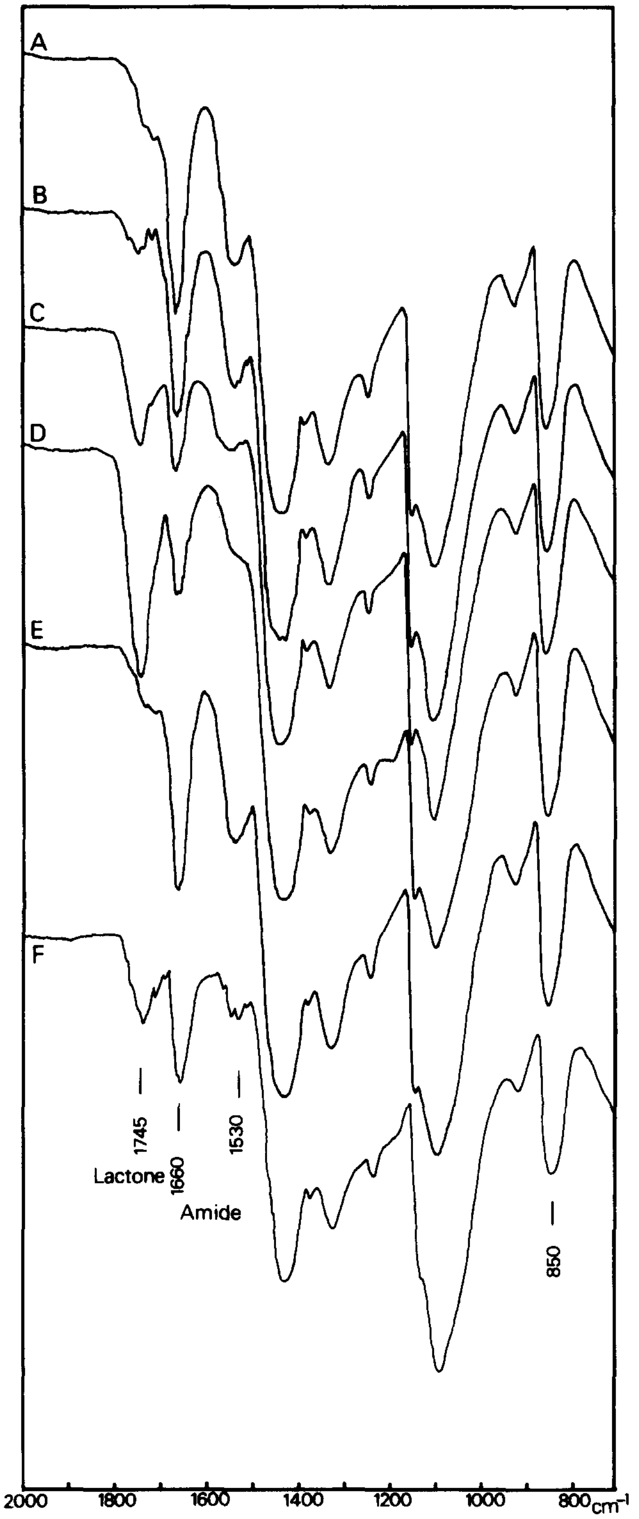
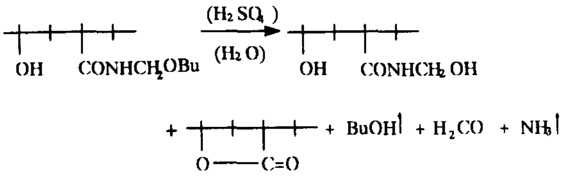


**Figure 3** The i.r. spectra of PVAL modified with 3.0 mol% of *N*-(butoxymethyl)-acrylamide. The five spectra are for the samples treated under the various conditions shown in *Table 3*. (A) Original. (B) Treatment by alkali in methanol. (C) Mixing with $H_2SO_4$ at 40°C (pH 3). (D) Mixing with $H_2SO_4$ at 80°C (pH 3). (E) Mixing with $NH_4Cl$ at 80°C (pH 6.2). (F) Crosslinked film made from the solution of sample (E).

In samples, C and D, mixing with $H_2SO_4$ at 40°C and 80°C respectively, a viscosity increase is observed together with a reduction of the 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% lactone are generated, as shown in equation (5).



$$\text{OH},\ \text{CONHCH}_2\text{OBu} \xrightarrow[(H_2O)]{(H_2SO_4)} \text{OH},\ \text{CONHCH}_2\text{OH} + \text{O—C=O} + \text{BuOH}\uparrow + H_2CO + NH_3\uparrow \quad (5)$$

The mixing with ammonium chloride in aqueous solution at 80°C (sample E) causes no change in the structure of the BMAM group nor in its viscosity. In the crosslinked film made from the aqueous solution of sample E followed by heat-treatment at 150°C for 20 min (sample F), almost all the amide linkage is not hydrolysed and makes the crosslinking shown in the equation (4), because sample F shows almost the same value of nitrogen by elemental analysis as sample A. A small amount of lactone due to the decomposition of the amide linkage, however, is regarded to be generated as a side reaction because of the absorption at 1745 $cm^{-1}$ observed in the i.r. spectrum[28]. From the intensity analysis, the amount of lactone can be estimated as about 0.2 mol%. The degree of decomposition of the amide linkage of BMAM is about 6% during heat-treatment.

### *Applications of the self-crosslinkable PVALs*

Using the specific properties of the present "cross-linkable and controllable" modified PVALs, various applications have been proposed, such as coating or sizing agent for paper[44,45], emulsifier[46], fibre[47] and others[48].

## CONCLUSIONS

(1) *N*-(Alkoxymethyl)-acrylamides, such as MMAM and BMAM, have been found useful for the production of self-crosslinkable PVAL by copolymerization and alcoholysis. A powder of the modified PVAL showing perfect solubility in water can be produced. Using the aqueous solutions, crosslinked and water-resistant materials can be prepared in the dry state with the aid of an acidic curing agent, ammonium chloride in particular. In this sense, the timing of crosslinking is controllable in the modified PVAL.

(2) Using a modified PVAL containing 1.0 mol% of BMAM units, crosslinked film showing high water-resistance, 0.8% of sol fraction and 2.4% (w/w) of swelling degree, can be obtained.

(3) The amide linkage of the BMAM group in the polymer chain is not hydrolysed in alcoholysis or in the aqueous solution containing ammonium chloride. On the other hand, a part of it is hydrolysed and converts to lactone in an aqueous solution containing sulfuric acid as a curing agent. Therefore, ammonium chloride is more advantageous as a curing agent.

(4) *N*-(Methylol)-acrylamide cannot be used for this purpose because crosslinking occurs in alcoholysis.

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