

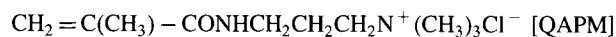
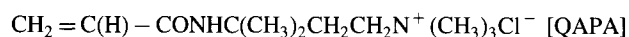
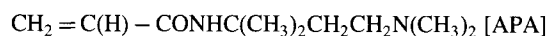
# Functional modification of poly(vinyl alcohol) by copolymerization III. Modification with cationic monomers

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Various methods for modifying poly(vinyl alcohol) with cationic groups have been investigated using two cationic reagents and 10 cationic monomers. The cationic monomers of acrylamide and methacrylamide derivatives such as N-(1,1-dimethyl-dimethylaminopropyl) acrylamide (APA) and N-(dimethyl aminopropyl) methacrylamide (APM) and their quaternary ammonium salts (QAPA and QAPM) shown below have been found useful to produce cationic poly(vinyl alcohol)s by copolymerization and alcoholysis because of their much higher reactivity in copolymerization and because the amido linkage has good stability for alkaline alcoholysis.



Modifications with dimethyl aminoethyl vinyl ether, 1-methyl vinyl imidazole and their quaternary ammonium salts have also been investigated and regarded as useful for the preparation of poly(vinyl alcohol)s having more stable cationic groups. The cationically modified poly(vinyl alcohol)s show specific functions such as high adsorption to fibrous pulp dispersed in water, formation of polyelectrolyte complex and emulsifying ability to make cationic emulsion. Partially hydrolysed poly(vinyl alcohol)s modified with QAPM have been found to show unusually high viscosity in aqueous solutions such as 2000 cP at 4 wt% and 20°C. © 1997 Elsevier Science Ltd.

(Keywords: poly(vinyl alcohol); copolymerization; cationic monomers)

## INTRODUCTION

Cationic modification has been common for industrial nonionic water-soluble polymers like starch and poly(acrylamide) because of its functional significance in industry. A typical application using cationic properties is as an internal reinforcing agent in paper-making<sup>1</sup> where cationically modified products can adsorb onto fibrous pulp dispersed in water owing to the electrostatic effects, while nonionic ones can not. In the case of poly(vinyl alcohol) (PVAL), however, cationic modification has not yet been commercialized before the present work probably due to the following reasons:

- (1) Modifying PVAL by aminoacetal reaction has been investigated for the purpose of improving dyeability of PVAL fibre<sup>2</sup>. This reaction, however, is accompanied by generating gel due to crosslinking, which makes it difficult to use the product as a water-soluble polymer. Another cationic modifier commercially used for starch, 3-chloro-2-hydroxypropyl trimethylammonium chloride (CTA) and its glycidyl type reagent (GTA)<sup>3</sup> shows poorer reactivity to PVAL, as reported in this paper. Other polymer reactions have been proposed in the

literature: modifications using aminobenzacetaldehyde<sup>4</sup>, diethylaminoethyl methyl ether<sup>5</sup>, acrylamide<sup>6</sup>, polyethylene-polyamide<sup>7</sup> or hydrazine<sup>8</sup>.

- (2) Instead of polymer reactions, copolymerizations have also been tried, but they also had difficulties because two typical cationic monomers cited in 'Functional Monomers' by Yocum and Nyquist<sup>9</sup>, vinyl pyridine and aminoalkyl (meth)acrylates cannot be applied for this purpose. The rate of copolymerization of vinyl acetate (VAc) and vinyl pyridine<sup>10</sup> is so slow that the practical production is impossible. Aminoalkyl (meth)acrylate is a common cationic modifier for vinyl polymers like poly(acrylamide), and the copolymerization with VAc can be carried out easily. However, the ester linkage connecting the (meth)acrylic part and cationic group in the monomer units inevitably breaks in the process of alcoholysis of modified poly(vinyl acetate) (PVAc). Other monomers for modification have also been proposed in the literature: N-vinyl phthalimide<sup>11</sup>, N-vinyl succinimide<sup>12,13</sup>, 4-vinyl imidazole<sup>14</sup>, 2-methyl-1-vinyl imidazole (MVI)<sup>15–17</sup> and dimethylaminoethyl vinyl ether(AE)<sup>18</sup>. The last two monomers have been investigated in this paper.

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In spite of many proposals, cationic modification of

Table 1 The cationic reagents and monomers used

			MW	r <sub>1</sub> , r <sub>2</sub> <sup>1</sup>
1	CTA	3-Chloro-2-hydroxypropyl trimethylammonium chloride	188.1	-
		$\text{ClCH}_2\text{CH}(\text{OH})\text{CH}_2\text{N}^+(\text{CH}_3)_3 \text{Cl}^-$		
2	CTA	Glycidyltrimethylammonium chloride	151.6	-
		$\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3 \text{Cl}^-$		
3	DMA	2-(Dimethylamino)ethyl acrylate	143.2	22.2, 0.03
		$\text{CH}_2=\text{CH}-\text{COOCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$		
4	QDMA	Trimethyl-(2-methacryloxyethyl)ammonium chloride	193.7	22.2, 0.03
		$\text{CH}_2=\text{CH}-\text{COOCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3 \text{Cl}^-$		
5	AE	Dimethylaminoethyl vinyl ether	115.2	0.0, 4.0
		$\text{CH}_2=\text{CH}-\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$		
6	QAE	Trimethyl-(vinylloxyethyl)ammonium chloride	165.7	0.0, 4.0
		$\text{CH}_2=\text{CH}-\text{OCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3 \text{Cl}^-$		
7	MVI	2-Methyl-1-vinylimidazole	108.1	0.62, 0.24
		$\text{CH}_2=\text{CH}-\text{N}(\text{CH}_3)\text{Im}$		
8	QMVI	1-Vinyl-2,3-dimethylimidazolium chloride	158.6	0.62, 0.24
		$\text{CH}_2=\text{CH}-\text{N}(\text{CH}_3)_2\text{Im}^+ \text{Cl}^-$		
9	APA	N-(1,1-Dimethyl-dimethylaminopropyl) acrylamide	184.3	50, 0.07
		$\text{CH}_2=\text{C}(\text{CH}_3)\text{CONHCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$		
10	QAPA	Trimethyl-(3-acrylamido-3-dimethylpropyl) ammonium chloride	234.8	50, 0.07
		$\text{CH}_2=\text{C}(\text{CH}_3)\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3 \text{Cl}^-$		
11	APM	N-(Dimethyl aminopropyl) methacrylamide	170.2	11.21, 0.0867
		$\text{CH}_2=\text{C}(\text{CH}_3)\text{CONHCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$		
12	QAPM	Trimethyl-(3-methacrylamidopropyl) ammonium chloride	220.6	11.21, 0.0867
		$\text{CH}_2=\text{C}(\text{CH}_3)\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3 \text{Cl}^-$		

<sup>1</sup>r<sub>1</sub> Monomer 1: Cationic monomer, Monomer 2: VAc

PVAL was not easy either by polymer reactions or by copolymerizations even on the experiment scale used so far.

In this paper, a novel effective method for the production of cationically modified PVALs by copolymerization has been reported using the (meth)acrylamide derivatives such as APA, APM, QAPA and QAPM shown in Table 1. The copolymers of vinyl alcohol and these monomers are novel substances which have not been known in the literature<sup>19,20</sup>.

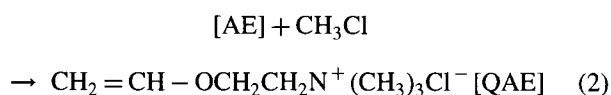
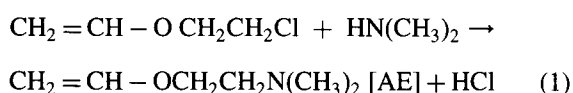
The commercial production of the cationic PVALs has already started based on the present work. The functions of cationic groups in the modified PVALs are useful for various applications such as reinforcing agent for paper<sup>21</sup>, sizing agent for fiber<sup>22</sup>, emulsifier<sup>23</sup>, ink-jet recording<sup>24</sup> and others<sup>25</sup>. Their usefulness in applications has been partly reviewed<sup>26,27</sup>.

In the series of the present work, the functional modification of PVAL with major three ionic groups, carboxylate<sup>28</sup>, sulfonate<sup>29</sup> and cationic, by the copolymerization method has been established.

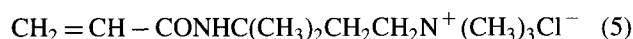
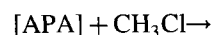
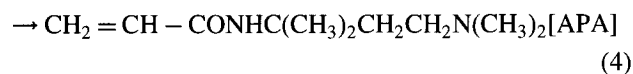
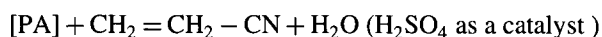
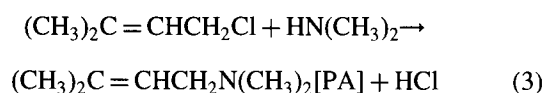
## EXPERIMENTAL

### Materials

The 12 cationic reagents, summarized in Table 1, were used for cationic modification of PVAL. Two modifiers used for the polymer reaction, 3-chloro-2-hydroxypropyl trimethylammonium chloride (CTA) and its glycidyl form reagent (GTA), were supplied from Yokkaichi Chemical Co., Yokkaichi, Mie, Japan. The three cationic monomers, dimethylaminoethyl acrylate (DMA), 1-methyl vinyl imidazole (MVI) and N-(dimethyl aminopropyl) methacrylamide (APM)<sup>30</sup> were obtained from commercial sources, Kohjin Co., BASF Japan Co. and Nitto Chemicals Co., respectively, all located in Tokyo. Their quaternary salts, trimethyl-(2-acryloxyethyl)ammonium chloride (QDMA), 1-vinyl-2,3-dimethylimidazolium chloride (QMVI) and trimethyl-(3-methacrylamidopropyl)ammonium chloride (QAPM), were synthesized in powder form by the reaction with trimethyl chloride in acetone. Dimethyl aminoethyl vinyl ether (AE), and its quaternary ammonium salt, trimethyl-(vinyl-oxyethyl)-ammonium chloride (QAE) were synthesized by the following reactions:



N-(1,1-Dimethyl-dimethylaminopropyl) acrylamide (APA) and its quaternary salt, trimethyl-(3-acrylamido-3,3-dimethylpropyl)ammonium chloride (QAPA) were synthesized by the following reactions reported in the literature<sup>31-33</sup>



The synthesis shown in equation (4) is an application of the method known as the 'Ritter reaction'. All the tertiary amino and quaternary ammonium monomers were purified by vacuum distillation and reprecipitation, respectively. The structure and purity were analyzed by <sup>1</sup>H n.m.r.

Vinyl acetate (VAc) used was a commercial product from Kuraray Co. PVAL used for the polymer reaction with CTA or GTA was also a product from the company, Poval PVA-117.

### Syntheses and characterization

**Reaction of PVAL with CTA or GTA.** Aqueous solution (500 g) dissolving 50 g of PVAL and 1 g of sodium hydroxide was prepared in a 1-l-glass reactor equipped with a stirrer. CTA (10 g) was added to the solution. The mixture was stirred for 20 h at 45°C, neutralized with acetic acid and poured into a large quantity of acetone. The precipitate was ground, washed with methanol in a Soxhlet's extractor and dried. The content of nitrogen in the polymer (CTA-PVAL) was analyzed as 0.08%: the degree of conversion of CTA is 5.0%. A similar procedure was performed using GTA instead of CTA and the polymer obtained (GTA-PVAL) contained nitrogen at 0.10%: the degree of conversion of GTA is 6.2%.

**Monomer reactivity ratios.** Copolymerizations at lower conversions were carried out for the determination of monomer reactivity ratios,  $r_1$  and  $r_2$ . The values,  $r_1/r_2$  for the copolymerization of APA/VAc have been determined as 50/0.07 from eight copolymer samples. Copolymerization at the concentrations of APA, 0.07, 0.10, 0.20, 0.398, 0.695, 0.99, 1.961 and 4.762 wt%/total monomers, and at the rates of conversion of VAc, 7.2, 1.2, 2.0, 3.2, 1.9, 2.5, 3.3 and 3.4% gave copolymers containing APA units of 0.41, 1.01, 1.67, 2.80, 9.96, 8.42, 15.1 and 35.4 mol%, respectively, determined by n.m.r. analysis. The values,  $r_1/r_2$ , for the copolymerization of QAPA/VAc were assumed to be the same as those of APA/VAc. The values,  $r_1/r_2$  for AE (or QAE) and VAc of 0.0/4.0 and those for MVI (or QMVI) and VAc of 0.62/0.24 have been determined based on a similar method. In the cases of APM (or QAPM)/VAc, the values,  $r_1/r_2$ , have been obtained as 11.21/0.0867 from the calculation using  $Q_1 = 0.289$ ,  $e_1 = -0.052$ <sup>34</sup>,  $Q_2 = 0.026$  and  $e_2 = -0.88$ <sup>35</sup>.

**Copolymerization.** Copolymerizations of VAc and cationic monomers were carried out using a 5-l-glass reactor equipped with a stirrer, reflux condenser and apparatus supplying methanol solution of cationic monomer. Tertiary amino monomers were used after neutralizing with acetic acid of the equivalent amounts. All the copolymerization reactions were carried out in homogeneous systems using methanol and 2,2'-azobis(isobutyronitrile) (AIBN) as solvent and initiator, respectively, at boiling temperatures of the system, 60–62°C under a nitrogen gas atmosphere. In order to obtain copolymers having a homogeneous monomer composition at any degrees of conversion during copolymerization,

the 'feeding-comonomer method'<sup>36,37</sup> was adopted, where a more reactive cationic monomer was continuously added to the reaction system. The balance amount of cationic monomer was determined from the monomer reactivity ratios,  $r_1$  and  $r_2$ , and from the solid content analyzed occasionally. In the cases of AE and QAE, however, copolymerization was carried out without any additional feeding because they have less reactivity than VAc. The procedures during and after copolymerization were similar to the method carried out in the preceding paper<sup>28</sup>. The small amount of cationically modified PVAC was purified by reprecipitation in cooled water twice and analyzed using <sup>1</sup>H n.m.r. and elementary analysis. Typical examples of copolymerization results are shown in Table 2 where feed amounts of reagents are described as weight part for convenience of comparison.

**Alcoholysis.** Cationically modified PVALs were obtained by alcoholysis of the modified PVACs obtained above. The methanol solution of sodium hydroxide was added to the methanol solution of the cationically modified PVAC with stirring at 40°C. The amount of sodium hydroxide used was 0.004 to 0.2 mole ratio to VAc units in the cases of modified copolymers with quaternary ammonium cationic monomers. More amounts of sodium hydroxide were used in the cases of modified copolymers with tertiary amino cationic monomers, where alcoholysis occurred by sodium hydroxide exceeding the amount of neutralization of acetic acid used. The gelatinous PVAL generated by alcoholysis was ground, washed with methanol and dried. The samples for analysis were washed with a Soxhlet's extractor and dried. Typical examples of modified PVALs are also shown in Table 2.

**<sup>1</sup>H n.m.r.** Spectra were obtained with Varian EM-390 at 90 MHz. As solvents and internal standard reagents, CDCl<sub>3</sub> and hexamethyldisiloxane were used for modified PVACs, while D<sub>2</sub>O and sodium 3-(trimethylsilyl)propionic acid-d<sub>6</sub>-sodium salt were used for modified PVALs. N.m.r. analysis was useful for the determination of the amount of cationic monomer units in the copolymers because of strong signals of dimethyl or trimethyl groups included in cationic units.

**Characterization of modified PVALs.** The degree of hydrolysis (D. H.) of vinyl acetate units in modified PVALs was measured both by <sup>1</sup>H n.m.r. and by a chemical method, alkaline re-hydrolysis followed by acid titration<sup>38</sup>. In the latter method, correction was made for errors caused in the cases of PVALs modified with DMA and QDMA because alkali is also consumed by the ring-opening reaction of lactone generated, as discussed later. Viscosity of aqueous solution (4 wt%) at 20°C ( $\eta_{4\%}$ ) was measured using a Brookfield viscometer at 60 rpm. The value was determined from the data of two solutions with different concentrations close to 4 wt%. Limiting viscosity number,  $[\eta]$  (dl/g), was measured for the samples which had been re-hydrolyzed by sodium hydroxide in methanol. The measurement using a capillary viscometer was carried out for the samples dissolved in an aqueous solution of sodium chloride (1 M) at 30°C. Viscosity-average degree of polymerization was calculated by the equation  $\bar{P}_v = ([\eta] \times 10^4 / 8.33)^{1/0.62}$ <sup>38-40</sup>.

#### Applications

**Adsorption on Pulp.** Bleached kraft pulp having a

beating degree of 466 ml CFS (Canadian Standard Freeness, an indication of the degree of beating) was used. Aqueous slurry dispersing the fibrous pulp of 0.25% and containing a cationically modified PVAL of 100 ppm was filtered with a wire gauze of 200 mesh. The filtrate was filtered again with filter paper (No. 5A). The adsorption degree of modified PVAL to fibrous pulp was determined from the concentration of PVAL in the aqueous filtrate by an iodine method<sup>41</sup>. 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 for the coloration reagent. A portion (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 500 to 700 nm. The maximum value of absorbance was determined. A similar procedure was carried out for an aqueous solution not including pulp as blank test. Calibration curves were made for each modified PVAL.

**Polyelectrolyte complexes with anionic polymers**<sup>42,43</sup>. The mixing experiment was performed in aqueous solution. The solution of the cationic PVAL modified with 2.0 mol% of QAPM (QAPM-PVAL, D.H.:98.8 mol%,  $\eta_{4\%}$ :28.5 cP) at the concentration of 0.5 wt% was used. Three anionic polymers used were: (a) Poly(vinyl sulfonic acid potassium salt) (PVS · K, N/400) supplied from Wako Pure Chemical Ind., Osaka; (b) Modified PVAL with sulfonate group<sup>29</sup> (SAMPS-PVAL, sodium 2-acrylamide-2-methylpropane sulfonate (SAMPS) units: 2.0 mol%, D. H.: 98.0 mol%,  $\eta_{4\%}$ :30.0 cP, Concentration: 0.5 wt%); (c) Modified PVAL with carboxylate group<sup>28</sup> (IA-PVAL, sodium itaconate units: 2.0 mol%, D. H.:97.0 mol%,  $\eta_{4\%}$ :29.0 cP, Concentration: 0.5 wt%). Transmittance at 450 nm was measured for the mixed aqueous solutions of the cationic PVAL and each anionic polymer at various compositions.

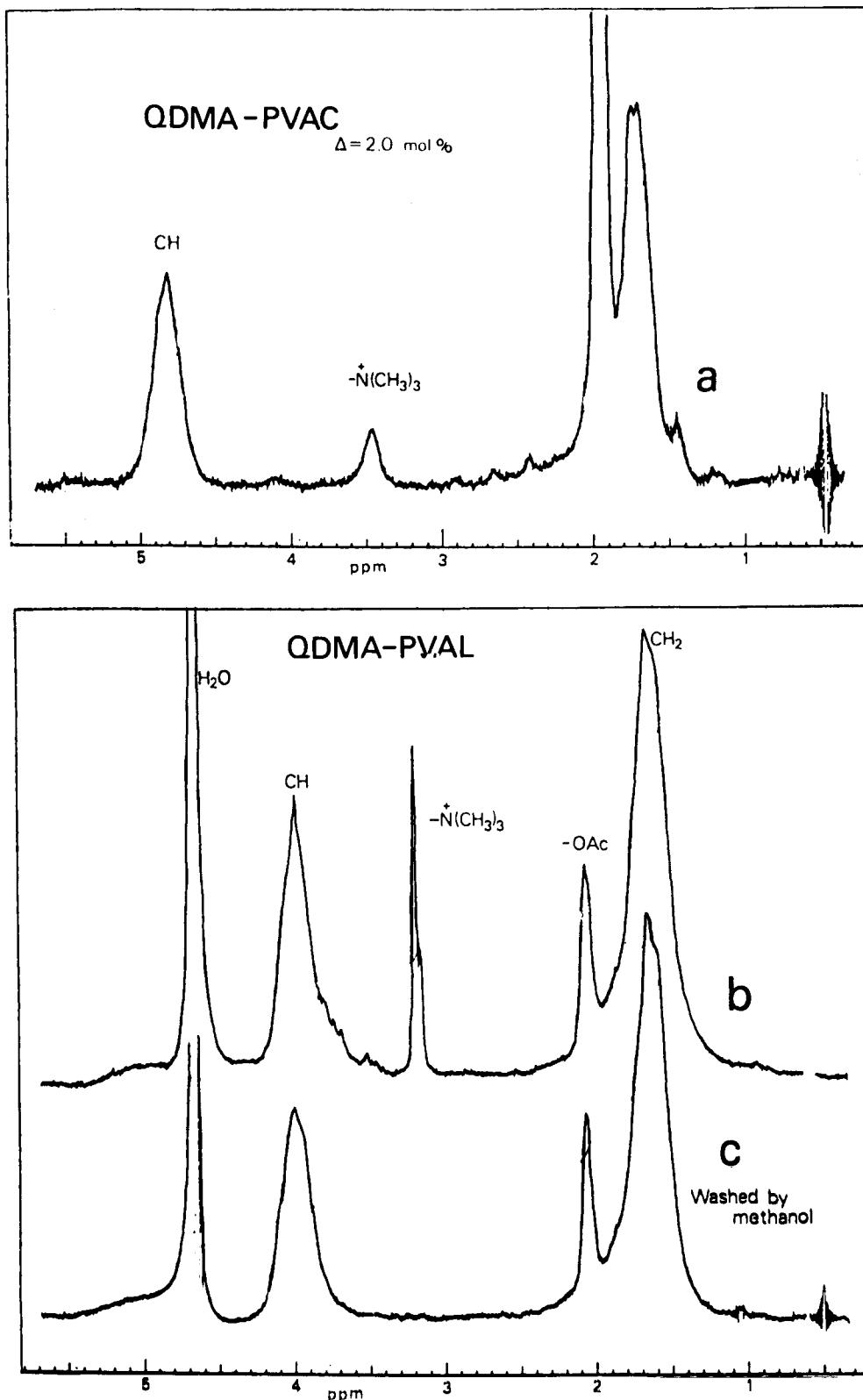
**Emulsion polymerization.** A 3-l-glass reactor equipped with a stirrer, thermometer, reflux condenser and dropping funnel was charged with 80 g of cationic PVAL (QAPM-PVAL, QAPM units: 1.0 mol%, D. H.:80.3 mol%,  $\eta_{4\%}$ : 9.0 cP) and 850 g of distilled water, and clear solution was prepared by stirring and heating. The system was cooled, adjusted to pH 4.0 with a 50% aqueous solution of acetic acid, 1000 g of VAc was added and the temperature was increased to 60°C. Polymerization was carried out for 135 min under a nitrogen gas atmosphere by the occasional addition of an aqueous solution of hydrogen peroxide and an aqueous solution of sodium pyrosulphate as an initiator system. The emulsion thus obtained contained 51 wt% of solid and showed 60 cP of a Brookfield viscosity at 25°C, using Rotor No.1 at 60 rpm. It showed good mechanical stability and dilution stability, and its zeta potential measured using a zeta meter was +28.5 mV, which means that it is positively charged or cationic.

A similar procedure was repeated, except that the modified PVAL was replaced with a non-modified PVAL (D. H.: 88.0 mol%,  $\eta_{4\%}$ : 8.0 cP), to prepare another PVAC emulsion as a control. This emulsion had a solid content of 50 wt%, 80 cP of a Brookfield viscosity at 25°C and -24.0 mV of a zeta potential, which means that it is negatively charged or anionic.

Table 2 Synthesis of cationic poly(vinyl alcohol)s by copolymerization and alcoholysis

No.	Cationic monomers	Feed in copolymerization (part)				Reaction time	Extent of conversion of VAc %	Modified PVAc Cationic group mol%	Degree of Polymerization $\bar{P}_n$	Modified PVAl Cationic group mol%	Degree of hydrolysis	Viscosity (4%, 20°C) cP	
		VAc	Cationic monomer	Acetic acid	Methanol								AIBN
		Initial/Additional	Initial/Additional	Initial/Additional	min								
1	DMA	1000	3.6/40.0	1.4/15.2	250/20	1.5	90	34	6.6	1551	0	89.6	25.7
2	QDMA	1000	1.2/20.0	- / -	250/20	0.3	185	41	2.0	1621	0	89.2	27.4
3	AE	1000	4.6/ -	2.2/ -	262/24	0.2	180	24	0.9	980	0.8	98.7	14.7
4	QAE	1000	75/ -	- / -	430/ -	1.5	190	30	1.5	821	1.5	98.9	15.0
5	MVI	1000	36/24	20/13	250/ -	1.3	225	18	10.2	NA(*1)	10.1	98.7	(*1)
6	QMVI	1000	4.4/9.2	- / -	250/27.8	1.4	180	31	1.0	1804	1.0	99.1	30.6
7	APA	1000	4.0/8.0	1.4/2.6	250/8.0	0.3	95	11	2.9	1711	2.8	98.0	28.0
8	QAPA	1000	8.0/60.0	- / -	332/340	0.8	390	74	3.6	1390	3.9	93.5	21.7
9	QAPA	1000	0.9/39	- / -	1857/39	8.0	160	67	2.0	474	2.0	81.8	7.1
10											2.0	96.9	7.3
11	APM	1000	1.0/33.0	0.4/10.8	250/88	1.0	170	45	3.0	1496	3.1	98.8	24.2
12	QAPM	1000	8.0/56.0	- / -	332/336	3.0	300	71	3.2	1420	3.3	92.3	19.8
13											3.3	70.7	7.2

\*1 Soluble in hot water above 80°C.



**Figure 1** The  $^1\text{H}$  n.m.r. spectra of (a) modified poly(vinyl acetate) with trimethyl-(2-acryloxyethyl) ammonium chloride (QDMA), (b) the corresponding poly(vinyl alcohol) by alcoholysis before purification and (c) the purified sample

## RESULTS AND DISCUSSION

### Syntheses of cationic PVALs

*Polymer reaction with CTA or GTA.* The modified PVALs containing cationic groups (0.08 or 0.10 wt% as nitrogen) were obtained from the reaction between PVAL and CTA or GTA. The degrees of conversion of CTA or GTA were observed only below 7%. These are in contrast

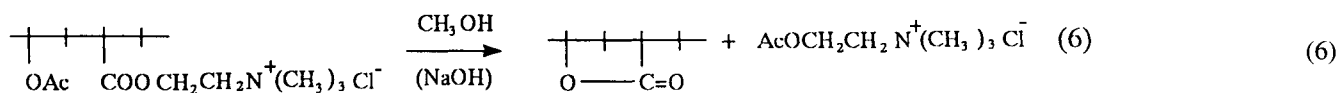
to the degree of conversion reported for the production of cationically modified starch containing 0.1–0.3% of nitrogen, approximately 70%, under similar reaction conditions<sup>44</sup>.

*Copolymerization with QDMA or DMA.* Figure 1 shows the  $^1\text{H}$  n.m.r. spectra for the copolymer of VAc and QDMA (QDMA-PVAC) and for its hydrolyzed product

by alcoholysis (QDMA-PVAL) (Sample 2 in Table 1). The amount of QDMA units is determined as 2.0 mol% for the QDMA-PVAC from the area intensity of absorption at 3.45 ppm which is assigned to trimethylammonium groups. The <sup>1</sup>H n.m.r. spectra of the un-purified sample of QDMA-PVAL shown in Figure 1b, shows an apparent signal of the group, but the spectra of the purified sample using a Soxhlet's extractor with methanol in Figure 1c shows no signal of the group. The cationic group is regarded as liberated during the alcoholysis procedure, as shown in the following reaction:

of VAc and alkyl (meth)acrylate<sup>28,45,46</sup>. The copolymerization with QDMA (Sample 1) cannot be applied for cationic modification of PVAL due to the low resistance of ester linkage to alkaline alcoholysis.

*Copolymerization with QAE or AE.* Figure 2 shows the spectra of the PVAL modified with QAE (QAE-PVAL) obtained from alcoholysis of the copolymer of VAc and QAE (Sample 4). The upper spectrum (a) is for the sample before purification and the lower (b) after purification. The amount of QAE units was determined as 1.5 mol%



A similar reaction generating a lactone ring in a PVAL chain is already known for the alcoholysis of the copolymer

for the purified sample. The apparent larger strength for the signal of trimethylammonium group in sample (a) must be

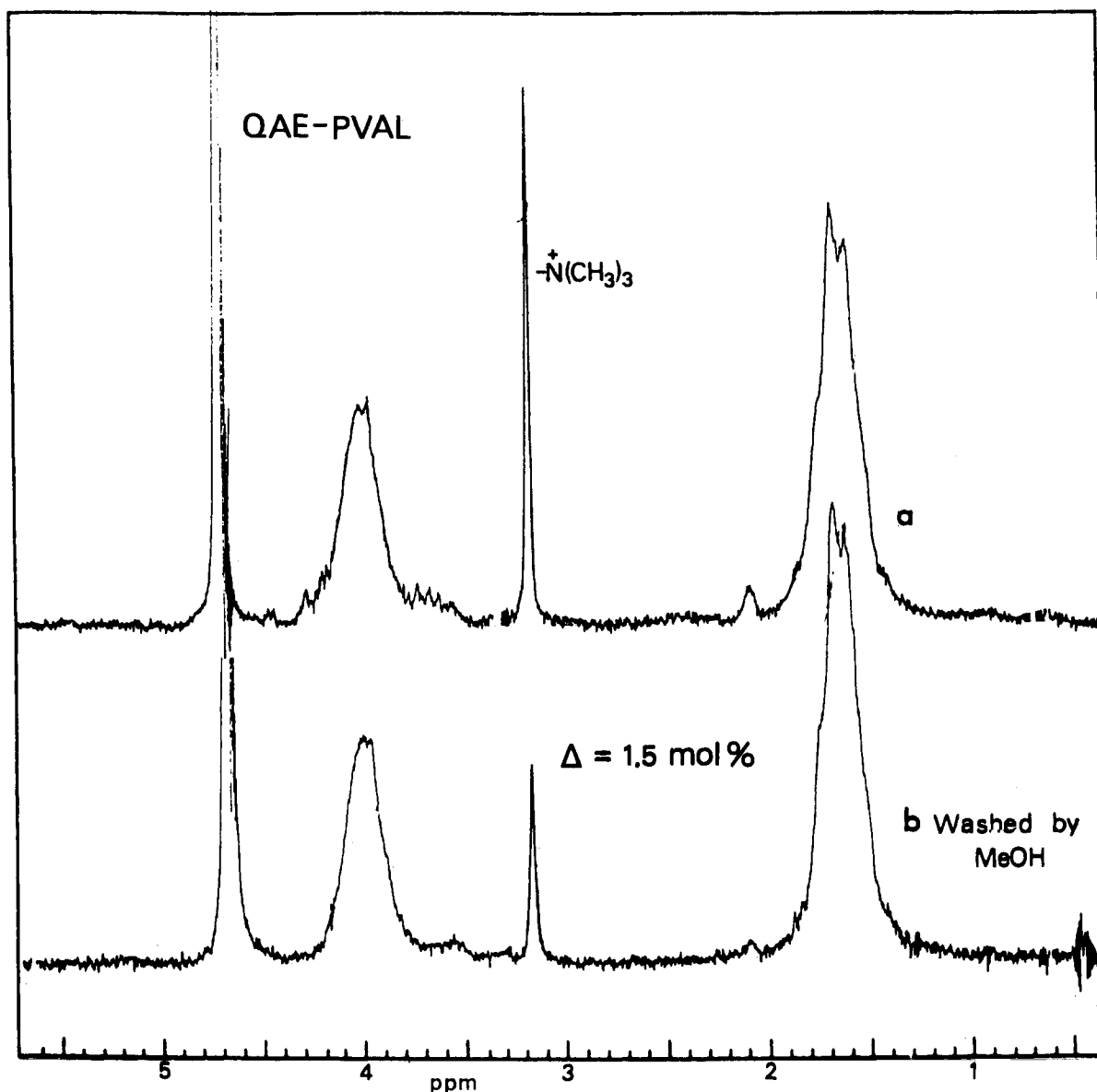


Figure 2 The <sup>1</sup>H n.m.r. spectra of (a) modified poly(vinyl alcohol) with trimethyl(vinyloxyethyl)ammonium chloride (QAE) before purification and (b) the purified sample

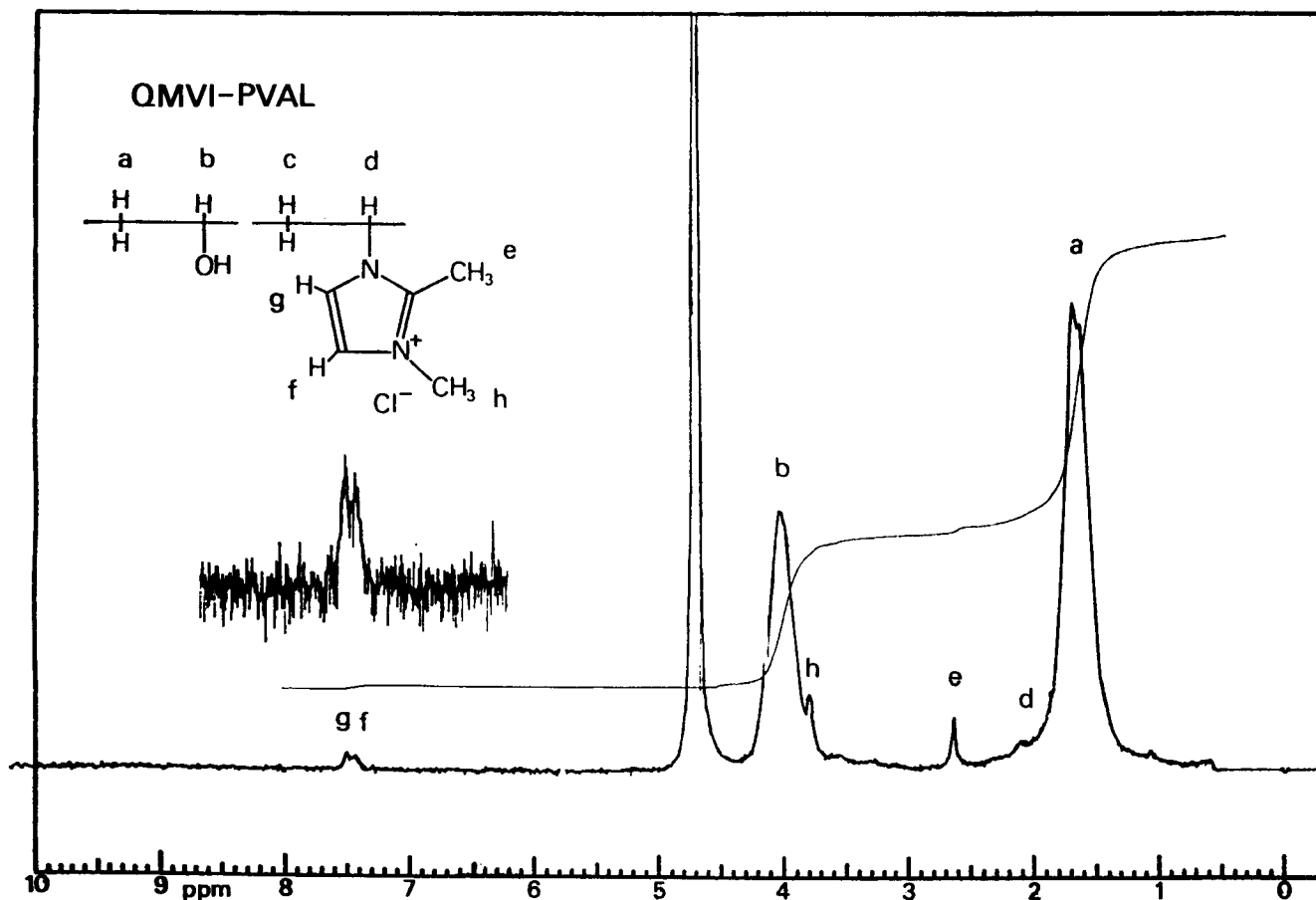


Figure 3 The  $^1\text{H}$  n.m.r. spectrum of modified poly(vinyl alcohol) with 1-vinyl-2,3-dimethylimidazolium chloride (QMVI)

due to a higher amount of residual monomer included in the sample, because QAE has a smaller reactivity in copolymerization. The modified PVAL with AE units was also obtained (Sample 3). Copolymerization with AE or QAE is regarded as a possible method for obtaining cationically modified PVALs, although they have the problem of less reactivity in copolymerization.

**Copolymerization with QMVI or MVI.** Figure 3 shows the spectrum of the PVAL modified with QMVI (QMVI-PVAL) containing QMVI units of 1.0 mol% (Sample 6). This was obtained from alcoholysis of the copolymer of VAc and QMVI. The modified PVAL with MVI units of 10.1 mol% (Sample 5) shows solubility in water only above  $80^\circ\text{C}$ . Copolymerization with MVI or QMVI is also regarded as another possible method for obtaining cationically modified PVALs<sup>47</sup>.

**Copolymerization with QAPA, QAPM, APA or APM.** Figure 4 shows the spectra of QAPA-PVAc (the copolymer of VAc and QAPA), QAPA-PVAL (alcoholysis product of the QAPA-PVAc), QAPM-PVAc and QAPM-PVAL (Samples 8 and 12). In the copolymerizations, the addition of QAPA or QAPM solution was stopped at 45% of the degree of conversion of VAc, and polymerization was subsequently continued by 71 or 74% of the degree of conversion of VAc, respectively. In this method, QAPA or QAPM monomer was almost perfectly consumed in copolymerization, and the mole fraction of the cationic monomer units in the copolymer can be determined from material balance. In the case of the copolymer with QAPA, the

mole fraction of QAPA units are: 3.3 mol% from material balance, 3.6 from n.m.r. analysis of the modified PVAc and 3.2 from n.m.r. analysis of the modified PVAL. In the case of the copolymer with QAPM, 3.4 mol% from material balance, 3.9 from the modified PVAc and 3.3 from the modified PVAL. The mole fractions obtained from three analytical methods can be regarded as consistent within experimental errors. QAPA and QAPM monomer units are so stable in the alcoholysis reaction that modified PVALs with cationic groups can be produced. On the other hand, however, it has been observed that stronger alkali conditions can cause the cleavage of the amido linkage. The original solid samples (5 g) of the QAPA-PVAL and the QAPM-PVAL (Samples 8 and 12) were immersed in methanol solution of sodium hydroxide (5 g/l, 200 ml) for 2 h at  $36^\circ\text{C}$ . From n.m.r. analysis for the samples after washing by Soxhlet's extraction with methanol, 3.7 mol% of QAPA units for the QAPA-PVAL and 1.0 mol% of QAPM units for the QAPM-PVAL were observed. It can be concluded that QAPM units partly lose cationic groups presumably due to the cleavage of the amido linkage, while QAPA units show resistance to cleavage under the same conditions.

It has also been confirmed that PVALs modified with the tertiary amino groups can be synthesized by copolymerization using APA or APM as a comonomer (Samples 7 and 11).

*Partially hydrolysed QAPM-PVALs and highly viscous aqueous solutions.* Table 3 shows the synthetic conditions and properties for QAPM-PVALs with the modification



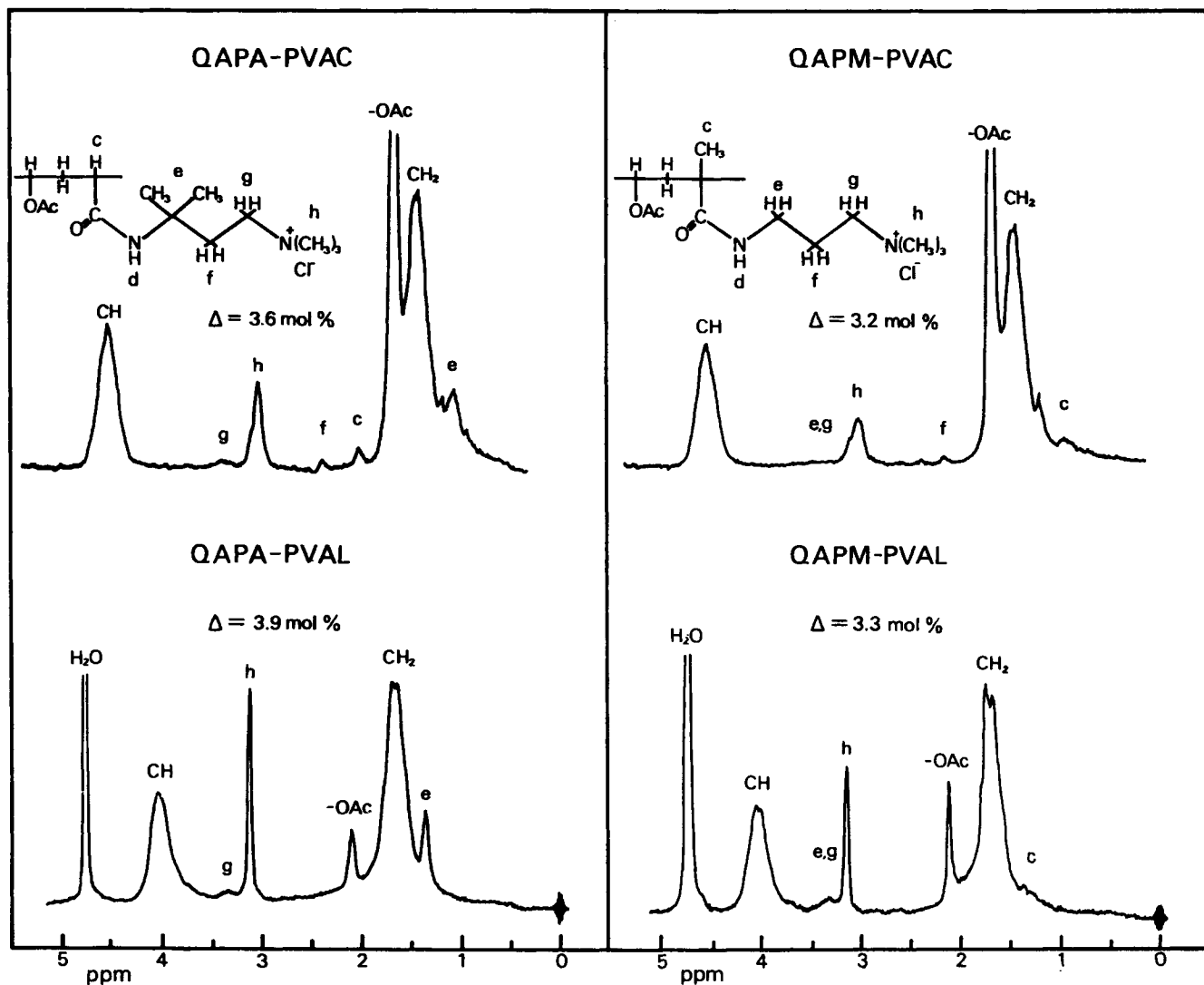


Figure 4 The  $^1\text{H}$  n.m.r. spectra of modified poly(vinyl acetate with trimethyl-(3-acrylamido-3,3-dimethylpropyl)ammonium chloride (QAPA-PVAC), modified poly(vinyl acetate) with trimethyl-(3-methacrylamidopropyl)ammonium chloride (QAPM-PVAC) and their hydrolyzed products (QAPA-PVAL and QAPM-PVAL) obtained by alkaline alcoholysis

degrees of 0.13 to 1.0 mol% and with various D. H., down to 54.8 mol%.

Firstly, it has been found that the modified PVALs of much lower D. H., even 54.8 mol% of D.H. for example, are soluble in water, although some of them show a slightly milky appearance: non-modified PVALs lose their solubility in water in cases for lower D. H. than about 80 mol%<sup>48,49</sup>. Such increased solubility in water for the partially hydrolyzed QAPM-PVALs is regarded as due to increased hydrophilic property of QAPM units. A similar phenomenon has already been found in the cases of the modification of PVALs with other ionic monomers like itaconic acid<sup>29</sup> and SAMPS<sup>30</sup>. Lower modification with QAPM at the mole fraction of 0.13 mol% has been found to be so effective that the PVAL of 77.1 mol% of D. H. shows solubility, although that of 70.3 mol% shows phase separation.

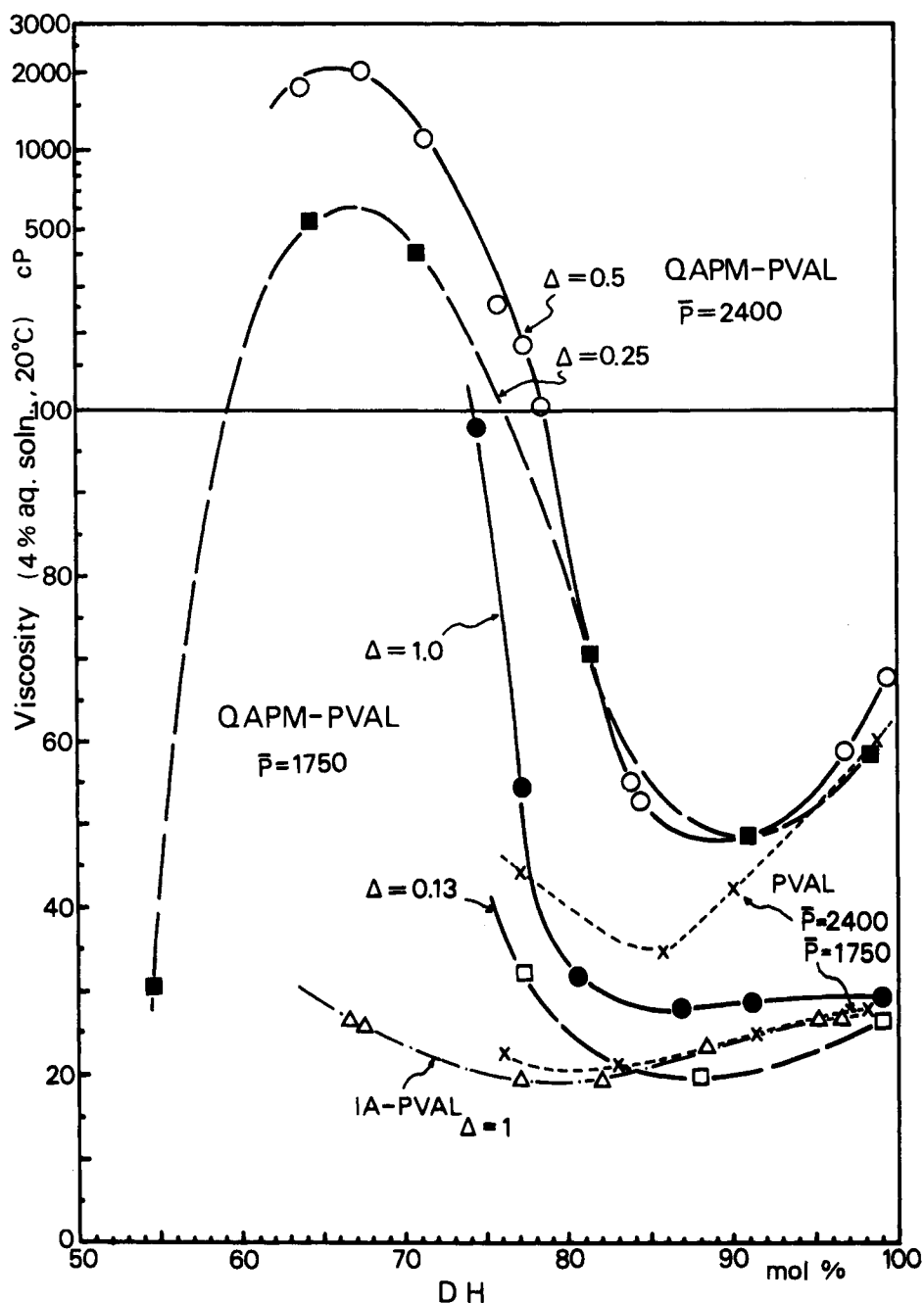
Secondly, anomalously high viscosity has been observed for the aqueous solution of partially hydrolyzed QAPM-PVALs, as shown in Table 3 and Figure 5. The viscosity depends prominently on the combinations of the mole fraction of QAPM units and D. H. The PVAL with 0.5 mol% of QAPM units and 67.5 mol% of D. H. shows the highest viscosity, 2000 cP at the concentration of 4 wt%

at 20°C. In the cases of the PVALs modified with sodium itaconate units (IA-PVALs) and non-modified PVALs having similar degrees of polymerization, such anomaly in viscosity has not been observed, as shown in Figure 5. A similar phenomenon showing a highly viscous aqueous solution has been known for the PVALs modified both with groups carrying hydrophobic chains and with sodium carboxylate groups<sup>50</sup>, where intermolecular hydrophobic interactions or association among hydrophobic chains has been assumed. The phenomenon observed in the present case could be explained by a similar mechanism. High viscous PVALs shown here are expected to be applied for thickener or viscosity-increasing agent.

*Monomer reactivity and industrial production.* Figure 6 shows 'copolymerization curves' of VAc and four cationic monomers used. Copolymerization with QAPA or QAPM shows curves so apart above the azeotropic line that lower mole fractions of cationic monomer in copolymerization give higher mole fractions of cationic units in copolymer. On the other hand, the curve for the copolymerization with QMVI locates closely on the azeotropic line of 'ideal copolymerization', while QAE shows much lower reactivity.

**Table 3** Syntheses of poly(vinyl alcohol)s modified with 3-trimethyl-(1-methacrylamidopropyl)ammonium chloride (QAPM)

No.	Feed in copolymerization (part)						Extent of conversion of VAc %	Cationic groups mol%	Degree of hydrolysis mol%	Viscosity of aqueous solution (4%, 20°C) cP	
	VAc	QAPM	Methanol	AIBN	Reaction time min	Initial/Additional					Initial/Additional
14								99.0	29.4		
15	1000	2.3 / 14.9	266 / 14.9	0.60	230		1.0	91.1	29.0		
16								80.6	31.8		
17								74.5	97.5		
18								99.4	67.6		
19								96.5	59.0		
20								84.3	53.0		
21	1000	1.1 / 5.7	163 / 5.7	0.36	145		0.54	78.3	103		
22								75.7	276		
23								71.3	1098		
24								67.5	2000		
25								63.8	1760		
26								98.2	58.8		
27								90.8	49.3		
28	1000	0.57 / 2.75	176 / 8.3	0.40	130		0.25	81.6	71.6		
29								70.9	408		
30								64.4	548		
31								54.8	31.2		
32								99.0	26.7		
33	1000	0.29 / 1.96	325 / 17.7	0.80	160		0.13	88.1	19.5		
34								77.1	33.3		
35								70.3	Phase separation		



**Figure 5** Viscosity for the 4 wt% aqueous solutions for PVALs modified with trimethyl-(3-methacrylamidepropyl)ammonium chloride (QAPM-PVAL), PVALs modified with itaconic acid (IA-PVAL) and non-modified PVALs, as functions of the degree of hydrolysis (D. H.). The degrees of modification ( $\Delta$ ) and the viscosity-average degrees of polymerization  $\bar{P}_v$  of the PVALs are also shown

From the industrial point of view, it can be concluded generally that the selection of comonomers like QAPA and QAPM showing curves apart from the azeotropic line is more beneficial because of the smaller amount of residue of expensive cationic monomer. In contrast, copolymerization using QMVI or QAE generates a higher volume of residue. This is also the case for the continuous copolymerization using flow tank reactor(s) adopted commercially instead of the semi-batch method shown in this paper.

#### Properties and applications of cationically modified PVALs

**Adsorption to pulp.** Figure 7 shows the data observed on the adsorption of a cationically modified PVAL to fibrous pulp dispersed in bulk of water. The cationic PVAL modified with 1 mol% of QAPM units shows that the degree of adsorption reaches as high as 85%. This makes a decided

contrast with the non-modified PVAL showing no adsorption. It has been observed that such a small amount of cationic group inside a PVAL chain functions as active site for adsorption to fibrous pulp, which is known as a typical substance charged negatively<sup>1</sup>. This functional property suggests that cationic PVALs have the possibility of application to internal reinforcing agent for paper.

**Polyelectrolyte complexes.** Another typical experiment has been carried out for the confirmation of cationic properties, the formation of polyelectrolyte complex<sup>42,43</sup>. Figure 8 shows the transmittance of aqueous dispersions obtained from mixing the aqueous solution of QAPM-PVAL with the aqueous solution of anionic polymers. Mixing with poly(vinyl sulphuric acid potassium salt) (PVS ·K) of N/400 indicates sharper clouding. Based on the assumption

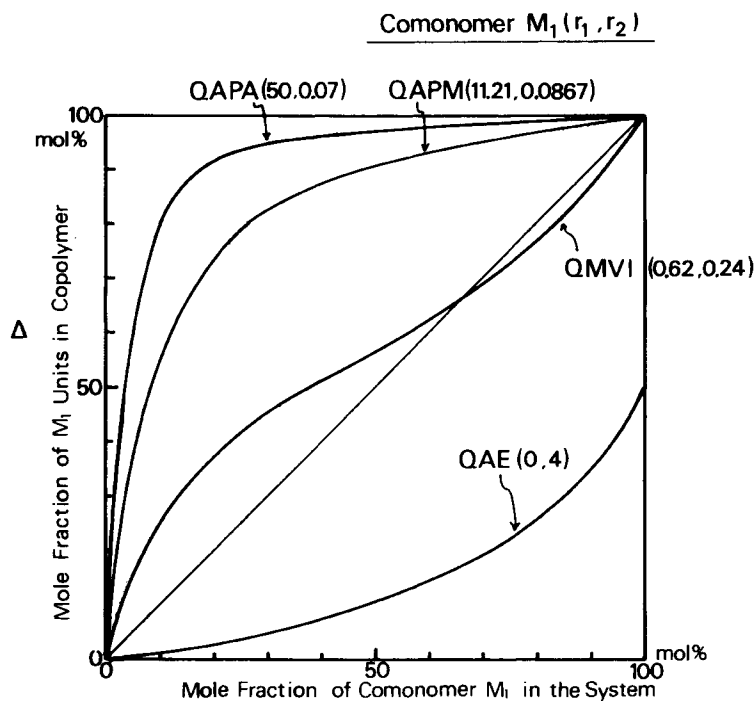


Figure 6 Copolymerization curves for various cationic monomers ( $M_1$ ) and vinyl acetate ( $M_2$ )

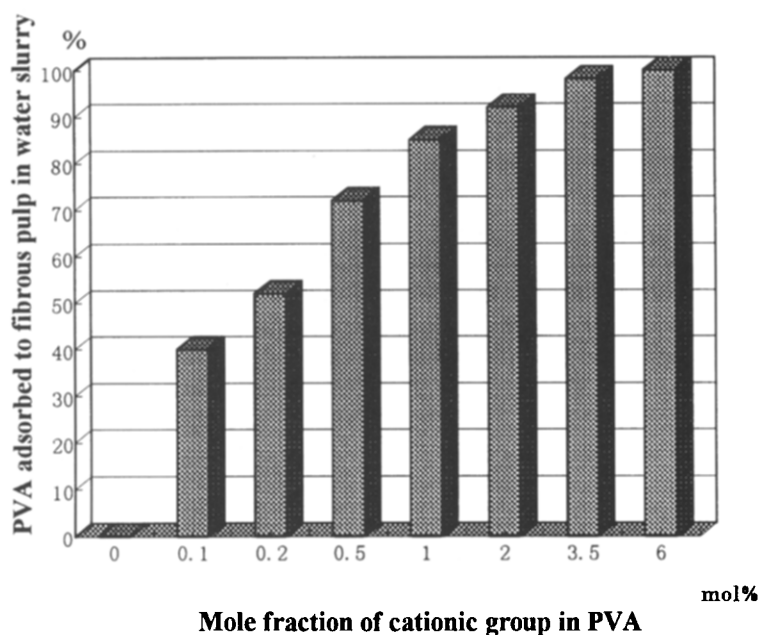


Figure 7 Adsorption of cationic PVAL onto fibrous pulp dispersed in bulk water

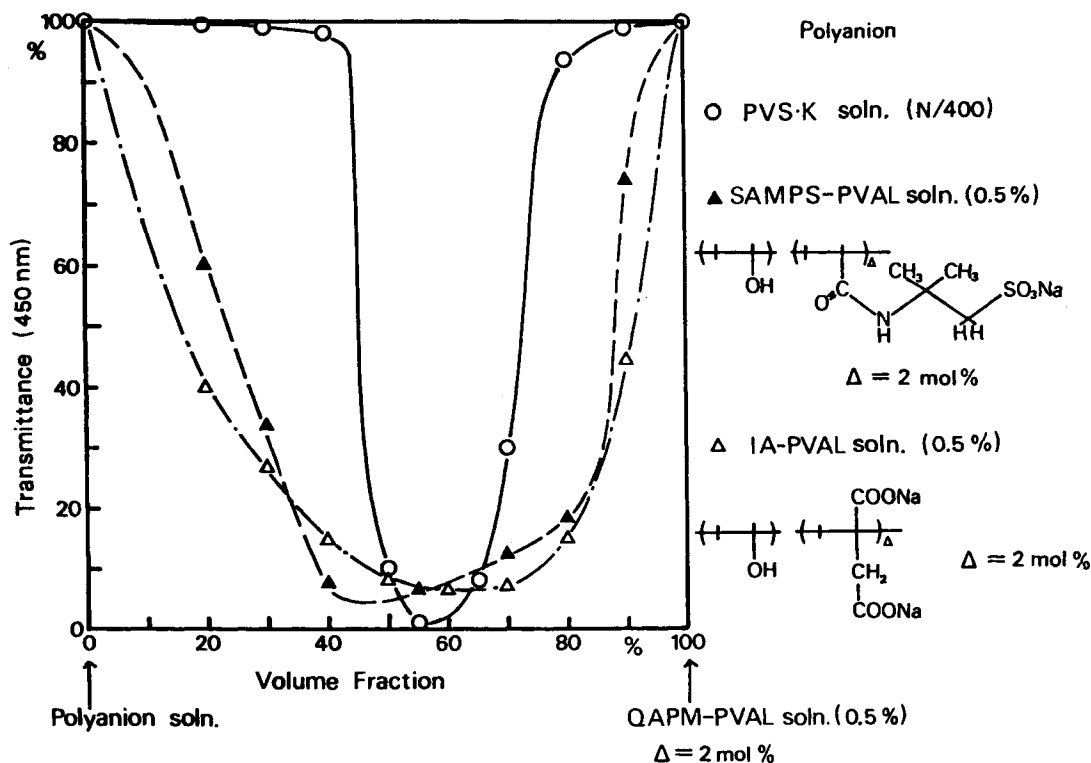
of maximum clouding caused at equivalence, the mole fraction of the cationic group in the polymer is calculated as 2.0 mol%, which is consistent with the results from  $^1\text{H}$  n.m.r. analysis. Mixing with the solution of IA-PVAL or SAMPS-PVAL also shows maximum clouding approximately at the respective equivalent points.

*Cationic polymer emulsion.* It has been found that cationic polymer emulsion can easily be produced by using the cationically modified PVALs as emulsifier or protective colloid. The emulsion using a cationic PVAL shows a positive value of zeta potential, + 28.5 mV, while the emulsion using a non-modified PVAL as control, a negative value of zeta potential, -24.0 mV. The cationic

emulsion can show specific characteristics in the interaction with materials having negative charge, pulp, cotton, glass and others.

#### CONCLUSIONS

(1) Cationic monomers of (meth)acrylamide derivatives such as APA and APM, and their quaternary ammonium salts (QAPA and QAPM) have been found useful for cationic modification of PVAL, since the amido linkage of the comonomer units has good resistance to alkaline alcoholysis. Much higher reactivity of the cationic monomers than that of vinyl acetate in copolymerization is beneficial from the industrial point of view.



**Figure 8** Formation of polyelectrolyte complex and turbidity in aqueous solution. Transmittance for the aqueous dispersions containing a cationic poly(vinyl alcohol) and polyanions as functions of the volume fraction of aqueous solutions used. Cationic poly(vinyl alcohol): PVAL modified with 2.0 mol.% of trimethyl-(3-methacrylamidopropyl) ammonium chloride (QAPM-PVAL, concentration: 0.5 wt%). Polyanions: (a) Poly(vinyl sulfuric acid potassium salt) of N/400. (b) Sulfonate-modified PVAL or PVAL modified with 2.0 mol% of sodium 2-acrylamide-2-methylpropane sulfonate (SAMPS-PVAL, concentration: 0.5 wt%). (c) Carboxylate-modified PVAL or PVAL modified with 2.0 mol% of itaconic acid (IA-PVAL, concentration: 0.5 wt%)

(2) In contrast, typical cationic (meth)acrylate derivatives such as DMA and its quaternary ammonium salt (QDMA) can not be used for this purpose because the ester linkage included in the comonomer units has no resistance to alkaline alcoholysis.

(3) Dimethyl aminoethyl vinyl ether (AE), 1-methyl vinyl imidazole (MVI) and their quaternary ammonium salts (QAE and QMVI) have been regarded useful for the preparation of PVALs having a more stable cationic group, although they have a problem of lower reactivity in copolymerization.

(4) Typical cationic reagents commercially used for the modification of starch, CTA and GTA show poorer reactivity to PVAL.

(5) The functions of cationic characteristics of the modified PVALs have typically been demonstrated for the experiments such as adsorption to fibrous pulp dispersed in water, formation of polyelectrolyte complex and the production of cationic emulsion.

(6) Unusually high viscosity has been observed for the aqueous solutions of partially hydrolyzed PVALs modified with QAPM. Association of the modified PVAL chain in solution has been assumed for the phenomenon.

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