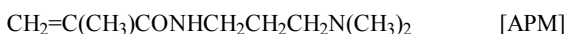
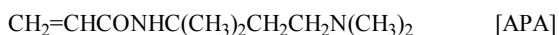


CHAPTER 9

MODIFICATION WITH CATIONIC MONOMERS

Various methods for modifying poly(vinyl alcohol) with cationic group have been investigated using two cationic reagents and ten 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 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 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 hydrolyzed poly(vinyl alcohol)s modified with QAPM have been found to show unusually high viscosity in aqueous solution such as 2000 cP at 4wt% and 20°C.

9.1 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 property is internal reinforcing agent in paper-making,¹ where cationically modified products can adsorb onto fibrous pulp dispersed in water owing to the electrostatic effects while nonionic one can not. In 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 fiber.² This reaction, however, is accompanied by generating gel due to crosslinking, which makes it difficult to use the product as water-soluble polymer. Another cationic modifiers commercially used for starch, 3-chloro-2-hydroxypropyl trimethylammonium chloride (CTA) and its glycidyl type reagent (GTA),³ show poorer reactivity to PVAL, as reported in this paper. Other polymer reactions have been proposed in literature: modifications using aminobenzacetaldehyde,⁴ dimethylaminoethyl methyl ether,⁵ acrylamide,⁶ polyethylene-polyamide⁷ or hydrazine⁸.

(2) Instead of polymer reactions, copolymerization has also been tried, but it has also been found difficult because two typical cationic monomers cited in "Functional Monomers" by Yocum and Nyquist,⁹ vinyl pyridine and aminoalkyl (meth)acrylates cannot be applied for this purposes. The rate of copolymerization of vinyl acetate (VAc) and vinyl pyridine¹⁰ is so quite 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 (meth)acrylic part and cationic group in the monomer units inevitably break in the process of alcoholysis of modified poly(vinyl acetate) (PVAC). Other monomers for modification have also been proposed in literature: N-vinyl phthalimide,¹¹ N-vinyl succinimide,^{12,13} 4-vinyl imidazole,¹⁴ 2-methyl-1-vinyl imidazole(MVI)¹⁵⁻¹⁷ and dimethylaminoethyl vinyl ether(AE).¹⁸ The last two monomers have been investigated in this paper.

In spite of many proposals, cationic modification of PVAL was not easy either by polymer reactions or by copolymerizations even on experimental scale 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

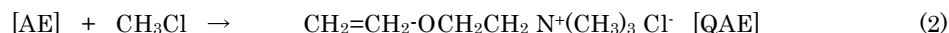
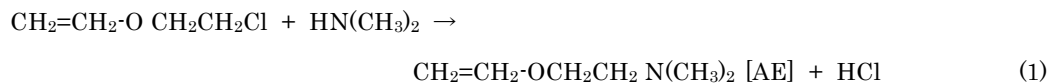
APA, APM, QAPA and QAPM shown in Table 19. The copolymers of vinyl alcohol and these monomers are novel substances which have not been known in literature.^{19,20} The commercial production of the cationic PVALs have already been started base on the present work. The functions of cationic group in the modified PVALs are useful for various applications such as reinforcing agent for paper,²¹ sizing agent for fiber,²² emulsifier,²³ ink-jet recording²⁴ and others;²⁵ their usefulness in applications has been partly reviewed.^{26,27}

In the series of the present work, there has been established the functional modification of PVAL with major three ionic groups, carboxylate,²⁸ sulfonate²⁹ and cationic, by copolymerization method.

9.2 EXPERIMENTAL

9.2.1 Materials

The twelve cationic reagents, summarized in Table 19, were used for cationic modification of PVAL. Two modifiers used for 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)³⁰ 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 as powder form by the reaction with trimethyl chloride in acetone. Dimethyl aminoethyl vinyl ether (AE), and its quaternary ammonium salt, trimethyl-(vinylxyethyl)ammonium chloride (QAE) were synthesized by the following reactions:



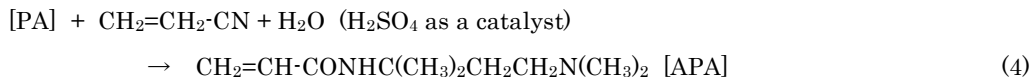
N-(1,1-Dimethyl aminopropyl) acrylamide (APA) and its quaternary salt, trimethyl-(3-acrylamido-3,3-dimethylpropyl)ammonium chloride (QAPA) were synthesized by the

Table 19 The cationic reagents and monomers used

		MW	r_1, r_2^{*1}
1	CTA 3-Chloro-2-hydroxypropyl trimethylammonium chloride	188.1	—
	$\text{C}(\text{CH}_2)_2\text{CH}(\text{OH})\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^-$		
2	GTA Glycidyltrimethyl ammonium chloride	151.5	—
	$\text{CH}_2-\text{CH}(\text{O})\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^-$		
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
	$\text{CH}_2=\text{CH}_2-\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$		
6	QAE Trimethyl-(vinylloxyethyl)ammonium chloride	165.7	0.0, 4.0
	$\text{CH}_2=\text{CH}_2-\text{OCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^-$		
7	MVI 2-Methyl-1-vinyl imidazole	108.1	0.62, 0.24
	$\text{CH}_2=\text{CH}-\text{N}(\text{CH}_3)\text{CH}_2$		
8	QMVI 1-Vinyl-2,3-dimethylimidazolinium chloride	158.5	0.62, 0.24
	$\text{CH}_2=\text{CH}-\text{N}(\text{CH}_3)_2$		
9	APA N-(1,1-Dimethyl-dimethylamino)propyl acrylamide	184.3	50, 0.07
	$\text{CH}_2=\text{CHCONHC}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$		
10	QAPA Trimethyl-(3-acrylamido-3'-dimethylpropyl ammonium chloride	234.8	50, 0.07
	$\text{CH}_2=\text{CHCONHC}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^-$		
11	APM N-(Dimethyl amino)propyl methacrylamide	170.2	11.21, 0.0867
	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$		
12	QAPM Trimethyl-(3-methacrylamidopropyl ammonium chloride	220.5	11.21, 0.0867
	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^-$		

*1 Monomer 1: Cationic monomer, Monomer 2: VAc.

following reactions reported in literature:³¹⁻³³



The synthesis shown in *Equation* (4) is an application of the method known as “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 ¹H-NMR.

Vinyl acetate (VAc) used were 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.

9.2.2 Syntheses and Characterization

9.2.2.1 Reaction of PVAL with CTA or GTA Aqueous solution (500g) dissolving 50g of PVAL and 1g of sodium hydroxide was prepared in a 1L-glass reactor equipped with a stirrer. CTA (10g) was added to the solution. The mixture was stirred during twenty hours 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%. Similar procedure was performed using GTA instead of CTA and the polymer obtained (GTA-PVAL) contained nitrogen of 0.10%: the degree of conversion of GTA is 6.2%.

9.2.2.2 Monomer Reactivity Ratios Copolymerization 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. Copolymerizations 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 NMR analysis. The values, r_1 / r_2 , for the copolymerization of QAPA / VAc were assumed as the same as those of APA / VAc. The values, r_1 / r_2 , for AE (or QAE) and VAc as 0.0 / 4.0 and those for MVI (or QMVI) and VAc as 0.62 / 0.24 have been determined based on 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 $Q_1=0.289$, $e_1=-0.052$,³⁴ $Q_2=0.026$ and $e_2=-0.88$.³⁵

9.2.2.3 Copolymerization Copolymerizations of VAc and cationic monomers were carried out using a 5L-glass reactor equipped with a stirrer, a reflux condenser and an 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 system using methanol and 2,2'-azobis(isobutyronitrile) (AIBN) as solvent and initiator, respectively, at boiling temperatures of the system, 60° to 62°C under the atmosphere of nitrogen gas. In order to obtain copolymers having homogeneous monomer composition at any degrees of conversion during copolymerization, the "feeding-comonomer method"^{36,37} was adopted, where 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.²⁸ The small amount of cationically modified PVAC was purified by reprecipitation in cooled water twice and analyzed using ¹H-NMR and elementary analysis. Typical examples of copolymerization results are shown in Table 20 where feed amounts of reagents are described as weight part for convenience of comparison.

9.2.2.4 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 for 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 20.

9.2.2.5 ¹H-NMR Spectra were obtained with Varian EM-390 at 90MHz. As solvents and internal standard reagents, CDCl₃ and hexamethyldisiloxane were used for modified PVACs, while D₂O and sodium 3-(trimethylsilyl)propionic acid-d₆-sodium salt were used for modified PVALs. NMR 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.

9.2.2.6 Characterization of Modified PVALs The degree of hydrolysis (DH) of vinyl acetate units in modified PVALs was measured both by ¹H-NMR and by a chemical method, alkaline re-hydrolysis followed by acid titration.³⁸ 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 capillary viscometer was carried out for the samples dissolved in aqueous solution. of sodium chloride (1M) at 30 °C . Viscosity-average degree of polymerization was calculated by the equation,

$$\overline{P}_v = \left([\eta] \times 10^4 / 8.33 \right)^{1/0.62} \quad .^{38-40}$$

9.2.3 Applications

9.2.3.1 Adsorption on Pulp Bleached kraft pulp having a beating degree of 466ml 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.⁴¹ The iodine solution with deionised 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. 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. Similar procedure was carried out for aqueous solution not including pulp as blank test . Calibration curves were made for each modified PVAL.

9.2.3.2 Polyelectrolyte Complexes with Anionic Polymers^{42,43} Mixing experiment was performed in aqueous solution. The solution of the cationic PVAL modified with 2.0 mol% of QAPM (QAPM-PVAL, DH: 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 sulfuric acid potassium salt) (PVS · K, N/400) supplied from Wako Pure Chemical Ind., Osaka; b) Modified PVAL with sulfonate group²⁹ (SAMPS-PVAL, sodium 2-acrylamide-2-methylpropane sulfonate (SAMPS) units: 2.0 mol%, DH: 98.0 mol%, $\eta_{4\%}$: 30.0 cP, Concentration: 0.5 wt%) c) Modified PVAL with carboxylate group²⁸ (IA-PVAL, sodium itaconate units: 2.0 mol%, DH: 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.

9.2.3.3 Emulsion Polymerization A 3L-glass reactor equipped with a stirrer, a thermometer, a reflux condenser and a dropping funnel was charged with 80 g of cationic PVAL (QAPM-PVAL, QAPM units: 1.0 mol%, DH: 80.3 mol%, $\eta_{4\%}$: 9.0 cP) and 850 g of distilled water, and clear solution was prepared

Table 20 Synthesis of cationic Poly(vinyl alcohols) by copolymerization and alcoholysis

No.	Feed in copolymerization (part)										Reaction time min	Extent of conversion of VAc %	Modified PVAc		Modified PVAl	
	Cationic monomers	VAc	Cationic monomer		Acetic acid		Methanol		AIBN	Cationic group			Degree of Polymerization \bar{P}_n	Cationic group	Degree of hydrolysis mol%	Viscosity (4%, 20°C)
			Initial/ Additional	Initial/ Additional	Initial/ Additional	Initial/ Additional	mol%	mol%								
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 ^(*)	10.1	98.7	(*)			
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.

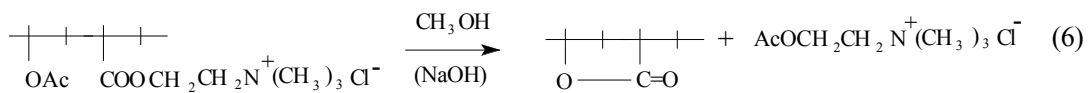
acid, 1000 g of VAc was added and the temperature was increased to 60°C. Polymerization was carried out for 135 min under the atmosphere of nitrogen gas by the occasional addition of an aqueous solution of hydrogen peroxide and an aqueous solution of sodium pyrosulfite as an initiator system. The emulsion thus obtained contained 51wt% 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. The similar procedure was repeated except that the modified PVAL was replaced with an non-modified PVAL (DH: 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.

9.3 RESULTS AND DISCUSSION

9.3.1 *Syntheses of Cationic PVALs*

9.3.1.1 *Polymer Reaction with CTA or GTA* The modified PVALs containing cationic group (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 to 0.3% of nitrogen, approximately 70%, under the similar reaction conditions.⁴⁴

9.3.1.2 *Copolymerization with QDMA or DMA* Figure 48 shows the ¹H-NMR spectra for the copolymer of VAc and QDMA (QDMA-PVAC) and for its hydrolyzed product by alcoholysis (QDMA-PVAL) (*Sample 2* in Table 19). The amount of QDMA units are 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 ¹H-NMR spectra of the un-purified sample of QDMA-PVAL shown in Figure 48-b, shows apparent signal of the group but the spectra of purified one using a Soxhlet's extractor with methanol in Figure 48-c shows no signal of the group. The cationic group is regarded as liberated during alcoholysis procedure, as shown in the following reaction:



Similar reaction generating lactone ring in PVAL chain has already been known for the alcoholysis of the copolymer of VAc and alkyl (meth)acrylate, as discussed in Chapter 7.^{28, 45, 46} The copolymerization with DMA (*Sample 1*) cannot be applied for cationic modification of PVAL due to the low resistance of ester linkage to alkaline alcoholysis

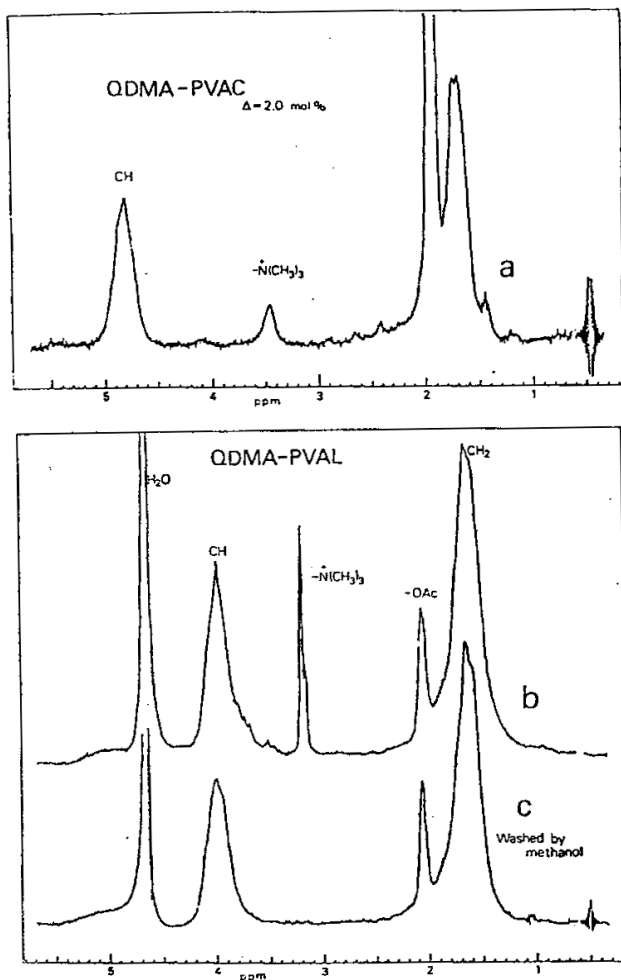


Figure 48 The $^1\text{H-NMR}$ spectra of (a) modified poly(vinyl acetate) with trimethyl-(2-acryloxyethyl) ammonium chloride (QDMA), (b) the corresponding poly(vinyl alcohol) by alcoholysis before purification, and (c) the purified sample.

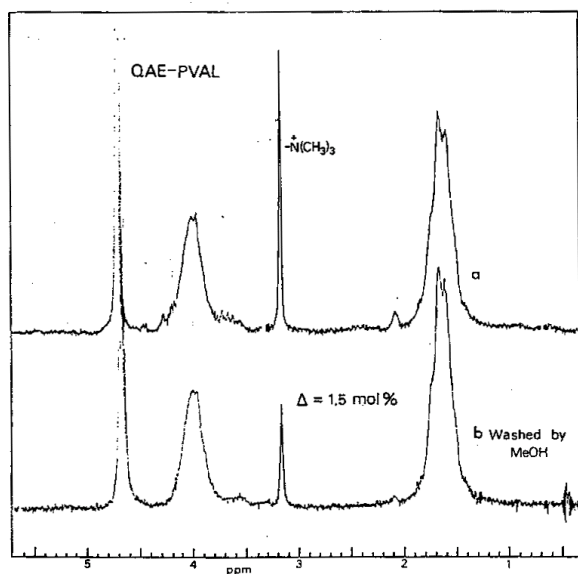


Figure 49 The ^1H -NMR spectra of (a) modified poly(vinyl alcohol) with trimethyl-(vinylxyethyl)ammonium chloride (QAE) before purification, and (b) the purified sample.

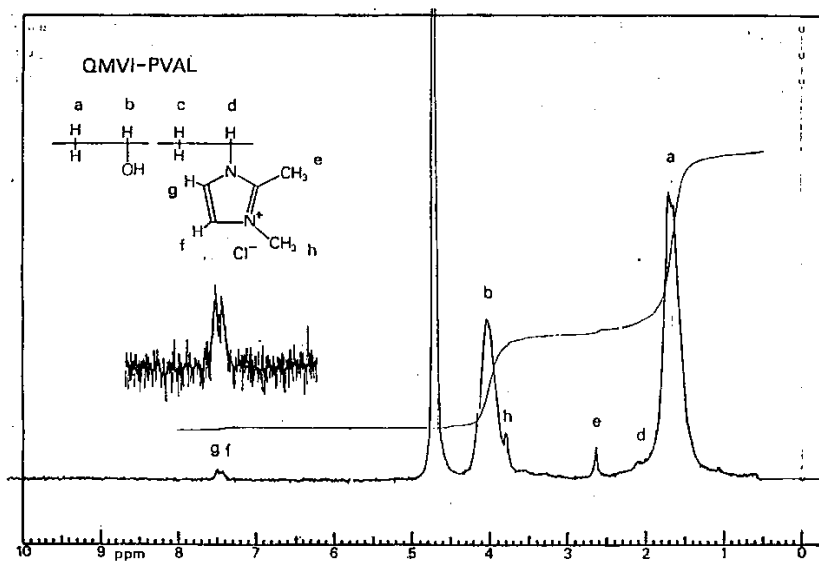


Figure 50 The ^1H -NMR spectrum of modified poly(vinyl alcohol) with 1-vinyl-2,3-dimethylimidazolium chloride (QMVI).

9.3.1.3 Copolymerization with QAE or AE Figure 49 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% for the purified sample. Apparent larger strength for the signal of trimethylammonium group in the sample (**a**) must be due to higher amount of residual monomer included in the sample because QAE has 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 a problem of less reactivity in copolymerization.

9.3.1.4 Copolymerization with QMVI or MVI Figure 50 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°C. Copolymerization with MVI or QMVI is also regarded as another possible method for obtaining cationically modified PVALs.⁴⁷

9.3.1.5 Copolymerization with QAPA, QAPM, APA or APM Figure 51 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 copolymer can be determined from material balance. In the case of the copolymer with QAPA, the mole fraction of QAPA units is: 3.3 mol% from material balance, 3.6 from NMR analysis of the modified PVAC and 3.2 from NMR 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 group can be produced.

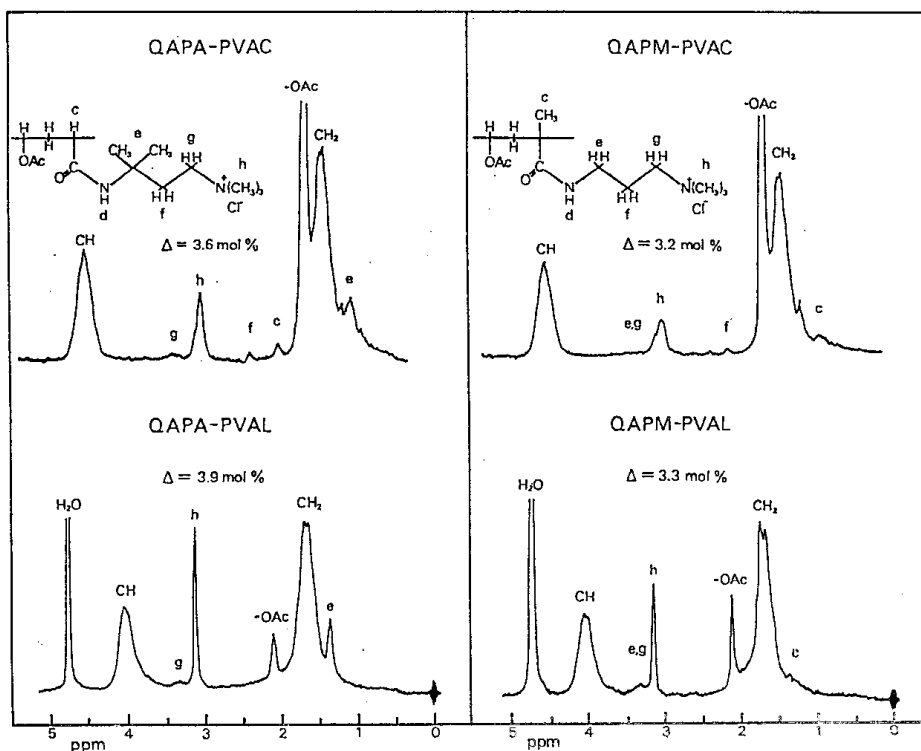


Figure 51 The $^1\text{H-NMR}$ spectra of modified poly(vinyl acetate) with trimethyl-(3-acrylamido-3,3-dimethylpropyl)ammonium chloride (QAPA-PVAC), modified poly(vinyl acetate) with trimethyl-(3-methacrylamidopropyl)ammonium chloride (QAPM-PVAC) and their hydrolyzed products (QAPA-PVAL and QAPM-PVAL) obtained by alkaline alcoholysis.

On the other hand, however, it has been observed that stronger alkali conditions can cause the cleavage of amido linkage. The original solid samples (5g) 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 two hours at 36°C . From NMR 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 loses cationic group presumably due to the cleavage of amido linkage while QAPA units show resistance to cleavage under the same conditions.

It has been also 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*).

9.3.1.6 Partially Hydrolyzed QAPM-PVALs and Highly Viscous Aqueous Solutions Table 21 shows the synthetic conditions and the properties for QAPM-PVALs with the modification degrees of 0.13 to 1.0 mol% and with various DH, down to 54.8 mol%. First, it has been found that the modified PVALs of much lower DH, even 54.8 mol% of DH for example, are soluble in water although some of them show slightly milky appearance; non-modified PVALs lose their solubility in water in cases for lower DH than about 80 mol%.^{48,49} Such increased solubility in water for the partially hydrolyzed QAPM-PVALs is regarded as due to increased hydrophilic property of QAPM units. Similar phenomenon has already been found in the cases of the modification of PVALs with other ionic monomers like itaconic acid²⁸ and SAMPS.²⁹ Lower modification with QAPM at the mole fraction like 0.13 mol% has been found so effective that the PVAL

Table 21 Syntheses of Poly(vinyl alcohol)s modified with 3-trimethyl-(1-methacrylamidopropyl) ammonium chloride (QAPM)

No.	Feed in copolymerization (part)			Reaction time min	Extent of conversion of VAc %	Cationic groups mol%	Degree of hydrolysis mol%	Viscosity of aqueous solution (4%, 20°C) cP
	VAc	QAPM Initial/ Additional	Methanol Initial/ Additional					
14							99.0	29.4
15	1000	2.3 / 14.9	266 / 14.9	0.60	230	64.1	1.0	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	44.6	0.54	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	48.0	0.25	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	65.8	0.13	19.5
34							77.1	33.3
35							70.3	Phase separation

of 77.1 mol% of DH shows solubility although that of 70.3 mol% shows phase separation. Secondly, anomalous high viscosity has been observed for the aqueous solution of partially hydrolyzed QAPM-PVALs, as shown in Table 21 and also in Figure 52. The viscosity depends prominently on the combination of the mole fraction of QAPM units and DH. The PVAL with 0.5 mol% of QAPM units and 67.5 mol% of DH shows the highest viscosity, 2000 cP at the concentration of 4 wt% at 20°C.

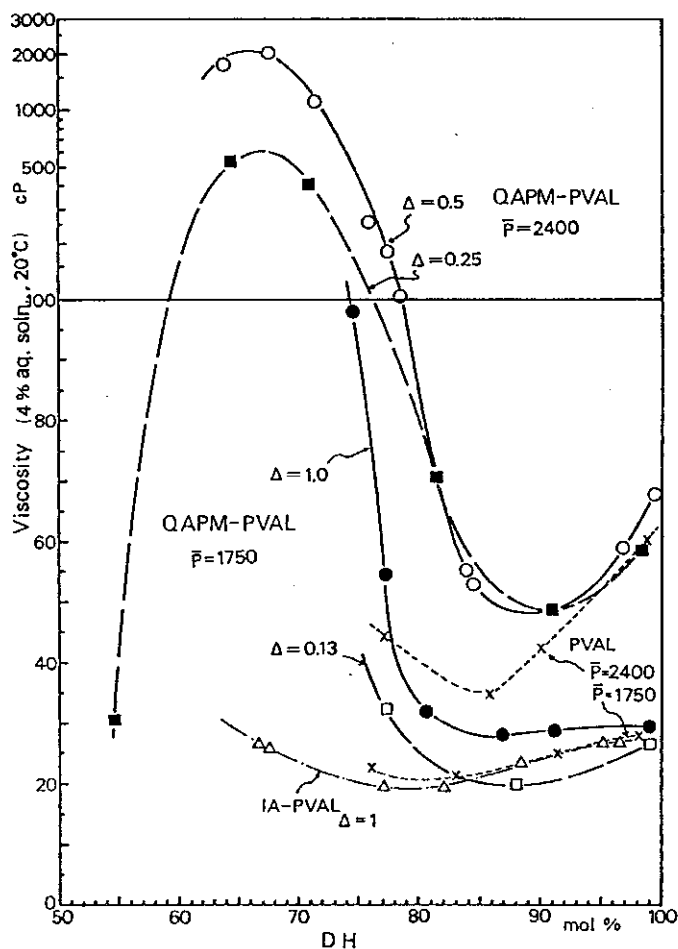


Figure 52 Viscosity for the 4 wt% aqueous solutions for PVALs modified with trimethyl-(3-methacrylamidopropyl)ammonium chloride (QAPM-PVAL), PVALs modified with itaconic acid (IA-PVAL), and non-modified PVALs, as functions of the degree of hydrolysis (D. H.). The degrees of modification (Δ) and the viscosity-average degrees of polymerization \bar{P}_v of the PVALs are also shown.

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 52. Similar phenomenon showing highly viscous aqueous solution has been known for the PVALs modified both with groups carrying hydrophobic chains and with sodium carboxylate group,⁵⁰ where intermolecular hydrophobic interaction or association among hydrophobic chains has been assumed. The phenomenon observed in the present case could be explained by similar mechanism. High viscous PVALs shown here is expected to be applied for thickener or viscosity-increasing agent.

9.3.1.7 Monomer Reactivity and Industrial Production Figure 53 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.

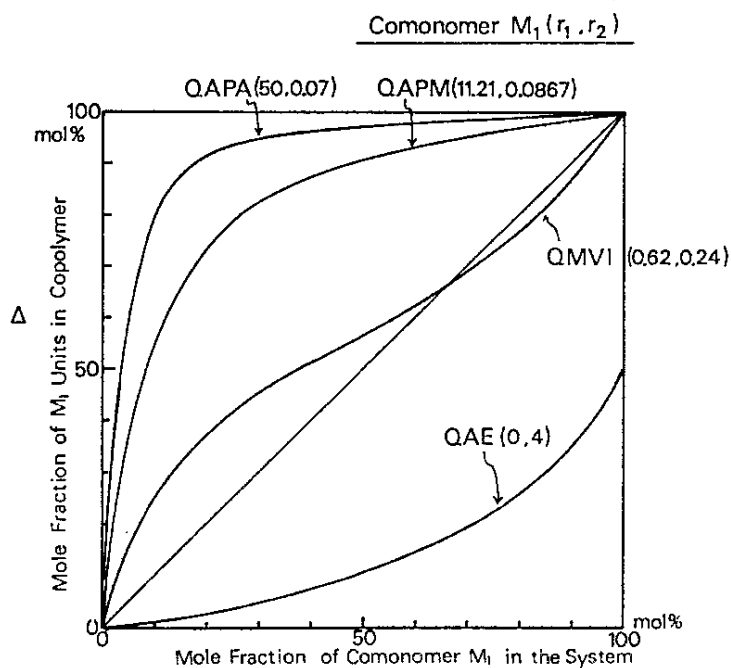


Figure 53 Copolymerization curves for various cationic monomers (M_1) and vinyl acetate (M_2).

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

9.3.2 Properties and Applications of Cationically Modified PVALs

9.3.2.1 Adsorption to Pulp Figure 54 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 small amount of cationic group inside PVAL chain functions as active sites for adsorption to fibrous pulp, which is known as a typical substance charged negatively.¹ This functional property suggests that cationic PVALs have the possibility of application to internal reinforcing agent for paper.

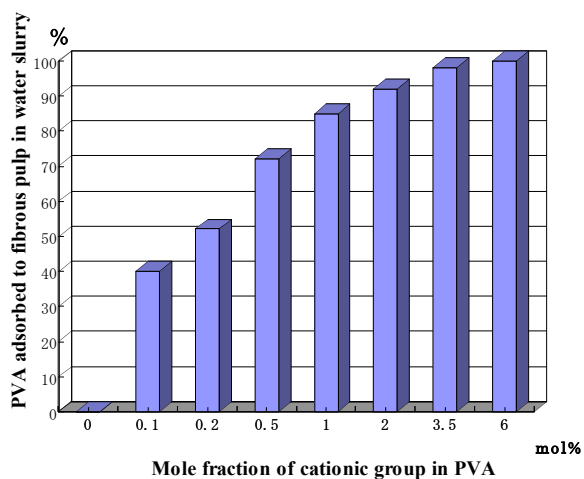


Figure 54 Adsorption of cationic PVAL onto fibrous pulp dispersed in bulk water.

9.3.2.2 Polyelectrolyte Complexes Another typical experiment has been carried out

for the confirmation of cationic properties: the formation of polyelectrolyte complex.^{42,43} Figure 55 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 sulfuric acid potassium salt) (PVS · K) of N/400 indicates sharper clouding. Based on the assumption of maximum clouding caused at equivalence, the mole fraction of cationic group in the polymer is calculated as 2.0 mol%, which is consistent with the results from ¹H-NMR analysis. Mixing with the solution of IA-PVAL or SAMPS-PVAL also shows maximum clouding approximately at the respective equivalent points.

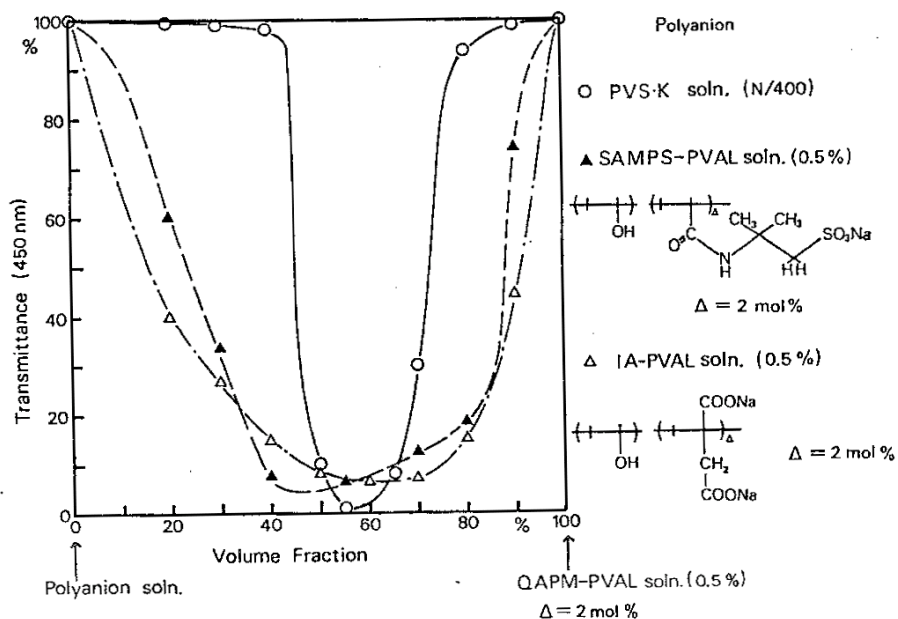


Figure 55 Formation of polyelectrolyte complex and turbidity in aqueous solution. Transmittance for the aqueous dispersions containing a cationic poly(vinyl alcohol) and polyanions as functions of the volume fraction of aqueous solutions used. Cationic poly(vinyl alcohol): PVAL modified with 2.0 mol% 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%).

9.3.2.3 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.

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