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Preparation of Polyvinylamine by the Hofmann Degradation of Polyacrylamide[1]

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Polyvinylamine which contained 95.6 mol% amine units was obtained when the Hofmann degradation was applied to polyacrylamide by use of a very slight excess of sodium hypochlorite and a large excess of sodium hydroxide at 0 to −15 °C for about 15 h. Polyvinylamine hydrochloride (PVAm·HCl) was isolated almost quantitatively as a white powder. PVAm·HCl was freely soluble in water, but insoluble in organic solvents such as methanol, acetone, dioxane, *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). The desalting of PVAm·HCl was performed by passing its aqueous solution through columns of ion exchange resins. The product containing 30.5% nitrogen was obtained in reasonable yield. Polyvinylamine was freely soluble in water, acetic acid, or lower alcohols, but insoluble in solvents such as acetone, dioxane, DMF, and DMSO.

It is well known that *N*-haloamides are highly stable at a temperature as low as 0 °C and activation energy of the Hofmann degradation is about 30 kcal/mol. Therefore, the Hofmann degradation is generally carried out by dissolving the amide in a very slight excess of cold aqueous hypohalite solution, followed by rapid warming.[2]

However, the Hofmann degradation of polyacrylamide (PAM) is exceptional. It has been previously shown in this laboratory that the Hofmann degradation of PAM is accelerated very much by the neighboring-group participation and the *N*-haloamide groups of PAM are easily converted to amino groups even at a temperature below 0 °C.[3] According to this procedure, the partial amination of PAM was easily accomplished while limiting the formation of carboxyl groups to a very small percentage.[4]

The present investigation was undertaken in order to find some suitable methods for increasing further the contents of amine units, and for the separation and the purification of polyvinylamine (PVAm). PVAm containing as much as 95.6 mol% amine units could be purely isolated almost quantitatively.

Experimental

Materials. Acrylamide and $K_2S_2O_8$ were recrystallized twice from benzene and water solution respectively. All of the other chemicals used were reagent grade.

Polymerization of acrylamide was carried out in 10% aqueous solution with the use of $K_2S_2O_8$-2-propanol redox initiator under nitrogen atmosphere at 60 °C for 60 min. The resulting polymer was purified by reprecipitating twice from water-methanol. The nitrogen content of PAM was 18.9% and the content of carboxyl groups was negligible small. The intrinsic viscosity of PAM was 2.1 dl/g at 30 °C.

Sodium hypochlorite solution was prepared by passing chlorine gas through a 7 M NaOH solution cooled with an ice bath. The concentration of NaOCl measured by the iodometry was 2.0 mol/l and that of NaOH by the acidmetry after removal of NaOCl with a small excess of H_2O_2 was 2.5 mol/l.

The ion exchange resins used were Amberlite IR-120B and IRA-400.

Reaction Procedure. Twenty-four grams of 10.3% PAM (1.4 mol/l per amide group) cooled to 0 °C were added into 10 ml of alkaline NaOCl cooled to about −5 °C with vigorous stirring. The resulting solution was cooled rapidly by dipping in a bath of −15 °C. When the temperature of the solution reached about −10 °C, a desirable amount (1—40 ml) of 10 mol/l NaOH cooled to −15 °C was added with stirring and maintained at −10 to −15 °C for 1—2 h. Then the reaction mixture was warmed to 0 °C and allowed to stand for 10—15 h.

Isolation and Purification. The polymer was isolated by pouring the mixture into about a 4-fold amount of methanol. The resulting precipitate was dissolved in about 25 ml of water and 6 M HCl was added dropwise to this solution with stirring. Although CO_2 gas evolved and the polymer precipitated once, it was soon dissolved completely by the continuous stirring, keeping the pH about 2. The resultant solution was poured into about a 4-fold amount of methanol again. The supernatant solution was decanted and the residual precipitate was filtered through the weighed sintered glass disk, then washed with methanol and ethanol successively and dried *in vacuo* over P_2O_5. The ash content of polyvinylamine hydrochloride (PVAm·HCl) obtained in this manner was less than 0.3%.

The repetition of the reprecipitations was undesirable because the purified PVAm·HCl was precipitated with great difficulty. Since PVAm·HCl is very hygroscopic, care had to be taken in handling it.

The aqueous solution (2—3%) of PVAm·HCl was passed through the columns of cation and anion exchange resins successively and the columns were washed with water about double in volume. The collected effluent from the columns was concentrated to about 5% under reduced pressure and the resultant solution was poured into a large amount of acetone. The precipitate obtained was filtered and dried *in vacuo*.

Analytical Method. Contents of both amino and carboxyl groups were measured by the colloid titration method.[5] For details of the analyses the previous paper[3] should be referred to.

The chlorine content of PVAm·HCl was determined as follows: Dilute sulfuric acid was added to 100 ml of the aqueous solution containing about 0.1 g PVAm·HCl to adjust the pH to about 2. A proper amount (50—100 ml) of 0.01 M potassium poly(vinyl sulfate)[5] was added to this solution until the supernatant solution became clear, and the resulting precipitate was filtered off and washed several times with a small amount of water. The combined filtrate was neutralized and titrated by 0.05 M $AgNO_3$ (Mohr method). If the PVAm was not removed, the end point of the titration became imprecise and the content of chlorine was overestimated.

TABLE 1. REACTION CONDITIONS OF THE HOFMANN DEGRADATION OF PAM AND THE ANALYTICAL RESULTS

No.	Reaction conditions			Analytical results			Analytical results of PVAm·HCl				
	PAM (mol/kg)	NaOCl (mol/kg)	NaOH (mol/kg)	Amino group (mol/kg)	Degree of amination (%)	Carboxyl group (mol%)	Yield (g)	Ash (%)	Chlorine (%)	Nitrogen (%)	Carboxyl group
1	0.740	0.751	1.16	0.395	53.4	5	1.49	0.3	25.9	17.2	neg. small
2	0.500	0.507	2.99	0.435	87.0	4	1.52	0.2	40.3	16.0	neg. small
3	0.385	0.394	4.14	0.354	92.0	3	1.54	0.3	43.0	16.0	neg. small
4	0.263	0.268	5.28	0.253	95.6	2	1.55	0.1	43.3	16·1	neg. small
5	0.288	0.294	8.15	0.273	94.8	2	1.54	0.1	42.9	15.9	neg. small
6	0.257	0.259	5.09	0.227	88.3	1	1.53	0.1	40.7	15.5	neg. small
7	0.255	0.261	5.09	0.205	80.4	1	1.51	0.2	38.3	16.0	neg. small
8	0.218	0.220	4.86	0.191	87.6	1	1.53	0.2	40.2	15.5	neg. small
						PVAm·HCl (calcd)	1.61	0	44.6	17.6	0

In the case of Nos. 6—8, 3 ml of dioxane (No. 6), 3 ml of methanol (No. 7) or 10 ml of water saturated with NaCl (No. 8) were added to 14 g of 10.3% PAM solution before mixing it with the alkaline NaOCl.

Nitrogen contents were determined by the Kjeldahl method.

Results and Discussion

Effect of NaOH Concentration on Yields of Amine Units. During the progress of the Hofmann degradation, the isocyanato groups which are formed as transient intermediates react with water to yield the objective amino groups on the polymer chain in the presence of excess alkali[2)] On the other hand, a part of these resulting amino groups give the urea derivatives due to the reaction between the amino and isocyanato groups. These two reactions can be illustrated as follows:

$$\text{R-CONH}_2 \xrightarrow{\text{OCl}^-} \text{R-CON}^-\ \text{Cl} \longrightarrow$$

$$[\text{R-N=C=O}] \xrightarrow{\text{OH}^-} \text{R-NH}_2 \qquad (1)$$

$$\text{R-N=C=O} + \text{R-NH}_2 \longrightarrow \text{R-NHCONH-R} \qquad (2)$$

Therefore the yields of amine increase with an increase in concentration of NaOH. When PAM was subjected to the Hofmann degradation in the presence of 4.2 mol/l NaOH, 88% of the amide units converted to amine, as described earlier[3)]. Although the yields of amine units could be expected to increase further if an additional amount of NaOH was applied, the salting-out of the polymer, which took place on the occasion of mixing the PAM solution with alkaline aqueous NaOCl, precluded an experiment with a high concentration of NaOH.

After various attempts were made, it was found that the concentrations of NaOH could be increased still more, without any salting-out of the polymer, by adding the large amount of 10—20 mol/l NaOH to the mixrure of PAM and NaOCl prepared in the presence of a small amount of NaOH. This may be responsible for the fact that the *N*-chlorinated PAM salt outed with more difficulty than the PAM.

Results are shown in Table 1. The degrees of amination based on amide groups were 53.4 and 87.0% in the presence of 1.16 and 2.99 mol/kg NaOH respectively. Since these experimental data are similar to the results of the paper reported previously,[3)] the degree of amination has been found to be little influenced by the addition procedures of NaOH.

The degree of amination increased further with increase of the concentration of NaOH and amounted to 95.6 mol% in the presence of 5.28 mol/kg NaOH. However, when an excess concentration of NaOH such as 8.15 mol/kg (No. 5) was applied, the degree of amination was limited to 94.8 mol% because the polymer salt outed as a pasty cake. The higher limit of NaOH concentration in the homogeneous reaction seemed to be 6—7 mol/kg.

In the cases shown above (No. 1—5), 2—5 mol% of carboxyl groups were formed, even though PAM cooled to 0 °C was used. It may be preferable to mix alkaline NaOCl with PAM at a lower temperature to reduce the formation of carboxyl groups[3)]. Further, it has already been found that the degree of amination increases with decrease of the reaction temperature[3)]. No. 6—8 were the cases in which PAM cooled to −5 to −10 °C after the addition of dioxane, methanol, or water saturated with NaCl was mixed with an alkaline NaOCl to −15 °C. As can be seen from Table 1, the formation of carboxyl groups was less than 1%. However, the degree of amination was reduced also, contrary to our expectation. That the degree of amination is particularly low in the presence of methanol may be due to the formation of some urethane linkages.

Isolation of PVAm·HCl and Analytical Results. Results are shown in Table 1. The products of 1.49—1.55 g were obtained from 1.44 g PAM. Since the molecular weight of monomer units of PAM and PVAm·HCl are 71.1 and 79.5 respectively, the theoretical yield of PVAm·HCl is 1.61 g. In the case of No. 4 in which 95.6% of the amide units converted to amine, 1.55 g of PVAm·HCl was obtained.

The ash contents of the products were very small (0.1—0.3%). The chlorine contents of the products increased with increase of amine units. The chlorine content (43.3%) of No.4 is 97.1% of the theoretical

Table 2. Analytical results of PVAm desalted from PVAm·HCl by ion exchange

No.	Yield (%)		Nitrogen (%)	Molecular weight per nitrogen	Molecular weight per amino group	Carboxyl group
	found	calcd				
1	72.5	73.1	22.0	63.7	104.9	neg. small
2	57.3	58.4	25.0	56.0	59.1	neg. small
3	54.0	55.5	28.5	49.2	49.9	neg. small
4	53.7	55.4	30.5	45.9	46.5	neg. small
PVAm (calcd)		54.2	32.5	43.1	43.1	0

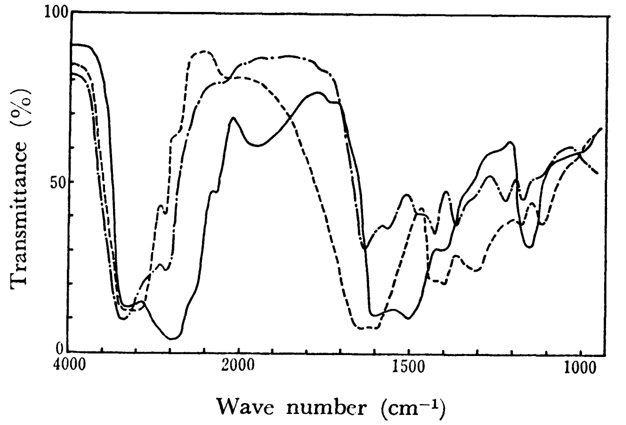

Fig. 1. IR spectra of PAM, PVAm·HCl(No. 4) and PVAm(No. 4).
----: PAM, ——: PVAm·HCl, —-—: PVAm.

value (44.6%). This value agreed closely with the degree of amination (95.6%) determined by colloid titration.

The carboxyl contents were negligible small. The disappearance of carboxyl groups appeared to be due to the formation of methyl ester which occured during the isolations and purifications, because methanol was detected in the hydrolysis solutions of purified products by the gas chromatography.

PVAm·HCl was highly hygroscopic and freely soluble in water. However, it was insoluble in pure organic solvents such as methanol, acetone, dioxane, *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), though soluble in methanol, DMF, or DMSO containing 10—20% water.

The infrared absorption spectrum of PVAm·HCl (No.4) in a KBr disk is shown in Fig. 1 and compared with that of PAM. The absorption band at 1640 cm^{-1} in PAM, which was assigned to CONH$_2$, diminished and new bands due to NH$_3^+$ appeared at 2800, 1950, and 1500 cm^{-1}. A very weak absorption band due to the ester was observed at 1700 cm^{-1}. The absorption bands due to NH$_2$ exist at 3335 and 1610 cm^{-1}.

Preparation of PVAm from PVAm·HCl. Attempts to obtain the pure PVAm by pouring the PVAm·HCl solution with a small excess of NaOH into various organic solvents were unsuccessful. Even if the above solution was added into a large amount of methanol the solids did not appear. Although some milky precipitates were obtained by pouring such a solution into ethanol or 2-propanol, the filtration was actually impossible. By using the acetone–ethanol (4 : 1) or dioxane–ethanol (2 : 1) mixture as precipitant, precipitates which could be filtered easily were obtained, but these contained as much as 30—60% ash.

The ion exchange resins were also applied to desalt PVAm·HCl. Results are shown in Table 2. The yields of products were satisfactory, as can be seen from comparison of found and calculated values, and accordingly the amount of PVAm bound to cation exchange resins was extremely small.

The nitrogen contents of the products were 22.0—30.5%. The latter value (30.5%) approximates adequately to the theoretical nitrogen content of PVAm (32.5%). Then the equivalent molecular weights per nitrogen (EW-N) were compared with those per amino group (EW-A) determined by colloid titration. In the case of No. 1, EW-N was 63.7 and EW-A 104.9. This serious difference shows that No. 1 contains a large amount of non-amine-type nitrogens. EW-N and EW-A are brought close together with increase of the degree of amination. In the case of No. 4 (degree of amination: 95.6%), the nitrogen was found to be virtually an amine-type one since EW-N was 45.9 and EW-A 46.5.

The contents of carboxyl groups were small enough to neglect. The ester seems not to be hydrolyzed by passing it through the ion exchange resins.

PVAm was hygroscopic and freely soluble in water, acetic acid, or lower alcohols such as methanol, ethanol, and 2-propanol. However, it was insoluble in organic solvents such as acetone, dioxane, tertahydrofuran, DMF, DMSO, benzene, and choroform.

The infrared absorption spectrum of PVAm in a KBr disk is shown in Fig. 1, in comparison with that of PVAm·HCl. The absorption bands due to NH$_2$ existed at 3340 and 1635 cm^{-1}, although the bands at 2800, 1950, and 1500 cm^{-1} in PVAm·HCl, which were assigned to NH$_3^+$, diminished.

The intrinsic viscosity of PVAm (No.4) measured at 30 °C in 0.1 M NaCl solution was 0.70 dl/g.

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