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Group Interactions in Polyelectrolytes. X. The Amination Kinetics of Poly(vinyl haloacetals) and Related Compounds

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Polyvinyl chloroacetal (PVCA) and polyvinyl bromoacetal (PVBA) were prepared from polyvinyl alcohol, whose acetal contents were close to the value expected on the basis of Flory's calculation for the intramolecular reaction between neighboring substituents. The amination of these polyvinyl haloacetals and polyvinyl chloroethyl ether with 2-aminobutanol and diethanolamine was investigated kinetically in dimethyl sulfoxide. The $\Delta G^{\neq}$ values in the amination of these polymers were much higher than that of chloromethylated polystyrene (CMPS) reported previously; this was because of their higher $\Delta H^{\neq}$ values. The lower $\Delta H^{\neq}$ of CMPS was ascribed to the resonance structure of the activation complex due to the phenyl substituent at the α-carbon of the chloromethyl group. This was ascertained by comparing the $\Delta H^{\neq}$ value in the amination of phenethyl chloride with that of benzyl chloride. The amination of PVBA was faster than that of PVCA as a result of the lower $\Delta H^{\neq}$ of the former.

The amination of haloacetalized polyvinyl alcohol has already been investigated for the purpose of improving vinylon fibers[1] and for the preparation of ion-exchange fibers.[2] The amination proceeded in a heterogeneous system, and the reaction was reported to be accompanied by cross-linking. The amination kinetics of polyvinyl haloacetal in a homogeneous system has not yet been studied, though. The present author has now prepared chloroacetal and bromoacetal of polyvinyl alcohol (PVA); their acetal contents are very close to the value calculated by Flory.[3] The amination of these polyvinyl haloacetals with diethanolamine or 2-aminobutanol in dimethyl sulfoxide (DMSO) has been found to proceed to nearly a 100% conversion in a homogeneous system.

The amination rate of polyvinyl bromoacetal (PVBA) was higher than that of polyvinyl chloroacetal (PVCA). The amination rates of these polyvinyl haloacetals are, however, much lower than that of chloromethylated polystyrene (CMPS), which was reported previously.[4,5] The present author has also investigated the amination of polyvinyl chloroethyl ether (PVCE) of a low molecular weight; the rate was only a little higher than that of PVCA. The higher amination rate of CMPS, as compared with PVBA, PVCA, and PVCE, may be ascribed to its resonance structure in the transition state. Then, the amination rate of benzyl chloride, which is a model of the structural unit of CMPS, has been compared with that of phenethyl chloride, which is considered to lack in resonance. Further, the amination rates of both benzyl chloride and cuminyl chloride with several amines have been measured in order to examine the propriety of the compounds as structural unit models of CMPS.

The amination rates of PVBA, PVCA, and phenethyl chloride with diethanolamine have been found to be a little lower than the corresponding amination rates with 2-aminobutanol. On the other hand, each amination of CMPS and benzyl chloride with diethanolamine was a little faster than that with 2-aminobutanol.[4,5] This reverse reactivity of the two aminoalcohols has been discussed with the aid of the amination data on PVCA and phenethyl chloride with several alkylamines, in addition to the published data on CMPS and benzyl chloride.

Experimental

Materials. The polyvinyl alcohols used were Gohsenols of Nihon Gosei Chem. Ind. Co., NH-18 (degree of hydrolysis: 99.0—100%; degree of polymerization, $\overline{P}$=over 1500) and KH-17 (degree of hydrolysis: 78.5—81.5%; $\overline{P}$=over 1500). The cuminyl chloride was prepared by treating cumen (0.4 mol) and chloromethyl ether (0.87 mol), with stanic chloride (0.096 mol) as the catalyst, in toluene at −10°C. The yield of the purified product (bp 110 °C/15 mmHg, $n^{21.5}$ 1.5224) was 52.6%. The 2-aminobutanol was prepared by the procedure described in a previous paper;[6] n^{20} 1.4529, $[\alpha]^{20}_{D}$ −10.23. The other chemicals and solvents were of a reagent grade and were distilled before use; they were proved to be pure by their refractive indices.

Preparation of Polyvinyl Haloacetals. To ethylene dichloride, which absorbed dry hydrogen chloride, we added PVA (equivalent to a 1% concentration) and chloroacetaldehyde diethyl acetal (equimolar to the hydroxyl group of PVA), after which the mixture was left for several days at 20 °C. The mixture was then poured into methanol to precipitate the polymer. The polymer was purified by reprecipitation with ethylene dichloride-methanol and by washing it thoroughly with methanol. The polyvinyl chloroacetal (PVCA) thus obtained was dried *in vacuo* at 40 °C. The content of acetal (E%) in the polymer was calculated from the content of chlorine (Cl%) in the polymer by means of:

$$E\% = 145.64 \times [\text{Cl}\ \%]/(58.62-[\text{Cl}\ \%]) \qquad (1)$$

Polyvinyl bromoacetal (PVBA) was also prepared by the same procedure except that the reprecipitation was carried out with DMSO-methanol. The acetal content was calculated from the bromine content (Br%) in the polymer by means of:

$$E\% = 83.97 \times [\text{Br}\ \%]/(76.15-[\text{Br}\ \%]) \qquad (2)$$

Preparation of Polyvinyl Chloroethyl Ether. To a solution of 2-chloroethyl vinyl ether (10.6 g) in diethyl ether (50 ml), we added, drop by drop, a solution of boron trifluoride etherate (0.15 g) in diethyl ether (50 ml), after which the mixture was kept for 200 min at 25 °C. The mixture was then washed with 5% aqueous sodium hydroxide and water. The ethereal solution was then dried with calcium chloride, and the diethyl ether was removed by the use of an evaporator. The molecular weight of the polyvinyl chloroethyl ether

(PVCE) thus obtained was 945 ($\bar{P}=9$). Found: C, 44.53; H, 6.56; Cl, 30.35%. Calcd for $(C_4H_7OCl)_n$: C, 45.08; H, 6.63; Cl, 33.27%.

Amination Kinetics Measurements. The amination rates of PVBA, PVCA, PVCE, phenethyl chloride, cuminyl chloride, and benzyl chloride were measured by the procedures described previously for the amination of CMPS and benzyl chloride.[4]

Results and Discussion

Haloacetalization of Polyvinyl Alcohol (PVA). Noma *et. al.*[7] reported that, in the chloroacetalization of PVA with chloroacetaldehyde diethyl acetal in ethylene dichloride containing hydrogen chloride, the fractional conversion, after repeated treatments, nearly reached the calculated maximum value of 0.8647 which was given by Flory for the intramolecular reaction between neighboring substituents of a polymer having the 1.3-structure.[3] In the present study, the chloroacetalization of PVA by Noma's procedure has been examined in an attempt to prepare the PVCA of maximum acetal content by only one treatment. The acetalization of PVA with bromoacetaldehyde diethyl acetal has also been investigated by means of the same procedure. The results are shown in Tables 1 and 2. The results of the elementary analysis of the haloacetals with the highest acetal content, which are shown in Table 3, indicate that the C, H, and halogen contents of each polymer are very close to the values calculated on the basis of the maximum conversion given by Flory.

Table 1. Chloroacetalization of PVA (NH-18) in dichloroethane at 20 °C[a)]

HCl concn. M	Time day	Cl %	Acetal %
0.36	8	21.36	83.5
0.50	8	20.09	75.9
0.79	7	19.97	75.3
0.50	11	21.34	85.3
0.35	13	21.57	84.7
0.48	13	21.59	84.8
0.50	13	21.74	85.9
Calcd value (Flory)		21.83	86.47

a) Concentration of PVA: 1%.

Table 2. Bromoacetalization of PVA (NH-18) in dichloroethane at 20 °C[a)]

HCl concn. M	Time day	Br %	Acetal %
0.42[b)]	10	34.63	70.3
0.52	7	37.43	81.2
0.62[c)]	7	37.01	79.7
0.50	7	38.85	87.5
0.50	10	38.34	85.1
0.50	13	38.14	84.2
Calcd value (Flory)		38.64	86.47

a) Concentration of PVA: 1%. b) Concentration of PVA: 0.56%. c) Room temp.

Table 3. Elementary analysis of chloroacetal and bromoacetal of PVA (NH-18)

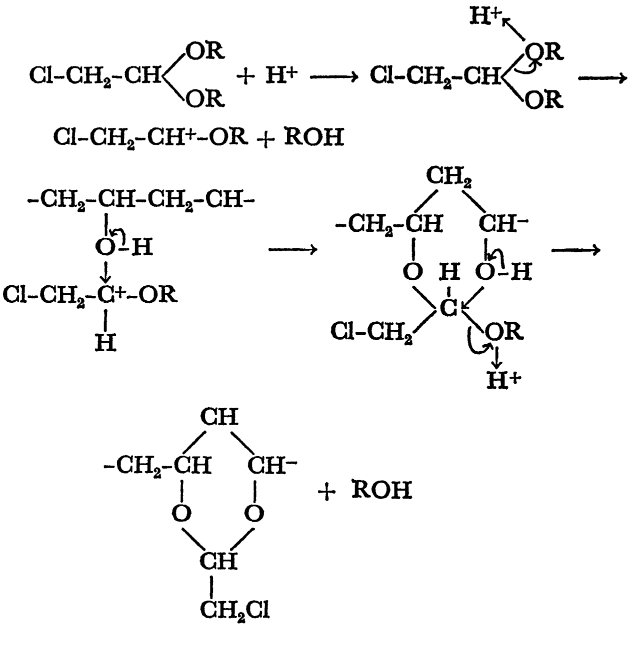
Chloroacetal	C %	H %	Cl %	Acetal %
Found (PVCA)	49.03	6.38	21.74	85.9
Calcd (Flory)	49.01	6.36	21.83	86.47
Bromoacetal	**C %**	**H %**	**Br %**	**Acetal %**
Found (PVBA)	38.95	4.92	38.44	85.6
Calcd (Flory)	38.48	5.00	38.64	86.47

Table 4. Chloroacetalization of PVA in DMSO

PVA	Concn. %	HCl concn. M	Temp. °C	Time day	Acetal %
KH-17	1	0.25	Room	1	5.6
	1	0.50	Room	2	9.5
	1	0.50	Room	6	45.2
	1	1.00	30	1	11.2
	1	0.50	40	2	22.2
	2	0.50	40	1	24.6
	2	0.50	40	1	Gel
NH-18	2	0.50	30	8	33.8
	2	0.50	30	8	Gel

In the above procedure, the reaction proceeded initially in a heterogeneous system, though the polymer was gradually swollen and finally dissolved in ethylene dichloride as the acetalization proceeded. The acetalization of PVA with chloroacetaldehyde diethyl acetal has also been investigated in DMSO; the results are summarized in Table 4. Although the reaction proceeded thoroughly in a homogeneous system, the acetal content of the product was low, and occasionally the gelation of the solution took place.

In the acetalization of PVA catalyzed by a proton, the probable mechanism of which is shown in the following scheme, the carbonium cation formed from the acetal may be subject to the nuclephilic attack by the oxygen of PVA to form the ether link, and the



succeding reaction with the neighboring hydroxyl group in the same mechanism may result in the formation of the acetal ring. Since DMSO is a basic aprotic solvent and since cations are very likely to solvate in this solvent, the activation energy of the acetalization in DMSO is possibly enhanced by this solvation.

Amination of Polyvinyl Chloroacetal (PVCA). The amination kinetics of PVCA with 2-aminobutanol and diethanolamine in DMSO can be fully expressed by this second-order rate equation:

$$kt = \frac{1}{a-b}\ln\frac{b(a-x)}{a(b-x)} \tag{3}$$

where k is the rate constant, where a and b are the initial concentrations of the amine and halogen groups respectively, and where x is the concentration of halide ions formed after time, t.

During the amination of chloromethylated polystyrene (CMPS) with diethanolamine in DMSO, the second-order rate constant, computed on the basis of Eq. (3), decreased as the amination proceeded; this deceleration was ascribed to the steric obstruction in the transition state by the neighboring substituted group.[5] The lack of this steric obstruction in the amination of PVCA with diethanolamine, which is indicated by its ordinary kinetic behavior, can be explained by the fact that the distance between the reactive groups in PVCA is longer than that in CMPS.

Table 5. Amination of PVCA in DMSO[a,b,c]

Amine	Temp. °C	$k\times10^3$ l/mol min	E_a kcal/mol	log A[d]
2-Aminobutanol	90	0.740	19.6±0.2	8.68±0.09
	100	1.57		
	110	3.15		
	120	5.93		
Diethanolamine	90	0.470	18.9±0.1	8.06±0.05
	100	0.953		
	120	3.43		
	130	6.43		

a) PVCA was prepared from NH-18. b) Concentrations: a is about 0.757 M and b is about 0.038 M. c) Amination rates of PVCA prepared from KH-17 with diethanolamine were also measured to give the values, E_a of 18.9±0.7 and log A of 8.10±0.38. d) A is expressed by l/mol min.

Table 6. Amination of PVBA in DMSO[a,b]

Amine	Temp. °C	$k\times10^2$ l/mol min	E_a kcal/mol	log A[c]
2-Aminobutanol	70	0.977	16.8±0.1	8.70±0.06
	80	1.91		
	90	3.74		
	100	7.05		
Diethanolamine	79.9	1.12	16.5±0.2	8.26±0.12
	85	1.49		
	90	2.08		
	100	3.77		
	110	7.05		

a) PVBA was prepared from NH-18. b) Concentrations: a is about 0.36 and b is about 0.017 M. c) A is expressed by l/mol min.

The numerical values of k at different temperatures are tabulated in Table 5, together with the values of E_a, the activation energy, and A, the frequency factor expressed by l/mol min, both of which were computed by the least-squares method.

Amination of Polyvinyl Bromoacetal (PVBA). The amination kinetics of PVBA with 2-aminobutanol and diethanolamine also fit Eq. (3). The results of the amination are tabulated in Table 6. The amination rate of PVBA is about fifty times that of PVCA; this is a result of the lower E_a value of PVBA.

Amination of Polyvinyl Chloroethyl Ether (PVCE). The amination of PVCE with diethanolamine conformed to Eq. (3), and no deceleration was observed during the course of amination. Since the degree of polymerization of this polymer is very low ($\bar{P}=9$), and since its side chain is rather flexible, the steric obstruction between the reactive groups may be avoided by the free rotation in the main and side chains. The results of the kinetic measurements are shown in Table 7. The amination of PVCE is several times faster than that of PVCA.

Amination of Phenethyl Chloride. The amination rate of CMPS is much higher than those of PVCA, PVBA, and PVCE. In the comparison of the rate constants at 60 °C, for example, constants which are given by the extrapolation of the Arrhenious plots, the amination rate of CMPS is about ten thousand times that of PVCA. This large difference in their amination rates may be considered to originate in the stabilization of the transition state of CMPS because of its

Table 7. Amination of PVCE in DMSO[a]

Amine	Temp. °C	$k\times10^3$ l/mol min	E_a kcal/mol	log A[b]
Diethanolamine	60	0.370	18.2±0.2	8.52±0.11
	70	0.797		
	80	1.73		
	85	2.52		
	90	3.56		

a) Concentration: a is about 0.574 M and b is about 0.029 M. b) A is expressed by l/mol min.

Table 8. Amination of phenethyl chloride in DMSO

Amine	Temp. °C	$k\times10^2$ l/mol min	E_a kcal/mol	log A[c]
2-Aminobutanol[a]	90	0.882	16.9±0.1	8.13±0.07
	100	1.70		
	110	3.05		
	120	5.22		
	130	9.28		
Diethanolamine[b]	90	0.610	16.9±0.3	7.96±0.14
	100	1.17		
	111	2.29		
	120	3.50		
	130	6.30		

a) Concentration: a is about 0.400 M and b is about 0.040 M. b) Concentration: a is about 0.800 M and b is about 0.040 M. c) A is expressed by l/mol min.

TABLE 9. COMPARISON IN AMINATION RATES OF BENZYL CHLORIDE AND CUMINYL CHLORIDE[a)]

Amine	Solvent	Temp. °C	Chlodide	$k\times10^3$ l/mol min	k_{CC}/k_{BC}
Isobutyl	DMF	50	B C	9.97	
			C C	10.3	1.03
	Dioxane	90	B C	1.18	
			C C	1.23	1.04
s-Butyl	DMF	50	B C	3.79	
			C C	4.12	1.09
	Dioxane	90	B C	0.556	
			C C	0.583	1.05
2-Amino-butanol	DMF	50	B C	2.81	
			C C	3.03	1.08
Diethanol	DMF	40	B C	2.90	
			C C	3.17	1.09
Diethyl	DMF	30	B C	2.82	
			C C	3.22	1.14
Triethyl	DMF	50	B C	0.376	
			C C	0.490	1.30

a) In the table, BC represents for benzyl chloride and CC represents for cuminyl chloride.

TABLE 10. AMINATION OF PHENETYL CHLORIDE AND PVCA WITH ALKYLAMINES IN DMSO

Chloride	Amine	Temp. °C	k l/mol min
Phenethyl	Isobutyl	90	3.35×10^{-2}
	s-Butyl	90	1.09
	Diethyl	90	1.15
PVCA	Isobutyl	90	1.81×10^{-3}
		110	6.70
	s-Butyl	110	3.35
	Diethyl	110	2.29

resonance structure, associated with the phenyl substituent at the chloromethyl group. This conception has been examined by comparing the amination rate of benzyl chloride with that of phenethyl chloride, which has one methylene group between the phenyl group and the chloromethyl group. Table 8 lists the results of the amination of phenethyl chloride with 2-aminobutanol and diethanolamine. The amination rate of phenethyl chloride is considerably lower than that of benzyl chloride or CMPS; the former rate is almost comparable to those of the polymers without a phenyl group, as had been expected.

Amination of Cuminyl Chloride. In previous papers, benzyl chloride was chosen as a model of the structural unit of CMPS, and its amination rate was taken as a criterion. Another appropriate model of CMPS is cuminyl chloride, *p*-isopropyl chloromethyl benzene. The amination rates of cuminyl chloride with various amines have been measured; the rate constants are compared with those of benzyl chloride in Table 9. No significant difference is shown in the amination rate between the two chlorides in most cases. This result supports the propriety of benzyl chloride as a unit model of CMPS.

Amination of PVCA and Phenethyl Chlordie with Isobutylamine, s-Butylamine, and Diethylamine. As is shown in Tables 5, 6, and 8, the amination rates of PVCA, PVBA, and phenethyl chloride with 2-aminobutanol in DMSO are higher than the corresponding rates with diethanolamine. In the amination of CMPS and benzyl chloride in dimethyl formamide (DMF) and DMSO, however, the published data[4,5)] show that the amination rate with diethanolamine is higher than the rate with 2-aminobutanol. This difference in the reactivities of the two aminoalcohols is due to the difference in their enthalpy and entropy of activation, as will be discussed in the following section. It will serve as a reference to examine the reactivities of some alkylamines in the amination of PVCA and phenethyl chloride and compare it with that in the amination of CMPS and benzyl chloride. In view of the data shown in Table 10, the reactivities of the amines decrease in the following order:

isobutyl>*s*-butyl>diethyl (PVCA; DMSO)
isobutyl>*s*-butyl≈diethyl (phenethyl chloride; DMSO)

On the other hand, in the amination of CMPS and benzyl chloride, the following order is given by the present author's previously published data.[5,8,9)]

diethyl>isobutyl>*s*-butyl (CMPS; DMF)
diethyl≈isobutyl>*s*-butyl (benzyl chloride; DMF)
isobutyl>*s*-butyl (CMPS, benzyl chloride; dioxane)

The order anticipated from the basicity of the amines is this: diethyl>isobutyl≈*s*-butyl, while the order anticipated from the steric hindrance in the transition state is: isobutyl>*s*-butyl>diethyl. Actually, the results indicate that isobutyl>*s*-butyl in all the cases; however, the reactivity of diethylamine is higher for CMPS and benzyl chloride and lower for PVCA and phenethyl chloride. The steric effect can be expected to be more significant for PVCA and phenethyl chloride than for CMPS and benzyl chloride, since the transition states in the amination of the former two are less polar and tighter than those of the latter two. The resonance in the transition states of the latter two, due to the phenyl substituent attached to the chloromethyl group, is thought to make their structures more polar and looser.

Activation Parameters. The activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$) in the amination of PVCA, PVBA, PVCE, and phenethyl chloride are calculated and summarized in Table 11, in which the parameters of CMPS and benzyl chloride are also listed for comparison. The $\Delta G^{\neq}$ values of CMPS and benzyl chloride are much lower than those of the other polymers and phenethyl chloride. This difference in $\Delta G^{\neq}$ is due to the difference in $\Delta H^{\neq}$. In the amination of CMPS and benzyl chloride, the positive charge on the α-carbon of the chloromethyl group in the transition state can be delocalized because of the π-electrons of the phenyl group, and this resonance may lower the enthalpy of activation to a large extent.

The lower reactivity of PVCA than PVBA is contrary to expectation in view of the inductive effect of the halogen group. The lower $\Delta G^{\neq}$ of PVBA is due to the lower $\Delta H^{\neq}$. This difference in $\Delta H^{\neq}$ is considered

Table 11. Activation parameters of the aminations[a)]

Amine	Halide	Temp. °C	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ e. u.	$\Delta G^{\neq}$ kcal/mol
2-Aminobutanol	PVBA	100	16.1±0.1	−29.3±0.3	27.0
	PVCA	100	18.9±0.2	−29.4±0.4	29.8
	PC	100	16.2±0.1	−31.9±0.3	28.1
	BC	25	11.9	−34.4	22.2
	CMPS	25	11.6	−36.2	22.4
Diethanolamine	PVCE	100	17.5±0.2	−30.1±0.5	28.7
	PVBA	100	15.8±0.2	−31.3±0.6	27.5
	PVCA	100	18.2±0.1	−32.2±0.2	30.0
	PC	100	16.2±0.3	−32.7±0.7	28.4
	BC	25	11.2	−35.0	21.6
	CMPS	25	11.2	−35.4	21.7

a) In the table, BC and PC represent for benzyl chloride and phenethyl chloride respectively.

to reflect mainly the difference in bond energy between the α-carbon and the leaving halogen group. The effect of solvation on the leaving halogen group may be minor in such a dipolar aprotic solvent as DMSO, unlike protic solvents, though the solvation resulting from the mutual polalization may be stronger for bromide ions than chloride ions.

As is shown in Table 11, the $\Delta G^{\neq}$ of the amination with diethanolamine is lower than that with 2-aminobutanol for CMPS and benzyl chloride, and *vice versa* for PVBA, PVCA and phenethyl chloride. The $\Delta H^{\neq}$ of the amination with diethanolamine is lower than that with 2-aminobutanol not only for CMPS and benzyl chloride, but also for PVCA and PVBA. Further, the higher $\Delta G^{\neq}$ of the amination of PVCA and PVBA with diethanolamine can be ascribed to the lower $\Delta S^{\neq}$ of the amination with diethanolamine. In view of the basicity of the aminoalcohols, the amination rate with 2-aminobutanol can be expected to be higher than that with diethanolamine. The lower $\Delta H^{\neq}$ of the amination with diethanolamine may, then, be ascribed to a certain stabilizing factor in the transition state. A possible factor is the hydrogen bonding between the hydroxyl group of aminoalcohol and the leaving chlorine group, which is considered to be more significant in the amination with diethanolamine. The lower $\Delta S^{\neq}$ values in the amination of PVCA and PVBA with diethanolamine than the corresponding values with 2-aminobutanol can be explained in terms of such a steric fatcor as has been discussed in the preceding section. Since the transition state in the amination of the halide without a phenyl substituent at the α-carbon lacks the resonance effect, and since its structure is considered to be tighter than that with the phenyl group, the former may be more susceptible to the steric effect. Therefore, the reverse reactivity of 2-aminobutanol and diethanolamine in the amination of CMPS and polyvinyl haloacetals can be referred to the same steric effect which brings about the reverse reactivity of *s*-butylamine and diethylamine in the amination of CMPS and PVCA.

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