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Solvation–Desolvation Effect in Polyelectrolyte Catalysis: Cyanoethylation of Amino Acid in Aqueous Me_2SO Mixtures

KO YAMASHITA, HIROMI KITANO, and NORIO ISE*

Department of Polymer Chemistry, Kyoto University, Kyoto, Japan.

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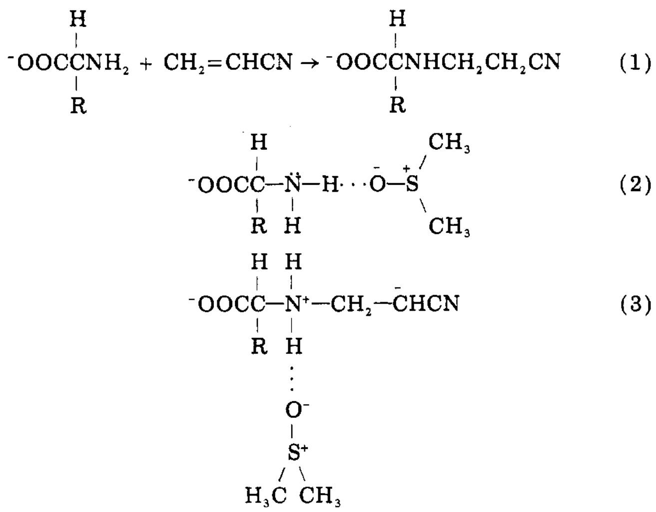
Catalytic influence of polyelectrolytes has been studied by various research groups and it has been found that reactions between similarly charged ionic species could be enormously accelerated by oppositely charged polyions and those between cationic and anionic species could be hindered by both cationic and anionic polyions.[1] With regards to the cause of this distinct polyelectrolyte effect, we pointed out that desolvation and solvation of the reactant and/or activated complex by the polyions might be important, in addition to the purely electrostatic interaction between the polyions and the reactants and/or activated complex.[2] The pressure effect studied was not inconsistent with the solvation–desolvation hypothesis.[3] In this paper, we wish to report the selective solvation effect, which affected clearly the catalysis by polyelectrolytes on cyanoethylation of an amino acid (eq 1 in Scheme I).

This reaction system (in the absence of polyelectrolyte) was studied by Friedman et al. in the 1960's.[4,5] They found that the reaction rates in the mixed solvent, especially in the Me_2SO–H_2O equal volume mixture, were much larger than in pure water, and this phenomenon was attributed to the increase in the nucleophilicity of the amino group of the amino acid by hydrogen-bond formation between Me_2SO oxygen and NH_2 hydrogen (eq 2). If the catalysis by polyelectrolytes is partly attributable to desolvation of the reactants by polyions, the rate-enhancing effect of Me_2SO would be weakened if the polyions can be strongly solvated by Me_2SO. Thus, in the present work, the experiment was designed to check this anticipation by using quaternized poly(vinylpyridine) derivative, a cationic polymer which may be solvated by Me_2SO preferentially.

Experimental Section

L-Phenylalanine (L-Phe), ninhydrin, and other reagents were obtained from Wako Pure Chemical Co. Acrylonitrile and Me_2SO were distilled before use. The details about the preparation of poly(4-vinyl-*N*-benzylpyridinium chloride) (BzPVP) and sodium poly(styrene sulfonate) (NaPSt) were described elsewhere.[6] The procedure of kinetic measurement followed was described by Friedman et al.[5] A Hitachi UV spectrophotometer (EPS-3T) was used in order to follow the ninhydrin reaction.

Scheme I



$$^{-}\mathrm{OO}\underset{R}{\overset{H}{\mathrm{C}}}\mathrm{CNH_2} + \mathrm{CH_2{=}CHCN} \rightarrow {}^{-}\mathrm{OO}\underset{R}{\overset{H}{\mathrm{C}}}\mathrm{CNHCH_2CH_2CN} \quad (1)$$

$$^{-}\mathrm{OOC}\underset{R}{\overset{H}{\mathrm{C}}}\!-\!\underset{H}{\overset{\cdot\cdot}{\mathrm{N}}}\!-\!\mathrm{H}\cdots\overset{-}{\mathrm{O}}\!-\!\overset{+}{\mathrm{S}}(\mathrm{CH_3})_2 \quad (2)$$

$$^{-}\mathrm{OOC}\underset{R}{\overset{H}{\mathrm{C}}}\!-\!\underset{H}{\overset{H}{\mathrm{N}^{+}}}\!-\!\mathrm{CH_2}\!-\!\overset{-}{\mathrm{C}}\mathrm{HCN}\cdots{}^{-}\mathrm{O}\!-\!\mathrm{S}^{+}(\mathrm{CH_3})_2 \quad (3)$$

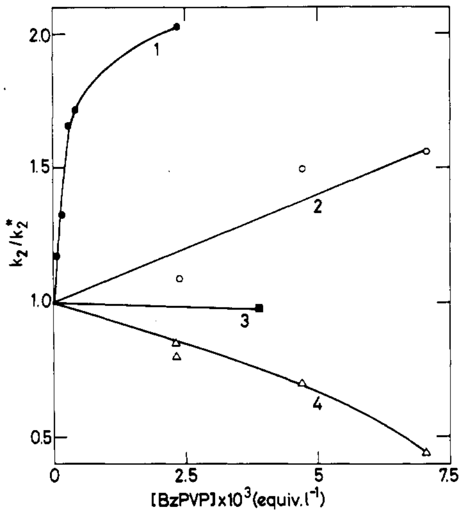


Figure 1. Polyelectrolyte influence on the cyanoethylation of L-phenylalanine at 30 °C ([acrylonitrile] = 0.2 M, [L-Phe] = 1 mM): (1) pH 10.06 buffer; (2) 50(v/v)% pH 10.06 buffer–Me_2SO; (3) pH 8.48 buffer; (4) 50 (v/v)% pH 8.48 buffer–Me_2SO.

Results and Discussion

The influence of the cationic polyelectrolyte, BzPVP, on this reaction system is shown in Figure 1, where k_2 and k_2^* are the second-order rate constants in the presence and absence of polyelectrolyte, respectively. k_2^* were 2.1×10^{-3}, 5.3×10^{-3}, 0.48×10^{-3}, and 5.0×10^{-3} M^{-1} s^{-1} for pH 10.06 buffer, 50(v/v)% pH 10.06 buffer–Me_2SO, pH 8.48 buffer, and 50(v/v)% pH 8.48 buffer–Me_2SO, respectively. These were in agreement with literature values[5] (k_2^* were 0.35×10^{-3} and 5.0×10^{-3} M^{-1} s^{-1} under slightly different conditions, namely, for pH 8.4 buffer and 50(v/v)% pH 8.4 buffer–Me_2SO, respectively). Clearly Me_2SO accelerates the reaction. By the addition of BzPVP, the reaction rate was increased by a factor of 2 at most in the pH 10.06 buffer solution (curve 1). This can be explained by the electrostatic interaction between anionic L-Phe ($pK_2 = 9.0$[4]) and cationic BzPVP and hydrophobic interaction between acrylonitrile and BzPVP.

In the 50(v/v)% pH 10.06 buffer–Me_2SO, however, the reaction rate was increased only slightly. This can be understood as follows: BzPVP accumulates the reactants in its domain similarly as in the pH 10.06 buffer. Me_2SO, which accelerated the reaction rate in the absence of polyelectrolyte, solvates the cationic polyions (as will be discussed below) in such a way that it does not so strongly

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Table I
Viscosity of BzPVP in Me_2SO-H_2O at 25 °C[a]

	Me_2SO, (v/v) %				
	0	12.5	25	37.5	50
η_{sp}/c,[b] dL g^{-1}	0.84	0.94	0.95	0.78	0.41
$[\eta]$, dL g^{-1}	0.64		0.90		0.37

[a] In pH 8.48 borate buffer. [b] [BzPVP] = 12.0 g L^{-1}.

increase the nucleophilicity of L-Phe. This is because Me_2SO solvates the polyions with its oxygen atom directed to the polyions. Thus, the unfavorable factor (weaker solvation of L-Phe by Me_2SO in the reaction site) suppresses the favorable one (accumulation of reactants).

In binary mixtures of Me_2SO and H_2O, selective solvation of cationic small ions was observed,[7] that is, Me_2SO was preferred and H_2O was rejected by the ions. Selective solvation of Me_2SO to the cationic polyelectrolyte was qualitatively confirmed by the viscosity measurement (Table I). Both η_{sp}/c and $[\eta]$ increased and then decreased by the addition of Me_2SO. The initial increase may be attributed to the expansion of the polymer chain by the solvation of Me_2SO and the following decrease would be due to the shrinkage of the polymer chain by the increase of electrostatic interaction between the polyions and gegenions, because the bulk dielectric constant of the solvent was decreased.

In the pH 8.48 buffer, the reaction rate was unaffected by the polyions because L-Phe exists as a zwitterion. In the 50(v/v)% pH 8.48 buffer-Me_2SO, however, the reaction was *retarded* by the addition of BzPVP ($k_2/k_2^* < 1$). This can be accounted for as follows. As was suggested by Friedman et al. from the observed pH shift, all compounds of pK_2 of 9 or less would be completely ionized (the amino group is deprotonated) in the 50% pH 8.48 buffer-Me_2SO. Therefore L-Phe ($pK_2 = 9.0$) and acrylonitrile must be accumulated in the polymer domain. Nevertheless, the unfavorable selective solvation (BzPVP was solvated by Me_2SO and L-Phe cannot be solvated as a consequence of the specific orientation of the Me_2SO molecule) might overwhelm the accumulation effect of the reactants. As the acceleration effect by Me_2SO was larger at pH 8.48 than at pH 10.06 (compare k_2^* values given above), desolvation of the Me_2SO from the reactants should give larger decrease in the acceleration effect by Me_2SO at pH 8.48 than at pH 10.06, causing $k_2/k_2^* < 1$. Though Friedman did not definitely confirm, Me_2SO seems to stabilize the transition state by the hydrogen bonding effect (eq 3). If so, the addition of polyelectrolyte might diminish this hydrogen bonding effect by the induction of the specific orientation of the Me_2SO molecule. Our results obtained here do not exclude this possibility.

In the case of NaPSt, on the other hand, no influence on rate was observed except small decreases in the 50(v/v)% pH 8.48 buffer-Me_2SO which may be due to the enhanced viscosity of the solution. We note that Me_2SO does not solvate PSt anions.

In conclusion, the selective solvation effect, though small but definite, was observed in catalysis by polyelectrolytes.

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A Relationship between Steady State Shear Compliance and Molecular Weight Distribution

PAWAN K. AGARWAL

Corporate Research Laboratories, Exxon Research and Engineering Company, Linden, New Jersey 07036.

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The preponderant effect of polydispersity on the viscoelastic behavior of polymers is now well recognized.[1,2] Various empirical correlations of the experimental data of steady state recoverable compliance J_e and molecular weight distribution characterizing parameters have appeared in the literature. None of these correlations is widely accepted, which should not be surprising in view of the disagreement between the experimental data and the theoretical expectations in monodisperse systems.[2,3]

Ferry[4] was perhaps the first who proposed a functional relationship between J_e and molecular weight distribution in a polydisperse system. Extending the Rouse theory he showed

$$J_e = {}^2\!/_5 M_{z+1} M_z / M_w \rho R T \qquad (1)$$

where ρ is the density of the polymer, R is the gas constant, T is the absolute temperature and M_w, M_z, and M_{z+1} are the usual molecular weight averages. The following was obtained by Ninomiya[5] on the basis of his experimental success with Rouse's blending law for viscosity,

$$J_{e_b} = w_1 J_{e_1} (M_1/M_w)^2 + w_2 J_{e_2} (M_2/M_w)^2 \qquad (2)$$

where J_{e_b} is the steady state compliance for the blend and w_1 and w_2 are the weight fraction of monodisperse polymers having molecular weights M_1 and M_2 and steady state compliance J_{e_1} and J_{e_2}, respectively. M_w is the weight average molecular weight of the blend.

Several other linear and higher order blending laws have been proposed on the basis of the Rouse model. One due to Ninomiya and Ferry[6] is:

$$H_b(\tau) = v_1 H_1(\tau/\lambda_1) + v_2 H_2(\tau/\lambda_2) \qquad (3)$$

where the H's are the relaxation spectra and the λ's are dimensionless shift factors, which represent the amount of shift of relaxation times of the monodisperse polymers in the blend. To deal with the problem more generally and to get rid of shift factors, Masuda[7] et al. proposed a quadratic mixing law

$$H_b(\tau) = w_1^2 H_{11} + 2 w_1 w_2 H_{12} + w_2^2 H_{22} \qquad (4)$$

where $H_{12}(\tau)$ is the cross-relaxation spectrum. On the basis of results on the blends of polystyrene for which J_e becomes proportional to the inverse of the square of high molecular weight fraction w_2, when $w_2 \rightarrow 1$, Bogue[8] et al. presented a quadratic blending law.

$$H_b(\tau) = v_1^2 H_{11}(\tau/\lambda_{11}) + 2 v_1 v_2 H_2(\tau/\lambda_{12}) + v_2^2 H_{22}(\tau/\lambda_{22}) \qquad (5)$$

Mills,[9] based on his experimental results on poly(dimethylsiloxane), polystyrene, and polyethylene, proposed the following empirical relationship.

$$J_e \propto (M_z/M_w)^{3.7} \qquad (6)$$

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