Ternary Copolymers of Hemin, Styrene, and 1-Vinylimidazole or 1-Vinyl-2-methylimidazole as Cyanide Ion Exchanger

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Synopsis

Ternary copolymers, involving hemin (H) (ferri-protoporphyrin IX chloride), styrene, and 1-vinylimidazole (VI) or 1-vinyl-2-methylimidazole (VMI) in the different proportions, were synthesized by radical copolymerization. All the copolymers obtained were insoluble in aqueous solvents. No dissolution of H from the copolymers was observed even when the extraction with 0.5N NaOH or HCl was allowed to continue for a total time of 50 days. To clarify the functional capabilities of the ternary copolymers as a cyanide ion exchanger, the adsorption of cyanide ion onto the copolymers was investigated at different pHs. The amount (A_{cn}) of the adsorbed cyanide ion was found to be dependent on the content of H residue in the copolymer, thus indicating that the adsorption site for the cyanide ion consists of ferri-protoporphyrin IX (FP). Another important feature is that A_{cn} increases in proportion to the VI or VMI content of the copolymer. This result was discussed in terms of the coordination structure of the FP and also of the coordination reaction of cyanide ion to the FP.

INTRODUCTION

The present authors have reported the syntheses of water-insoluble copolymers containing hemin (H) (ferri-protoporphyrin IX chloride) by radical polymerization with several vinyl monomers, together with their functional properties as a cyanide ion exchanger.[1,2] Additionally, we also reported that the affinity of ferri-protoporphyrin IX (FP) for cyanide ion is enhanced by occupying one coordination site of FP by polymer ligands, especially by a polymer containing 1-vinylimidazole (VI) or 1-vinyl-2-methylimidazole (VMI).[3] These facts prompted us to prepare a cyanide ion exchanger by the copolymerization of H with a vinyl monomer such as VI or VMI.

In this study, VI and VMI were copolymerized with a mixture of H and styrene (St) to obtain the corresponding ternary copolymers, i.e., copoly(H, St, VI) and copoly(H, St, VMI).
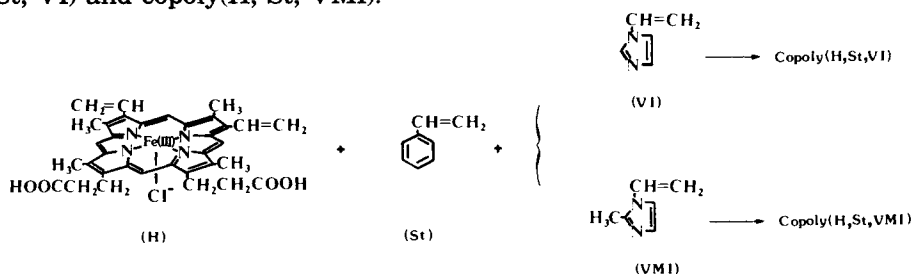
To clarify their functional properties as cyanide ion exchanger, the adsorption and desorption behavior of cyanide ion were investigated at different pHs. It was found that both copolymers have a large adsorptive capacity for cyanide ion, compared with previously prepared H-containing polymers[1,2] into which imidazole groups were not introduced. The present paper describes in detail the preparations and properties of both copoly(H, St, VI) and copoly(H, St, VMI) as cyanide ion exchanger.

EXPERIMENTAL

Preparation Methods

All the monomers were the same samples as used previously.[1-3] The copolymerization was carried out in a sealed tube at 85°C for 48 h under reduced pressure using 6.14 mL of purified dimethylformamide (DMF) as the solvent and 1.83 mmol of α,α'-azobisisobutyronitrile (AIBN) as the initiator. A large scale copolymerization was also carried out in a nitrogen atmosphere with stirring under the same conditions described above, except the size was enlarged three times. The reaction mixture was poured slowly into a 3:1 mixture of methanol and distilled water to precipitate the copolymer, which was then separated by filtration, washed with methanol, and dried under vacuum. The crude copolymer was reprecipitated three times from chloroform with methanol, dried under vacuum, alternately washed with a large amount of $0.5N$ NaOH and HCl, rewashed with distilled water, and then dried at 50°C for 3 days under vacuum.

Characterization Methods

The copolymers were identified by spectroscopic analyses. The instruments used were: a Hitachi IR 260-50 spectrophotometer for infrared (IR) spectrum and a Hitachi 220-20 spectrophotometer for visible and ultraviolet spectra. The reduced viscosity (η_{sp}/C) for the copolymers was measured at $C = 0.5$ g/dL in DMF at 25 ± 0.005°C with an Ubbelohde viscometer having a flow time of 184.7 s for DMF at 25°C. The copolymer composition was determined by a combination of elemental and iron analyses.[2]

Adsorption Experiment

The adsorption of cyanide ion onto the copolymer was, unless otherwise noted, carried out in various buffer solutions (ionic strength 0.15) containing equimolecular quantities (2×10^{-5} mol/L) of potassium cyanide and the polymer-bound H. The buffer solutions used were: NaCl–HCl, pH 0.9–3.2; CH_3COONa–CH_3COOH, pH 3.2–5.5; $Na_2B_4O_7$–KH_2PO_4, pH 5.5–9.2; $Na_2B_4O_7$–Na_2CO_3, pH 9.2–11.0; NH_4OH–NH_4Cl, pH 8–11.0; Na_2HPO_4–NaOH, pH 11.0–12.0; NaOH–NaCl, pH 12.0–14.0. The sample was prepared by dispersing the copolymer into buffer solution (50 mL). The dispersion was always sealed in a vial to avoid volatilization of hydrocyanic acid, stirred at 25 ± 0.1°C for 12 h, and then allowed to stand for 12 h to precipitate the copolymer. The cyanide concentration of the supernatant was measured by the pyridine–pyrazolone method.[4]

Column Experiment

The separation of the cyanide ions from the KCN-containing buffer solution (pH = 9, ionic strength = 0.15, and KCN concn = 13.9 mg/L) of $Na_2B_4O_7$–KH_2PO_4 was carried out using a glass column (50 cm × 6 mm diameter) packed with the copolymer (2 g). The KCN solution was effused through the column at a constant flow rate of 0.2 mL/min, and the effluent fraction (10 mL) was received in a measuring flask (20 mL) into which $0.1N$ NaOH (10 mL) was admitted before receiving the effluent. The cyanide ion bound to the copolymer was eluted with $0.5N$ NaOH. To avoid volatilization of hydrocyanic acid, all the experiments were made in a closed system.

RESULTS AND DISCUSSION

Preparation and Characterization of the Copolymers

All the copolymers obtained were insoluble in aqueous solvents. No dissolution of H from the copolymers was observed even when the extraction with $0.5N$ NaOH or HCl was allowed to continue for a total time of 50 days at 25 ± 2°C. The IR spectra (KBr disk) showed the characteristic absorption bands due to the C = N stretch (1620 cm^{-1}) and to the C = C stretch (1600, 1495, and 1455 cm^{-1}). The visible spectra measured in purified chloroform were in accord with those of heme compounds.[5] In addition, the Soret band was shifted to about 5 nm lower wavelength before and after the copolymerization. According to Fuhrhop et al.,[5] this is accepted as evidence supporting that one of the two vinyl groups in FP takes part in the polymerization.

The results for the preparation and characterization of copoly(H, St, VMI) and copoly(H, St, VI) are summarized in Table I, together with those for copoly(H, St) (i.e., copolymer of H and St) already reported.[1] The content of H residue in the polymer was determined by iron analysis, and those of VMI and VI residues were also determined on the basis of the nitrogen content obtained by subtracting the nitrogen due to the H residue from the total nitrogen.

From Table I, it is found that the H content for all the copolymers generally agrees with the molar ratio of H monomer. Furthermore, the contents of VMI and VI residues in the ternary copolymers are found to be independent of the concentration of H monomer. Nishide et al.[6] has reported that, with the aid of AIBN, the dimethyl ester (HDME) of H reacts with St monomer to yield the copolymer but not with VMI monomer. When a HDME and St mixture containing VMI or VI as third component was subjected to the radical copolymerization,[5] however, the corresponding ternary copolymers were obtained in reasonable yield. The present authors[2] also reported that the ternary copolymer consisting of H, St, and 1-vinyl-2-pyrrolidone (VP) can be prepared by radical copolymerization with AIBN, although VP monomer does not copolymerize with H or HDME. Taking into account these facts, the present results could be explicable as follows: H monomer preferentially reacts with St monomer rather than VMI or VI monomer to link the neighboring position of the St residue in the polymer chain.

TABLE I
Preparation and Characterization of Copoly(H, St, VMI), Copoly(H, St, VI), and Copoly(H, St)[a]

Sample code	Feed[b] (mmol)				Yield (%)	Composition of copolymer (mol %)			$\eta_{ap}/C \times 10^2$ (dL/g)
	H	St	VMI	VI		H	VMI	VI	
HMiS1	0.35 (0.58)	30.0 (49.7)	30.0 (49.7)		43.1	0.47	21.2		10.9
HMiS2	0.70 (1.15)	30.0 (49.4)	30.0 (49.4)		31.5	1.04	20.5		7.41
HMiS3	1.05 (1.72)	30.0 (49.1)	30.0 (49.1)		25.3	1.50	21.6		6.26
HMiS4	1.40 (2.28)	30.0 (48.9)	30.0 (48.9)		18.1	2.21	21.5		5.07
MiSH1	0.70 (1.15)	55.5 (90.6)	5.0 (8.24)		34.5	1.12	8.0		10.6
MiSH2	0.70 (1.15)	50.0 (82.3)	10.0 (16.5)		32.5	1.08	11.4		9.26
MiSH3	0.70 (1.15)	40.0 (65.9)	20.0 (32.9)		33.1	1.25	15.1		8.92
MiSH4	0.70 (1.15)	35.5 (58.5)	25.0 (41.2)		29.9	1.13	18.6		7.65
HIS1	0.35 (0.58)	30.0 (49.7)		30.0 (49.7)	40.3	0.46		22.1	9.98
HIS2	0.70 (1.15)	30.0 (49.4)		30.0 (49.4)	33.1	1.00		21.7	7.61
HIS3	1.05 (1.72)	30.0 (49.1)		30.0 (49.1)	22.7	1.43		21.9	6.81
HIS4	1.40 (2.28)	30.0 (48.9)		30.0 (48.9)	16.2	2.14		20.8	5.45
ISH1	0.70 (1.15)	55.0 (90.6)		5.0 (8.24)	35.1	1.08		6.0	10.8
ISH2	0.70 (1.15)	50.0 (82.3)		10.0 (16.5)	34.0	0.99		11.1	9.45
ISH3	0.70 (1.15)	40.0 (65.9)		20.0 (32.9)	29.1	1.03		15.0	8.75
ISH4	0.70 (1.15)	35.0 (58.5)		25.0 (41.2)	30.1	1.09		18.4	8.03
HS1	0.23 (0.39)	58.7 (99.6)			75.6	0.53			9.96
HS2	0.55 (0.93)	58.4 (99.1)			68.5	0.93			9.67
HS3	1.13 (1.91)	57.9 (98.1)			60.7	1.94			8.66
HS4	1.47 (2.49)	57.5 (97.5)			52.4	2.55			7.82
HS5	1.96 (3.32)	57.0 (96.7)			41.7	3.31			7.65
HS6	2.82 (4.78)	56.2 (95.2)			37.3	4.49			6.87
HMiS3L15[c]	15.75 (1.72)	450 (49.1)	450 (49.1)		28.9	1.42	22.3		7.41
HIS3L15[c]	15.75 (1.72)	450 (49.1)		450 (49.1)	26.7	1.39		21.5	7.52
HS4L10[a,c]	14.30 (2.49)	560 (97.5)			56.3	2.52			7.86

[a] Copoly(H, St) was obtained previously under the same conditions as used for the ternary copolymers, except for use of pyridine as the solvent, and the data in this table were cited from Ref. 1.

[b] The values in parentheses are mol % of each monomer.

[c] Obtained by a large scale copolymerization which was carried out in 92 mL DMF containing 27.5 mmol of AIBN for the ternary copolymers and in 62 mL of pyridine containing 18.3 mmol of AIBN for copoly(H, St).

Another characteristic of Table I is that there is no distinguishable difference in the contents of the imidazolated monomer residues between copoly(H, St, VMI) and copoly(H, St, VI). Thus, it could be indicated that the molar ratio of the imidazole to the iron(III) in the copolymer, regarded as an important factor controlling the coordination structure of FP in the adsorption site, is unchanged by the species of VMI and VI monomers. This could be understood by assuming that VMI and VI monomers are not different from each other with respect to polymerizability with St monomer in the presence of H monomer.

In addition to the results reported above, a further important feature of Table I is that the yield and viscosity decrease proportionally with the feed concentration of H monomer, whereas the effects of the VMI and VI monomers are not as marked as that of the H monomer. It has been found that the homopolymers of H and other metalloporphyrins are not obtained by radical polymerization.[7] Furthermore, several vinyl monomers, e.g., St monomer, show a low tendency to polymerize in the presence of H or HDME,[1,6] and the polymers obtained contain the H residue in the end of the polymer chain.[6] These results have been interpreted by considering degradative chain transfer of propagating chain radicals to the H monomer.[1,2] Such consideration could be also reasonable to understand the results obtained here. Thus, it is difficult to synthesize the copoly(H, St, VMI) and copoly(H, St, VI) having high molecular weight by radical copolymerization [this problem will be dealt with elsewhere, although high molecular weight copoly(H, St, VMI) has been obtained by crosslinking with divinylbenzene].[8] However, the ternary copolymers prepared here are considered to be adequate for use as a cyanide ion exchanger, since they were insoluble in aqueous solvents and also did not lose H residues by extracting with acid and base (see above).

Cyanide Ion Exchange Properties of the Copolymers

To clarify the functional capability of copoly(H, St, VMI) and copoly(H, St, VI) as cyanide ion exchanger, the adsorption and desorption behavior of cyanide ion were investigated. The adsorptive amount (A_{cn}) was expressed as the weight (mg) of the adsorbed cyanide ions per 1 g dry copolymer.

The changes in A_{cn} with the content of H residue for copoly(H, St, VMI) and copoly(H, St, VI) are shown in Figure 1, together with that for copoly(H, St).[1] It is observed that the increase in the H content of each copolymer tends to increase the A_{cn} value, therefore indicating that the adsorption site for the cyanide ion consists of the FP bonded to the polymer. Another remarkable feature of Figure 1 is that the values of A_{cn} for copoly(H, St, VMI) and copoly(H, St, VI) are much larger than that for copoly(H, St), although there is no distinguishable difference between both ternary copolymers. Thus, the VMI and VI residues in the copolymers appear to contribute to raising the adsorptive capacity for the cyanide ion. More definitive evidence for such contribution of the imidazolated monomers is obtained when the contents of VMI and VI residues were varied under conditions where the H content was kept constant (see Fig. 2).
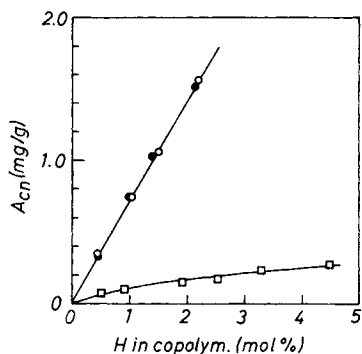
Fig. 1. Change in A_{cn} with the H content of the copolymers: (○) copoly(H, St, VMI) (sample code, HMiS1-4); (●) copoly(H, St, VI) (sample code, HIS1-4); (□) copoly(H, St) (sample code, HS1-6). Adsorption conditions: adsorbent concn (C_a), 106–458 mg/L for copoly(H, St, VMI), 106–456 mg/L for copoly(H, St, VI), and 200–240 mg/L for copoly(H, St); initial concn (C_i) of KCN, 1.30 mg/L for the ternary copolymers and 14.5 mg/L for copoly(H, St); pH, 9 for the ternary copolymers and 8 for copoly(H, St), which correspond to the pH value of a maximum adsorption for each polymer; ionic strength, 0.15 for each.

Our previous study[2] demonstrated that the ability of copoly(H, St) to adsorb cyanide ion is enhanced by introducing acrylamide (AAm) residue. However, compared with the AAm-introduced copolymer, i.e., copoly(H, St, AAm), both ternary copolymers obtained here exhibit a fairly large adsorption capacity. For example, the values of A_{cn} at pH 9 for each polymer containing about 2 mol % H are as follows: 1.5 mg/g for both copoly(H, St, VMI) and copoly(H, St, VI); 0.45 mg/g for copoly(H, St, AAm); and 0.15 mg/g for copoly(H, St). This also reveals that the imidazole-introduced copolymer is excellent in the ability to adsorb cyanide ion.

Figure 3 shows the dependence of A_{cn} on pH for copoly(H, St, VMI), copoly(H, St, VI), and copoly(H, St).[1] The samples used here were prepared by a large scale polymerization (see Table I). Unless otherwise noted, these
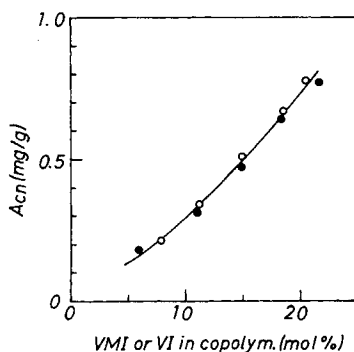

Fig. 2. Effect of the content of the imidazolated monomer residues on A_{cn}: (○) copoly(H, St, VMI) (sample code, MiSH1-4 plus HMiS2); (●) copoly(H, St, VI) (sample code, ISH1-4 plus HIS2). Adsorption conditions: C_a, 183–204 mg/L for copoly(H, St, VMI) and 198–219 mg/L for copoly(H, St, VI); C_i, 1.30 mg/L; pH, 9; ionic strength, 0.15.
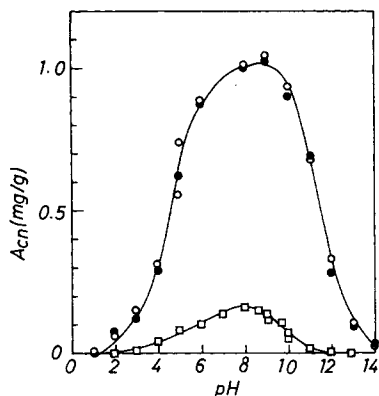
Fig. 3. Dependence of A_{cn} on pH: (○) copoly(H, St, VMI) (sample code, HMiS3L15); (●) copoly(H, St, VI) (sample code, HIS3L15); (□) copoly(H, St) (sample code, HS4L10). Adsorption conditions: C_a, 159 mg/L for copoly(H, St, VMI), 157 mg/L for copoly(H, St, VI), and 240 mg/L for copoly(H, St); C_i, 1.30 mg/L for the ternary copolymers and 14.5 mg/L for copoly(H, St); ionic strength, 0.15.

were subjected to all the experiments described below. It is observed that the absorption of cyanide ion shows a maximum value at pH 9, while cyanide ion is little adsorbed at pH ranges below 1 and above 14 where the binding of water molecules and hydroxyl ions becomes the dominant factor.[9] Therefore, the adsorption and desorption of cyanide ion are found to be controllable by the adjustment of pH, which indicates the functional capability of the ternary copolymers as exchanger of cyanide ion.

The ion exchange abilities of copoly(H, St, VMI) and copoly(H, St, VI) were further confirmed by column experiment (Fig. 4). When the $Na_2B_4O_7-$
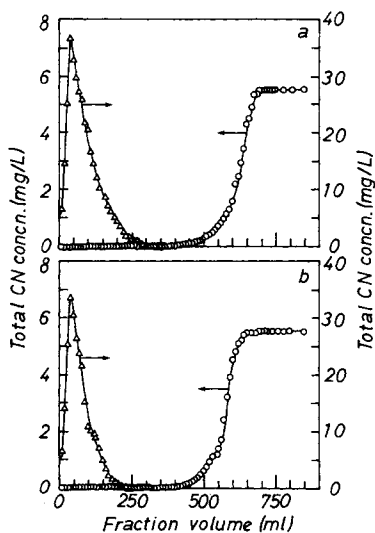

Fig. 4. Column separations of cyanide ion with copoly(H, St, VMI) (a) and copoly(H, St, VI) (b) which have the same sample codes as described in Figure 3: (○) and (△) represent the adsorption and desorption of cyanide ion, respectively. The experimental conditions were mentioned in the text.

KH$_2$PO$_4$ buffer solution (pH 9 and ionic strength 0.15) containing 13.9 mg/ L potassium cyanide (corresponding to 5.46 mg/L total CN) is effused through a column of the copolymer (2 g), the cyanide concentration in the fraction is found to be kept below 0.2 mg/L until the total fraction volume goes up to over 400–500 mL. The adsorbed cyanide ion is 1.72 mg/g for copoly(H, St, VMI) and 1.57 mg/g for copoly(H, St, VI), as estimated from Figure 4. These amounts are 3–10 times those of the previously prepared exchangers,[1,2] and also correspond to 48–52% of the maximum adsorption capacity (A_{cn}^{max}), which can be determined from the total H content of the ternary copolymer. The elution pattern of the adsorbed cyanide ions with 0.5N NaOH is also shown in Figure 4. Most of the adsorbed ions are eluted with the NaOH solution (recovery above 95%). The adsorption and desorption were reproduced reversibly over different runs of the column experiments.

On the basis of the results reported here, it may be concluded that copoly(H, St, VMI) and copoly(H, St, VI) have a function as a cyanide ion exchanger. Moreover, in their abilities to adsorb and desorb cyanide ion, the VI or VMI residue in the copolymer plays an important role.

Coordination Properties of Cyanide Ion to the Copolymers

The adsorption of cyanide ion onto H-containing polymers is based on the coordination reaction of cyanide ligand to the adsorption site consisting of FP.[1,2] Previously we demonstrated that the affinity of FP for cyanide ion is strengthened by occupying one coordination site of FP by polymer ligands, especially the copolymers of VP with VMI, copoly(VP, VMI), and with VI, copoly(VP, VI).[3] Thus, it seems desirable to discuss a large adsorptive capacity for cyanide ion of copoly(H, St, VMI) and copoly(H, St, VI) in terms of the coordination structure of FP and also of the coordination behavior of cyanide ion to FP.

The moles (n_{cn}) of cyanide ions coordinated to 1 mol FP in the copolymer and the equilibrium constant (K_{cn}) for the coordination reaction can be estimated by the following equation.

$$\log\left(\frac{Y}{1 - Y}\right) = n_{cn} \log[CN^-]_{eq} + \log K_{cn} \tag{1}$$

where $Y\,(=A_{cn}/A_{cn}^{max})$ represents the degree of the saturation of the Fe(III) in FP with cyanide ion, and $[CN^-]_{eq}$ is the equilibrium concentration (mol/ L) of cyanide ion which was replaced by that ($[KCN]_{eq}$) of potassium cyanide in the actual calculation. Although the initial molar concentration ($[KCN]_0$) of KCN was used in Ref. 3 to analyze experimental data, the equilibrium concentration was adopted in this study because of a large ability of the copolymers to absorb cyanide ion. The logarithmic plots of $Y/(1 - Y)$ vs. $[KCN]_{eq}$ at pH 9 and 12 for the ternary copolymers are shown in Figure 5, together with that for copoly(H, St). It is observed that all the plots are straight lines with the correlation coefficient 0.994–0.998. The values of n_{cn} and K_{cn}, determined by means of the slope and intercept of the straight lines, are summarized in Table II. The n_{cn} values for copoly(H, St, VMI)
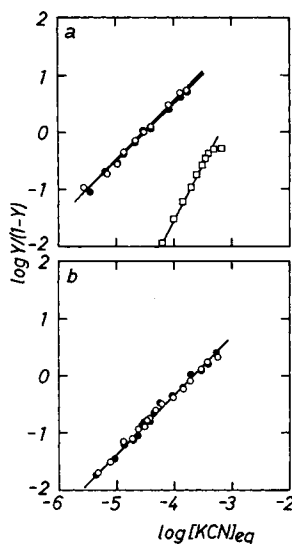
Fig. 5. Logarithmic plots of $Y/(1 - Y)$ vs. $[KCN]_{eq}$ at pHs 9 (a) and 12 (b): (○) copoly(H, St, VMI); (●) copoly(H, St, VI); (□) copoly(H, St). The sample codes correspond to those in Figure 3. Adsorption conditions: initial H concn ($[H]_0$), 2×10^{-5} mol/L (equal to each C_a in Fig. 3); $[KCN]_0$, 5×10^{-6} to 6×10^{-4} (equal to C_i of 0.326 to 39.1 mg/L), ionic strength, 0.15.

and copoly(H, St, VI) are found to be close to 1, while that for copoly(H, St) is about 2. Therefore, it can be seen that only one cyanide ion binds to the FP of each ternary copolymer because of occupying the fifth coordination site of Fe(III) by polymer-bound ligand unit, perhaps the imidazolyl group in the VMI or VI residue. This is supported by the fact that two cyanide ions coordinate to the FP of copoly(H, St) which contain no ligand residues.

From the electron spin resonance study for H covalently and noncovalently combined with the copolymer of St and VI,[5] Fuhrhop et al. have

TABLE II
Values of n_{cn} and K_{cn} for H-containing Copolymers and Hemichromes

Sample	pH	n_{cn}	$K_{cn} \times 10^{-3}$ [c]	Solvent[d]
Copoly(H, St, VMI)[a]	9.0	1.01	43.7	I
	12.0	1.02	5.89	II
Copoly(H, St, VI)[a]	9.0	1.00	41.7	I
	12.0	1.04	6.31	II
Copoly(H, St)[a]	9.0	1.94	1778	I
Hemichromes composed of[b]				
Copoly(VP, VMI)	9.0	1.02	3.55	III
	12.0	1.06	1.19	IV
Copoly(VP, VI)	9.0	0.98	2.82	III
Free H[b]	9.0	1.91	224	V

[a] Determined from Figure 5.
[b] Cited from Ref. 3 to compare with the results of the copolymers.
[c] Expressed in L^2/mol^2 for copoly(H, St) and free H and in L/mol for the others.
[d] Abbreviations used: I, $NaHCO_3$–Na_2CO_3 buffer; II, Na_2HPO_4–NaOH buffer; III, a 1:1 mixture of ethylene glycol (EG) and $NaHCO_3$–Na_2CO_3 buffer; IV, a 1:1 mixtue of EG and Na_2HPO_4–NaOH buffer; V, NaCl–NaOH buffer containing 2 wt % polyvinylpyrrolidone.

reported that the six-coordinated low spin type of FP is formed when the content of VI is 10 mol % or more, while the copolymers containing less than 1 mol % of VI yields the high spin FP of coordination no. 5. They also reported that H is incorporated with the copolymer of St with VMI or 1-vinyl-2-phenylimidazole to form only the high spin type. These are analogous to our previous result[3] which illustrated that the five- and six-coordinate hemichromes are formed by complexing H with copoly(VP, VMI) and copoly(VP, VI), respectively. Thus, it is reasonable to consider that the adsorption site of copoly(H, St, VMI) consists of the five-coordinate type of FP, while the six-coordinate FP is the adsorption site of copoly(H, St, VI) (this could be true at least for the copolymer of code number HIS3L15 because of the VI content = 21.5 mol %). However, the n_{cn} value for copoly(H, St, VI) is close to 1. As was pointed out previously,[3] this conflict can be resolved by considering that one of the two ligands coordinated to FP is exchanged with cyanide ion.

The investigation of the dependence of Y on the ratio of $[KCN]_0$ to $[H]_0$ (initial H concn in mol/L) is a useful approach to elucidate a difference in the affinities for cyanide ion between copoly(H, St) and copoly(H, St, VMI) or copoly(H, St, VI) (as noted in Ref. 3, it is impossible to investigate this difference by comparing the K_{cn} values in Table II because of the disagreement in the dimensions of K_{cn} between the samples with $n_{cn} \cong 1$ and 2). The curves of Y vs. $[KCN]_0/[H]_0$ for three copolymers are given in Figure 6, together with those[3] of free H plus the hemichromes consisting of copoly(VP, VMI) and copoly(VP, VI). The initial slopes of the curves for the hemichromes are found to be much larger than that for H. As was mentioned previously,[3] this is an indication of increasing the affinity of FP for cyanide ion caused by occupying the fifth coordination site of the Fe(III) by polymer ligand. By comparing the curves for the ternary copolymers with that for copoly(H, St), a remarkable difference is also observed in the initial slopes. It is therefore indicated that, compared with copoly(H, St), both copoly(H, St, VMI) and copoly(H, St, VI) have a much strong affinity for cyanide ion
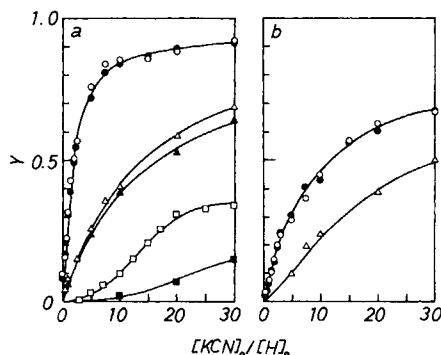

Fig. 6. Curves of Y vs. $[KCN]_0/[H]_0$ at pHs 9 (a) and 12 (b): (○) copoly(H, St, VMI); (●) copoly(H, St, VI); (□) copoly(H, St); (△) copoly(VP, VMI)-containing hemichrome; (▲) copoly(VP, VI)-containing hemichrome; (■) free H. The results for the copolymers were obtained under the same conditions as described in Figure 5, while those for the others were cited from Ref. 3.

owing to the structural contribution of the adsorption site which consists of either five- or six-coordinate FP.

From the curves in Figure 6, it is further observed that the initial slopes for the ternary copolymers is larger than those for the hemichromes, indicating that the former are superior to the latter with regard to the affinity for cyanide ion. An analogous results can be obtained by comparing the K_{cn} values (Table II). This difference could be due to whether the coordination reaction of cyanide ion to FP takes place in the liquid phase or on the solid surface, since it could be convenient to assume that hydrophobic domain constructed around the adsorption site in the copolymers serves to eliminate a coordinating and solvating medium like the water surrounding the FP, and accordingly to increase the affinity of the FP for cyanide ion. This can be supported by the fact that the K_{cn} and Y values of copoly(H, St) are much larger than those of free H sample.

From the results mentioned above, a large adsorptive capacity of the ternary copolymers is explicable in terms of the coordination reaction of cyanide ligand to the five- or six-coordinate FP situated in hydrophobic domain on the copolymer surface, although for the six-coordinate type it must be kept in mind that the ligand exchange with the cyanide ion takes place during the course of the reaction.

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