

Divinylbenzene-crosslinked Terpolymer Consisting of Hemin, Styrene, and 2-Methyl-5-vinylpyridine as Cyanide Ion Exchanger. Preparation of the Polymer in the Form of Beads by Suspension Polymerization

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Synopsis

Bead-shaped, divinylbenzene-cross-linked terpolymers, consisting of hemin (ferri-protoporphyrin IX chloride), styrene, and 2-methyl-5-vinylpyridine, were prepared by suspension polymerization in which all or part of styrene monomer was replaced with divinylbenzene. Analogous terpolymers of the cross-linked and uncross-linked formless types were also prepared by solution polymerization. All the terpolymers obtained were characterized by electron spin resonance spectroscopy, scanning electron microscopy, and measurement of specific surface area. The characteristic of the adsorption of cyanide ion onto the terpolymer beads was investigated and compared with those adsorbed onto their analogs. The column separation of cyanide ion with the terpolymer beads was carried out to examine the ion-adsorbing capacity. It was found that the suspension polymerization is just appropriate to prepare a cyanide ion exchanger in the form of beads.

INTRODUCTION

We have studied the synthesis of a cyanide ion exchanger by radical terpolymerization among hemin (H) (ferri-protoporphyrin IX chloride), styrene (St), and 1-vinylimidazole (VI) or 1-vinyl-2-methylimidazole (VMI).¹ It has been shown that the ability of the exchanger to adsorb cyanide ion is enhanced by introducing VI or VMI, mainly because their imidazolyl group binds to H in the polymer to form the five-coordinated high-spin type of ferri-protoporphyrin IX, which has a strong affinity toward cyanide ligand. However, it was difficult to synthesize a high-molecular weight polymer, which causes a lowering of yield of the product. With a view to raising yield, we have also carried out the terpolymerization by replacing a part of St monomer with divinylbenzene (DVB).² It was found that crosslinking with DVB affords an excellent yield of the polymers without causing a large undesirable influence on their abilities to adsorb cyanide ion. This gives an indication as to the preparation of a cyanide ion exchanger in the form of beads by applying the technique of suspension polymerization.

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In this work we describe the synthesis of bead-shaped, DVB-cross-linked terpolymers by the suspension polymerization, together with their functional capabilities as a cyanide ion exchanger. Water-insoluble 2-methyl-5-vinylpyridine (MVP) was employed in place of VI or VMI.

The term *ternary copolymer* or *terpolymer* was previously used to describe polymers composed of H, St, and VI or VMI.^{1,2} When the polymers are crosslinked with DVB, they contain it as the fourth component. However, in the networked chain, the monomer units consisting of St and of DVB cannot be experimentally differentiated, and in this study there is no necessity to do so. In this article, thus, the description *crosslinked* or *uncrosslinked* is used to distinguish whether the polymers contain DVB or not.

EXPERIMENTAL

Suspension Polymerization

All the monomers, other than MVP, were the same samples as used previously.^{1,2} MVP, commercially obtained from Aldrich Chemical Co. Inc., was twice distilled under reduced pressure (55°C/5 mmHg) immediately before use. The suspension polymerization was carried out with a standard suspension polymerization apparatus; namely, a four-necked and round-bottomed separable flask (300 mL) equipped with a mechanical stirrer, a thermometer, an argon gas inlet tube, and a reflux condenser with a gas outlet tube at the top. The monomer feed was prepared by mixing each monomer (H, St, DVB, and MVP) in different molar ratios. Quinoline, *n*-octane, and α, α' -azobisisobutyronitrile (AIBN) were used as the solvent, precipitant, and initiator, respectively. A solution composed of the monomer feed (about 13 g), diluent (6.9 g quinoline plus 11.4 g *n*-octane), and initiator (0.3 g) was added to 125 mL distilled water containing 130 mg sodium dodecylbenzenesulfonate. The mixture was agitated until the organic component was dispersed as fine droplets, and then heated at 90°C for 4 h. The resulting polymer beads were collected by filtration, and purified via the following procedures; (i) repeated washing with purified dimethylformamide (DMF) and dichloromethane until the washing had no UV absorption bands at 238–300 nm, (ii) extracting with acetone in a Soxhlet apparatus for one week, (iii) vacuum drying at 40°C for 3 days, (iv) washing with 0.1 N HCl and then with a large amount of distilled water, and (v) vacuum drying to constant weight at 50°C. Preliminary experiments revealed that the present purification method is sufficient to remove residual monomers from crosslinked terpolymer and also to form the MVP-coordinated and chloride-bound Fe(III)-protoporphyrin IX as the adsorption site.

Solution Polymerization

DMF (6.9 g) containing 0.1 g AIBN was mixed with the same monomer feed (about 13 g) as subjected to the suspension polymerization (this system essentially corresponds to that of bulk polymerization because of using a slight amount of the solvent). The mixture was loaded into a test tube, which was then sealed under reduced pressure and heated at 86°C for 36 h. The solidified or gelificated reaction mixture was pulverized well and purified in the same manner as described in the previous section.

The solution polymerization was also carried out to prepare uncross-linked terpolymer (formless type) consisting of H, St, and MVP. The methods for the preparation and purification were the same as those already reported.¹

Characterization Methods

The polymer composition was determined by a combination of elemental and iron analysis.¹ Electron spin resonance (ESR) spectroscopy with a JEOL JES-FELX spectrometer was carried out to examine the coordination structure of the adsorption site. The morphological observation was made by using a Hitachi S-450 scanning electron microscope (SEM). The surface area was measured by the BET nitrogen adsorption method.

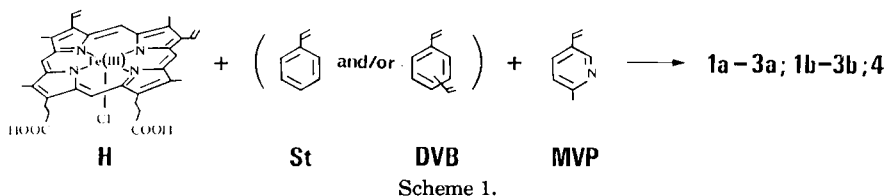
Cyanide Ion-Exchange Properties

The functional capability of the prepared polymers was evaluated by both adsorption and column experiments. The adsorption experiment was carried out at 25°C for 12 h by stirring 0.155–0.189 g resin in 50 mL Na₂B₄O₇-KH₂PO₄ buffer solution (pH 9; ionic strength 0.1) containing different amounts of KCN. The column experiment was made by passing the same buffer solution containing 20 mg/L cyanide ion through a column (1 m × 10 mm diameter) packed with 11.3 g resin. Detailed procedures for all the experiments have been described previously.¹

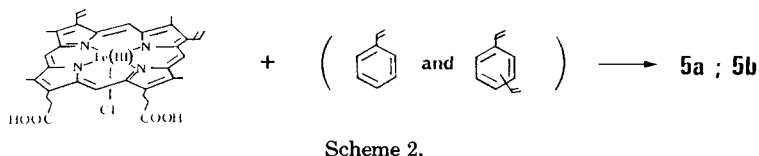
RESULTS AND DISCUSSION

Preparation and Characterization

Bead-shaped, cross-linked terpolymers **1a–3a** were prepared by the suspension polymerization in which all or part of St was replaced with DVB, while their analogs **1b–3b** (cross-linked terpolymers of the formless type) and **4** (uncross-linked terpolymer of the formless type) were obtained by the solution polymerization:



In this work, polymers **5a** (bead type) and **5b** (formless type) into which MVP is not introduced, were also prepared to investigate its effect on the ability to adsorb cyanide ion:



The synthetic methods for **5a** and **5b** were the same as those for the cross-linked terpolymers of the bead and formless types, except the polymerization was done in the absence of MVP.

In the extraction test with 0.5 N NaOH or HCl for one month, no dissolution of H from all the prepared polymers was observed. The visible spectrum of **4** in purified chloroform showed that the Soret band was shifted to about 5 nm lower wavelength before and after the polymerization. According to Fuhrhop et al.,³ this means that one of the two vinyl groups in H takes part in the polymerization.

The results for the preparation and characterization are summarized in Table I. Included in this table for comparison are the previous results¹ for uncross-linked terpolymer **HMiS2** (formless type) involving H, St, and VMI. First, we note from Table I that there is a marked difference in yield between the polymers uncrosslinked and crosslinked with DVB. We have reported in this series^{1,4,5} that radical copolymerization of H with various vinyl monomers is unsuitable for obtaining a high-molecular weight copolymer, because of (a) stabilizing the radical produced in the vinyl group of H by its resonance with the conjugated porphyrin ring and/or (b) losing the activity of the radical by its oxidation with the Fe(III) in the porphyrin ring. This caused a lowering of yield, and the obtained copolymers contained the H residue in the end of the chain. However, crosslinking with DVB affords an excellent yield of the polymers by solution polymerization and also by suspension polymerization. This could be due to an increase in molecular weight by crosslinkages forming between the DVB-containing oligomer chains.

We can also see from Table I that there are no distinguishable differences in the H and MVP contents between the bead (**1a-3a**) and the formless (**1b-3b**) types of the cross-linked terpolymers. Furthermore, similar result can be obtained by comparing **4** with all the cross-linked terpolymers. These are of importance in the synthesis of cyanide ion exchanger by employing the technique of suspension polymerization, since both H and MVP residues play a crucial role in the formation of the adsorption site having a strong affinity for cyanide ion.

Another important feature of Table I is that the internal surface of the bead-shaped polymers (**1a-3a**; **5a**) is larger than that of the formless polymers (**1b-3b**; **5b**), though for both types an increase in the amount of DVB enhances the internal surface. Sederel and Dejong⁶ have reported that suspension copolymerization of St and DVB in the presence of both solvating and nonsolvating diluents yields porous copolymer beads, that is, PPS (porous by precipitator and solvent) resin having *microporosity* and *macroporosity*. By considering the mechanism of pore-structure formation during the polymerization, they defined microporosity as the pores present within the microspheres composed of copolymer nuclei and of their agglomerations and macroporosity as the pores among the microspheres and their agglomerations with the bead. In this study, the suspension polymerization was carried out by adding quinoline as the solvating diluent and *n*-octane as the nonsolvating diluent at the same time to the monomer mixture (see experimental section). The existence of the microspheres within the bodies of the prepared polymer beads was confirmed by the morphological observations with a SEM (Fig. 1). This indicates that the bead-shaped polymers contain more or less the

TABLE I
Data for Preparation and Properties of Prepared Polymers

Samplecode	Feed ^a (mmol)			Yield (%)	Composition of polymer (mol%)			Surface area (m ² /g)
	H	MVP	VMI		St	DVB	H	
1a	0.70 (1.15)	30.0 (49.4)		22.1 (36.4)	7.9 (13.0)	0.74	35.9	1.11
2a	0.70 (1.15)	30.0 (49.4)		11.8 (19.4)	18.2 (30.0)	0.70	34.2	205
3a	0.70 (1.15)	30.0 (49.4)			30.0 (49.4)	0.72	33.7	332
1b	0.70 (1.15)	30.0 (49.4)		22.1 (36.4)	7.9 (13.0)	0.76	35.4	0.21
2b	0.70 (1.15)	30.0 (49.4)		11.8 (19.4)	18.2 (30.0)	0.72	35.8	179
3b	0.70 (1.15)	30.0 (49.4)			30.0 (49.4)	0.70	34.9	300
4	0.70 (1.15)	30.0 (49.4)		30.0 (49.4)		0.78	36.5	
5a	0.70 (1.15)			30.0 (49.4)	30.0 (49.4)	0.80		362
5b	0.70 (1.15)			30.0 (49.4)	30.0 (49.4)	0.84		356
HMIS2 ^b	0.70 (1.15)		30.0 (49.4)	30.0 (49.4)		1.04		20.5

^aThe values in parentheses are mol% of each monomer.

^bCited from Ref. 1.

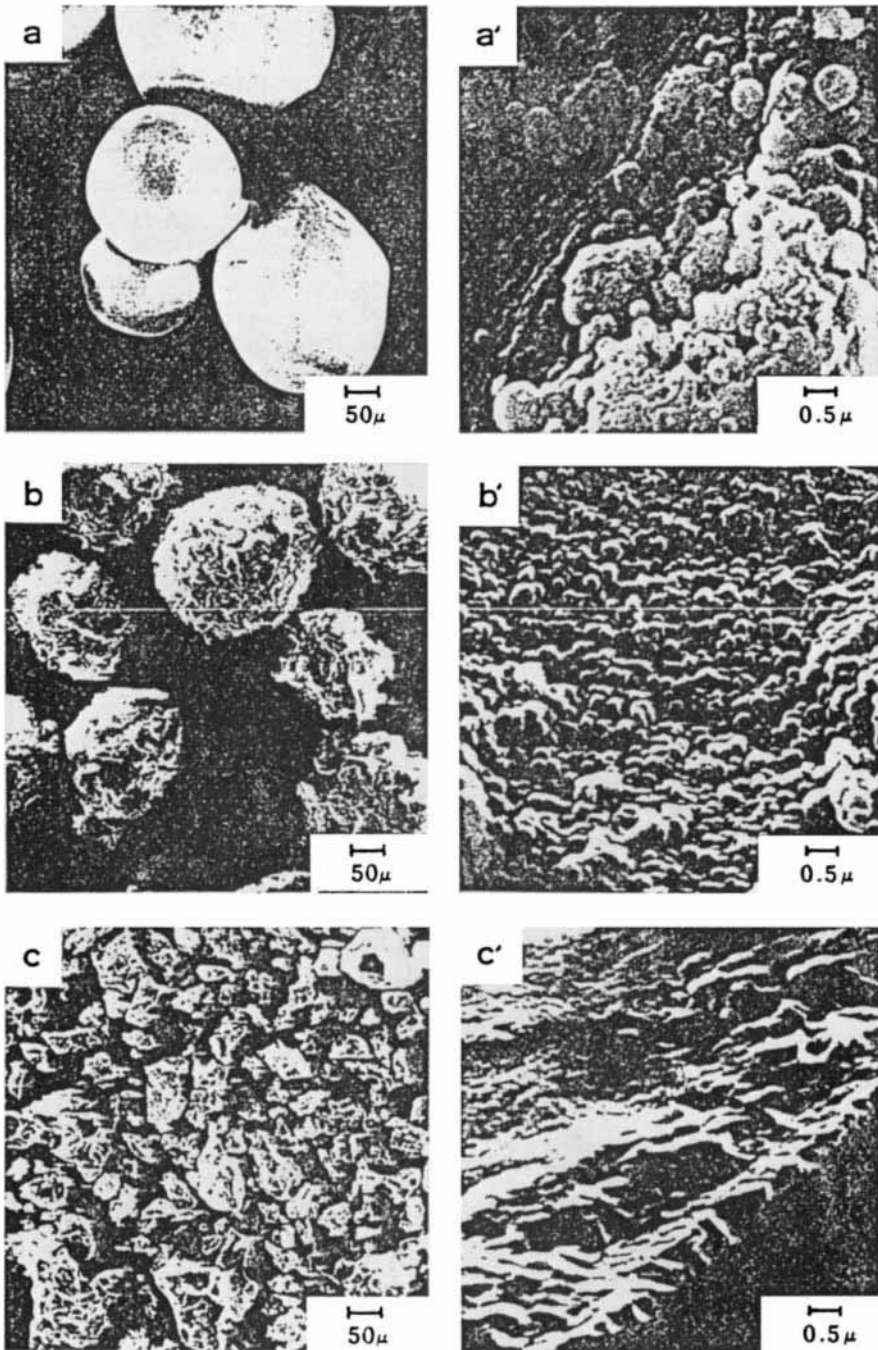


Fig. 1. Scanning electron micrographs of 1a (a, a'), 3a (b, b'), and 3b (c, c'). 1a and 3a are bead-shaped resins containing the microspheres within their bodies. 3b is an example of pulverized formless resins in which no microspheres are observed.

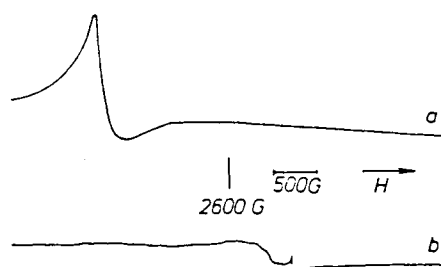


Fig. 2. ESR spectra of **3a** at liquid nitrogen temperature: (a) in 0.001 N HCl and (b) in phosphate buffer (pH 9) containing 0.1 M KCN.

macroporosity, although it is likely that **1a** is lacking in the microporosity because of forming gelificated microspheres due to inadequate crosslinking. In contrast to the suspension polymerization, solution polymerization affords the formless polymers (**1b-3b**; **5b**), whose bodies consist of continuous polymeric phase (Fig. 1), showing that they have not the macroporosity. Therefore, the difference in the internal surface between the polymers of the bead and formless types at the same DVB content can be explained in terms of macroporosity.

Cyanide Ion-Exchange Properties

A main factor affecting the ability of H-containing polymer to adsorb cyanide ion is the coordination structure of H.^{1,7} The coordination sphere around the central iron of H in the prepared polymers was thus examined prior to studying their function capabilities as cyanide ion exchanger. As can be seen from Figure 2, the ESR spectra of **3a** before and after the cyanide adsorption are in accord with those of high- and low-spin Fe(III)-porphyrins, respectively. The same spectral changes were observed in all the polymers. However, as shown in Table II, the axial coordination numbers (n_{cn}) of cyanide ion can be distinguished by whether the polymers contain MVP or not (i.e., n_{cn} is close to one for **1a-3a**, **1b-3b**, and **4**, and to two for **5a** and **5b**). These indicate that one coordination site of iron(III)-protoporphyrin IX existed in all the MVP-containing polymers is occupied by the pyridyl group as an axial base, while both 5th and 6th coordination sites of the porphyrin in **5a** and **5b** are free from occupying by axial bases.

Table II includes the results for the adsorption of cyanide ion onto each of the polymer samples. The amount (A_{cn}) of cyanide ion adsorbed was expressed as moles of the adsorbed ions per 1 mol polymer-bound H to avoid the effect of a slight difference in the H content between the samples. The investigation of the adsorption data gives the following two characteristics: (a) the A_{cn} values of **1a-3a** and **1b-3b** are much higher than those of **5a** and **5b**, and (b) there is no remarkable difference in the A_{cn} value between **4** and **HMiS2**, respectively, into which MVP and VMI are introduced. The result in (b) is further supported by comparing the equilibrium constants (K_{cn}) for the coordination reaction of cyanide ion to the polymer-bound H. Taking into account the results mentioned above, these suggest that occupying one coordination position of iron(III)-protoporphyrin IX by the pyridyl group in MVP

TABLE II
 Adsorption Characteristic of Cyanide Ion onto Prepared Polymers

Sample code	A_{cn}^a (mol/L mol H in polym.)	n_{cn}^b	$K_{cn} \times 10^{-2b}$ (L/mol)
1a	0.411	1.01	3.61
2a	0.579	0.99	6.37
3a	0.762	1.00	16.1
1b	0.371	1.02	3.22
2b	0.550	1.00	6.02
3b	0.644	1.02	10.2
4	0.837	1.02	29.5
5a	0.147	2.02	—
5b	0.101	2.00	—
HMiS2	0.858 ^c	1.00 ^c	30.9 ^c

^aDetermined at pH 9, initial KCN concn. = 2.14 mmol/L, and initial H concn. = 0.214 mmol/L.

^bEstimated from the adsorption data (pH 9) according to the same manner as described in Ref. 7.

^cObtained in this study from the adsorption experiment for the previously prepared HMiS2.

or by the imidazolyl group in VMI is effective for increasing the affinity of the adsorption site toward cyanide ion, although the pyridyl and imidazolyl groups are not different from each other with respect to ability to enhance the affinity. This is of great importance in preparing cyanide ion exchanger by the suspension polymerization.

The cyanide adsorption data also show that the A_{cn} or K_{cn} values for the cross-linked terpolymers (1a-3a; 1b-3b) are lower than that for the uncross-linked terpolymer (4). This means that crosslinking with DVB more or less leads to a lowering of the capability to adsorb cyanide ion. Thus, it is likely that the effective adsorption site is reduced by forming crosslinkages, because

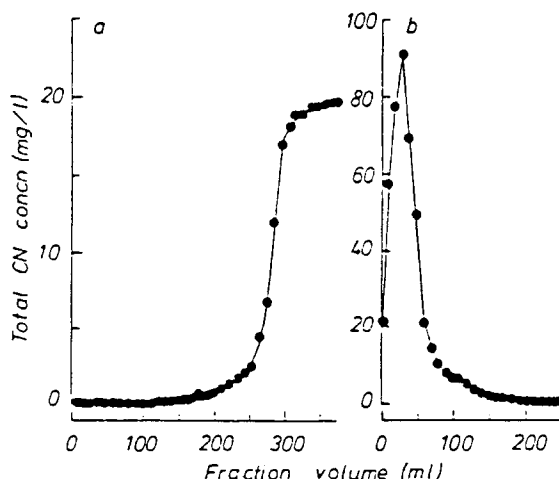


Fig. 3. Column separation of cyanide ion with 3a: (a) the separation of cyanide ions from KCN-containing phosphate buffer solution (pH 9, CN = 20 mg/L) and (b) the elution of the adsorbed cyanide ion with 0.1 N NaOH solution.

a part of the H sites in the resin may be unable to contact with cyanide ion. However, the comparison of Table I with Table II reveals that increasing the internal surface of the polymer serves to compensate such a reduction. Therefore, the suspension polymerization is just appropriate to prepare a cyanide ion exchanger, since the bead-shaped resins obtained possess the macroporosity which is more effective for enhancing the internal surface.

The ion-exchange characteristics of the bead-shaped resins were further investigated by column experiments. Figure 3 shows typical experimental data for column separation of cyanide. When the phosphate buffer solution (pH 9) containing 20 mg/L cyanide ion was effused through a column of **3a**, the cyanide concentration of the fractions was observed to be kept below 0.01–0.1 mg/L until the total fraction volume exceeds 200 mL. The adsorbed cyanide ion (0.357 mg/g, corresponding to 56 mol% of total H bound to polymer) was then almost entirely eluted with 0.1 N NaOH solution (recovery, ca. 98%). The adsorption and desorption were reproduced reversibly over different runs of the column experiments.

This work was partially supported by a Grant-in-Aid for Scientific research from the Ministry of Education, Japan (No. 575576).

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Received November 1, 1985

Accepted December 7, 1985