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Terpolymers

Synthesis of Divinylbenzene-Crosslinked Terpolymer Consisting of Hemin, Styrene, and 1-Venyl-2-Methylimidazole as Cyanide Ion Exchanger

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Summary

Crosslinked terpolymers, consisting of hemin (ferri-protoporphyrin IX chloride), styrene (St), and 1-vinyl-2-methylimidazole, were obtained in satisfactory yield (>70 %) by radical polymerization in which a part of St monomer was replaced with divinylbenzene. These terpolymers showed an ability to function as a cyanide ion exchanger.

Introduction

Recently we have studied the radical terpolymerization among hemin (H) (ferri-protoporphyrin IX chloride), styrene (St), and 1-vinyl-2-methylimidazole (VMI), together with a functional property of obtained water-insoluble terpolymers as cyanide ion exchanger (1). It has been shown that the ability to adsorb cyanide ion is enhanced by introducing VMI, mainly because its imidazolyl group binds to H in the polymer to form the five-coordinated high spin ferri-protoporphyrin IX which has a strong affinity toward cyanide ion. However, it was difficult to synthesize a terpolymer having high molecular weights, and the product was obtained in low yields. In this study, we tried to carry out the terpolymerization by replacing a part of St monomer with divinylbenzene (DVB). It was found that the present method affords an excellent yield of DVB-crosslinked porous terpolymer which was able to function as a cyanide ion exchanger.

Experimental

All the monomers, other than DVB, were the same samples as used previously (1). Technical grade DVB (containing ca. 40% ethylbenzene) was of commercial origin (Wako Pure Chemical Industries, Ltd., Japan). The purification of DVB was made in the same manner as described in a literature (2). The terpolymerization was carried out in a sealed tube at 86 °C for

36 h under reduced pressure, using 1.83 mmol of α,α'-azobisisobutyronitrile as the initiator and 6.14 mL of purified dimethylformamide (DMF) as the solvent. The solidified or gelificated reaction mixture was crushed and pulverized well before subjecting to the purification.

The purification of resin consisted of the following procedures; (I) the removal of residual monomers and uncrosslinked oligomers by repeated washing with DMF and dichloromethane (DCM) until the washing has no UV absorption bands at 238 - 300 nm, (II) the removal of DMF by extracting with acetone in a Soxhlet apparatus for a week, (III) the removal of acetone by 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. It should be noted that the procedure (I) is suitable for removing residual monomers and uncrosslinked oligomers, since (a) not only all the monomers used here but also the uncrosslinked terpolymers prepared previously (1) are highly soluble in both DMF and DCM, and (b) swelling and contraction of crosslinked terpolymer take place in DMF and DCM, respectively. Moreover, the procedure (II) is necessary because DMF behaves as a ligand for ferri-porphyrins. The procedure (IV) is done with view to forming the imidazole-coordinated chloride-bound high spin ferri-protoporphyrin IX in the polymer.

The polymer composition was determined by a combination of elemental and iron analyses. Electron spin resonance (ESR) spectroscopy, scanning electron microscopy (SEM), and BET nitrogen adsorption were further carried out to examine crosslinked terpolymer. The capability as cyanide ion exchanger was evaluated by investigating the adsorption of the cyanide ion from KCN solution and the desorption of the adsorbed ion by 0.5 N NaOH. The axial coordination number of cyanide ion was estimated from data of the cyanide adsorption. Detailed procedures for all the experiments have been described previously (1,3).

Results and Discussion

The results for the preparation and characterization of the terpolymers (HMiS2D1 to HMiS2D3) crosslinked with DVB are summarized in Table 1, where the results of the crosslinked binary copolymer (HS2D3) prepared here in the same manner as used for the terpolymers are also shown for comparison. Additionally, included in this table for comparison are the results for their uncrosslinked polymers (HMiS1, HMiS2, HS2, and HS3) already reported (1,3). There is a marked difference in yield between the terpolymers synthesized in the absence and presence of DVB. Similar effect of DVB is also observed in the copolymerization of H and St.

TABLE I

Preparation and Characterization of Various H-Containing Polymers Uncrosslinked and Crosslinked with DVB

Sample code	Feed (mmol)				Yield (%)	Composition of polymer (mol%)		Surface area (m^2/g)	A_{cn}[a] (mol/mol H)
	H	VMI	St	DVB		H	VMI		
HMiS2D1	0.70	30.0	28.8	1.2	76	0.69	21.9	0.02	0.49
HMiS2D2	0.70	30.0	22.1	7.9	81	0.72	18.6	18.0	0.56
HMiS2D3	0.70	30.0	11.8	18.2	73	0.65	16.4	237.0	0.78
HMiS1[b]	0.35	30.0	30.0		43	0.47	21.2	6.9	0.89
HMiS2[b]	0.70	30.0	30.0		32	1.04	20.5	7.1	0.91
HS2D3[c]	0.70		41.8	18.2	87	0.87		294.4	0.14
HS2[d]	0.55		58.4		69	0.93		4.21	0.32
HS3[d]	1.13		57.9		61	1.94		4.22	0.32

[a] Determined under the conditions of [H] = $2X10^{-5}$ mol/L, $[KCN]_i$ = $4X10^{-4}$ to $5X10^{-4}$ mol/L, ionic strength = 0.1, and pH 9 (phosphate buffer)

[b] Cited from ref. 1

[c] Prepared here in the same procedure as used for HMiS2D1 to HMiS2D3

[d] Cited from ref. 3

The previous study (4) dealing with radical homopolymerization of H monomer demonstrated that the polymer is not obtained with radical initiator. Furthermore, several vinyl monomers (e.g., St monomer) show a low tendency to polymerize in the presence of H monomer, and the polymers obtained contain the H residue at the end of the polymer chain (5). These results have been explained in terms of degradative chain transfer of propagating chain radical due to the H monomer (1,3). This chain transfer may be ascribed to (a) stabilizing the radical produced in the vinyl group of H by its resonance with the conjugated porphyrin ring and/or (b) lossing the activity of the radical by its oxidation with the Fe(III) in the porphyrin ring. The radical polymerization is consequently anticipated to be unsuitable for obtaining a high molecular weight polymer containing H. In fact, increasing the feed concentration of H monomer caused rapid decrease in the viscosity and yield of the terpolymer (1). However, crosslinking with DVB affords an excellent yield of the terpolymer. This could be due to an increase in molecular weight by the formation of crosslinkages between the DVB-containing oligomer chains.

Another remarkable feature of Table 1 is the fact that the polymerization of the 30% DVB-containing monomer feeds gives rise to the products (HMiS2D3 and HS2D3) with a large surface area, although such a product is not obtained from the monomer feeds at low DVB content (see HMiS2D1 and HMiS2D2). It is thus found that the internal surface of the crosslinked polymers increases with an increase in the feed concentration of DVB. This can be directly supported by the morphological observation with SEM (see Figure 1).

A main factor affecting the ability of H-containing polymer to adsorb cyanide ion is the coordination structure of the H (1). Taking this into account, the coordination sphere around the central iron of the H in the obtained crosslinked polymers was characterized prior to investigating their functional capabilities as cyanide ion exchanger. The ESR spectra of all the crosslinked polymers were in accord with those of high spin Fe(III)-porphyrins. However, the axial coordination number of cyanide ion was close to one for HMiS2D1 to HMiS2D3 and to two for HS2D3. These results are taken to assume that the imidazolyl group of VMI in the crosslinked terpolymers coordinates to the Fe(III) to form the five-coordinated high spin Fe(III)-protoporphyrin IX as the adsorption site for cyanide ion.

The adsorption characteristics of cyanide ion for the crosslinked polymers are also shown in Table 1, together with those for the polymers prepared previously (1,3). In the adsorption experiments, the initial KCN concentration ($[KCN]_i$) was adjusted to 20 to 25 times the H concentration ([H]), because under such conditions the amount (A_{cn}) of cyanide ion adsorbed is little altered by change in $[KCN]_i$. A_{cn} was

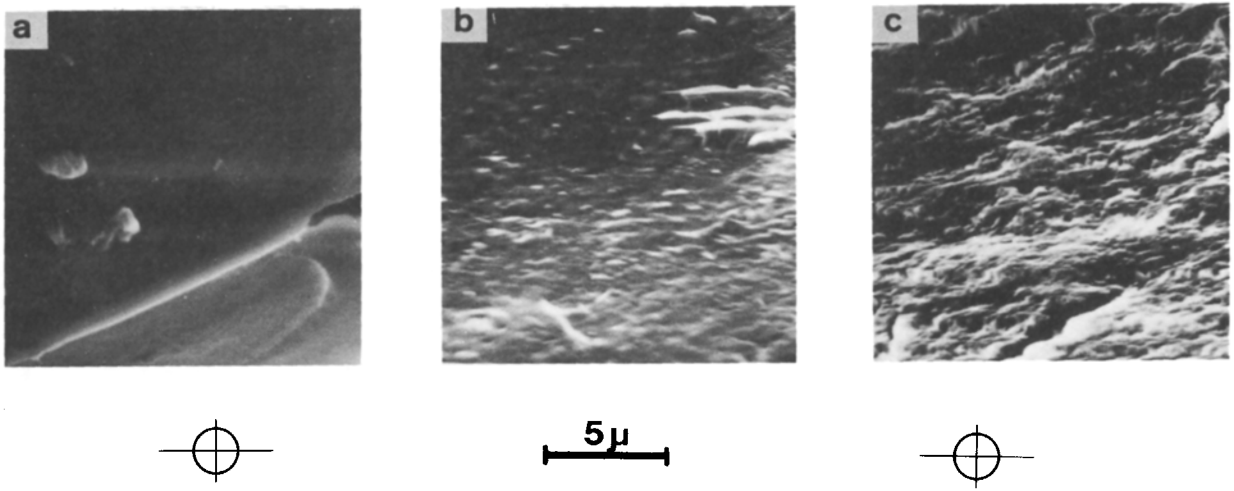

Fig. 1. Scanning electron micrographys of DVB-crosslinked terpolymers: (a) HMiS2D1; (b) HMiS2D2; (c) HMiS2D3

then expressed as moles of adsorbed cyanide ion per 1 mol polymer-bound H to avoid the effect of the difference in the H content between the samples. The comparisons of the results for the uncrosslinked and crosslinked polymers show that, regardless of ternary and binary copolymers, crosslinking with DVB leads to a decrease in the A_{cn} value. It is thus likely that the effective adsorption site is reduced by forming crosslinkages, because a part of the H in resin may be unable to contact with cyanide ion. However, increasing the internal surface of the terpolymer by satisfactory crosslinking serves to compensate such a reduction (see HMiS2D3). Another important feature of the crosslinked polymers is that the A_{cn} values of HMiS2D1 to HMiS2D3 are much higher than that of HS2D3, indicating that the high affinity of the imidazole-coordinated high spin Fe(III)-porphyrin for cyanide ion is unchanged by crosslinking with DVB. In addition to these results, a complete removal of the adsorbed cyanide ion from each of the uncrosslinked and crosslinked polymers was established by the desorption experiments with 0.5 N NaOH solution.

In conclusion, it becomes apparent that crosslinking with DVB is favorable for raising the yield of the terpolymer without a large undesirable influence on its functional capability as cyanide ion exchanger.

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