

Preparation and Characterization of Polyoxetane Resins Anchoring the Pendant Spacer-Separated Hydroxamic Acid Residue

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ABSTRACT: Polyoxetane resins, **IVa** and **IVb**, anchoring the hydroxamic acid residue were prepared with high degree of functionality (DF) by polymer reactions from aliphatic NH_2 groups at pendant spacer-ends of **IIa** and **IIb**. The pendant hydroxamic acids adsorbed Cu(II) ions from aqueous solution of Cu(II) acetate at pH 6 to show capacity beyond that calculated for the ordinary Cu(II)-complex chelated with the two pendant ligands, probably due to the formation of uncompleted chelate structures. The corresponding aromatic NH_2 groups of **IIc** and **IIId** showed very low DF in the same polymer reactions. At pH 6, amines of **IIc** and **IIId** adsorbed Cu(II) ions to a certain extent, although those of **IIa** and **IIb** could adsorb no Cu(II) ions. A soft, expansible polyoxetane network, as a supporting matrix, may importantly affect Cu(II)-adsorption at high capacity.

KEY WORDS Cationic Ring-Opening Polymerization / Polyoxetanes / Polymer Reaction / Pendant Hydroxamic Acid / Chelating Resins /

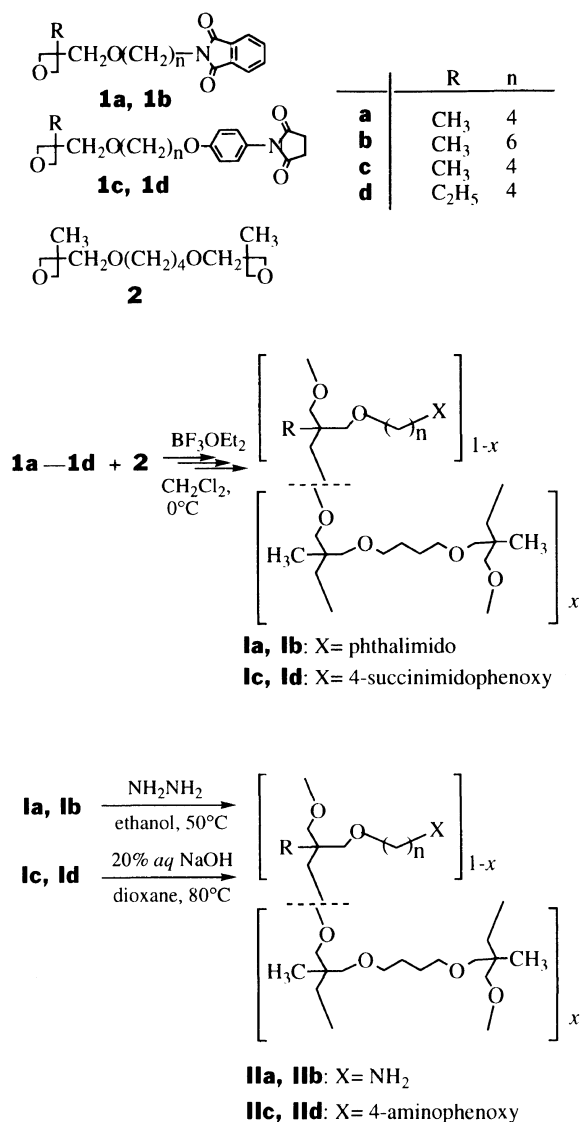
We prepared polyoxetane resins and studied applications to functional polymers.¹ For one pendant spacer-separated functional group of the resins, we prepared primary amines, such as alkylamine and aniline moieties, regarded as an important reaction site for chemically modifying resins.^{2,3}

We are interested in chelating resins, since they are convenient adsorbents for selective removal and recovery of heavy metals useful or undesirable for living organisms. A hydroxamic acid group has chelating ability with heavy metals, and several chelating resins were prepared using pendant groups, such as CO_2CH_3 , CONH_2 , and $\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)_2$, of polyvinyl and polystyrene backbones.^{4–6} In our synthesis and characterization of functional polyoxetanes, we prepared polyoxetane resin anchoring a pendant hydroxamic acid group through a moderately long spacer arm, since we considered that the flexible and somewhat polar polyoxetane networks are applicable to supporting matrices of chelating resins, *i.e.*, these resins are pressed to smoothly change conformation of polymer backbones so as to chelate with metal ions, and often used in aqueous media dissolving metal ions. The above polymer reactions may smoothly proceed due to the desired character of polyoxetane matrices. Herein, we describe the preparation and characterization of several chelating resins anchoring pendant hydroxamic acid groups, derived by polymer reaction from the pendant primary amines of cross-linked polyoxetanes.

RESULTS AND DISCUSSION

Preparation of Resins Anchoring Pendant Spacer-Separated Hydroxamic Acid Residue

As shown in Scheme 1, polyoxetane resins with pendant primary amines were obtained by BF_3 -initiated cationic ring-opening polymerization of imide-containing monomers, **1a–1d**, with cross-linking agent, **2**, followed by complete conversion of the imide moieties by hydrazinolysis or hydrolysis into amino ones, as previously reported,^{2,3} and the resulting resins are listed

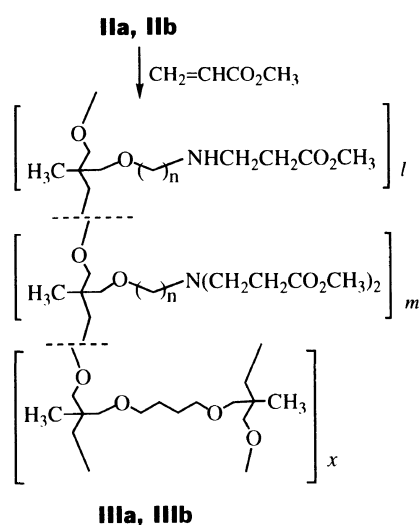


Scheme 1. Synthetic routes of polyoxetane resins, **IIa–d** and **IIa–d** from oxetanes, **1a–d** and **2**.

Table I. Preparation of polyoxetane resins, **IIa–d**, anchoring pendant amino groups and imide-protected derivatives, **Ia–d**

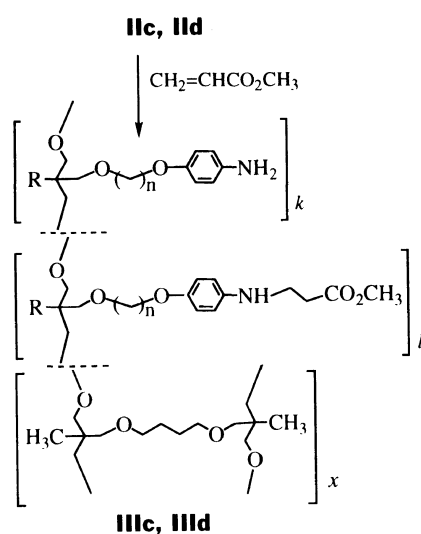
| Monomers in feed ^a | R ^b | n in spacer ^b | X ^b | Polymer products | | Amine polymers | |
|-------------------------------|-------------------------------|--------------------------|----------------|-------------------|-------------------------|----------------|-------------------------|
| | | | | Name | Yield ^c % | Name | Yield ^d g |
| Ia | CH ₃ | 4 | PI | Poly(Ia) | 85 ^{e,f} | — | — |
| Ia/2 (20) | CH ₃ | 4 | PI | Ia | 87 | IIa | 0.84 |
| Ib | CH ₃ | 6 | PI | Poly(Ib) | 43 ^{e,g} | — | — |
| Ib/2 (30) | CH ₃ | 6 | PI | Ib | 97 | IIb | 0.90 |
| Ic/2 (30) | CH ₃ | 4 | SI | Ic | 99 | IIc | 0.94 |
| Id | C ₂ H ₅ | 4 | SI | Poly(Id) | 78 ^{e,h} | — | — |
| Id/2 (45) | C ₂ H ₅ | 4 | SI | Id | 80 | IIId | 0.88 |

^a Monomers for polymerization in dichloromethane (DCM) at 0°C for 50h with 0.08 molar amount of BF₃OEt₂ to monomer. Figures in parentheses show mol% **2**. ^b See structures of monomers in Scheme 1. In X, PI and SI refer to phthalimido and 4-succinimidophenoxy, respectively. ^c Based on weights of monomers in feed. ^d Weights of products obtained from 1g **Ia–d**. ^e Obtained by reprecipitation with DCM–methanol solvent. ^{f–h} Molecular weights of uncross-linked polymers estimated by GPC based on standard polystyrenes: ^f 24500; ^g 5700; ^h 8800.

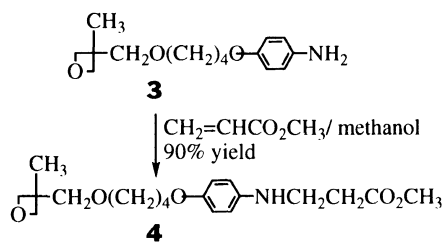
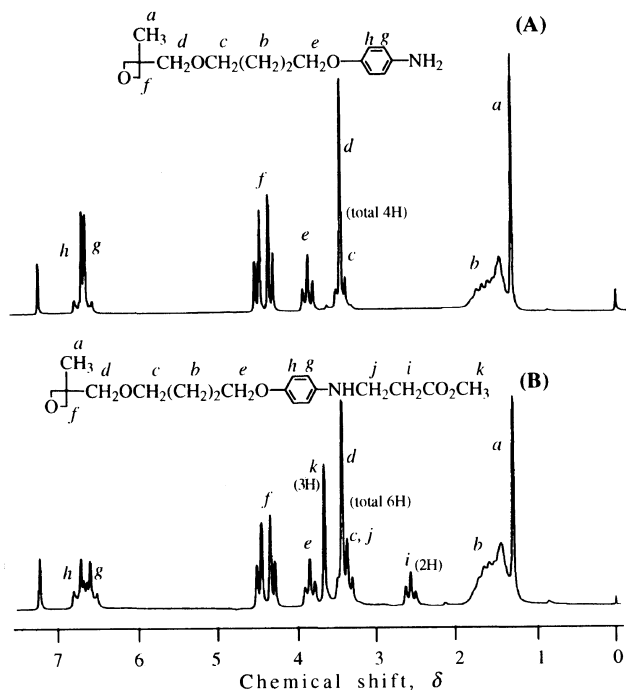
**Scheme 2.** Synthetic routes of polyoxetane resins, **IVa** and **IVb**, or **Va** and **Vb** from **IIa** or **IIb** through **IIIa** or **IIIb**.

in Table I.

The polymer reactions are shown in Scheme 2 for aliphatic amines of **IIa** and **IIb**, and in Scheme 3 for aromatic amines of **IIc** and **IIId**. In the first step of the polymer reactions, amines of **IIa–d** were converted to β -aminopropionic methyl ester residues of **IIIa–d** by

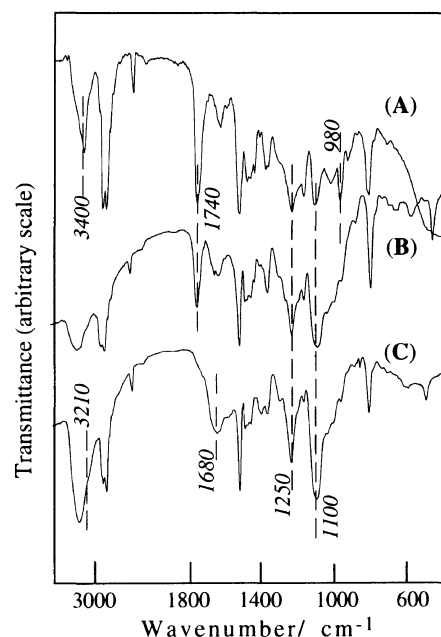
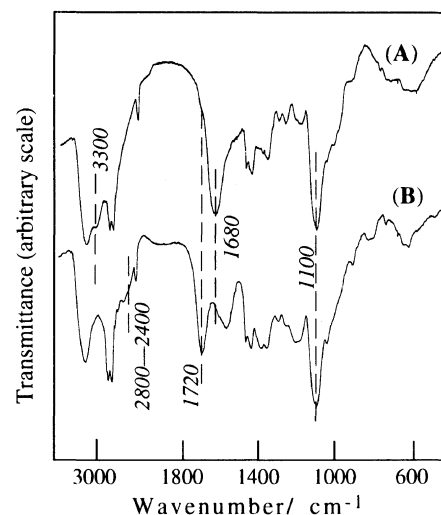
**Scheme 3.** Synthetic routes of polyoxetane resins, **IVc** and **IVd**, or **Vc** and **Vd** from **IIc** or **IIId** through **IIIc** or **IIIId**.

Michael addition reaction with excess methyl acrylate in methanol. To confirm the structure of the the Michael addition product, we examined a reaction using the anilino residue of **3**, a model compound for the pendant

Scheme 4. Model reaction producing **4** from **3**.Figure 1. ^1H NMR spectra of **3** (A) and **4** (B).

aniline of **IIc**, with methyl acrylate under the same reaction conditions as for **IIc**, as shown in Scheme 4. This model reaction gave the single Michael addition product, **4**, in 90% yield, as indicated by ^1H NMR (Figure 1) and IR spectra (Figure 2). In comparison with the ^1H NMR spectrum of **3**, the spectrum of **4** indicates additional signals, (i), (j), and (k), assignable to a β -aminopropionic methyl ester moiety, at integral intensities of 2H, 2H, and 3H, respectively, although chemical shifts and patterns of the other signals resemble those of **3**. The IR spectrum of **4** shows distinctive bands due to NH (amine) and C=O (ester) stretching vibrations, respectively, at 3400 and 1740 cm^{-1} . As shown in Figure 2, the IR spectrum of **IIIc** is very similar to that of **4**, although the IR band assignable to the oxetane ring disappears at 980 cm^{-1} in the spectrum of **IIIc**. Hence, from results of the model reactions, it is reasonable to consider that the anilino residues of **IIc** are converted by polymer reaction to the single Michael addition product of **IIIc**, without forming the double Michael addition product. In reactions of **IIa** and **IIb** with methyl acrylate, the double Michael addition product was formed besides the single Michael addition product, as described below.

Pendant ester groups of **IIIa–d** were subjected to the further reaction with 3 equiv hydroxyammonium chloride in the presence of 6 equiv NaOH in 30% aqueous

Figure 2. IR spectra of **4** (A), **IIIc** (B), and **IVc** (C).Figure 3. IR spectra of **IVa** (A) and **Va** (B).

dioxane at room temperature to give pendant hydroxamic acid residues of **IVa–d**. The IR spectra are exemplified in Figures 2 and 3. The IR spectra of **IVa** and **IVc** indicate a broad band due to C=O (amide) stretching vibration at 1680 cm^{-1} , although the band of **IVc** is weaker than that of **IVa**. A characteristic IR band of the unchanged ester is not observed at 1740 cm^{-1} , and an IR band assignable to the C=O stretching vibration of carboxylic acid residues also hardly appears at 1720 cm^{-1} . The NaOH base is thus consumed to generate hydroxylamine from its hydrochloride, but not to hydrolyze the pendant ester. When resins **IIIa–d** were acidified after heating with excess NaOH in 50% aqueous 1,4-dioxane at 80°C, pendant ester groups were completely converted to the corresponding carboxylic acids of **Va–d**, which showed IR bands at 1720 cm^{-1} . When the resins were not acidified after the alkaline hydrolysis, broad bands of the sodium carboxylate at 1570 cm^{-1} were seen. Therefore, for resins **IIIa–d**, nearly all the ester groups seem to be converted to hydroxamic acid residues, *i.e.*, Y =

Table II. Polymer reaction products, **IIIa–d**, obtained from pendant primary amines with methyl acrylate

| Name | Yield ^a g | Monomeric unit fractions ^b | | | | | | DF ^c % |
|-------------|-------------------------|---------------------------------------|----------|----------|----------|------|------|----------------------|
| | | <i>x</i> | <i>k</i> | <i>l</i> | <i>m</i> | | | |
| IIIa | 1.42 | 0.25 | 0.32 | 0.34 | 0 | 0.48 | 0.18 | 100 |
| IIIb | 1.29 | 0.35 | 0.40 | 0.40 | 0 | 0.38 | 0.22 | 100 |
| IIIc | 1.37 | 0.37 | 0.37 | 0.40 | 0.46 | 0.14 | 0 | 23 |
| IIId | 1.26 | 0.54 | 0.58 | 0.59 | 0.36 | 0.05 | 0 | 12 |

^a Weights of products obtained from 1 g **IIa–d**. ^b See the structures in Schemes 2 and 3. Cross-linking, *x*, estimated from elemental-analysis data of imido-type resins (left), primary amino-type resins (middle), and resins of β -aminopropionate- and hydroxamic-types (right columns). ^c Degree of functionalization (DF) of pendant amines, $(1-x-k)/(1-x)$.

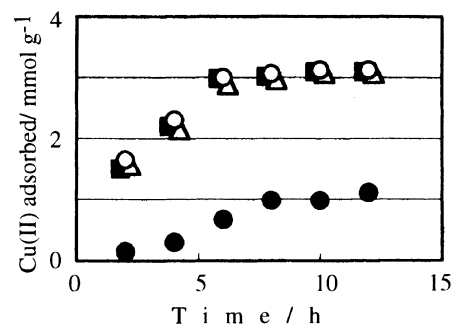
Table III. Hydroxamic and carboxylic acid-containing resins, **IVa–d** and **Va–d**, obtained by polymer reactions of the pendant β -aminopropionic esters and the Cu(II)-adsorption capacities of the pendant acids

| Name | Yield ^a g | Capacity/mmol g ⁻¹ | | |
|------------------------|-------------------------|-------------------------------|--------------------|-------------------------|
| | | Adsorption ^b | | Desorption ^d |
| | | Found | Calcd ^c | Found |
| IIa^c | | 0.00 | | |
| IIc^c | | 0.98 | | |
| IVa | 0.96 (13) | 3.12 | 1.3–1.5 | 2.90 |
| IVb | 0.98 (7) | 3.20 | 1.3–1.4 | 2.97 |
| IVc | 0.97 (9) | 1.28 | 0.3 | 1.20 |
| IVd | 1.05 (8) | 0.74 | 0.1 | 0.72 |
| Va | 0.92 | 1.11 | | |
| Vd | 0.91 | 2.01 | | |
| Vc | 0.92 | 0.95 | | |
| Vd | 0.93 | 0.62 | | |

^a Weights of products obtained from 1 g of each resin. Figures in parentheses are considered wt% (at maximum) for moisture in products, based on elemental-analysis data. ^b Determined after immersing a resin in 10^{-2} mol dm⁻³ Cu(II) acetate at room temp for 48 h. ^c Calculated on the basis of structure A. ^d After immersing a dried Cu(II)-adsorbing resin in 1 mol dm⁻³ aqueous HCl at rt for 24 h, amount of Cu(II) ions desorbed was determined for 1 g dried Cu(II)-adsorbing resin. ^e Obtained from **Ia** or **Ic**, as shown in Table I.

CONHOH in **IVa–d**.

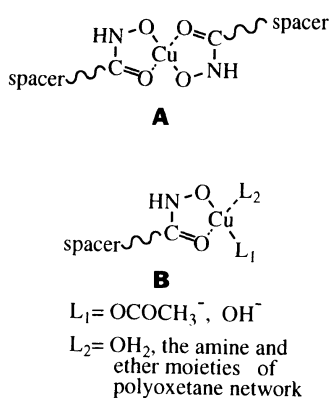
Monomeric unit fractions, *k*, *l*, and *x*, of **IIIa** (and also **IVa**) were calculated using elemental-analysis data for carbon and nitrogen atoms in **IIIa** and in **IVa**. Cross-linking, *x*, was calculated from elemental-analysis data of **Ia** and **IIa**. Monomeric unit fractions were obtained for **IIIb–d**. In each resin, *x*, calculated in three cases, were close to each other, although deviation was observed for **IIIa**. Thus, the pendant anilines of **IIc** and **IIId** gave single Michael addition products in **IIIc** and **IIId**, respectively, in degree of functionality (DF), $(1-x-k)/(1-x)$, of 0.23 and 0.12. The reactivity of the pendant anilines in the polymer reaction with methyl acrylate is somewhat lowered by crowded polymer matrices of **IIId**, which has a bulkier ethyl side chain and higher cross-linking than **IIIc**. The polymer reactions of the pendant aliphatic amines of **IIa** and **IIb** gave the double Michael addition product besides the single Michael addition product in **IIIa** and **IIIb**. That is, all

**Figure 4.** Plots of adsorbed Cu(II) ions against immersing time with resins: 1st (○), 2nd (■), and 3rd cycles of repeated use with **IVa** (△) and with **Va** (●).

the primary aliphatic amines first gave the single Michael addition product with methyl acrylate, and then 27–37% of the resultant secondary amines were changed to give the double Michael addition product with additional methyl acrylate. The results of the polymer reactions are shown in Tables II and III. Thus, the aliphatic amines react more smoothly with methyl acrylate than the corresponding aromatic amines, presumably owing to the higher nucleophilicity of the aliphatic amines relative to that of the aromatic ones. Resins, **VIa** and **VIb**, anchor two pendant-terminal functional groups, $-\text{NH}_2\text{--}_a(\text{CH}_2\text{CH}_2\text{CONHOH})_a$ where $a = 1$ and 2, and the pendant hydroxamic acid is a major functional group, whereas the pendant carboxylic acid is a minor functional group that may be neglected in comparison with that of the hydroxamic acid. When the pendant CONH_2 groups based on 5 mol% *N,N'*-methylenebisacrylamide-cross-linked polyacrylamide were allowed to react with 3 equiv hydroxyammonium hydrochloride in the presence of 1 equiv NaOH in water at room temperature, hydroxamic acid groups were formed in DF of 70%, and 25% of the amide groups were unreacted.⁶ In polystyrene networks of macroreticular (20 mol% divinylbenzene (DVB)) and gel (5–20 mol% DVB) types, pendant ethyl malonates gave 2.0–2.9 mmol g⁻¹ of the carboxylic acid groups and 2.1–3.7 mmol g⁻¹ of the hydroxamic acid groups by polymer reaction using hydroxylamine and sodium methoxide in methanol at 70°C. The resulting resins indicated distinctive IR bands due to the carboxylic acid at 1710 cm⁻¹, besides IR bands due to the hydroxamic acid at 1680 cm⁻¹.⁵ Thus, the structures of the resins **IVa–d** were confirmed, and DF of polymer reactions were fairly good for aliphatic amines, although unsatisfactory for the aromatic amines.

Binding Ability of Resins, **IVa–d**, with Cu(II) Ion

Hydroxamic and carboxylic acids bind Cu(II) ions in the form of a chelate or salt. The binding ability of pendant acid residues was examined for resins obtained in the present study. A resin was immersed in aqueous solution of Cu(II) acetate buffered at pH 6 with sodium acetate–acetic acid, and the concentration of Cu(II) ions in the supernatant was determined by ethylenediaminetetraacetic acid (EDTA) titration to determine the amount of Cu(II) ions adsorbed on the resin. The results of the Cu(II)-adsorption capacity are summarized in Table III, and plots of the amount of the adsorbed



Scheme 5. Structures of Cu(II)-complexes formed with pendant hydroxamic ligands.

Cu(II) against the immersing time, in Figure 4. As shown in Figure 4, the adsorption reaction of Cu(II) ions with resin **IVa** reached equilibrium so as to adsorb 3.1 mmol Cu(II) ions per 1 g of dry **IVa** after 8 h. This Cu(II)-adsorption capacity of **IVa** is comparable to 3.0 mmol per 1 g dry resin obtained as a hydrophilic gel of poly-(acrylohydroxamic acid) cross-linked with 5 mol% *N,N'*-methylenebisacrylamide.⁶

In the ordinary form of chelating Cu(II) ions with hydroxamic acids, such as acetohydroxamic acid, two molecules of hydroxamic ligands should bind to one molecule of the Cu(II) ions, as shown by structure A in Scheme 5.⁴ In each resin, the amount of Cu(II) ions adsorbed was higher than the capacity calculated for structure A on the basis of content of the pendant hydroxamic acids. Therefore, uncompleted structures, such as B, may be formed with ligands L_1 and L_2 other than the pendant hydroxamic acid groups. The aliphatic amine and ether moieties of **IIa** and **IIb** may not act for ligand binding Cu(II) ions, since **IIa** adsorbed no Cu(II) ions dissolved in water at pH 6. Yokoi *et al.* studied interactions between Cu(II) ions and poly(acrylic acid) (PAA) in aqueous solution. At pH 3–8, mononuclear Cu(II) complexes with one and two carboxyl groups of PAA always were found to exist in equilibrium between these complex species, and these two complexes have the same coordination structures as the low-molecular-weight acetate complexes Cu(II)(OAc)^+ and Cu(II)(OAc)_2 , where OAc denotes acetate anions, suggesting that coordination of Cu(II) ions to carboxyl groups of PAA is strain-free.⁷ Thus, the structures A and B may exist in Cu(II)-complex formation with ligands of the present polyoxetane resins. In such a case, structure B may be formed more easily than structure A, since, in the formation of intermolecularly chelated structure of A, the coordination of pendant ligands to Cu(II) ions is blocked by the cage of polymer matrices and the polymer backbones are pressed to take deformed conformations, which are strained, possibly due to restrained movability of polymer backbones by cross-linking. **IIc** could adsorb Cu(II) ions from water at pH 6, indicating that the aromatic amines were ligands capable of binding to Cu(II) ions. Poly(4-aminostyrene) acts as a polymeric ligand for the formation of several Co(III) complexes.⁸ Judging from a comparison of capacity of **IVc** and **IIc**, most adsorbed Cu(II) ions appear to bind to aromatic amines.

Carboxylic acids **Va** and **Vb** adsorbed 1.1 and 2.0 mmol Cu(II) ions per g-resin, respectively. These values are very inferior to those observed with the hydroxamic acids of **IVa** and **IVb**. The carboxylic acids of **Vc** adsorbed 0.95 mmol Cu(II) ions per g-resin, which was very close to capacity, 0.98 mmol per g-resin, for Cu(II)-adsorption with **IIc**. At this time, why the pendant carboxylic acids indicate lowered Cu(II)-capacity is not clear.

When immersed in aqueous solution of Cu(II) acetate, hydroxamic acid-containing resins, **IVa** and **IVb**, were colored from white to green, and carboxylic acid-containing resins, **Va** and **Vb**, from white to blue, although such color changes were not observed for aromatic resins, **IVc**, **IVd**, **Vc**, and **Vd**, since these resins are dark brown. Cu(II)-adsorbing **IVa–IVd** indicated broad bands at $1620\text{--}1600\text{ cm}^{-1}$, but not IR bands at 1680 cm^{-1} due to amide groups of **IVa–IVd**. The hydroxamic acid residue is thus a major binding group in chelating resins of aliphatic-amino types, **IVa** and **IVb**. This was proved from observation of IR spectra of **IVa** and **IVb**.

The Cu(II)-adsorbing resins were immersed in dilute hydrochloric acid for 20 h to completely desorb Cu(II) ions, to an extent comparable to that on the virgin resin. The resin recovered was used to adsorb Cu(II) ions again. Repeated use results of **IVa** are shown in Figure 4.

Polyoxetane resins anchoring pendant spacer-separated hydroxamic and carboxylic acid moieties were readily prepared with high DF through polymer reaction steps using methanol, ethanol, and aqueous 1,4-dioxane solvents, poor solvents for polystyrene resins widely used as supporting matrices in functional polymers synthesis. This is ascribed to the flexibility and moderate polarity of polyether networks, which swell in protic and aqueous organic solvents. When such pendant groups as hydroxamic and carboxylic acids and aromatic amines were anchored to polyoxetane resins, the supporting matrices could take Cu(II) ions even from water. This behavior of supporting matrices is facilitated by the expansion of polyether networks rather than hydrophilicity, which may be much lowered (see below), *i.e.*, they expand enough to interfuse hydrated ionic species into networks from aqueous media by attraction between pendant ligands and ions.

Diethyl ether shows solubility in water comparable to that of 1-butanol, *i.e.*, both are soluble to the extent of about 8 g per 100 g water.⁹ However, it is difficult to dissolve ethers with bulkier or longer alkyl groups in water, *e.g.*, diisopropyl and dibutyl ethers are hardly soluble in water. A resin of 3-(4-bromobutoxy)methyl-3-methyloxetane cross-linked with 30 mol% of **2**, considered as a model of supporting matrices for resins obtained in this study, did not seem to swell in water. This resin is composed of ether moieties analogous to ethers with neopentyl and butyl groups.

Uncross-linked polyoxetanes with the pendant NH_2 groups, *e.g.*, **IIa** and **IIb** with $x=0$, were soluble in water,² obviously due to the hydrophilicity of NH_2 groups immobilized on polymer backbone. Thus, pendant hydrophilic groups, such as NH_2 , CONHOH , and CO_2H , may be important to interfuse aqueous media into the hydrophobic resin.

Glass transition temperatures (T_g) of several poly-

oxetanes having alkyl side chains at the C-3 position of the oxetane unit were determined to be below 0°C, *e.g.*, T_g of -31°C was reported for poly(3-methyl-3-propyloxetane), which may be regarded as a model for the main chain part of resins used in this study.¹⁰ We confirmed that 3-(4-bromobutoxy)methyl-3-methyloxetane gave a viscous grease-like polymer under ring-opening polymerization conditions, probably, showing that T_g of this polymer is below room temperature.¹¹ Thus, polyoxetane chains become flexible, although exceptions have been found, as in the case of crystalline polymers of 3,3-dimethyl- and 3,3-diethyloxetanes and so on.¹²⁻¹⁴

Oxetane monomers having functional groups of amines and *N*-unsubstituted amides at the side chain-end could not give the corresponding polymers by BF_3 -initiated ring-opening polymerization, possibly due to character of the amino and amido nitrogen atoms, which interfere with the initiation step with BF_3 through Lewis acid-base interaction. Ring-opening polymerization with BF_3 was quite unsusceptible to phthalimide and *N*-phenylsuccinimide moieties of oxetane monomers. Therefore, pendant aliphatic and aromatic amines anchored to polyoxetane networks through spacers can be prepared with varied cross-linking.

In conclusion, pendant primary aliphatic amines immobilized in flexible, expansible polyoxetane networks are considered as reaction sites useful for producing various functional polymers, although the corresponding aromatic amines must be further investigated to improve the DF of polymer reactions.

EXPERIMENTAL

Materials

Polyoxetane resins, **Ia—d**, were obtained by BF_3 -initiated ring-opening polymerization of oxetanes **Ia—d** with a cross-linking agent, **2**, and then the pendant imides of **Ia—d** were completely converted to the corresponding primary amines of **IIa—d** using hydrazine monohydrate in ethanol at 50°C or using 20% NaOH in 50% aqueous 1,4-dioxane at 80°C.^{2,3} The elemental analysis data of the products are as follows.

Anal. (Found). **Ia**: C, 66.01%; N, 3.55%. **Ib**: C, 67.09%; N, 2.96%. **Ic**: C, 65.37%; N, 3.27%. **Id**: C, 65.21%; N, 2.09%. **IIa**: C, 61.12%; N, 4.55%. **IIb**: C, 64.67%; N, 3.69%. **IIc**: C, 64.99%; N, 3.27%. **IId**: C, 53.61%; N, 5.76%.

Resins with the Pendant β -Aminopropionic esters; Typical Procedure. Resin **IIa** (2.88 g, about 1.0 mmol of the pendant NH_2) was stirred in methanol (35 cm^3) at room temperature for 1 h, and then methyl acrylate (1.8 g, 21 mmol) was added into the resin dropwise at 0°C. The contents were stirred at room temperature for 20 h. The resultant resin was filtered, washed successively with methanol and ether, and then dried in a vacuum. The products gave the following elemental-analysis data.

Anal. (Found). **IIIa**: C, 59.66%; N, 3.25%. **IIIb**: C, 61.88%; N, 2.79%. **IIIc**: C, 62.01%; N, 2.86%. **IIId**: C, 57.27%; N, 1.82%.

The anilino group of **3**³ was also allowed to react with the acrylate in the same manner as the above-mentioned procedure, and the crude product was purified by column

chromatography to give **4** as a viscous oil in a 90% yield. The structure of **4** was confirmed by its ¹H NMR and IR spectra, shown in Figures 1(B) and 2(A), respectively.

Resins with the Pendant Hydroxamic and Carboxylic Acids; Typical Procedure. Resin **IIIa** (1.53 g, about 4.6 mmol of the pendant ester) was stirred in a mixture of 1,4-dioxane (15 cm^3) and water (3 cm^3) at 40°C for 1 h, and hydroxyammonium chloride (0.92 g, 13.3 mmol) was added into the contents. A 6 mol dm^{-3} aqueous NaOH solution (4.5 cm^3) was added dropwise into the resin with stirring at 0°C, and the mixture was stirred at 0°C for 1.5 h and then at room temperature for 7.5 h. After removing the solvent by means of an evaporator, the residue was acidified at pH 4 with diluted HCl, filtered, washed successively with water and methanol, and dried under vacuum to give resin **IVa**. The products gave the following elemental-analysis data.

Anal. (Found). **IVa**: C, 49.94%; N, 7.33%. **IVb**: C, 55.34%; N, 6.74%. **IVc**: C, 60.91%; N, 3.49%. **IVd**: C, 61.30%; N, 2.81%.

Carboxylic acid-containing resins, **Va—d**, were obtained by alkaline hydrolysis of **IIIa—d** with an excess of NaOH in 50% aqueous 1,4-dioxane at 80°C for 24 h, followed by the same post-treatment as that for **IVa—IVd**.

Adsorption of Cu(II) with the Pendant Ligands of Resins

The typical procedure is as follows. Dried resin, **IVa**, (0.1 g) was placed in an 100 cm^3 -graduated flask containing 50 cm^3 of a buffer solution (sodium acetate-acetic acid) at pH 6 overnight. Into this flask, 10 cm^3 of a 0.1 mol dm^{-3} aqueous solution of Cu(II) acetate and an adequate volume of the buffer solution were added to adjust the solution volume at the marked line. Aliquots (each 5 cm^3) were drawn out from the supernatant of the solution at appropriate intervals of immersing time to determine the amount of the Cu(II) ion adsorbed on the resin by an EDTA titration method, till the chelation reaction reached its equilibrium state. The Cu(II)-adsorbing resin was collected by filtration, and immersed in an 1 mol dm^{-3} aqueous HCl solution (10 cm^3) for 20 h to determine the amount of the Cu(II) ion desorbed from the resin. The recovered resin was repeatedly examined in three cycles of the adsorption-desorption for the Cu(II).

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