

# Preparation and Characterization of Amidoxime Resins Based on Poly(Acrylonitrile-co-Vinylidene Chloride-co-Divinylbenzene)

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## SYNOPSIS

The poly(acrylonitrile-co-vinylidene chloride-co-divinylbenzene) beads with macroporous morphology were synthesized by suspension polymerization. The use of dichloroethane as a solvating diluent resulted in copolymer beads having highly porous structures. These have been reacted with hydroxylamine in methanol, which generates amidoxime groups. The precursory resins were readily functionalized within 0.5–1 h. A detailed analysis is made of the pore structure of resins in the anhydrous state including pore size distribution and specific surface area. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Homopolymers of vinylidene chloride have not been used to any extent commercially because they have very high softening temperatures. Also, they are insoluble in common solvents. Copolymerization with another monomer avoids many of the difficulties in the handling of the homopolymer. Best known of their polymers are vinylidene chloride–vinyl chloride copolymers. In addition, vinylidene chloride copolymerizes readily with acrylonitrile. The resulting copolymers offer especially interesting possibilities in the film and textile fields. The “saran” copolymers represent a series of vinylidene chloride copolymers with vinyl chloride or acrylonitrile.<sup>1–2</sup>

Limited work on the chelating resins derived from the copolymers of vinylidene chloride with other monomers have been reported. Egawa and Maeda<sup>3</sup> prepared a number of chelating resins based upon poly(vinylidene chloride-co-divinylbenzene) by direct reaction of copolymers with ligands containing amino groups. The capacity of the chelating resins was tested for the adsorption of various metal ions such as Cu(II), Hg(II), Cd(II), Zn(II), and

Mg(II). The resins were also identified as potentially useful for separation of these metal ions.

The present research describes the preliminary efforts to provide a basis in preparing chelating resins based upon poly(acrylonitrile-co-vinylidene chloride-co-divinylbenzene) containing amidoxime groups.

## EXPERIMENTAL

### Materials

Acrylonitrile was distilled under nitrogen before use. A commercial divinylbenzene solution with a known content of divinylbenzene was shaken with NaOH solution (1 mol dm<sup>-3</sup>) three times to remove the stabilizer, three times with deionized water until the washings become alkali-free, and finally dried over silica gel. Vinylidene chloride was supplied by the Asahi Chemical Co. and used without further purification. All diluents were G.P.R. grades, used as supplied. Azobisisobutyronitrile (AIBN) purchased commercially was purified by recrystallization from ethanol prior to use as a polymerization initiator.

### Resin Syntheses and Functionalization

Poly(acrylonitrile-co-vinylidene chloride-co-divinylbenzene) and poly(acrylonitrile-co-vinylidene

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chloride) beads (symbolized as RN-VC) were synthesized by suspension polymerization. A solution of comonomers (50 mL) in diluent and polymerization initiator (AIBN 180 mmol/L monomer mixture) were suspended in a solution of Na<sub>2</sub>SO<sub>4</sub> (30 g), gelatin (0.3 g), and CaCO<sub>3</sub> (5 g) in 500 cm<sup>3</sup> of deionized water by stirring (250–280 rpm) in an autoclave. The suspension was heated to 60°C. Polymerization was carried out at 60–70°C for 4 h. Then, the suspension was heated to 90°C and kept at this temperature for 1 h. The product was filtered off and washed with HCl solution (1.0 M) to hydrolyze any adhering CaCO<sub>3</sub>, washed with deionized water until the washings are neutral to pH paper, and finally with MeOH to remove any traces of diluent. After drying, the copolymer beads with desired diameter (32–60 mesh) were selected. The amidoxime-functionalized resins (symbolized as RNH-VC) were prepared using 3% NH<sub>2</sub>OH in MeOH at 80°C. Both RN-VC and RNH-VC were purified by extraction in a Soxhlet with acetone or methanol before the chemical and spectral analyses.

### Analyses and Spectroscopy

Elemental analyses (C, H, and N) were performed on a Yanaco CHN Corder (Model MT-3) instrument. The Cl analysis was carried out by titrations with Hg(NO<sub>3</sub>)<sub>2</sub> after combustion of the sample.

The IR spectra were recorded in KBr pellets on a Jasco J-0055 spectrophotometer (400–4000 cm<sup>-1</sup>).

The specific surface areas were determined using a Yuasa Surface Area apparatus. The pore volume and the pore size distribution were obtained by mercury porosimeter with a Carlo-Erba porosimeter.

### Measurement of Anion-Exchange Capacity

A 0.5 g sample of RNH-VC and 100 mL of hydrochloric acid solution (0.1 M) were shaken at 30°C for 15 h. The anion exchange capacity of the resin was measured by determining chloride in the supernatant by means of argentometry.

### Measurement of Cation-Exchange Capacity

The resin used for the measurement of anion-exchange capacity was washed with deionized water until the washings are acid-free, air-dried, and dried at 40°C under vacuum. The resulting resin (0.25 g) and 25 mL of sodium hydroxide solution (0.1 M) were shaken at 30°C for 15 h. A 5 mL portion of supernatant was titrated with a 0.1 M solution of HNO<sub>3</sub> using methyl orange indicator. After this reached methyl orange end-point, the chloride released was titrated with a 0.05 M K<sub>2</sub>CrO<sub>4</sub> solution for the detection of end-point. The cation exchange capacity was determined by subtracting the amount of chloride from the amount of sodium hydroxide exhausted.

### Swelling Measurements

About 0.5 g of resin was weighed,  $W$  (g); after immersion in deionized water at room temperature for 24 h, the volume of wet resin  $V$  (cm<sup>3</sup>) was measured. The swelling volume  $V$  (H<sub>2</sub>O) was calculated according to the following equation:

$$\text{swelling volume} = V/W \text{ (wet-mL/dry-g)}$$

**Table I** Syntheses of RN-VC

Copolymer	AN <sup>a</sup>	VC <sup>b</sup>	DVB <sup>c</sup>	EVB <sup>d</sup>	Toluene (vol %)	Elemental Analysis (%)			
						H	N	C	Cl
RN-VC1	90	10	—	—	100	5.15	21.33	59.90	13.12
RN-VC2	90	10	—	—	80	5.03	20.18	60.25	14.03
RN-VC3	90	10	—	—	60	5.00	21.08	60.26	13.10
RN-VC4	90	10	—	—	40	5.00	21.23	60.31	13.02
RN-VC5	90	5	3	2	80	5.69	19.34	66.78	7.59
RN-VC6	86.7	5	5	3.3	100	5.86	19.29	68.62	5.78

<sup>a</sup> Acrylonitrile.

<sup>b</sup> Vinylidene chloride.

<sup>c</sup> Divinylbenzene.

<sup>d</sup> Ethylvinylbenzene (commercial divinylbenzene containing 57% DVB, a mixture of para and meta isomers, and 38% EVB was used during copolymerization).

**Table II Effect of Diluent on Specific Surface Area of RN-VC**

Copolymer	Toluene (vol %)	Specific Surface Area (m <sup>2</sup> /g)	
		32 Mesh	32-60 Mesh
RN-VC1	100	4.56	3.55
RN-VC2	80	3.60	3.25
RN-VC3	60	3.81	3.15
RN-VC4	40	4.16	4.80
RN-VC5	80	24.25	23.17
RN-VC6	100	28.93	28.25

The swelling volume  $V$  (NaCl) was measured after immersing the resin in 3% NaCl. In addition, the swelling volume of the alkali-treated resin  $V$  (NaOH) was also measured. Alkaline treatment was performed by immersing 0.5 g of resin into 50 mL of NaOH solution (1  $M$ ) at 30°C for 72 h.

## RESULTS AND DISCUSSION

### Preparation of RNH-VC

The first four copolymers of acrylonitrile and vinylidene chloride (RN-VC1, RN-VC2, RN-VC3, and RN-VC4) in Table I were synthesized using toluene (40–100 vol %) as the diluent in the absence of cross-linking agent. Also, two copolymers with 3 mol % and 5 mol % of divinylbenzene (RN-VC5 and RN-VC6) were prepared for comparison. Tables I–IV give the properties of the resins, and the structure of the cross-linked resins is shown in Scheme 1. The data in Tables II–IV showed that the lightly cross-linked copolymers (RN-VC5 and RN-VC6) and

their amidoxime derivatives (RNH-VC5 and RNH-VC6) displayed enhanced physical properties with respect to their larger specific surface area and smaller pore radius. Comparison of these data with those of noncross-linked ones allows us to see the effect of cross-linking on physical properties of the copolymer and its amidoxime derivative.

The swelling ratios of the chelating resins are illustrated in Table IV. The effect of cross-linking agent is very marked, in particular by the alkaline treatment. The absence of cross-linking agent resulted in a collapsing structure by very high swelling. The ion exchange capacities of each resin were similar as shown in Table IV.

### Effect of Diluent

The modification of polymer networks by a porogenic agent has long been known to produce significant changes in their properties.<sup>4–8</sup> The influence of various porogenic agents such as tetrachloroethane, dichloroethane, and chloroform on the properties of the lightly cross-linked copolymers of acrylonitrile–divinylbenzene and their amidoxime derivatives has already been embodied.<sup>9–10</sup> With these in mind, the suspension polymerization of acrylonitrile and vinylidene chloride was performed in the presence of various organic solvents employed as a diluent. As summarized in Table V, the use of dichloroethane resulted in resins that are characterized by a relatively large specific surface area and a small pore radius.

An attempt has been made to produce the lightly cross-linked resins that have more porous network. This was achieved by the employment of dichloroethane as a diluent. The data in Table VI show that the use of dichloroethane yielded copolymer beads

**Table III Porosities of RN-VC and Their Amidoxime Derivatives (RNH-VC)**

Copolymer	RN-VC		Resin	RNH-VC <sup>a</sup>	
	Pore Volume (cm <sup>3</sup> /g)	Average Pore Radius (Å)		Pore Volume (cm <sup>3</sup> /g)	Average Pore Radius (Å)
RN-VC1	1.164	4157	RNH-VC1	0.968	4561
RN-VC2	0.924	4429	RNH-VC2	0.924	4981
RN-VC3	0.637	2992	RNH-VC3	0.637	3372
RN-VC4	0.450	1339	RNH-VC4	0.399	1579
RN-VC5	1.133	728	RNH-VC5	0.845	976
RN-VC6	1.098	593	RNH-VC6	0.746	776

<sup>a</sup> NH<sub>2</sub>OH treatment: NH<sub>2</sub>OH/CN = 0.6, 80°C, 2 h.

**Table IV** Specific Surface Areas, Swelling Ratios, and Ion Exchange Capacities of RNH-VC

Resin <sup>a</sup>	SSA <sup>b</sup> (m <sup>2</sup> /g)	V <sub>1</sub> <sup>c</sup>	V <sub>2</sub> <sup>d</sup>	V <sub>3</sub> <sup>e</sup>	V <sub>4</sub> <sup>f</sup>	Swelling Ratios		C <sub>a</sub> <sup>g</sup> (meq/g)	C <sub>c</sub> <sup>h</sup> (meq/g)
						V <sub>2</sub> /V <sub>1</sub>	V <sub>4</sub> /V <sub>1</sub>		
RNH-VC1	2.25	2.6	3.6	3.8	30.0	1.38	11.54	3.1	1.4
RNH-VC2	2.75	2.4	3.4	3.4	23.8	1.41	9.92	3.0	1.4
RNH-VC3	2.06	2.1	3.0	2.9	21.2	1.43	10.10	3.0	1.5
RNH-VC4	3.45	1.7	2.4	2.4	20.0	1.41	11.76	3.0	1.4
RNH-VC5	14.00	2.6	3.2	3.2	6.6	1.23	2.54	3.4	1.3
RNH-VC6	16.24	2.3	3.0	3.0	5.3	1.30	2.30	3.1	1.2

<sup>a</sup> RNH-VC1: 32-mesh size, others in the range of 32–60 mesh size. NH<sub>2</sub>OH treatment: NH<sub>2</sub>OH/CN (mol ratio) = 0.6, 80°C, 2 h.

<sup>b</sup> Specific surface area.

<sup>c</sup> Dry volume.

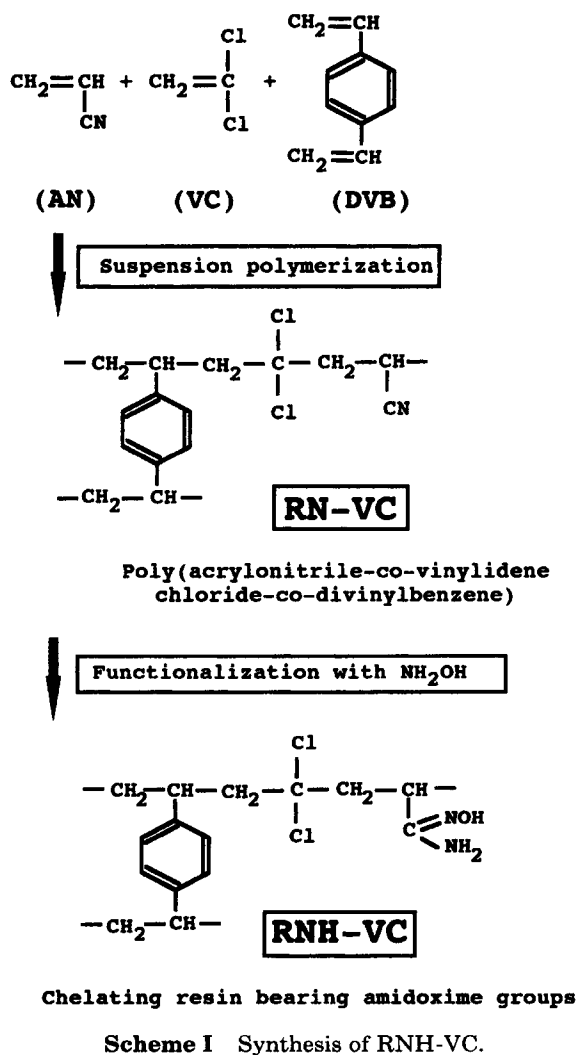
<sup>d</sup> Wet volume in deionized water.

<sup>e</sup> Wet volume in 3% NaCl.

<sup>f</sup> Wet volume in alkali (after immersing in 1M NaOH at 30°C for 72 h).

<sup>g</sup> Anion exchange capacity.

<sup>h</sup> Cation exchange capacity.



having a large specific surface area and a small pore radius.

The elemental analyses of RN-VC are given in Table VII. The sum of each analysis does not add up to 100% (i.e., 99.4, 99.4, and 99.7%, respectively). The deviations are probably caused by incomplete combustion of the sample during the chlorine analysis.

The IR spectrum of RN3-VC5 shows a very strong peak at 2230 cm<sup>-1</sup>, corresponding to the nitrile vibration. The C—Cl stretching vibration appears at 1250 cm<sup>-1</sup> [Figure 1(A)].

### Reaction Time

The functionalization of RN2-VC5 was carried out using 3% NH<sub>2</sub>OH in MeOH (NH<sub>2</sub>OH/CN (mol ratio): 1.5 : 1.0) with variations in reaction time. The data in Table VIII show that the chlorine content decreased with increasing reaction time, perhaps reflecting a possible hydrolysis of chlorine in the reaction medium. The microanalyses for C, H, and N did not give any distinct information about the resulting chemical structure. The IR spectrum of RNH3-VC5 shows that the characteristic peak corresponding to the nitrile group at 2230 cm<sup>-1</sup> disappeared remarkably after the reaction with NH<sub>2</sub>OH for 1 h. Also, the peaks at 3000–3500 cm<sup>-1</sup> (broad N—H and/or O—H stretching vibrations), 1650 cm<sup>-1</sup> (C=N stretch vibration) and 920 cm<sup>-1</sup> (N—O stretch vibration) confirmed the functionalization of RN3-VC5 [Figure 1(B)].

**Table V Specific Surface Areas and Porosities of RN-VC Synthesized Using Various Diluents**

Copolymer <sup>a</sup>	Diluent <sup>b</sup>	SSA (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Average Pore Radius (Å)
RN-VC7	Dichloroethane	5.92	0.98	2328
RN-VC8	Tetrachloroethane	5.00	0.98	4393
RN-VC9	Chloroform	3.03	1.00	4894
RN-VC10	MIBK	Powder	—	—
RN-VC11	<i>o</i> -Dichlorobenzene	3.86	1.10	3985
RN-VC12	<i>n</i> -Hexanol	Powder	—	—
RN-VC13	<i>i</i> -Amyl alcohol	Powder	—	—
RN-VC14	<i>p</i> -Xylene	3.49	0.99	4983
RN-VC15	Chlorobenzene	3.13	1.08	5080
RN-VC16	Dichloromethane	3.93	—	—
RN-VC17	Tetrachloromethane	3.43	—	—

(—): not measured.

<sup>a</sup> VC 10 mol %, DVB 0 mol %.

<sup>b</sup> 80–100 vol %.

**Table VI Specific Surface Areas and Porosities of RN-VC Synthesized Using Dichloroethane as Diluent**

Copolymer	DVB (mol %)	SSA (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Average Pore Radius (Å)
RN2-VC5	2	39.6	0.64	291
RN3-VC5	3	44.8	0.56	194
RN5-VC5	5	62.4	0.52	172

VC: 5 mol %, DVB: 2, 3, and 5 mol %, respectively. Diluent: Dichloroethane (100 vol %).

As summarized in Table IX, the specific surface area of RNH2-VC5 increased slightly up to 2 h of reaction time and then leveled off. In addition, swelling ratios of RNH2-VC5 as a function of reaction time are given in Table IX. There was almost no dependence on reaction time. However, a large swelling ratio was obtained by the alkaline treatment due to the increase in hydrophilicity.

**Table VII Elemental Microanalysis**

Copolymer	DVB (mol %)	Microanalysis (%)			
		C	H	N	Cl
RN2-VC5	2	65.70	5.59	22.15	5.94
RN3-VC5	3	66.72	5.75	21.07	5.83
RN5-VC5	5	68.00	5.97	19.27	6.41

Table X shows the properties of RNH2-VC5 as a function of reaction time. The results of porosity measurements confirmed the remarkable discrepancy with regard to pore radius and pore volume as a function of reaction time. The anion exchange ca-

**Table VIII Effect of Reaction Time on Functionalization of RN2-VC5 With NH<sub>2</sub>OH**

Reaction Time (h)	Microanalysis (%)			
	C	H	N	Cl
0.5	46.15	6.40	23.95	3.60
1	46.48	6.48	23.78	3.21
2	46.03	6.48	23.73	3.12
4	43.73	6.49	23.40	2.50
6	43.03	6.44	23.05	2.38
8	45.09	6.50	24.78	2.20

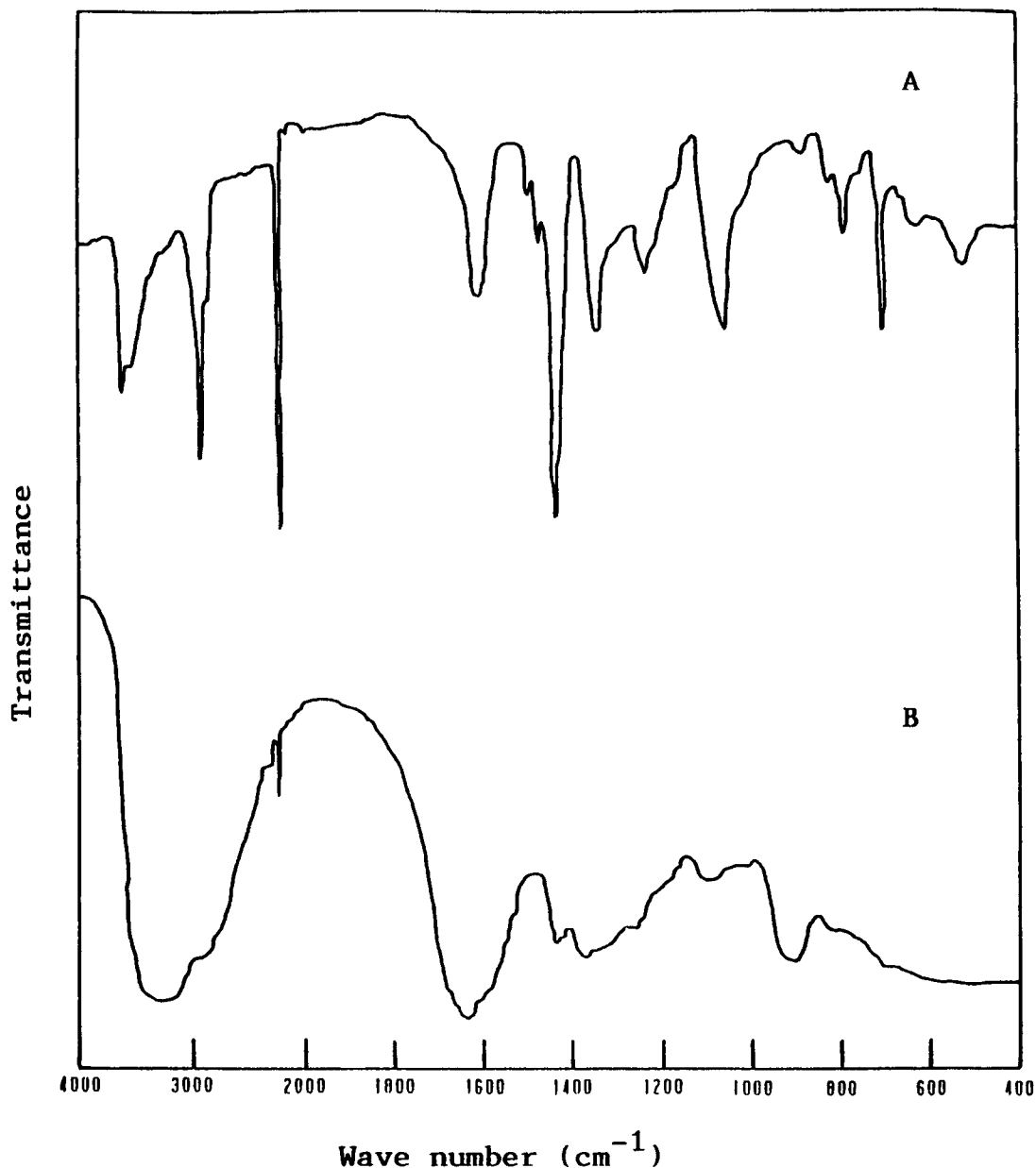


Figure 1 IR spectra: (A) RN3-VC5, (B) RNH3-VC5.

capacity did not change significantly with increasing reaction time, showing the precursory resin was readily functionalized within 0.5–1 h. A slight increase in cation exchange capacity is probably due to the hydrolysis of nitrile groups over the functionalization. The results of porosity measurements confirmed the remarkable discrepancy with regard to pore radius and pore volume as a function of reaction time.

The data summarized in Table XI refer to the

chelating resins RNH3-VC5 based on a 3 mol % cross-linked poly(acrylonitrile-*co*-vinylidene chloride-*co*-divinylbenzene). The chelating resins RNH3-VC5 behaved very similarly to RNH2-VC5 nominally 2 mol % cross-linked as a function of reaction time.

The present research has shown that the amidoxime-functionalized chelating resins based on the lightly cross-linked poly(acrylonitrile-*co*-vinylidene chloride-*co*-divinylbenzene) displayed highly porous

**Table IX Specific Surface Areas and Swelling Ratios of RNH2-VC5 as a Function of Reaction Time**

Reaction Time <sup>a</sup> (h)	SSA (m <sup>2</sup> /g)	V <sub>1</sub> <sup>b</sup> (mL/g)	V <sub>2</sub> <sup>c</sup> (mL/g)	V <sub>3</sub> <sup>d</sup>	Swelling Ratios	
					V <sub>2</sub> /V <sub>1</sub>	V <sub>3</sub> /V <sub>1</sub>
0.5	15.9	2.4	3.8	9.9	1.6	4.1
1	15.3	2.1	3.4	9.8	1.6	4.7
2	20.3	2.4	3.4	9.6	1.4	4.0
4	20.3	2.2	3.3	9.6	1.5	4.4
6	20.8	2.4	3.4	9.6	1.4	4.0
8	21.8	2.4	3.2	9.6	1.3	4.0

<sup>a</sup> NH<sub>2</sub>OH/CN (mol ratio); 1.5 : 1.0, 80°C.

<sup>b</sup> Dry volume.

<sup>c</sup> Wet volume in deionized water.

<sup>d</sup> Wet volume in 1M NaOH.

**Table XI Properties of RNH3-VC5 as a Function of Reaction Time<sup>a</sup>**

Reaction Time (h)	SSA (m <sup>2</sup> /g)	C <sub>a</sub> (meq/g)	C <sub>c</sub> (meq/g)	V-NaCl (cm <sup>3</sup> /g) <sup>b</sup>	
				NT	AT
0.5	20.9	3.7	1.9	3.0	6.6
1	19.9	4.0	2.1	3.0	6.0
2	22.9	3.9	2.2	3.0	5.7
4	24.6	4.1	2.5	3.0	5.8
6	25.4	3.8	2.5	3.0	5.8
8	26.7	3.8	2.5	3.0	6.2

NT: Nontreated resin; AT: alkali-treated resin (1M NaOH, 30°C, 72 h).

<sup>a</sup> NH<sub>2</sub>OH/CN (mole ratio): 1.5 : 1.0, 80°C.

<sup>b</sup> Volume in 3% NaCl.

**Table X Properties of RNH2-VC5 as a Function of Reaction Time**

Reaction Time (h)	Pore Volume (cm <sup>3</sup> /g)	Average Pore Radius (Å)	C <sub>a</sub> (meq/g)	C <sub>c</sub> (meq/g)
0.5	0.280	289	4.3	2.8
1	0.270	245	4.2	2.9
2	0.444	406	4.0	3.0
4	0.490	439	4.1	3.3
6	0.523	488	4.0	3.4
8	0.653	521	3.9	3.4

structure when dichloroethane is used as a porogen during the suspension copolymerization.

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