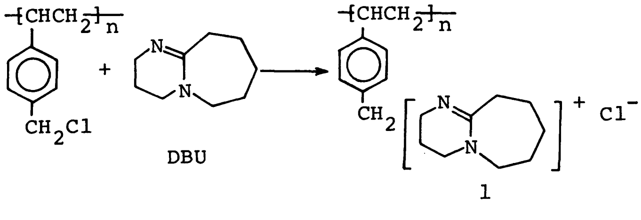
Ion Exchange Resins Anchoring 1,8-Diazabicyclo[5.4.0]undec-7-ene

Tomomichi Ishikawa* and Atsushi Yoneyama
Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, Fukasawa, Setagaya-ku, Tokyo 158

(Received September 13, 1983)

The synthesis of polymeric quaternary ammonium salts linked 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU) to chloromethylated polystyrenes is described. The polymers so obtained become anion exchangers with both quaternary ammonium and tertiary amino groups. The values of the total ion-exchange capacities indicated that the quaternization of the tertiary amino groups on the polymers with hydrochloric acid is difficult. The chloride forms of the resins, in spite of their bulky and steric quaternary ammonium groups containing DBU, were effective as ion exchangers for a variety of bulky anions such as sulfate, oxalate, hexacyanoferrate(II), hexacyanoferrate(III), and tris(oxalato) ferrate(III) ions. The free base forms of the resins gave low reactivity for chloride and sulfate ions. Some examples of the application of the resins is also reported.

Quaternary ammonium polymers have been used as ion exchange resins, catalysts and polyelectrolytes for a long time, and have also generated considerable interest in biological and medical fields in recent years.[1] The reaction of chloromethylated polystyrene with a variety of tertiary amines yields polymeric ammonium salts. On the other hand, "ionen polymers" can be prepared from tertiary diamino compounds with dihaloalkanes. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) possessing two tertiary amino groups is a potent organic base which is useful for the dehydrohalogenation of alkyl halides,[2] the *O*-alkyl cleavage of hindered methyl esters[3] and the oxidative coupling of diphenylmethanimine.[4] Because it is known that one mole of two functional compounds can be reacted with one chloromethyl group on the polymers,[5] anion exchange resins containing both strongly and weakly basic groups will be obtained by treating chloromethylated polystyrene with DBU:



1

We have studied the reactivity of these basic groups, especially the basicity of the weakly basic groups. In this paper we describe new anion exchange resins of this type which have been prepared for the first time, and the properties of these resins have been investigated.

Experimental

Materials. Chloromethylated polystyrenes were prepared by chloromethylation of soluble polystyrene (DP 1100; Asahi Dow Chem. Co.) and 2% divinylbenzene-styrene copolymer(200—400 mesh; Eastman Kodak Co.) according to Ref.[6,7] Commercial DBU (Extra Pure; Sanyo Kasei Kogyo Co.) was purified by distillation; bp 88—89 °C (400 Pa). *N,N*-Dimethylformamide(DMF) was dried by the usual method and distilled befor use. The other materials were of reagent grade.

Preparation of Quaternary Ammonium Polymers. A 300 cm³, four necked round bottomed flask equipped with a stirrer, reflux condenser, and thermometer was charged with the desired amount of chloromethylated polystyrenes, DBU, and DMF. The reaction mixture was stirred at 40 °C for 6—7 h, and then filtered (in the case of the soluble chloromethylated polystyrene, after poured into ethyl acetate) and washed several times with methanol. The product was dried under reduced pressure.

Determination of Ion-exchange Capacities. Salt splitting capacity and total ion-exchange capacity were determined by the general method[8] for strongly and weakly basic anion exchange resins.

General Method of Ion Exchange. About 0.3 g of the chloride forms of the resins was shaken overnight with 100 cm³ of 0.1 mol cm^{-3} salts aq solution, and then recovered by filtration. The resin was washed with water, dried *in vacuo* and submitted to elemental analysis.

Adsorption Measurement. Metalic Salts: About 0.3 g of the chloride forms of the resins was shaken for 4 d with 100 cm³ of 0.1 mol cm^{-3} copper(II) or mercury(II) chloride aq solution, and then recovered by filtration. The resin was washed with water, dried *in vacuo* and submitted to elemental analysis.

Iodine: About 0.1 g of the chloride forms of the resins was shaken overnight with 30 cm³ of the desired concentration of iodine-chloroform solution or iodine-potassium iodide aq solution, and then recovered by filtration. The resin was washed with water, and dried *in vacuo*. The iodine adsorbed was determined by iodometry and elemental analysis.

Results and Discussion

Quaternary Ammonium Polymers. Polymer-supported quaternary ammonium salts were prepared from polystyrenes by a route which involves chloromethylation and subsequent amination. Styrene homopolymer and 2% divinylbenzene–styrene copolymer were used in this work, because higher crosslinking and poorer swelling chloromethylated polystyrenes seem to be insufficient for practical amination with bulky amine such as DBU. Egawa and co-worker[9] also reported that the anion exchange resins derived from the styrene copolymers containing divinylbenzene of less than 2% are useful for the absorption of the metalic ions.

The chloromethylation of styrene homopolymer and 2% divinylbenzene–styrene copolymer gave two chloromethylated polymers containing 19.3 and 21.4% of chlorine, respectively. The chloromethylated polymers were treated with the various amounts of DBU. The yields of the aminated polymers were based

TABLE 1. REACTION OF DBU WITH CHLOROMETHYLATED POLYSTYRENE[a]

Run[b]	Material mol ratio DBU/CSU[c]	Product					
			Content[d]		Relative distribution of constitutional sequence[e]		
		Yield	DBU	Cl	*l*	*m*	*n*
		%	mequiv g^{-1}	mequiv g^{-1}			
1	1.69	72.5	1.91	1.84	0.078	0.548	0.374
2	1.80	76.6	2.31	2.13	0.078	0.418	0.504
3	1.00	87.3	2.78	2.74	0.078	0.228	0.694
4	1.20	94.4	2.89	2.81	0.078	0.137	0.785
5	1.50	97.7	3.10	2.90	0.078	0.055	0.867
6	2.06	97.5	3.05	2.88	0.078	0.082	0.840
7	1.49	91.9	3.04	2.98	0.170	0.006	0.824

a) At 40 °C for 6 h in DMF. b) Runs 1—6; 2% divinylbenzene-styrene copolymer, Run 7; styrene homopolymer. c) CSU : Chloromethylstyrene unit. d) Determined by elemental analysis. e) See Fig. 1.

on the chloromethylated polystyrenes. The DBU and chlorine contents of the products were determined by elemental analysis. The results are summarized in Table 1. It is apparent that the chlorine contents are in good agreement with the DBU contents which were calculated on the basis of the nitrogen contents. These results indicate that one molecule of DBU reacted with one chloromethyl group to give the ion pairs of the chloride ion with the quaternary ammonium ion. Notwithstanding that all the chloromethyl groups had reacted, they do not convert quantitatively into quaternary ammonium groups.

The IR spectrum of the quaternary ammonium polymer shows an absorption band at 3350 cm^{-1} (OH of alcohol). On the other hand, the absorption responsible for the C-Cl bond (660 cm^{-1}) in the chloromethylated polystyrenes disappeared.

From these results, all the chloromethyl groups unreacted with DBU appeared to be changed to hydroxymethyl groups by the hydrolysis, perhaps because of the presence of a small amount of water in the reaction mixture. Therefore, the constitutional sequence of the polymers obtained in this work will be presented as Fig. 1.

The value of *l*, *m*, and *n* in the Fig. 1 were determined on the basis of the chlorine contents of the original chloromethylated polystyrenes and the nitrogen contents of the aminated polymers. The results are given in Table 1. In such Runs 1—3 which were carried out in the insufficiently dehydrated DMF, the value of *m* becomes higher than those of Runs 4—7 in the almost anhydrous DMF.

The reaction of the soluble chloromethylated polystyrene with DBU was completed under homogeneous condition in DMF. However, the aminated products, which were precipitated with ethyl acetate and then dried, were insoluble in DMF, perhaps because of the formation of crosslinks.

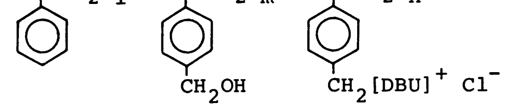


Fig. 1. Constitutional sequence.

Exchange Capacities of Basic Resins. The aminated polymers described in this paper can behave as a strongly basic anion exchanger as well as a weakly basic anion exchanger, because of the presence of both the quaternary ammonium groups and the tertiary amino groups in the polymers. The anion exchange capacities (salt splitting capacities) and total ion exchange capacities are given in Table 2. As can be seen from this table, the values of salt splitting capacity are considerably lower in comparison with the values for commercial strongly basic anion exchange resins. The salt splitting capacity was determined by titrating the sodium hydroxide which is formed according to Scheme 1.

$$\underset{\mathbf{1}}{\text{(P)-}[\text{DBU}]^{+}\text{Cl}^{-}} \xrightarrow{\text{NaOH}} \underset{\mathbf{2}}{\text{(P)-}[\text{DBU}]^{+}\text{OH}^{-}} \xrightarrow{\text{NaCl}} \underset{\mathbf{3}}{\text{(P)-}[\text{DBU}]^{+}\text{Cl}^{-}} + \text{NaOH}$$

Scheme 1.

Table 2 also gives the DBU and chlorine contents of the starting chloride form **1**, the intermediate free base form **2**, and the resulting chloride form **3** of the polymers in the Scheme 1. It was shown that **2** contained negligible chlorine, showing that all the chloride ions had been virtually displaced by hydroxide ions, while the chlorine content of **3** was extremely low in comparison with that of **1**. From these results, for this polymer the low values of salt splitting capacity seem to be ascribable to the higher selectivity of adsorption of hydroxide ion than that of chloride ion.

The total exchange capacities were calculated from the amounts of hydrochloric acid reacting with the polymer **2** according to Scheme 2.

$$\underset{\mathbf{2}}{\text{(P)-}[\text{DBU}]^{+}\text{OH}^{-}} \xrightarrow{\text{HCl}} \underset{\mathbf{4}}{\text{(P)-}[\text{DBU}]^{2+}\text{-H }2\text{Cl}^{-}}$$

Scheme 2.

Table 2. Ion-exchange capacity

Resin		SSC[c)]	TIEC[d)]	[TIEC]	Content	
					DBU	Cl
No[a)]	Form[b)]	mequiv g^{-1}	mequiv g^{-1}	2 [DBU]	mequiv g^{-1}	mequiv g^{-1}
2	1	0.61	2.62	0.567	2.31	2.13
2	2	—	—	—	2.65	0.16
2	3	—	—	—	2.58	0.41
2	4[e)]	—	—	—	2.16	2.30
4	1	0.65	3.33	0.576	2.89	2.81
5	1	0.68	3.43	0.553	3.10	2.90
7	1	0.73	3.64	0.596	3.05	2.98

a) Run number in Table 1. b) In Scheme 1. c) Salt splitting capacity. d) Total ion-exchange capacity. e) Product obtained by treating the chloride forms of the resin with hydrochloric acid.

In the Table 2 the values of the ratio of the total exchange capacities to the number of nitrogen atoms are relatively low in comparison with the value expected from the polymer **4**. This result indicates that the reaction of the tertiary amino groups on the polymer **2** with hydrochloric acid is very difficult. This appears to be caused by an electrostatic effect owing to the close contacts[10)] between the quaternary ammonium groups derived from the two tertiary amino groups on the DBU molecule.

The pK_a of DBU was 11.5, while that of the DBU bound on the polymer was 5.1, which is nearly equal to that of pyridine.

Application of Polymer Anchoring DBU. In this work, polymers anchored by bulky quaternary ammonium groups were prepared. Therefore, the ion exchange reactions with a variety of bulky anions such as sulfate, oxalate, hexacyanoferrate(II), hexacyanoferrate(III), and tris(oxalato)ferrate(III) were carried out. The chloride forms of the polymers were used in these reactions. The results are given in Table 3. In the determination of the ion exchange capacity, a difference of less than 5% was found between the values determined by elemental analysis of the Na_2SO_4-treated polymer and by titration of the sodium chloride produced in the solution after treatment. For potassium hexacyanoferrate(III), moreover, the value determined by iodometry of $K_3[Fe(CN)_6]$ remaining in the solution after the treatment was in near agreement with that by elemental analysis of the treated polymer. Therefore, in the other cases the exchange capacities were determined by elemental analysis. The results show that the polymers allow an ion exchange reaction with each bulky anion.

Table 3. Ion exchange with various salts[a)]

Salt used	Ion exchange capacity[b)]	Content of Cl[b)]
	mequiv g^{-1}	mequiv g^{-1}
Na_2SO_4	1.22 (1.17)[c)]	0.33
$Na_4[Fe(CN)_6]$	0.691	0.11
$K_3[Fe(CN)_6]$	0.852 (0.888)[c)]	0.30
$(NH_4)_3[Fe(C_2O_4)_3]$	0.730	0.34
$Na_2C_2O_4$	1.43	0.21
$(NH_4)_2C_2O_4$	1.45	0.13

a) The chloride forms of the resin containing 2.89 mequiv g^{-1} of DBU was used. b) Determined by elemental analysis. c) Determined by volumetric analysis.

The absorption of metalic ions with the anion exchange resin bound tetraethylenepentamine has been investigated[9)] at various pH values. It is found that the absorption increases with an increase of the pH value; at pH 4.5, it is nearly maximized in mercury(II) chloride but reaches only half a maximum value in copper(II) chloride. Table 4 gives the DBU and chlorine contents of the products obtained by treating the chloride forms

Table 4. Adsorption of $CuCl_2$ and $HgCl_2$[a)]

Salt used	pH	Content	
		DBU	Cl
		mequiv g^{-1}	mequiv g^{-1}
$CuCl_2$	4.5	2.84	2.80
$HgCl_2$	4.2	1.78	2.30

a) The chloride forms of the resin containing 2.89 mequiv g^{-1} of DBU was used.

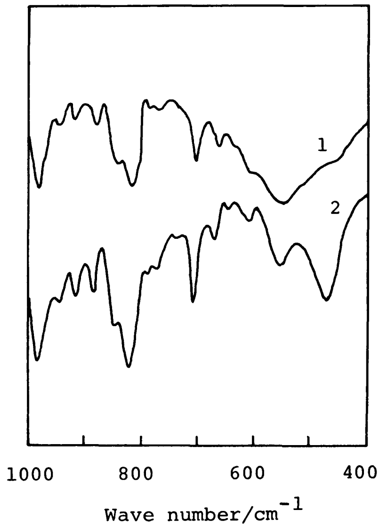


Fig. 2. IR spectra of the polymers.
1: Starting polymer. 2: Polymer treated with $HgCl_2$.

TABLE 5. ADSORPTION OF IODINE a)

Meterial mole ratio I_2/DBU	Solvent	Observed ratio	
		I/DBU b)	I/DBU c)
0.471	$CHCl_3$	0.924	0.924
1.09	$CHCl_3$	1.69	1.67
1.42	$CHCl_3$	1.94	1.80
1.89	$CHCl_3$	1.98	1.92
1.81	KI aq	3.05	1.82

a) The chloride forms of the resin containing 2.89 mequiv g^{-1} of DBU was used. b) Determined by elemental analysis. c) Determined by iodometry.

of the aminated polymers with aqueous solutions of mercury(II) or copper(II) chloride at pH 4—5. The values were determined by elemental analysis. The product obtained by treatment with mercury(II) chloride gave a lower DBU content than for the starting polymer. The IR spectrum of this product is shown in Fig. 2; it indicates the characteristic absorption band at 460 cm^{-3}, perhaps on $\nu_{\text{N-Hg}}$ 11), which is not observed for the starting polymers. These results are probably associated with the formation of a polymer–mercury complex. The mercury content of the product determined by atomic absorption analysis was 2.13 mequiv g^{-1}, which is reasonably consistent with that calculated from the nitrogen content. On the other hand, in the case of copper(II) chloride the DBU and chlorine contents of the product are almost consistent with those of the starting polymer. Both the starting and $CuCl_2$-treated polymers gave identical IR spectra. These results indicate that this resin can be used for separation of mercury and copper ions.

The reaction of iodine with the chloride forms of the aminated polymers was carried out in chloroform or in aqueous solution of potassium iodide. The amounts of iodine adsorbed were determined by elemental analysis and iodometry. The values of the ratio of iodine atoms to one DBU-moiety in the polymers are given in Table 5. In chloroform, the values by iodometry were closely consistent with those calculated from the nitrogen content. In this case, about one molecule of iodine seems to be adsorbed with one DBU-moiety on the polymers. On the other hand, in the KI aq solution the value I/DBU by elemental analysis is about one and a half times the number of the value by iodometry. This result indicates that the chloride ions on the polymer were displaced with triiodide ions formed from iodine and potassium iodide.

References.

1) "Polymeric Amines and Ammonium Salts," ed by J. Goethals, International Symposium on Polymeric Amines and Ammonium Salts, Ghent, Belgium, September 1979, IUPAC Publication, Pergamon, London (1980).

2) H. Oediger and Fr. Moler, *Angew. Chem., Int. Ed. Engl.*, **6**, 76 (1967).

3) E. J. Parish and D. H. Miles, *J. Org. Chem.*, **38**, 1223 (1973).

4) H. Hayashi, T. Tanaka, N. Shigemoto, and T. Okazaki, *Chem. Lett.*, **1977**, 981.

5) C. C. Leznoff and J. Y. Wong, *Can. J. Chem.*, **50**, 2892 (1972).

6) G. D. Jones, *Ind. Eng. Chem.*, **44**, 2686 (1952).

7) R. S. Feimberg and R. B. Merrifield, *Tetrahedron*, **30**, 3209 (1974).

8) "Kinosei-Kobunshi," in "Kobunshi-Jikkengaku," 1st ed by S. Kambara, Kyoritsu-Shuppan, Tokyo (1974), Vol. 7, Chap. 1, p. 25.

9) H. Egawa and H. Saheki, *Kogyo Kagaku Zasshi*, **74**, 772 (1971).

10) A. Rembaum, *J. Polym. Sci.*, **B6**, 159 (1968).

11) K. Ueno and A. E. Matell, *J. Phys. Chem.*, **59**, 998 (1955); **60**, 934, 1270 (1956); S. Mizushima, I. Nakagawa, and D. M. Sweeny, *ibid.*, **25**, 1006 (1956).