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Aminobutadienes. XIII. Anion-exchange Resins from Imidobutadiene Polymers[1]

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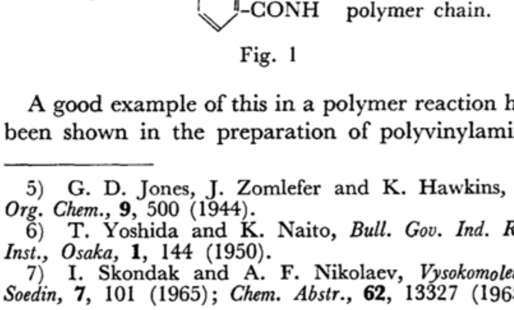
A method of preparing new-type anion-exchange resins from 1-phthalimido-, 1-succinimido-, and 2-phthalimido-1,3-butadiene polymers is shown. The procedure consists of two steps, the hydrolysis of the imido groups into free amine, followed by heating with hydrochloric acid to make the amino groups into the hydrochloride, and *N*-methylation by the Schotten-Baumann method. The anion-exchange resins obtained from the former two polymers show high exchange capacities, such as 5.85 and 7.21 meq/g of dry resin respectively. However, their salt-splitting capacities are not high. The mechanisms of their crosslinking on hydrolysis and of their heat-aging are also discussed.

During the studies of aminobutadiene chemistry which have been carried out in our laboratory, we attempted to prepare a new type of anion-exchange resin from the imidobutadiene polymers we had previously obtained. For the use of anion-exchange resin, a high exchange capacity per unit of volume is the chief requirement. From this point of view, it would be advantageous to use a monomer which had an amino group in a highly concentrated state per unit of weight. Since 2-phthalimido-1,3-butadiene (2-PB), on bulk polymerization by radical initiators, usually affords a tough resin as a homogeneous gel, as has already been reported,[3] we initially thought that the use of gelation agents such as divinylbenzene, divinylether, and divinylsulfide for the formation of crosslinkage in the 2-PB polymer could be unnecessary, and also that the gelation tendency of the 2-PB monomer itself was the most convenient way to introduce the exchange groups into the resin particles in a high concentration. On the other hand, in the case of 1-phthalimido-1,3-butadiene (1-PB) and 1-succinimido-1,3-butadiene (1-SB) polymers, it was usually possible to prepare soluble polymers.[4] However, insoluble gels were always afforded in the hydrolysis stage of their imido groups; this would also facilitate the preparation of the crosslinked polymers of anion-exchange-resin particles.

Although imido groups as those used here for the protection of the primary amino group can be altered into the corresponding primary amino group by a somewhat severe hydrolysis using either strong acid or alkali, hydrazinolysis by heating with hydrazine hydrate is a more effective and more moderate method for the same purpose. Several workers[5-7] have recommended the use of hydrazinolysis in preparing primary amino compounds from the corresponding phthalimides. The procedure usually consists of two cources. The first is hydrazinolysis, which gives primary amine and phthalhydrazide, commonly less soluble in solvents, while the second is treatment by hydrochloric acid, which changes the free amine into hydrochloride usually soluble in water. If a large excess of hydrazine is used, the formation of primary amine will be encouraged, as may be seen in Fig. 1.



where R shows the residual polymer chain.

Fig. 1

A good example of this in a polymer reaction has been shown in the preparation of polyvinylamine

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[1] Partly reported in Japanese Patent 468683 (March 12, 1966).

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[3] K. Murata and A. Terada, *J. Polymer Sci., A*-1, **4**, 2989 (1966).

[4] A. Terada and K. Murata, *ibid., A*-1, **5**, 2219 (1967).

[5] G. D. Jones, J. Zomlefer and K. Hawkins, *J. Org. Chem.*, **9**, 500 (1944).

[6] T. Yoshida and K. Naito, *Bull. Gov. Ind. Res. Inst., Osaka*, **1**, 144 (1950).

[7] I. Skondak and A. F. Nikolaev, *Vysokomolekul Soedin*, **7**, 101 (1965); *Chem. Abstr.*, **62**, 13327 (1965).

from polyvinylphthalimide;[6] it was concluded that the reaction took place quantitatively.

The present paper deals with the hydrazinolysis of our imidobutadiene polymers and with the following quaternarization to make a new type of anion-exchange resin.

Experimental

Materials. Polymers of 1-PB, 1-SB, and 2-PB, and a copolymer of 2-PB with *N*-vinylphthalimide were prepared by radical polymerization, either in bulk or in solution process, according to the method previously reported (see also the footnotes of Table 1).[3,4]

Nitrogen Analysis. The nitrogen contents of the starting and the resulting polymers were determined by the usual Micro-Dumas method.

Hydrolysis of Imidobutadiene Polymer. On the hydrolysis of the imidobutadiene polymers, the following convenient type of procedure was usually carried out. For example, a mixture of 0.74 g of the 1-PB polymer and 16 m*l* of 80% hydrazine hydrate was refluxed for 15 hr. The mixture, which was a clear solution in the first stage of the reaction, coagulated after a while, and then a sponge-like mass separated. This cake was repeatedly washed with water to remove the excess hydrazine, and was then heated in 15 m*l* of 20% hydrochloric acid in a boiling-water bath for 6 hr to convert the free aminobutadiene polymer to the corresponding hydrochloride and to remove any phthalhydrazide formed. After the hydrochloride had been repeatedly washed with water, it was immersed in a large amount of 5% aqueous sodium hydroxide and gently heated for a while so as to generate free amine again; then it was repeatedly washed with hot water to remove any alkali and dried under a vacuum at room temperature. The yield was 0.23 g.

***N*-Methylation of Aminobutadiene Polymer.** A sample of 0.21 g of aminobutadiene resin, in a dried free-amine form, in 15 m*l* of ethanol was methylated with 5 g of methyl iodide by the Schotten-Baumann method in the presence of a small excess of 10% alcoholic potassium hydroxide. After the mixture had been refluxed for 10 hr, the resin was collected on a glass filter and washed with water. The resulting I-type resin was converted to the OH-type resin by treating it with 5% aqueous potassium hydroxide, and finally to the Cl-type resin by treating it with hydrochloric acid. This resin was then sufficiently washed with ethanol and dried under a vacuum at room temperature over potassium hydroxide pellets. The yield was 0.34 g.

Determination of Salt-splitting Capacity. A sample of dried Cl-type resin, exactly weighed and found to be from 100 to 200 mg, was immersed in 100 m*l* of 1 N sodium hydroxide for 24 hr at room temperature, and then repeatedly washed with water to remove the excess alkali. The resin was immersed in 100 m*l* of 1 N sodium chloride for 24 hr, gathered on a glass filter, and repeatedly washed with other portions of 1 N sodium chloride; the final volume of the filtrate with the gathered washings was then exactly adjusted to 200 m*l* using a volumetric flask. A 50 m*l* portion of the solution was titrated with 0.1 N hydrochloric acid in the presence of a methyl orange indicator to determine the amount of free alkali.

Determination of Total Anion-exchange Capacity. The sample used in the above salt-splitting-capacity determination was again immersed in 100 m*l* of 1 N hydrochloric acid for 24 hr, washed completely with methanol until the washings became neutral to remove the excess acid, and then immersed in 100 m*l* of 1 N sodium sulfate for 24 hr. The resin was repeatedly washed with other portions of 1 N sodium sulfate, after which the total volume of the filtrate and the washings was exactly adjusted to 200 m*l*. A 50 m*l* portion of the solution was titrated as usual with 0.1 N silver nitrate to determine the quantity of free chloride ions present.

Aging Test of the Cl-type Resin. The aging test of the *N*-methylated resin at room temperature and on heating under an atmospheric pressure was carried out using two different samples, which had been obtained from 1-PB and 1-SB polymers respectively. Both samples were successively heated at 60, 90 120, 150, and 180°C in that order for 24-hr periods; at the end of each heating step, the total anion-exchange and salt-splitting capacities were measured as mentioned.

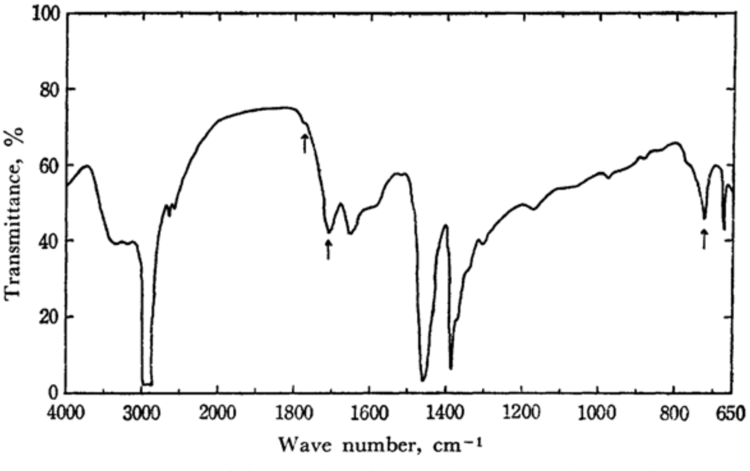
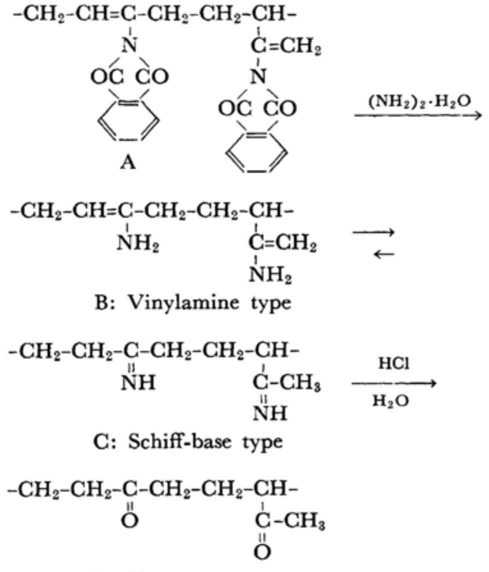


Fig. 2. Infrared spectrum of 2-aminobutadiene polymer (sample No. 6) in Nujol paste.

Results and Discussion

The hydrazinolysis and subsequent hydrochloric acid treatment of the 1-PB and 1-SB polymers gave crosslinked aminobutadiene polymers in good yields; they could be recognized as almost pure samples by their nitrogen contents. In the case of the 2-PB polymer, however, this treatment was unsatisfactory, giving a quite different result. The hydrolysis of the 2-PB polymer did not take place smoothly, and the resulting aminobutadiene polymer had less nitrogen content than in the other cases. Moreover, the yields were low, as Table 1 shows. This low yield seems to indicate a considerable loss of the used sample during the hydrolysis procedures.

Their low nitrogen contents may be considered to indicate a difficulty in the hydrolysis of the phthalimido group in the 2-PB polymer, because the infrared spectrum of the sample No. 6, for example, leaves phthalimido-carbonyl bands at 1770 (shoulder) and 1710 cm^{-1} and an *O*-disubstituted benzene band at 725 cm^{-1}, as is shown in Fig. 2. On the other hand, the 2-PB polymer, on hydrolysis, always gives a vinylamine structure in each of monomer unit, and this structure is generally in an equilibrium state with the ketimine structure—indeed, the latter form is usually preferable (Fig. 3, B and C).[8] This ketimine can be easily hydrolyzed partially with the concentrated hydrochloric acid of the post-treatment, and affords a ketone structure, which must reduced the nitrogen content of the resulting polymer less than the original one. On the direct hydrolysis of the 2-PB polymer with concentrated hydrochloric acid or 10% aqueous sodium hydroxide, the resulting polymers showed nitrogen contents of 1.92 and 2.62% respectively. This may show phthalimide elimination during hydrolysis, as is shown in Fig. 4, because of the phthalimido group attached to the carbon of the double bond.



B: Vinylamine type

C: Schiff-base type

D: Ketone type

Fig. 3.

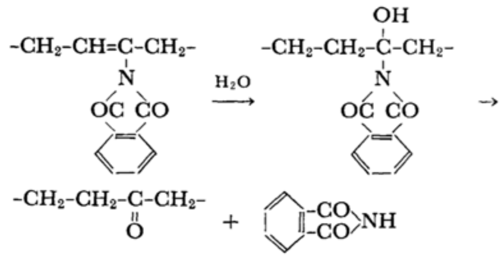


Fig. 4.

Also, both the 1-PB and 1-SB polymers contain approximately 80% of the 1,4-configuration and 20% of the 3,4-configuration.[4] On hydrolysis, the structure of the latter configuration should afford an aldmine structure analogous to that above. As to the crosslinking of these hydrolyzed polymers, some assumptions are possible. Some of these aldmine and ketimine will preferentially react with hydrazine to form their hydrazones by exchange reactions,[9] and these ammonia- and hydrazine-derivatives of the carbonyl groups will partially react with each other to form intra- and inter-molecular crosslinking spontaneously,[10] as with the samples shown in Fig. 5. Carbon-carbon condensations of the aldol type often occur if there is an α-methylene group.[10]

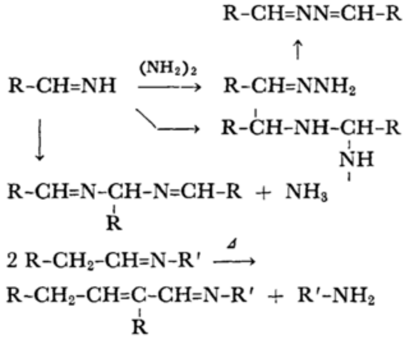


Fig. 5.

The results of the *N*-methylation of the aminobutadiene polymers obtained from the above hydrolysis are shown in Table 2. Their total anion-exchange capacities were in the range between 2.6 and 7.2 meq/g of dry resin; however, their salt-splitting capacities were not high. For

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[8] For example, P. A. S. Smith, "The Chemistry of Open-chain Organic Nitrogen Compounds," Vol. I, W. A. Benjamin, New York (1965), p. 295.

[9] Ref. 8, p. 301.

[10] Ref. 8, p. 298.

TABLE 1. HYDROLYSIS OF IMIDOBUTADIENE POLYMERS[a]

Sample No.	Polymer[b] (g)		Hydrazine hydrate (ml)	Reaction time (hr)	Yield (g)	Nitrogen[h] content (%)	Yield as amino-butadiene polymer (%)
1	1-PB[c]	0.74	16	15	0.23	19.71	89
2	1-SB[d]	0.77	16	15	0.22	21.29 21.03	82
3	2-PB[e]	0.17	5	15	—	7.00 7.06	—
4	2-PB[e]	0.57	10	24	0.15	9.16 9.34	75
5	2-PB[f]	0.34	8	15	0.08	10.11	67
6	2-PB[f]	1.00	15	15	0.21	9.10 9.01	60
7	2-PB-VPI copolymer[g]	0.82	10	20	0.15	15.46 15.32	56[i]

a) The reactions were usually carried out under reflux, except in the case of No. 4. The reaction temperature for No. 4 was 180°C in a sealed tube. Each of sample numbers used from Table 1 through Table 3 indicate the same sample.

b) All the polymers were prepared by radical polymerization, using benzoyl peroxide as an initiator.

c) Obtained at 116°C in a bulk state, $\eta_{sp}/c=3.0$.

d) Obtained at 60°C in an acetylene tetrachloride solution, $\eta_{sp}/c=0.35$.

e) Obtained at 85°C in a bulk state.

f) Obtained at 60°C in an acetylene tetrahloride solution, $\eta_{sp}/c=1.0$.

g) Obtained by the copolymerization of 2-PB with *N*-vinylphthalimide at 60°C in an acetylene tetrachloride solution, N%; 7.22, 7.27%.

h) The theoretical nitrogen contents of phthalimidobobutadiene, succinimidobutadiene, and aminobutadiene polymers are 7.03, 9.27, and 20.27%, respectively.

i) Calculated on the assumption that this product is the homopolymer of 2-aminobutadiene.

TABLE 2. *N*-METHYLATION OF AMINOBUTADIENE POLYMERS[a] AND THEIR ANION-EXCHANGE CAPACITIES

Sample No.	Weight (g)	Methyl iodide (g)	Ethanol (ml)	Reaction time (hr)	Yield[b] (g)	Nitrogen[c] content (%)	Total anion-exchange capacity (meq/g of dry resin)
1	0.21	10	15	10	0.28	11.87 11.46	5.85
2	0.21	5	15	10	0.34	11.28 11.54	7.21
4	0.11	5	8	10	0.12	7.37 7.85	3.22
5	0.07	5	7	10	0.09	6.87 7.14	2.62
6	0.13	5	10	14	0.20	8.57	3.52

a) The reactions were carried out under reflux.

b) The yields show those of the Cl-type resins.

c) As Cl-type resins vacuum-dried at room temperature.

TABLE 3. HEAT-AGING TEST OF *N*-METHYLATED RESIN HYDROCHLORIDES

Temperature (°C)	Sample No. 1		Sample No. 2	
	Salt-splitting capacity (meq/g of dry resin)	Total anion-exchange capacity (meq/g of dry resin)	Salt-splitting capacity (meq/g of dry resin)	Total anion-exchange capacity (meq/g of dry resin)
60	1.19	5.83	1.05	6.78
90	0.52	5.36	0.69	5.85
120	0.38	4.80	0.53	5.09
150	0.20	4.43	0.31	4.65
180	—	2.85	—	3.08

example, sample No. 1 showed a value of 0.84, while No. 2 showed 1.01 meq/g of dry resin.

The aging test of the *N*-methylated resin hydrochlorides showed that the usual keepting of them for two years under an atmospheric pressure and at room temperature was harmless to their total anion-exchange capacities. Table 3 shows the results of the heat-aging test.

The more rapid decrease in the rate of the salt-splitting capacity than in the rate of the total anion-exchange capacity indicates that there is a methyl chloride elimination[11] from a quaternary ammonium chloride group which reduces the salt-splitting capacity.

The authors wish to thank Professor Shizunobu Hashimoto of Doshisha University and Dr. Isao Shiihara of this Institute for their helpful suggestions during this work.

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[11] I. T. Millar and H. D. Springall, "Sidgwick's Organic Chemistry of Nitrogen," Clarendon Press, Oxford (1966), p. 114.