[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

Variable Capacity Anion Exchange Resins from Quaternized Diimethylaminostyrene-styrene Bead Copolymers

BY RICHARD H. WILEY AND J. M. SCHMITT

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A series of bead copolymers of dimethylaminostyrene and styrene cross-linked with 1–20% of divinylbenzene have been quaternized with methyl iodide at room temperature. Divinylbenzene cross-linked (10%) resins having exchange capacities of 1.47, 2.35, 2.80 and 3.00 meq./g. are described. These capacity values are in agreement with theoretical values calculated on the basis of the copolymer composition and establish 96–100% effective quaternization. Partially quaternized resins, quaternized by previously described techniques which give no more than 52% of the theoretical amount of quaternization, can be quaternized up to 88% of the theoretical amount by additional treatment with methyl iodide at room temperature.

In previous communications[1] we have stated the basis for the interest in series of ion exchange resins which have the same exchange group distributed at varying intervals along the polymer chain. Previous studies of polymers of this type have been made only with cation exchange units on the chain. We now wish to report the successful preparation and characterization of a series of anion exchange cross-linked bead polymers of variable capacity along with data obtained in the course of these studies which makes possible the preparation of new types of high capacity anion exchange resins.

There are three obvious methods for the preparation of strongly basic anion exchange resins. The commercial polymers are prepared by trimethylamine quaternization of chloromethylated styrene–divinylbenzene copolymer. In this process the maximum capacity of the resins is limited by the degree to which chloromethylation can be achieved. It is also possible to quaternize cross-linked dimethylaminostyrene–styrene copolymers[2a] but such resins, prepared as previously reported, have capacities indicating that only one in four dimethylamino groups is quaternized.[2b] A third possibility lies in polymerizing a monomer containing quaternary groups. The maximum capacities achieved by such techniques using allylic quaternary salts have not exceeded 3.89 meq./g. or 76.7% of the theoretical value.[3]

Of these preparative methods, the most attractive in terms of preparing polymers with varying distribution of the ionic groups along the chain, appears to be that of quaternizing cross-linked copolymers of dimethylaminostyrene with styrene. The most obvious advantage of this method is that the copolymerization reactivity ratios of these two monomers are known[4] to be nearly equivalent ($r_1 = 1.02$, $r_2 = 0.84$) so that the monomer units will be fairly evenly distributed along the copolymer chain in a series of copolymers prepared from different ratios of monomers. This is important in providing a uniform dilution of the charge density. The most obvious disadvantage is that no one has previously obtained quantitative quaternization of the dimethylamino groups. Unless complete quaternization can be achieved the exchange resin obviously would consist of a mixture of weak and strong base exchange units making interpretations of exchange data complicated if not impossible. There remains also the minor problem of devising a satisfactory method for the bead copolymerization of these monomers.

We have prepared a series of bead copolymers of dimethylaminostyrene and styrene containing 1, 5, 10 and 20 mole per cent. divinylbenzene as cross-linking agent. The bead copolymerization is conveniently carried out in aqueous suspensions at 80° using 0.1% polyvinyl alcohol as dispersing agent and azo-bis-(isobutyronitrile) as initiator. Yields of 66–90% of copolymer beads regularly were obtained. The data for the series of copolymers are summarized in Table I.

TABLE I

BEAD COPOLYMERS FROM *p*-DIMETHYLAMINOSTYRENE, STYRENE AND DIVINYLBENZENE

o.	Mole[a] ratio	DMAS[b]	S[c]	DVB[d]	EVB[e]	Yield, %
1	90/10	8.50	..	0.84[f]	0.84	90
2	75/25	6.00	0.79	.79[f]	.79	80
3	50/50	3.97	2.19	.78[f]	.78	66
4	25/75	2.00	3.63	.78[f]	.78	90
5	50/50	6.00	4.16	.11[g]	.11	70
6	50/50	4.50	2.83	.43[h]	.43	80
7	50/50	3.97	1.42	1.76[i]	1.76	90
8	90/10	8.50	..	0.84[f]	0.84	90[j]
9	75/25	4.41	0.58	.58[f]	.58	83[k]
10	50/50	3.50	1.93	.69[f]	.69	90[l]
11	25/75	2.00	3.63	.78[f]	.78	90[m]

[a] Mole per cent. *p*-dimethylaminostyrene to styrene. Ethylvinylbenzene added with divinylbenzene is included in the quantity expressed as styrene. [b] *p*-Dimethylaminostyrene, grams. [c] Styrene, grams. [d] Divinylbenzene, grams. [e] Ethylvinylbenzene, grams. [f] 10 mole per cent. [g] 1 mole per cent. [h] 5 mole per cent. [i] 20 mole per cent. [j] *Anal.* Calcd.: N, 7.95. Found: N, 8.05. [k] *Anal.* Calcd.: N, 6.85. Found: N, 7.17. [l] *Anal.* Calcd.: C, 86.58; H, 8.52. Found: C, 85.43; H, 8.57. [m] *Anal.* Calcd.: C, 89.17; H, 8.18. Found: C, 88.88; H, 8.41.

The quaternization of these copolymers has been studied under a variety of conditions with the results listed in Table II. The available data establish that the exchange capacity of these quaternized resins decreases as the time during which quaternization is carried on is lengthened. This can be illustrated with the data for polymers number 1 and 8 both of which are dimethylaminostyrene polymers. Quaternization for 22 hours with di-

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[1] Richard H. Wiley and S. F. Reed, Jr., *J. Phys. Chem.*, **60**, 533 (1956); Richard H. Wiley and S. F. Reed, Jr., THIS JOURNAL, **78**, 2171 (1956); Richard H. Wiley and J. M. Schmitt, *ibid.*, **78**, 2169 (1956).

[2] (a) E. L. Kropa, U. S. Patent 2,663,702 (1953); (b) it has been pointed out by a Referee that commercial resins are 90% quaternized.

[3] G. B. Butler, *et al.*, THIS JOURNAL, **76**, 2418 (1954); **78**, 4797 (1956).

[4] C. Walling, *et al.*, *ibid.*, **70**, 1537 (1948).

methyl sulfate at 110° is 52% complete; for 144 hours this drops to 20%. Similarly the 50/50 copolymers number 3 and 5 showed 52% quaternization after 4 hours and a drop to 41% after 48 hours. Without respect to the copolymer composition, quaternization for 4 hours is about 52% complete; for 22 hours, 49 to 52%; for 48 hours, 41%; and for 144 hours, 20 to 25% complete. If one reduces the temperature to 80° and runs the quaternization in the presence of bicarbonate for 48 hours, the reaction is only 30% complete. If, however, such partially quaternized resins are retreated with methyl iodide at room temperature the capacity can be increased significantly—in some cases doubled, in others raised to 88% of theoretical.

TABLE II

QUATERNIZATION AND TOTAL CAPACITY OF CROSS-LINKED DIMETHYLAMINOSTYRENE–STYRENE RESINS

No.[a]	Quaternization[b] Methyl sulfate[c]	Quaternization[b] Methyl iodide[d]	Capacity[e] Calcd.	Capacity[e] Obsd.
1	52(22)		3.14	1.63T
1[f]	(22)	80(48)	3.14	2.50W
2	49(22)		2.88	1.41T
2[f]	(22)	88(48)	2.88	2.53W
3	52(4)		2.33	1.21T
3[f]	(4)	83(48)	2.33	1.93W
4[f]	(22)	51(48)	1.49	0.73W
5	41(48)		2.52	1.04T
5[f]	(48)	58(96)	2.52	1.47W
6[f]	(48)	53(96)	2.44	1.28W
7[f]	(22)	81(48)	2.12	1.72W
8	29(48)[g]		3.14	0.91W
8	20(144)		3.14	0.63W
8[f]	(144)	54(48)	3.14	1.70W
8		96(24)	3.14	3.00W[h]
9		97(24)	2.88	2.80W[h]
10		100(24)	2.33	2.35W
11	30(48)[g]		1.49	0.45W
11	25(144)		1.49	0.37W
11[f]	(144)	54(48)	1.49	0.79W
11		99(24)	1.49	1.47W[h]

[a] Numbers correspond to those in Table I. [b] Per cent. quaternization; time in hours in parentheses. [c] Procedure a. [d] Procedure c. [e] Meq./g.; T, titration method; W, weight difference method. [f] Quaternized first with methyl sulfate; then with methyl iodide. [g] Procedure b. [h] The capacities of these resins also has been determined as follows. The resins were converted to the chloride form with excess hydrochloric acid, and dried at 65° *in vacuo*. The chloride, from weighed samples, was then eluted with sodium nitrate and titrated with silver nitrate to give these capacities as calculated for the chloride form. Calcd. for no. 8, 4.15 meq./g., found 4.08; calcd. for no. 9, 3.77 meq./g., found 3.59; calcd. for no. 11, 1.70 meq./g., found 1.63. The authors are indebted to Dr. Siegfried Lindenbaum, Oak Ridge National Laboratories, for these data.

The observations that a slight increase in percentage quaternization apparently resulted on lowering the temperature from 110 to 80° and that significantly increased quaternization took place at room temperature prompted the quaternization of a series of copolymer beads (numbers 8, 9, 10 and 11) at room temperature. The results given in Table II establish that these conditions afford 96–100% complete quaternization. The cross-linked copolymer beads thus obtained provide the type of uniformity in varied charge distribution required for the study of relations between selectivity coefficients and copolymer composition. The distribution of the ionic charge is probably uniform over the length of the polymer chain and the type of exchange unit is quantitatively uniform. Studies of the selectivity coefficients will be conducted elsewhere. It further appears from these studies that the capacity of quaternary salt copolymers useful as exchange resins can be greatly increased using more efficient quaternization procedures—particularly lower temperatures.

A white haze is formed and minute quantities of a white solid deposit during the first few moments that methyl iodide comes in contact with the dimethylaminostyrene copolymers. This solid material was isolated and identified as the methiodide of dimethylaminostyrene by comparison of its infrared spectrum with that of a sample prepared from the monomer and methyl iodide. Apparently traces of unpolymerized monomer contained in the copolymer are extracted by the methyl iodide. These could not have been greater than trace quantities; otherwise the measured and theoretical capacities would have differed by amounts greater than those observed.

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Experimental[5]

p-N,N-Dimethylaminostyrene was prepared by a modification of the previously described method.[6] The carbinol was dehydrated by flash distillation at 150° under vacuum. This procedure gave reproducible 50% yields of redistilled monomer, b.p. 77–78° (2 mm.), $n^{27}\text{D}$ 1.6097, m.p. 16.5°. The monomer was stored at −20° and redistilled just prior to use. Styrene also was distilled at reduced pressure just prior to use. Divinylbenzene solution (Koppers Co.) containing 50% of divinylbenzene in ethylvinylbenzene was washed three times with 5% sodium hydroxide to remove stabilizer, washed with water, and dried over magnesium sulfate prior to use. The nitrogen was freed of oxygen by passing through alkaline β-anthraquinone sulfonate–sodium hydrosulfite solution.

Polymerizations.—The following procedure was used for the preparation of the polymers and copolymers listed in Table I. All operations were carried out under oxygen-free nitrogen.

A 200-ml., three-necked flask equipped with stirrer and nitrogen inlet and outlet connections was placed in a constant temperature bath at 80°. To this flask was added a solution of 0.051 g. of polyvinyl alcohol (du Pont Elvanol 50–42) in 51 ml. of distilled water, a solution of 8.5 g. (0.0577 mole) of *p*-dimethylaminostyrene, 1.68 g. of 50% divinylbenzene solution (0.84 g. of divinylbenzene or 10 mole per cent. and 0.84 g. of ethylvinylbenzene) and 0.0093 g. (0.1%) of the weight of monomers of azobis-isobutyronitrile. The stirrer speed was adjusted for the size beads desired. After 48 hours at 80° the beads were heated to 110° for an additional 48 hours. The hard, transparent, amber beads were collected on a filter, washed with ether, and dried. The yield of beads was 90% of the weight of the monomers charged.

Quarternization of the Resins.—Three procedures were used. The data are summarized in Table II. Typical procedures are described.

(a) **With Dimethyl Sulfate.**—The ratio of dimethyl sulfate to dimethylamino groups used was twenty-to-one. A mixture of 4.56 g. of beads of resin 1 (Table I) and 64.89 g. of dimethyl sulfate was heated in a stoppered flask at 110° for 22 hours. The beads were washed with water to remove

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(5) Analyses by Micro Tech Laboratories, Skokie, Ill.

(6) C. S. Marvel, *et al.*, THIS JOURNAL, **68**, 736 (1946); R. W. Strassburg, *et al.*, *ibid.*, **69**, 2141 (1947).

excess dimethyl sulfate and dried. Alterations in reaction time of from 4 to 144 hours gave 20–52% complete quaternization. Requaternization according to procedure c below gave the increased values noted in the table.

(b) **With Dimethyl Sulfate, Sodium Bicarbonate and Water.**—A four-to-one mole ratio of dimethyl sulfate to amino groups was used. A mixture of 0.8717 g. of resin 8 (Table I), 2.52 g. of dimethyl sulfate, 1.88 g. of sodium bicarbonate and 2.58 ml. of distilled water was heated in a closed flask at 80° for 48 hours. The beads were washed with water and dried.

(c) **With Methyl Iodide.**—A twenty-to-one mole ratio of methyl iodide to amino groups was used. A mixture of 1.196 g. of resin 8 (Table I) and 19.9 g. of freshly distilled methyl iodide was allowed to stand at room temperature in a stoppered flask for 24 hours with frequent shaking. A small amount of white precipitate formed in the first few minutes. The beads were collected on a filter, washed with water and dried. A sample of the white precipitate was collected and its infrared spectrum found to be identical with that from *p*-dimethylaminostyrene methiodide prepared from the styrene and methyl iodide, m.p. 193–194°.

Anal. Calcd. for $C_{11}H_{16}NI$: C, 45.69; H, 5.58; I, 43.88. Found: C, 45.32; H, 5.68; I, 43.61, 43.68.

Total Capacity Measurements.—Results of the capacity determinations are given in Table II. Some of these measurements were made by the titration procedure previously described[7] and others were made by the following weight difference procedure.

The resin in the iodide form was washed thoroughly and dried to constant weight (one week) under vacuum in a rotary drier. This resin (1.9346 g. of resin 8) was placed in a column, washed with 2 liters of 1 *N* sodium sulfate, and then washed with water until the effluent no longer contained sulfate. The resin was then redried as before and weighed (1.4802 g.) in the sulfate form. The difference in weight for the beads in the iodide and in the sulfate forms (0.4544 g.) was divided by the difference (78.89) in molecular weight of iodine (126.92) and one-half sulfate (48.03) to give the meq. of replaceable ionic groups. The meq. of replaceable ions divided by the weight of resin in the iodide form gave the total capacity (3.0) in meq. per g. of dried resin in the iodide form.

LOUISVILLE, KY.

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[7] R. Kunin and R. J. Myers, "Ion Exchange Resins," John Wiley and Sons, Inc., New York, N. Y., 1950, p 153.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS]

Factors Controlling Position of Alkylation of Alkali Metal Salts of Phenols, Benzyl and Allyl Halides[1,2]

BY DAVID Y. CURTIN, ROBERT J. CRAWFORD AND MAX WILHELM

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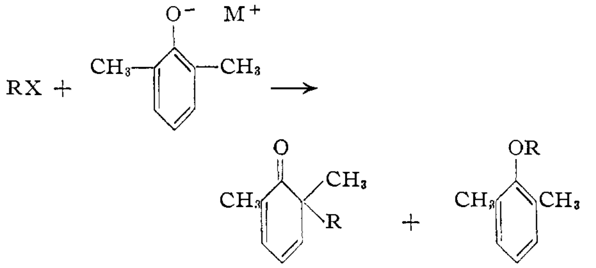
The alkylation of metal salts of 2,6-dimethylphenol and its 4-methyl and 4-bromo derivatives with benzyl and allyl halides has been examined. In general a mixture of allyl or benzyl aryl ether and 6-allyl (or benzyl) 2,4-cyclohexadienone is obtained and the objective of this study has been to determine some of the factors which influence the dienone/ether ratio. It has been found that dienone formation is favored by non-polar solvents, use of salts of less acidic phenols, higher salt concentrations, use of the lithium rather than sodium and sodium rather than potassium salt, and allyl or benzyl rather than saturated halides, and markedly decreased by the addition of tetrabutylammonium bromide. The ratio seems to be independent of the nature of the halide in a comparison of chloride, bromide and iodide. Only *ortho* alkylation is found. These results readily can be interpreted in terms of a postulation made in 1926 by Ingold that dissociated ions give a preponderance of allyl or benzyl ether and that ion aggregates give largely dienone.

In the course of a study of the *para* Claisen rearrangement, it was found[2,3] that sodium 2,6-dimethylphenoxide can be made to react with allyl halides, the attack occurring at an *o*-position with the formation of 6-allyl-2,6-dimethyl-2,4-cyclohexadienone (I). The conditions employed (suspension of the sodium salt in benzene) were patterned after those previously shown by Claisen and his associates[4,5] to cause *o*-alkylation of sodium phenoxide and salts of certain other phenols with unoccupied *o*-positions. It has been of interest to attempt to learn more about the factors controlling the relative amounts of carbon- and oxygen-alkylation of phenol salts. A study of the alkylation with benzyl and allyl halides of sodium 2,6-dimethylphenoxide is reported here.



I (R = allyl) II (R = allyl)
III (R = benzyl) IV (R = benzyl)

Certain examples of the formation of dienones by the direct carbon-alkylation of phenols have been reported which differ in important respects from the alkylations to be discussed but which should be mentioned briefly. The abnormal Reimer–Tiemann reaction[6] introduces a dichloromethyl unit into an *o*- or *p*-position of a methylated phenol. This reaction has two unique features. The product of oxygen attack is an α-halo ether which is probably immediately reconverted to the starting phenol in the reaction medium. Further, the reaction in which the position of substitution is deter-

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[2] Most of this work was presented at the Fifteenth National Organic Symposium, Rochester, N. Y., June, 1957. A preliminary report was made by David Y. Curtin and Robert J. Crawford, *Chemistry & Industry*, 313 (1956).

[3] D. Y. Curtin and R. J. Crawford, THIS JOURNAL, **79**, 3156 (1957).

[4] L. Claisen, *Z. angew. Chem.*, **36**, 478 (1923).

[5] L. Claisen, F. Kremers, F. Roth and E. Tietze, *Ann.*, **442**, 210 (1925).

[6] K. Auwers and F. Winternitz, *Ber.*, **35**, 465 (1902).