leading to a yellow solid, 1.3 g., which was chromatographed on alumina. The portion eluted by 95:5 ethanol–acetone was concentrated and dried in vacuum, washed with petroleum ether and treated with a small quantity of water, leading to white crystals, 0.102 g. (0.44 mmole), 14%, pinacol hydrate, m.p. 35–37°. A portion of this, 0.05 g., was dissolved in 10 ml. of water and treated with 0.25 g. of periodic acid in 40 ml. of water at room temperature overnight. The solution was distilled into a solution of dinitrophenylhydrazine in acidified ethanol–water, which was allowed to stand for two hours and then was evaporated, leading to acetone 2,4-dinitrophenylhydrazone, 0.017 g., m.p. and mixed m.p. with an authentic sample, 125–127°.

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WALTHAM, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Organoboron Compounds. X.[1,2] Popcorn Polymers and Highly Cross-linked Vinyl Polymers Containing Boron

BY ROBERT L. LETSINGER AND STEPHEN B. HAMILTON

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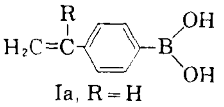
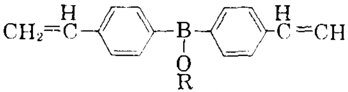
Several substituted styrene compounds possessing boron functional groups were synthesized and subjected to polymerization conditions. A popcorn-type copolymer was obtained from the ethyl tartrate ester of *p*-vinylbenzeneboronic acid, styrene and diallyl maleate. Although highly insoluble, this polymer reacted with phenylenediamine, alcohol and hydrogen peroxide. Copolymerization of 2-aminoethyl bis-*p*-vinylphenylborinate and styrene yielded a highly cross-linked, powdery solid, from which ethanolamine could be removed by hydrolysis. The resulting polymer readily adsorbed amino alcohols from solutions.

For studies on the catalytic action of organoboron compounds it was desirable to have a low density, porous, highly insoluble polymer that contained firmly bound $-B(OH)_2$ or $>B-OH$ groups. We undertook the preparation of two different types of polymers which held promise of exhibiting such properties. One was a "popcorn-type" polymer[3] derived from *p*-vinylbenzeneboronic acid (Ia). It should contain relatively few cross links. The other was a copolymer of styrene and an ester of bis-*p*-vinylphenylborinic acid (II), which should be highly cross-linked. The first section of this paper deals with the synthesis of the monomers, and the second, with the preparation and some properties of the polymers. Vinyl-type polymers containing boron have not previously been reported.

Monomer Synthesis.—Initial efforts were directed toward the preparation of *p*-vinylphenyllithium, from which the boron compounds should be obtainable by reaction with butyl borate. Unfortunately, all attempts to prepare this lithium compound were attended by extensive polymer formation. Thus, *p*-bromostyrene reacted with butyllithium in ether solution; however, the arylcarboxylic acids obtained on carbonation were all polymeric.[4] From the carbonation products of a similar interchange reaction which was carried out in pentane a small amount of *p*-vinylbenzoic acid was isolated, but the quantity was not of preparative significance.



Ia, R = H
Ib, R = CH_3

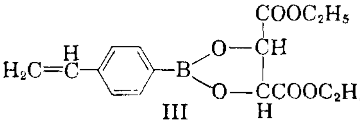


II

We next turned to *p*-bromo-α-methylstyrene, which polymerizes much less readily than *p*-bromostyrene. An interchange reaction with butyllithium proceeded satisfactorily to give, on carbonation, *p*-isopropenylbenzoic acid. With butyl borate the interchange products yielded *p*-isopropenylbenzeneboronic acid (Ib).

At this phase of the research the method of Leebrick and Ramsden for preparation of *p*-vinylphenylmagnesium chloride[5] appeared in the literature. Following their procedure, we prepared this Grignard reagent and treated it with butyl borate. A 60% yield of *p*-vinylbenzeneboronic acid was isolated from the reaction mixture.[6]

Compounds Ia and Ib rapidly decolorized bromine in carbon tetrachloride solution and yielded sharp melting dihydrobenzoboradiazole derivatives[7] with *o*-phenylenediamine. *p*-Vinylbenzeneboronic acid also furnished a solid ester (III) when heated in toluene with (+)-ethyl tartrate; the corresponding derivative of Ib did not crystallize.



III

The reaction of two mole equivalents of *p*-vinylphenylmagnesium chloride with butyl borate yielded bis-*p*-vinylphenylborinic acid, which was

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[1] This work was supported by the National Science Foundation, Grant G-2361.

[2] For the previous paper in this series see R. L. Letsinger and S. Dandegaonker, THIS JOURNAL, **81**, 498 (1959).

[3] For a review of popcorn polymerization see (a) E. H. Immergut, *Makromol. Chem.*, **10**, 193 (1953); (b) J. L. Amos, K. E. Coulter and F. M. Tennant in "Styrene," edited by R. H. Boundy and R. F. Boyer, Reinhold Publishing Corp., New York, N. Y., 1952, p. 729.

[4] Similar results were reported by G. B. Bachman, C. L. Carlson and M. Robinson, THIS JOURNAL, **73**, 1964 (1951).

[5] J. R. Lubrick and H. E. Ramsden, *J. Org. Chem.*, **23**, 935 (1958).

[6] A. Hoffman and W. M. Thomas recently prepared *p*-vinylbenzeneboronic acid by dehydrohalogenation and hydrolysis of *p*-(α-bromomethyl)-phenylboroxine, THIS JOURNAL, **81**, 580 (1959). Also, H. R. Snyder, M. S. Konecky and W. J. Lennarz, THIS JOURNAL, **80**, 3611 (1958), listed some frequencies at which *p*-vinylbenzeneboronic acid absorbs in the infrared, without however, giving any further information about the compound.

[7] R. L. Letsinger and S. B. Hamilton, *ibid.*, **80**, 5411 (1958).

isolated as the aminoethyl ester[8] II in 38% yield. A portion of II was converted to 2-amino-1-methylethyl bis-*p*-vinylphenylborinate by hydrolysis and reaction with 1-amino-2-propanol.

Polymerization. Popcorn Polymers.—Staudinger and Husemann[9] observed that styrene would copolymerize with small amounts of divinylbenzene to give two types of polymers. One, relatively dense and glassy in appearance, would form a gel in benzene. The other, which has since acquired the name "popcorn polymer" from its appearance, was opaque, possessed a low density, and was subject to only slight swelling in benzene. It has been found that *p*-chlorostyrene also yields popcorn polymer,[10] and a variety of divinyl compounds, including butadiene,[11] diallyl maleate[12] and methallyl cinnamate,[13] may function as the crosslinking agent in place of divinylbenzene.

For the preparation of the organoboron polymers we selected diallyl maleate as the polyvinyl component. Data on a series of reactions are summarized in Table I. In general, the components, along with a seed of popcorn polymer to serve as initiator, were sealed in erlenmeyer flasks (25-ml. capacity except for the larger scale reactions) and held at 80° for the indicated periods. The popcorn polymer, which filled a good portion of the flask when the yield was high, was separated mechanically and by use of benzene to soften and swell the glassy polymer.

Preliminary experiments with styrene confirmed the report that popcorn polymers could be readily obtained with diallyl maleate.[12] Unseeded mixtures yielded approximately equal amounts of popcorn and glassy polymer (expt. 1), whereas mixtures seeded with popcorn polymer gave almost quantitative amounts of the popcorn variety (2). It is interesting that the carbonyl band (5.8 μ) in the infrared spectrum of the popcorn polymer was even less intense than that in the glassy polymer, indicating that less cross-linking agent (maleate) was present in the non-swelling polymer.[14,15] Otherwise, the spectra of the two polymers could not be distinguished.

Attempts to prepare popcorn polymers with *p*-vinylbenzoic acid (expt. 6, Table I), α-methylstyrene (7) and compound III (8) were unsuccessful, and only a low yield (10%) of popcorn polymer was obtained with *p*-bromostyrene (5). An excellent conversion to popcorn polymer resulted, however, when an equimolar mixture of *p*-chlorostyrene and *p*-bromostyrene was employed as the monovinyl component (9). By use of an analogous copolymerization process we were able to prepare boron-containing popcorn polymers.[16] Thus, mixtures containing ester III and styrene (75 mole per cent. or more) afforded essentially quantitative amounts of popcorn polymer (12, 13). With somewhat higher proportions of III, glassy polymer also developed (14). It may be noted that styrene gave popcorn polymer in the presence of *p*-isopropenylbenzeneboronic acid (11); however, this polymer did not contain boron (flame test).

TABLE I

FORMATION OF POPCORN POLYMERS

Expt.	Vinyl components	Wt., g.	Diallyl maleate, g.	Benzene, g.	Time,[a] hr.	Yield of popcorn polymer, %
1	Styrene[b]	8.6	0.8	0.8	72	$\sim$50[c]
2	Styrene	8.6	.8	.8	24	95
3	Styrene	3.0	0	.24	240	0[c]
4	*p*-Chlorostryene	1.4	0.1	.1	24	100
5	*p*-Bromostyrene	1.85	.1	.1	48	10[c]
6	*p*-Vinylbenzoic acid	1.49	.1	.5	168	0[c]
7	α-Methylstyrene	1.2	.1	.1	30 days	0[d]
8	III[e]	2.91	.1	.1	168	0[c]
9	[*p*-Bromostyrene[f]	0.92	.1	.1	47	90
	p-Chlorostyrene]	0.7				
10	Ia,[g] *p*-chlorostyrene	0.32, 1.10	.1	.1	48	50[h]
11	Ib,[j] styrene	2.0, 7.6	.8	.8	48	65[i]
12	III, styrene	0.85, 1.50	.15	.15	23	95[h]
13	III, styrene	1.0, 1.0	.1	.1	54	90[h]
14	III, styrene	1.5, 1.0	.14	.2	36	20[h]
15	III, styrene	0.98, 0.30	.005	.05	72	10[h]

[a] This is the time elapsed before flask was opened. Generally the popcorn polymer had formed long before this. [b] No popcorn seed was used. [c] The remaining product was glassy polymer. [d] Did not polymerize. [e] Ethyl tartrate ester of *p*-vinylbenzeneboronic acid. [f] Brackets signify a copolymerization with two monovinyl components. [g] *p*-Vinylbenzeneboronic acid. [h] The popcorn polymer contained boron. [i] The popcorn polymer did not contain boron. [j] *p*-Isopropenylbenzeneboronic acid.

The boronate groups in the popcorn copolymer of styrene, III, and diallylmaleate were available, at least in part, for the usual types of chemical reactions. Thus, hydrogen peroxide cleaved the carbon–boron bonds to give a boron-free polymer, *o*-phenylenediamine reacted to yield a dihydrobenzoboradiazole derivative (about 40% of the boronate groups reacted), and water hydrolyzed the boronate esters, liberating boronic acid groups. The hydrolyzed polymer readily absorbed 2-aminoethanol from alcohol–water solution.

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(8) 2-Aminoethanol has proved to be of general use in the isolation and characterization of aromatic borinic acids; see for example (a) R. L. Letsinger, I. Skoog and N. Remes, THIS JOURNAL, **76**, 4047 (1954); (b) R. L. Letsinger and I. Skoog, *ibid.*, **77**, 2491 (1955); (c) **77**, 5176 (1955); (d) R. L. Letsinger and N. Remes, *ibid.*, **77**, 2489 (1955); and (e) R. L. Letsinger and J. R. Nazy, *J. Org. Chem.*, **23**, 914 (1958).

(9) H. Staudinger and E. Husemann, *Ber.*, **68B**, 1618 (1935).

(10) J. W. Breitenbach, H. Preussler and H. Karlingen, *Monatsh.*, **80**, 150 (1950). This seems to be the only substituted styrene previously reported to enter into popcorn polymers. Other monovinyl compounds found to give popcorn polymers include methyl acrylate and vinyl acetate (see above) and methyl methacrylate; J. R. Panchak, T. T. Kryza and T. G. Fox, Abstr. of A.C.S. Meeting, Sept., 1952.

(11) M. S. Kharasch, W. Nudenberg, E. Jensen, P. Fischer and D. Mayfield, *Ind. Eng. Chem.*, **35**, 830 (1947); L. M. Welch, M. W. Swaney, A. H. Gleason and R. K. Beckwith, *ibid.*, **35**, 826 (1947).

(12) E. C. Britton, G. H. Coleman and J. W. Zemba, U. S. Patent 2,331,263 (1943).

(13) E. C. Britton, H. B. Marshall and W. J. LeFevre, U. S. Patent, 2,341,175 (1944).

(14) By contrast, Staudinger and Husemann (note 6) suggested that the low swelling capacity of popcorn polymer, as compared to the glassy polymer formed simultaneously, resulted from a concentration of the cross-linking agent (divinylbenzene in their case) in the popcorn polymer.

(15) In order to extract any monomeric maleate which may have been retained by the glassy polymer we treated a portion of the polymer with boiling benzene for two hours. The polymer swelled markedly. After separation and drying it gave an infrared spectrum indistinguishable from the original glassy polymer.

(16) Mixtures containing two monovinyl compounds do not seem to have been employed previously in popcorn polymerization except in the case of styrene and vinylidene chloride (note 10), and it was not shown in that case that vinylidene chloride had been incorporated into the polymer.

Polymer from II.—A copolymer (IV) was prepared by heating 2-aminoethyl bis-*p*-vinylphenylborinate and styrene in the presence of α,α'-azodiisobutyronitrile. It crumbled easily and was insoluble and non-swelling in refluxing benzene, toluene, acetone, ethanol and acetic acid. It did not melt on heating to 400°, but began to darken about 280°. Further evidence of the polymeric nature of this product was provided by the infrared spectrum, which contained no peaks in the 6–6.2 μ region (C=C) although both styrene and the vinylphenylborinate monomer absorbed strongly in this region (6.11 and 6.15 μ, respectively).

On hydrolysis with hydrochloric acid in aqueous ethanol IV yielded a nitrogen-free polymer which still contained boron. This product reacted with 2-aminoethanol to give a polymer possessing 90% of the amount of aminoethanol originally present in IV (see Table II). The hydrolyzed polymer also reacted, though to a less extent, with 1-amino-2-propanol and ephedrine. The data in Table II are in accord with the assumption that the number of boron sites available for reaction decreases as the bulk of the aminoalcohols increases. Simple amines (ethylamine and ethylenediamine) were bound to the polymer to a less extent even than ephedrine, which must be related to the fact that borinate–ammonia complexes are much less stable than aminoethyl esters of borinic acids.[8b]

TABLE II

BINDING OF AMINES AND AMINOALCOHOLS BY N-FREE STYRENE–II COPOLYMER

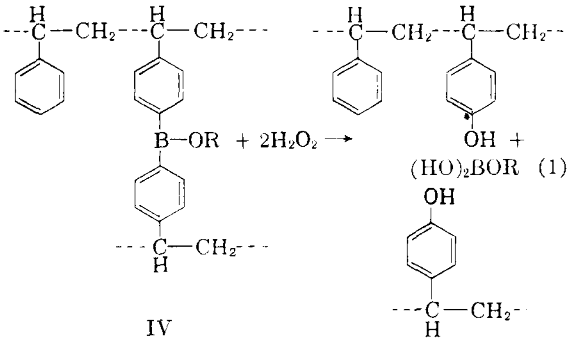
Amine	% N found	% B groups reacted[a]
2-Aminoethanol	4.01	91
1-Amino-2-propanol	3.44	80
Ephedrine	2.01	51
Ethylamine	1.94	41
Ethylenediamine	3.99	43

[a] The original polymer, for which 100% of the boron groups were combined with 2-aminoethanol, contained 4.36% N by analysis; therefore the equivalent wt. of the fragment containing one boron atom in the polymer chain was [100/4.36](14) = 321, and the equivalent weight after hydrolysis was 278. The "% B reacted" was calculated from the equation

$$\frac{\%\text{N}}{100} = \frac{(N_\text{B})/(14n)}{(N_\text{B})/\Delta E + 278}$$

where N_B is the mole fraction of boron that has reacted with amine, ΔE is the increase in equivalent weight attending reaction of one amine per boron, and n is the number of nitrogen atoms in the amine; "% B reacted" = 100 N_B. The accuracy of the values for the % B groups reacted should be of the order of ±5%.

In contrast to the insolubility in acetic acid, polymer IV readily dissolved in acetic acid solutions of hydrogen peroxide. Addition of water to the solution precipitated a new polymer which was free of boron, possessed hydroxyl groups (infrared), and was soluble in alcohol and in acetone. This change in solubility may be attributed to a decrease in the number of cross-links as a result of oxidation of carbon–boron bonds (equation 1). The intrinsic viscosity ($\eta = [\ln \eta_r/c]_{c \to 0}$) of this material, obtained from viscosity measurements in absolute ethanol at 22.5°, was 0.099. This is indicative of a relatively low degree of polymerization.



IV

(1)

Experimental Section

Carbon, hydrogen and nitrogen analyses were performed by Miss Hilda Beck unless otherwise indicated. The infrared spectra were determined with a Baird recording spectrophotometer, with the sample in potassium bromide. A nitrogen atmosphere was used in all reactions with organometallic reagents and in the polymerizations. Melting points were taken on a Fisher–Johns apparatus and are uncorrected.

***p*-Isopropenylbenzeneboronic Acid (Ib) and *p*-Isopropenylbenzoic Acid.**—Butyllithium (258 ml. of 0.853 *M* ether solution) was added with stirring to a solution of 43.2 g. (0.217 moles) of *p*-bromo-α-methylstyrene in 250 ml. of ether. The solution was allowed to warm to room temperature; then it was cooled to −70° and added over a period of two hours to a well-stirred solution of 115 g. of *n*-butyl borate in 365 ml. of ether. After the mixture had warmed to room temperature it was acidified with dilute hydrochloric acid. The ether layer (along with the ether from a wash of the aqueous layer) was extracted with sodium hydroxide solution and the alkaline extract then separated and acidified. From an ether extract of this solution was obtained 29.0 g. (82.5%) of crude solid product (a mixture of the monomeric acid and polymer). On recrystallization from water 13.0 g. (37%) of the purified *p*-isopropenylbenzeneboronic acid was obtained, m.p. 152–155°.

Anal. Calcd. for $C_9H_{11}O_2B$: C, 66.72; H, 6.84; neut. equiv., 161. Found: C, 63.40[17]; H, 7.37; neut. equiv., 162 (detn. by titration with alkali in presence of mannitol).

The dihydrobenzoboradiazole derivative has been reported previously.[7]

From a similar, smaller scale reaction (2.356 g. of *p*-bromo-α-methylstyrene) which was carbonated on Dry Ice (rather than added to butyl borate) was isolated 1.45 g. of crude *p*-isopropenylbenzoic acid. Recrystallization yielded a sample melting at 158–160° (lit.[4] 156–158°).

***p*-Vinylbenzeneboronic Acid (Ia).**—*p*-Vinylphenylmagnesium chloride was prepared from 27.6 g. of *p*-chlorostyrene by the procedure of Leebrick and Ramsden,[5] with the exception that ethyl bromide was not used as an activator. Tetrahydrofuran (200 ml.) was added, the mixture cooled to −78° and a solution of 100 g. of *n*-butyl borate in 200 ml. of tetrahydrofuran, also at −78°, added over a period of 5 to 10 minutes. The solution was stirred for 30 min., allowed to warm to room temperature, and stirred for two additional hours, whereupon it was hydrolyzed with dilute hydrochloric acid. An isolation procedure similar to that used for *p*-isopropenylbenzeneboronic acid yielded 17.68 g. (60%) of *p*-vinylbenzeneboronic acid, m.p. 188–190°. The weight of polymer obtained from this reaction was 12.7 g. (38%).

Anal. Calcd. for $C_8H_9O_2B$: C, 64.93; H, 6.13; B, 7.31. Found: C,[18] 60.50, 63.03, 58.05; H, 6.07, 6.13, 6.09; B, 7.32.

2-(4-Vinylphenyl)-1,3-dihydrobenzo[2,1,3]boradiazole.—A toluene solution containing 1.0 g. of *p*-vinylbenzeneboronic acid and 0.732 g. of *p*-phenylenediamine was heated

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[17] A black ash remained; see note 18.

[18] Many aromatic organoboron compounds yield a black ash (probably a mixture of boron carbide and boron oxide) on combustion. Such an ash was obtained from each of three analyses of *p*-vinylbenzeneboronic acid. As expected, the carbon results were low and erratic. It may be noted, however, that the hydrogen results were satisfactory.

to reflux. The water azeotrope and a portion of the toluene was removed by distillation. On cooling, 1.32 g. of the dihydrobenzoboradiazole derivative was obtained. Recrystallization from carbon tetrachloride yielded 1.12 g. (75%) of purified material, m.p. 246–247°.

Anal. Calcd. for $C_{14}H_{13}BN_2$: C, 76.40; H, 5.95; N, 12.79. Found: C, 76.47[19]; H, 5.85[19]; N, 13.18.

Ethyl Tartrate Ester of *p*-Vinylbenzeneboronic Acid (III).—A benzene solution (25 ml.) containing 2.035 g. of (+)-ethyl tartrate and 1.460 g. of *p*-vinylbenzeneboronic acid was refluxed in a flask fitted with a take-off adapter to remove the water azeotrope. The benzene was then removed *in vacuo* until the solution was one-half its original volume. On addition of pentane white needles separated; weight 2.78 g. (89.6%), m.p. 58–59°.

Anal. Calcd. for $C_{16}H_{19}BO_6$: C, 60.41; H, 6.02; neut. equiv. for boronate ester, 318. Found: C, 60.0, 59.8; H, 5.94, 5.91; neut. equiv. (titration in the presence of mannitol), 313.

2-Aminoethyl Bis-*p*-vinylphenylborinate.—To a solution of 0.2 mole of *p*-vinylphenylmagnesium chloride in 200 ml. of tetrahydrofuran at −78° was rapidly added 21.8 g. (0.09 mole) of *n*-butyl borate in 100 ml. of tetrahydrofuran. After warming to room temperature and three hours of stirring, the mixture was hydrolyzed with dilute hydrochloric acid. The ether layer was treated with 15 ml. of 2-aminoethanol. Evaporation of the ether and addition of water yielded the solid ester, which after recrystallization from toluene melted at 181–182° and weighed 9.99 g. (37.7%).

Anal. Calcd. for $C_{18}H_{20}BNO$: C, 78.00; H, 7.27; N, 5.05. Found: C, 73.03[17]; H, 7.09; N, 5.12.

2-Amino-1-methylethyl Bis-*p*-vinylphenylborinate.—Three grams of 2-aminoethyl bis-*p*-vinylphenylborinate was shaken with 200 ml. of ether and 20 ml. of dilute hydrochloric acid under a nitrogen atmosphere. The ether layer was separated and mixed with 25 ml. of an acetone–water solution containing 5 ml. of 1-amino-2-propanol. Distillation of the ether *in vacuo* and addition of 20 ml. of water to the residue yielded a solid, which was recrystallized from benzene; 86.5% yield, m.p. 185–187°.

Anal. Calcd. for $C_{19}H_{22}ONB$: C, 78.36; H, 7.61; N, 4.82. Found: C, 78.02[19]; H, 7.79[19]; N, 4.87.

Reactions of Styrene–III Popcorn Polymer.—Polymer prepared from expt. 12, Table I, was used in these tests. The infrared spectrum showed strong absorption at 5.75 (ester C=O) and 7.3 μ (B—O). The polymeric nature of this and the other materials described as "popcorn polymers" was indicated by the insolubility of the materials in all solvents examined, the high melting temperature (307–312°, preliminary softening at about 280°) and the absence of vinyl absorption in the infrared spectra.

(a) **Hydrogen Peroxide.**—A suspension of 0.20 g. of polymer in a solution of 10 ml. of acetic acid and 1 ml. of 30% hydrogen peroxide was allowed to stand three hours; then the polymer was separated by filtration, washed, and dried for two hours at 100° and 15 mm. It burned without a green flame. The infrared spectrum showed a new band of medium intensity at 3.0 μ (O–H), only a weak carbonyl band at 5.8 μ (presumably most if not all tartrate had been removed) and very weak absorption in the 7.3–7.7 μ region (region for B–O).

(b) **Alcohol.**—A sample of the popcorn polymer was heated in a dilute solution of hydrochloric acid in ethanol for an hour, while another sample was soaked in 95% ethanol for 66 hours at room temperature. The infrared spectra of the recovered polymers were identical (except that the C=O band in the acid treated sample was slightly less intense) and indicated that most of the tartrate had been removed; λ 2.9 μ (OH, mod. intensity), 5.8 μ (C=O, weak, similar to intensity for product of peroxide reaction) and 7.5 μ (B—O, strong and broad band).

(c) **2-Aminoethanol.**—Some of the hydrolyzed polymer was heated one hour with ethanol which contained 2-aminoethanol; then it was separated, washed with water and ethanol and dried. The nitrogen analysis (Found: N, 1.03) corresponded to one aminoethanol molecule per 1.5 boronic acid groups ($-B(OH)_2$ concn. in polymer assumed equal to that in mixture of monomers).

(d) ***o*-Phenylenediamine.**—The insoluble material obtained by heating the popcorn polymer an hour with *o*-phenylenediamine in benzene exhibited bands at 2.9 and 7.0 μ (characteristic for dihydrobenzoboradiazole system[7]), 7.4 (B–O or B–N) and 5.8 μ (C=O, sufficient intensity to indicate that some tartrate was still present). The nitrogen analysis (Found: N, 1.30) corresponded to conversion of about 40% of the $-B(OR)_2$ groups to dihydrobenzoboradiazole groups. (In the absence of boron groups, *o*-phenylenediamine was not bound to the polymer, as shown by the nitrogen analysis [Found: N, 0] for a styrene–diallyl maleate popcorn polymer which had been treated with *o*-phenylenediamine in benzene.)

Copolymerization of Styrene and II.—A mixture of 0.64 g. of aminoester II, 0.25 g. of styrene, 1.0 g. of toluene and 0.01 g. of α,α'-azodiisobutyronitrile was sealed in a tube under nitrogen and heated for 10 hr. at 80° and one hour at 100°. The polymer was washed with hot toluene and dried; wt. 0.72 g.

A nitrogen analysis on the polymer indicated that the percentage of II incorporated in the polymer was somewhat higher than the percentage of II in the monomer mixture (%N calcd. for monomer mixture of styrene and II, 3.64; %N calcd. for pure II, 5.05; %N found, 4.36%).

A similar polymerization with 0.625 g. of 2-amino-1-methylethyl bis-*p*-vinylphenylborinate, 0.25 g. of styrene, 0.01 g. of the azo catalyst and 1.00 g. of toluene yielded a polymer of the same appearance and properties as that prepared from the 2-aminoethyl ester II; wt. 0.81 g. (%N calcd. for a mixture of monomers, 3.45; %N found, 3.89).

Reactions of Styrene–II Copolymer. (a) **Hydrogen Peroxide.**—A suspension of 0.1 g. of the polymer in 10 ml. of acetic acid was swirled with 1.0 g. of 30% hydrogen peroxide. Virtually all of the polymer dissolved. The solution was filtered and polymer reprecipitated by addition of water. This material (0.067 g.) was quite soluble in ethanol and acetone but not in benzene. No green (due to B) could be seen in the flame when the polymer was burned. The infrared spectrum showed strong absorption at 3.0 μ (O–H) and the 7.3–7.7 μ region was free of the strong absorption characteristic of trivalent boron.

(b) **Hydrolysis.**—The copolymer (0.50 g.) was heated for an hour on a steam-bath with ethanol which contained hydrochloric acid. Separation by filtration yielded 0.48 g. of polymer which was insoluble in common organic solvents, contained boron (green flame on burning, λ 7.5–7.7 μ) and was free of nitrogen (quantitative analysis).

The polymers in Table II were obtained by heating 0.10 g. samples of the N-free polymer with the indicated amine in acetone solution for one hour. The products were washed thoroughly with acetone and water to remove any loosely adhering amine. The infrared spectrum of the polymer after addition of 2-aminoethanol was identical with that of the original polymer IV; λ 3.05 μ (N–H of complexed amine); the strong absorption in 7.3–7.7 μ region characteristic of trivalent boron compounds was absent.

EVANSTON, ILL.

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[19] Analyses by Micro-Tech Laboratories, Skokie, Ill.