

***p*-Vinylbenzoic Acid: A Convenient Preparation, Copolymerization, and Examination as Dye Receptive Modifier for Acrylic Fibers and as Ion Exchange Resin Component**

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SUMMARY:

A convenient preparation of *p*-vinylbenzoic acid from β -haloethylbenzene with 67% overall yield was described. Monomer reactivity ratio of *p*-vinylbenzoic acid (1) to acrylonitrile (2) was determined:

$$\text{Free acid: } r_1 = 1.8 \pm 0.05; \quad r_2 = 0.076 \pm 0.001$$

$$\text{Na salt: } r_1 = 0.26 \pm 0.06; \quad r_2 = 0.09 \pm 0.08$$

p-Vinylbenzoic acid increased the affinity of acrylic fibre toward cationic dye when copolymerized with acrylonitrile, but was less effective than sulfonic acids as dye receptive site. Acid ion exchange resins based on *p*-vinylbenzoic acid possessed a high selection factor of Ca^{2+} over Mg^{2+} .

ZUSAMMENFASSUNG:

Eine vorteilhafte Synthese von *p*-Vinylbenzoesäure, ausgehend von β -Halogenäthylbenzol, wird beschrieben (67% Ausbeute). Die Copolymerisationsparameter für das System *p*-Vinylbenzoesäure (1)/Acrylnitril (2) wurden bestimmt:

$$\text{Freie Säure: } r_1 = 1,8 \pm 0,05; \quad r_2 = 0,076 \pm 0,001$$

$$\text{Na-Salz: } r_1 = 0,26 \pm 0,06; \quad r_2 = 0,09 \pm 0,08$$

p-Vinylbenzoesäure als Comonomeres erhöht die Affinität von Polyacrylnitrilfasern gegenüber kationischen Farbstoffen; ihre Wirkung ist jedoch geringer als die von Sulfonsäuregruppen.

Saure Ionenaustauscherharze auf der Basis von *p*-Vinylbenzoesäure besitzen ein hohes Selektionsvermögen für Ca^{2+} gegenüber Mg^{2+} .

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1. Introduction

In view of the recent increase of papers¹⁻⁸ dealing with improvement of *p*-vinylbenzoic acid (VBA) synthesis⁹, it seems worthwhile to publish a rather straightforward preparation of VBA, which has been used routinely in this laboratory. In addition are described in this paper: monomer reactivity ratio of VBA with acrylonitrile, examination as dye receptive in acrylic fiber and attempted preparation and some properties of weak acidic cation exchange resins based on VBA.

2. Experimental

2.1. Preparation of *p*-vinylbenzoic acid (VBA)

p-(β -Bromoethyl)benzoic acid

β -Bromoethylbenzene was acetylated and oxidized according to the directions of FOREMAN and McELVAIN¹⁰ with 77% yield. M.p. 208–210°C. (from benzene, reported¹⁰) 205 to 207°C.). Strong IR-bands at 1689, 1605, 1425, 1314, 1290, 1172, 858, 758, and 702 cm⁻¹.

p-(β -Chloroethyl)acetophenone

β -Chloroethylbenzene was acetylated in the same way as above. Yield 81%; b.p._{4.5} 133–134°C.; n_D^{30} 1.5498; d_4^{25} 1.1428. Strong IR-bands at 1680, 1606, 1430 sh, 1410, 1356, 1263, 1184, 1016, 956, and 817 cm⁻¹.

Anal. (C₁₀H₁₁ClO) Calcd. C 65.75 H 6.07 Cl 19.41

Found C 65.34 H 6.29 Cl 19.35

2,4-Dinitrophenylhydrazon

Bright red needles from ethanol/ethyl acetate (2:3); m.p. 185–186°C. (reported¹¹) 184°C.).

Anal. (C₁₆H₁₅ClN₄O₄) Calcd. C 52.97 H 4.17 Cl 9.77 N 15.45

Found C 53.11 H 4.21 Cl 9.76 N 15.31

p-(β -Chloroethyl)benzoic acid

β -(Chloroethyl)acetophenone was oxidized with alkaline hypobromite¹⁰. Yield 88%; m.p. 185–186°C. (from benzene). Strong IR-bands at 1684, 1605, 1418, 1310, 1285, 1174, 756, and 719 cm⁻¹.

Anal. (C₁₀H₁₁OCl) Calcd. C 58.55 H 4.91 Cl 19.21

Found C 58.70 H 5.18 Cl 19.27

Oxidation by alkaline potassium permanganate solution gave terephthalic acid.

Anal. (C₈H₆O₄) Calcd. C 57.83 H 3.64

Found C 57.67 H 3.91

p-Vinylbenzoic acid (VBA)

To a solution of 11.5 g. (0.05 mole) of *p*-(β -bromoethyl)-benzoic acid in 100 ml. of hot ethanol was added the solution of 4.8 g. (0.12 mole) of sodium hydroxide and 0.2 g. of hydroquinone in 50 ml. of hot ethanol/water (8:2), and refluxed for 1.5 hrs. The reaction mixture was poured into 700 ml. of dil. HCl, the precipitate collected, washed with 2% HCl and recrystallized from ethanol/water (2:8). The yield of VBA, colorless plates, was 6.4 g. (86.5%). On heating in a melting apparatus the crystal mass contracted markedly at 142–143°C. but did not melt up to 360°C. in accordance with the description of MERRILL¹¹. Vinyl group equivalent (bromine addition method¹²) 143.0 (Calcd. 148.5). Strong IR-bands at 1674, 1603, 1417, 1405, 1316, 1280, 1174, 1108, 984, 914, 902, 855, 780, 750, and 708 cm⁻¹. When the reaction was conducted in 99.5% ethanol, the voluminous precipitate of the sodium salt of benzoic acid tends to form, unless made in large dilution and with a rather poor yield (71%). In water, the yield was also unsatisfactory. (59% at 85°C., 10 min.; 15% at 40°C., 2.5 hrs.).

2.2. Monomer reactivity ratio of VBA and VBNa with acrylonitrile

Low conversion copolymerization of VBA with acrylonitrile in dimethylformamide

About 0.5 g. of monomer mixture and 4 mg. of azo-bis-isobutyronitrile in 2 to 4 ml. of dimethylformamide was warmed at 50°C. under nitrogen in a sealed tube for 0.5 to 1 hr. The content was poured into a large volume of methanol and the precipitated polymer collected. The polymer was purified by repeated reprecipitations. Copolymer composition based on nitrogen analysis is shown in Table 1.

Monomer reactivity ratios were calculated by intersection method of MAYO and LEWIS¹³.

Table 1. Copolymerization of *p*-vinylbenzoic acid (VBA) with acrylonitrile (AN) in dimethylformamide at 50°C.

No.	Monomer molar composition		Polymerization period (hrs.)	Conversion (%)	N-content of polymer (%)	Polymer molar composition	
	AN	VBA				AN	VBA
6	0.9616	0.0384	0.5	8.5	13.05	0.7314	0.2686
7	0.9177	0.0823	0.5	10.9	9.81	0.6226	0.3774
8	0.8670	0.1330	0.5	9.0	7.83	0.5406	0.4594
9	0.8073	0.1927	1.0	13.4	6.57	0.4802	0.5198

Medium conversion copolymerization of sodium *p*-vinylbenzoate (VBNa) with acrylonitrile in water

Portions of VBNa mother liquor (0.356 *M*) which had been prepared by dissolving VBA in an equivalent volume of ca. 0.03 *N* NaOH solution and adjusting the *p*_H of the solution to 7.5 with dil. H₂SO₄, were mixed with acrylonitrile in various proportions and warmed to 50°C. in a sealed tube with K₂S₂O₈ (0.8%) and NaHSO₃ (0.8%). After suitable periods the content of the reaction tube was poured into hot water containing CaCl₂ and NH₄Cl.

The polymer was collected on a glass filter, washed with a small amount of water, dried repeatedly and weighed. Table 2 shows the results.

Since conversions all exceeded 10%, monomer reactivity ratios were calculated by integration method¹³.

Table 2. Copolymerization of sodium *p*-vinylbenzoate (VBNa) with acrylonitrile (AN) in water at 50°C.

No.	Monomer molar composition		Polymerization period (hrs.)	Conversion (%)	N-content of polymer (%)	Polymer molar composition	
	AN	VBNa				AN	VBNa
10	0.9656	0.0344	0.5	31.19	20.65	0.7031	0.0116
11	0.9640	0.0361	1.0	14.35	20.06	0.8537	0.0252
12	0.9586	0.0414	0.4	13.59	16.58	0.8654	0.0243
13	0.9019	0.0981	2.5	24.78	12.23	0.7623	0.0476
14	0.7939	0.2061	3.5	33.14	9.74	0.6208	0.1000
15	0.6563	0.3437	2.7	20.19	5.78	0.5786	0.2572
16	0.4757	0.5243	3 days	13.12	3.35	0.4398	0.4472

2.3. Examination of VBA as dye receptive units in acrylic fiber

Copolymerization of VBNa, acrylonitrile, and methyl acrylate

As an example, the procedure for the preparation of copolymer No. 20 (Table 4) is described below. VBA (1.50 g.) was dissolved in *ca.* 300 ml. of water containing 1.5 g. of NaOH in a flask fitted with water-sealed mechanical stirrer, reflux condenser, thermometer, two dropping funnels and inlet and outlet tubes for nitrogen. The flask was put into a water-bath. After adjusting the p_H of the solution to 5.8 by addition of 1 *N* H₂SO₄, a total volume of 500 ml. was made up. Then, acrylonitrile (46.50 g.), methyl acrylate (2.00 g.), and EDTA (0.5 mg.) were added and the flask was heated at 40°C. under stirring in an atmosphere of nitrogen. When the mixture became homogeneous, 4.5 ml. of 0.54 *M* aqueous solution of thioglycolic acid and 1.50 g. of ammonium persulfate were added in this order. After a few min. the solution became milky and temperature began to rise. The temperature was kept at 50°C. for 4 hrs. under stirring at a speed of 300 r.p.m. White polymer was collected on a cloth filter, washed with water and dried. Yield 45.8 g.

Titration of acid groups in polymer

To liberate the free acid form, the polymer was trituated in 0.1 *N* H₂SO₄ for 1 hr. and washed with water until neutral. The polymer was dissolved in dimethylformamide to 0.4% concentration and titrated conductometrically with 0.01 *N* methanolic KOH solution.

Yellowness index after and before heating

Polymer particles (diameter < 70 μ) were heated for 60 min. at 170°C. in a small test tube, taken out and pressed at 400 kg./cm² to a tablet. HUNTER-values *L*, *a* and *b* were

measured by photoelectric colorimeter and the yellowness index (Y.I.) was calculated according to the equation²⁰⁾

$$\text{Y.I.} = (0.700 a + 1.75 b)/L$$

The Y.I. of unheated polymer was determined by the same procedure.

Spinning

10 to 18 wt.-% solution of polymer in dimethylformamide was forced by means of compressed air through 0.08 mm. \times 50 HOLE-spinnerett into a coagulant bath containing *p*-xylene/dimethylformamide (9:1) at room temperature. After running for 1 m. in the bath, fibre bundle was rolled up, dried at reduced pressure, drawn 3 times on a metal plate heated at 180°C., and contracted by 20% on a plate at 200°C. Final fiber denier *ca.* 3.

Saturation dyeing with Sevron Blue B

Fiber samples were dyed at various dye concentration ranging from 12 to 40% on weight of fiber for 2 hrs. at 120°C. in a glass pressure tube (liquor ratio to fiber 100:1). Dye uptake F_F and the residual dye concentration in the bath F_L were determined colorimetrically. Plot of reciprocals of these two quantities, $1/F_F$ and $1/F_L$, invariably gave a straight line. The intercept of this line at the $1/F_F$ axis, $(1/F_F)_{F_L=\infty}$, may be assumed to be the reciprocal of saturation dye-uptake at infinite dye-bath concentration at 120°C. Preliminary experiments have been carried out to ascertain that 2 hrs. are sufficient to reach the dyeing equilibrium at these conditions. Saturation uptake of Sevron Blue B by Orlon 42 more dyeable by the present procedure was 125 mg. per 1 g. fibers.

Measurement of half-dyeing rate

Sample fiber (1 g.) which was tied loosely to a mechanical stirring rod was immersed into dye-liquor in a 200 ml. round bottom flask fitted with thermometer, reflux condenser, air-tight stirrer, and sampling device; the dye-liquor consisted of 30 mg. of a cationic dye and 100 ml. of buffer solution (p_H 4.5; $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$) and was heated to 96°C. Stirring is started immediately and dyeing was continued at 96°C. until apparent equilibrium was substantially attained, judged from the exhaustion curve. Usually, dyeing was continued for 3 hrs. One half of dye uptake at equilibrium (F) divided by one half of dyeing time (τ), $F/2\tau$ was tentatively termed "half-dyeing rate", which corresponds to the slope of initial straight portion of the exhaustion curve.

Half-dyeing rate determination was repeated 3 times using different colors: Sevron Orange L, Maxilon Red BL and Genacryl Green GF, which had been examined to give favorable shapes of exhaustion curves for the present purpose.

Since the rates are different among these dyes and it is desirable to use a single figure as a measure of dyeing rate, arithmetic mean of relative rates

$$\frac{1}{3} \left\{ (k_{\text{orange}}/0.406) + (k_{\text{red}}/0.774) + (k_{\text{green}}/0.761) \right\} \cdot 100 (\%)$$

was computed and included in the Table 4 as "relative half-dyeing rate". Denominators of each term 0.406, 0.774 and 0.761 are half-dyeing rates for Orlon 42 with S. Orange L, M. Red BL, and G. Green GF, respectively. The relative half-dyeing rate is reproducible within 10% variation and seems to deserve to practical usage.

2.4. Cation exchange resin based on VBA

Methyl *p*-vinylbenzoate (VBMe)

VBA was esterified according to the direction of MARVEL and OVERBERGER⁹. M.p. 34–35°C. (reported⁹) 35–36°C.).

Divinylbenzene (DVB)

Commercial reagent DVB was shaken with one-fourth part of 5% NaOH solution, washed with water, dried with Na₂SO₄ and distilled *i. vac.* in the presence of sulfur. Fraction of b.p.₅ 60–61°C. was immediately used for copolymerization. Divinylbenzene content of this fraction analyzed by nitrosite method¹⁴) was $52.6 \pm 1.5\%$.

Suspension copolymerization of VBMe and DVB

Essentially the procedure described by TROMMSDORFF¹⁵) was followed. As for runs No. 1, 2, 4, 7 and 10 in Table 5, the volume of water was 10 times the monomer mixture. Carboxymethyl cellulose (0.7%) was used as an emulsifier. Polymerization was initiated with 1 wt.-% (of monomer) of dibenzoyl peroxide and continued at 90°C. for 4 hrs. with stirring (350–400 r.p.m.) in an atmosphere of nitrogen. Run No. 6 is a direct copolymerization of VBA with DVB in a similar process: 300 ml. of water containing 0.5% of carboxymethyl cellulose, a solution of 9.8 g. of VBA, 3.0 g. of DVB, and 100 mg. of dibenzoyl peroxide in 80 ml. of benzene/xylene (1:3) were mixed at 60°C. and stirred at 80°C. for 4 hrs. at a speed of 300 r.p.m. When temperature reached 80°C., the suspension was disturbed to a fine emulsion. In all runs, the bead or powder polymer was collected, washed, dried, and extracted with nitromethane or benzene for 8 hrs. in a SOXHLET extractor to remove non-crosslinked molecules.

Saponification of VBMe-DVB Copolymer

Bead polymer (10 g.) was stirred in 50 ml. of dioxane at reflux temperature for 2 hrs. Then 50 ml. of 10% alcoholic KOH was added and the mixture refluxed for 24 hrs. with stirring. Cation exchange capacity and apparent acidity constants of the resins were determined according to the procedure given by KUNIN¹⁶).

Separation factor K_{Mg}^{Ca} of VBA-VBMe-DVB type cation exchange resin

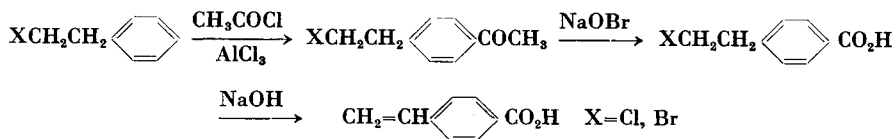
Several 0.25 g. portions of a resin in Na-form were each immersed in 50 ml. of aqueous solutions of various mixtures of CaCl₂·2H₂O and MgCl₂·6H₂O, the total salt concentration being kept to 0.04 M, the *p*_H adjusted to 10.1 by addition of ca. 0.5 ml. of 0.1 N NaOH solution. After shaking thoroughly and standing 5 min., 5 ml. of the solution was taken out and the concentration of both salts determined by standard complexon titration. Under these conditions, the extent of exchange of Na by Ca or Mg was over 70%. The same procedure was repeated to obtain value $K \frac{Ca}{Mg}$ of Amberlite IRC-50.

3. Results and Discussion

3.1. Preparation of vinylbenzoic acid (VBA)

Although several new syntheses of VBA have been reported¹⁻⁸) since the first classical preparation by MARVEL and OVERBERGER⁹), it was

rather surprising that the dehydrohalogenation of *p*-(haloethyl)benzoic acid has never been examined. In 3 steps from β -haloethylbenzene, VBA was now obtained with 67 % overall yield^{*)}:



The first two steps were described by FOREMAN and McELVAIN¹⁰⁾. Since these processes can be conducted at moderate temperatures and need no special apparatus, they provide a convenient laboratory method.

3.2. Monomer reactivity ratio of VBA with acrylonitrile

Monomer reactivity ratios of free VBA and its sodium salt (VBNa) in copolymerization with acrylonitrile in dimethylformamide and water were determined by the usual manner¹³⁾. Results are shown in Table 3.

Table 3. Monomer reactivity ratios of free vinylbenzoic acid (VBA) and its sodium salt (VBNa) (1) with acrylonitrile (AN) (2)

Monomer 1	2	Medium	Temp. (°C.)	r_1	r_2	$r_1 r_2$	Monomer 1 Q	e
VBA	AN	DMF	60	1.8 ± 0.05	0.076 ± 0.001	0.14	1.0	-0.2
VBNa	AN	water	50	0.26 ± 0.06	0.09 ± 0.08	0.023	0.3	-0.7
(Styrene)	AN		50	0.37 ± 0.02	0.05 ± 0.02	0.02	1.0	-0.8 ^{a)}

^{a)} K. R. HENNERLY-LOGAN and R. V. V. NICHOLLS, J. Res. nat. Bur. Standards **41** (1948) 521.

VBA and VBNa both copolymerize with acrylonitrile. The *e*-value of VBA, which is more positive than that of styrene on account of the electron attracting effect of the carboxyl group, decreased to -0.7 in VBNa because of the electron donating influence of the carboxylate group. On the other hand a decrease of the *Q*-value from 1.0 to 0.3 on neutralizing VBA to VBNa means that the stabilization of the radical by resonance is weakened in the latter. Such a decrease of both *Q*- and *e*-values by con-

^{*)} The maximum overall yield of VBA ever reported was 32 % in 5 steps from *p*-dichlorobenzene²⁾.

versions of COOH to COO⁻ has also been observed in acrylic¹⁷⁾ and methacrylic¹⁸⁾ acid.

3.3. Examination of VBA as dye receptive in acrylic fiber

In view of the good copolymerizability of VBA with acrylonitrile and of the now widely accepted efficacy of small amounts of copolymerized acidic monomer in improving the dyeing properties of acrylic fibers, copolymers of acrylonitrile, methyl acrylate, and VBA were prepared, spun into fiber, and the behavior towards cationic dyes examined.

Table 4. Polymerization conditions, polymer properties and dyeing behavior of acrylonitrile (AN)/methyl acrylate (MA)/VBNa copolymers

No.		17	18	19	20
Monomer composition (wt.-%)	AN	93.00	92.95	92.86	92.57
	MA	7.00	6.49	5.99	3.98
	VBNa	0	0.56	1.15	3.45
Conversion (%)		86	81	76	92
N-content of polymer (%)		24.17	24.57	24.94	24.70
(Acid equivalent of polymer ^{a)}) · 10 ⁻⁶ (equiv./g.)		0	26.8	69.8	156
Polymer composition (wt.-%)	AN ^{b)}	91.56	93.07	94.47	93.56
	MA	8.44	6.42	4.17	3.40
	VBNa ^{c)}	0	0.51	1.36	3.04
$\tau_{sp}/c^d)$		0.192	0.411	0.550	0.841
Yellowness index	befor heating	-0.006	0.003	0.004	0.083
	after heating ^{e)}	0.441	0.477	0.393	1.023
Saturation uptake of Sevron Blue B (mg./g. fibers)		71.4	86.4	103.7	134.4
Half-dyeing rate (mg. dye/g. fiber per min.)	Sevron Orang L	0.196	0.284	0.229	0.302
	Maxilon Red BL	0.290	0.275	0.409	0.547
	Genacryl Green GF	0.397	0.356	0.336	0.916
Relative half-dyeing rate ^{f)}		46.0	47.5	51.2	88.5

^{a)} Balance polymer No. 17 had $33.2 \cdot 10^{-6}$ equiv./g. acidic groups. Difference between titration value and this value is listed.

^{b)} Calculated from N-content of polymer.

^{c)} Calculated from acid equivalent of polymer.

^{d)} 2 g. per litre dimethylformamide at 25 °C.

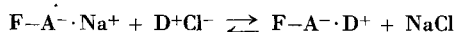
^{e)} 170 °C., 60 min.

^{f)} See experimental part.

In Table 4 are summarized polymerization conditions, composition and viscosity of polymers, yellowness indices before and after heating, and dyeing properties.

Reduced viscosity number of the polymers in dilute dimethylformamide solution increased rapidly with VBNa content, which indicate that polymers containing even a small amount of VBNa act as polymer electrolytes. VBNa content in polymers No. 18, 19, and 20 was essentially parallel to the initial composition.

Polymers thus prepared were spun into fiber and dyed. Both saturation dye uptake and relative rate of dyeing with cationic dyes increased with the increment of VBNa content (Fig. 1). Efficacy of VBNa as dye-site is, however, inferior to sulfonate group containing vinyl monomers such as sodium allylsulfonate and sodium acryloyloxybenzenesulfonate*). Since the slope of line in Fig. 1 corresponds to the number of dye molecules bound to an acidic site in the polymer, less carboxylate groups are bound than sulfonate groups. In other words, the dyeing equilibrium reaction



where F denotes fiber backbone, A⁻ is acidic site in fiber and D⁺ is dye cation will be shifted more to the left side with the former than with the latter.

The increment of dyeing rate by incorporation of VBNa was also small compared with sulfonate-monomers as shown in Fig. 1. To raise dye-receptive capacity and dyeing rate to the level of commercial Orlon 42, it was necessary to copolymerize more than 1 mole-% of VBNa, while 0.1 to 0.3 mole-% was sufficient for allylsulfonate and acryloyloxybenzenesulfonate.

Resistance to yellowing on heating which is of practical significance was only slightly lowered by incorporation of VBNa while it is not affected by copolymerization of sulfonate monomers. On the other hand, acrylic and methacrylic acid severely affect the thermal stability of acrylic fibers¹⁹⁾. In view of these results, the effect of the acidic species on the discoloration of polyacrylonitrile seems to offer an interesting problem.

3.4. Cation exchange resin based on VBA

Since cation exchange properties of resins of the carboxylated polystyrene type which resemble in structure the most well known strongly

*) Prepared by condensation of sodium *p*-hydroxybenzenesulfonate with acryloyl chloride in the presence of sodium carbonate in water below 10°C.

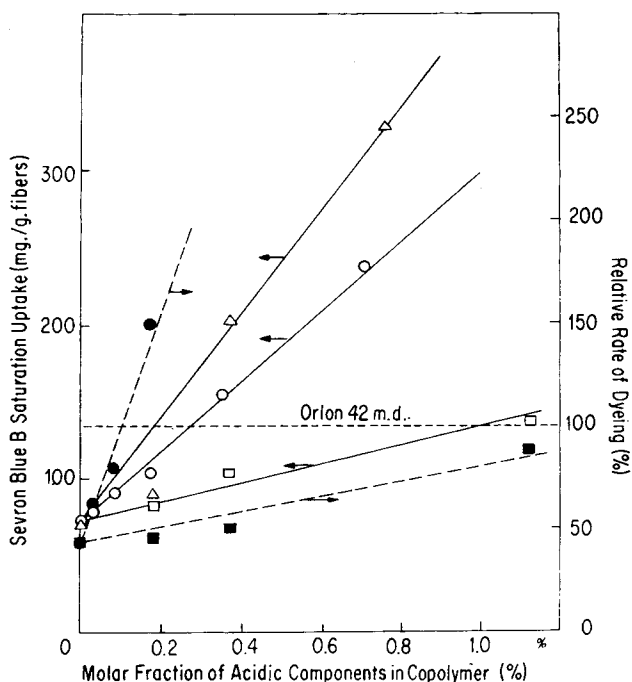


Fig. 1. Relationship between Sevron Blue B saturation uptake at 120°C. and molar fraction for three kinds of acidic components in modified acrylic fiber

△ = Sodium allylsulfonate; ○,● = Sodium acryloyloxybenzenesulfonate
□,■ = Sodium *p*-vinylbenzoate

acidic ion exchange resin, sulfonated polystyrene, are not known, bead polymers based on VBA were prepared.

Because of the high melting point and low solubility of VBA in organic solvents, an attempt to prepare pearl polymers by suspension copolymerization of VBA dissolved in xylene/benzene with divinylbenzene (DVB) was unsuccessful and a powder polymer resulted (No. 6 in Table 5). Therefore, the methyl ester of VBA (VBMe, m.p. 35°C.) was copolymerized with DVB by the usual suspension method at 90°C. and the pearl-shaped product was saponified with alcoholic KOH after preliminary swelling of the pearls in hot dioxane. Results of some ion exchange measurements are presented in Table 5.

Elementary analysis of the VBMe-DVB copolymer agreed well with the calculated composition based on the assumption that the monofunctional impurity in DVB is ethyl vinylbenzene. Saponification of resins

Table 5. Copolymerization of methyl *p*-vinylbenzoate (VBMe) and divinylbenzene (DVB). Saponification, analysis, densities, and ion exchange properties of the copolymers

Exp. No.	Copolymerization				Conv. (%)	VBMe-DVB copolymer				d ¹⁵	
	Monomer composition wt.-%		Approx. particle size (mm.)	Soluble part ^{c)} (%)		C		H			
	VBMe	DVB Mixture				DVB	M.F. a)	found	calcd. d)		found
1	100	0	0	50	2.0	—	73.79	74.05	6.15	6.22	—
2	90.9	5.1	4.0	81	0.9	2.1	75.06	75.65	6.53	6.42	1.03
4	81.7	10.2	8.1	86	0.9	2.6	76.87	77.25	6.71	6.61	1.05
6 ^{b)}	(76.5)	12.5	10.9	74	powder	11.7	—	—	—	—	—
7	66.6	18.7	14.7	90	1.2	4.8	79.14	79.92	7.08	6.93	0.98
10	53.9	25.8	20.4	89	0.8	3.2	81.25	81.17	7.18	7.21	1.06

Exp. No.	Saponified copolymer (VBA-VBMe-DVB structure)										pK _a
	Cation exchange capacity (mequiv./g.)		Extent of saponification ^{e)} (%)	C		H		Degree of cross-linking ^{f)} (%)	d ¹⁵		
	found	calcd.		found	calcd.	found	calcd.		H	Na	
1	—	—	—	—	—	—	—	0	—	—	—
2	6.18	6.14	100	70.74	6.00	5.71	1.01	5.5	1.01	1.49	6.3
4	4.61	5.53	83.4	74.08	6.39	6.08	1.10	10.9	1.10	1.26	6.2
6 ^{b)}	6.40	5.17	—	73.07	6.15	6.14	0.84	12.5	0.84	1.51	—
7	3.46	4.51	76.7	76.18	6.86	6.33	1.10	19.6	1.10	1.29	6.3
10	2.25	3.64	68.0	79.14	7.10	6.95	1.05	26.7	1.05	1.24	6.5

a) Monofunctional vinyl compound.

b) VBA instead of VBMe was copolymerized with DVB.

c) Extracted with nitromethane or benzene in a SOXHLET extractor for 8 hrs.

d) On the assumption that the monofunctional vinyl compound in the DVB mixture is ethyl vinylbenzene.

e) [(Found exchange capacity)/(Calcd. exchange capacity)]·100. f) Weight content of DVB unit.

tended to slow down as the degree of cross-links increased. Calculated elementary composition of saponified and acidified resins based on the cation exchange capacity did not agree with the observed, presumably due to relatively large errors in capacity determination.

Cation exchange resins prepared here had a high separation factor for Ca^{2+} over Mg^{2+} ($K_{\text{Mg}}^{\text{Ca}}$) at p_{H} 10.1, especially for high degrees of cross-linking (Fig. 2). It is well known that cross-linked polymethacrylic acid, Amberlite IRC-50, does not separate alkaline earth cations (Fig. 2). Since apparent acidity constants (pK_a) of these carboxylic resins are all 6.2 to 6.5 (Table 5), including 6.2 of Amberlite IRC-50, the observed high $K_{\text{Mg}}^{\text{Ca}}$ -value of the resins based on VBA cannot be interpreted in terms of acidity of the carboxyl group. Further informations will be needed for understanding of this anomaly.

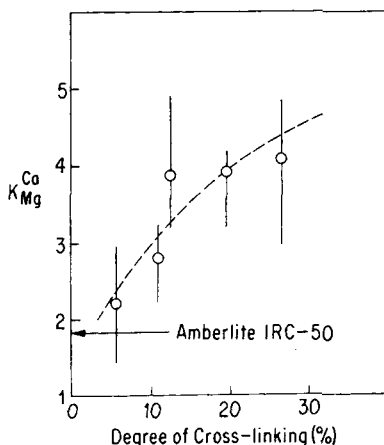


Fig. 2. Relationship between the separation factor for Ca^{2+} over Mg^{2+} ($K_{\text{Mg}}^{\text{Ca}}$) at p_{H} 10.1 and degree of cross-linking of VBA-VBMe-DVB cation exchange resin

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