

[CONTRIBUTION FROM THE RESEARCH LABORATORY, ROHM & HAAS CO.]

Methoxymethyl Vinyl Sulfide, Vinyl Thiocyanate and Allied Polymers¹

BY JESSE C. H. HWA

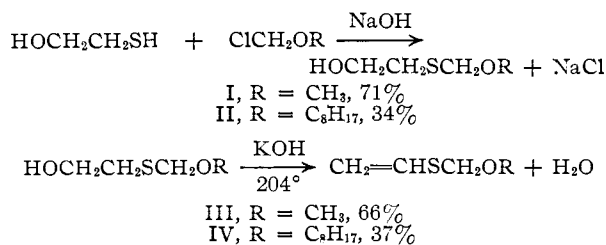
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Methoxymethyl vinyl sulfide (MMVS) and vinyl thiocyanate have been synthesized by conventional methods to provide for new vinyl sulfide-type monomers suitable for second-stage oxidation to polymers having ethylene sulfonic acid units. MMVS could be homo- and copolymerized readily with several common vinyl and polyvinyl monomers. Oxidation of poly-(MMVS) by aqueous hydrogen peroxide in acid medium gave a good yield of poly-(ethylenesulfonic acid). Oxidation of MMVS-divinylbenzene copolymer gave insoluble poly-(ethylenesulfonic acid) ion exchange resins having exchange capacities somewhat greater than those of poly-(styrenesulfonic acid)-type. A MMVS-ethyl acrylate-divinylbenzene terpolymer has been converted stepwise to a sulfocarboxylic acid ion exchange resin. Poly-(MMVS) and MMVS-methyl methacrylate copolymers could be cured by heat to become insoluble by second-stage crosslinking. Vinyl thiocyanate was similar to but somewhat less reactive than MMVS in many respects.

Most commercial sulfonic acid ion exchange resins are of crosslinked poly-(styrenesulfonic acid) type. It is of interest to synthesize a crosslinked poly-(ethylenesulfonic acid) ion exchange resin which has a higher exchange capacity (lower equivalent weight). Ethylenesulfonic acid or its alkyl esters are not suited as the starting monomers for such synthesis because of poor copolymerization behavior² and/or water solubility and instability³ which are not desirable for conventional suspension polymerization practice. Synthesis by oxidation of polymeric simple alkyl vinyl sulfides is not satisfactory because the corresponding sulfones will be stable toward further oxidation. Brubaker⁴ has oxidized poly-(vinyl thioacetate) to poly-(ethylenesulfonic acid).

The purpose of this work was to prepare new vinyl sulfide type monomers having labile sulfide functional groups, to study the preparation and properties of polymers and copolymers from these monomers and to examine methods of converting the crosslinked polymers to polyethylenesulfonic acid ion exchange resins.

Methoxymethyl vinyl sulfide (MMVS) (III) was synthesized by reaction of equimolar quantities of sodium 2-hydroxyethyl mercaptide and chloromethyl methyl ether to give 4-methoxy-3-thiabutanol (I) in 71% yield, and by dehydration of I in 66% yield over hot caustic. 2-Ethylhexoxymethyl vinyl sulfide (IV) was prepared in a similar manner.



MMVS has been homopolymerized in bulk under nitrogen atmosphere, using dimethyl azobisisobutyrate as the catalyst. The solvent-purified polymer was obtained in 72% yield and its molecular weight by ebulliometry was about 14,000.

(1) This paper was presented before the Division of Organic Chemistry at the first Delaware Valley Regional Meeting of the American Chemical Society, at Philadelphia, Pa., on February 16, 1956.

(2) C. G. Overberger, D. E. Baldwin and H. P. Gregor, *THIS JOURNAL*, **72**, 4864 (1950).

(3) J. Ferns and A. Lapworth, *J. Chem. Soc.*, **101**, 273 (1912).

(4) M. M. Brubaker, U. S. Patent 2,378,536 (1945).

Poly-(methoxymethyl vinyl sulfide) was clear, tacky and capable of cold flow at room temperature. MMVS also has been copolymerized with *n*-butyl acrylate and methyl methacrylate. The copolymerization of MMVS with several crosslinking agents has been studied; some typical results are listed in Table I. The best yield of the crosslinked resin was obtained when MMVS was copolymerized with divinylbenzene in bulk (79%). Suspension polymerization of the same two monomers resulted in a lower yield (41%). The amount of MMVS found in the purified resin, based on sulfur analysis, was less than that in charge. This disparity may be explained by the greater reactivity of a styrene than a vinyl sulfide.⁵

TABLE I
COPOLYMERIZATION OF MMVS WITH CROSSLINKING AGENTS

Cr. link. agent	Wt. % agent	Wt. % cata. ^a	Time, hr.	Temp., °C.	Yield, %	% S in copolymer Calcd. ^b Found	
DVB ^a	4.0	1	16	70-75	79	28.7	26.4
DVB	8.5	2	16	70-75	79	26.4	21.0
DVB	8.5	4	16	80-85	35
DVB ^{c,d}	8.5	2	48	60	61
DVB ^c	12.0	2	65	65-70	54	24.4	21.3
TVB ^e	4.0	2	16	60-75	64
1,5-BP ^f	8.5	2	16	70-75	65

^a Dimethyl azobisisobutyrate. ^b From charge. ^c Expt. conducted in presence of saturated brine, MgSiO₃ wax (Eyrite) and a buffer. ^d A similar suspension polymerization resulted in 41% yield. ^e 1,3,5-Trivinylbenzene; cf. D. T. Mowry and E. L. Ringwald, *THIS JOURNAL*, **72**, 2037 (1950). ^f 1,5-Bis-(vinylmercapto)-pentane, prepared at Rohm and Haas Co. by the vinylation of 1,5-pentanedi-thiol; W. P. Hall and E. E. Reid, *THIS JOURNAL*, **65**, 1466 (1943), by the method of R. C. Morris and G. W. Conklin, U. S. Patent 2,664,414 (1953). ^g Commercial divinylbenzene containing 55-60% of divinylbenzene.

Poly-(methoxymethyl vinyl sulfide) has been oxidized by acidic 10% aqueous hydrogen peroxide in an estimated 95% yield to poly-(ethylenesulfonic acid). Oxidation of crosslinked MMVS polymers to insoluble poly-(ethylenesulfonic acid) ion exchange resins was achieved readily by the same method. The results are shown in Table II. A comparison of the ion exchange capacity data obtained with those theoretically obtainable shows that a substantial chemical conversion of the sulfide to sulfonic acid functional groups was effected. No attempt has been made to account for the discrepancy found between salt-splitting cation ca-

(5) C. C. Price and J. Zomlefer, *THIS JOURNAL*, **72**, 14 (1950).

TABLE II
 OXIDATION OF MMVS-DVB COPOLYMERS TO INSOLUBLE POLY-(ETHYLENESULFONIC ACID) RESINS

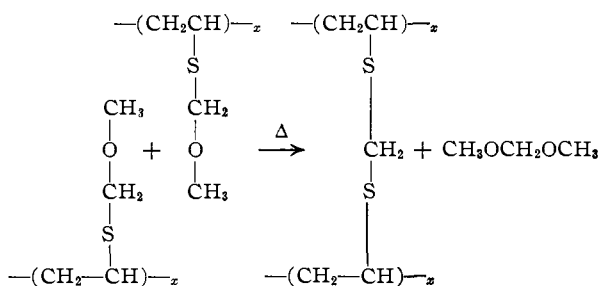
% DVB	% H ₂ O ₂ ^a	Time, hr.	Temp., °C.	Solids, %	CEC		SSCC ^b		Density lb./cu. ft.
					meq./g.	meq./ml.	meq./g.	meq./ml.	
4	5	10	45-55	23.2	7.7	1.35	6.50	1.18	48.3
4	10	6	50-55	17.1	7.43	0.94	5.70	0.72	45.9
8.5	10 ^c	10	25	~30	4.80
8.5	10	6	50-55	25.4	7.68	1.30	6.15	1.04	41.5
8.5	10 ^c	10	45-55	30.5	7.53	1.63	5.55	1.21	44.4
8.5	35	5	50-55	39.0	5.20	..	4.44
8.5 ^d	10	6	50-55	9.6	8.35	0.45	5.42	0.29	35.1
12.0	10	6	54-57	34.4	6.1	..	5.23

^a 8-15 moles of H₂O₂ used per mole MMVS; oxidation mixture consisted of H₂O₂ and 4% H₂SO₄. ^b Calcd. SSCC for the oxidized copolymers containing 4, 8.5 and 12% DVB, based on % S found in the intermediates, are 8.3, 6.6 and 6.7 meq./g., respectively. ^c Oxidation mixture contained equimolar (based on H₂O₂) quantities of acetic acid. ^d 1,5-Bis-(vinylmercapto)-pentane being the crosslinking agent.

capacity⁶ (SSCC)—a measure of strong (sulfonic) acid capacity—and cation exchange capacity⁶ (CEC)—a measure of total (strong and weak) exchange capacity. In any event the magnitude of the salt splitting cation capacity obtained (5.2-6.5 meq./g.) showed some improvement over that of a conventional poly-(styrenesulfonic acid) type resin (~5.0 meq./g.).

MMVS also has been utilized in synthesizing mixed functional sulfocarboxylic acid ion exchange resins. A MMVS-ethyl acrylate-divinylbenzene (20:65:8.5) terpolymer was first prepared by suspension polymerization. From the intermediate, an insoluble sulfocarboxylic acid resin, having 9.65 and 1.63 meq./g. of CEC and SSCC, respectively, was obtained first by the hydrolysis of the ester units and then by the oxidation of the sulfide units.

MMVS homopolymer and MMVS-methyl methacrylate copolymers could be crosslinked by curing with heat alone. Table III lists the results. The data show that crosslinking was enhanced by longer time, higher temperature of cure and greater concentration of MMVS in the resin. The second-stage crosslinking phenomenon may best be explained by a disproportionation reaction between two monothioformal functional groups to a dithioformal and a formal.⁷



The second monomer examined was vinyl thiocyanate⁸ (VII); von Braun and Kirschbaum attempted but failed to prepare vinyl thiocyanate by alkaline degradation of N-β-thiocyanatoethyl-

(6) S. Fisher and R. Kunin, *Anal. Chem.*, **27**, 1191 (1955).

(7) F. W. Wenzel and E. E. Reid, *This Journal*, **69**, 1090 (1937); H. Hochme and H. Bentler, *Ber.*, **89**, 1470 (1956).

(8) VTC may be considered as a vinyl pseudohalide. Three other known members of the family are: vinyl cyanide (acrylonitrile); vinyl isocyanate, CH₂=CHN=C=O, G. D. Jones, J. Zomlefer and K. Hawkins, *J. Org. Chem.*, **9**, 500 (1944); and vinyl isothiocyanate, CH₂=CHN=C=S, G. D. Jones and R. L. Zimmerman, U. S. Patent 2,757,190 (1956).

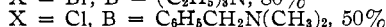
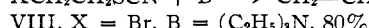
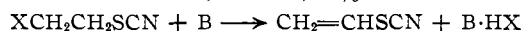
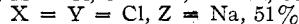
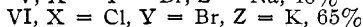
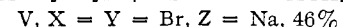
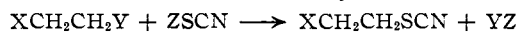
TABLE III

SECOND-STAGE CROSSLINKING OF METHOXYMETHYL VINYL SULFIDE POLYMERS

Com- position by weight MMA: MMVS ^a	Cure		Data after cure		
	Time, hr.	Temp., °C.	Wt. loss, %	Solv. in EDC ^d	Swelling ratio ^e
0:100 ^b	1	105	..	+ ^f	..
0:100 ^c	5	140	..	- ^g	..
90:10	1.5	150	..	+	..
90:10	4	150	1.5	-	5.3
90:10	4	180	5.0	-	2.8
90:10	4	200	4.4	-	2.9
95:5	4	150	..	+	..
95:5	4	180	2.3	-	4.3
95:5	4	200	3.9	-	4.2

^a Polymers obtained by bulk polym. at 60° for 40 hr., 0.025% dimethyl azobisisobutyrate as catalyst. ^b Polym. under nitrogen atm. and at 0.5% catalyst. ^c Sample was amber colored after cure; all the rest of the samples were clear. ^d Ethylene dichloride. ^e Vol. swollen resin/vol. dry polymer; in EDC. ^f Cold-flow. ^g Rubbery.

methylaniline methiodide.⁹ Vinyl thiocyanate was prepared by the dehydrohalogenation of the β-bromo- and β-chloroethyl thiocyanates (V and VI) with a tertiary amine in 80 and 50% yields, respectively. The β-haloethyl thiocyanates were prepared by treating the appropriate ethylene dihalide with an alkali metal thiocyanate.



Vinyl thiocyanate (VTC) was similar to methoxymethyl vinyl sulfide in polymerization characteristics. Vinyl thiocyanate has been homopolymerized in bulk to a brittle resin soluble in dimethylformamide and acetone. It could also be copolymerized with common acrylic monomers and divinylbenzene in moderate yields.

Vinyl thiocyanate polymers and certain copolymers were also capable of second stage crosslinking. Poly-(vinyl thiocyanate), whether in the solid state or in solution, slowly became partially insoluble upon standing in air at room temperature. A *n*-butyl acrylate-VTC (95:5) emulsion

(9) J. v. Braun and G. Kirschbaum, *Ber.*, **53**, 1399 (1920).

could be air-dried on glass to form a continuous, tacky but insoluble film.

Oxidation of crosslinked vinyl thiocyanate polymers to poly-(ethylenesulfonic acid) type ion exchange resins proceeded with considerable difficulty. Generally either the oxidation conditions were not vigorous enough that no apparent oxidation took place, or, under more energetic conditions, sulfonic acid groups were formed but at the expense of extensive degradation. Among the common reagents, alkaline hydrogen peroxide achieved best results; a VTC-6% divinylbenzene copolymer has been so converted to a resin having 3.46 meq./g. CEC and 1.52 meq./g. SSCC.

In conclusion, methoxymethyl vinyl sulfide appears to be a versatile monomer capable of copolymerization and second-stage crosslinking. Oxidation of crosslinked MMVS polymers readily yields ion exchange resins containing ethylenesulfonic acid units. Vinyl thiocyanate is similar to MMVS but is generally less reactive.

Acknowledgment.—The author is indebted to the assistance of Messrs. L. Miller, W. A. Fleming and E. Mowrey who conducted part of the experiments and to Dr. E. F. Meitzner who encouraged the undertaking of the work.

Experimental¹⁰

4-Methoxy-3-thiobutanol (I).—A mixture of 80.0 g. (1.94 moles) of sodium hydroxide pellets, 156 g. (2.0 moles) of 2-mercaptoethanol and 700 ml. of anhydrous 2B ethanol (commercial grade) was stirred at 25–50° until solution was complete. After the solution was cooled to 0–5° by means of an ice-water-bath, 155 g. (1.86 moles) of chloromethyl methyl ether (technical grade, about 95%) was added slowly in a course of 30–45 min. while maintaining the temperature at 8–12°. The ice-water-bath was removed and the mixture was stirred at room temperature overnight. The precipitated salt was removed by filtration and washed twice with 150-ml. portions of 2B ethanol. The washings were combined with the mother liquor to which 0.5 g. of quinone was added. The liquid was fractionally distilled at diminished pressure; 163 g. (71%) of the product was obtained, b.p. 57–58° (1 mm.), n_D^{20} 1.4873, d_4^{20} 1.1109, (M)²⁰D 31.59 (calcd.¹¹ 31.69), OH number 459 (calcd. 459); λ_{max} 3440s(C-OH), 1187s cm.⁻¹(C-O-C-S-C).

Anal. Calcd. for C₄H₁₀O₂S: C, 39.31; H, 8.18; S, 26.2. Found: C, 39.27; H, 7.90; S, 25.9.

Methoxymethyl Vinyl Sulfide (III).¹²—In a 150-ml. stainless steel beaker equipped with a stainless steel stirrer, dropping funnel and take-off condenser, 30 g. of potassium hydroxide pellets was heated to and maintained at 204–208° (bath), by means of a hydrogenated linseed oil-bath, for 30 min. A mixture of 83.4 g. (0.68 mole) of 4-methoxy-3-thiobutanol and 0.5 g. of quinone was added dropwise into the molten caustic in a course of 2 hr. during which water and MMVS were distilled simultaneously. The aqueous phase was separated from the distillate. The organic phase was dried over anhydrous potassium carbonate and then fractionally distilled; 47 g. (66%) of a colorless oil was collected at 78–80° (190 mm.), n_D^{20} 1.4807, d_4^{20} 0.9955, (M)²⁰D 29.80 (calcd.¹¹ 29.69); λ_{max} 3080vs(=C-H stretch), 1590m (C=C stretch), 1187m, 1088s (C-O-C-S-C), 957 cm.⁻¹ (H-C=CH₂ wagging).

Anal. Calcd. for C₄H₈OS: C, 46.15; H, 7.73; S, 30.79. Found: C, 45.91; H, 7.82; S, 30.60.

(10) All boiling points and melting points are uncorrected. Ion exchange capacity determinations and elementary analyses were made by the Control Laboratories of the Rohm and Haas Co. Infrared spectra were determined with a Perkin-Elmer double beam infrared spectrophotometer, model 21, and interpreted by Dr. J. D. Stroupe and his staff.

(11) A. I. Vogel, *J. Chem. Soc.*, 1833 (1948).

(12) T. F. Doumani, U. S. Patent 2,402,878 (1946).

4-(2-Ethylhexoxy)-3-thiobutanol (II).—By the method similar to the preparation of I, from 234 g. (3.0 moles) of 2-mercaptoethanol, 124 g. (3.0 moles) of sodium hydroxide, 1050 ml. of absolute alcohol and 520 g. (2.91 moles) of 2-ethylhexyl chloromethyl ether, II was isolated as an azeotrope, b.p. 104° (0.6 mm.), n_D^{20} (mixture) 1.4581, d_4^{20} (mixture) 0.9180; λ_{max} 3420m (C-OH), 1180w, 1150m, 1073s (C-O-C-S-C), 1117m (C-O-C-O-C),¹³ 1055s cm.⁻¹ (C-OH). The product amounted to 347 g. or 33.5% yield at 62.0% purity, assuming the other component in the azeotropic mixture was di-(2-ethylhexyl)-formal.

Anal. Calcd. for C₁₁H₂₄O₂S (as 62.0% azeotrope with di-(2-ethylhexyl)-formal): S, 9.04; OH no., 158. Found: S, 9.04; OH no., 157.

2-Ethylhexoxymethyl Vinyl Sulfide (IV).—A mixture of 60 g. (0.17 mole) of the above azeotropic mixture, 0.5 g. of quinone and 60 g. of potassium hydroxide pellets was stirred in a stainless steel beaker at 210–220° for 8 hr. After cooling, the liquid portion was removed by decantation and fractionally distilled under diminished pressure. The product, 13.8 g. (37.1%), was obtained as a colorless oil, b.p. 93° (4 mm.), n_D^{20} 1.4698, d_4^{20} 0.8986, (M)²⁰D 62.63 (calcd. 62.22); λ_{max} 3075vw (=C-H stretch), 1590m (C=C stretch), 1155m, 1088s (C-O-C-S-C), 956m (CH=CH₂ wagging) cm.⁻¹.

Anal. Calcd. for C₁₁H₂₂OS: S, 15.8. Found: S, 16.0.

The Homopolymerization of MMVS.—In two 20-ml. vials with metal-foil lined screw caps, duplicate charges of a mixture of 5.00 g. of MMVS and 0.050 g. of dimethyl azobisisobutyrate were heated at 66° under nitrogen atmosphere for 40 hr. Weight losses of 0.021 g. and 0.014 g., respectively, were noted. The sirupy contents were combined, dissolved in 15 ml. of acetone and the solution precipitated from 100 ml. of methanol. Poly-(MMVS) was isolated by decantation and drying over anhydrous calcium chloride *in vacuo*, at room temperature. The product, weighing 7.20 g. (72%), was clear and tacky. It was soluble in ethylene dichloride and toluene and insoluble in water and methanol. Its molecular weight by ebulliometry (in acetone) was 13,600 ± 20%. The infrared absorption spectrum of poly-(MMVS) showed the two absorption bands at λ_{max} 1183m, 1080s cm.⁻¹ which appear to be characteristic of the C-O-C-S-C system associated with the -C-O-C- stretching; the spectrum also showed absence of band at 1590 cm.⁻¹ (C=C stretch).

Copolymerization of MMVS with Crosslinking Agents.—The copolymerizations were conducted in 20-ml. vials with metal-foil lined screw caps. The vial charged with ca. 5 g. of the monomer-catalyst mixture was flushed with nitrogen, capped and placed in a heated oil-bath. After a length of time, the gel was removed, extracted with ethylene dichloride in a Soxhlet for 4 hr. and dried at 65° for 5 to 8 hr. The results of the various experiments are listed in Table I.

Suspension Copolymerization of MMVS and Divinylbenzene.—A mixture of 11.4 g. of sodium chloride, 1.76 g. of a 3% aqueous suspension of magnesium silicate wax (Eyrrite), 20 ml. of water and 7.5 ml. of a borate-buffer solution prepared from 43 ml. of 0.1 N sodium hydroxide, 50 ml. of 0.2 M boric acid and 7 ml. of water was stirred for 20 min. under nitrogen atmosphere. The monomer solution consisting of 17.1 g. of MMVS, 2.8 g. of commercial divinylbenzene (Koppers Chemical Co., 59.8% active, inhibitor removed by washings with 5% sodium hydroxide) (8.5% divinylbenzene based on the monomers) and 0.40 g. of dimethyl azobisisobutyrate was added. The suspension was agitated at such a rate that the oil droplets had diameters of ca. 0.30–1.40 mm. The mixture was heated at 80–85° for 22 hr. At this time the mixture still had a strong MMVS odor, the aqueous phase had a pH of 7 and the beads were soft. The resin was removed by filtration, stirred twice with 200-ml. portions of alcohol and extracted with ethylene dichloride in a Soxhlet for 4 hr. The dried resin weighed 8.1 g. (41%).

Anal. Calcd. for (C₄H₈OS)_n (85% copolymer): S, 26.4. Found: S, 21.0.

Poly(-ethylenesulfonic Acid).—A mixture of 0.900 g. of poly-(MMVS), 28 g. of 35% hydrogen peroxide, 61 g. of water and 11 g. of concentrated hydrochloric acid (d. 1.178) was heated at 50–55° for 10 hr. and at 60–65° for 6.5 hr. The clear solution was evaporated to dryness at 80°. Water

(13) H. Tschamler and R. Leutnar, *Monatsh.*, **83**, 1502 (1952).

was added to the residue to give a solution weighing 2.13 g. and containing ca. 40% solids. By titration with 0.1 *N* sodium hydroxide, the solution contained 0.888 g. (95%) of poly-(ethylenesulfonic acid) by calculation.

A Sulfocarboxylic Acid Ion Exchange Resin from MMVS and Ethyl Acrylate.—A mixture of 0.0096 g. of gelatin, 0.96 g. of a commercial dispersing agent (Amberlite W-1, 20% aqueous solution), 0.5 g. of sodium bicarbonate and 149 g. of water was stirred for 30 min. under nitrogen atmosphere. The monomer mixture consisting of 10.0 g. of methoxymethyl vinyl sulfide, 32.6 g. of inhibitor-free ethyl acrylate (EA), 7.4 g. of commercial divinylbenzene (57.4% active, weight proportion of 20:65:8.5, respectively) and 1.0 g. dimethyl azobisisobutyrate was added. The oil-in-water suspension was stirred at an appropriate rate (168 r.p.m.) and heated at 70–75° for 8 hr. The resin was separated by filtration, rinsed thoroughly with water and dried at 105° for 4 hr. The EA–MMVS–DVB terpolymer was obtained in 86.6% yield (43.3 g.).

Hydrolysis of the terpolymer to a carboxylic acid resin was effected by refluxing 43.3 g. (0.280 mole ester unit) of the terpolymer with a mixture consisting of 12.9 g. (0.322 mole) of sodium hydroxide, 14.6 g. of water and 58.4 g. of ethanol for 16 hr. After cooling, 300 ml. of water was added in a period of 1 hr. The mixture was filtered. The resin was then stirred, and alternately isolated by filtration, with three 300-ml. portions of 2 *N* sulfuric acid. The moist resin weighed 49 g.; 24.5 g. of the moist resin was thoroughly rinsed with deionized water until the washing was neutral to litmus. The product, a carboxylic acid resin, weighed 22.7 g., and had 76.4% solids, 7.6% S (dry basis, calcd. 7.5%), 7.39 meq./g. of CEC^s and 0.14 meq./g. of SSCC^s (calcd. 8.0 and 0 meq./g., respectively).

Oxidation of the carboxylic acid resin to sulfocarboxylic acid resin was effected by heating 24.5 g. of the above acid-laden resin with a mixture of 400 ml. of 10% hydrogen peroxide, 9 ml. of concentrated sulfuric acid and 10 ml. of water at 50–55° for 5 hr. After usual washings, the product weighed 31.7 g. and had 52.0% solids, 7.3% S (dry basis, calcd. 7.4%), 9.65 meq./g. of CEC and 1.63 meq./g. of SSCC (calcd. 10.3 and 2.3 meq./g., respectively).

β -Bromoethyl Thiocyanate (V).—A mixture of 325 g. (4.0 moles) of sodium thiocyanate, 1840 g. (1035 ml., 12.0 moles) of ethylene dibromide and 400 ml. of absolute alcohol was refluxed for 16 hr. The sodium bromide precipitate was removed by filtration and washed with two 175-ml. portions of alcohol. The combined liquid containing 0.5 g. of added quinone was distilled under reduced pressure. An oil-bath should be used and the pot temperature should not exceed 150–155°. This precaution was necessary because the product, as well as the β -chloro analog VI, often would decompose and polymerize when superheated, leading to run-away reactions. Fractionation of the liquor gave 1487 g. of recovered ethylene dibromide, b.p. 89° (197 mm.), 57° (50 mm.); 130 g. of residue which was chiefly ethylene dithiocyanate; and 303 g. (46%, based on sodium thiocyanate; lit.¹⁴ 2%) of the product, b.p. 99° (8 mm.), 78° (2 mm.), n_D^{20} 1.5512.

Anal. Calcd. for C₂H₄BrNS: Br, 48.2. Found: Br, 48.0.

β -Chloroethyl Thiocyanate (VI).—A mixture of 891 g. (712 ml., 9.0 moles) of ethylene dichloride, 243 g. (3.0 moles) of sodium thiocyanate and 300 ml. of alcohol was heated with stirring in a stainless steel autoclave at 125° and 67–70 p.s.i.g. for 7 hr. The resultant mixture was worked up similar to the preparation of V; 183 g. (51%) of the product was obtained, b.p. 83–87° (9 mm.) (lit.¹⁵ b.p. 106° (25 mm.)), n_D^{20} 1.5145.

Vinyl Thiocyanate (VTC) (VII).—A mixture of 166 g. (1.0 mole) of V, 114 g. (1.1 moles) of triethylamine, 0.5 g. of quinone and 300 ml. of benzene was heated with stirring under nitrogen atmosphere by means of a water-bath at 65–75° for 2.75 hr. At the end of this period no further increase in the amount of salt deposited was noticeable. The reaction mixture promptly was cooled. The salt was removed by filtration and washed with 30 ml. of benzene. The combined liquid was distilled carefully under reduced pressure and nitrogen atmosphere. The pot temperature should be kept as low as practical. The portion boiling at

54° (62 mm.), 51° (55 mm.) or 122° weighed 68 g. (80%), n_D^{20} 1.4880, d_4^{20} 1.036, (M)²⁰_D 23.67 (calcd.^s 23.24), molecular weight by ebulliometric method 86 ± 4 (calcd. 85.1); λ_{max} 1600s (C=C stretch), 909s, 950s, (C=C–H wag), 2170s (–S–C≡N) cm.⁻¹, no absorption at 2050–2080 cm.⁻¹ (–N=C=S).

Anal. Calcd. for C₃H₃NS: C, 42.4; H, 3.55. Found: C, 42.7; H, 3.65.

Vinyl thiocyanate, when freshly obtained, was a colorless liquid of repulsive odor. Upon standing in air at room temperature it gradually turned red. Upon mixing with equal parts of diethylenetriamine, VTC reacted explosively yielding a water-soluble polymer. Upon standing with twice its volume of thioacetic acid at room temperature for 10 days, a monoadduct was obtained, m.p. 124–127° (recrystallized once from ethanol-water).

Anal. Calcd. for C₆H₇NOS₂: N, 8.7; S, 39.8. Found: N, 8.6; S, 40.4.

Homopolymerization of Vinyl Thiocyanate.—A mixture of 2.0 g. of freshly distilled vinyl thiocyanate and 0.025 g. of dimethyl azobisisobutyrate was degassed and evacuated to 1.0 × 10⁻⁵ mm. at liquid nitrogen temperature in an ampoule. The ampoule was sealed and then heated at 70° for 64 hr. at which time the mass turned to dark red in color. The viscous sirup was mixed with 10 ml. of acetone and the solution added to 100 ml. of methanol with stirring. The polymer was purified by precipitation in this manner for two more times. The powdery product was dried at room temperature in vacuum overnight.

Anal. Calcd. for (C₃H₃NS)_x: N, 16.5; S, 37.7. Found: N, 14.0; S, 33.2.

Poly-(vinyl thiocyanate) was soluble in dimethylformamide and acetone and insoluble in methanol, water, benzene, carbon tetrachloride, acetic acid and carbon disulfide. On drying its solution in acetone, the polymer that remained was brittle. Upon standing in air at room temperature, poly-(vinyl thiocyanate), whether in the dry form or in acetone solution, gradually became partially insoluble in acetone.

Copolymerization of Vinyl Thiocyanate.—A methyl methacrylate–ethyl acrylate–vinyl thiocyanate terpolymer (52:43:5) was prepared in 40% toluene solution at 80° using benzoyl peroxide as catalyst. The polymer was obtained in 96.2% conversion.

Anal. Calcd. for (C₃H₃NS)_x (from charge): N, 1.0. Found: N, 0.7.

Stable emulsions of 95:5 and 90:10 *n*-butyl acrylate–vinyl thiocyanate copolymers were prepared in 96 and 100% yields, respectively, by a conventional oxidation–reduction recipe. The 95:5 copolymer was air-dried to a clear continuous film which was tacky but did not dissolve in acetone.

Preparation of a Sulfonic Acid-type Ion Exchange Resin from Vinyl Thiocyanate.—In a manner similar to that described for the suspension polymerization of methoxymethyl vinyl sulfide and divinylbenzene, an insoluble vinyl thiocyanate–divinylbenzene copolymer was obtained in the form of small beads. A mixture of 25.5 g. (0.30 mole) of freshly distilled vinyl thiocyanate, 2.91 g. (0.0135 mole) of commercial divinylbenzene (Dow Chemical Co., 58% active) and 0.30 g. of dimethyl azobisisobutyrate was suspended in 90 ml. of deionized water containing 0.67 g. of Amberlite W-1 (Rohm and Haas Co., 20% solids) by stirring. The suspension was heated at 88–92° for 8 hr. after which the hardened beads were isolated by filtration. The copolymer was purified by washing with four 200-ml. portions of acetone over a period of 6 hr. and then dried at 65° for 16 hr. The yield was 15.3 g. (54%).

Anal. Calcd. for (C₃H₃NS)_x (94% copolymer): N, 15.5; S, 35.3. Found: N, 11.6; S, 29.3.

A mixture of 5.0 g. of the vinyl thiocyanate–6 weight % divinylbenzene copolymer, 10 g. of sodium hydroxide, 80 ml. of 30% hydrogen peroxide, 40 ml. of water and a trace of commercial antifoam was heated gradually from 50 to 80° in 1 hr. and maintained at 80° for 8 more hr. The mixture was cooled, diluted with 200 ml. of water and filtered. The beads were washed with three 200-ml. portions of 2 *N* hydrochloric acid in a course of 18 hr. and then with four 300-ml. portions of water in a course of 6 hr. The washed beads were dried at 110° for 3 hr. The yield was 1.2 g. The resin had 3.46 meq./g. of CEC and 1.52 meq./g. of SSCC.

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