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Sulfonium Polymers Derived from Ar-Vinylbenzyl Chloride. I. Exploratory Study of the Preparation and Properties of the Monomers and Polymers

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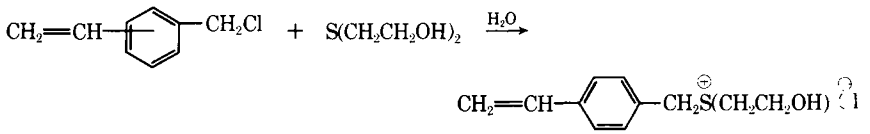
Synopsis

Although sulfonium salts are well known, polymeric sulfonium salts seldom have been mentioned in the chemical literature. This paper describes exploratory work in the preparation of various sulfonium monomers and polymers from ar-vinylbenzyl chlorides (*ortho* and *para* isomers). These chlorides—particularly the *para* isomer—reacted readily with 2,2′-thiodiethanol and water to yield the corresponding ar-vinylbenzyl sulfonium chloride monomers in aqueous solution.



The odorless, reactive monomer mixture polymerized readily with persulfate or hydroperoxide catalysts; however, polymerization could be inhibited with cupric salts. Copolymerization with trimethyl(ar-vinylbenzyl)ammonium chloride was random. In copolymerization with acrylamide or acrylonitrile, the sulfonium monomer was more reactive. Analogous sulfonium monomers were made by reaction of ar-vinylbenzyl chlorides with various sulfides. In general, all the sulfonium monomers yielded homopolymers which were fairly stable in aqueous solution in the absence of strongly nucleophilic agents which would attack the sulfonium groups. However, when dried at room temperature the polymers would crosslink; and when heated, the polymers became hydrophobic also. Scrambling of the sulfonium group substituents during drying, and nucleophilic displacement reactions by chloride ion during heating were likely explanations. The high cationic charge on the polymers made them substantive to cellulose fibers. This property, when coupled with high nucleophilic reactivity of the sulfonium groups with the carboxylate sites of the pulp or other anionic counterions during drying and heating, made the polymers very effective as beater additives for imparting wet strength to paper.

INTRODUCTION

Sulfonium salts have been known for over a century, and there exists a voluminous literature regarding them. However, high polymeric sulfonium salts have seldom been reported. Perhaps the fact that sulfonium

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compounds are relatively unstable and break down to generally smelly sulfides has discouraged much work on incorporation of the sulfonium functionality into polymeric systems.

There are sulfonium salts derivable from nonodorous sulfides, however, and the very reactivity of the sulfonium functionality can convey interesting properties to polymers. Thus, one of the present workers (M. J. H.) found that the water-swollen gel particles of poly[dialkyl(ar-vinylbenzyl)-sulfonium chloride], made by reaction of alkyl sulfides with chloromethylated, divinylbenzene-crosslinked polystryene, were very reactive to water-soluble nucleophiles. As a result, a wide variety of ion-exchange resins, including chelating ion-exchange resins, could be synthesized readily from these crosslinked sulfonium polymers and the appropriate nucleophiles.[1]

As an outgrowth of the studied of such crosslinked sulfonium polymers, the present workers have explored the synthesis and some properties and uses of water-soluble ar-vinylbenzylsulfonium monomers and polymers. The availability to this laboratory of large quantities of mixed *ortho* and *para* isomers of vinylbenzyl chloride, made by the process of McMaster and Stowe,[2] made the synthesis of the sulfonium monomers relatively simple. The ar-vinylbenzyl chlorides were sufficiently reactive so that many of the sulfonium salts could be made readily by simple agitation of the chlorides with water and the appropriate organic sulfide.

Thus, the first sulfonium monomer prepared in this laboratory was produced upon stirring at room temperature a mixture of water, 2,2′-thiodiethanol (thiodiglycol or diethanol sulfide are other names), and mixed *ortho* and *para* vinylbenzyl chloride isomers ($o/p \cong {}^1/_2$). The resulting aqueous mixture of sulfonium monomers (*ortho* and *para* isomers) was not isolated. After several days, during which the oil layer had progressively decreased in volume, the mixture gradually became quite viscous, indicating that the sulfonium monomers had polymerized spontaneously.

Sulfonium polymer from this reaction was purified by precipitation in acetone, and immediate redissolution of the gummy mass in water. The solution was colorless, odorless, and quite stable at room temperature. But the dry (or almost dry) polymer would crosslink on standing overnight. The polymer was effective as a beater additive for giving wet strength to paper handsheets.[3] (See data presented later in this article.)

No offensive odors were evolved when the treated paper was dried and oven-cured, since 2,2′-thiodiethanol has little odor, is rather innocuous, and is high-boiling (283°C).[4] These interesting and possibly useful properties of the sulfonium polymer stimulated further studies.

PREPARATION OF BIS(2-HYDROXYETHYL)-(AR-VINYLBENZYL)SULFONIUM CHLORIDE AND RELATED MONOMERS

Aqueous solutions of the bis(2-hydroxyethyl)sulfonium monomers were prepared by stirring inhibited ar-vinylbenzyl chloride with 2,2-thiodiethanol and water which contained small amounts of Cu^{II} salts. From a purified sample of *p*-vinylbenzyl chloride, the corresponding bis(2-hydroxyethyl)(*p*-vinylbenzyl)sulfonium chloride was obtained as a relatively pure, white hydroscopic solid. The product was characterized by chemical and spectroscopic analyses, and by conversion to the picrylsulfonate salt.

Solutions which contained very predominately the ortho isomer were prepared readily by reaction of high-*ortho* mixtures of *o*- and *p*-vinylbenzyl chloride ($o/p \cong 9$) with 2,2′-thiodiethanol and water. Most of the experimental studies, however, were conducted with the use of an easily obtained mixture of *ortho* and para isomers of the sulfonium monomers ($o/p \cong {}^1/_2$), made from a corresponding mixture of *ortho* and *para* isomers of vinylbenzyl chloride. The sulfonium monomers in aqueous solution were characterized by chloride ion, hydrogen ion, and unsaturation analyses.

To optimize the preparation of the usual mixed sulfonium monomers, temperatures and concentrations were varied in the stirred heterogeneous mixture of organic chloride, sulfide, and water. Figures 1–3 show the results. Increasing concentrations of reactants increased the rate of reaction until the amounts of organic chloride and sulfide became large relative to the amount of water. The rate then leveled off. Thus, the rate was essentially the same when 1.4 mole (25 g) or 2.8 mole (50 g) of water was present per mole of chloride (152 g) and sulfide (122 g) (Fig. 1).

The effect of the reaction temperature is shown in Figure 2. Increasing the temperature increased the rate of reaction, of course; however, side-reaction hydrolysis also increased. This hydrolysis—either of starting chloride or product sulfonium salt—produced

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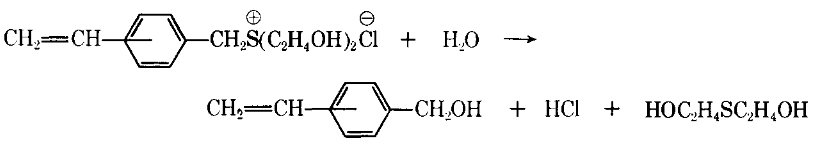
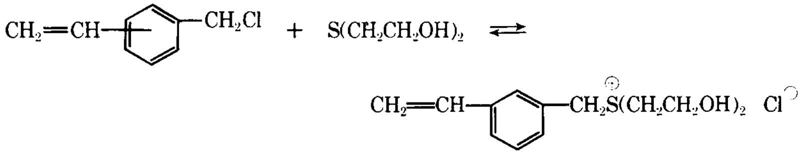


(2)

over three times as much acid (HCl) in 4 hr at 50°C as it did in 40 hr at 85°C, even though the total conversion to sulfonium monomer was somewhat less in the 50°C experiment. Compromise conditions, shown in Figure 3 were considered as optimum: about 2.8 mole of water per mole of chloride and sulfide at 40°C gave near-maximum conversion (about 75%) in 10–12 hr with only 2% hydrolysis.

In all mixed-chloride runs, conversion leveled out at about 75–80%, which indicated that the reactions came to equilibrium, due to nucleophilic attack of chloride ion on the sulfonium salt to re-form starting materials [eq. (3)].



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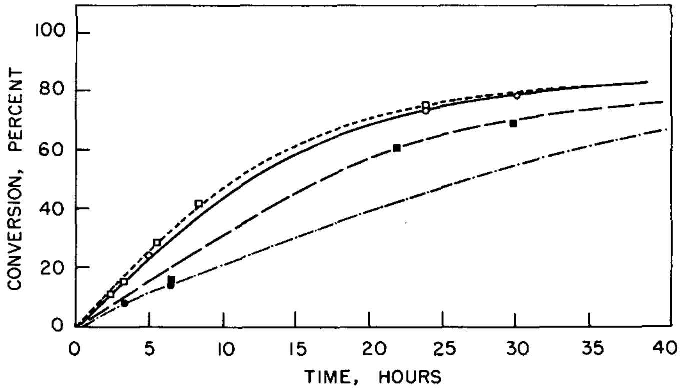


Fig. 1. Effect of concentration on rate of stirred reaction of mixed *ortho* and *para* vinylbenzyl chlorides ($o/p \cong {}^1/_2$, 1 mole, 152.5 g) and 2,2′-thiodiethanol (1 mole, 122 g) at 25°C. Mls H_2O: -□---□--- 25 -○——○- 50 -■— —■- 100 ●-·-·-● 200.

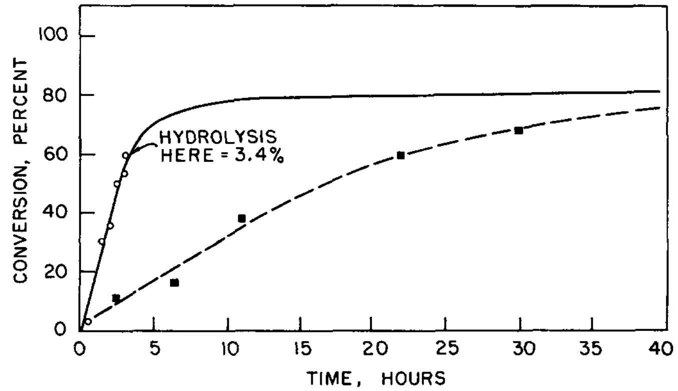


Fig. 2. Effect of temperature on rate of stirred reaction of mixed *ortho* and *para* vinylbenzyl chlorides ($o/p \cong {}^1/_2$, 1 mole, 152.5 g) and 2,2′-thiodiethanol (1 mole, 122 g) in water (5.55 mole, 100 g). Temperatures: -○——○- 50°C ---■---■--- 25°C.

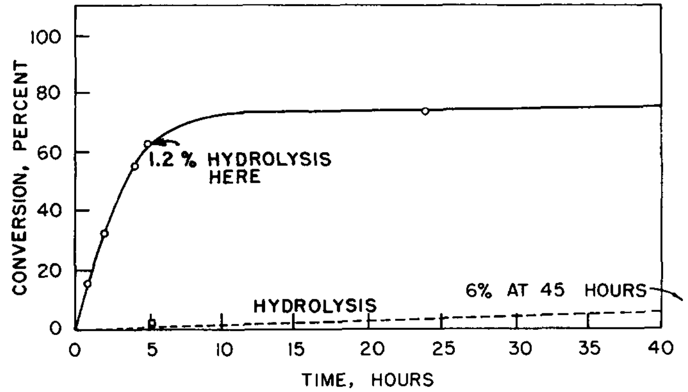


Fig. 3. Reaction of mixed *ortho* and *para* vinylbenzyl chlorides ($o/p \cong {}^1/_2$, 1 mole, 152.5 g) and 2,2′-thiodiethanol (1 mole, 122 g) in water (2.8 mole, 50 g) in water (2.8 mole, 50 g) under optimum conditions.

The equilibrium point was different for the *ortho* and the *para* isomers. A preparation from high-*ortho* vinylbenzyl chloride ($o/p \cong 9$) leveled out at about 75% conversion, but a preparation from purified *para* isomer went to about 95% conversion. The less favorable equilibrium for the *ortho* isomer may be due to the presence of some steric strain between the vinyl group and the rather bulky bis(2-hydroxyethyl)sulfonium group of the product.

Kinetic studies also showed that the *ortho* isomer reacted at a slower rate with the 2,2′-thiodiethanol than did the para isomer. Thus, a high-*ortho* vinylbenzyl chloride mixture ($o/p \cong 3$) reached only about 8% reaction by the time purified *para* isomer had reached 30% reaction (Fig. 3 conditions).

The above equilibrium and kinetic results were consistent with those found in a large-scale preparation (several gallons, Fig. 3 conditions), with the use of the usual *ortho* and *para* mixture of ar-vinylbenzyl chlorides ($o/p \cong {}^1/_2$). In this preparation, the product solution was diluted with water and extracted with perchloroethylene. The unreacted vinylbenzyl chloride recovered from this extract was mainly the *ortho* isomer, although the starting mixture was mainly *para* isomer.

Various sulfonium monomers other than bis(2-hydroxyethyl) sulfonium chloride were made by reaction of different sulfides with the usual mixtures of ar-vinylbenzyl chlorides ($o/p \cong {}^1/_2$). Ordinarily, the sulfonium monomers were polymerized without isolation, since the objective was primarily to evaluate the polymers directly as additives to paper.

Table I shows a summary of the monomer preparations. The ar-vinylbenzyl chloride mixture, sulfide, and water were stirred together at about 35°C, and conversions to sulfonium monomers and to by-products were determined by analyses of the aqueous solutions. The experiments indicated that oil-soluble, bulky sulfides reacted much less readily than smaller, water-soluble sulfides. Apparently, reaction between a sulfide and the ar-vinylbenzyl chlorides was facilitated if it could occur at the water–oil interface, where the high dielectric constant and solvation of the highly polar transition state molecules would help lower their free energies.

POLYMERIZATION OF BIS(2-HYDROXYETHYL(AR-VINYLBENZYL) SULFONIUM CHLORIDE AND RELATED MONOMERS

In the absence of inhibitors, the usual aqueous mixtures of *ortho* and *para* isomers of bis(2-hydroxyethyl)(ar-vinylbenzyl)sulfonium chlorides polymerized on standing at or below room temperature. The best inhibitor found was Cu^{II} in quite high concentrations. Thus, the aqueous monomer solutions (25–50%) could be stored in the refrigerator for several months without significant polymer formation in the presence of 2000 ppm of $CuSO_4$.

An interesting feature of the spontaneous polymerization of uninhibited monomer solutions was the formation of highly crosslinked gels, even in the presence of considerable residual monomer. Addition of water-soluble

TABLE I

Preparation of ar-Vinylbenzylsulfonium Monomers and Polymers[a]

Run	Organic sulfide	Sulfide, mmole	ar-Vinyl-benzyl chloride (VBC), mmole	Vol water, ml	Reaction time, hr	VBC converted, %: Sulfonium product	VBC converted, %: Hy-drolysis product	Polymerization conditions	Viscosity of polymer solution, cP[b]
1	CH_3SCH_3[c]	1370	1100	100	72	70	2	Long standing at 5°C[d]	—
2	$S(CH_2)_4$[c,e]	43	39	6.5	120	67+[f]	—	Polymerized during monomer preparation	1.39
3	$C_6H_5CH_2SCH_3$[c]	65	65	17	143	7[g]	3	$Na_2S_2O_3$ + HOC_2H_4SH or UV light[h]	—
4	$CH_3SCH_2CH_2OH$	230	230	50	96	96	4	Polymerized during monomer preparation	1.02
5	$CH_3SCHOHCH_2OH$	111	222	30	24	87	3	Polymerized during monomer preparation[i]	1.06
6	$CH_3SCH_2CONH_2$	38	38	25	144	62[j]	10	UV light, 4 hr	2.20
7	$CH_3SCH_2CH_2CONH_2$	84	84	50	22	74[k]	2	UV light, 4 hr	1.95
8	CH_3SCH_2COONa	113	113	10	46	90+[l]	5[l]	Standing 5 days at 5°C	—
9	$S(CH_2CH_2COOH)_2$	178	179	100	120	26[m]	9[m]	UV light several days	2.1
10	$CH_2CH_2CH_2OH$ / S \\ CH_2CH_2OH	1000	1000	100	30	70	1–3	—	—

[a] Vinylbenzyl chloride (mixed isomers, $o/p \cong {}^1/_2$, except for use of purified *para* isomer in run 2), sulfide, and water were stirred at ca. 35°C (air atmosphere). Chloride and hydrogen ion analyses used to determine conversion to products. If polymerization occurred during monomer preparation, polymer was precipitated with acetone and redissolved immediately in water. Otherwise, the aqueous phase was extracted with ether, polymerized under N_2, and polymer produced was isolated as described. Polymer content of final polymer solutions was found by ionic chloride analysis or by vacuum drying at room temperature over P_2O_5.

[b] Viscosities were taken at 25°C on 0.5% solutions of polymer in 2% NaCl (aq.).

[c] Odorous sulfide.

[d] Two years storage at 5°C. Conversion to polymer was 30%.

[e] Tetrahydrothiophene.

[f] Yield of isolated polymer (in aqueous solution) was 67%.

[g] Note low conversion. Use of mixed $CH_3OH—H_2O$ solvent gave better conversion (45% sulfonium salt, 9% solvolysis in 120 hr).

[h] Polymer was insoluble.

[i] A few gels, easily removable by filtration, were formed.

[j] The sulfonium salt presumably was the expected $RS^{\oplus}(CH_3)CH_2CONH_2Cl^{\ominus}$, since the homologous monomer of run 7 had not hydrolyzed at the amide group under similar, acidic conditions.

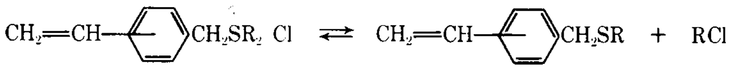
[k] Proton magnetic resonance analysis of product for NH_4^+ content showed that hydrolysis of amide groups must have been less than 10 percent. Titration of product solution with NaOH caused rapid breakdown, apparently by a facile reverse Michael (elimination) reaction: $RS^{\oplus}(CH_3)CH_2CH_2CONH_2 + OH^{\ominus} \rightarrow H_2O + RSCH_3 + CH_2{=}CHCONH_2$.

[l] The values are approximate. It was assumed that no vinylbenzyl ester formed since VBC + CH_3COONa gave less than 2% reaction under similar conditions.

[m] The aqueous phase was extracted with ether until the $[H^+]/[Cl^-]$ ratio remained constant.

mercaptans, such as 2-mercaptoethanol, did not stop the polymerization, but usually led to soluble polymers, presumably due to molecular weight reduction by chain transfer.

The crosslinking which occurred with unmodified monomer solution may be explained by the postulate that a small amount of *scrambling* (interchange) of the substituent groups of the sulfonium monomer occurred *during or after* its preparation. This scrambling would form some (2-hydroxyethyl)bis(ar-vinylbenzyl)sulfonium chloride crosslinker.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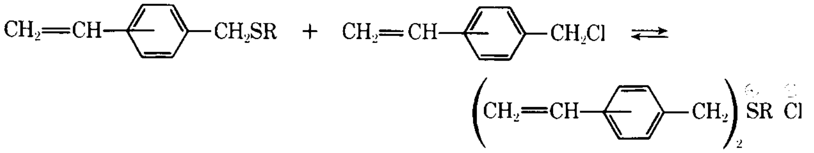
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R = CH_2CH_2OH etc.

A series of polymerization experiments were made in which various amounts of $Na_2S_2O_5$, $HOCH_2CH_2SH$, $Na_2S_2O_8$, *t*-BuOOH, etc., were added to perchloroethylene-extracted monomer solutions. The conversion of monomer to polymer was followed by measuring the decrease in ultraviolet absorption due to conjugation of the vinyl group and the aromatic ring. Thus the para isomer had one of its ultraviolet absorption maxima at 295 mμ (molar absorptivity, $\epsilon \simeq 1000$). The *ortho* isomer had much less absorption ($\epsilon \simeq 220$) and no distinct maximum in this region; and the polymer from the mixed isomers had very much less absorption ($\epsilon \simeq 20$, ϵ being based on mer weight and the usual log base 10). Consequently, the absorbance at the 295 maximum minus the baseline absorption between 300 and 293 provided a measure of the *para sulfonium monomer content* (Fig. 4).

In the experiments, the polymerization behavior was somewhat erratic, possibly due to certain differences in the ar-vinylbenzyl chloride samples used, and, therefore, in the resulting sulfonium monomers. Various experiments are summarized in Table II. The results indicated that use of $HOCH_2CH_2SH$, in conjunction with $Na_2S_2O_8$ or *t*-BuOOH at temperatures up to 50°C, would yield high conversions (over 90%) to soluble polymer which was very effective as a wet-strength additive to paper. The pH of the system could be under 1 without any apparent deleterious effect. In large preparations of the polymer, therefore, the practical approach was to make stepwise additions of the above modifier and catalyst to the perchloroethylene-extracted monomer solution and polymerize for several days at room temperature under nitrogen (at higher temperatures, shorter schedules were satisfactory). Residual monomer could be removed by cation exchange on a strongly acidic exchanger.

The actual degree of copolymerization of the *ortho* monomer with the *para* monomer in the polymerizations of the mixed monomers was not measured directly. The *ortho* monomer appeared to enter into polymerization less readily than the *para* isomer, however, as indicated by cation-exchange

TABLE II

Polymerization Experiments with Aqueous Bis(2-hydroxyethyl)(ar-vinylbenzyl)sulfonium Chloride[a,b]

Run	Monomer solids (total), %	Temperature, °C	$Na_2S_2O_8$ added, %	*t*-BuOOH added, %	$HOCH_2CH_2SH$, added, %	Conversion rates, days/% polymer[d]		
						Time/polymer	Time/polymer	Time/polymer
1	52	25	—	—	—	0/5	3/x	—
2	52	25	—	—	1.0	0/5	3/90	6/99
3	50	25	—	0.5	0.5	0/13	0.75/85	3/x
4	52	25	1.0	—	1.0	0/5	3/94	6/99
5	52	50	—	—	—	0/5	0.7/x	—
6	52	50	—	—	1.0	0/5	0.7/?	6/x
7	50	50	—	0.5	0.5	0/15	0.17/80	3/x
8	52	50	1.0	—	1.0	0/5	0.12/60	3/x
9	35	50	—	1.0	1.0	0/20	0.35/96	5/x
10	35	50[c]	0.75[c]	—	0.75	0/18	0.27/77	3/91

[a] The pH (less than 1) of the monomer solutions was not adjusted, the solutions being used as prepared (See footnote b). Tabulated runs all were under nitrogen. Other runs indicated that small amounts of air had little effect. Continuous bubbling of air (through solutions) inhibited polymerization, however (25°C). Addition of excess $Na_2S_2O_5$ to $Na_2S_2O_8$ catalyzed systems caused conversions to stop very much short of completion (pH 5). The rates of conversion to polymer were found by ultraviolet absorption analysis for *para* isomer content, and strictly speaking measure only the rates of conversion to polymer of this isomer, which likely polymerized somewhat faster than the *ortho* isomer.

[b] Monomer used was an *o,p* mixture of isomers ($o/p \cong 1/2$). Monomer preparation was essentially as shown in Figure 3. The aqueous monomer solutions were prepared and extracted with perchloroethylene shortly before use. The starting vinylbenzyl chloride mixture (VBC) was inhibited with ca. 100 ppm of *t*-butylcatechol and 100 ppm of *m*-nitro-*p*-cresol for monomer of runs 3, 4, 9, and 10. Remaining runs were from monomer prepared from VBC inhibited only with *t*-butylcatechol.

[c] Three-step addition of $Na_2S_2O_8$ and $HOCH_2CH_2SH$ (0, 2, 5 hr). Sample let stand at 25°C after 18 hr.

[d] Crosslinked polymer denoted by x.

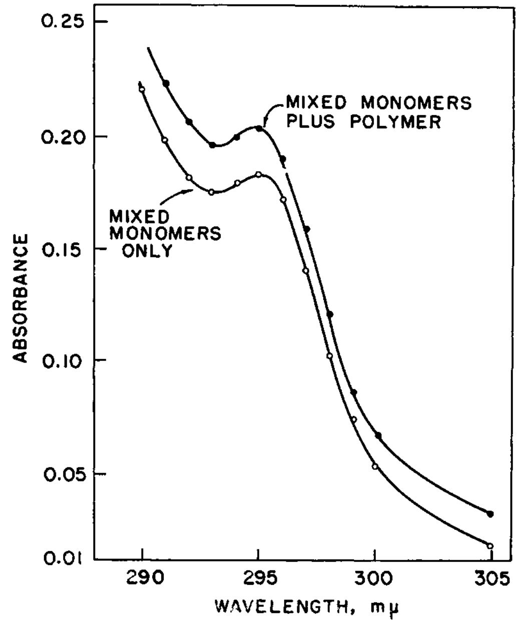


Fig. 4. Ultraviolet absorption in the 295 mμ region of mixed *ortho* and *para* isomers ($o/p \cong 1/2$) of bis(2-hydroxyethyl) (ar-vinylbenzyl)sulfonium chloride ($2.32 \times 10^{-3}N$) alone, and in the presence of its polymer ($2.59 \times 10^{-3}N$).

conversion of residual monomers to HCl and comparison of the amount of HCl with the amount of residual *para* monomer, as determined by ultraviolet absorption. Thus, in one case, conversion of *ortho* monomer was only 82% while the conversion of *para* monomer (measured by ultraviolet absorption) was 94%. This interpretation of the cation-exchange data assumed that because of size exclusion of large molecules, no appreciable amount of sulfonium polymer was exchanged onto the resin.

No systematic studies were made of the polymerization of any of the sulfonium monomers except the *o,p* mixture of bis(2-hydroxyethyl)(ar-vinylbenzyl)sulfonium chloride. The other sulfonium polymers, which formed spontaneously or by application of ultraviolet light or peroxide catalysis, were isolated by precipitation into acetone and redissolved immediately in water to avoid crosslinking. The polymer solutions then were evaluated directly as wet strength resins for paper.

PREPARATION OF COPOLYMERS OF BIS(2-HYDROXYMETHYL)(AR-VINYLBENZYL) SULFONIUM CHLORIDE

Copolymers were prepared from Cu^{++}-inhibited *o,p* mixtures of the sulfonium chloride monomer, sodium hydroxide, excess ethylendiaminetetraacetic acid (to complex Cu^{++}), phosphate buffer (pH of 5), sodium persulfate, and 2-mercaptoethanol. The comonomers were added to this mix-

TABLE III

Copolymers of Bis-(2-hydroxyethyl)(Ar-vinylbenzyl)sulfonium Chloride[a]

Run	Comonomer	Composition of charge polymerized				Time of polymerization, hr	Yield of copolymer, wt-%	Composition of copolymer, mer % sulfonium, monomer[d]
		Sulfonium monomer, mole-%	Total solids, %[b]	$Na_2S_2O_8$, %[c]	$HSCH_2$-CH_2OH, %[c]			
1-a	Trimethyl (ar-vinylbenzyl) ammonium chloride	61	62	0.9	0.9	24	63	63
1-b	"	44	47	0.9	0.9	24	53	48
1-c	"	28	40	0.9	0.9	24	64	33
2-a	Acrylonitrile	22	62[e]	0.5	0.5	90[e]	33	63
2-b	"	33	58[f]	0.7	0.7	90[f]	48	72
3-a	Acrylamide	6	35	1.0	0.2	72	37	25
3-b	"	12	42	0.8	0.8	72	—	37
3-c	"	22	37	1.5	0.6	24	42	60

[a] Ar-vinylbenzyl monomers all were *o,p* mixtures of isomers ($o/p \cong 1/2$).

[b] Per cent solids equals total grams of monomers per 100 grams of the solutions (aqueous in all cases).

[c] Per cent $Na_2S_2O_8$ and per cent $HSCH_2CH_2OH$ each as grams per 100 grams of total monomer solids present.

[d] Since the sulfonium monomers were mixtures of *o* and *p* isomers, the copolymers were actually at least three-component interpolymers in all cases. Compositions reported are based on ultimate S and N analyses, and give the total sulfonium monomers content, likely accurate to ±5 mole-%.

[e] The solution was diluted with water to 21% solids after polymerization for 2 hr.

[f] After 2 hr, the solution was stored at 5°C for 16 hr, then diluted to 25% solids and allowed to stand at room temperature.

ture, and standing at room temperature yielded the copolymers. The copolymers were precipitated into acetone and immediately redissolved in water. Like the polymers derived from the mixed *o,p*-sulfonium monomers only, these copolymers (which strictly speaking, were terpolymers or tetrapolymers) would crosslink if the precipitated masses were allowed to stand at room temperature.

The copolymer preparations are summarized in Table III. The results may be qualitatively stated. The sulfonium monomer(s) gave copolymers with *o,p* mixtures of trimethyl(ar-vinylbenzyl)ammonium chloride which were randomly uniform. However, the sulfonium monomer(s) gave copolymers with acrylonitrile or acrylamide which were enriched in the sulfonium monomer (mer) content.

BEHAVIOR OF SULFONIUM POLYMERS ON WET STORAGE, ON DRYING, AND ON HEATING

Once the various ar-vinylbenzylsulfonium polymers had been purified by precipitation and immediate redissolution in water, they were relatively stable. Thus, tests showed that 25–35% aqueous solutions of poly[dimethyl(ar-vinylbenzyl)sulfonium chloride] ($o/p \cong {}^1/_2$) or poly[bis(2-hydroxyethyl) (ar-vinylbenzyl)sulfonium chloride] ($o/p \cong {}^1/_2$) maintained essentially all their activity as wet strength additives for paper after storage for several months at room temperature. The solutions showed a gradual increase in viscosity and in acidity over a period of time, and many of the various sulfonium polymers prepared (See Tables I and III) crosslinked on long storage.

Wet storage at low temperatures (10°C) gave improved stability, of course, relative to room temperature storage. After 6 years storage at 5–10°C, three out of four samples of poly[bis(2-hydroxyethyl) (ar-vinylbenzyl)sulfonium chloride] were still not crosslinked, and one was fairly strongly crosslinked. One sample, density of 1.13 g/cc at 25°C, initially had $[Cl^-] = 1.59$, and $[H^+] = 0.34$, and a Brookfield viscosity of 52 CP at 25°C. After the 6 years storage, (Cl^-) was 1.66 (apparently some water had evaporated), $(H^+) = 0.52$, and the Brookfield viscosity was 170 CP. The viscosity of a 0.5% solution in 2% NaCl was 1.07 CP. Thus, about 13% of the sulfonium groups originally present had hydrolyzed during the long storage. Other polymers which still were not crosslinked after 6 years of low temperature storage were an aqueous 35% solution of poly[(2-hydroxyethyl)methyl(ar-vinylbenzyl) sulfonium chloride], an aqueous 8% solution of poly[(2-hydroxyethyl)(3-hydroxypropyl)(ar-vinylbenzyl)-sulfonium chloride], and an 18% solution of the copolymer of bis(2-hydroxyethyl)(ar-vinylbenzyl)sulfonium chloride and acrylonitrile.

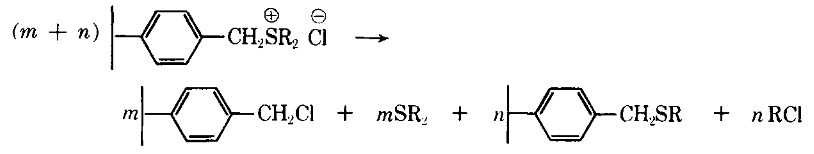
Qualitative studies were made of the drying of films of poly[bis(2-hydroxyethyl)(ar-vinylbnezyl)sulfonium chloride] and poly[dimethyl(ar-vinylbenzyl)sulfonium chloride]. Films of the former generally would crosslink mildly on air drying for a day or two at relative humidities of 50% or less, so that in water they then would form some highly swollen gels, rather than completely soluble solutions; films of the latter required several days longer to crosslink similarly. The gels vanished when treated for a few hours with excess aqueous trimethyl amine, but not when treated with excess dimethylsulfoxide. Therefore the aqueous gels were caused by a small number of covalent crosslinks which could be broken by trimethylamine.

The gels could not have been due to association of numerous benzylic chloride or other nonpolar groups produced by the mild drying, since titrations ($AgNO_3$) for ionic chloride indicated that within experimental error (ca. ±5%) essentially all the sulfonium chloride groups were still present, and such association of groups should have been broken in the excess dimethyl sulfoxide.

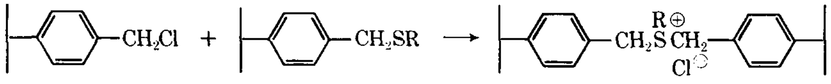
The great decrease in stability of the sulfonium polymers when dried even under mild conditions, compared to their relatively much greater stability in aqueous solution, is rather striking. Qualitatively, however, the decreased stability (increased reactivity) is readily explained. The primary step of breakdown of the sulfonium polymers should be nucleophilic attack by chloride ion or other nucleophilic species. This suggestion is in accord with the established S_{N2} mechanism of reaction of several benzylic dimethylsulfonium salts (aq.) with OH^- ion,[6] or the reaction of $(CH_3)_3S^+$ in ethanol even with very weak nucleophiles or solvent.[7] Since the time required to complete a specified fraction of an S_{N2} reaction is inversely proportional to the initial concentration of reactants, the high concentration of sulfonium groups and chloride in the amorphous polymer film as the solution dries out will naturally produce a higher reactivity, provided that the sulfonium groups and chloride ions are not fixed in unfavorable orientations in the semisolid or solid film. The fact the dried polymer will be an amorphous solid, rather than a crystalline solid (such as formed by relatively stable low molecular weight sulfonium salts) means that fixed unfavorable orientations are quite unlikely. Also, a crystalline cage effect, tending to cause recombination of sulfide and organic chloride reaction products would not be present, and diffusion of the sulfide would be relatively easy through the amorphous solid.

As the polymer dries, the loss of solvating water molecules and the likely decrease in the dielectric constant of the system could both play a very significant role in the decreasing stability (increasing reactivity) of the sulfonium polymer. This suggestion is in accord with the known facts that trimethylsulfonium bromide decomposes 10^4 times more rapidly as the anion-solvating power decreases from methanol to dimethylformamide,[8] and that the decomposition is faster also in solvents of lower dielectric constant.[7,9]

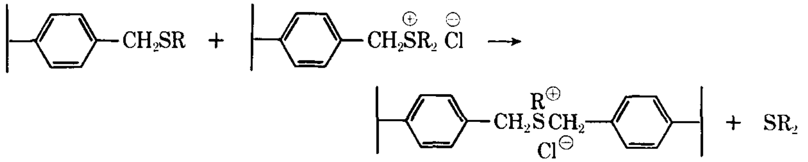
Thus, in the dried polymer, some nucleophilic attack by chloride ion at the sulfonium groups should occur *readily*. This in itself does not explain the formation of crosslinked (yet highly *hydrophilic*) polymer on drying, however. A simple extension is required. These crosslinking results may be explained by a sulfonium scrambling mechanism. As the polymers dry out, some nucleophilic attack on the various carbon atoms adjacent to the sulfonium sulfur gives benzylic chloride groups and benzylic thioether groups [eq. (6)], part of which then could react together to form sulfonium crosslinks [eq. (7a)]. Or, alternately, sulfonium scrambling might occur by direct attack of a benzylic thioether group on a benzylic sulfonium group to form the same type of sulfonium crosslink [eq. (7b)].



(6)

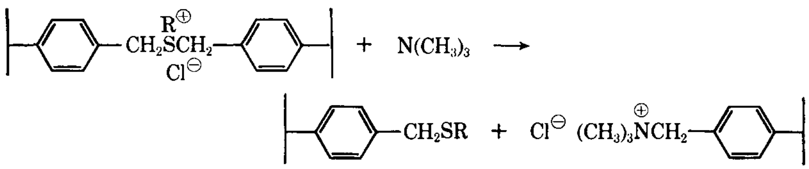


(7a)



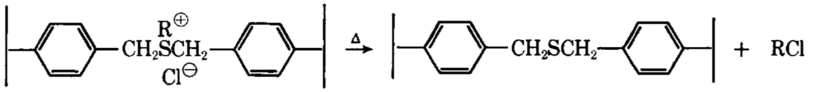
(7b)

Cleavage of the sulfonium crosslinks would then occur to a major extent when they were exposed to nucleophilic attack by trimethylamine, to give soluble polymer again [eq. (8)].



(8)

The effect of heating the polymer films was noted. An air-dried film of the bis(hydroxyethyl)sulfonium polymer was heated at 100°C for $^1/_2$ hr and suspended in water. It swelled modestly, which indicated that part of the sulfonium groups remained. Potentiometric titration of the swollen film with $AgNO_3$ showed that indeed about half of the original ionic chloride which was due to sulfonium chloride groups was still present. Overnight treatment of the film with excess aqueous trimethylamine caused it to swell considerably more, but it was far from being soluble. Apparently the heat treatment had converted a significant portion of the first-formed sulfonium crosslinks to sulfide crosslinks. Although the trimethylamine treatment could convert the benzylic chloride groups present to hydrophilic quaternary ammonium groups, it could not cleave the sulfide crosslinks, of course.



(9)

The above results may be compared with those reported by Berger,[10] who found that a benzylic dimethylsulfonium ion exchange resin lost 55% of its ionic chloride capacity on heating for 8 hr at 78°C, and that it lost all of its capacity after 8 hr at 100°C. Berger recognized the formation of benzylic chloride and benzylic sulfide groups in explaining these results. However, since he was dealing with a highly crosslinked ion exchange resin (7% divinylbenzene content), he never noted the scrambling and crosslinking possibilities which are elucidated in the present work.

EFFECT OF SULFONIUM POLYMER STRUCTURE ON WET STRENGTH ACTIVITY

As Table IV indicates, the various ar-vinylbenzylsulfonium polymers made by simply polymerizing the mixed *ortho* and *para* sulfonium monomers generally showed high activity in improving the wet strength of paper handsheets when small amounts were added to the dilute pulp slurry before the sheet was formed. The wet bursting strength, as per cent of dry bursting strength usually ranged from 15 to 30% at 0.5 to 1% loading of the polymers, based on the weight of the pulp. The dry bursting strength also generally was increased by about 30 to 70% over the strength of the untreated control sheets.

However, two polymers, poly[methyl(ar-vinylbenzyl)thetin], $[CH_2CH\text{-}C_6H_4CH_2S^{\oplus}(CH_3)CH_2COO^{\ominus}]_n$, and poly[bis(2-carboxyethyl)(ar-vinylbenzyl) sulfonium chloride], $[CH_2CHC_6H_4CH_2S^{\oplus}(CH_2OOH)_2Cl^{\ominus}]_n$, produced very little effect on wet or dry strength. These results, it is felt, demonstrate that the polymers needed a definite net positive charge in order to be adsorbed well at the negatively charged sites (carboxylate groups, presumably) of the paper pulp. Since both of the ineffective polymers would be in the zwitterionic form in dilute aqueous solution at a pH near 7, they likely did not absorb on the pulp appreciably, and so little or no effect on the strength properties resulted.

There were significant differences in the wet strength activity of the fully cationic polymers, also, which might have been caused by the differing structures of the alkyl and substituted alkyl groups of the sulfonium functionality. Thus, poly[(2,3-dihydroxypropyl)methyl(ar-vinylbenzyl) sulfonium chloride] was somewhat unusual, since it gave good wet strength (19% of dry), but it gave poor dry-strength improvement (10%). However, since the polymers may not have been fully comparable in molecular weights, degree of branching, etc., one properly can compare only the gross activities. Such comparison indicates that the activity certainly was not sensitively dependent on the nature of the pendant alkyl or substituted alkyl groups, as long as the substituents were not anionic groups which would detract from the fully cationic nature of the polymer.

That the sulfonium functionality as such was vitally important to the effectiveness of the polymers as wet strength resins for paper is established quite definitely by the data of Table IV. Thus, the interpolymers of bis(2-hydroxyethyl)(ar-vinylbenzyl)sulfonium chloride with trimethyl(ar-vinylbenzyl)ammonium chloride, or with acrylamide, or with acrylonitrile

TABLE IV

Effect of Sulfonium Polymers on the Dry and Wet Strength of Paper Handsheets[a]

Run	Mer constituents of polymers added to paper pulp slurry	Polymer loading, %	Dry burst factor	Increase over control, %	Wet burst factor	Wet burst, % of dry burst[b]
1	Bis(2-hydroxyethyl)(ar-vinylbenzyl) sulfonium chloride (VBS)	0.5	36.2	62.3	8.7	24.0
2	"	1.0	41.7	71.6	11.9	28.0
3	Dimethyl(ar-vinylbenzyl)sulfonium chloride	1.0	38.7	46.6	12.6	32.5
4	(2-Hydroxyethyl)methyl(ar-vinylbenzyl) sulfonium chloride	0.5	32.8	33.9	5.3	16.2
5	(2,3-Dihydroxypropyl)methyl (ar-vinylbenzyl)sulfonium chloride	0.5	37.3	9.7	7.2	19.3
6	(2-Carbamoylmethyl)methyl (ar-vinylbenzyl)sulfonium chloride	0.5	33.9	38.4	6.9	20.4
7	(2-carbamoylethyl)methyl (ar-vinylbenzyl)sulfonium chloride	0.5	31.1	26.9	5.1	16.4
8	Methyl(ar-vinylbenzyl)thetin	1.0	28.3	6.4	1.6	5.7
9	Bis(2-carboxyethyl)(ar-vinylbenzyl) sulfonium chloride	1.0	—	−4.4	—	4.5
10	VBS (48 mole-%) and trimethyl (ar-vinylbenzyl)ammonium chloride (52 mole-%)[c]	1.0	30.8	25.7	6.1	24
11	VBS (37 mole-%) and acrylonitrile[d]	0.5	—	35.8	—	20.9
12	VBS (25 mole-%) and acrylamide[e]	1.0	26.7	20.8	3.3	12
13	VBS (37 mole-%) and acrylamide[f]	1.0	32.7	48.0	6.8	20.8

[a] Pulp was unbleached hardwood soda, beaten to a Canadian Standard Freeness of about 400 ml., and the loading of sulfonium additive was based on the weight of the dry pulp. The handsheets were prepared using a modification of TAPPI Standard Method T 205-m-53. The pulp slurries which contained the sulfonium additive were at a pH range of 6.5–7. The handsheets were cast and then conditioned at least 48 hr at 21°C and 62% RH. Tests for dry burst were made by using TAPPI Standard Method T220-m-53. Wet bursting strengths were made after soaking the test samples in deionized water for 4–24 hr. All test results were corrected for the basis weight of the sheets. All test data were obtained by C. G. Humiston, Biochemical Research Laboratory, The Dow Chemical Company, Midland, Mich. All ar-vinylbenzyl polymers contained *ortho* and *para* mers. Thus, strictly speaking, the polymers of runs 1–8 were copolymers of the *ortho* and *para* sulfonium monomer isomers, with the *para* isomer content = *ca.* 67 mole-%; the polymers of runs 8–11 were terpolymers of the *ortho* and *para* sulfonium monomers and the listed comonomer; and the polymer of run 7 was from the mixture of *ortho* and *para* sulfonium monomers and the mixture of *ortho* and *para* quaternary ammonium monomers.

[b] The dry burst referred to is the dry burst of the treated paper, not the dry burst of the control.

[c] 54 wt-% sulfonium mer.

[d] 89 wt-% sulfonium mer.

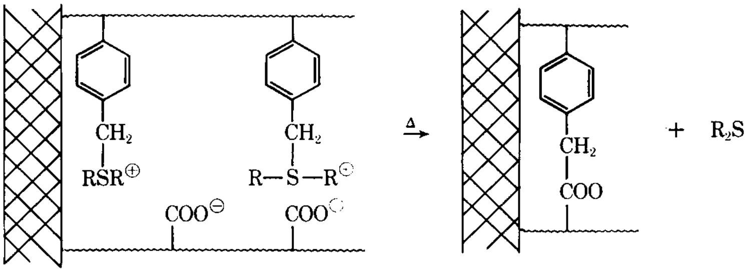
[e] 56 wt-% sulfonium mer.

[f] 69 wt-% sulfonium mer.

all were active as wet strength resins. However, these interpolymers lost activity as the sulfonium monomer (mer) content decreased.

Morgan and one of the present authors studied the effect of anionic polymers as coadditives to the paper pulp, along with the sulfonium polymers.[5] This work showed that the dry and wet strength properties could be improved more by application of sulfonium polymer plus anionic coadditive such as methacrylic acid, than by use of sulfonium polymer alone. This was especially the case under conditions of low degree of thermal cure. Thus, a loading of 0.33% of poly[bis(2-hydroxyethyl)(ar-vinylbenzyl)-sulfonium chloride] plus 0.17% of poly(methacrylic acid), added to a soda pulp slurry (pH 6), gave handsheets which when cured for 1 min at 102°C had a dry burst improvement of 43% and a wet burst retention of 17% relative to the control. A loading of 0.50% of the sulfonium polymer gave handsheets with only 13% improvement in dry burst and 11% retention of wet burst under the same conditions.[5]

Apparently the sulfonium polymer was adsorbed well on the anionic sites of the cellulosic pulp fibers and ionized poly(methacrylic acid) was coadsorbed onto cationic sites of the sulfonium polymer which were not associated with anionic fiber sites. Then, when the handsheets were dried mildly, the carboxylate groups of both the ionized poly(methacrylic acid) and the fiber sites produced nucleophilic displacement reactions at the sulfonium groups of the sulfonium polymer [eq. (10)]. As a result, the composite established interfiber bonding more readily than would have been the case if the sulfonium polymer only had been present.



(10)

Probably the establishment of such polymeric ester interfiber bonding is the vital factor in the efficient production of wet strength, and the formation of hydrophobic but nonbonding benzylic chloride or benzylic sulfide groups probably is only a minor factor. If so, the ease of displacement reactions at the carbon atom which attaches the sulfonium group to the polymer chain is of high importance to the functioning of the polymer as a wet strength resin. One does expect that nucleophilic attack on the benzylic carbon atom present in all the polymers studied would be much easier than attack on ordinary alkyl carbon atoms. This expectation is confirmed by the work of Berger[10] which was mentioned earlier. He found that a thermally fully decomposed benzylic dimethylsulfonium chloride ion exchange resin contained about twice as much chlorine as sulfur by ultimate analysis (12.3% compared to 6.2%).

Although the above suggestions on mechanism of wet strength performance by the sulfonium resins are only speculative, the following conclusions are offered. (*1*) High cationic character of the sulfonium resins, coupled with reasonably high molecular weights, causes the resins to *adsorb* strongly to the anionic (carboxylate) sites of the paper fibers. (*2*) Drying and thermal cure causes the formation of interfiber bonds at the contact areas of the fiberous paper mat through the formation of a plurality of ester links between the carboxylate sites of the fibers and the polymer. (*3*) These ester links are obtained as a result of nucleophilic displacement reactions by these carboxylate groups on the benzylic carbon atoms attached to the sulfonium sulfur atom, with concurrent liberation of organic sulfide. (*4*) Attack of the carboxylate groups at other carbon atoms attached to the sulfonium sulfur is of minor importance to the development of wet strength, as also is, attack by any other nucleophilic ions on any of the sulfonium carbon atoms. (*5*) The charge density of the sulfonium polymers is so high that a considerable portion of the sulfonium groups in an adsorbed polymer do not have fiber carboxylate groups associated with them. (*6*) Coaddition of proper amounts of certain carboxylic, soluble polymers results in a secondary adsorption of the carboxylic polymer to the paper fibers by adsorption onto the primarily adsorbed sulfonium polymer: and increased buildup of interfiber bonding under mild thermal cure is the result.

EXPERIMENTAL

Preparation of Purified para and High-ortho Vinylbenzyl Chlorides

These materials were obtained from several different workers connected with The Dow Chemical Co., Midland, Mich., and were typically prepared from a usual mixture of *ortho* and *para* isomers ($o/p \cong {}^1/_2$) of vinylbenzyl chloride, obtained by dehydrochlorination of mixed *o* and *p*-(1-chloroethyl)-benzyl chlorides.[2] Careful fractional distillation (all-glass still, good vacuum, dinitro-*o*-cresol or other inhibitor), yielded an early cut, bp 56–57°C/1 mm) which was 80% *ortho* isomer, 10% *para* isomer, 10% impurities by gas-chromatographic analysis (0.25 in. × 6 ft stainless steel column, 15% acid-washed Chromosorb at 150°C. On-column injection was necessary to prevent considerable decomposition or polymerization).

A later cut, bp ~ 60°C/1 mm, crystallized on storage at −25°C. Decantation of the liquid phase, washing of the melted crystals then with sodium bisulfite and water to remove aldehydes, and flash distillation *in vacuo* yielded the *para* isomer in about 99% purity, as estimated by gas chromatography, infrared spectroscopy, and freezing curve (freezing point −12.86°C).

ANAL. Calcd for C_9H_9Cl: Cl, 23.3%. Found: Cl, 23.2%.

Sources and Preparation of Sulfides and Monomers

Dimethyl sulfide, 2,2′-thiodiethanol, tetrahydrothiophene, benzyl methyl sulfide, 3,3′-thiodipropionic acid, acrylamide, and acrylonitrile all were commercial materials. 2-Hydroxyethyl methyl sulfide was prepared by the reaction in ethanol of 2-hydroxyethyl mercaptan, sodium hydroxide, and methyl iodide; product bp, 65°C/20 mm: reported,[11] bp 81°C/30 mm. Trimethyl (ar-vinylbenzyl)ammonium chloride ($o/p = {}^1/_2$) was made by reaction of ar-vinylbenzyl chloride isomers with trimethylamine.[12]

Methylthioacetamide

To 10 g of methyl methylthioacetate was added 20 ml of concentrated aqueous ammonia. The resulting two-phase system was shaken overnight. The solid amide which formed was filtered and washed with ice water, and the filtrate was concentrated to yield more solid amide. The combined solid was air dried overnight to yield the product (7.0 g); mp 95–102°C, reported[14] mp 99–102°C.

Methylthiopropionamide

To dry acrylamide (43 g, 0.6 mole) in methanol (100 ml) was added 50 g (1.0 mole) of methyl mercaptan, in methanol (80 ml). (The reaction vessel used was equipped with a Dry Ice-cooled condenser. The methyl mercaptan and methanol had been precooled before mixing, to avoid volatilization losses.) Sodium methoxide (0.5 g) was added, and the mixture was warmed gently until it refluxed. After 28 hr without any further heating, the reaction vessel contents were removed and the volatiles were allowed to evaporate in a hood. The solid product remaining was methylthiopropionamide (68 g, essentially 100% yield); mp 74–78°C, mixed mp with acrylamide of mp 77–79°C was 60°C.

ANAL. Calcd for C_4H_9ONS: S, 26.9%. Found: S, 26.9%.

2,3-Dihydroxypropyl Methyl Sulfide

A solution of 2,3-dihydroxypropyl mercaptan (0.52 mole of commercial material) in water (total volume 125 ml) was neutralized with NaOH (21 g, 0.52 mole). Then methyl iodide (0.79 mole) in methanol (350 ml) was added stepwise under nitrogen. The mixture was stirred overnight and added to a mixed bed (600 ml) of strongly acidic and strongly basic ion exchange resins (Dowex 50, hydrogen form, and Dowex 1, hyroxide form).

The mixture was filtered after 1 hr and the resins were washed with 500 ml of methanol. The combined filtrates were treated again with mixed ion exchange resins (500 ml), after which no mercaptan or iodide was detectable by titration with $AgNO_3$. The methanol was removed by vacuum distillation to give the product, which was used without further purification.

Carboxymethyl Methyl Sulfide and Carbomethyoxymethyl Methyl Sulfide

Thioglycolic acid (95%, 138 g, 1.4 mole), dissolved in aqueous methanol (200 ml water and 400 ml methanol), was neutralized by cautious stepwise addition of sodium hydroxide pellets (120 g, 3.0 mole). After the solution had cooled, methyl iodide (225 g, 1.6 mole) was added slowly and the mixture was heated at reflux (40–50°C) overnight. Addition of hydrochloric acid (190 ml, 2.3 mole) in water (300 ml) gave a clear solution, which was then extracted with methylene chloride twice (500 ml. each). Distillation of the extract yielded the methyl ester of thiomethylacetic acid (carbomethyoxymethyl methyl sulfide) (bp 57–59°C/15 mm; reported[15] bp 53–55°C/11 mm). The yield was 60 g. (35%). The distillation also gave thiomethylacetic acid (carboxymethyl methyl sulfide) (54 g, 33% yield, bp 116.5°C/15 mm.; reported[16] bp 130–131°C/27 mm).

2-Hydroxyethyl 3-Hydroxypropyl Sulfide

2-Mercaptoethanol (78 g, 1.0 mole) and allyl alcohol (58 g, 1.0 mole) were mixed together in a beaker (hood). The temperature of the mixture rose to 68°C. and continued at this point for about 20 minutes before it dropped. This preparation was repeated twice more and the combined reactions were heated on a steam bath overnight in a vessel equipped with a condenser, while a slow steam of air was bubbled through the mixture. Titration with iodine then indicated that reaction was 80% complete (50% before heating). The mixture yielded pure product on distillation (312 g, 76%); bp 144°C/2.5 mm). The NMR spectrum showed no indication of $HOCH_2CH_2SCH_2CH(CH_3)OH$ in the product.[13]

Preparation of Bis(2-hydroxyethyl)(p-Vinylbenzyl)sulfonium Chloride

Purified *p*-vinylbenzyl chloride (freshly flash-distilled, 3.05 g, 0.0200 mole), 2,2′-thiodiethanol (2.45 g, 0.0200 mole), and water (2.00 ml) were stirred together at 37°C for 18 hr in the presence of 2 mg of hydroquinone and 2 mg of $CuCl_2$. Conversion to the sulfonium chloride was quantitative (within ±5% experimental error), based on $AgNO_3$ titration of an aliquot for ionic chloride. The mixture was extracted with ether and blown out with nitrogen. The aqueous solution of sulfonium salt, $[Cl^-] = 3.6$, $[H^+] = = 0.11$, appeared to be at least 90% pure from the NMR spectrum.[13]

Addition of aqueous picrylsulfonic acid to an aliquot of the solution yielded bis(2-hydroxyethyl) (*p*-vinylbenzyl)sulfonium picrylsulfonate, which was dried over P_2O_5; mp 86–87.5°C.

ANAL. Calcd for $C_{19}H_{21}O_{11}N_3S_2$: C, 42.9%; H, 3.98%. Found: C, 43.0%; H 4.08%.

The NMR spectrum of the picrylsulfonate (in D_3CSOCD_3) was consistent with the assigned structure.[13]

Repeated extraction of a portion of the aqueous sulfonium chloride (1.27 g) with anhydrous ether (ca. 25 ml, four times) removed most of the water and left a thick liquid which crystallized. The solid was titurated several times with more ether, and was dried several days *in vacuo* over P_2O_5 to give a quite-hard, white solid; mp (preheated block) 72.5–75°C (decomposition; vinylbenzyl chloride odor evident).

ANAL. Calcd for $C_{13}H_{19}ClO_2S$: C, 56.8%; H, 6.97%; vinyl unsaturation $CH_2{=}CH$. 9.83%; ionic Cl, 12.9%. Found. C, 56.5%; H, 7.01%; vinyl unsaturation (bromination), 10.1%; ionic Cl ($AgNO_3$, small sample), 11.5%.

The ultraviolet spectrum in the 250–300 mμ region (in water, Cary 15 spectrophotometer) had a broad peak at 256.5 mμ (molar absorptivity, ϵ = 22300) and weak peaks at 285 mμ (ϵ = 2230) and 295 mμ (ϵ = 1040). The NMR spectrum (in D_2O) was consistent with the proposed structure.[13]

Preparation of High-ortho Bis(2-hydroxyethyl)(ar-vinylbenzyl) Sulfonium Chloride

A mixture of high-*ortho* vinylbenzyl chloride ($o/p \cong 9$, ca. 10% other materials; 9.62 g, ca. 56 mmole), 2,2′-thiodiethanol (7.35 g, 60 mmoles), and water (6.00 ml) were stirred at 35–40°C for 18 hr in the presence of $CuCl_2$ inhibitor (0.006 g). Chloride and hydrogen ion content then indicated conversion to sulfonium monomer was 75%, and hydrolysis was 3%. The mixture was extracted with ether, and residual ether was blown out with air: $[Cl^-] = 2.63$; $[H^+] = 0.07$. The ultraviolet absorption showed small shoulders at 285 mμ (ϵ = 650) and 295 mμ (ϵ = 300). Subtracting the ~10% *para* isomer contribution eliminated the shoulders and left residual ϵ at 285 mμ of about 490 and at 295 mμ of about 220.

Rate Studies of Formation of Mixed ortho and para Isomers of Bis(2-hydroxyethyl)(ar-vinylbenzyl)sulfonium Chloride

The reactants (vinylbenzyl chloride, $o/p \cong {}^1/_2$, 2,2′-thiodiethanol, and water) were stirred in a flask immersed in a constant temperature bath. Samples of the total well-stirred mixture were removed at intervals and titrated with $AgNO_3$ to determine ionic chloride content and with NaOH to determine HCl content. Samples also were titrated in acid with bromide-bromate reagent. This reagent gave Br_2, which reacted with the vinyl groups and with 2,2′-thiodiethanol. Thiodiethanol interference with the $AgNO_3$ titration was significant early in the runs only.

$$\%\ \text{conversion} = \frac{100 \times [Cl^-]}{\text{theoretical (calcd) } [Cl^-] \text{ for } 100\% \text{ conversion}}$$

Thiodiethanol reaction with Br_2 was fairly quantitative:

$$R_2S + Br_2 + H_2O \rightarrow R_2SO + 2HBr$$

$$\%\ \text{conversion} = 100 \times \frac{\text{initial} - \text{found } Br_2 \text{ titer}}{0.500 \times \text{initial } Br_2 \text{ titer}}$$

A typical set of experimental data is shown in Table V (Fig. 3 conditions).

Preparation of Dimethyl(ar-vinylbenzyl)sulfonium Salts

To aqueous dimethyl(ar-vinylbenzyl)sulfonium chloride ($o/p \cong {}^1/_2$), prepared as in run 1, Table I, was added three volumes of 2% aqueous $KClO_4$. A dense, crystalline precipitate formed (white). After drying *in vacuo* at room temperature over P_2O_5, it reacted with the theoretically correct amount of Br_2 by titration to correspond to pure dimethyl(ar-vinylbenzyl)sulfonium perchloriate, mp 140–141°C. The NMR spectrum showed the product was pure *para* isomer.

TABLE V

Time, hr	Vol $N/2$ Br^-BrO_3, ml/ml sample	Conversion, %	Vol $N/10$ $AgNO_3$, ml/ml sample	Conversion, %	Vol $N/10$ NaOH, ml/ml sample	% Hydrolysis 100-$[H^+]/[Cl]$
0	27.2	0	4	—	—	—
0.67	25.2	15	7	17	—	—
1.93	22.7	33	13	32	—	—
4.00	19.7	55	21	52	—	—
5.00	18.7	63	24	60	0.3	1.2
24.00	17.2	73	29	72	—	—
45.00	17.3	73	30	75	1.8	6.0
71.75	16.9	75	31	78	2.3	7.4

ANAL. Calcd for $C_{11}H_{15}ClO_4S$: $CH_2{=}CH$, 9.7%; C, 47.4%; H, 5.4%. Found: $CH_2{=}CH$, 9.7% (by Br_2 titration); C, 47.7%; H, 5.6%.

Vinylbenzyl chloride ($o/p \cong {}^1/_2$) (30.4 g, 0.20 mole), dimethyl sulfide (11.6 g, 0.20 mole), and absolute ethanol (50 ml) were mixed and allowed to stand overnight. A portion (10 ml) of this solution was mixed with $BiCl_3$ (in 150 ml ethanol solution, filtered), and yielded a dense, white precipitate which soon solidified. The solid was recrystallized twice from hot methanol and dried over P_2O_5.

ANAL. Calcd for $(C_{11}H_{15}SCl)_3\cdot(BiCl_3)_2$: C, 31.1%; H, 3.6%; S, 7.5%; Cl, 25.0%, Found: C, 31.2%; 3.4%; S, 7.8%; Cl, 24.1%.

Preparation of Copolymers of Bis(2-hydroxyethyl)-(ar-vinylbenzyl)-sulfonium Chloride

The preparations of these copolymers are summarized in Table III. The sulfonium monomer mixture (Cu^{++}-inhibited, $o/p \cong {}^1/_2$) was treated with NaOH to a pH of 5, buffered with NaH_2PO_4, and the comonomer was added, along with sufficient ethylenediamine-tetraacetic acid to sequester the Cu^{++} inhibitor. (Under the conditions used, all comonomers were soluble in the aqueous system, even acrylonitrile, which apparently was "salted in" by the high concentration of sulfonium monomer present.) Then $Na_2S_2O_8$ and $HOCH_2CH_2SH$ were added, the solution was blown out with N_2, and allowed to stand at room temperature.

Some of the polymerizations (runs 1-a, 1-b, and 1-c of Table III) exothermed (peak temperatures under 50°C) during the early stages of the runs.

Product copolymer was isolated by addition of the polymerized solution (or an aliquot) to an acetone–water mixture (95 vol-% acetone). The gummy solid which formed was redissolved immediately in water to avoid crosslinking. Determination of per cent solids was made by drying a portion of the final solution as a thin film in a vacuum desiccator over P_2O_5 at room temperature overnight. The composition of product copolymer was calculated based on ultimate analyses of the dried films for S and N. It was verified that such drying did not cause significant loss of any sulfur-containing volatiles from some possible breakdown of the sulfonium mers of the copolymer. A concentrated aqueous mixture of bis(2-hydroxyethyl) (ar-vinylbenzyl)sulfonium chloride and tetramethylammonium chloride and a vacuum-dried film, cast from the mixture, both were analyzed for S and N. Within experimental error of the analyses, the found ratios of S/N were the same.

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