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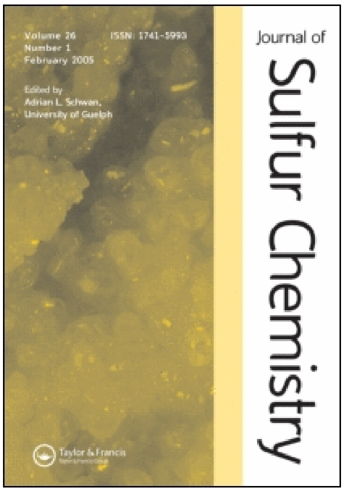

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Summary of my Work on Sulfur Compounds

C. S. Marvel[a]
[a] Department of Chemistry, The University of Arizona Tucson, Arizona, U.S.A.

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SUMMARY OF MY WORK ON SULFUR COMPOUNDS

C. S. MARVEL

Department of Chemistry, The University of Arizona Tucson, Arizona 85721, U.S.A

ABSTRACT

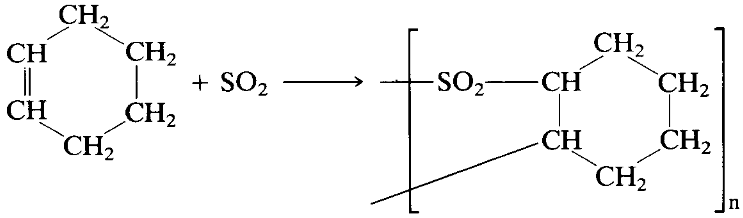
(by Lamar Field)

From time to time, SULFUR REPORTS plans to invite distinguished chemists to summarize the research of their careers as it has related to sulfur chemistry. This contribution by Professor C. S. Marvel, the first such account, is an informal résumé of his research with organic sulfur compounds that has occurred in a career spanning more than 60 years. Professor Marvel received his Ph.D. degree at the University of Illinois (Urbana) in 1920. He remained there on the faculty until he became Professor Emeritus in 1961 and relocated to the University of Arizona, where he has continued his research vigorously. His recognition as a towering figure in organic and polymer chemistry of the twentieth century is illustrated by award to him of the Priestley, Perkin, Nichols, and Gibbs medals, along with a host of named lectureships, honorary degrees, and other awards. He has been a member of the National Academy of Sciences (U.S.A.) since 1938 and has served as President of the American Chemical Society (1945) and on numerous editorial boards and advisory panels. An instructive (and entertaining) autobiography appeared in CHEMTECH, **10**, 8–11 (1980). Although Professor Marvel's primary career interest has been in polymers, he has made many significant contributions to organic sulfur chemistry; these are described in 100 publications listed in the bibliography. His present account describes his adventures with polymeric sulfides, disulfides, thiol esters, mercaptals, and sulfones. His research has not been confined to polymeric compounds, however, and he summarizes contributions as well to the chemistry of many classes of sulfur compounds, including thiols, disulfides, thio acids, sulfinic and sulfonic acids and derivatives, and sulfur-containing heterocycles.

My research with sulfur compounds is rather heterogeneous but I shall try to summarize it as much as I can. The major thrust is the use of sulfur compounds in polymer chemistry, but there are a few other items included.

My first research involving sulfur compounds was the preparation of a variety of arene- and alkanesulfonamides of low molecular weight amines to obtain well crystalline and sharp melting derivatives for their characterization. These were needed at that time for the qualitative course in organic analysis which I was teaching (in early 1920). I found that the *p*-bromobenzenesulfonamides and *m*-nitrobenzenesulfonamides were easily prepared and easy to characterize. Methanesulfonamides were also prepared and had the advantage that they could be used to separate primary and secondary amines and the amines could be obtained by hydrolysis. The aromatic sulfonamides were difficult to hydrolyze.(1,2,3,6,7)

My first major work in the sulfur field was a result of a discussion with Dr. Elmer Bolton of the DuPont Experimental Station (in 1928) when he called my attention to a 1914 British patent by Mathews and Elder, which stated that simple olefins such as ethylene and propylene would react with sulfur dioxide to make polymers. This seemed like an unusual reaction, and he asked me if I thought it would occur. I said I was very doubtful, for it did not seem like ordinary chemistry, but that if he was interested I would try it out and see if I could make polymers in that way. In Urbana, I tried the reaction using cyclohexene and sulfur dioxide and found that it did occur on catalysis with peroxides and that beautiful white polysulfones were obtained.[13] I extended the reaction



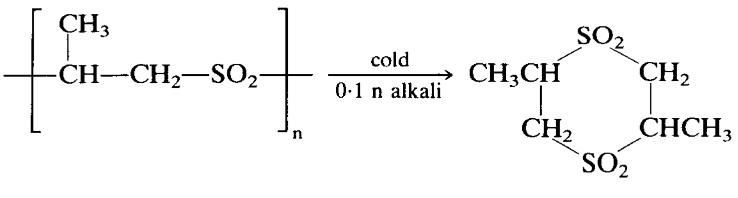
to propylene, butylene, and pentenes and found that they also gave good polymers with sulfur dioxide. I did very little work with ethylene because pressure equipment was not available. Later I found that it also gave polymers which were very intractable and hard to fabricate. The polymers from the other simple olefins were white, soluble in ordinary solvents, and could be melt-pressed to give beautiful clear poker chips. However, at the melting point they always decomposed slightly and the poker chips were blemished with little stars so that they did not prove to be practical polymers for a molding resin.(14,15,16 and following)

We found that with 1-olefins and 1-acetylenes and with many 2-olefins and many of their derivatives the reaction ran well to give quantitative yields of polymeric products. However, all of these products decomposed at their melting points. In general, we obtained polymers that had a ratio of one olefin molecule to one sulfur dioxide molecule, as illustrated by the equation

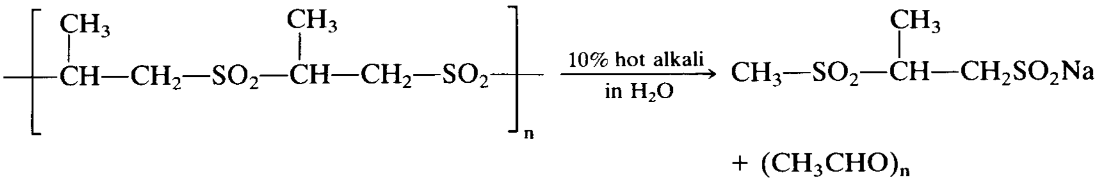
$$CH_3CH{=}CH_2 + SO_2 \longrightarrow [CH_3{-}CH{-}CH_2{-}SO_2]_n.$$

Later work in other laboratories indicated that in certain cases, by changing the temperature, some variations in composition could be obtained. In our work, vinyl chloride[22] was one exception which we found reacted with sulfur dioxide to give two vinyl chloride units for each unit of sulfur dioxide.

When heated with alkalies



the polymers degraded to cyclic sulfones. A study of polypropylenesulfone showed that the mid hydrolysis produced a composition containing four carbons and two sulfur atoms, which seemed unusual to come from a three-carbon olefin and sulfur dioxide, but we observed that the hydrolysis produced acetaldehyde which polymerized in the process. The other product was a sulfone sulfinic acid that is noted in the following structure.



$$\left[\overset{CH_3}{\overset{|}{CH}}{-}CH_2{-}SO_2{-}\overset{CH_3}{\overset{|}{CH}}{-}CH_2{-}SO_2\right]_n \xrightarrow[\text{in } H_2O]{10\%\text{ hot alkali}} CH_3{-}SO_2{-}\overset{CH_3}{\overset{|}{CH}}{-}CH_2SO_2Na + (CH_3CHO)_n$$

In the first study of this structure we were confused by a rearrangement which occurred in the synthesis of the sulfone sulfinic acid, and believed that the original structure of the polymer was of a head-to-head, tail-to-tail arrangement.[14] On a restudy of the synthesis,[52] we found that a rearrangement had occurred which had caused the original error in our results. Other olefins gave similar products. Olefins in which the double bond was conjugated with carbonyl or cyano groups would not give the sulfur dioxide adducts. But other substitution of the olefin did not interfere with the reaction. Although all of these polymers could be melt-pressed into films, none of them gave films without blemishes and they never were useful molding products.

When polysulfones were first made, the heat instability of the polymers seemed to preclude any usefulness. But, this very property has made them extremely important in recent years as photo-resist products [L. F. Thompson, M. J. Bowden, *J. Electro. Chem. Soc.*, **120**, 1722 (1973); M. J. Bowden, L. F. Thompson, *Solid State Technol.*, **22**, 72 (1979)]. This is another case of fundamental research which seemed relatively unimportant when first performed that has turned out to be a useful industrial development.

My next study in the sulfur series was another polymeric product which we prepared from alkylene and arylenedithiols (1950 and following). [29 and following] These thiols reacted with nonconjugated diolefins to give polyalkylene or polyarylene sulfides such as

$$n\,HS(CH_2)_nSH + n\,CH_2{=}CH(CH_2)_x{-}CH{=}CH_2 \xrightarrow[\text{catalyst}]{\text{peroxide}} \left[S(CH_2)_nSCH_2CH_2(CH_2)_xCH_2CH_2\right]_n$$

Some of these products were highly crystalline, and cold drawing gave good fibers. Some of the alkylene and arylene polysulfides produced excellent films which were sensitive to ultraviolet light. They were not commercially useful products. The reaction was very general and the products could be obtained at high yield.

When the olefins were irregular in structure, the polyalkylene sulfides were rubbery in character.[36] Some interesting rubbery materials were obtained from vinylcyclohexene by adding to the polymerization mixture some 2,6-diallylphenol to give polysulfides which could be cross-linked through the phenol group. Some of the rubbery products were promising but never actually were used as rubbers.

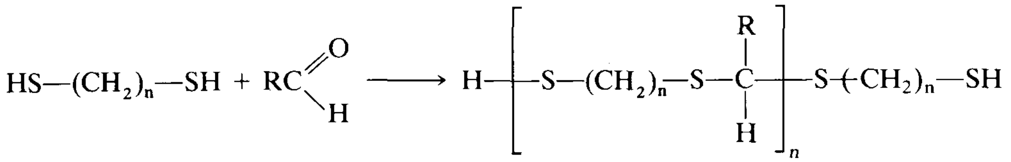
We found that the termination reaction of the addition reaction was the formation of a disulfide unit by oxidation.[47] This unit could be reduced to give a lower molecular weight polymer with thiol end groups and these could be reoxidized to give back the original polysulfide material.

Another polymeric reaction was the addition of dithiol acids, $HSOC(CH_2)_nCOSH$, to diolefins to give polythiol esters as shown by the equation

$$HSCO(CH_2)_xCOSH + CH_2{=}CH(CH_2)_xCH{=}CH_2 \longrightarrow \left[SCO(CH_2)_xCOSCH_2CH_2(CH_2)_xCH_2CH_2\right]_n$$

(in the 1950's).[41,48] These were easily prepared in good yields with good melting points and were reasonably stable but did hydrolyze easily with 5% sodium hydroxide and water. X-ray patterns showed they were definitely crystalline products when either aryl or aromatic thio acids were used. We obtained the same polymers by using diacid chlorides and dithiols so we knew the structure of the polymers. We found that the addition reaction of thiol acids with nonconjugated diolefins was easily carried out in emulsion,[48] and that high molecular weight polyesters could be obtained by this process.

Another group of polymers were prepared (in the 1950's) from dithiols and aromatic aldehydes[34] to give polymer mercaptals such as



$$HS-(CH_2)_n-SH + RC\overset{O}{\underset{H}{\diagup}} \longrightarrow H\left[S-(CH_2)_n-S-\underset{H}{\overset{R}{C}}\right]_n S-(CH_2)_n-SH$$

An interesting observation was that when the dithiol was 1,10-decanedithiol and the aldehyde was benzaldehyde, the product in 50% yield was a crystalline 26-membered cyclic dimercapal.[53] Autenreith and Butell had observed earlier that xylene dithiols reacted with aldehydes to give similar big rings.

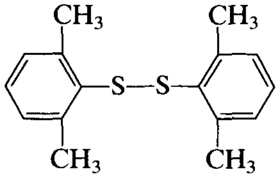
Another polymerization reaction was developed in the late 1950's by the air oxidation of dithiols in alkaline emulsions to give polydisulfides that were somewhat similar to those prepared by Patrick from ethylene dichloride and sodium disulfide.[59,60] The alkylene disulfides were heated with sulfur and formed

$$HS-(CH_2)_xSH \xrightarrow[\text{oxidation}]{\text{air}} [S-(CH_2)_x-S]_n \xrightarrow[\text{heat}]{S} \text{chain extension crosslinking}$$

polysulfides which were rubbery in character but were somewhat too expensive for practical use.

All of this research using dithiols gave us a bad reputation in the chemistry building because the hoods were poor and the compounds were very odoriferous. More than that they eventually became allergens for all the chemists who worked with them. As a result, the chemists had swelling of their arms and hands, severe itching, and general discomfort. In every case it became necessary to terminate the work for the chemist and shift to another problem to get relief. The alkylene dithiols seemed to be the worse offenders. The thiol acids and thiol esters were disagreeably smelling materials, but did not seem to cause allergic reactions to those who worked with them.

In our study of the polymerization of styrene and butadiene to make GRS as part of the government's synthetic rubber program (1941–1945), we found that thiols were excellent chain transfer agents for controlling the molecular weight of the product and giving a good rubber.[30] The chain length of the thiol was most important. We also found out that ortho-disubstituted aryl disulfides were efficient chain transfer agents for this polymerization.[55a] It was found that the disulfide shown



was as effective as dodecanethiol. When only one methyl group was present in the ortho position in each ring, the disulfide was less efficient as a chain transfer agent. On the other hand, if there was ortho diethyl substitution in each ring, the disulfide was totally ineffective as a chain transfer agent apparently due to severe steric hindrance.

Another study, illustrated in the equation,

$$CH_2Br{-}CHBr{-}COCl \xrightarrow{RSH} CH_2Br{-}CHBr{-}COSR \xrightarrow{NaI} CH_2{=}CH{-}CO{-}SR$$

in the rubber program led to the synthesis of a number of a alkyl thiolacrylates[56] which were copolymerized with butadiene and styrene to improve the oil resistance of the synthetic rubber. These esters could not be prepared by a direct reaction of acrylyl chloride and the thiol because of the rapid addition of the mercaptan to the acrylic acid double bond. α,β-Dibromopropionyl chloride and thiols gave good yields of esters and the removal of the bromine atoms afterward gave excellent yields of the acrylic thio esters. These esters were copolymerized with butadiene and styrene, but they were slower in reaction than acrylic esters. Dithiofumaric ester was also prepared and found to copolymerize with styrene and butadiene.[61]

One piece of research carried out in 1954–1955 was the development of improved procedures for making dithio esters from imidoesters, and the study of some reactions of thiol esters and dithio esters.[55] Some new thio amides were also prepared. As a result of these new materials, our specialists in infrared work determined that the $\nu(C=S)$ for thiol esters was 1170–1195 cm^{-1}, and for thioamides it was 1180–1765 cm^{-1}. The importance of avoiding hydrolysis in making these materials was emphasized. It was shown that the reaction of dithio esters with ammonia is almost as rapid as of acid chlorides with ammonia.

In our work on thermally stable polymers, we have studied a variety of thiazines,[71,72] thiazoles,[64] arylene sulfides,(77 and following) aryl sulfonamides,[69] and aryl sulfones,(76 and following) which are sulfur-containing molecules, but we have not used the chemistry of sulfur to obtain the products we desired, so I'm not describing them in detail. It is significant that aromatic heterocyclics containing sulfur atoms are especially stable at elevated temperatures. The remarkable stability of thiazole fibers, which resemble carbon fibers, is an interesting fact.

In isolated research on sulfur compounds we have synthesized and resolved the naturally occurring amino acid methionine[8,9] We also found a way to prepare aliphatic sulfinic acids[31,38] and studied some of their reactions. We developed a method of reducing sulfonyl chlorides to thiols by use of lithium aluminum hydride.[32] We studied the directive influence of alkylsulfamido and dialkylsulfamido groups in the benzene ring on substitution reactions.[10] We developed a method of making higher alkyl sulfonates,[11] and we found a method of extending carbon chains by three atoms by the action of Grignard reagent on 3-chloropropyl *p*-toluenesulfonate.[5]

I have never considered myself a sulfur chemist, but I certainly have found many useful places in my research where sulfur compounds were important. In summarizing my work, I found that I have had about 100 articles which deal with sulfur compounds.

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