

# Homogeneous and Heterogeneous Sulfonation of Polymers: A Review

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This paper reviews the various reactions used to sulfonate polymers, especially polystyrene. The mechanisms for the sulfonation of low molar mass compounds are also discussed. The commonly used sulfonation reagents are described, with an emphasis on  $\text{SO}_3$  and its physical and chemical properties. Polymer sulfonations can be grouped into two general routes: one involving homogeneous sulfonation and the other heterogeneous reactions.

## 1. INTRODUCTION

Sulfonation is defined as a substitution reaction used to attach the  $\sim\text{SO}_3\text{H}$  group on a molecule of an organic compound via chemical bond to carbon or, less frequently, to a nitrogen atom of the organic compound. Compounds such as  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_3$  and its complexes, such as acyl and alkyl sulfates and chlorosulfonic acid, are commonly used as sulfonating agents. Less frequently, other compounds, such as fluorosulfonic acid, sulfur dioxide, sulfites and acid sulfites, sulfonyl chloride alkyl sulfates, and N-pyridinium-sulfonic acid, were utilized. Substantial difference between mechanism of sulfonation onto aliphatic and aromatic compounds has been observed. Sulfonation proceeds easily for the aromatics, even though the dissociation energy of the C-H bond is higher in aromatic (428 kJ/mol) than in aliphatic (374–384 kJ/mol) compounds. This phenomenon is assumed to be caused by the two-step reaction mechanism where the rate of  $\text{SO}_3$  insertion to hydrocarbons alone cannot control the reaction rate. One, two, or three  $\sim\text{SO}_3\text{H}$  groups may be attached to one carbon atom of the aliphatic chain, whereas only one  $\sim\text{SO}_3\text{H}$  group may be attached to the carbon atom of an aromatic ring.

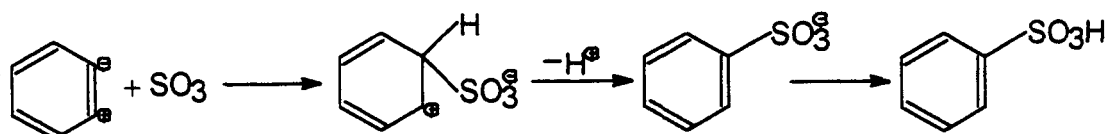
The methods for preparation of sulfonated low molar mass organic compounds are well known (1–8), especially for the molecules containing aromatic rings, which are sulfonated easily in contrary to aliphatic compounds, and which have much greater commercial importance than aliphatic sulfonic acids. The actual mechanisms of sulfonation of low molar mass hydrocarbon compounds are expected to be the same as in the case of high molecular mass polymer substrates.

The first information on sulfonation of high polymers such as polystyrene (PS) was published before World War II. Ever since, the utilization of sulfonated polymers in various industrial, domestic, and medical applications has been increasing steadily. Sulfonated ionomers were defined as macromolecular compounds containing sulfonic  $\sim\text{SO}_3$  groups. These compounds are utilized satisfactorily, because of their interesting chemical and mechanical properties, in a number of industrial applications, e.g., for production of compatible blends of nonmiscible polymers, ion exchange materials, membranes for reverse osmosis and ultra-filtration, plasticizers for macro-defect-free concretes, and conductive composites.

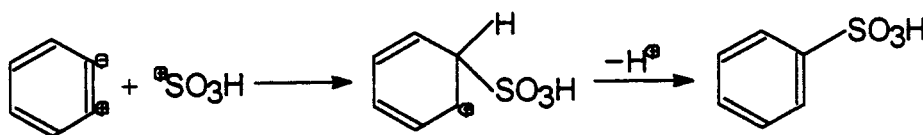
## 2. MECHANISMS OF $\sim\text{SO}_3$ INSERTION

### 2.1. Sulfonation

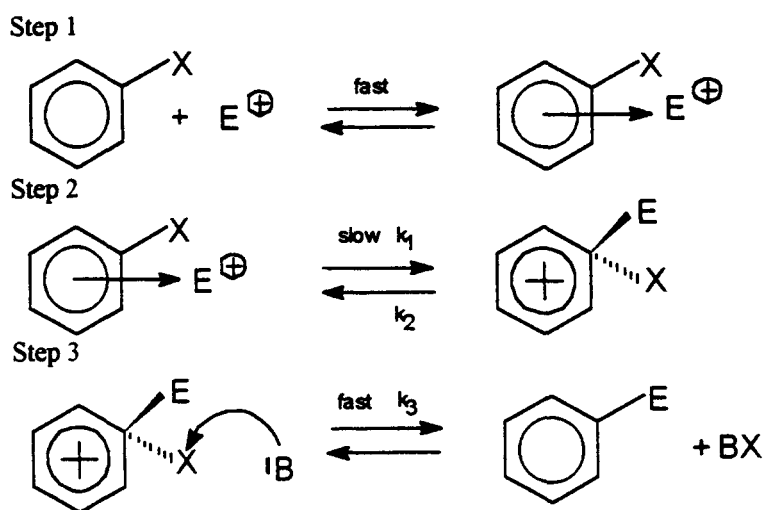
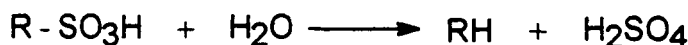
Sulfonation reactions are typical electrophilic substitutions when more electronegative atoms of oxygen draw the electron density from the sulfur atom, which then becomes an electrophilic center. This electrophilic center can react with the delocalized  $\pi$ -electron system of an aromatic ring at the position with the highest electron density, which is controlled by the position and type of other groups located around the aromatic ring. Sulfonation reaction proceeds easily in the presence of groups such as  $\text{Cl}\sim$ ,  $\text{NH}_2\sim$ ,  $\text{OH}\sim$ ,  $\text{SH}\sim$ , etc., known for increasing electron density at the aromatic ring. On the other hand, sulfonation runs poorly in the presence of substituents reducing electron density, such as  $=\text{NR}_2$ ,  $=\text{O}$ , etc., at the aromatic ring. See the reaction schemes for aromatic sulfonation utilizing  $\text{SO}_3$  (Scheme 1) and  $\text{SO}_3\text{H}^\oplus$  (Scheme 2) sulfonating agents.



Scheme 1. Sulfonation of aromatic systems with sulfur trioxide.



Scheme 2. Sulfonation of aromatic systems with sulfonic cation.

Scheme 3. General mechanism of the sulfonation reaction: Step 1.: Formation of the  $\pi$ -complex, Step 2.: Formation of the arenium ions ( $\sigma$ -complex), Step 3.: Termination of the sulfonation by the release of  $X^\oplus$ .

Scheme 4. Desulfonation by a reaction with water (hydrolysis).

General reaction *Scheme 3* is assumed (9) to describe the kinetics of sulfonation satisfactory. In agreement with the proposed *Scheme 3* and results of kinetic studies (10, 11), both reacting molecules determine the rate of sulfonation, and this electrophilic substitution can be considered a bimolecular reaction of the second order ( $S_E2$  mechanism).

At first, an origin of the  $\pi$ -complex is presumed to be a fast reversible reaction between an aromatic compound and an electrophilic agent, e.g.,  $SO_3$  (*Scheme 3*: step 1). Experimental evidence for an existence of the  $\pi$ -complex has not yet been published; however, it is assumed that the  $\pi$ -complex can be transformed slowly from  $\pi$ - to  $\sigma$ -complex (= arenium ions) by the second reaction (*Scheme 3*: step 2). This reaction then becomes the rate determining step. Although the  $\sigma$ -complex was isolated, it is a highly reactive intermediate that must stabilize itself by a further reaction step. At the end, this electrophilic substitution is quickly terminated by the release of  $X^\oplus$  (5). If  $X^\oplus$  is a

proton, then a base B is necessary to ensure its removal (*Scheme 3*: Step 3).

## 2.2. Desulfonation

The sulfonation of aromatic compounds can be very complex because of its reversibility. Then, the term desulfonation (or hydrolysis of  $\sim SO_3H$  group) is commonly used (12, 13) to describe the reverse process. Reaction conditions are set such that an equilibrium between the sulfonation and desulfonation reactions is usually shifted toward the prevailing sulfonation. The  $\sim SO_3H$  groups can be removed from sulfonated compounds with dilute solutions of acids or with water (*Scheme 4*).

The hydrolysis is represented by the electrophilic release of the  $\sim SO_3H$  group by a participation of a proton in this reaction. In the presence of sulfuric or chloric acid, hydrolysis can run simultaneously with the sulfonation because of high concentration of  $H^\oplus$



Scheme 5. Crosslinking reaction.



Scheme 6. Decomposition of sulfones.

ions. Reaction conditions determine the prevailing direction of the reaction. Sulfonation itself prefers high concentrations of sulfuric acid; however, partial desulfonation was observed even in the most concentrated sulfuric acid (6).

Desulfonation probably has several causes: (i) the  $\sim\text{SO}_3\text{H}$  group is not conjugated with the benzene ring; (ii) a strong, partially positive charge on the sulfur atom increases electron density at a meta-position of the benzene ring and on the carbon atom from C—S bond; (iii) after the release of a proton, a negative charge located on the  $\sim\text{SO}_3\text{H}$  group can make hydrolysis of the  $\sim\text{SO}_3\text{H}$  group more probable. Substituents that support sulfonation can also promote hydrolysis of the  $\sim\text{SO}_3\text{H}$  group, because of the increase of the electron density on the carbon atom of the C—S bond. When the formation of the sulfonic acid is easy, the hydrolysis also runs easily.

### 2.3. Sulfone Formation

Because of the presence of relatively highly reactive  $\sim\text{SO}_3\text{H}$  groups, a following crosslinking reaction between the molecules of the sulfonated product can occur, adding more complexity to the assumed reaction scheme (Scheme 5).

Very little information on the crosslinking mechanism has been found (14); however, it seems that its rate increases with increasing the reaction temperature. Crosslinked sulfones are very stable compounds. Their decomposition can be achieved only by melting with alkaline hydroxides (Scheme 6).

### 2.4. Influence of Other Substituents on Sulfonation

The presence of various substituents can result in preferential insertion of  $\sim\text{SO}_3\text{H}$  and formation of specific isomers. In general, sulfonation of aromatic compounds, using substituents of the first class ( $\text{NR}_2$ ,  $\text{NHR}$ ,  $\text{NH}_2$ ,  $\text{NHCOR}$ ,  $\text{OH}$ ,  $\text{OR}$ ,  $\text{HS}$ ,  $\text{RS}$ , alkyl, halo-,  $\text{NO}$ ), resulted in more para-isomers than ortho-isomers. Sulfonation with substituents of the second class ( $\text{R}_3\text{N}^\oplus$ ,  $\text{R}_2\text{S}^\oplus$ ,  $\text{NO}_2$ ,  $\text{CN}$ ,  $\text{HCO}$ ,  $\text{ClCO}$ ,  $\text{SO}_2\text{R}$ ,  $\text{SO}_3\text{H}$ ,  $\text{COOR}$ ,  $\text{CONH}_2$ ) results in the predominant placement of the  $\sim\text{SO}_3\text{H}$  group at the meta-position (15–17). For example, a location of the second  $\sim\text{SO}_3\text{H}$  group on the aromatic ring by sulfonation to a higher level is directed by the first  $\sim\text{SO}_3\text{H}$  group to the meta-position of the aromatic ring, resulting in the reduced possibility that another  $\sim\text{SO}_3\text{H}$  will be attached. In some cases, the sulfonation produces only the para-isomer (for halogenated benzenes). It is assumed that this

effect is caused by the steric effect and repulsion of the  $\sim\text{SO}_3\text{H}$  groups. The ratio of formed isomers is determined also as the function of the overall conditions of the sulfonation reaction. Sulfonation at a higher temperature, proceeding for a longer time, produces isomers more stable to desulfonation than isomers prepared at a lower temperature for a short time. In the case in which two isomers were formed in sulfonation reaction, the elevated reaction temperature increased the yield of the isomer, which was already dominant at the lower reaction temperature.

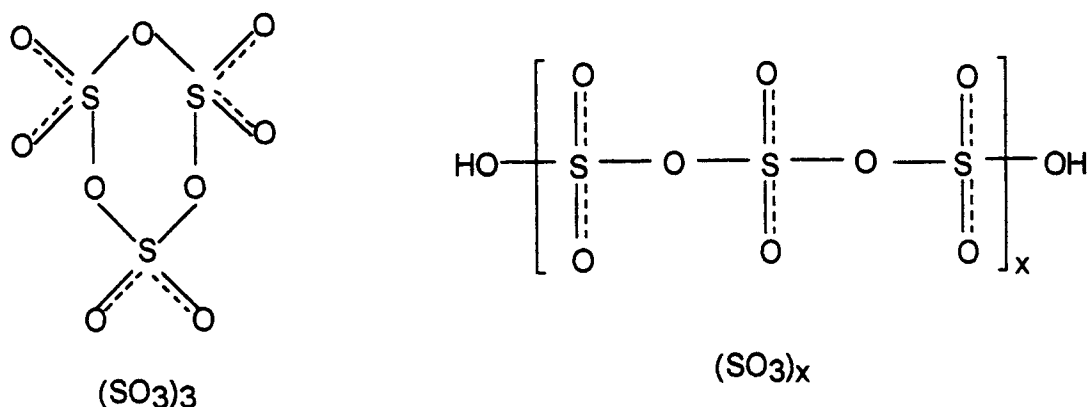
### 2.5. Reaction Conditions for Sulfonation

The choice of reaction conditions for the sulfonation is usually made considering three factors: (i) sulfonation level (number of the  $\sim\text{SO}_3\text{H}$  group entering into the aromatic ring), (ii) the type of formed isomers, and (iii) a yield of sulfonic acid (reduction of desulfonation).

The sulfonation reactions described in the literature were carried out over a wide range of temperatures, usually from  $-20^\circ\text{C}$  to  $300^\circ\text{C}$ . Sulfonation gives a better yield at elevated temperatures, especially in the case of sulfonation to higher levels. However, sulfone formation is also increased by enhanced reaction temperatures. In addition, the concentration of the sulfuric acid or oleum used as the sulfonating agent influences the course of sulfonation. Sulfonation prefers high concentrations of sulfonating agents, while water formed as a side product in the sulfonation reaction reduces the rate of sulfonation. A catalyzing influence of inorganic compounds was not observed except of mercuric compounds (i.e.  $\text{HgSO}_4$ ). These compounds, at concentrations above 1 wt%, changed the ratio and yield of formed isomers, when oleum was used as the sulfonating agent (18, 19).

## 3. SULFONATING AGENTS

Sulfonating agents are distinguished by the type of the reaction they enter into three groups. Sulfuric acid, oleum, chlorosulfonic acid, fluorosulfonic acid, amidosulfonic acid, free sulfur trioxide and its complexes, halogen derivatives of sulfuric acid, etc., form the first group of sulfonating agents derived from sulfur trioxide. They are designated as electrophilic reacting agents. The second group contains nucleophilic agents such as sulfites and hydrogen sulfites, and sulfur dioxide, which react with halogen derivatives and unsaturated compounds containing multiple bonds. The third group consists of the radically reacting agents, i.e. sulfonylchloride ( $\text{SOCl}_2$ ), blends of gases: sulfur dioxide and chlorine ( $\text{SO}_2 + \text{Cl}_2$ , sul-



Scheme 7. Ice-like structure of  $\gamma$ -SO<sub>3</sub> modification [(SO<sub>3</sub>)<sub>3</sub>] and asbestos-like structure of  $\beta$ -SO<sub>3</sub> modification [(SO)<sub>x</sub>].

fenchloration), sulfur dioxide and oxygen (SO<sub>2</sub> + O<sub>2</sub>, sulfoxidation), etc. The reagents of the first group are used most frequently to sulfonate aromatic compounds. They exhibit the most effective sulfonation capability of all the agents described above and are widely used to manufacture sulfonic acids. It seems reasonable to describe the properties and reactivity of some of these agents.

### 3.1. Sulfur Trioxide (SO<sub>3</sub>)

Sulfur trioxide (SO<sub>3</sub>) is manufactured on a large scale for production of sulfuric acid by a continuous catalytic oxidation of sulfur dioxide (SO<sub>2</sub>). Sulfur trioxide is available for laboratory purposes as a freshly distilled or stabilized liquid, or as fuming sulfuric acid (oleum). Pure and dry SO<sub>3</sub> can be kept in the liquid state for a few months, but it will polymerize in the presence of a trace content of water (above 10 ppm) to form polysulfuric acid. In order to prevent polymerization of freshly distilled SO<sub>3</sub> in the course of storage, various stabilizers can be used satisfactorily. The liquid sulfur trioxide can be stabilized by the addition of a small quantity (up to 2 wt%) of various derivatives of boron, sulfur, and phosphorus, such as SOCl<sub>2</sub>, BCl<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, TiCl<sub>4</sub>, SbCl<sub>5</sub>, SbF<sub>5</sub>, Na<sub>3</sub>SiF<sub>6</sub>, P<sub>4</sub>O<sub>10</sub>, or other compounds such as aliphatic ethers, esters and chlorides of sulfuric acid, aromatic amines, amides and nitrocompounds, nitriles, and aliphatic ethers. However, the most effective SO<sub>3</sub> stabilizers (as low as 0.1 wt%) are (CH<sub>3</sub>O)<sub>3</sub>B, (CH<sub>3</sub>O)<sub>3</sub>B<sub>2</sub>O<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub> and B<sub>2</sub>O<sub>3</sub> (20, 21). Laboratory preparation of SO<sub>3</sub> commonly relies on repeated distillations of oleum.

#### 3.1.1. Physical Properties of SO<sub>3</sub>

Sulfur trioxide occurs in a monomeric form and in several polymeric forms. The colorless SO<sub>3</sub> gas appears to be mostly monomeric. However, as determined by Raman spectral analysis, freshly distilled SO<sub>3</sub> is a colorless liquid containing 90% of the trimeric and 10% of the monomeric form (22). On the other hand, some investigators claim that the distilled SO<sub>3</sub> contains 20% of trimer and 80% of monomer (23).

However, most authors consider a trimeric form (S<sub>3</sub>O<sub>9</sub>) to be the main ingredient of liquid SO<sub>3</sub> (20, 21).

The polymerization of sulfur trioxide gives rise to three solid polymeric modifications (Scheme 7) (24). The  $\alpha$ -SO<sub>3</sub> is the most stable at laboratory temperature. It consists of a higher linear polymer with a layered structure. The asbestos-like structure of  $\alpha$ -SO<sub>3</sub> is formed by cooling dry SO<sub>3</sub> vapor at temperatures below -80°C. It has the lowest vapor pressure of all the SO<sub>3</sub> forms.

The  $\beta$ -SO<sub>3</sub> consists of linear polymeric macromolecules assuming a helical conformation. It is a polymer with lower molar mass than  $\alpha$ -SO<sub>3</sub>. Needle-like crystals of  $\beta$ -SO<sub>3</sub> are formed by spontaneous polymerization of the liquid or  $\gamma$ -SO<sub>3</sub> (ice-like modification) in the presence of a trace content of water (1 mol H<sub>2</sub>O in 10<sup>5</sup> mol SO<sub>3</sub>) acting as an initiator. Depolymerization of  $\beta$ -SO<sub>3</sub> to liquid SO<sub>3</sub> is observed in the course of an incomplete melting at 32°C to 45°C. This modification consists of a mixture of polymers, and it is neither well defined nor thermally stable. The formed crystalline polysulfuric acid has a crystal needle-like structure with a melting point between 32°C and 62°C depending on the molar mass and the type of end groups.

The  $\gamma$ -SO<sub>3</sub> is a thermodynamically unstable cyclic trimer S<sub>3</sub>O<sub>9</sub> and exists in a reversible equilibrium with monomeric SO<sub>3</sub>. The melting point of  $\gamma$ -SO<sub>3</sub> (ice-like solid) is 16.86 ± 0.02°C (25). The orthorhombic S<sub>3</sub>O<sub>9</sub> molecules of  $\gamma$ -SO<sub>3</sub> are formed by cooling the liquid SO<sub>3</sub> to lower temperatures. The upper polymerization temperature for the polysulfuric acid is around 30°C. Important physical properties of SO<sub>3</sub> are shown in Table 1 (24, 26–28).

#### 3.1.2. Chemical Properties of SO<sub>3</sub>

Sulfur trioxide is one of the most reactive inorganic compounds known (29, 30). From the character of its reactivity, SO<sub>3</sub> is defined as an oxidative agent and a Lewis-acid. Sulfur trioxide is also known for its high strength for withdrawing a water from organic compounds. Sulfur trioxide is a typical electrophilic agent, reacting at the location of the highest electron density in a molecule of a substrate. The possibility of using

Table 1. Physical Constants of the Dry SO<sub>3</sub>.

Melting point ( $\alpha$ -SO <sub>3</sub> )	16.8°C
Boiling point	44.5°C
Critical temperature	217.7°C
Critical pressure	7.93 MPa
Density of liquid SO <sub>3</sub>	1.9255 g/cm <sup>3</sup>
Relative density of gaseous SO <sub>3</sub>	2.77 (to air)
Critical density	0.633 g/cm <sup>3</sup>
Viscosity 30°C	$1.59 \times 10^{-3}$ Pa.s
Specific heat (25–35°C)	257.94 J/mol
Heat of dilution	168.83 kJ/mol
Van der Waals constants	a = 2.105 b = 0.964
Dielectric constant (18°C)	3.11
Heat of polymerization (O°C)	-125.5 kJ/mol
3 SO <sub>3</sub> to S <sub>3</sub> O <sub>9</sub>	
Dissociation energy of (O <sub>2</sub> S–O) bond	342.5 kJ/mol

Table 2. Pressure of SO<sub>3</sub> Vapors Above the 50% and 60% Oleum.

Temperature (°C)	50% Oleum (torr)	60% Oleum (torr)
20	40	80
40	90	220
60	260	600

solvents in the sulfonation reaction is, thus, reduced, as a result of the high reactivity of free SO<sub>3</sub>. The sulfonation reaction can be carried out without solvents in gaseous or liquid phase (heterogeneous sulfonation) or with the use of sulfur dioxide as the best solvent for sulfur trioxide (homogeneous sulfonation). The typical feature of sulfur trioxide is the formation of adducts when it reacts with Lewis-bases (30). These complexes (or adducts) were also used as sulfonating agents. For example, SO<sub>3</sub> gives the SO<sub>3</sub>-O(CH<sub>2</sub>)<sub>2</sub>O-SO<sub>3</sub> complex in the reaction with dioxan. The reaction with trimethyl phosphate [(MeO)<sub>3</sub>PO] and triethyl phosphate [(EtO)<sub>3</sub>PO] gives adducts soluble in dichloroethane, which are also good sulfonating agents. Stable chlorosulfonic acid (HSO<sub>3</sub>Cl) results from the reaction with HCl at low temperatures. A crystalline compound with a melting point of 240°C arose from the reaction of SO<sub>3</sub> with (CH<sub>3</sub>)<sub>3</sub>N. The stable NH<sub>2</sub>-SO<sub>3</sub>H complex was formed by reacting SO<sub>3</sub> with NH<sub>3</sub>, and converting the resulting product to N(SO<sub>3</sub>)<sub>3</sub> by the consequent reaction with SO<sub>3</sub>.

Dry sulfur trioxide reacts only very slowly with most metals, such as Cu, Ag, Mg, Zn, Fe, at room temperature because the surface of metals is often passivated

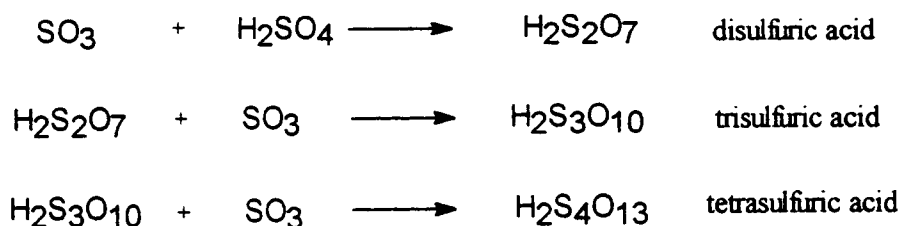
with reaction products such as oxides. In order to initiate any reaction with such a metal surface, a temperature increase is necessary. Sulfates and oxides of metals are the products of these reactions.

Although oleum is a very strong oxidative and dehydration agent for most organic compounds, it can also be used successfully for direct sulfonation of organic compounds. Distillation of oleum is important for laboratory preparation of SO<sub>3</sub>, since the simple preparation of SO<sub>3</sub> is based on the SO<sub>3</sub> vapor condensation (vapor pressure shown in Table 2) and consequent drying with P<sub>4</sub>O<sub>10</sub> (31, 32). Oleum is usually produced by dissolving the SO<sub>3</sub> in a concentrated H<sub>2</sub>SO<sub>4</sub>. In addition to formed polysulfuric acids (H<sub>2</sub>S<sub>n</sub>O<sub>3n+4</sub>), oleum contains free SO<sub>3</sub> and (SO<sub>3</sub>)<sub>3</sub>. The commercial oleum contained 25 or 65 wt% SO<sub>3</sub> dissolved in H<sub>2</sub>SO<sub>4</sub> in the form of a polysulfuric acid (Scheme 8).

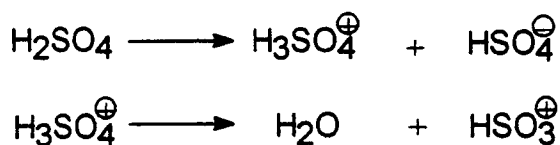
#### 4. SULFONATION OF SMALL ORGANIC MOLECULES

Conventional methods for preparation of sulfonated, low molar weight aromatic compounds by homogeneous sulfonation in a solution, frequently used H<sub>2</sub>SO<sub>4</sub> as the sulfonating agent. This sulfonation process is well described in literature (1–13). Yet other, less well-known methods also exist, that have the potential to be used for sulfonation of high polymers. These are based mostly on sulfonation of organic compounds with SO<sub>3</sub> in a heterogeneous phase, i.e., the compound and sulfonating agent exist in different phases. Although details of these reactions are not described in most of the papers reviewed, they are very important for further research and potential industrial applications.

Sulfuric acid, which may be considered as the SO<sub>3</sub>-H<sub>2</sub>O system, is a sulfonating agent employed most frequently. Sulfuric acid is a weaker oxidative agent and dehydration agent for hydroxycompounds than oleum. A number of side reactions (i.e., oxidation, dehydration) accompanying sulfonation took place as a result of reactions of H<sub>2</sub>SO<sub>4</sub> with alifatic compounds. Sulfuric acid is also a good sulfonating agent, especially for sulfonation of aromatic compounds. An aromatic ring can be sulfonated in a reaction with sulfonic cation (SO<sub>3</sub>H<sup>+</sup>), which arises from concentrated sulfuric acid (Scheme 9) (33). Acetic acid, acetanhydride, tetrachloromethane, or an excess of substrate were the preferred solvents used in these sulfonation reactions.



Scheme 8. Formation of polysulfuric acid by dissolving SO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub>.



Scheme 9. Origin of sulfonic cation by disproportionation of  $\text{H}_2\text{SO}_4$ .

Gilbert (29) described the utilization of the  $\text{SO}_3$  in homogeneous sulfonation of small organic molecules. Using  $\text{SO}_3$ , oxidation of the aliphatic compounds runs parallel to the sulfonation, and the formation of unsaturated compounds, alcohols, ketones, and carboxylic acids as side products was observed. The addition of stabilizing acetic acid was used to reduce the formation of sulfones in this reaction. The reaction of  $\text{SO}_3$  with acetic acid can be described using Scheme 10. The concentration of free  $\text{SO}_3$  decreased after addition of the acetic acid and sulfur trioxide; the acetyl sulfate and sulfuric acid were found to exist in equilibrium.

The reaction of  $\text{SO}_3$  with small aromatic molecules proceeds very quickly in the initial stage, and a complex of  $\text{SO}_3$  with a sulfonated product is formed at the end of the sulfonation. For example, benzene can react with the liquid  $\text{SO}_3$  for a time shorter than 1 s, and toluene can react even more quickly (34). The reaction of benzene with two molecules of  $\text{SO}_3$  is suggested in Scheme 11.

The formation of sulfones by reacting two  $\sim\text{SO}_3\text{H}$  groups was also observed. The sulfone yield was dependent on the reaction temperature. About 30% of the sulfone was formed within a temperature range from 70°C to 80°C and about 50% of the sulfone arose when reaction was carried out between 150°C to 200°C. The sulfone yield was reduced by the sulfonation with liquid  $\text{SO}_3$  at about -10°C, or by addition of the acetic acid.

The most important industrial sulfonation process, which produces sulfonated compounds for detergents, is based on the heterogeneous reaction using  $\text{SO}_3$  as the sulfonating agent and fatty acid as the substrate. Sulfonation in a thin film achieved by using stabilized liquid  $\text{SO}_3$  successfully produced sulfonated alkylbenzenes (35). A method for the continuous sulfonation of fatty acids by means of a gaseous blend of sulfur trioxide with air in a volume ratio of 5:85 at about 90°C was patented by the Henkel Company (36). This method with a 93% conversion yield gives a good product used in detergent production. The yield of the di-substituted product was only about 1 wt%. In a following patent (37), a method for preparing a paste containing a blend of 60%–75% surface-activated

compounds was described. Eniricerce and Snam Progetti patented a method for sulfonation of asphalt (38) by reacting the asphalt solution with gaseous  $\text{SO}_3$  in tetrachloromethane at a temperature ranging from 0°C to 60°C.

## 5. SULFONATION OF POLYMERS

The principles of the sulfonation reactions described for the low molar mass compounds in the preceding paragraph can also be used in the case of polymer sulfonation. Identical sulfonating agents and similar reaction conditions can also be used. Sulfonation kinetics is, however, altered and some hindrances to sulfonation arise as a result of steric effects caused by the size of substrate molecules.

Generally, polymer sulfonation can be carried out as a heterogeneous reaction or as a homogeneous reaction in hydrocarbons or chlorinated solvents. Sulfonating compounds such as  $\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{ClSO}_3\text{H}$ , acetyl sulfate,  $\text{C}_{12}$ -lauryl sulfate,  $\text{C}_{18}$ -stearyl sulfate, and complexes of  $\text{SO}_3$  with alkylphosphates and dioxan, were commonly used for sulfonation of various polymers, namely polystyrene (PS).

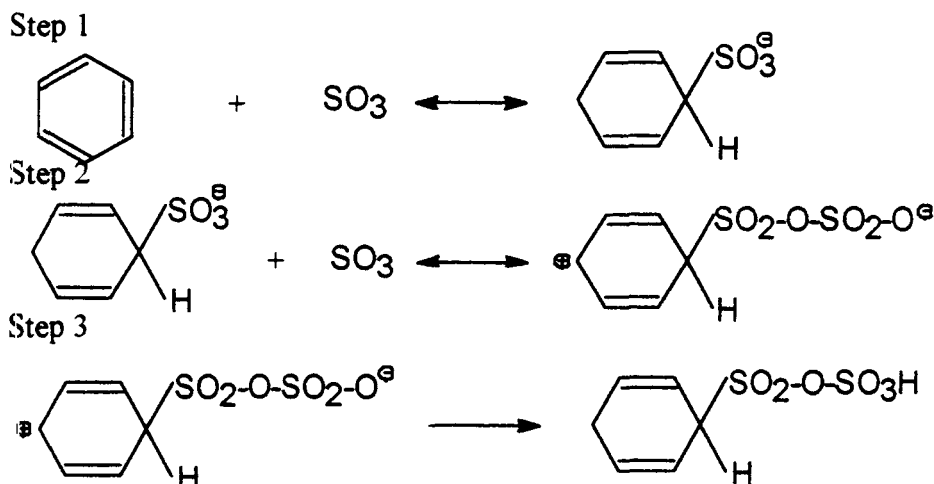
### 5.1. Homogeneous Sulfonation of Polymers

Homogeneous sulfonation of PS was first carried out in a chloroform solution at -20°C with  $\text{SO}_3$  or  $\text{HSO}_3\text{Cl}$  as sulfonating agents (39, 40).

Turbak (41) sulfonated poly(vinyltoluene) and polystyrene in the homogeneous phase without significant crosslinking by using higher complexes of  $\text{SO}_3$  with triethyl phosphate as sulfonating agents. These polymers were sulfonated by adding a 2 wt% dichloroethane solution of the polymer to the solution of the sulfonating agent. This complex agent was formed by dropping liquid  $\text{SO}_3$  into a dichloroethane solution of the triethyl phosphate at a temperature of about 25°C. A solid polymeric form  $(\text{SO}_3)_x$  was not useful for sulfonation of the polymers. A complex of 2-to-1 molar ratio of  $\text{SO}_3$  to  $(\text{EtO})_3\text{PO}$  was used successfully in this work. Sulfonated polymer was obtained as a clear solution with low viscosity [which is a good parameter for measurements of crosslinking density (42)]. In any case, when  $\text{SO}_3$  was first complexed with phosphate, a higher reaction temperature or extended sulfonation time did not cause substantial crosslinking of the resulting sulfonated polystyrene (SPS). Although the SPS was not obtained in the solid state, a 2-hour filtration of the reaction mixture resulted in a separation of sulfonated PS product. Uncrosslinked and ungelled, completely water soluble polymer was produced in this process. The resulting SPS contained, according to elemental analysis, about 15 wt% of sulfur independent of the polystyrene molecular weight



Scheme 10. Mechanism of acetic acid effect on the sulfonation agent.



Scheme 11. Mechanism of the benzene reaction with two molecules of the liquid  $\text{SO}_3$ : Step 1.: Insertion of the  $\text{SO}_3$  to the benzene ring, Step 2.: Insertion of the second  $\text{SO}_3$  molecule, Step 3.: Stabilization of the formed arenium ion.

ranging from 100,000 to 5 million. The 1-to-1 complex of  $\text{SO}_3$  with triethyl phosphate was found to be too inactive to sulfonate polystyrene; the 3-to-1 and 4-to-1 complexes gave sulfonated products that filtered in less than 2 minutes.

Makowski *et al.* (43) prepared a lightly sulfonated polystyrene by a reproducible reaction of dichloroethane solution of polystyrene with acetyl sulfate at a temperature of  $50^\circ\text{C}$  for 1 hour. Acetyl sulfate as the sulfonating agent was prepared by mixing concentrated sulfuric acid and acetic anhydride in a solution of dichloroethane at temperatures lower than  $10^\circ\text{C}$ . The sulfonated product was isolated by steam stripping and pulverized with water in a high-speed mixer for liquids; the SPS was then filtered and dried in a vacuum oven. The sulfonated polystyrene that was obtained contained from 0.1 to 1.3 wt% of sulfur. The molecular weight of the starting polystyrene ( $M_w = 228,000$ ) was not substantially reduced after sulfonation, and a statistical placement of  $\sim\text{SO}_3\text{H}$  groups was assumed. The sulfonation can also proceed by using a 1,2,4-trichlorobenzene as a solvent. No cross-linking was observed in reaction utilizing these sulfonating agents.

Makowski *et al.* (43) also sulfonated a *t*-butyl-styrene-isoprene copolymer. This copolymer was dissolved in a methylene chloride, and then the sulfonating mixture, prepared from  $\text{SO}_3$  and  $(\text{EtO})_3\text{PO}$ , was added by rapid stirring. After 2.5 hours, the sulfonated copolymer was poured into a large amount of methanol, and after its precipitation, it was isolated by evaporation of the solvents.

Weiss (44) sulfonated a triblock copolymer of poly(styrene-ethylene/butylene-styrene) ( $M_w = 50,000$ ) up to a concentration of the  $\sim\text{SO}_3\text{H}$  groups of 18 mol%. Acetyl sulfate and dichloroethane solutions of polymer were used in this sulfonation according to the method developed by Makowski (43), except that the reaction time was extended from 1 to 2 hours.

Both these methods resulted in a good accord of results.

The sulfonation of polyphenylene oxide (PPO) (45, 46) was conducted in chloroform ( $\text{CHCl}_3$ ) by using chlorosulfonic acid ( $\text{ClSO}_3\text{H}$ ) as the sulfonating agent. The PPO was dissolved in  $\text{CHCl}_3$  to form a 3% solution, and the desired amount of  $\text{ClSO}_3\text{H}$  was added with careful stirring over a 20-minute period. The sulfonated PPO that was obtained was used for reverse osmosis applications.

In the same way, Huang and Kim (47) sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) by using chlorosulfonic acid and a solution of copolymer in chloroform, and then neutralized it by forming a sodium salt. The kinetics of the sulfonation reaction depended on the concentration of both reactants, and the reaction was irreversible.

The sulfonation reactions of model compounds of diene monomers used EPDM rubber was studied by Thaler (48). The sulfonation of small molecular models of EPDM [such as ethylenenorbornane (ENB), dihydrocyclopentadiene (DCPDH)] was reported. These two model compounds behaved quite differently. The ENB model (I) gave a skeletally rearranged  $\gamma$ -sulfone by the reaction with acetylsulfate. In contrast, the dicyclopentadiene (DCPD) model gave rise to a single allylic sulfonic acid. These reactions were due to a low solubility of acetyl sulfate carried out in solutions of the olefins in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) at reaction temperatures ranging from  $-75^\circ\text{C}$  to  $-30^\circ\text{C}$ .

Thaler and de Brevil (49) attempted to determine the mechanism of sulfonation reactions on another model of noncyclic olefins such as 3-hexene, 1-butene (II), and cyclic olefins such as cyclopentene, dihydrocyclopentadiene, ethylidene cyclopentene, and ethylidene cyclohexane (III) in  $^{13}\text{C}$ -NMR studies. These three major types of model olefins gave different sulfonation mechanisms. Reaction with the small olefin molecule (II) produced rather stable but highly reac-

tive  $\beta$ -sulfones, while the multicyclic olefins as DCPDH gave sulfonic acid instead. The cyclic olefins (III) reacted to form allylic sulfonic acids, while the latter produced a skeletally rearranged  $\gamma$ -sulfone. The sulfonation chemistry of end-capped olefins (I), which could have produced  $\gamma$ -sulfone, proved to be more difficult.

The preparation of sulfonated ethylene-propylene elastomer (EPDM) by continuous process in an extruder was achieved by Siadat *et al.* (50). The copolymer was initially heated to 85°C under a nitrogen atmosphere in a single-screw extruder reactor. Then sulfuric acid and acetic anhydride were fed into the extruder. Sulfonation was carried out for 5–10 min. The resulting sulfonated EPDM was only partially neutralized by the reaction with zinc stearate in a series of static mixers at a temperature of about 93°C. The unreacted acetyl sulfate was later removed from the sulfonated product by steam stripping. The absence of solvents and shorter processing time were the advantageous factors in using the extruder for continuous sulfonation.

Jin *et al.* (51) sulfonated poly(ether-ether-ketone) (PEEK) by the reaction of PEEK and concentrated sulfuric acid and prepared its sodium and zinc salts ranging from 4 to 100 mol% of substitution. Cross-linking reaction was not observed in the presence of water during the sulfonation reaction. The unsulfonated and lightly sulfonated PEEK (to 5 mol% of  $\sim\text{SO}_3\text{H}$  groups) were soluble only in strong acids. Ionomers of a medium level of sulfonation (to 32 mol%) swelled in strong polar solvents and phenols; however, they were insoluble in these solvents. The highly sulfonated polymers (above about 75 mol%) were dissolved in strong polar solvents such as DMFA, DMSO, pyridine, etc.

Attempts to sulfonate highly unsaturated polymers such as isoprene or butadiene were not successful because of the high reactivity of the resulting sulfonated product. To form a chemically crosslinking product, however, Zhou *et al.* prepared sulfonated polyisoprene in a very diluted solution of chloroform by the reaction with acetyl sulfate (52, 53).

Vink (54) prepared sulfonated polystyrene (SPS) by using a homogeneous reaction of a PS solution in cyclohexane with a mixture of concentrated  $\text{H}_2\text{SO}_4$  and phosphorous pentoxide ( $\text{P}_4\text{O}_{10}$ ). The reaction was carried out at about 40°C for 30 min with agitation. A yellowish-white sticky mass was obtained after cooling of the reaction mixture with ice. The sulfonated product was purified by dialyzing it in cellophane tubing against distilled water. The yield of sulfonation reaction was found in the range of 90–95 mol%.

Thaler (55) found that the sulfonation of PS with acetylsulfate, which was facile in chlorinated solvents, was ineffective in cyclohexane. The low sulfonation yield was probably caused by a lower solubility of the acetyl sulfate in hydrocarbon solvents. This problem was obviated by using fatty acid sulfates of a higher molecular weight as the sulfonating agents. Lauric ( $\text{C}_{12}$ ) and stearic ( $\text{C}_{18}$ ) acids were treated with

liquid  $\text{SO}_3$  (or  $\text{ClSO}_3\text{H}$ ) to form cyclohexane soluble reagents. Sulfonation was carried out similarly as in the case of acetyl sulfate (43). Another way is based on the formation of sulfonating agents *in situ* by the reaction of  $\text{H}_2\text{SO}_4$  with chlorides of carboxylic acid. Cyclohexanol soluble acyl sulfates were formed in this reaction; however the commercial utility of this method is limited by the formation of a gaseous  $\text{HCl}$  as a by-product.

## 5.2. Heterogeneous Sulfonation of Polymers

Although little has been published about preparation of SPS via sulfonation in a heterogeneous phase, this method is assumed to be advantageous over the homogeneous processes described earlier, because it avoids problems with solvents and the separation of a sulfonated product from the reaction mixture. The heterogeneous sulfonation reaction, i.e., solid-liquid (s-l) (such as  $\text{PS}-\text{H}_2\text{SO}_4$ ) or solid-gaseous (s-g) (such as  $\text{PS}-\text{SO}_3$ ), can be used in commercial manufacturing of cheap sulfonated ionomers from waste polymers.

Kim *et al.* (56) described a method that utilized monodisperse crosslinked PS beads as the substrate. The treatment of these beads with gaseous  $\text{SO}_3$  above fuming sulfuric acid was used to sulfonate the PS. Monodisperse PS beads (450 nm in diameter) were sulfonated in the gaseous phase for 3 days at room temperature to obtain a yellowish sulfonated product. The sulfonated PS beads were used for the preparation of a conducting polymer by adding poly(xylylene tetrathiofenium chloride),  $\text{AsF}_5$ , and the poly(tetrafluoroethylene). Kim's paper is the only reference dealing with the (s-g) heterogeneous sulfonation method.

Regas (57) sulfonated polystyrene-divinylbenzene networks ( $M_w$  from 1000 to 50,000) by reaction of crosslinked polystyrene-divinylbenzene beads swollen in dichloroethane with concentrated  $\text{H}_2\text{SO}_4$  at 80°C for about 10 min. In this case, when the  $\text{ClSO}_3\text{H}$  was used as a sulfonating agent, the reaction temperature had to be decreased below 0°C because of the high reactivity. The prepared product was used for ion-exchange capacity measurements.

Carrol *et al.* (58) developed (s-l) heterogeneous sulfonation of a finely divided PS powder ( $M_w = 240,000$ ). The PS powder was prepared by precipitation of a diluted PS solution in methyl-ethyl ketone with methanol. Sulfonation of this PS powder was conducted using 100%  $\text{H}_2\text{SO}_4$  as the sulfonating agent in the presence of  $\text{Ag}_2\text{SO}_4$  as a catalyst at room temperature for 10 min. The  $\text{Ag}_2\text{SO}_4$  prevented the formation of side products in this reaction. A 100% yield of the sulfonation reaction was achieved within 5 to 15 min. A gelatinous colorless mass was obtained, and no change after 24 hours or further reaction was observed. It seems that mono-substitution at the para-position was the only reaction proceeding in the described process.

Bishop *et al.* (59) investigated the behavior of diluted solutions of poly(oxy-1,4-phenyleneoxy-1,4-phenylene



carbonyl-1,4-phenylene) (PEEK) in strong acids (i.e.  $\text{H}_2\text{SO}_4$ ,  $\text{ClSO}_3\text{H}$ ). The copolymer became sulfonated upon its dissolution in  $\text{H}_2\text{SO}_4$  or  $\text{HSO}_3\text{Cl}$ . Aggregation of the polymer chains was caused by an electrostatic interaction between the sulfonated chains, and, in addition, a chemical crosslinking was observed as a result of side reaction accompanying the sulfonation process.

### 5.3. Preparation of Sulfonated Polymers by Polymerization of Sulfonated Monomer

In order to present a complete picture of the sulfonation reactions used, the polymerization method for preparation of sulfonated ionomers is briefly reviewed. Weiss *et al.* (60, 61) described the radical emulsion copolymerization of styrene and sodium styrene sulfonate (NaSS) as a feasible route to ionomeric SPS. Lightly sulfonated PS was obtained by copolymerization of styrene with 4 wt% of NaSS by addition of potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_5$ ), and n-dodecylthiol ( $\text{C}_{12}\text{H}_{25}\text{SH}$ ). Copolymerization can also be initiated with redox systems such as diisopropylbenzene hydroperoxide and trimethylenetetraamines by obtaining a similar copolymer composition. Polymerization was carried out in a water emulsion at about 50°C for about 6 hours. An enhanced rate of copolymerization of NaSS with styrene over the homopolymerization of styrene, due to alteration of the polymerization kinetics, was observed. Weiss *et al.* (62) also studied the copolymerization of butadiene with NaSS and the effect of the reaction conditions on the properties of a sulfonated product. Siadat *et al.* (63) described the preparation of a sulfonated rubber by emulsion copolymerization of styrene sulfonic acid esters with isoprene.

## 6. CONCLUSIONS

The analysis of mechanisms and kinetics of sulfonation of small organic molecules described in the first part of this review article is used to suggest the feasibility of polymer sulfonation in a heterogeneous reactions using gaseous or liquid  $\text{SO}_3$  as a sulfonating agent. The sulfonation of high polymers can be achieved using two basic routes, i.e., via sulfonation of high polymers or via copolymerization of sulfonated monomers. This review is concerned with the sulfonation reactions of high polymers with PS as the primary one. Generally, the sulfonation of high polymers as the method for sulfonated ionomers preparation has several basic features:

- (i) a random distribution of inserted  $\sim\text{SO}_3\text{H}$  groups along the PS chain;
- (ii) a minimum of chain-to-chain heterogeneity;
- (iii) the sulfonation proceeds without any significant polymer degradation;
- (iv) the characterization of SPS can be simplified by using polymers with narrow molar mass distributions.

The most frequently quoted process for the preparation of a lightly sulfonated polystyrene was the method of homogeneous sulfonation of PS with acetyl sulfate in a solution of dichloroethane described by Makowski *et al.* (43). Only the paper by Carrol (58) described the preparation of highly sulfonated polystyrene in the heterogeneous (s-l) phase.

The heterogeneous sulfonation of solid waste PS by gaseous  $\text{SO}_3$  is considered the most viable way to produce sulfonated PS commercially. Sulfonated PS has a wide range of commercial applications, i.e., sulfonation of waste PS to obtain a water-soluble polymer additive for concrete is one of the alternative recycling ways. It seems that such a technique could become an economically attractive way of recycling waste PS. Modification of concrete mixtures by addition of sulfonated PS as a superplasticizer can result in macro-defect-free (MDF) cements with tensile moduli on the order of 150 GPa and tensile strengths of 150–250 MPa. These materials have substantially better mechanical properties than unmodified concrete, because of the much smaller size of inherent structural defects (64). The SPS, because of its macromolecular character, could bring good results in concrete modification. However, its application has been limited so far, because a viable industrial sulfonation process has not yet been developed.

## REFERENCES

1. P. H. Groggins and W. A. Simpson, *Chemical Engineering Series*, New York (1947).
2. J. March, *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure*, Wiley, New York (1991).
3. R. Taylor, *Electrophiles Aromatic Substitution*, Wiley, New York (1990).
4. D. M. Brouwer, E. L. Mackor, C. MacLean, G. A. Olah, and P. von R. Schleyer, *Carbonium Ions*, **2**, 837–97, Wiley, New York (1970).
5. F. Muth, in *Houben-Weyl*, Bd.9 p. 429, (1955).
6. H. Cerfontain, *Mechanistic Aspects in Aromatic Sulfonation and Desulfonation*, Wiley, New York (1968).
7. E. E. Gilbert, *Sulfonation and Related Reactions*, Wiley, New York (1965).
8. C. M. Suter and A. W. Weston, *Org. React.* **3**, 141 (1946).
9. O. Cervinka and V. Dědek, *Organic Chemistry*, pp. 217–9, SNTL Alfa Prague, Czech Republic (1982).
10. H. Cerfontain and A. Telder, *Rec. Trav. Chim.*, **84**, 1613 (1965).
11. H. Cerfontain, H. J. Hofman, and A. Telder, *Rec. Trav. Chim.*, **83**, 493 (1964).
12. F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).
13. R. O. C. Norman and R. Taylor, *Electrophilic Substitution in Benzenoid Compounds*, p. 225, Elsevier, Amsterdam (1965).
14. O. Cervinka, *Chemistry of Organic Compounds*, p. 812, SNTL Alfa Prague, Czech Republic (1985).
15. H. Cerfontain, *Rec. Trav. Chim.*, **80**, 296 (1961).
16. H. Cerfontain, *Rec. Trav. Chim.*, **84**, 551 (1965).
17. A. A. Spryskov and S. P. Srarkov, *Zh. Obshch. Khim.*, **26**, 2962 (1956).
18. K. Lauer, *J. Pract. Chem.*, **135(81)**, 424, (1933).
19. H. Vollmann, H. Becker, M. Corell, and H. Streeck, *Ann. Chem.*, **531**, 1 (1937).
20. D. C. Abercromby, R. A. Hyne, and P. F. Tiley, *J. Chem. Soc.*, 5832 (1963).

21. Urban @ Schwarzenberg, *Ullmans encyklopedia of technical chemie*, 3.ed., 15.teil, Munich, Berlin (1964).
22. R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **39**, 2189 (1961).
23. G. E. Walrafen and T. F. Young, *Trans. Faraday Soc.*, **56**, 1419 (1960).
24. Gmelin, *Handbuch der Anorg. Chemie, Schwefel B, Lieferungen I, II, III*, Verlag Chemie, Weinheim, Germany (1953, 1960, 1963).
25. J. H. Colwell and G. D. Halsey, *J. Phys. Chem.*, **66**, 2179 (1962).
26. R. A. Hyne and P. F. Tiley, *J. Chem. Soc.*, 2348 (1961).
27. H. A. Lehmann and G. Ladwig, *Z. Anorg. Allgem. Chem.*, **284**, 1 (1956).
28. R. Steudel, *Z. Anorg. Allgem. Chem.*, **346**, 255 (1966).
29. E. E. Gilbert, *Chem. Rev.*, **62**, 549 (1962).
30. G. Nickless, *Inorganic Sulphur Chemistry*, p.3884, Elsevier, New York (1968).
31. H. S. Makowski, R. D. Lundberg, L. Westerman, and J. Block, *Ions in Polymers, ASC Symposium Series, Adv. Chem. Ser.*, **187**, 3 (1980).
32. J. C. D. Brand and A. Rutherford, *J. Chem. Soc.*, 3916 (1952).
33. R. J. Gillespie, *Rev. Pure Appl. Chem.*, **9**, 1 (1959).
34. G. A. Ratclif, *Diss. Abstracts*, **14**, 2018 (1954).
35. E. A. Knaggs, *Chemtech*, **22**, 436 (1992).
36. K. D. Henkel Offen 4,034.242 (1990).
37. A. G. Henkel DE. 4,109.250 (1991).
38. Eniricerce S.p.A., Snam Progetti, Eur. P. 450.201 (1989).
39. W. Breuers, H. Mark, and E. Konrad, U.S. Patent 2,031,929 (1936).
40. C. Wulf, Ger. 580,366 (1933), Brit. 367,416 (1933).
41. A. F. Turbak, *Ind. Eng. Chem., Prod. Res. Dev.*, **1(4)**, 275 (1962).
42. H. H. Roth, *Ind. Eng. Chem.*, **46**, 2435 (1954).
43. Makowski *et al.*, U.S. Patent 3,870,841 (Nov. 3, 1975).
44. R. A. Weiss, A. Sen, C. L. Willis, and L. A. Pottick, *Polymer*, **32(10)**, 1867 (1991).
45. C. W. Plummer *et al.*, *Development of Sulfonated PPO for Reverse Osmosis, OSW Research and Development Report*, **551** (1970).
46. P. J. Chlodzinski, A. P. Fickett and A. B. Laconti, *Polym. Prepr.*, **12(2)**, 276 (1971).
47. R. Y. M. Huang and J. J. Kim, *J. Appl. Polym. Sci.*, **29**, 4017 (1984).
48. W. A. Thaler, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 875 (1982).
49. W. A. Thaler and C. du Brevil, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 3905 (1984).
50. B. Siadat and R. D. Lundberg, *Polym. Eng. Sci.*, **20**, 530 (1980).
51. K. Jin, M. T. Bishop, T. S. Ellis, and F. E. Karasz, *Br. Polym. J.*, **17**, 4 (1985).
52. Z. L. Zhou and A. Eisenberg, *J. Polym. Sci., Polym. Phys. Ed.*, **27**, 657 (1982).
53. D. Rahrig, W. J. MacKnight and R. W. Lenz, *Macromolecules*, **12**, 195 (1979).
54. H. Vink, *Macromol. Chem.*, **182**, 279 (1981).
55. W. A. Thaler, *Macromolecules*, **16**, 623 (1983).
56. G. Y. Kim, R. Salovey, and J. J. Aklonis, *Polym. Bulletin*, **23**, 543 (1990).
57. F. P. Regas, *Polymer*, **25**, 249 (1984).
58. W. R. Carrol and H. Eisenberg, *J. Polym. Sci., Part A-2*, **4**, 599 (1966).
59. M. T. Bishop, F. E. Karasz, P. S. Russo, and K. H. Langley, *Macromolecules*, **18**, 86 (1985).
60. R. A. Weiss, S. R. Turner, and R. D. Lundberg, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 525 (1985).
61. S. R. Turner, R. A. Weiss, and R. D. Lundberg, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 535 (1985).
62. R. A. Weiss and R. D. Lundberg, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 3427 (1980).
63. B. Siadat and R. W. Lenz, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 3273 (1980).
64. V. M. Malhotra, *Superplasticizers and Other Chemical Admixtures in Concrete*, Proc. Third International Conference, Ottawa (1989).

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