

Polymeric Decontaminant: *N,N*-Dichloro Poly(styrene-*co*-divinyl benzene) Sulfonamide—Synthesis, Characterization and Efficacy against Simulant of Sulfur Mustard

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ABSTRACT: *N,N*-Dichloro poly(styrene-*co*-divinylbenzene) sulfonamide (1) reacts with 2-chloro ethyl phenyl sulfide (2), a simulant of sulfur mustard (SM), at room temperature, yielding corresponding nontoxic sulfones and sulfoxides in aqueous as well as aprotic medium. The decontamination reaction was monitored by gas chromatography, and products were identified by gas chromatography–mass spectrometry. *N,N*-dichloro poly(styrene-*co*-divinylbenzene) sulfonamide was synthesized by three steps from a commercial starting material sulfonate cation-exchange resin and characterized by FTIR, and TGA, and

compressive strength by universal testing machine. The positive chlorine content of this polymer was checked by standard iodometry titration. The synthesized positive chlorine compound is observed to be a promising against a simulant of SM, chiefly in the situation where use of aqueous medium is precluded. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2203–2207, 2007

Key words: *N,N*-dichloro poly(styrene-*co*-divinylbenzene) sulfonamide; 2-chloro ethyl phenyl sulfide; sulfur mustard (SM); decontamination; positive chlorine compound

INTRODUCTION

Poly(styrene divinylbenzene) copolymer¹ beads are widely used as adsorbents² support for catalysis,^{3,4} anion-exchangers,^{5,6} and cation-exchange^{7,8} precursors for carbon spheres. Cation-exchange is among the most important commercial products derived from styrene–divinylbenzene (St-DVB) copolymer for use in chromatographic separations⁹ and acid catalysis.¹⁰ Porous styrene St-DVB beads are produced by suspension polymerization.¹¹

A macroporous poly(styrene-*co*-divinylbenzene) resin having *N,N*-dichloro sulfonamide groups sulfonamide have been used as a polymer-supported reagent for oxidation of residual sulfides,¹² cyanides,¹³ thiocyanates,¹⁴ water disinfection,¹⁵ and some application in synthetic organic chemistry.¹⁶ In the present study we report macromolecular dichloroamine as a polymeric decontaminant against simulant of sulfur mustard (SM). SM is highly toxic and persistent blistering agent. It is one of the oldest and most important chemical warfare agents, being a cytotoxic alkylating agent.¹⁷ Hence decontamination of this compound and its simulant has evinced considerable interest. The chemical decontamination of SM immediately after contact is still the best method of protection. The

prerequisite for such a decontaminant is that it must instantly convert SM into nontoxic products. Various methods for the decontamination of SM are known in the literature, amongst them hydrolysis and oxidation are the most preferred. However, destruction of SM by hydrolysis is not suitable for the decontamination in large quantity. Other alternative methods such as hydrogenolysis, super critical water oxidation, and electrochemical oxidation have not ached upto the practical utility. The most common and widely used process is the oxidation¹⁸ of SM using organic chloramines,^{19–21} which is rapid enough to decontaminate it instantly. We report here reaction profile of 2-chloro ethyl phenyl sulfide as a simulant of SM, with polymeric chloramines as a decontaminating agent in aqueous as well as aprotic medium at room temperature. Keeping in view the requirement for large quantity of polymeric decontaminant, an easily and commercially viable synthetic procedure for *N,N*-dichloro poly(styrene-*co*-divinylbenzene) sulfonamide is also reported. Starting from a commercial sulfonate cation-exchange resin via sulfonyl chloride and sulfonamide resins, a macromolecular dichroamine was prepared.

EXPERIMENTAL

Synthesis of *N,N*-dichloro poly(styrene-*co*-divinylbenzene) sulfonamide

The copolymer was synthesized in three steps, and its structure is given in the Figure 1. In the first step,

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—SO₃H group of commercial sulfonate polystyrene-divinylbenzene copolymer was converted into corresponding —SO₂Cl by refluxing using excess amount of phosphorus oxychloride for 4–6 h. In the second step, —SO₂Cl group of aforementioned resin was readily converted into —SO₂NH₂ using excess concentrated ammonia reflux for 3–4 h. The final step chlorination of amide group was carried out using freshly prepared sodium hypochlorite at 5°C for 2 h in acidic medium, using acetic acid. The positive chlorine content of this polymer checked by standard iodometry titration²² was found to be 8.2%.

CHARACTERIZATION

Thermal stability of commercial sulfonate cation-exchange resins (1a), corresponding sulfonyl chloride (1b), sulfonamide resins (1c), and macromolecular dichloroamine (1d) was studied by TA instrument TGA 2950 at a heating rate of 10°C min⁻¹ using nitrogen. Infrared (IR) spectra of all cation-exchange resins (1a–1d) were also identified by FTIR as KBr pellets. IR spectra were recorded on a Perkin-Elmer 1720x FTIR spectrophotometer. Compressive strength of all beads (1a–1d) was measured using Good brand's Universal Testing Machine, and tension was applied at the constant rate of 0.5 cm min⁻¹. GC/MS analysis was performed in EI mode in order to identify the decontaminated products. The GC conditions used were as follows: column BP-5 (30 m × 0.32 mm) with a temperature programme of 80°C for 2 min followed by a gradient to 280 at 20°C min⁻¹. The injector temperature was maintained at 250°C while the transfer line was at 280°C. The EI analysis was performed at 70 eV with ion source temperature at 200°C and emission current of 400 μA.

Reaction of 2-chloro ethyl phenyl sulfide (2) and polymeric decontaminant (1)

To a stirred solution of simulant (0.01 mole) in CH₃CN : H₂O (2 : 1) was added polymeric decontaminant (0.04 mole). Aliquots were taken at different time intervals (upto 24 h) and extracted with dichloromethane. The organic phase was analyzed for the residual simulant and degradation products by GC using BP-5 column and FPD sulfur mode as a detector. The reaction of 1 with 2 was also monitored in toluene as aprotic medium, using a similar procedure as aqueous medium.

RESULTS AND DISCUSSION

Sulfonate-(St-DVB) copolymer is easily available and very cheap. *N,N*-Dichloro poly(styrene-*co*-divinylbenzene) sulfonamide is prepared by three-step process,

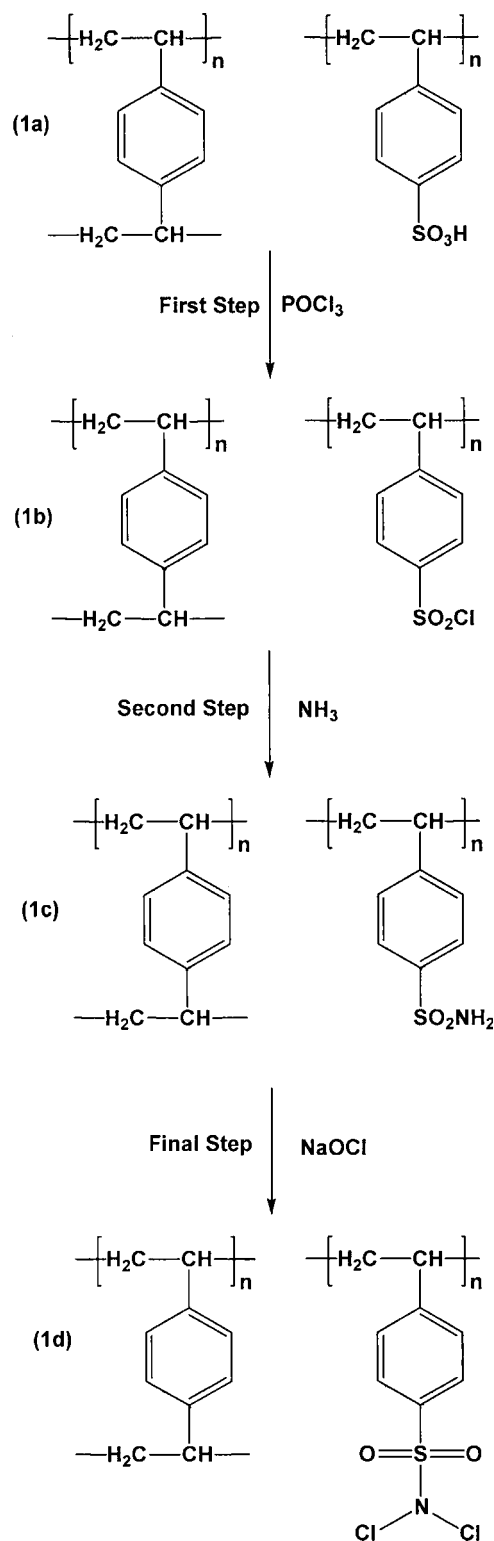


Figure 1 Synthesis of *N,N*-dichloropoly(styrene-*co*-divinylbenzene) sulfonamide (1a–1d).

starting from a commercial sulfonate cation-exchange resin via sulfonyl chloride and sulfonamide resins, a macromolecular dichloroamine was prepared, and active chlorine was determined by iodometry titration using sodium thiosulfate and found to be 8.2%.

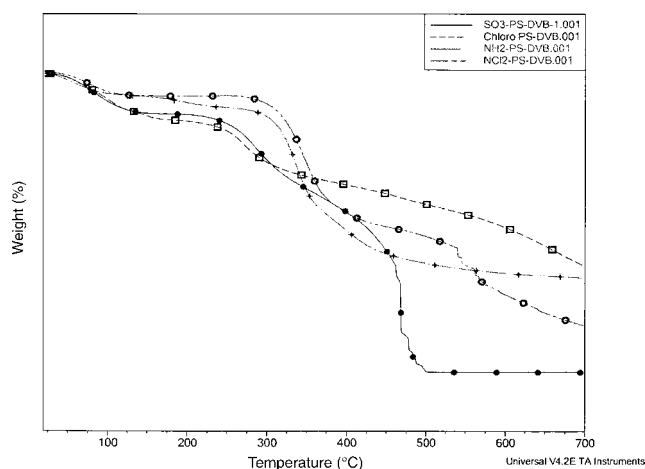


Figure 2 TGA of the polymers (1a–1d).

In the FTIR spectra of sulfonate poly(styrene-*co*-divinylbenzene) samples, absorption bands were observed around 3440, 1060, 1024, and 674 cm^{-1} . The broad band at 3440 cm^{-1} is assigned to O–H stretch in $-\text{SO}_3\text{H}$ as well as to absorbed moisture. The other bands are due to various sulfur–oxygen vibrations; symmetric O=S=O (1060 cm^{-1}), S=O stretch (1024 cm^{-1}), S–O stretch (675 cm^{-1}). In sulfonyl chloride polystyrene divinylbenzene, OH absorption band disappeared and a new band was observed at 736 cm^{-1} due to C–Cl stretching band. The FTIR spectra of resins (1c) show strong absorption at 3357 cm^{-1} due to NH_2 . The final polymer (1d) showed absorption bands at 3357 cm^{-1} (NH_2), 3362 cm^{-1} (Ar-H), 1374, 1172 ($-\text{SO}_2$) cm^{-1} , and 822(C–Cl) cm^{-1} . These beads (1a–1d) are subjected to compressive strength measurements results into values in the range of 19.2–24.9 MPa, and in TGA (Fig. 2) showed multistep mass loss in all resins (1a–1d). In starting sulfonate-PS-DVB, the mass loss upto 200°C was due to physically bound water and mass loss in the range of 200–300°C may be attributed to decomposition of sulfonic acid groups. The breakdown of polymer backbone takes place above 400°C. Thermal stability after substitution in SO_3 -PS-DVB was found to increase in polymers (1b–1d), and the results are given in Table I.

The first decontaminant used was bleaching powders and to a lesser extent potassium permanga-

nate. The reactions of chemical warfare agents with excess bleach are so vigorous, and these agents can be converted to less or nontoxic products at the liquid–liquid (bleach solution) or liquid–solid (bleach powder) interface in a few minutes. However, there are some disadvantages in using bleaches as a decontaminant.

- The active chlorine content of the bleach gradually decreases with storage time, so that a fresh solution must be prepared prior to each use.
- A large amount of bleach is required for the oxidation of the agents, and most importantly,
- Bleach is corrosive to many surfaces.

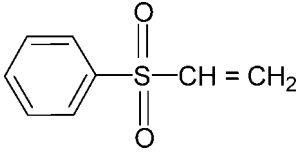
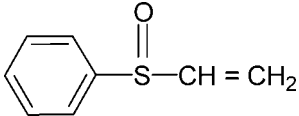
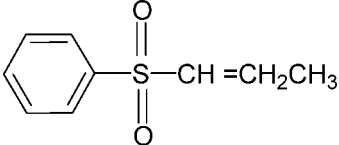
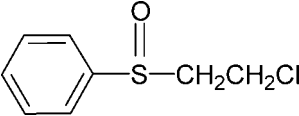
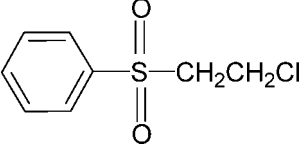
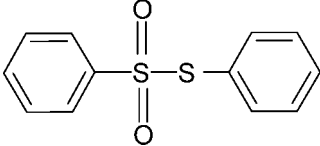
Decontamination of SM by hydrolysis is somewhat problematic than oxidation. SM has low solubility in water due to which decontamination of SM by hydrolysis is very slow. Decontamination of SM by oxidation is a preferred method. *N*-Chloramines have been used to overcome some of these difficulties.

Oxidative chlorination is the oldest and most widely used decontamination method against CW agents. The term oxidative chlorination covers the active chlorine chemicals like hypochlorite, which under certain conditions can generate a positive-charged chlorine (Cl^+), which is an oxidizing species. Oxidation reaction removes the lone pair on sulfur, thus making the molecules no more reactive to biological systems. SM bears oxidizable bivalent sulfur atom. Oxidation reactions are relatively faster than hydrolysis reactions. *N*-Chloramines, in which chlorine is directly attached to nitrogen, can generate positively charged chlorine (Cl^+), which is an oxidizing species. The additional advantage of polymeric chloramines is higher stability as compared to low-molecular chloramine, such as chloramine-T and dichloroamine-T. Active chlorine content does not decrease with prolonged storage time. Presence of strong electron withdrawing benzene sulfonyl group is expected to release positive chlorine, thereby facilitating the decontamination reaction. Homogenous reactions are preferred. But two-phase systems, with the agents as the organic phase and ionic reactions in the aqueous phase, are also under consideration. We therefore used the concept to synthesize (1) and monitor decomposition reaction with (2).

TABLE I
Decomposition of Polymers (1a–1d) by TGA

Polymers	10% loss temp (0°C)	20% loss temp (0°C)	50% loss temp (0°C)	Final decomposition temp (0°C)	Residue at 700 (0°C)
SO_3 -PS-DVB (1a)	104	268	416	500	–
ClSO_2 -PS-DVB (1b)	107	254	583	696	35.5
NH_2SO_2 -PS-DVB (1c)	205	319	388	693	31.24
Cl_2NSO_2 -PS-DVB (1d)	298	332	432	697	15.32

TABLE II
Identified Decontamination Products from 2-Chloro Ethyl Phenyl Sulphide with Polymeric Decontaminant in Aqueous Medium

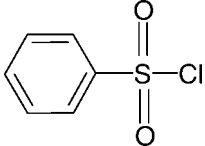
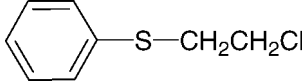
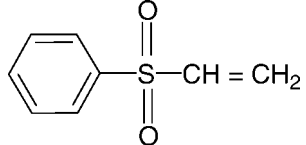
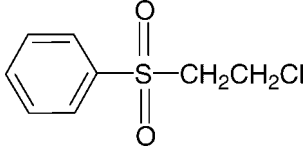
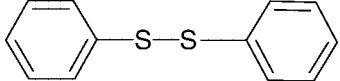
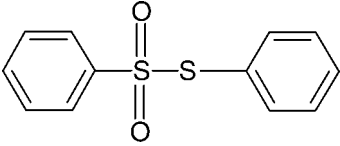
R_t (min)	m/z	Identified compounds
8.16	168	
8.27	152	
9.15	183	
9.29	188/190	
9.39	204/206	
11.73	250	

Decontamination studies of 2-chloro ethyl phenyl sulfide with polymeric decontaminant were carried out in aqueous medium, using acetonitrile : water mixture, as well as in aprotic medium, using toluene at room temperature with stirring. Decontaminated products were separated by GLC and identified by GC/MS in EI mode, and the results are given in the Tables II and III. The reaction profile of simulant of SM (2) and polymeric decontaminant (1) was studied. It was observed that the decontamination reaction was found to be faster in aqueous medium as compared to aprotic medium. In aqueous medium, 95% simulant was decomposed within 30 min, and after 1 h 100% simulant was decomposed into mainly phenyl vinyl sulfoxide. In aqueous medium, as shown in Table II, simulant was converted into a series of oxidation and elimination products, the first

step in chlorination of sulfide is electrophilic attack of chlorine on sulfur, generating sulfonium cation. Subsequently, nucleophilic displacements of chlorine by water with elimination of HCl produce corresponding sulfoxide. Second, such attack of chlorine on sulfur in a similar manner produces corresponding sulfones. Subsequently, both oxidation products undergo elimination reactions in the basic solution to produce phenyl vinyl sulfones, benzene(2-chloro ethyl sulfonyl), benzene(2-chloro ethyl sulfone), benzene sulfono thionic acid *S*-phenyl ester, benzene (1-propenyl sulfonyl sulfonic-4 hydroxy), and benzene ethyl sulfonyl.

In aprotic medium, according to GC results, the extent of reaction was 85% after 24 h with 1 and 2. The other decontamination products as shown in Table III were benzene-2-chloro ethyl sulfonyl, benzene-2-chloro ethyl sulfones, benzene ethyl sulfonyl, benzene sulfonyl chloride, and diphenyl disulfide and benzene sulfonothioic acid-*S*-phenyl ester.

TABLE III
Identified Decontamination Products from 2-Chloro Ethyl Phenyl Sulphide with Polymeric Decontaminant in Aprotic Medium

R_t (min)	m/z	Identified products
6.92	176/178	
7.52	172/174	
8.13	168	
9.38	204/206	
10.63	218	
11.74	250	

CONCLUSION

N,N-Dichloro poly(styrene-*co*-divinylbenzene)sulfonamide was synthesized by three steps. Decontamination efficacy of this polymer was determined at room temperature in aqueous as well as aprotic medium, using 2-chloro ethyl phenyl sulfide a simulant of SM. Nontoxic sulfones and sulfoxide in aqueous as well as aprotic medium were the decontaminated products of the simulant. Decontamination reaction was monitored by gas chromatography, using FPD as detector. Products were identified by GC-MS. Results were encouraging in aqueous medium when compared with aprotic medium. Presence of positive chlorine in polymeric chloramines makes it an efficient oxidant against SM stimulant, which bears oxidizable divalent sulfur.

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