

Contents list available at **IJND**
International Journal of Nano Dimension

Journal homepage: www.IJND.ir

Preparation of *N, N*-dichloropolystyrene sulfonamide nanofiber as a regenerable self-decontaminating material for protection against chemical warfare agents

ABSTRACT

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Received: 22 August 2011
Accepted: 05 November 2011

N,N-dichloropolystyrene sulfonamide as a decontaminant was synthesized in 5 steps from styrene monomer. Styrene was first polymerized. Then, sulfonation reaction was performed by H₂SO₄ (c) followed by chlorination with POCl₃ obtain chlorosulfonated polystyrene. Amidification reaction was then applied to get sulfonamide resin. Sulfonamide resin was treated with sodium hypochloride to obtain *N,N*-dichloropolystyrene product. The products of each step were characterized by FT-IR technique. The active chlorine content of final product was measured by standard iodometry titration. Composite nanofibers of polystyrene – *N,N*-dichloropolystyrene sulfonamide (PS/DPSA) were prepared with electrospinning technique. The appropriate nanofibers obtained under optimized conditions such as applied voltage, distance between the collection plate and nozzle, kind of solvent and concentration of composite solution. The diameter of nanofibers was determined by scanning electron microscope (SEM) and range of nanofiber was about 160-300nm. The decontamination reaction of 2-chloroethyl ethyl sulfide (2-CEES) a simulant of sulfur mustard (S.M.) by composite nanofibers of PS/ DPSA was monitored by gas chromatography (GC). Also the reaction products of decontamination reaction were identified by gas chromatography – mass spectroscopy (GC-MS). These composite nanofibers are able to decontaminate 2-CEES in 7 minutes.

Keywords: *2-chloroethyl ethyl sulfide; N,N-dichloropolystyrene sulfonamide; Nanofiber; Self-decontamination; Electrospun.*

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INTRODUCTION

The Chemical Weapons Convention (CWC), which have become effective since April 1997. It has also forbids development, production, stockpiling, and uses of chemical weapons [1].

Perhaps the most notable record of chemical warfare agent (CWA) use was the campaign led by Fritz Haber of Germany, wherein chlorine, phosgene, and mustard gases were used against the Allies on Europe's western front within numerous occasions during World War I [2]. Since then, nations have sought practical ways to decontaminate mustard agents and similar vesicants. Ideally, a decontaminating agent should act fast and produces low toxicity products, and performs in all weather conditions. During World War II, the various methods for the decontamination of mustard gas were presented in the literature, among them hydrolysis and oxidation reactions were preferred. However, destruction of sulfur mustards by hydrolysis is not suitable for the decontaminating procedure for large quantity one. The most common and widely used process is the oxidation [3] reaction of sulfur mustards, using organic chloramines [4-6] which is rapid enough to decontaminate. Oxidation reactions remove the lone pairs of sulfur compound, making the molecules no more reactive toward biological system. Various oxidizing agents have been used for this decontamination reaction, including peracids of the oxone type [7], oxaziridines [8], peroxides [9], or magnesium monoperoxyphthalate

[10]. A more recent development is the use of *N*-chloramide hydantoin as "self-decontaminating" components that are used to such militarily relevant materials as tents, paints, and uniforms. Hydantoin chloramides are nontoxic, regenerable, and are easily attached to polymer. Polymers have been functionalized to incorporate functional groups of many types [11, 12]. Many useful procedures for the oxidation of alcohols to the corresponding carbonyl compounds using polymer supported reagents have been reported [13, 14]. Our interest in polymer-supported reactions [15] and synthesis of polymeric analogues of well known halogeno-sulfonamides and their applications have been reported [16].

In this work, DPSA (Figure 1) was synthesized by different steps from monomer of styrene and followed by sulfonation, chlorosulfonation and amidification. Halogeno-sulfonamide was obtained by treatment of sodium hypochlorite with sulfonamide resin. Then, PS/DPSA solution was electrospun to preparation of nanofibers under optimized conditions. Nanofibers were measured for content of active oxidizing agent and finally, decontamination efficiency of this material on 2-CEES was investigated by GC-MS technique.

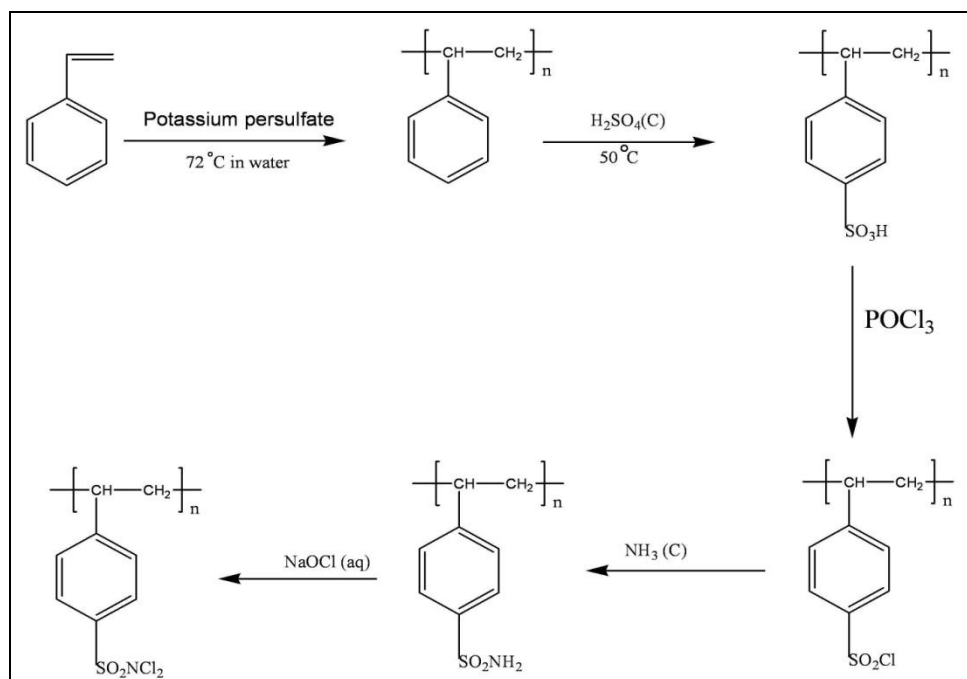


Fig.1. Synthesis of *N,N*-dichloropolystyrene sulfonamide.

EXPERIMENTAL

Chemical reagents

2-chloroethyl ethyl sulfide and Styrene were purchased from Aldrich. Chloroform, acetic anhydride, sulfuric acid, $K_2S_2O_8$ (KPS), methanol, *N,N*-dimethylformamide (DMF), $POCl_3$, NaCl, ammonia, and sodium hypochlorite solution of AR grades were purchased from Merck and were used as received.

Experimental procedure

The polymer was synthesized in five steps, and its structure is given in Figure 1.

- **Synthesis of polystyrene(PS)**

Deionized H_2O (220 ml), CH_3OH (25 ml), NaCl (0.65 g), styrene (50 g), and KPS (0.30 g) were introduced into a three-necked round-bottomed flask and stirred. The mixture was then deoxygenated by bubbling oxygen-free nitrogen through it for 15 min. The polymerization reaction was allowed to proceed at $72^\circ C$ for 12 h and then at $85^\circ C$ for 2 h. The strict solid of PS was produced after this step.

- **Synthesis of sulfonated polystyrene**

15 g of PS was dissolved in 150 mL of chloroform and 80 mL of conc. H_2SO_4 was added dropwise to the solution at $50^\circ C$ with continuous stirring for 3 h. After completing the reaction, the dark brown sulfonated PS was allowed to dry in air for 12 h at room temperature.

- **Synthesis of Chloro sulfonation polystyrene**

Sulfonated PS (15 g) was mixed with 150 mL of $POCl_3$ and refluxed for 5–6 h. $POCl_3$ was distilled off after completion of the reaction. The chloro sulfonated PS was washed with methanol.

- **Synthesis of Polystyrene sulfonamide**

Chloro sulfonated PS (15 g) was refluxed with aqueous conc. Ammonia (200 mL) for 5–6 h.

- **Synthesis of DPSA**

DPSA was easily obtained by stirring polystyrene sulfonamide (15 g) in 200 mL of sodium hypochlorite solution in acidic medium using acetic acid for 3–4 h at $5^\circ C$. The product was

filtered and dried in air. The positive chlorine content of this polymer was checked by standard iodometry titration and it was found to be 19.8%.

Electrospinning process

Initially, the solutions were prepared by dissolving PS and DPSA in DMF at room temperature. The concentration of these mixtures was constant in 30% (w/v) but ratio of PS: DPSA was varied from 10:1 to 2:1. Finally, in optimized conditions, the nanofibers were produced by PS:DPSA mixture with ratio of 3:1. The solution was loaded into a plastic syringe equipped with stainless steel needle. The syringe was positioned in the Plexiglas box and raised from a metallic support and a needle was connected to the positive electrode of high-voltage (15-20 kV) supply. The solution was fed at a constant rate (0.2 ml/ h) using a syringe pump (Top Syringe Pump Top-5300). A piece of flat aluminum foil was placed below the tip of the needle to collect the nanofibers. Aluminum foil was connected to ground and the distance to needle was 12 cm.

Characterization

Infrared (IR) spectra of all polymers were identified by FT-IR as KBr pellets. IR spectra were recorded on a Perkin Elmer Spectrum 100 in the range $4000-450cm^{-1}$. Scanning electron microscopy (SEM) was obtained with using HITACHI S-3000N JAPAN. The diameter of nanofibers were measured by using image analyzer (adobe photoshop 7.0) and evaluated about in the range of 160-1900 nm. The decontamination efficiency of PS/DPSA nanofibers was studied by comparing GC results for blank solution and after applying it with PS/DPSA nanofiber. The blank solution was consisted of 2-CEES and methanol (solvent) the reaction was carried out under N_2 atmosphere. The extracted products were analyzed by HP-Agilent GC-MS system and Varian Star 3400 CX gas chromatography with flame ionization (FID) detector. A fused-silica capillary column DB-1701(30m \times 0.25mm \times 0.25 μm) was chosen. The initial and final temperatures of the oven were programmed at $60^\circ C$ (held for 6.00 min) and $200^\circ C$ respectively, the rate increasing $20^\circ C/min$ was selected. The separated products were identified by comparison of experimental mass spectra with references.

RESULTS AND DISCUSSION

Characterization of DPSA

Polystyrene was synthesized from styrene by using KPS as initiator [17]. The sulfonation, chlorosulfonation, amidification and halogenation steps were carried out by slightly modifying the method proposed by Gutch et al [18]. FT-IR spectra of products are shown in Figure 2.

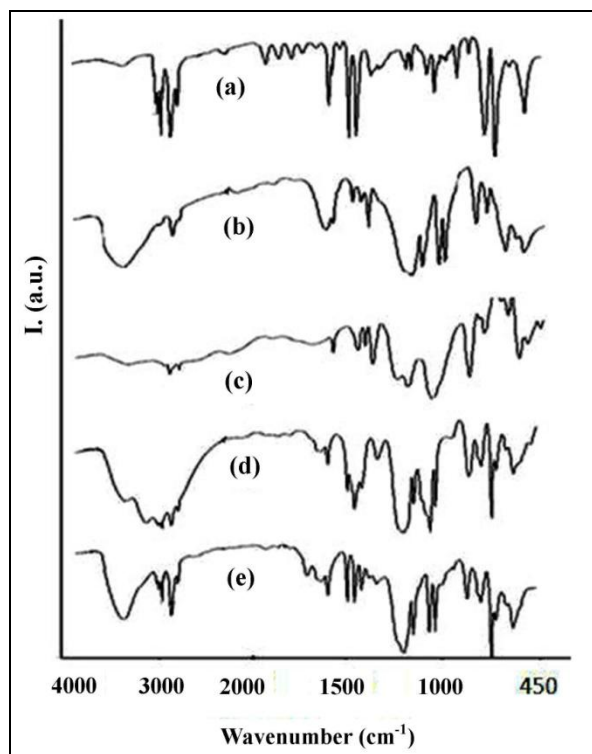


Fig. 2. FT-IR spectra of the PS (a), PS -SO₃H (b), PS -SO₂Cl (c), PS -SO₂NH₂ (d) and PS -SO₂NCl₂(e)

The typical absorption peaks of pure PS (Figure 2a) at 3082/3059, 2922/2849, 1604/1493, and 755/696 cm⁻¹ were attributed to aryl C-H vibration bands, the alkyl C-H vibration bands, the benzene ring backbone vibration mode, and the out-of-plane C-H bending vibration mode of the mono-substituted benzene ring, respectively. Other peaks were observed at 1177/1154 cm⁻¹ which represent C-C bond. Sulfonated polystyrene (Figure 2b) absorption bands were observed around 3454, 1413, 1183, and 695 cm⁻¹. The broad band at 3445 cm⁻¹ is assigned to O-H stretch in -SO₃H as well as to absorbed moisture. The other bands are due to various sulfur-oxygen vibration; asymmetric (1413

cm⁻¹) and symmetric O=S=O (1183 cm⁻¹). In sulfonylchloride polystyrene (Figure 2c) -OH absorption band was disappeared and new band was observed at 760 cm⁻¹ due to C-Cl stretching band. The FTIR spectra of polystyrene sulfonamide (Figure 2d) show strong absorption at 3448 cm⁻¹ due to NH₂. The final polymer, DPSA, (Figure 2e) showed absorption bands at 3448 cm⁻¹ (NH₂), 3050/2900 cm⁻¹ (C-H), 1382, 1184 (-SO₂) cm⁻¹, and 832(N-Cl) cm⁻¹.

Preparation of electrospun PS/ DPSA fiber

All the attempts to prepare nanofiber of DPSA were inconclusive but PS/ DPSA composite fiber was prepared with ease. Figure 3 show the SEM images of PS/ DPSA (70:30 w/w). In presence of DPSA, fiber diameter were increased to 200 nm which could possibly due to the addition of DPSA it seems resistance of spinning solution increased thereby increases fiber diameter.

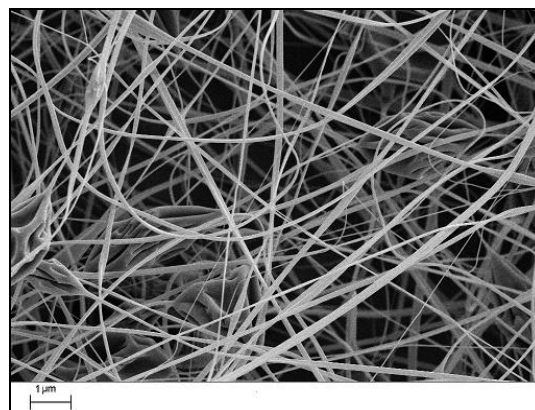


Fig.3. SEM images of PS/DPSA(70:30 w/w) nanofibers

Reaction of 2-CEES and composite nanofiber

A variety of oxidative chemicals have been used for decontamination agent. Oxidation by chlorine compound is the oldest and most widely used decontamination method against CW agents. PS/DPSA composite nanofibers can physically capture the chemical agents and destruct them. The degradation products of 2-CEES by PS/DPSA nanofibers were identified by GC/MS. Two samples were prepared to investigate the concentration effect of Cl⁺ on decontaminating of 2-CEES. In samples of 1 and 2, ratio of 2-CEES:Cl⁺ were (1:4) and (1:6) respectively, and decontamination yield of both samples studied in 7,

20 minutes. The GC results indicated that 99% of 2-CEES was decomposed by sample 1 in 7 minutes and in other tests 100% of S.M. was decomposed in the given time. Chromatograms of 2-CEES and reaction sample 1 with 2-CEES (after 7 minute) have been showed in Figure 4 and the major decontamination products were summarized in Table 1.

This results showed that ratio of (1:4) from (2-CEES:Cl⁺) in 7 minutes destroyed the 99% of 2-CEES and it concluded the decontamination reaction could be completed by an increase in concentration of Cl⁺ (i.e. decontamination reaction with ratio of (1:6) from (2-CEES:Cl⁺) was completed in 7 minutes) or prolongation of time. Presence of strong electron withdrawing compound, benzene sulfonyl group is expected to release (Cl⁺), thereby facilitating the decontamination reaction. PS/DPSA as a source of Cl⁺ can be oxidized sulfur atom of 2-CEES and therefore convert 2-CEES to nontoxic or less-toxic products.

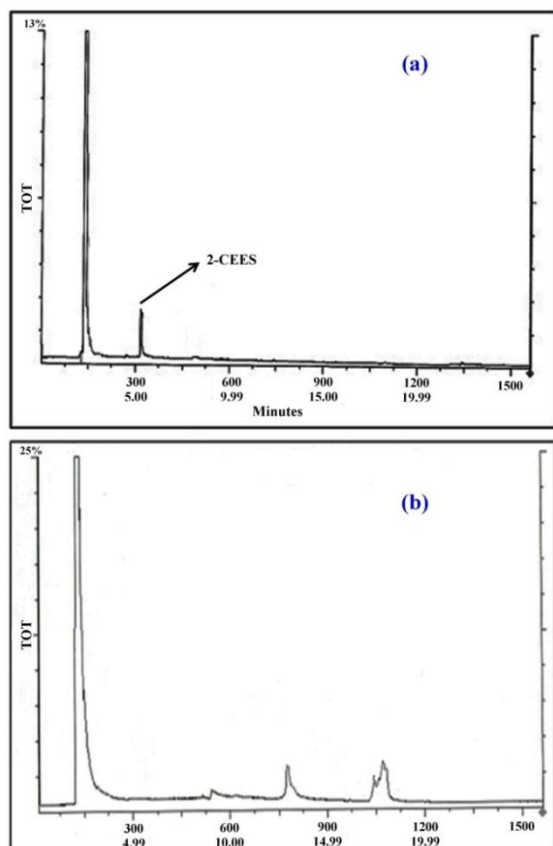


Fig. 4. Chromatograms of (a) 2-CEES and (b) reaction sample 1 with 2-CEES (after 7 minute) in methanol.

Table.1. Results of decontamination reaction of 2-CEES with PS/DPSA composite nanofiber

Sample	Rt(min)	2-CEES:Cl ⁺	Identified product
1	20	1 : 4	Ethyl vinyl sulfone (2-chloroethyl)ethyl sulfone
	7		Ethyl vinyl sulfone (2-chloroethyl)ethyl sulfone (2-chloroethyl)ethyl sulfoxide
2	20	1 : 6	2-chloroethyl)ethyl sulfone Ethyl vinyl sulfone
	7		Ethyl vinyl sulfone (2-chloroethyl)ethyl sulfone

Stability of PS/DPSA composites nanofiber

By measuring active chlorine during the time, the stability of PS/DPSA as a decontaminate agent can be estimated. To investigate the degree of PS/DPSA stability, the amount of active chlorine was measured by utilization of Iodometric titration with respect to time. The amount of active chlorine in PS/DPSA was measured in three different time-tables; the first one was on daily base, for one week the quantity of chlorine was constant. The second measurement was carried-out on weekly base, it was done by for one month and finally the last measurement of chlorine was performed monthly base. The results are shown in Table 2.

Table.2. Results of Stability test of PS/DPSA composites nanofiber

Time (day)	Cl ⁺ %	Time (day)	Cl ⁺ %
1	5.95	28	5.35
2	5.81	60	5.25
3	5.95	90	5.15
4	5.95	120	5.10
5	5.90	150	5.05
6	5.91	180	4.90
7	5.91	-	-
14	5.60	-	-
21	5.46	-	-

As it is observed in Table 2, six months after fabrication of PS/DPSA nanofiber composites small reduction in quantity of active chlorine was observed which claims that the stability of this fiber confronting the temperature and humidity of environment is acceptable.

Regeneration ability of PS/DPSA composites nanofiber

The mechanism proposed by Dubey and et al [19], showed that dichloro amine-T is converted to its related amine by reacting with vesicant agents, considering the DPSA structure resemblance of dichloroamine-T, by addition of sodium hypochlorite, it is expected to recapture Cl and initial compound is regenerated. To conform with the above claim, an experimental procedure has been defined, 0.2 g of DPSA nanofiber was treated with 8 μ L of 2-CEES simulant agent in 1 mL of methanol as solvent, then potassium iodide solution was added to eliminate the active chlorine which isn't participated in reaction. Chlorination reaction was carried-out on nanofiber and Iodometric test was performed on regenerable fiber. The recycling between chlorine and amine were repeated three times and the results are summarized on Table 3.

Table.3. Results of regeneration ability test of PS/DPSA composites nanofiber

Sample	Primary compound	Recycling (1)	Recycling (2)	Recycling (3)
percentage of active chlorine	5.60%	6.73%	6.91%	6.89%
Percentage of active chlorine to Primary compound	-	120.2%	102.7%	99.7%

Due to formation of nanofiber, those NH_2 functional groups that did not react with sodium hypochlorite in DPSA synthesis stage, their numbers has been increased over the surface of nanofiber, it may explain the unusual chlorination of nanofiber (above 100% in Table 3). The

presence of additional NH_2 functional group is observed in FT-IR spectra of final product (Figure 2e). We conclude that after participation of PS/DPSA in decontamination reaction, due to its re-treatment by sodium hypochlorite, PS/DPSA nanofiber can regain its active chlorine, and it can be also concluded the nanofiber is recyclable.

CONCLUSION

In this study we produced PS/DPSA electrospun nanofibers with the goal to convert the 2-CEES to nontoxic or less-toxic products. PS/DPSA nanofiber ability was destroyed 2-CEES, after 7 minutes. GC and GC/MS analysis have been provided valuable information about the efficient decontamination of PS/DPSA electrospun nanofibers on 2-CEES. These results demonstrate the potential of using PS/DPSA nanofibers as a unique decontamination agent and protective clothing against blistering agents.

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