N,N-Dichloro Poly(styrene-*co*-divinyl benzene) Sulfonamide Polymeric Beads: An Efficient and Recyclable Decontaminating Reagent for *O,S*-Diethyl Methyl Phosphonothiolate, a Simulant of VX

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ABSTRACT: An efficient and operationally simple method is developed for chemical decontamination of simulant of VX. A new chlorine bearing reagent *N,N*-dichloro poly(styrene-*co*-divinyl benzene) sulfonamide was developed to deactivate the simulant of VX in aqueous medium. This decontamination reaction was monitored by gas chromatography (GC), and the products were analyzed by gas chromatography-mass spectrometry (GC-MS). This reagent has advantage over earlier reported reagents in terms of effectiveness, stability, nontoxicity, cost, ease of synthesis, recyclablity (collected after filtration, rechlorinated, and used for further reaction), and decontamination of simulant of VX to give single nontoxic product at room temperature. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2250–2256, 2011

Key words: *O,S*-diethyl methyl phosphonothiolate; *N,N*-dichloro poly(styrene-*co*-divinyl benzene) sulfonamide; decontamination; active chlorine; GC–MS

INTRODUCTION

Organophosphorus compounds (OPCs) have been widely used in the industries, veterinary and human medicines,[1] in the agriculture as pesticides, or can be misused for military purpose as chemical warfare agents (CWAs).[2] There are various intoxications reported in the past because of their broad use over the world.[3,4] The number of intoxications with OP pesticides is estimated at some 3 millions per year resulting in 300,000s deaths and causalities.[5]

Highly toxic OPCs that are nerve agents such as sarin, soman, tabun, cyclosarin, and VX are lethal CWAs, which were developed during and after World War-II.[6] They were selected for their extreme and acute mammalian toxicity via inhalation or skin penetration and for a variety of technological and military tactical reasons.[7] Despite the continued world wide efforts to prevent synthesis, storage, and use of these compounds, the repeated use of nerve agents during military conflicts[2] and terrorist attacks[8,9] displays that they constitute a major threat for the civilization. The intoxication with nerve agents leads to inhibition of activity of enzyme acetylcholinesterase by phosphorylation of its active site serine residue.[10] The subsequent accumulation of the neurotransmitter acetylcholine and over-stimulation of cholinergic receptors result in a generalized cholinergic crisis including breakdown of the neuromuscular function.[11] VX, a sulfur containing organophosphate is the most toxic[12] CWA among nerve agents.

The decontamination of CWAs[13–16] from structure, environment, media, and even personal has become an area of particular interest in recent years because of increased homeland security concern. In addition to terrorist attacks scenario such as accidental releases of CWA or from historic, buried, munitions are also subjects from response planning. VX is one of the most difficult CWA to destroy. In general, the decontamination of VX can be achieved either by hydrolysis or by oxidation. However, hydrolysis of VX leads to toxic hydrolyzed products. Therefore, decontamination of VX by oxidation is the preferred method. VX contain bivalent sulfur atoms that can be readily oxidized . Further oxidation reaction is relatively faster than hydrolysis. In the past, VX was generally decontaminated by using chlorine based decontaminants, NaY and AgY zeolites, alumina-supported fluoride reagents, nanosize CaO, Catalytic methods, *N*-chloroamide, vaporized hydrogen peroxide, peroxybenzoic acid, *o*-iodosylbenzoic acid complex, peroxymonopersulphate in oxone, magnesium monoperoxy phthalate, and mildly basic solution.[17–26]

A macroporous poly(styrene-*co*-divinylbenzene)[27] (PS-DVB) resin having *N,N*-dichloro sulfonamide groups have been used as a polymer supported

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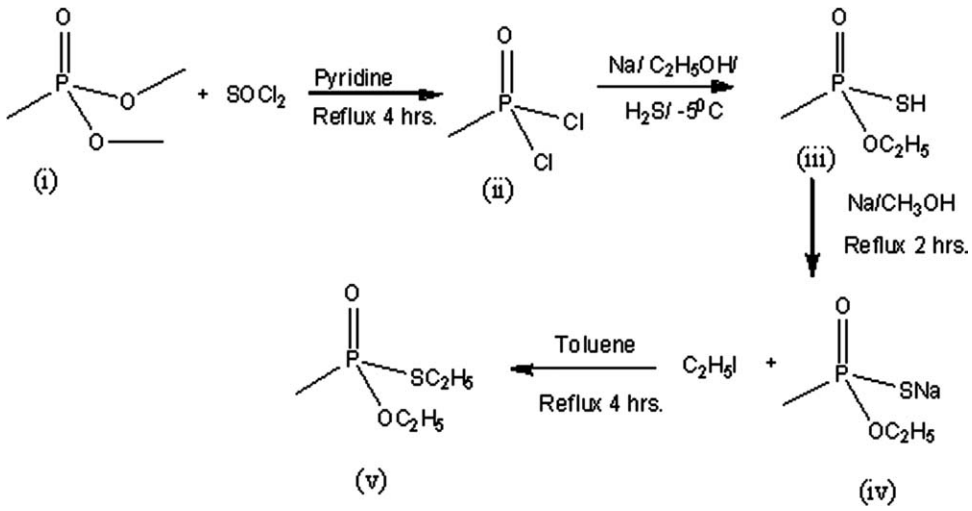


Scheme 1 Synthesis of O,S-diethyl methyl phosphonothioate (OSDEMP) (v).

reagent for chlorination, oxidation for residual sulfides,[28] cyanides,[29] thiocyanates,[30] water disinfection,[31] and some application in synthetic organic chemistry.[32] Although a variety of decontaminating agents have been reported over the years, however, most of them suffer from drawbacks such as the use of hazardous solvents and prolonged decontamination time. Further, these reagents can not be used on skin because of the toxicity of solvent and reagents. Our aim in this work is to overcome the limitation and drawbacks of the reported decontaminants.

In recent years, the use of recyclable reagents[32,33] has received considerable interest in organic synthesis due to stringent environmental rules. This prompted us to explore the possibility of using a stable, nontoxic, recyclable, easy to synthesize, cheap, and efficient positive chlorine releasing reagent *N,N*-dichloro poly(styrene-*co*-divinyl benzene) sulfonamide.

We have already reported *N,N*-dichloro poly(styrene-*co*-divinyl benzene) sulfonamide polymeric beads[34] for decontamination of simulant of sulfur masturd, another class of chemical warfare agent. We investigated its use as an alternative reagent for decontamination of simulant of VX at room temperature. To gain more complete understanding of agent chemistry, a simulant of VX, *O,S*-diethyl methyl phosphonothiolate (OSDEMP) was synthesized initially for decontamination study. The most common and widely used process is the oxidation of VX using *N*-chloro compounds, which decontaminates it with the formation of nontoxic product.

EXPERIMENTAL

Materials

Sulfonated PS-DVB was purchased from Ion Exchange India Limited, Mumbai, India. Thionyl chloride, acetone, methanol, ethanol, pyridine, ethyl iodide, sodium, toluene, NH_3, and acetic acid of AR grade were purchased from S.D. Fine-Chem, India. NaOCl was prepared by passing chlorine gas at flow of 1 g/min in NaOH solution (15%, 100 mL) for 30 min. at 5°C. Dimethyl methyl phosphonate (DMMP) was prepared in-house.

Synthesis of OSDEMP

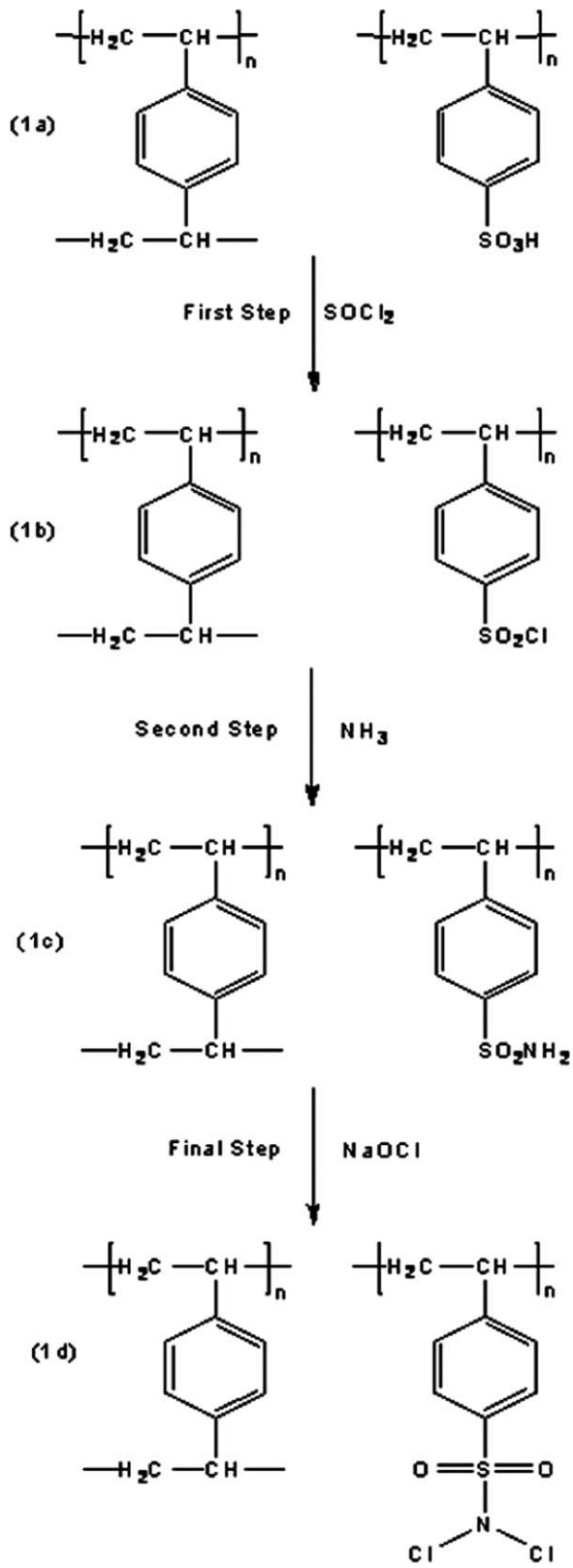
The synthesis of *O,S*-diethylmethyl phosphonothioate, was achieved in four steps (Scheme 1) starting from DMMP. The purity was checked by GC and GC–MS, and the structure was confirmed by fourier transform-infrared (FT-IR) spectroscopy, H^1 NMR and P^{31} NMR, and mass spectrometry.

Preparation of methyl phosphonic dichloride (ii)

DMMP (**a**), 7.0 g (0.056 mol) was taken in a 50-mL, two-neck round-bottom-flask equipped with a condenser, calcium chloride guard tube, and magnetic stirrer. To this, thionyl chloride 20.0 g(0.17 mol) was added drop wise over a period of 30 min at room temperature with stirring. After the complete addition of thionyl chloride, pyridine (0.5 mL) was added. It was then refluxed for 4 h in an oil bath with stirring. Excess thionyl chloride was then removed by distillation. The product, methyl phosphonic dichloride was then distilled at 153–161°C at atmospheric pressure. Yield: 6.5 g (86.6%).

Preparation of ethyl methyl phosphonothioic acid (iii)

Dry ethanol 100 mL was taken in a 250-mL three necks round-bottom-flask equipped with a condenser, pressure equalizing dropping funnel, calcium chloride guard tube, and magnetic stirrer. To this, sodium metal 3.1 g (0.135 mol) was added in small pieces and dissolved at room temperature. The reaction mixture was then cooled to 0–5°C under ice-salt bath. Dry H_2S was



Scheme 2 Synthesis of N,N-dichloro poly(styrene-co-divinylbenzene) sulfonamide (1a–1d).

then passed to the reaction mixture until it was saturated. Methyl phosphonic dichloride 6.0 g (0.0045 mol) was then added drop wise over a period of 3 h at −5°C with stirring. The ice bath was then removed and the reaction mixture was stirred at room temperature followed by reflux for 4 h. Excess ethanol was distilled off; the crude product was dissolved in minimum amountof water and extracted with diethyl ether. Diethyl ether layer was discarded and aqueous layer was acidified by concentrated hydrochloric acid to pH ~ 2. It was then extracted with diethyl ether repeatedly. The ether layer was dried over anhydrous magnesium sulphate and solvent removed by distillation. The residue, ethyl methyl phosphonothioic acid was distilled under vacuum. Yield: 4.7 g (74.5%), B.P.: 92°C at 1.0 mmHg

Preparation of ethyl methyl sodiumphosphonothioate (iv)

Dry methanol 7 mL was taken in a 25-mL two-neck round-bottom-flask equipped with a condensor, calcium chloride guard tube, and magnetic stirrer. Sodium metal 0.2 g (0.0086 mol) was dissolved in it at room temperature with stirring. To this was added ethyl methyl phosphonothioic acid 1.27 g (0.01 mol) slowly over a period of 30 min. It was then refluxed for 2 h. Excess methanol was then removed by distillation followed by washing with toluene to give the desired product sodium ethyl methyl phosphonothioate (iv). Yield: 1.2 g (81.7%).

Preparation of OSDEMP (v)

Ethyl methyl sodiumphosphonothioate 1.2 g (0.0074 mol) was taken in toluene (8.0 mL) in a 25-mL two-neck round-bottom-flask. To this was added ethyl iodide 2.5 g (0.016 mol) drop wise over a period of 10 min. The reaction mixture was then refluxed for 4 h. It was then cooled to room temperature and filtered to remove the sodium iodide salt. Washed with dry hexane. The filtrate was distilled off to remove the solvent and the residue distilled under vacuum to give the final product OSDEMP (v). Yield: 1.12 g (90%), B.P.: 51°C at 0.5 mmHg.

Characterization of OSDEMP is as given:

IR: (KBr, cm^{-1}) 3478 (m), 2981 (vs), 1774 (vs), 1449 (m), 1301 (s), 1267 (m), 1223 (vs), 64 (m), 1033 (vs), 957 (s), 883(s), 779 (m) 741 (m), 650 (vw), 531(s).

^{1}H NMR ($CDCl_3$/TMS 400 MHz): δ ppm; 1.3–1.4(m, 6H), 1.8 (d, 3H), 2.8–2.9 (m, 2H), 4.1–4.2(m, 2H).

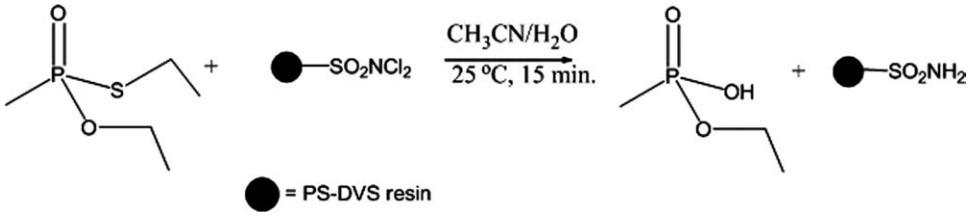
^{31}P NMR ($CDCl_3/Ph_3PO_4$ 400 MHz): δ ppm; 53.79

Mass: *m/z*: 168 (M^+), 140 (M-18), 124 (140-14), 108 (140-32), 95 (124-29), 79(108-29), 65 (79-14), 47 (65-18).

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

Chloro sulfonation of PS-DVB

Sulfonated PS-DVB (10 g) was mixed with 100 mL of $SOCl_2$ and refluxed for 4–6 h. $SOCl_2$ was distilled



Scheme 3 Decontamination of OSDEMP with polymeric Beads in aqueous medium.

off after completion of the reaction. The chloro sulfonated PS-DVB was washed with methanol (Scheme 2).

PS-DVB sulfonamides

Chloro sulfonated PS-DVB (10 g) was refluxed with aqueous concentrated ammonia (150 mL) for 4–6 h. The sulfonated form of the beads was then filtered, washed with water and finally dried in air.

Conversion of sulfonamide into chloro sulfonamide

This final conversion was easily achieved by stirring PS-DVB sulfonamide (10 g) in 150 mL of freshly prepared sodium hypochlorite solution in acidic medium using acetic acid (99.5%) for 2–4 h at 5°C, filtered, and dried in air. The positive chlorine content of this polymer checked by standard iodometric titration[35] was found to be 5.8%.

Characterization

Infrared (IR) spectra were recorded as KBr pellets on a Perkin-Elmer BX-2 FT-IR spectrophotometer. ^{1}H NMR and ^{31}P NMR were recorded by BRUKAR AVANCE 400 MHz instrument. The GC–MS analyses were performed in electron ionization mode (70 eV) with an Agilent 6890 GC, equipped with model 5975C mass selective detector (Agilent Technologies, San Jose, CA). Separation was carried out on an HP-5 MS column, 30 m × 0.25 mm internal diameter, 0.25 μm film thickness, together with a 2-m precolumn (Agilent Technologies). Splitless injections of 1 min were performed. The temperature program used with CH_2N_2 derivatisation was: 50°C, held for 2 min, ramped at 10°C min^{-1} to 250°C and held for 5 min. The carrier gas was helium at a flow rate of 35 cm s^{-1}. The split/splitless injector was maintained at 25°C, whereas the transfer line was maintained at 280°C. All analyses were performed in GC–MS full scan mode over the range of m/z 40–550 at a scan rate of 1.49 scans s^{-1}. The MS source and quadruple were maintained at 230°C and 150°C, respectively.

Thermal stability of commercial sulphonate cation-exchange resins (1a), corresponding sulphonyl chloride (1b), sulphonamide resins (1c), and macromolecular dichloroamine (1d) was studied by TA instrument Waters, TGA 2950 at a heating rate of 10°C min^{-1} using nitrogen.

Reaction of OSDEMP and *N,N*-dichloro poly(styrene-*co*-divinyl benzene) sulfonamide beads

A test-tube containing OSDEMP (0.1 mmol) in 3 mL CH_3CN:H_2O (5 : 1) was added *N,N*-dichloro poly (styrene-*co*-divinyl benzene) sulfonamide (0.8 mmol of active chlorine)[35] and the mixture allowed to stir at room temperature (Scheme 3). Aliquots were taken at different time interval (~ 1 h). To this, a solution of diazomethane in diethyl ether was added slowly at 5°C for methylation of decontaminated products (e.g., phosphonic acids) of OSDEMP. The solvent was then evaporated by purging dry nitrogen to the mixture and dried under anhydrous Na_2SO_4. The organic phase was analyzed for the residual OSDEMP and degradation products were identified as their corresponding methyl ester derivatives by GC and GC–MS analysis. After complete removal of active chlorine in decontamination reaction, the *N,N*-dichloro poly(styrene-*co*-divinyl benzene) sulfonamide converts into corresponding poly(styrene-*co*-divinyl benzene) sulfonamide beads.

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

Polymers	10% Loss temperature (0°C)	20% Loss temperature (0°C)	50% loss temp (0°C)	Final decomposition temperature (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

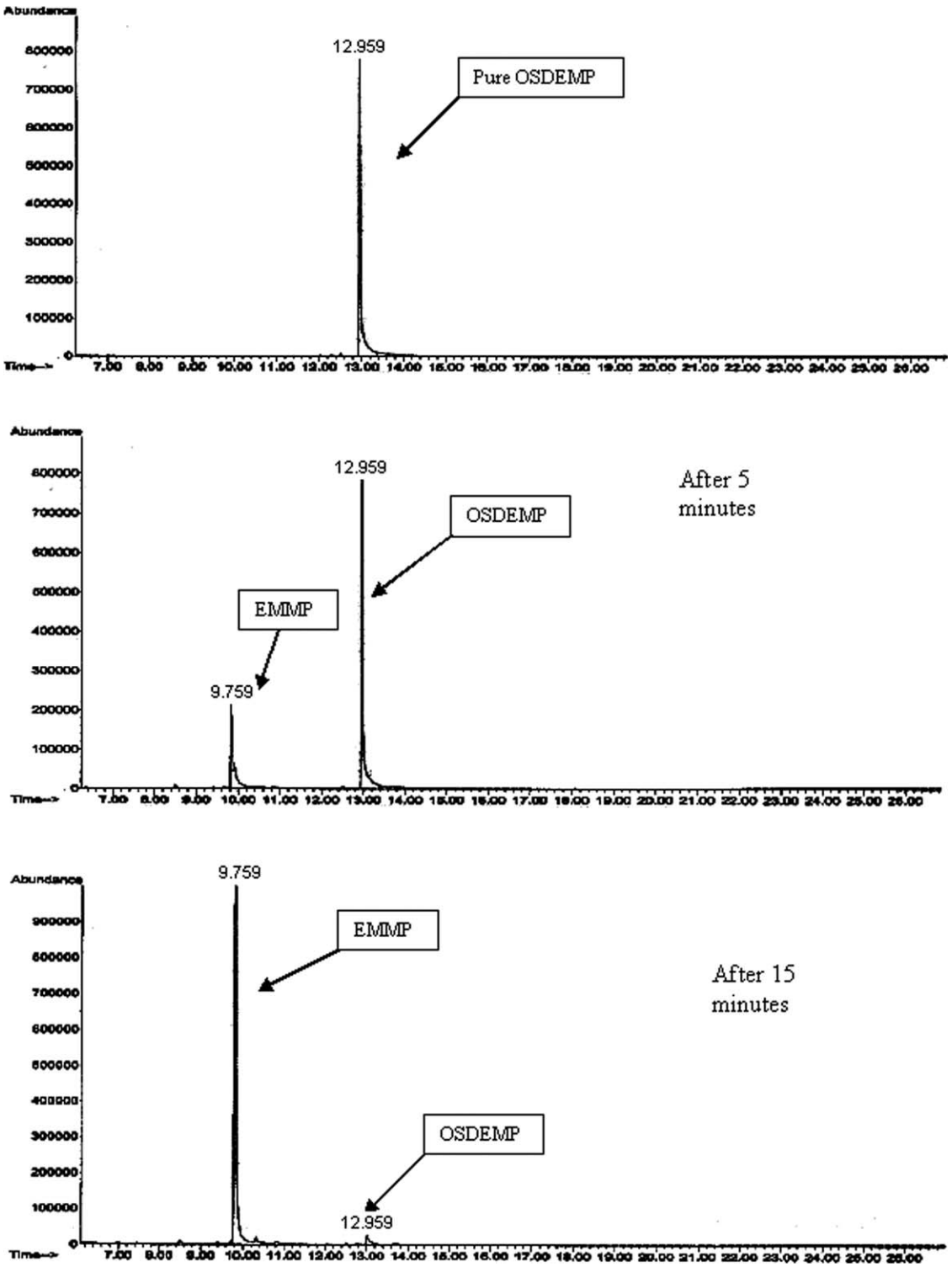


Figure 1 Progress of a decontamination reaction as monitored by GCMS analysis at different time intervals.

RESULT AND DISCUSSION

TGA studies were carried out to characterize each step of synthesis of polymers (1a–1d). TGA overlay thermogram of polymers (1a–1d) showed multistep mass loss in all resins (1a–1d). In starting sulphonated- PS-DVB, the mass loss upto 200°C was because of physically bound water and mass loss in the range of 200–300°C may be attributed to decomposition of sulfonic acid groups. The complete breakdown of polymer backbone takes place at 500°C. Thermal stability after substitution in SO_3-PS-DVB was found to be increase in polymers (1b–1d) and 50% decomposition in sulfonyl chloride of PS-DVB was found at 500°C and at 700°C residue

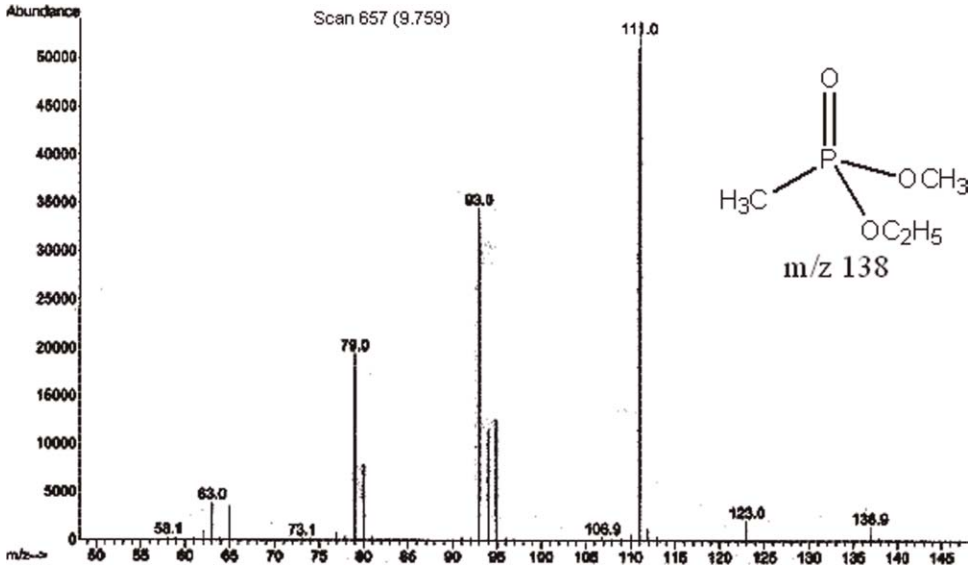


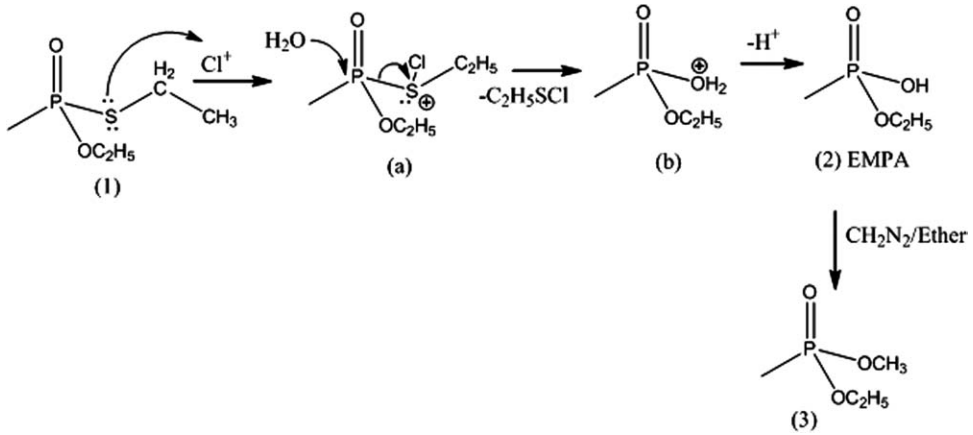
Figure 2 GC–MS data of derivatized (EMMP) decontaminated product of OSDEMP.

left was found 35.5%. Weight loss of 10% in polystyrene sulfonamide was found at 205°C, which clearly indicate increase in the thermal stability. Weight loss of 10% in *N,N*-dichloro poly(styrene-*co*-divinylbenzene) sulphonamide was found at 298°C and at 700°C residue left was found 15.32% and results are given in the Table I.

In the FT-IR Spectra of *N,N*-dichloro poly(styrene-*co*-divinylbenzene) sulphonamide, absorption bands were observed at 2931 cm^{-1} due to C—H. The other bands were observed at 1406 and 1159 cm^{-1} because of stretching of SO_2 and 675 cm^{-1} due to N—Cl bond.

Oxidative chlorination is the oldest and most widely used decontamination methods for CWAs. The term oxidative chlorination includes the active chlorine containing reagents like hypochlorite, which under certain conditions generate positively charged chlorine, which is an oxidizing species. VX is the most toxic CW agents, and therefore handling of this agent is extremely hazardous. Hydrolysis of VX is very slow and leads to toxic hydrolyzed products. Therefore, decontamination of VX by oxidation is the preferred method. VX contain bivalent sulfur atoms containing lone pair of electrons that can be readily oxidized. For the standardization of the chemical reactions, simulants of VX may be used. The simulant OSDEMP was prepared by four steps and structure of OSDEMP was confirmed by FT-IR, ^{1}H NMR, ^{31}P NMR, and GC–MS, and purity was checked by GC and found >98.8%. *N,N*-Dichloro poly(styrene-*co*-divinyl benzene) sulfonamide, a new class of readily available, economical, commercially viable, and recyclable reagent was chosen for use as a decontaminating agent in this study. Decontamination studies of OSDEMP were carried out at room temperature in aqueous medium using a mixture of acetonitrile and water (5 : 1). Decontaminated product was separated by GC and identified by GC–MS in EI mode.

OSDEMP was decontaminated 100% with *N,N*-dichloro poly(styrene-*co*-divinyl benzene) sulfonamide.



Scheme 4 Mechanism of decontamination of OSDEMP via P—S cleavage.

The decontaminated product was analyzed as their methyl ester derivatives by reacting with freshly prepared diazomethane in ether. Decontaminated product was identified by GC–MS and results are given in Figures 1 and 2. The organic layer did not show any peak corresponding to OSDEMP indicating the reaction of *N*,*N*-dichloro poly(styrene-*co*-divinyl benzene) sulfonamide with OSDEMP. The degradation of OSDEMP with *N*,*N*-dichloro poly(styrene-*co*-divinyl benzene) sulfonamide followed by P—S bond cleavage via oxidation and hydrolysis leading to the formation of nontoxic product ethyl methylphosphonate (EMPA) (**2**). The decontamination proceeded as per the mechanism given in Scheme 4.

The formation of product EMPA (**2**) proceeded with the oxidation of the sulfur and the subsequent cleavage of the P—S bond of OSDEMP, which contain oxidizable bivalent sulfur atom containing lone pair of electrons. Electrophilic attack of positive chlorine on sulfur atom gives intermediate **a**, followed by nucleophilic attack of water on phosphorus atom resulting in the cleavage of P—S bond to eliminate the C_2H_5SCl (which is highly volatile and easily escape the reaction mixture) to give intermediate **b** from which a proton is eliminated to give EMPA (**2**). The formation of (**2**) is identified by its corresponding methyl ester, i.e., ethyl methyl methylphosphonate (EMMP; **3**;*m*/*z* 138).

When all of the OSDEMP has been consumed (Fig. 1), the reaction was decanted and the beads were washed with a little water followed by chloroform. After removing the solvent by distillation, the consumed polymeric reagent from the oxidation or halogenations can be regenerated in a single step without the loss of activity, by simply suspending the consumed polymeric reagent in hypochlorite solution. The PS-DVB beads were recovered and rechlorinated using the reported method. These beads could be reused for decontamination of OSDEMP.

CONCLUSION

In conclusion, the study reveals that *N*,*N*-dichloro poly(styrene-*co*-divinyl benzene) sulfonamide works as an excellent decontaminating agent against OSDEMP, which bears oxidizable bivalent sulfur by its oxidation followed by hydrolysis to nontoxic product EMMP in aqueous medium at room temperature. This reagent has advantage over earlier reported reagent in terms of effectiveness, stable, nontoxic, cheap, easy to synthesize, recyclablity (collected after filtration, rechlorinated, and used for further reaction), and decontamination of simulant of VX to give nontoxic product at room temperature.

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