Polymeric Decontaminant 2 (*N,N*-Dichloropolystyrene Sulfonamide): Synthesis, Characterization, and Efficacy Against Simulant of Sulfur Mustard

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ABSTRACT: A polymeric decontaminant *N,N*-dichloropolystyrene sulfonamide was synthesized by different steps from starting material polystyrene and followed by sulfonation, chlorosulfonation, and amidification. Halogeno-sulfonamide was obtained by treatment of sodium hypochlorite with sulfonamide resin. It was characterized by FTIR, solubility, viscosity, DSC, and TGA techniques. Efficiency of this polymer as decontaminant was evaluated by reaction with 2-chloro ethyl phenyl sulfide, a simulant of sulfur mustard (SM) at room temperature. This decontamination reaction was monitored by gas chromatography (GC) and products were identified by gas chromatography-mass spectrometry (GC-MS). The positive chlorine content of this polymer was checked by standard iodometry titration. The synthesized positive chlorine compound is observed to be a promising decontaminant against simulant of sulfur mustard, chiefly in the situation where use of aqueous medium such as acetonitrile : water (2 : 1) is precluded. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 4109–4115, 2008

Key words: *N,N*-dichloro polystyrene sulfonamide; 2-chloro ethyl phenyl sulfide; sulfur mustard; decontamination and positive chlorine compound

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INTRODUCTION

Sulfur mustard (SM) is highly toxic and persistent blistering agents. It is one of the oldest and most important chemical warfare agents, being a cytotoxic alkylating agent.[1] 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 reached up to the practical utility. The most common and widely used process is the oxidation[2] of SM using organic chloramines[3–5] which is rapid enough to decontaminate it instantly. Oxidation reactions remove the lone pairs on sulfur making the molecules no more reactive to biological system. Various oxidizing agents have been used for this decontamination reaction, including hypochlorite,[6] peracids of the oxone type,[7] oxaziridines,[8] peroxides,[9] or magnesium monoperoxyphthalate (MMPP).[10] With regard to the chemical decontamination of a potent toxic compound like SM, it is necessary to know the nature of the products arising from such decontamination reaction for obvious reasons.[11]

Polymers have been functionalized to incorporate functional groups of many types.[12,13] Many useful procedures for the oxidation of alcohols to the corresponding carbonyl compounds using polymer supported reagents have been reported.[14,15] Our interest in polymer-supported reactions[16] and synthesis of polymeric analogues of well known halogeno-sulfonamides and their applications have been reported.[17] A macro porous poly(styrene-*co*-divinylbenzene) resin having *N,N*-dichloro sulfonamide groups[18–20] have been used as a polymer supported reagent for chlorination, oxidation for residual sulfides,[21] cyanides,[22] thiocyanates,[23] water disinfection,[18]and some application in synthetic organic chemistry.[24]

We have already reported *N,N*-dichloro poly (styrene-*co*-divinylbenzene) sulfonamide as a polymeric decontaminant[25] for simulant of sulfur mustard but this polymer have two disadvantages, first it is insoluble in almost all solvents and secondly, it showed prolonged decontamination time. Synthesis of soluble polymeric decontaminant have not been reported. For decontamination formulations soluble polymer gives better and efficient response. We have

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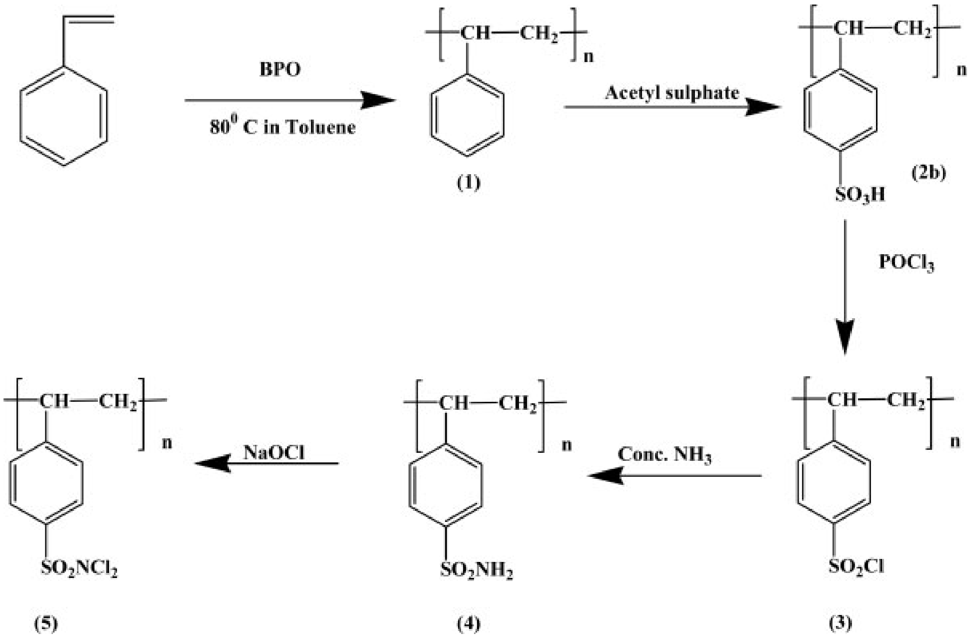


Figure 1 Synthesis of *N*,*N*-dichloropolystyrene sulfonamide.

synthesized soluble *N*,*N*-dichloro polystyrene sulfonamide for the decontamination of 2-chloro ethyl phenyl sulfide as a simulant of SM as a decontaminating agent at room temperature.

Keeping in view the requirement for large quantity of polymeric decontaminant, an easy and commercially viable synthetic procedure for *N*,*N*-dichloro polystyrene sulfonamide was reported. Starting from commercial styrene via polystyrene, sulfonation, sulfonyl chloride, sulfonamide resins, and a macromolecular dichroamine was prepared. We are therefore reporting here synthesis, characterization, and the reaction profile of polymeric chloramines with 2-chloro ethyl phenyl sulfide as a simulant of SM as a decontaminating agent in aqueous as well as nonaqueous medium at room temperature.

EXPERIMENTAL

Synthesis of *N*,*N*-dichloropolystyrene sulfonamide

The polymer was synthesized by different steps and given in the Figure 1.

a. Polystyrene (PS)(1): Styrene (20 g, inhibitor free) in a 150 mL dry toluene was placed in a three-neck round-bottomed flask fitted with condenser and droping funnel and then added benzoyl peroxide (150 mg) as initiator at 80°C and then reaction mixture was refluxed in an oil bath at 110–120°C for 4–6 h under nitrogen medium. After completing the reaction volume of toluene was reduced by using rotatory evaporator.
b. Synthesis of Sulfonated polystyrene (HSO_3-PS) (2a–c): Sulfonated polystyrene was prepared with three types of sulfonating agents such as acetyl sulfate, chloro sulfonic acid, and conc. H_2S0_4. Reaction condition with each type of sulfonating agents are in follows:
    1. Sulfonation by using chlorosulfonicacid (2a): In this method, 10 g of PS was dissolved in 100 mL of chloroform. A 5% (v/v) solution of chlorosulfonic acid in 100 mL of chloroform was added drop wise over a period of 20 min then mixture was allowed for stirring vigorously at 25°C under N_2 atmosphere.
    2. Sulfonation by Acetyl Sulfate (2b): PS (10 g) was dissolved in 1,2-dichloro ethane in a three-neck round-bottomed flask equipped with mechanical stirring, thermometer and droping funnel. The flask containing the solution was heated to 40°C in order to obtain total solubilization of PS and purged with N_2 for 30 min. A freshly prepared acetyl sulfate solution (by mixing 15.3 mL of acetic anhydride with 5.6 mL of sulfuric acid in 79 mL 1,2-dichloroethane) was added using the dropping funnel. The reaction mixture was maintained at 40°C under stirring for 2 h. The solution became clear yellow after adding an excess of 2-propanol in 30 min. Finally, the sulfonated polymer was isolated. Polymer (2b) was processed further due to high degree of sulfonation and high yield.
    3. Sulfonation by using conc. H_2SO_4 (2c): In this method, 10 g of PS was dissolved in 100 mL

TABLE I
Characterization of Polymers 1–5

Polymers	Reagent used	Nature of polymer	Yield (%)	Viscosity (Inh) dL/g in DMF, 35°C
PS (1)	Styrene + benzoylperoxide	Solid white powder	92	0.28
SO_3-PS (2a)	Polystyrene + chlorosulfonic acid	Solid, light brown tacky crumbs	62	0.33
SO_3-PS (2b)	Polystyrene + acetyl sulfate	Solid, brown, stiff, nontacky	84	0.61
SO_3-PS (2c)	Polystyrene + conc. H_2SO_4	Viscous, black solid	64	0.57
$ClSO_2$-PS (3)	SO_3-PS +$POCl_3$	Solid, black powder, nontacky	78	0.64
H_2NSO_2-PS (4)	$ClSO_2$-PS + conc. NH_3	Solid, yellow crumbs, nontacky	88	0.67
Cl_2NSO_2-PS (5)	NH_2SO_2-PS + sodium hypochlorite	Solid, pale yellow, crumbs, nontacky	86	0.70

of chloroform and 55 mL of conc. H_2SO_4 was added drop wise to the solution at 50°C with continuous stirring for 2 h. After completing the reaction sulfonated the dark brown PS was allowed to dry in air for 24 h at room temperature.

c. Chloro sulfonation of PS (3): Sulfonated PS (10 g) was mixed with 100 mL of $POCl_3$ and refluxed for 4–6 h. $POCl_3$ was distilled off after completion of the reaction. The chloro sulfonated PS was washed with methanol.
d. Polystyrene sulfonamides (4): Chloro sulfonated PS (10 g) was refluxed with aqueous conc. ammonia (150 mL) for 4–6 h.
e. Conversion of sulfonamide into halogeno sulfonamide (5): This final conversion was easily achieved by stirring polystyrene sulfonamide (10 g) in 150 mL of freshly prepared sodium hypochlorite solution in acidic medium using acetic acid for 2–4 h at 5°C temperature and filtering and drying in air. The positive chlorine content of this polymer was checked by standard iodometry titration[26] was found to be 8.7%.

Material and characterization

Styrene was purchased from Aldrich. Chloroform, 1,2 dichloromethane, acetic anhydride, sulfuric acid, Chlorosulfonic acid, $POCl_3$, and ammonia of AR grades were purchased from S. D. Fine Chem., Mumbai, India. Infrared (IR) spectra were recorded on a Perkin–Elmer 1720X FTIR Spectrophotometer. TA TGA 2950 and DSC 2920 instruments were used for thermal analysis. Thermal stability of polystyrene, sulfonated polystyrene, Cl-SO_2-PS, polystyrene sulfonamide, and *N*,*N*-dichloro polystyrene sulfonamide was studied at a heating rate of 10°C/min using nitrogen. Mass spectra were recorded on Agilent 5973 mass spectrometer coupled with GC and mass selective detector. GC/MS analysis was performed in EI mode in order to identify the decontaminated products. Chemito GC 1000 coupled with FPD sulfur mode detector was used for monitored decontamination reaction. 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. Gel permeation chromatography was obtained with a Waters instrument. Tetrahydrofuran (THF) was used as an eluent; a Styragel HR-4 (WAT044226) column (the column temperature was maintained at 100°C) was employed. The molecular weight and polydispersity are reported versus monodisperse polystyrene standards.

Reaction of 2-chloro ethyl phenyl sulfide (2) and *N,N* dichloropolystyrene sulfanamide (1)

Stirred solution of 0.01 mol 2-chloro ethyl phenyl sulfide in acetonitrile: water (2 : 1) was added to 0.05 mol *N*,*N*-dichloro polystyrenesulfonamide (M_w 34,210). Aliquots were taken at different time intervals (upto 24 h) and extracted with dichloromethane for analysis. The organic phase was analyzed for the residual 2-chloro ethyl phenyl sulfide 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 nonaqueous medium and aqueous medium.

RESULTS AND DISCUSSION

Polystyrene was synthesized by free radical polymerization of styrene by using benzoyl peroxide as initiator The PS exhibited weight-average molecular weights of up to 26,727, which depended on the exact repeating unit structure. Sulfonated polystyrene (2a–2c) was prepared by using three type of sulfonating agents such as chlorosulfonic acid (2a), acetyl sulfate (2b), and conc. sulfuric acid (2c) as per reported methods.[27–29] Polymeric decontaminant was characterized by various techniques such as FTIR, TGA, and DSC, viscosity determination, solubility behavior, and sorption study. In the FTIR Spectra of polystyrene was showed sharp peaks at 700 and 780 cm^{-1} due to C—H out of plane deformation

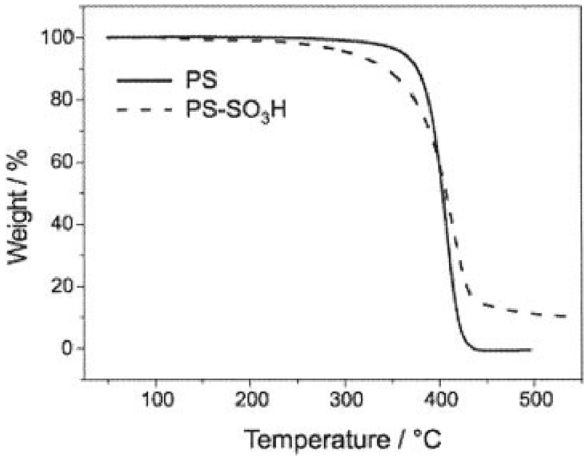


Figure 2 TGA curve of PS and PS-SO$_3$H.

which represents mono substitution. Other peaks were observed at 1160 and 1340 cm^{-1} which represent C—C and C—H bond, respectively. The disappearance of these peaks after sulfonation followed by the occurrence of a new peak at 520cm^{-1} representing para substitution is indicative of the attachment of sulfonic acid groups. Other peaks were observed at 2925 and 3000 cm^{-1} which represent C—C and C—H bond, respectively. Sulfonated polystyrene samples, absorption bands were observed around 3440, 1350, 1060, and 695 cm^{-1}. The broad band at 3440 cm^{-1} is assigned to O—H stretch in —SO$_3$H as well as to absorbed moisture. The other bands are due to various sulfur-oxygen vibration; asymmetric (1350 cm^{-1}) and symmetric O=S=O (1060 cm^{-1}), S—O stretch (695 cm^{-1}). In sulfonyl chloride polystyrene —OH absorption band was disappeared and new band was observed at 736 cm^{-1} due to C—Cl stretching band. The FTIR spectra of resins (4) 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 (—SO$_2$) cm^{-1}, and 822 (N—Cl) cm^{-1}. Viscosity was found in the range of 0.28–0.70 dL/g in DMF and results were shown in Table I. Table I shows the equilibrium percentage of methanol in the polystyrene and sulfonated polystyrene. The sulfonation level of PS-SO$_3$H samples was determined by titration with a standard 0.01 mol L^{-1} NaOH solution in methanol as per reported standard methods.[28] The sulfonation value obtained was high and is in the range of 23.0–27.8% indicating the presence of hydrophilic sites within the hydrophobic matrix. Sulfonation increases viscosity, hygroscopicity, and uptake of organic vapors.

The solubility behavior of all polymers was qualitatively tested in some of typical organic solvents. Starting polymer polystyrene (1) was soluble in acetone, acetonitrile, chloroform, toluene, and aprotic solvents such as NMP, DMAc, DMF, and DMSO and sulfonated polystyrene (2a–2c) was also soluble in water also. All other polymers (2–5) showed excellent solubility in aprotic dipolar solvents, such as NMP, DMAc, DMF, and DMSO. All the polymers were solids and yield of all the polymers (1–5) were found in the range of 62–92% and results shown in the Table I.

Thermal stability of PS and PS-SO$_3$H was studied under nitrogen atmosphere by TGA. This analysis shows (Fig. 2) that a decrease in thermal stability occurs for sulfonated polystyrene as a function of sulfonic groups concentration, as compared to PS. Pure PS shows a weight loss process with its onset at ~ 350°C. Sulfonated polystyrene shows weight loss starting at 200°C and results of thermal stability of other polymer (3–5) by TGA were given in the Table II.

The DSC curves for PS and PS-SO$_3$H are shown in Figure 3. The glass transition temperatures of PS-SO$_3$H are shifted to higher temperature, as compared to pure PS (100–140°C) due to the increase of structural rigidity of the materials as a function of the increase of the amount of sulfonic groups.

The first decontaminant used were bleaching powders and to a lesser extent potassium Permanganate.[7] The reactions of chemical warfare (CW) 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 to using bleaches as a decontaminant.

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

TABLE II
Thermal Stability of Polymers (1–5) by TGA

Polymers	10% loss temp (°C)	20% loss temp (°C)	50% loss temp (°C)	Final decomposition temp (°C)	Residue (%)
PS (1)	359	375	394	443	1.45
HSO$_3$-PS (2b)	107	254	583	615	33.80
ClSO$_2$-PS (3)	103	163	501	696	31.41
H$_2$NSO$_2$-PS (4)	326	358	495	692	34.63
Cl$_2$NSO$_2$-PS(5)	311	338	467	697	37.41

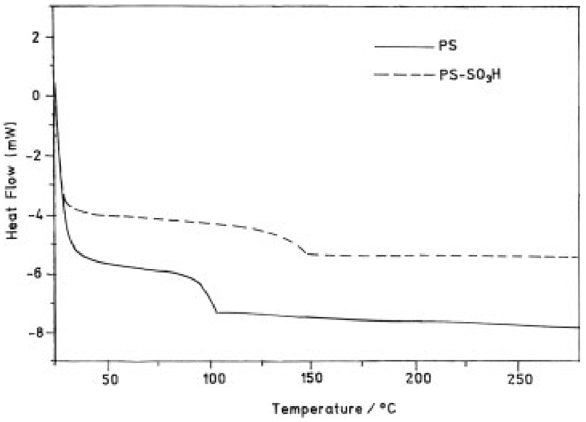


Figure 3 DSC curve of PS and PS-SO$_3$H (second heating run).

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 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. 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. Such decontaminants are also noncorrosive or nonreactive to the human skin. The additional advantages of polymeric chloramines are in terms of stability as compare 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 (Cl^+), thereby facilating the decontamination reaction. We therefore used the concept to synthesize (1) and monitor decomposition reaction with (2).

Decontamination studies 2-chloro phenyl ethyl sulfide with polymeric decontaminant was carried out in aqueous medium using acetonitrile: water mixture as well as in aprotic medium using toluene and isopropanol at room temperature with stirring. Decontaminated products were separated by GC and identified by GCMS in EI mode and results are given in the Tables III and IV. It was observed that reaction was more complete in aqueous medium in comparison to aprotic medium or isopropanol without water. GC results indicated in aqueous medium 100% simulant were decomposed within

TABLE III
Identification of the Decontamination Products from 2-Chloro Ethyl Phenyl Sulfide with Polymeric Decontaminant in Aqueous Medium

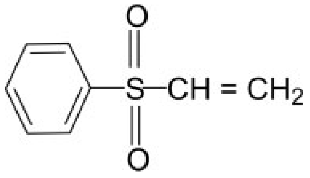
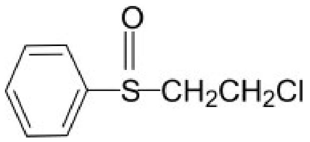
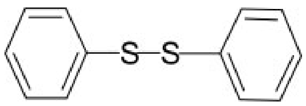
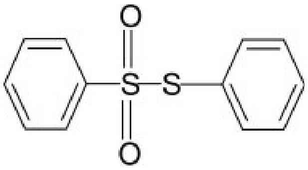
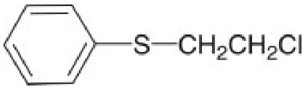
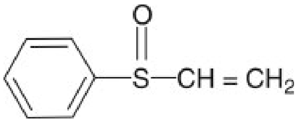
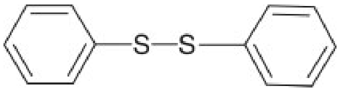
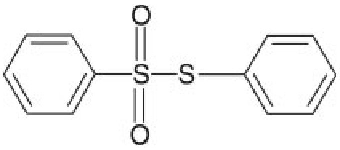
Rt (min)	m/z	Identified product	Percentage of decontaminated product
8.87	168		12.8%
10.53	188		79.4%
11.9	218		2.9%
11.48	250		5.9%

TABLE IV
Identification of the Decontamination Products from 2-Chloro Ethyl Phenyl Sulfide with Polymeric Decontaminant in Isopropanol (Without Water)

Rt(min)	m/z	Identified products	Percentage of decontaminated product
12.26	172/174		40%
12.60	152		49.5%
17.99	218		3.2%
20.28	250		7.3%

20 min. In present study 50% oxidation was completed in 7 min as compared to earlier published work (20 min)[25] Mechanism[7,30] of decontamination reaction in aqueous medium, 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 displacement of chlorine by water with elimination of HCl produces 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), diphenyl disulfide, and benzene sulfono thionic acid S-phenyl ester. It was observed that when reaction was carried out in isopropanol as nonaqueous medium only 60% simulant was decontaminated after 4 h. Main products were vinyl phenyl sulfoxide, diphenyl disulfide, and benzene sulfono thionic acid S-phenyl ester. It was observed that in aprotic[30] medium only 25–28% simulant was decontaminated after 8 h. Main products were chloro vinyl phenyl sulfide and dichloro vinyl phenyl sulfide.

CONCLUSION

Redox copolymer *N*,*N*-dichloro Polystyrene sulfonamide as a suitable material for macromolecular oxidant, for destruction of stimulant of SM which bear oxidizable divalent sulfur by its oxidation to nontoxic products in aqueous medium have been investigated in this report. The resin contains two atoms of active chlorine in functional groups and shows strong oxidizing properties. Decontamination reaction was monitored by gas chromatography using FPD as detector. Products were identified by GC-MS. Results were encouraging in aqueous medium as compared with nonaqueous and aprotic medium.

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References

1. Somani, S. M. In Chemical Warfare Agents; Somani, S. M., Ed.; Academic Press: San Diego, 1992; Chapter 2, p 13.
2. Yang, Y. C. Chem Ind 1995, 334.
3. Tsujihara, K.; Furukawa, N.; Oae, K.; Oae, S. Bull Chem Soc Jpn 1969, 42, 2631.
4. Kirk, R. E.; Othmer, D. F. Encyclopedia of Chemical Technology, 4th ed.; Wiley: New York, 1992; Vol. 4, p 274.
5. Dubey, D. K.; Ravindra Nath; Malhotra, R. C.; Tripathi, D. N. Tetrahedron Lett 1993, 47, 7645.
6. Arshady, R. J Chromatogr 1991, 586, 181.
7. Yang, Y. C.; Baker, J. A.; Ward, J. R. Chem Rev 1992, 92, 1729.
8. Leblanc, A.; Fosset, L.; Magnaud, G.; Desgranges, M.; Sentenac-Roumanon, H.; Lion, C.; Charvy, C.; Mohri, A. Phosphorus Sulfur Silicon 1993, 79, 141.

9. Yang, Y. C.; Szafraniec, L. L.; Beaudry, W. T. J Org Chem 1990, 55, 3664.
10. Drago, A. S. Coord Chem Rev 1992, 117, 185.
11. Deimas, G.; Desgranges, M.; Lion, C.; Magnaud, M.; Sentenac-Roumanon, H. Fr. Pat. C 2,676,368 (1991).
12. Mathur, N. K.; Narang, C. K.; Williams, R. E. Polymers as Aids in Organic Chemistry; Academic Press: New York, 1980.
13. Hodge, P.; Sherrington, D. C. Polymer Supported Reaction in Organic Synthesis; Wiley: New York, 1980.
14. Sreekumar, S.; Rajesekharan Pillai, V. N. Polymer 1987, 28, 1599.
15. Cainelli, G.; Cardillic, G.; Orena, A. M.; Sandri, S. J Am Chem Soc 1976, 21, 6737.
16. Salunkhe, M. M.; Thorat, M. T.; Mane, R. B.; Wadgaonkar, P. P. Eur Polym J 1989, 25, 1091.
17. Gupta, S. C.; Jain, S. K; Mehta, A.; Mathur, N. K.; Narang, C. K. J Polym Mater 1989, 6, 57.
18. Bogoczek, R.; Kociolek-Balawejder, E. Angew Makromol Chem 1989, 169, 119.
19. Emerson, D. W.; Shea, D. T.; Sorensen, E. M. Ind Eng Chem Prod Res Dev 1978, 17, 269.
20. Bogoczek, R.; Kociolek-Balawejder, E. Eur Polym Commmun 1986, 27, 286.
21. Kocioek-Balawejder, E. Eur Polym J 2002, 38, 953.
22. Kocioek-Balawejder, E. Eur Polym J 2000, 36, 295.
23. Kocioek-Balawejder, E. Eur Polym J 2000, 36, 1137.
24. Salunkhe, M. M.; Mane, R. B.; Kanade, A. S. Eur Polym J 1991, 27, 461.
25. Gutch, P. K.; Shrivastava, R. K.; Dubey, D. K. J Appl Polym Sci 2007, 105, 2203.
26. Vogel, A. I. Text Book of Quantitative Inorganic Analysis: Theory and Practice; Longmans Green: New York, 1951, p 348.
27. Kucera, F.; Jancar, J. Chem Pap 1996, 50, 224.
28. Smitha, B.; Sridhan, S.; Khan, A. A. J Membr Sci 2003, 225, 63.
29. Carretta, N.; Tricoli, V.; Picchion, F. J Membr Sci 2000, 166, 189.
30. Dubey, D. K.; Malhotra, R. C.; Swamy, R. V.; Vijayaraghavan, R. J Org Chem 1999, 64, 8031.