

## Poly(ether sulfonamide)s with glycidyl pendant units

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### SUMMARY

High molecular weight poly (ether sulfonamide) has been prepared by condensation of 4,4'-dichlorosulfonyldiphenylether with ethylenediamine. The reaction of potassium salt of poly (ether sulfonamide) with epichlorohydrin gives the corresponding N-glycidyl derivative in yield as high as 98%. The resulting polymer offers many functionalization possibilities through ring opening of the oxirane units. Also the glycidyl bearing polymer may act as multifunctional post-crosslinking agent for polymers carrying hydroxy, amino or carboxyl groups.

### INTRODUCTION

Polysulfonamides have been synthesized from aromatic and aliphatic disulfonyl chlorides and diamines, but most of works have focused on the preparation of polysulfonamides deriving from aryl disulfonyl chloride in order to obtain thermally stable polymers analogous to polyamides (1-5).

Polysulfonamides have been paid somewhat little attention due to the factors such as the purity of disulfonyl chloride, the organic solvents used, the temperature, and the pH of the system (1).

Polysulfonamides as well as sulfonamides (6) show excellent stability towards acid and base hydrolysis. Polysulfonamides are readily soluble in common organic solvents as well as in strongly basic aqueous solutions. Important aspect of polysulfonamides is that the reactive hydrogen of sulfonamide group permits chemical modification. Although nucleophilic substitution of low molecular weight sulfonamides (7) have been reported in literature, there are a few reports on modification of polysulfonamides such as N -chlorination (8) and N -alkylation (1).

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In our previous work (9), we demonstrated that crosslinked poly (styrene sulfonamide) was transformed into corresponding N-glycidyl derivative and the resulting polymer was modified with sorbitol, which was used to remove boron in ppm level.

In the present paper, we have prepared a polysulfonamide from 4,4'-dichlorosulfonyl diphenylether and ethylenediamine. Potassium salt of the polysulfonamide has been reacted with epichlorohydrin in N-methyl pyrrolidinone (NMP) to give glycidyl bearing polymer in 98% yield. The resulting polymer has been modified with glycerol to give water soluble polymer having hydroxy pendant units which may be of interest as polymeric surfactant.

## EXPERIMENTAL

### Materials:

Chlorosulfonic acid (Carlo Erba), ethylenediamine (Merck), epichlorohydrin (Merck), KOH (Merck), diphenylether (Merck) were used as supplied. The solvents were dried by usual methods.

### Measurements:

IR spectra were recorded on a Mattson 1000 FTIR spectrophotometer.  $^1\text{H}$  NMR spectra were obtained with a Bruker AC 200 spectrometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were conducted at a heating rate of  $10^\circ\text{C}/\text{min}$  in  $\text{N}_2$  on a Perkin Elmer DSC 6 and Shimadzu TG 50, respectively.

### Preparation of 4,4'-dichlorosulfonyl diphenylether (DCD):

This compound was prepared in pure form by modification of the procedure given in the literature (10). 20 g (0.117 mol) of diphenylether and 50 mL of cyclohexane are placed in a 250 mL two necked flask equipped with  $\text{CaCl}_2$  guard tube. While stirring at  $0^\circ\text{C}$ , 40 mL (0.6 m) of chlorosulfonic acid is added dropwise to the mixture. It takes about 45 minutes and stirring is continued for another 2 hours. As the reaction proceeds the mixture becomes viscous. The reaction content left overnight in refrigerator. The supernatant is decanted and the acid phase is extracted with two portions of 50 mL of dichloromethane. These solutions are combined with the supernatant and 3 g of granulated  $\text{CaCl}_2$  is added and shaken for removal of trace sulfonic acids. After filtering dichloromethane is distilled off. The product remains as hygroscopic white powder, yield 35 g (81.5 %), mp.  $125^\circ\text{C}$  (lit.  $128\text{-}129^\circ\text{C}$  (9)). For chlorine analysis, 0.1 g polymer was dissolved in 10 mL aqueous solution of NaOH (5%) and boiled and then neutralized with  $\text{HNO}_3$  solution. The neutral solution was diluted up to 50 mL and chlorine content of polymer determined colorimetrically by mercuric thiocyanate method (11) was found to be 19.31% which was consistent with theoretical value.

### Preparation of the polysulfonamide:

4 g (10.9 mmol) of DCD was dissolved in 10 mL of pyridine at 0 °C. To the solution was added dropwise 0.73 mL (10.9 mmol) of ethylenediamine with stirring. The stirring was continued for another 4 h and heated at 50 °C for 30 min. The resulting viscous solution was poured into 200 mL of cold water and 15 mL of concentrated HCl solution was added into the milky mixture. The precipitated polymer was filtered and washed with water. The crude product was dissolved in 100 mL of aqueous NaOH (5%) solution and precipitated in 120 mL of HCl (5%) solution to remove pyridine residues and washed with water and then dried. Yield : 8.8 g (98.5 %). <sup>1</sup>H NMR and IR spectra of the polymer are shown in Figures 1 and 3a, respectively. Inherent viscosity of the polysulfonamide was found to be 0.32 dL.g<sup>-1</sup> in NMP at 30°C (c = 0.375 g.dL<sup>-1</sup>). C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>S<sub>2</sub>O<sub>5</sub> Calcd. C% 47.46; H% 3.95; N% 7.91; Found C% 46.7; H%3.84; N%7.50.

### Reaction of the polysulfonamide with epichlorohydrine:

3 g of the polysulfonamide was dissolved in 15 mL of NMP. 20 mL of 2% KOH solution in methanol was then added to the reaction mixture and a voluminous precipitate of the polysalt formed. Methanol was distilled off and to the cooled residue, 15 mL (0.191 mol) of epichlorohydrin was added. The mixture was stirred at 40 °C for 72 h. To the end of the reaction, voluminous precipitate disappeared and tiny precipitate of KCl formed. The mixture was poured into 150 mL of water and the precipitate formed was filtered and washed with water. The product was dried under vacuo at room temperature for 24 h. Yield: 3.6 g. <sup>1</sup>H-NMR and IR spectra of the polymer with glycidyl pendant units are given in Figures 2 and 3b, respectively. The inherent viscosity of the polymer was found to be 0.33 dL.g<sup>-1</sup> in DMSO at 30 °C (c = 0.39 g.dL<sup>-1</sup>). C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>S<sub>2</sub>O<sub>7</sub> Calc. C% 51.5; H% 4.72; N% 6.01; Found C% 50.3; H% 4.59; N% 5.94.

### Determination of the epoxide content:

Pyridinium chloride method (12) was used to determine the epoxide content of the polymer which was found to be 4.22 mmol .g<sup>-1</sup> indicating 98.1% of conversion.

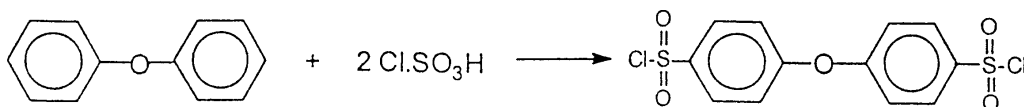
### Modification with glycerol:

1 g of the glycidyl bearing polymer was dissolved in 50 mL of NMP. The solution was filtered and reacted with 10 mL of glycerol and 0.5 mL of triethylamine with stirring for 2 h at 45 °C. After cooling, the mixture was poured into 100 mL of water. The mixture was filtered to remove trace amounts of suspended particles and 5 g of NaCl was added to the filtrate. The white precipitate was filtered and dried under vacuo for 24 h at 60 °C. Yield :1.3 g (93.5 % based on glycidyl bearing polymer). Inherent viscosity of glycerol modified polymer was

found to be  $0.54 \text{ dL.g}^{-1}$  in NMP at  $30 \text{ }^\circ\text{C}$  ( $c = 0.20 \text{ g.dL}^{-1}$ ).  $\text{C}_{26}\text{H}_{38}\text{N}_2\text{S}_2\text{O}_{13}$  Calc. C% 48.0; H% 5.84; N% 4.31; Found C% 46.1; H% 5.51; N% 4.64.

## RESULTS AND DISCUSSION

Diphenylether was chlorosulfonated with chlorosulfonic acid in dichloromethane affording pure compound (Scheme 1). The most tedious procedure in preparing chlorosulfones is to remove sulphuric acid residues formed by interaction of the eliminated water with the chlorosulfonic acid. In most procedures the reaction mixture is recommended to pour into ice-water for removal of sulphuric acid. This is based on the fact that aromatic sulfochlorides do not undergo a rapid hydrolyses in cold water. Inevitably the products obtained by this procedure contain trace quantities of sulfonic acids.

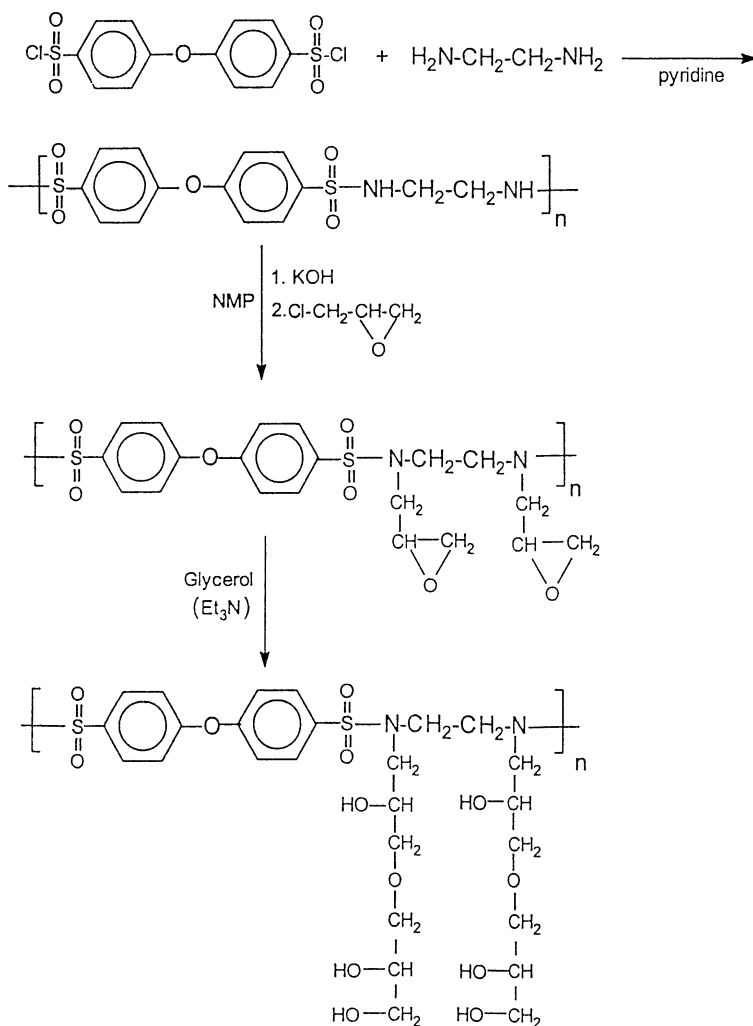


Scheme 1

This kind of impurity may not be very important for chlorosulfonation of low molecular weight organic compounds. However, in condensation polymerization, the sulfonic acid impurities retained is extremely important. Any minor deviation in the stoichiometry of the reaction causes a drastic decreasing in molecular weights as well as polymerization yields. Presumably, this is the main drawback in preparation of polysulfonamides with high molecular weights. For this reason, in the present study we have described an alternative procedure for preparing 4,4'-dichlorosulfonyl diphenylether. In the procedure presented we have used dichloromethane as solvent in which the dichlorosulfonated compound dissolves. The use of dichloromethane also allows dissipation of the reaction heat evolving. At the end of the reaction the upper organic layer containing the product is treated with anhydrous  $\text{CaCl}_2$ . This procedure provides easy removal of sulphuric acid or chlorosulfonic acid contaminants yielding a pure product.

### Polycondensation with ethylenediamine:

4,4'-dichlorosulfonyl diphenylether was condensed with ethylenediamine in usual manner in pyridine (Scheme 2). Ethylenediamine was deliberately chosen as diamine component because of the solubility characteristics of the resulting polysulfonamide. The polymer obtained has a reasonably high molecular weight.



Scheme 2

<sup>1</sup>H NMR spectrum of poly(ether sulfonamide) represents a sharp singlet at 2.8 ppm, which corresponds to ethylenic protons (Fig. 1). The multiplet signals appeared in 7-8 ppm range representing aromatic protons. Sulfonamide protons are observed at 3.6 ppm as a broad singlet. Exchangeable character of these protons has been

confirmed by D<sub>2</sub>O exchange. Glass transition temperature of polymer (T<sub>g</sub>) by DSC was observed at 140.9 °C (onset) and thermogravimetry of polymer demonstrated a 10% weight loss in nitrogen 320 °C. The polymer dissolves in NMP, DMSO, DMF and acetone.

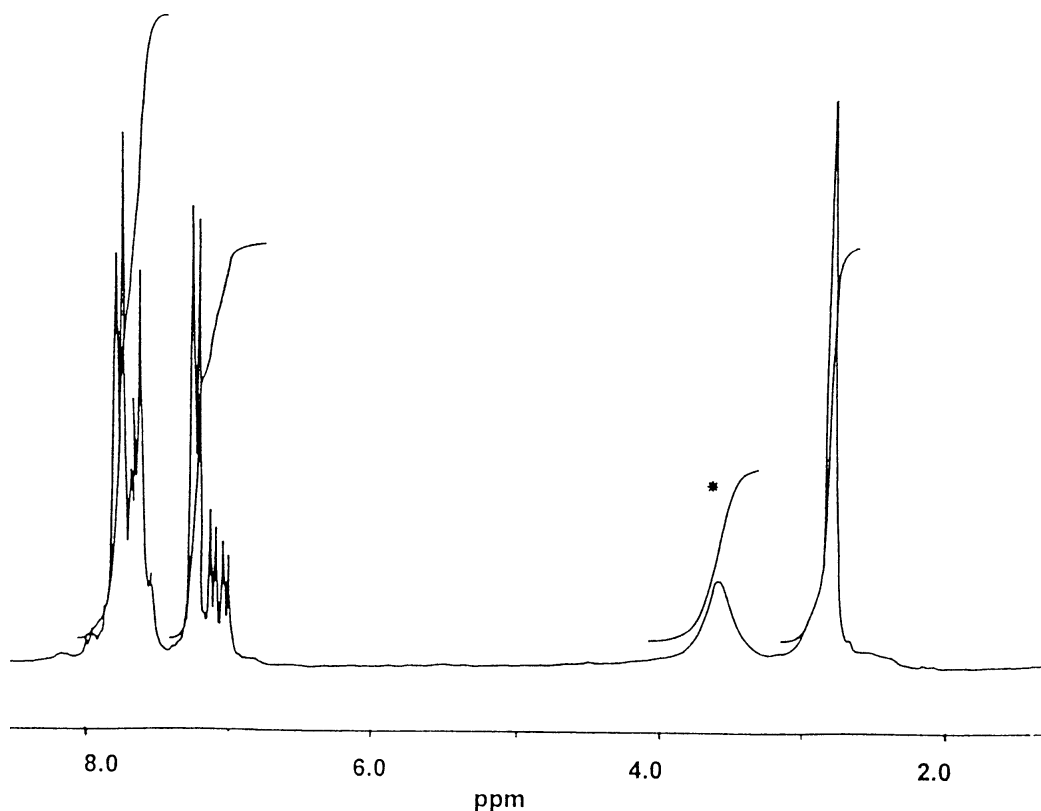


Figure 1. <sup>1</sup>H NMR spectrum of polysulfonamide in DMSO-d<sub>6</sub>.

#### **Functionalization of the polysulfonamide with epichlorohydrin:**

The reaction of potassium salt of the polysulfonamide with epichlorohydrin in NMP at 50°C affords a high yield of substitution. The resulting polymer with glycidyl groups dissolves in NMP, DMSO and DMF and determination of its epoxide content reveals 98.1% of substitution. Substitution of the glycidyl groups is clearly followed by its NMR spectrum in Fig.2. The broad signal of the sulfonamide proton in Fig.1 disappears due to complete substitution. Whilst multiplet signals of the aromatic protons remain at the same position, aliphatic protons of the ethylenediamine unit shift lower fields after substitution with the glycidyl groups. Protons of glycidyl and ethylenic groups give a broad multiplet in 2.7-3.8 ppm range. The integral ratio of the aliphatic protons to the aromatics implies approximately 91 % of substitution.

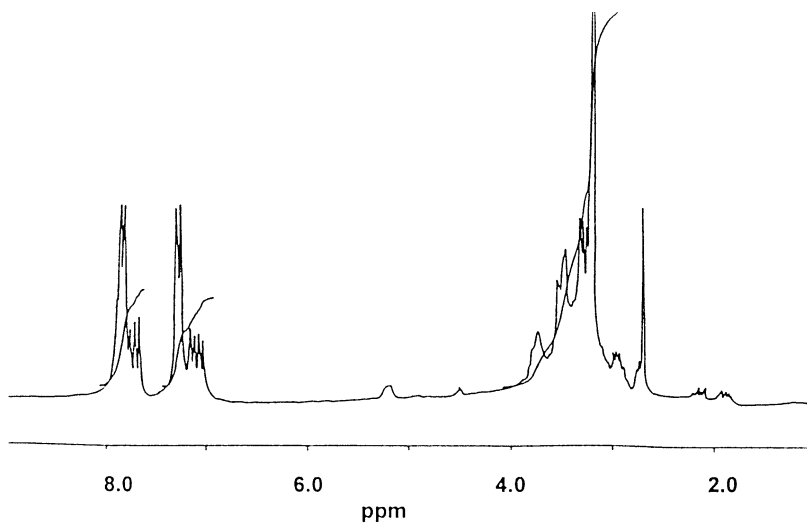


Figure 2.  $^1\text{H}$  NMR spectrum of polysulfonamide with glycidyl pendant units in  $\text{DMSO-d}_6$ .

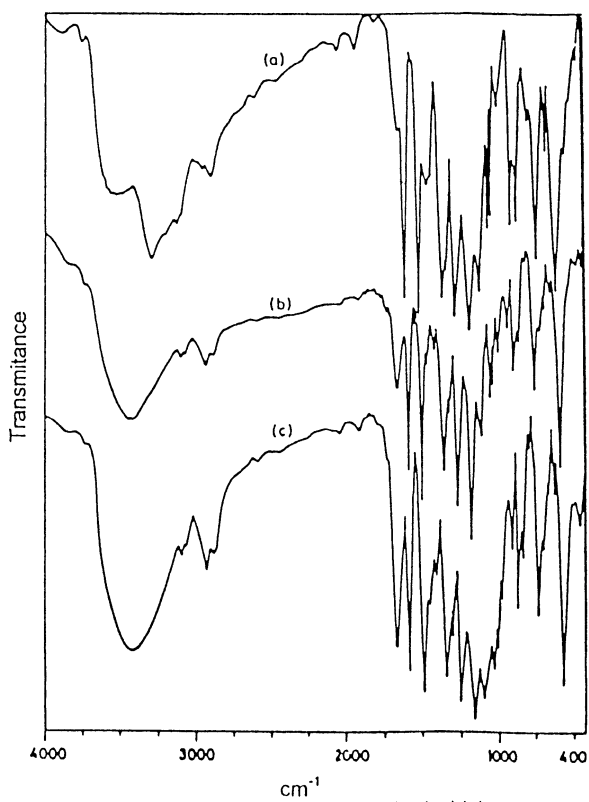


Figure 3. IR spectra of polysulfonamide (a), and with glycidyl units (b), and modified with glycerol (c).

Moreover incorporation of epoxide groups into the polysulfonamide is verified by comparison of IR spectra of the two polymers (Fig. 3a and 3b). N-H stretching vibration of the polysulfonamide at  $3250\text{ cm}^{-1}$  disappears and epoxide ring vibration band appears at  $950\text{ cm}^{-1}$ . Weak Tg of polysulfonamide containing glycidyl units was detected at  $139.4\text{ }^{\circ}\text{C}$  (onset).

#### **Modification with Glycerol:**

Water soluble polymer can only be prepared by dropwise addition of solution of polysulfonamide with glycidyl units to a large excess amount of glycerol, but when polymer is reacted directly with glycerol a crosslinked gel occurs. In Fig. 3c stretching vibrations of OH groups are observed at  $3300\text{-}3400\text{ cm}^{-1}$  range.

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