¬ STATEMENT

I hereby declare that the matter presented in this dissertation entitled, “Synthesis of monomer containing sulfonyl group and then polymerisation” is based on the results of investigations carried out by me in the School of Chemical Sciences, Goa University under the supervision of Prof. V.S. Nadkarni and the same has not been submitted elsewhere for the award of a degree of diploma.

Mr. Nitesh G. Venji

M.Sc. Part II, Organic Chemistry

School of Chemical Sciences

Goa University

CERTIFICATE

This is to certify that the dissertation entitled, "Synthesis of monomer containing sulfonyl group and then polymerisation" Herein I confirm that the work carried out by Mr. Nitesh G. Venji under my supervision in partial fulfilment of the requirements for the award of the degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa University.

Prof. V.S. Nadkarni

Project Supervisor

School of Chemical Sciences

Goa University

CERTIFICATE FROM HEAD

This is to certify that the dissertation entitled, Synthesis of monomer containing sulfonyl group and then polymerisation” Herein I confirm that work carried out by Mr. Nitesh G. Venji under the supervision of Prof. V.S. Nadkarni for the award of the degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa University.

Prof. V. S. Nadkarni

Dean of School of Chemical Sciences

Goa University

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Synthesis of monomer containing sulfonyl group and then polymerisation

INTRODUCTION

Polymer technology has developed tremendously in the past decades, as the uses of polymers in society have multiplied. Nevertheless, the technology in the processing of polymers remains empirical. The basic reason for this, is that not only are many important fundamental properties of these materials very difficult to measure, but the reaction mechanisms and flow behaviour in processing which yield these qualities are very complex.

The aim of the chemist working in the polymer area is to treat only those parts of the mechanism which are essential to obtaining a product with desired physical properties. In order to recognize and so simplify the situation in a reasonable way, today's chemical engineer in polymers requires a broad background in the polymer area. The scope of this dissertation was chosen with this requirement in mind. Methods of applying these new aids to the problems involved urgently require further exploration and development on a broad front.

MONOMERS

Monomers are small molecules which may be joined together in a repeating fashion to form more complex molecules called polymers. Monomers form polymers by forming chemical bonds or binding supramolecularly through a process called polymerization. Sometimes polymers are made from bound groups of monomer subunits called oligomers. To qualify as an oligomer, the properties of the molecules need change significantly if one or a few subunits are added or removed.

POLYMERS

Polymer refers to a molecule whose structure is composed of multiple repeating units. The units composing polymers derive, actually or conceptually, from molecules of low relative mass. Both synthetic and natural polymers play essential and ubiquitous roles. Many people use the term polymer and plastic interchangeably, polymer are much larger class of molecules which includes plastic and many other materials such as cellulose, amber and natural rubber.

Examples of polymers may include plastics such as polyethylene, silicones, biopolymers such as cellulose and DNA, natural polymers and other macromolecules. Polymers that contain only a single type of a repeat unit are known as homopolymer, while polymers containing two or more types of repeated units are called copolymer. When two or more different monomers unite together to polymerize, the product is called a copolymer and the process is called copolymerization. Copolymers may also be described in terms of the existence of or arrangement of branches in the polymer structure. Linear copolymers consist of a single main chain whereas branched copolymers consist of a single main chain with one or more polymeric side chain.

CLASSIFICATION OF POLYMERS

Polymers are classified as follows.

A. Classification based on sources of availability.

B. Classification based upon structure.

C. Classification based upon molecular forces.

D. Classification based upon modes of synthesis.

A. Classification of polymers on basis of sources of availability.

1. Natural Polymers.

These polymers are obtained from nature specially occurs in plants and animals hence they are called as natural polymers. For example cellulose, starch, natural rubber, proteins etc.

2. Synthetic polymers.

Synthetic polymers are the polymers which are prepared in laboratories these polymers are also called as manmade polymers. Examples are polyethylene, PVC, terylene etc.

3. Semi-synthetic polymers.

Semi-synthetic polymers are the polymers which are derived from naturally occurring polymers by chemical modification. For example cellulose diacetate polymer which is prepared by acetylation of naturally occurring cellulose with acetic anhydride. Other examples of synthetic polymers are vulcanized rubber, gun cotton which is cellulose nitrate etc.

B. Classification of polymers on the basis of structure.

1.Linear polymers.

Linear polymers are the polymers in which monomeric units are linked together to form long and linear chains. In these polymers chains are well packed therefore have high densities, high tensile strength, and high melting point. Some common examples are high density polythene, polyvinylchloride nylons, polyesters etc.

2.Branched chain polymers.

In this type of polymers monomers are joined to form long chains with side chains or branches of different length. These branched chain polymers are irregularly packed and therefore they have low tensile strength and melting point than linear polymers. Examples are low density polythene, glycogen, starch etc.

3.Crossed linked polymers

In this polymer monomer units are crossed linked together to form a three dimensional network. These polymers are also called three dimensional network polymers. These type polymers are hard, rigid and brittle because of extensive cross linking. Some common examples are Bakelite, melamine, formaldehyde resign etc.

C. Classification of polymers on basis of molecular forces.

1.Elastomers.

The presence of weak intermolecular forces like Van der Waals forces between monomer chains gives the elastic character to this polymer therefore called as elastic polymer. Because of presence of weak forces polymers can be easily stretched by applying small stress and regains its original shape when stress is removed. The important example of elastomer is natural rubber and other examples are buna-S, buna-N etc.

2.Fibres.

The polymer chain in fibre contains strong intermolecular forces like hydrogen bonding or dipole-dipole interactions between the chains. Because of strong forces polymer chains are closely packed and thus impart crystalline nature to polymer. Therefore the polymer has high tensile strength, less elasticity and sharp melting point because of crystalline nature.

3.Thermoplastic polymers.

Polymers belong to this class can be easily softened when heated and harden when cooled with little change in their properties. The types of intermolecular forces present between these polymer chains are intermediate between elastomers and fibres. There is no cross linking between the chains as result when these polymer is heated chains moves more and more freely. Therefore these polymers can be moulded into variety of shapes and then cooed to get desired product. Common examples of thermoplastic polymers are polythene, polystyrene, Teflon etc.

4.Thermo setting polymers.

These are type of polymers which shows permanent change in their structure on heating. On heating these polymers shows extensive cross linking in moulds and become hard and infusible therefore they cannot be reuse. The cross link holds the molecule in place so that heating does not allow them to move freely. Therefore these polymers are heavily branched molecules and permanently rigid. Examples are Bakelite, melamine, formaldehyde, etc.

D. Classification of polymers on basis of mode of synthesis.

1.Addition polymer.

In this polymerisation technique repeated addition of monomer is done without elimination of by product molecule. Monomers used are unsaturated compounds possessing double or triple bonds. Examples are polythene, polypropylene, polyvinyl chloride etc.

2.Condensation polymers.

In this polymerisation technique condensation of two or more than two monomers are done with the elimination of simple molecule like water, ammonia, hydrogen chloride etc.

The monomers used generally have different bi-functional or tri-functional groups. For example nylon-66 is obtained by condensation two monomers; hexamethylenediamine with adipic acid. Other examples are polyester, polyamide, etc.

Characteristics of Polymers

The majority of manufactured polymers are thermoplastic, meaning that once the polymer is formed it can be heated and reformed over and over again. This property allows for easy processing and facilitates recycling. The other group, the thermosets, cannot be remelted. Once these polymers are formed, reheating will cause the material to ultimately degrade, but not melt. Every polymer has very distinct characteristics, but most polymers have the following general attributes.

1. **Polymers can be very resistant to chemicals.** Consider all the cleaning fluids in your home that are packaged in plastic. Reading the warning labels that describe what happens when the chemical comes in contact with skin or eyes or is ingested will emphasize the need for chemical resistance in the plastic packaging. While solvents easily dissolve some plastics, other plastics provide safe, non-breakable packages for aggressive solvents.

2. **Polymers can be both thermal and electrical insulators.** A walk through your house will reinforce this concept, as you consider all the appliances, cords, electrical outlets and wiring that are made or covered with polymeric materials. Thermal resistance is evident in the kitchen with pot and pan handles made of polymers, the coffee pot handles, the foam core of refrigerators and freezers, insulated cups, coolers, and microwave cookware. The thermal underwear that many skiers wear is made of polypropylene and the fiberfill in winter jackets is acrylic and polyester.

3. **Generally, polymers are very light in weight with significant degrees of strength.** Consider the range of applications, from toys to the frame structure of space stations, or from delicate nylon fiber in pantyhose to Kevlar, which is used in bulletproof vests. Some polymers float in water while others sink. But, compared to the density of stone, concrete, steel, copper, or aluminum, all plastics are lightweight materials.

4. **Polymers can be processed in various ways.** Extrusion produces thin fibers or heavy pipes or films or food bottles. Injection molding can produce very intricate parts or large car body panels. Plastics can be molded into drums or be mixed with solvents to become adhesives or paints. Elastomers and some plastics stretch and are very flexible. Some plastics are stretched in processing to hold their shape, such as soft drink bottles. Other polymers can be foamed like polystyrene (Styrofoam™), polyurethane and polyethylene.

5. **Polymers are materials with a seemingly limitless range of characteristics and colors.** Polymers have many inherent properties that can be further enhanced by a wide range of additives to broaden their uses and applications. Polymers can be made to mimic cotton, silk, and wool fibers; porcelain and marble; and aluminum and zinc. Polymers can also make possible products that do not readily come from the natural world, such as clear sheets and flexible films.

6. **Polymers are usually made of petroleum, but not always.** Many polymers are made of repeat units derived from natural gas or coal or crude oil. But building block repeat units can sometimes be made from renewable materials such as polylactic acid from corn or cellulosics from cotton linters. Some plastics have always been made from renewable materials such as cellulose acetate used for screwdriver handles and gift ribbon. When the building blocks can be made more economically from renewable materials than from fossil fuels, either old plastics find new raw materials or new plastics are introduced.

7. **Polymers can be used to make items that have no alternatives from other materials.**

Polymers can be made into clear, waterproof films. PVC is used to make medical tubing and blood bags that extend the shelf life of blood and blood products. PVC safely delivers flammable oxygen in non-burning flexible tubing. And anti-thermogenic material, such as heparin, can be incorporated into flexible PVC catheters for open heart surgery, dialysis, and blood collection. Many medical devices rely on polymers to permit effective functioning.

PolymerizationTechniques

Bulk Polymerization :- In this technique final polymer obtained has high purity and insoluble iniator. In this technique chain transfer reagents are use to control molecular weights. Monomer is taken in mold of required size and shape and then heated to initiate polymerisation. This process is exothermic lot of heat is generated as a result during polymerization viscosity of medium increases, mixing become difficult and broad molecular weight distribution is obtained. Free radical polymerization is carried out using bulkpolymerization.

Solution polycondensation: In this polymerization technique solvent is chosen such that it dissolves the monomer. By using suitable solvent or water one can overcome problem of heat dissipation which encountered in bulk polymerization. Polymer obtained by this technique has low to medium molecular weight. Many free radical and ionic polymerization are carried out by this technique.

Emulsion polymerisation: In this technique water can be use for heat transfer. Uniform emulsion of monomer and dispersed phase is carried out. Water soluble initiator, soap, monomer and other ingredients are stirred in reaction vessel as a result micelle formation takes place. Micelle start growing as polymerization proceeds. The iniator enters micelle to initiate polymerization. As monomer enters inside micelle is consumed more and more monomer enter inside. After sufficient swelling of micelle it brust and milky white suspension result called latex which can be use in paints, adhesive etc. Polymer can be isolated from latex by destabilizing emulsion. Rate of polymerization is very high and high molecular weight product can be obtained.

Melt condensation: Monomers used this technique are solid and do not decompose at their melting point. Polymerization process is carried out in inert atmosphere to avoid oxidation, decarbonylation etc. And reduced pressure is also required. Molten polymer formed is discharge hot from the reactor and is passed directly for spinning, casting or extrusion. Nylon6,6 is prepared by this technique.

GENERAL INTRODUCTION TO POLYSULFONE POLYMERS AND POTENTIAL APPLICATION

Polysulfones are a family of thermoplastic polymers. These polymers are known for their toughness and stability at high temperatures. The simplest polysulfone poly(phenylenesulfone) was known as early as 1960. It can be produced in friedel-crafts reaction from benzenesulfonyl chloride. Since this polymer has melting point of over 500^0C, it is on one side very heat resistance, on other hand it is very difficult to process. In addition, its mechanical properties are rather poor. Therefore, thermoplastic polysulfones were researched as an alternative.

Polysulfone has one of highest service temperature among all melt process able thermoplastics. Its resistance to high temperature gives it role of flame retardant without compromising its strength that usually results from the addition of flame retardant. its high hydrolysis stability allows its use in medical application requiring autoclave and steam sterilization. However, it has low resistance to some solvents and undergo weathering.

Properties of polysulfone polymer

- Polysulfone polymer has high thermal, oxidative and hydrolytic stability.
- They are amorphous, transparent thermoplastic that can be molded, extruded or thermoformed into a wide variety of shapes.

- These polymers are highly resistance to aqueous mineral acid, bases and oxidizing agents and are fairly resistance to many non- polar solvents.
- These polymers are not resistant to low polar solvents such as esters, ketones, aromatic and chlorinated hydrocarbon.

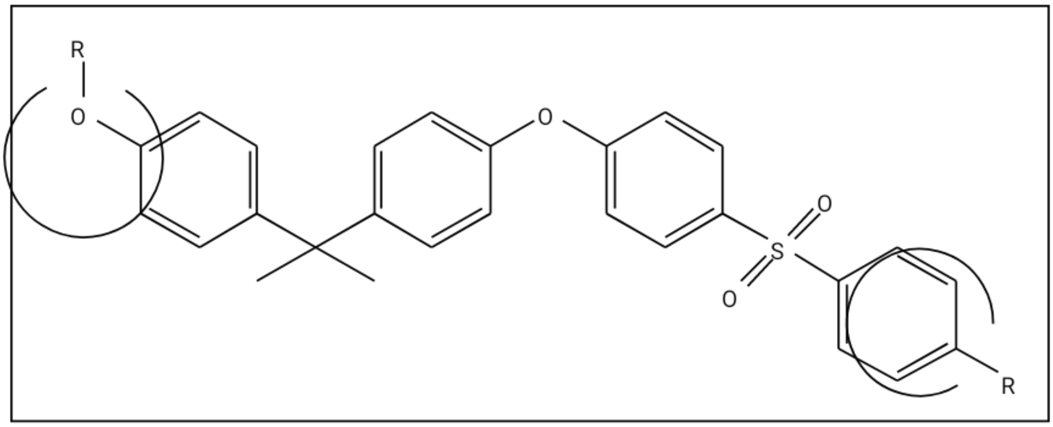
Polysulfone production.

There are five major types of polysulfones made by three companies.

1. union carbide - polysulfone
   > Udel
   > Radel
2. ICI – polyether sulfones
   > Victrex
   > Polyether sulfones 720 P
3. 3M – polyarylether sulfones
   > Astrel

1. Udel

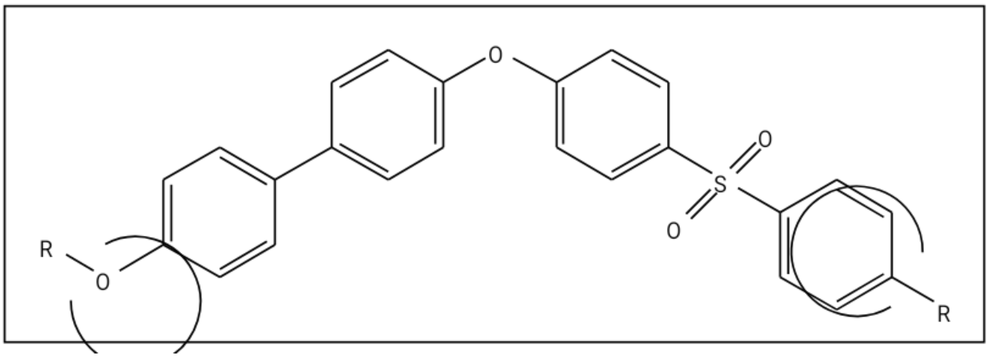
- Synthesized by nucleophilic replacement of the chloride from 4,4-dichlorodiphenylsulfone by anhydrous salt of bisphenol A.
- It exhibits a reasonably high glass transition temperature of 190-degree C.



2.Radel

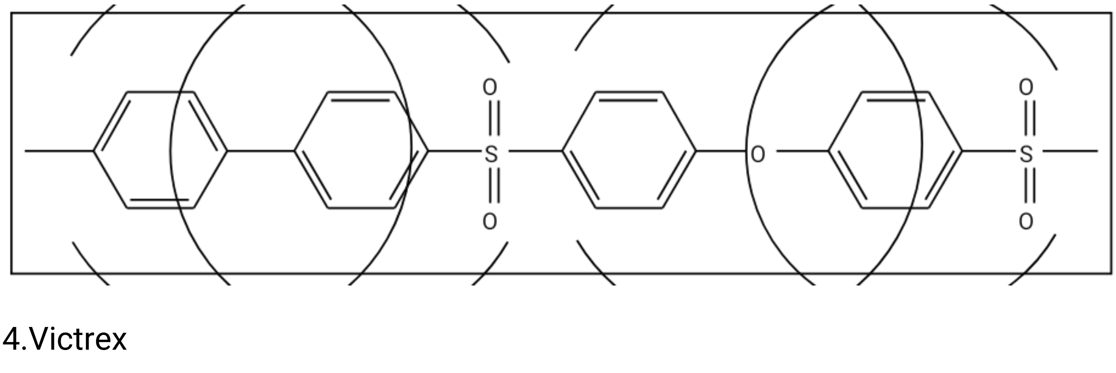
- Radel was formed from the reaction of a bisphenol and bis(p-chlorophenyl) sulfone.

- This polysulfone exhibits greater chemical or solvent resistance, a greater glass transition temperature of 220^0C, greater oxidative stability, and good toughness in comparison to Udel.



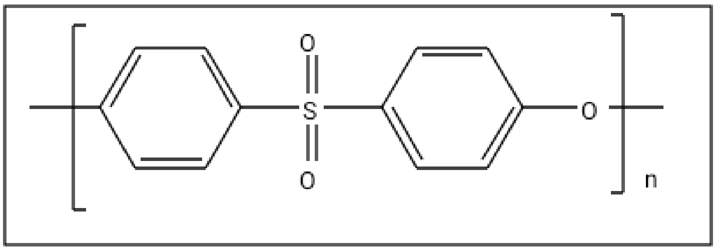
3.Astrel

- It's an especially high performance thermoplastic which requires specialized equipment with extra heating and pressure capabilities for processing.
- It has glass transition temperature of 285^0 C.



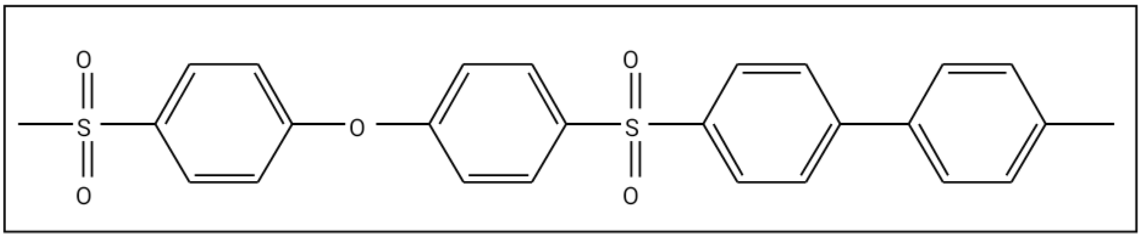
4.Victrex

- It has glass transition temperature of 230^0 C.



5.Polyether sulfone

- It has glass transition temperature of 250^0 C.



Literature Work

General synthetic route for monomer tetrakis(2-hydroxyethylsulphone) monomer

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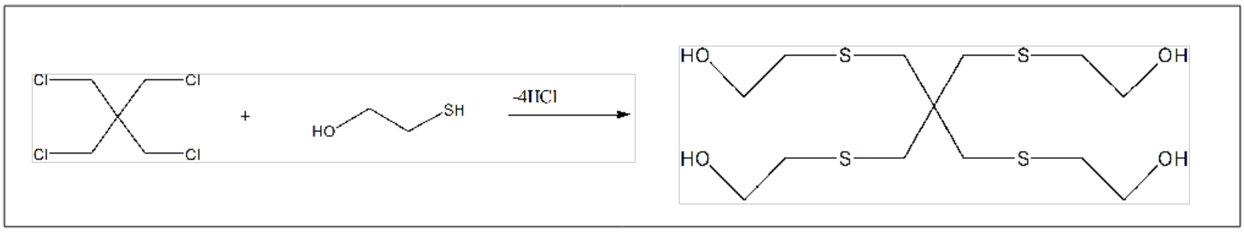
2)



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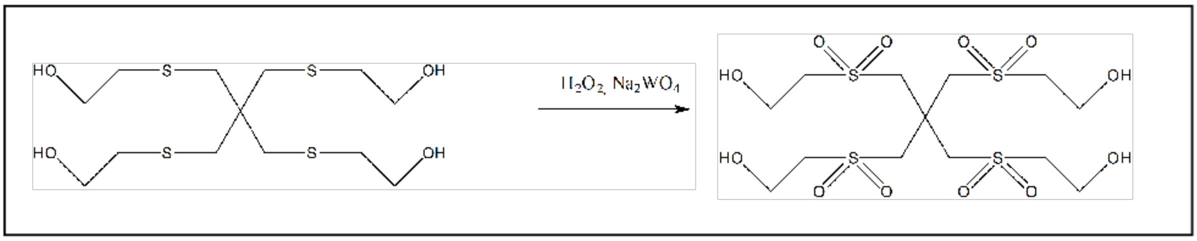
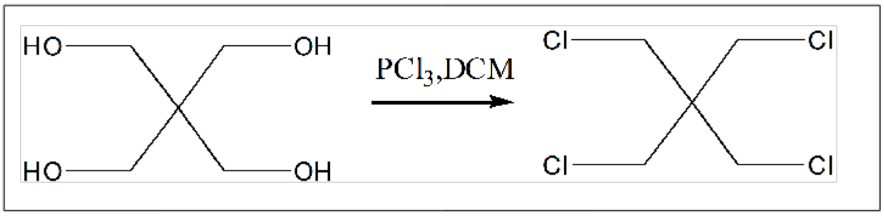


PROCEDURES FOR INDIVIDUAL REACTION STEPS

1. In the first step of the reaction 2,2-Bis(hydroxymethyl)propane1,3-diol (pentaerythritol) is chlorinated with the help of PCl_3

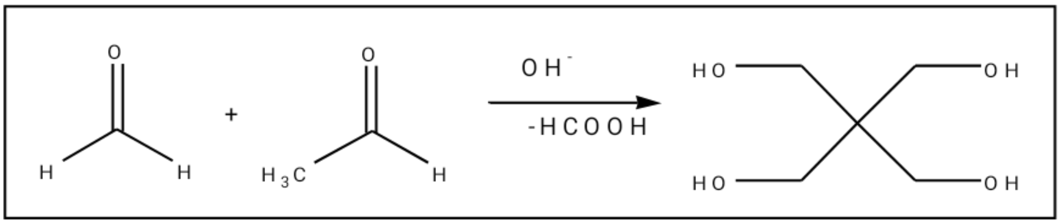


The reaction was carried out using following procedure.

1. In a 250 ml round bottom flask, 3g of pentaerythritol (22.03 mmol) is dissolved in dichloromethane and was taken and kept at 0 ^{0}C in an icebath.
2. 20 ml of PCl_3 (excess) was slowly added in dropwise and solution was stirred at room temperature for 24 hours.
3. After the completion of reaction, the solvent was removed by distillation to yield a white halogenated precipitate of 2,2-bis(chloromethyl)1,3-dichloropropane.

Pentaerythritol

Synthesis



Commercial uses of Pentaerythritol

The main commercial and industrial role of mono pentaerythritol is as a chemical intermediate as its basic material for polymer production. It is mainly employed in the manufacture of alkyd resins and paints, where it enhances the drying speed hardness and water resistance of this paints.

The second largest market for mono pentaerythritol is in production of neopolyol ester for synthetic lubricants. It enhances both the hydrolytic resistance and viscosity control of this lubricant.

It is also employed in preparation of polyvinyl chloride stabilizer, plasticizers, antioxidant, adhesive and sealant, varnishes and inks. It is also use to make radiation curing monomers and rosin ester.

Health hazards of Pentaerythritol.

The pentaerythritol is not at all hazardous to health and environment.

First aid measures.

- Incase if one inhaled fumes of pentaerythritol first aid measure is not require but person may expose himself / herself to fresh air for personal comfort.
- If pentaerythritol gets in contact with eye or skin one must was eye with fresh water and wash skin with soap.
- Incase if someone ingested large quantities of pentaerythritol one must seek medical advice / attention.

Health hazard of phosphorus trichloride

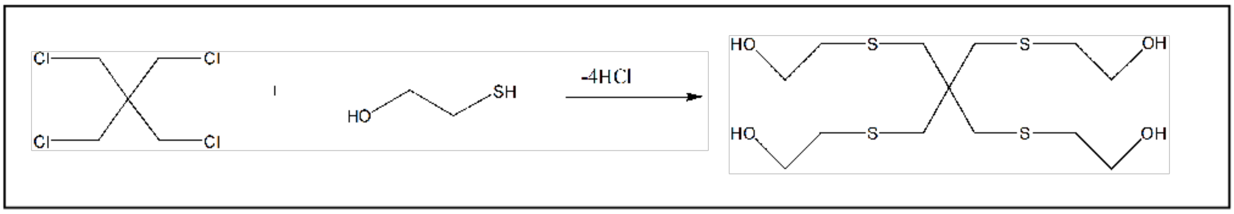
PCl_3 is corrosive and irritating to eyes, skin, and mucous membranes. Inhalation may result in chemical pneumonitis and pulmonary edema.

First aid measures

- If PCl_3 gets in contact with eye, then wash eye for 15 minutes with fresh water and seek immediate medical attention.
- In case of skin contact with PCl_3 one must remove contaminated clothing as rapidly as possible. Flush affected area with excess water and seek immediate medical attention.
- If someone inhaled fumes of PCl_3 then victim should be assisted to uncontaminated area and inhale fresh air.

2. In the second step

2,2bis(chloromethyl)1,3dichloropropane is further reacted with 4 molecules of 2-mercapto ethanol leading to formation of desired product by the elimination of 4 HCL molecules.

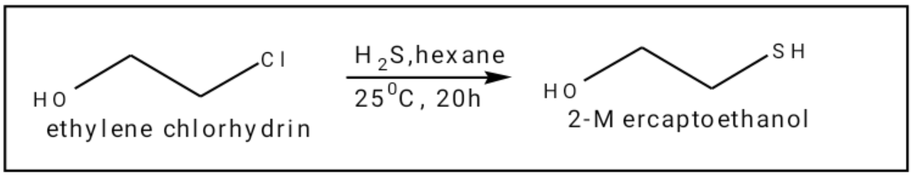


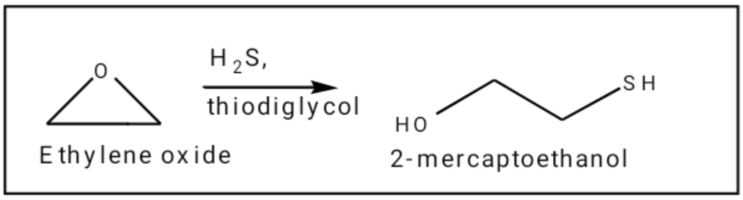
The above reaction was carried out using the following procedure.

1. To 400 parts of ethanol 9.2 parts of metallic sodium was added along with 31.2 parts of 2-mercaptoethanol and 38.8 parts pentaerythrititol tetrachloride this mixture heated under reflux.
2. Deposited NaCl was removed by adding non polar solvent and filtering the solution and solvent ethanol was removed by distillation to give us product tetrakis(2-hydroxyethylthiomethyl)-methane

2- mercaptoethanol

Synthesis





Commercial application of 2-mercaptoethanol

It is use for denaturation of proteins since it cleaves the sulfide bonds that form between thiol groups of cysteine residues. It is often use in preventing protein oxidation and denaturing ribonucleic acid.

Health hazard of mercaptoethanol

- Inhalation of fumes of mercaptoethanol leads to destruction to the tissues of the mucus membrane and upper respiratory tract.
- Can cause skin burns if absorb through skin.
- Contact with eye causes eye burns and toxic if swallowed.

First aid measures

If inhaled, move the person into fresh air. If not breathing, give artificial respiration and consult physician.

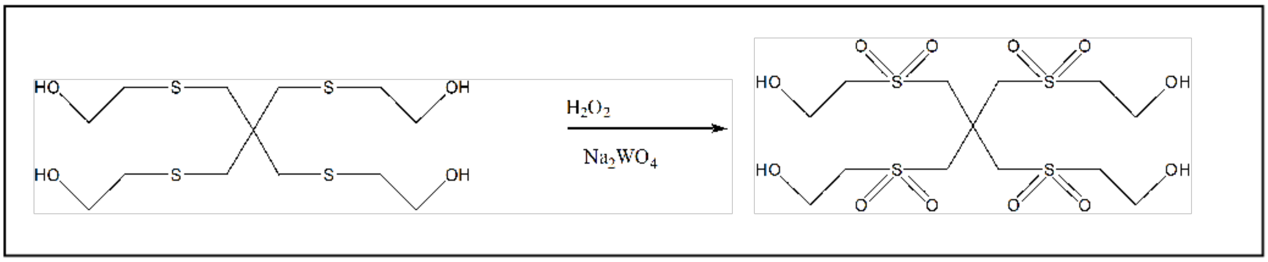
In case of eye contact rinse eyes with plenty of water for 15 minutes and consult a physician. Continue rinsing through eyes during transport to hospital.

In case of skin contact wash, the skin with plenty of water and take immediately to hospital.

If swallowed rinse mouth with water and consult physician.

3.Third Step

In third and final step of reaction the sulfide group of tetrakis(2-hydroxyethylthiomethyl)-methane are oxidize to sulfone group using hydrogen peroxide.



The reaction was carried out using following procedure

1. In 100 ml round bottom flask 2mmol of our sulfide solution was taken in a 1:1 mixture of methanol and DCM (10ml)
2. 30% of hydrogen peroxide (3-8 equivalent) was added along with tungsten oxide catalyst
3. The reaction mixture was stirred magnetically at room temperature the progress of reaction was monitored using TLC.
4. After completion the reaction mixture was filtered off and rinsed twice using 25-30ml DCM
5. Excess solvent was removed under reduced pressure.

Experimental work

Step 1

Aim: Chlorination of pentaerythritol to pentaerythritol tetrachloride

Apparatus required: 100mL round bottom flask, hot plate, magnetic needle, dropping funnel.

Chemicals required: pentaerythritol, thionyl chloride, pyridine, ethanol.

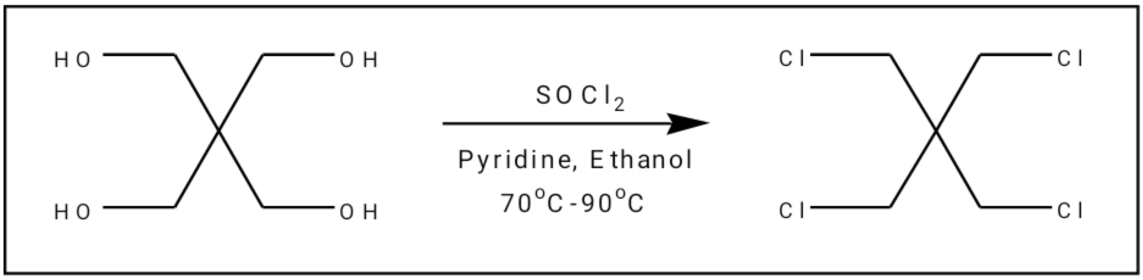


Figure 1: Chlorination of pentaerythritol to pentaerythritol tetrachloride

- To 100mL round bottom flask 11.5mL of pyridine was added.
- The mixture was kept for stirring by maintaining temperature between 70 – 90°C on hot plate.
- To above mixture 12.8mL of thionyl chloride was added dropwise with help of dropping funnel over course of 1 – 2 hrs.
- When addition was over the reaction mixture was heated overnight until no more sulphur dioxide gas is evolved.
- After gas evolution ceases the flask was cooled slightly and to it 50mL cooled water and ethanol mixture was added with stirring which results in precipitation of required product
- The product obtain was filtered using Buchner funnel washed with water and kept for drying.

Step 2

Aim: To convert 1,3-dichloro-2,2bis(chloromethyl)propane to Tetrakis[(2-hydroxyethylthio) methyl] methane.

Apparatus required: 100mL round bottom flask, dropping funnel, hot plate, magnetic needle.

Chemical required: methanol, 2-mercaptoethanol, sodium hydroxide.

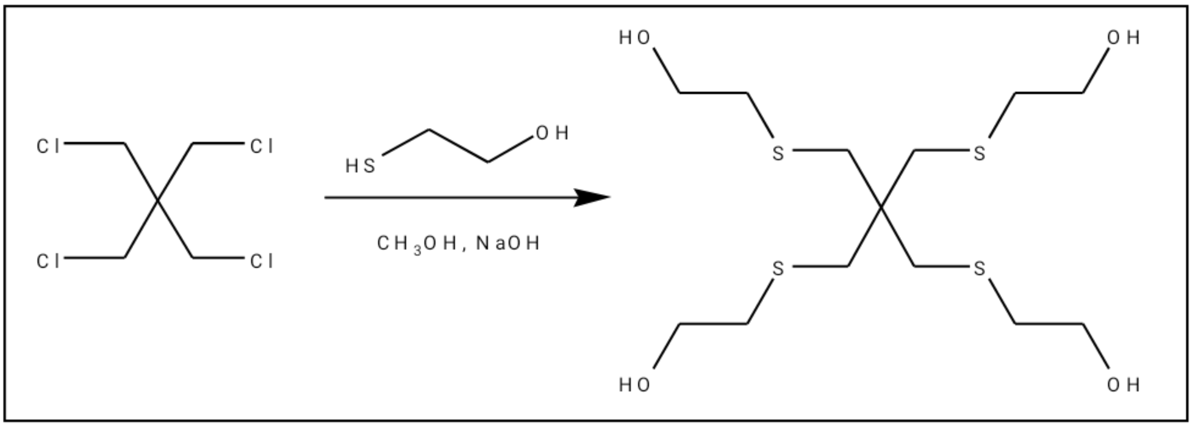


Figure 2: 1,3-dichloro-2,2bis(chloromethyl)propane to Tetrakis[(2-hydroxyethylthio) methyl] methane.

- A solution of 1,3-dichloro-2,2bis(chloromethyl)propane (0.3g,1.429mmol) in 15mL of methanol was added dropwise over 30 minutes with stirring to mixture of 2-mercaptoethanol and 11M sodium hydroxide which was taken in 100mL round bottom flask.
- The reaction mixture was stirred at 90^0C for 3 hr.
- The solvent was evaporated under vacuum and residue was poured in water and extracted with diethyl ether.
- The combined ether extracts were washed with saturated $NaCl_{aq}$ dried over anhydrous magnesium sulphate and filtered.
- The filtrate was evaporated under vaccum.

Result and Discussion

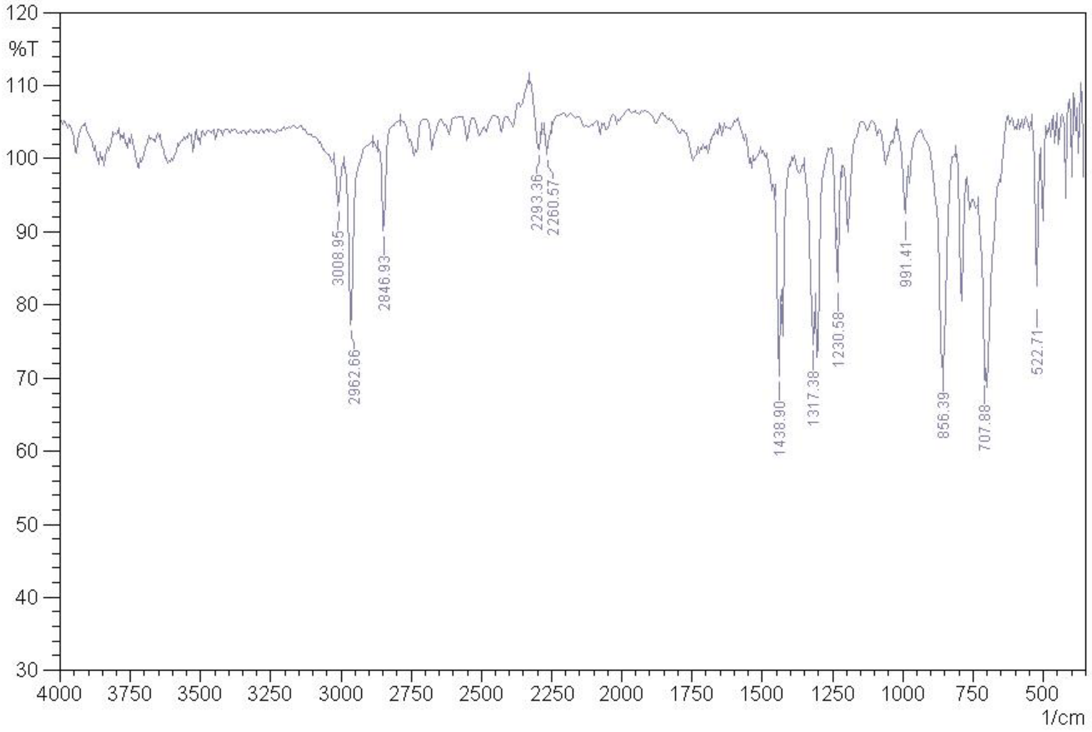


Figure 1: IR spectrum of Pentaerythritol Tetrachloride

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