Chapter II: Materials, Methods and Characterizations
2.1 Materials: The materials used to carry out the current study were obtained as follows

2.1.1 Chemicals: The synthesis of the monomers and initiators were performed using the chemicals obtained from M/s e-Merck, India, M/s Sigma-Aldrich chemicals, USA, M/s Loba chemie, India, M/s Qualigens Fine Chemicals, India and M/s Molychem, India. The chemicals were purified whenever required and dried using the appropriate procedures given in the literature.¹⁰⁹

2.1.2 Monomers: The monomers used in the study were synthesized in special laboratory, with controlled dust environment. The polymers were also prepared in similar environment. The monomers were purified using activated charcoal treatment followed by vacuum distillation wherever possible. Some of the thermally unstable monomers were purified by column chromatography, over 60-120 mesh silica gel, using the mixture of n-hexanes 60 - 80 °C and ethyl acetate.

2.1.3 Initiators: The initiators used for polymerization were IPP and BP. IPP was synthesized in our laboratory, and being highly unstable, was used without further purification. Commercially available moist BP (M/s Loba chemie) was crystallized from chloroform methanol mixture and used after drying.

2.1.4 Plasticizers: Commercially available dioctyl phthalate (M/s Loba chemie) of "GR" grade was used without further purification.

2.2 Mold design: Optical glass plates from (Schott, Germany) were used to assemble the mold. Commercial Teflon sheet of 500 µm thickness was cut in a square shaped gasket having a width of 1.2 - 1.3 cm as shown in figure below and a small opening to inject monomer was made. The gasket was sandwiched between the glass plates previously greased on the sides.
2.2.1 Preparation of films by cast polymerization: Purified monomer is first filtered through a micro filter of pore 500 µm and then through 200 µm pore filter to remove any suspended particles. The monomer is held under a high vacuum of 0.2 mbar for 15 minutes and then dry nitrogen is flushed for 15 minutes to remove dissolved oxygen. The process is repeated twice to remove the dissolved oxygen from the monomer. Initiator and the plasticizer are added to the flask and the contents are homogenized by stirring. The polymerization mixture is taken into a syringe and carefully injected into the mold, through the opening in the teflon gasket. Care was taken to avoid the formation of air bubbles which hinders the process of polymerization. After completely filing the mold, the opening is sealed using a teflon plug and the molds were
sandwiched between flat aluminium plates as shown in the figure 2.2.

Figure 2.2: Mold assembly.

The above molds are placed in a mold pressurizing assembly. It consists of a stainless steel base and a screw-type piston which can be tightened to apply the pressure on the molds. The molds prepared are pressurized during polymerization from time to time using the mold polymerization assembly (Figure 2.3).

Figure 2.3: Mold pressurizing assembly.

The whole assembly is placed into the polymerization bath and heated according to the predetermined heating profile. The molds are tightened periodically to avoid the cracks from shrinkage dur-
ing polymerization. After completion of polymerization, the molds are allowed to cool for 12 hrs and opened.

2.2.2 Polymerization: The molds were sandwiched between aluminium plates in a pressurizing assembly. The polymerization is carried out using heating profiles having a temperature range of 40 - 95 °C and 70 - 95 °C depending on the type of initiator used. The different polymerization heating profiles used are depicted in figure 2.4.

![Fig 2.4](image)

Figure 2.4: Heating profiles for polymerization of different polymers.

The whole assembly is placed between spiral heating coils (figure 2.5) in the polymerization bath. A constant temperature polymerization was employed for some thermally unstable mono-
mers. The bath temperature was controlled by external heating using programmable water bath (Julabo, F 25 HP, Germany) with a temperature accuracy of ± 0.01 °C.

Figure 2.5: Polymerization bath.

2.3 **Study of kinetics of polymerization:** Kinetic of polymerization was studied by analyzing the amount of monomer and initiator concentration at different time intervals. 20 g of purified monomer is first taken in a round bottom flask and flushed with dry nitrogen for 30 minutes. The initiator is added as per the requirements and the contents are mixed thoroughly. 2 g of this mixture is transferred in 8 - 10 test tubes each and flushed again with dry
nitrogen and sealed with a rubber cork. The test tubes are then heated at a specified constant temperature and after particular time interval a test tube is removed and analyzed for its residual unsaturation and initiator concentration. Similarly, all the test tubes are analyzed at particular intervals.

2.3.1 Determination of residual unsaturation and initiator concentration: The amount of unsaturation left or the amount of monomer converted to the polymer can be estimated by Wij’s iodometric estimations. The solutions of Wij's reagent (iodine monochloride in acetic acid), 0.1 N Na$_2$S$_2$O$_3$, 10 % KI solution, 0.1 N KIO$_3$ solution, starch indicator were prepared using the standard methods. The solutions were standardized wherever required.

i) Peroxide estimation: A known quantity of initiator (30 - 50 mg) is dissolved in acetic anhydride and treated with solid KI. The mixture is swirled and kept in dark for 20 minutes. After 20 minutes the mixture is diluted with glacial acetic acid and water. The liberated iodine is titrated against standard 0.01 N Na$_2$S$_2$O$_3$ solution using starch indicator. The chemical processes involved in the reaction are

\[ R-\text{CO-O-O-CO-R} + \text{KI} \quad \rightarrow \quad \text{I}_2 + R-\text{CO-O-K}^+ \quad 2.1 \]

\[ \text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \quad \rightarrow \quad 2 \text{NaI} + \text{Na}_2\text{S}_4\text{O}_6 \quad 2.2 \]

From the relation,

2000 mL of 1 N Na$_2$S$_2$O$_3$ is equivalent to molecular weight of initiator used. The relation can be conveniently used to determine the amount of initiator in the sample. The method can be used to estimate the amount of initiator left during the polymerization kinetic study. 1 g of monomer containing the initiator is dissolved in acetic anhydride and treated with solid KI. Further analysis remains same as given in the procedure above. The amount of initia-
tor can be determined by using the relation

\[ X \times g = \frac{\text{Burette reading} \times \text{Normality of } \text{Na}_2\text{S}_2\text{O}_3 \times \text{Molecular weight}}{2 \times 2000} \]

**ii) Determination of unsaturation:** The method involves a back titration of liberated iodine with standardized 0.1 N \( \text{Na}_2\text{S}_2\text{O}_3 \) solution. A known amount of monomer (30 - 50 mg) is dissolved in chloroform and a known amount of ICl in acetic acid is added. The mixture is kept in the dark for 60 minutes and 20% KI solution is added. The liberated iodine is titrated against standard 0.1 N \( \text{Na}_2\text{S}_2\text{O}_3 \) solution using starch indicator. The chemical reactions involved in the process are

\[
\begin{align*}
2 \text{P-CH}_2\text{-CH=CH}_2 + \text{ICl} & \rightarrow \text{P-CH}_2\text{-CHCl-CH}_2\text{I} + \text{P-CH}_2\text{-CHI-CH}_2\text{Cl} \\
(\text{P} = \text{Polymer chain}) \\
\text{ICl} + \text{KI} & \rightarrow \text{I}_2 + \text{KCl} \\
\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 & \rightarrow 2 \text{NaI} + \text{Na}_2\text{S}_4\text{O}_6 \\
\text{2000 mL of 1 N Na}_2\text{S}_2\text{O}_3 = 1 \text{I}_2 = n \times C = C, \text{ i.e. the molecular weight of the monomer, } n \text{ is the number of double bonds. This method is used to determine the unsaturation amount during the kinetic studies. The 30 - 50 mg of mixture containing the monomer and initiator is dissolved in chloroform and analyzed as per the procedure. Reading corresponding to the initiator is subtracted from the main reading.} \\
\end{align*}
\]

**2.4 Instrumentation:**

**2.4.1 Optical microscope:** The particle tracks were counted after chemical etching using a trinocular optical microscope. The microscope (Axiostar, Carl Zeiss, Germany) had optical magnifications of 5 x, 10 x, 40 x and 100 x.

**2.4.2 Vacuum pump:** A high vacuum pump (Hind Hivac, India) was used to generate vacuum of the order of 0.1 - 0.2 mbar re-
quired to distill monomers and to determine the alpha particle sensitivity of the polymer.

2.4.3 Thickness measurements: The thickness of the films prepared and analyzed is measured, over the entire surface of the films, randomly at 50 different points, for a film of size 8 cm x 8 cm, using a digital thickness gauge (Alpha meter, Para Electronics, India).

2.4.4 Exposure to radiation sources: Polymer samples of size 1 x 1 cm² are cut and exposed to ²⁵²Cf source at a distance of 1 mm. In order to expose the detector to low energy alpha particles, the detector is exposed to alpha particles from the source at a distance of 1, 2 and 3 cm. The exposure assembly is as shown in the figure 2.6 below.

![Figure 2.6: Exposure assembly.](image)

The films are placed on the stage and the height can be adjusted by using the screw nuts.
2.4.5 Etching of the detector film: The films exposed to radiation source are etched in chemical etching bath made of glass as shown in Figure 2.7. The bath is provided with a thermometer, hot water jacket, stainless steel holder and a magnetic stirrer. The apparatus is filled with etchant and heated by external circulation of hot water through the jacket. The polymer samples are placed in stainless steel cage. Once the etching temperature is attained the cage is dipped into the etchant.

![Figure 2.7: Glass assembly for chemical etching of polymer samples.](image)

The bulk etch rate is the important parameter which is analyzed during the process of chemical etching. The bulk etch rate of
the polymer can be determined by following methods

i) **Weight loss method**: In this method the weight of the test film is determined before and after the etching of the polymer film. This method is sometimes referred to as gravimetric method and is limited by the accuracy of mass measurements. The bulk etch rate is determined by using formula.  

\[
V_b = \frac{(M_1 - M_2) T_i}{2 M_2 t}
\]

Where, \(M_1\) and \(M_2\) are final and initial masses respectively, \(T_i\) is initial thickness and \(t\) is the time interval between the two measurements.

ii) **Fission fragment track diameter method**: This is the most frequently used method for determination of bulk etch rate. The rate of change of diameter of fission fragments tracks in the detector material exposed to \(^{252}\text{Cf}\) source after etching is determined at regular intervals. The diameters of fission fragments are determined by using an optical microscope. The bulk etch rate of the polymer was found by using the formula

\[
V_b = \frac{D_t}{2 t}
\]

Where, \(D_t\) is the diameter of fission fragment track and \(t\) is the time.

iii) **The change in thickness method**: The thickness of the material is determined using different methods of thickness measurements over its entire surface. The method can be used for detectors having uniform thickness. However the method renders error due to swelling of the polymer during chemical etching and hence is rarely used.

**2.4.6 Counting of particle tracks under an optical microscope**: The detector films after chemical etching are washed under running tap water and dried under an IR lamp. The dry films are
mounted on glass slide and placed on the microscope stage. The film is focused under the specific magnification and numbers of tracks per view are counted. In a 1 x 1 cm² film 100 views are counted using the X - Y stage. As per the given magnification, area under the observed view was determined using the stage micrometer. The track density was determined using the relationship.

\[
\text{Track density} = \frac{\text{Total number of tracks counted}}{\text{Total number of views} \times \text{area of the view}}
\]

2.4.7 Sensitivity study: The polymer samples which detect alpha and fission fragment particles are anchored on aluminium support and are exposed to \(^{252}\text{Cf}\) source in a vacuum dessicator.

![Diagram of vacuum descicator and exposure film](image)

Figure 2.8: Exposure of SSNTD film to \(^{252}\text{Cf}\) source for sensitivity measurements.

The distance of 5 cm is kept between the source and the
polymer. The films are exposed for 5 hrs at a vacuum of 0.2 mbar, applied using a high vacuum pump. After exposure, the films are etched and increase in the track diameter at every hour interval is noted. Once the diameters of the tracks are determined the alpha sensitivity of the detector film is determined by using the formula.\textsuperscript{17,66,73,76,78,111,113}

\[
S = \frac{1+\left(\frac{d_\alpha}{d_f}\right)^2}{1 - \left(\frac{d_\alpha}{d_f}\right)^2}
\]

Where

d_\alpha is the diameter of the alpha particle track.
d_f is the diameter of fission fragment track.

2.5 Spectral characterization: The monomers after synthesis were characterized using various spectral techniques. IR spectra were recorded on Shimadzu FT-IR spectrophotometer with KBr discs for liquids and KBr/compound powdered mixture for solids. \textsuperscript{1}H and \textsuperscript{13}C spectra were recorded on Bruker 300 MHz spectrophotometer with CDCl\textsubscript{3} as solvent and TMS as an internal standard. Mass spectra were recorded on QStar XL MS-MS system.

2.6 Monomer synthesis:

2.6.1 Allyl chloroformate:\textsuperscript{114,115} Triphosgene (9.3 g, 0.0316 mol) was dissolved in 70 mL dichloromethane in a two neck round bottom flask fitted with rubber septum. The mixture was cooled to 0 °C. Allyl alcohol (5.0 g, 0.086 mol) and pyridine (6.8 g 0.086 mol) were injected through the rubber septums in the reaction flask, simultaneously at such a rate that pyridine always remain in excess in the reaction mixture. After completion of addition, reaction mixture was stirred for 1 hr at 0 °C. The septum was removed and
reaction mixture was washed with $3 \times 25 \text{ mL}$ of ice cold water and the organic layer was dried over anhy. $\text{Na}_2\text{SO}_4$. Dichloromethane was removed by fractional distillation to afford (6.9 g, 67 %) allyl chloroformate. Figure 2.9 gives infrared spectrum of allyl chloroformate $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3091, 1770, 1267 and 1157 see next page 85).

![Scheme 2.1: Synthesis of allyl chloroformate.](image)

**2.6.2 Isopropyl chloroformate:**$^{73,115}$ A procedure was same as that used for the preparation of allyl chloroformate (Section 2.6.1) except that, isopropyl alcohol was used instead of allyl alcohol.

**2.6.3 Diallyl carbonate:**$^{116}$ A process earlier standardized in our laboratory was used to prepare diallyl carbonate. Allyl alcohol (300 mL, 4.4 mol) was taken in a round bottom flask along with 60 mL of cyclohexane. The mixture was heated to 60 °C under vigorous stirring and KOH (1.5 g) was added. The reaction was heated to around 70 °C and drop by drop dimethyl carbonate (123.5 mL, 1.47 mol) was added through a dropping funnel. After completion of addition, the mixture of methanol and cyclohexane was removed by azeotropic distillation using a dufton column for 6 hrs. After removal of 60 mL of methanol the unreacted allyl alcohol and dimethyl carbonate were removed by downward normal distillation.

The unreacted allyl alcohol and dimethyl carbonate could be recycled in the next batch of monomer synthesis. The mixture was washed with $3 \times 50 \text{ mL}$ distilled water and dried over anhy. $\text{Na}_2\text{SO}_4$. The product was finally distilled under reduced pressure to give pure diallyl carbonate (118 g, 56.73 %) as a colorless liquid.
Figure 2.9: Infrared spectrum of allyl chloroformate.
Infrared spectrum and the HRMS of DAC is given in Figures 2.10 and 2.11 respectively (pages 87-88). $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3088, 1747, 1253 and 968; m/z (TOF ES) 143.0708 ($\text{M}^+ + \text{Na}$, C$_7$H$_{10}$O$_3$ requires 143.0705)

**2.6.4 Allyl diglycol carbonate:** Diethylene glycol (12 g, 0.113 mol) was taken in a three neck flask equipped with thermometer, a dropping funnel and a magnetic stirrer. Diallyl carbonate (160 g, 1.13 mol) was charged in the flask and heated using oil bath under dry nitrogen atmosphere. At temperatures of around 60 °C, 500 mg of KOH was added. The temperature was raised to 114 °C and the allyl alcohol was continuously distilled out. After about 13 g of allyl alcohol was distilled, diallyl carbonate was distilled under reduced pressure. The crude ADC was suspended in 50 mL diethyl ether, washed with 3 x 30 mL of distilled water and dried over anhy. Na$_2$SO$_4$. Ether was carefully removed on water bath and finally, ADC monomer was distilled under reduced pressure of 0.2 mbar at 160 °C. Pure ADC (31.42 g, 80.63 %) was obtained as colorless liquid. The synthetic scheme for the process is as follows.

![Chemical reaction image](image-url)
Figure 2.10: Infrared spectrum of diallyl carbonate.
Figure 2.11: HRMS of diallyl carbonate.
Figure 2.12: Infrared spectrum of allyl diglycol carbonate.
**Diallyl sulphite (DAS):**\(^{118,119,120,121}\) Allyl alcohol (200 g, 3.44 mol) and 50 mL of dichloromethane was charged in a three neck flask fitted with a reflux condenser and a thermometer pocket. The reaction mixture was cooled to 10 °C and drop by drop thionyl chloride (205.81 g, 1.73 mol) was added to the reaction mixture. A vigorous reaction started and large amount of HCl gas was evolved. After complete addition of thionyl chloride the mixture was refluxed until no more gas was evolved. The solvent was removed and the product was vacuum distilled to get diallyl sulphite (180 g, 64 %) as a colorless liquid. The reaction scheme is as depicted below.

![Reaction Scheme](image)

**Scheme 2.4: Synthesis of Diallyl sulphite.**

The structure of DAS was characterized by following spectral data. 
\(\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1} 3088, 1647, 1207, \text{ and } 972; \delta H(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si}) 4.45 (4H, m, 2 x SO-O-CH\_2), 5.23 (4H, dd, 2 x CH\_2=), 5.85 (2H, m, 2 x -CH\_=); \delta C(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si}) 64.1 \text{ppm} (2 x t), 120.3 (2 x t), 133.3 (2C x d). m/z (TOF ES) 185.0248 (M\text{+} + \text{Na}. \text{C}_6\text{H}_{10}\text{O}_3\text{S requires } 185.0246)\)

The different spectra (IR, PMR, CMR & HRMS) recorded are given in Figures 2.13 to 2.16 respectively (pages 91-94).
Figure 2.13: Infrared spectrum of diallyl sulphite.
Figure 2.14: $^1$H NMR spectrum of diallyl sulphite.
Figure 2.15: $^{13}$C NMR spectrum of diallyl sulphite.
Figure 2.16: HRMS of diallyl sulphite.

Calcd Mass = 185.0246 \((M+Na)^+\)
2.6.6 Allyl diglycol sulphite (ADS):\textsuperscript{122,123} In a three neck round bottom flask provided with a dry nitrogen gas inlet, a thermometer and a distillation assembly was charged (150 g, 0.93 mol) of DAS. Diethylene glycol (9.858 g, 0.093 mol) was added the mixture was flushed with a stream of dry nitrogen. The temperature of the reaction mixture was raised to 60 °C and 1 g of KOH was added. The mixture was heated under stirring to 110 °C and maintained until allyl alcohol (10.80 g, 0.17 mol) gets distilled. After completion of reaction the excess DAS was removed by vacuum distillation. The remaining mixture was taken in ether and washed with 3 x 50 mL of distilled water. The product was distilled under reduced pressure of 0.02 mbar at 160 °C to afford ADS (23.36 g, 80 %) as a light brown colored liquid. The reaction scheme is as depicted below.

```
\begin{align*}
\text{Diethylene glycol} & \quad + \quad \text{Diallyl sulphite} \\
& \rightarrow \quad \text{Allyl Diglycol Sulphite} \\
& + \quad 2 \text{Allyl alcohol}
\end{align*}
```

Scheme 2.5: ADS monomer synthesis.

The structure of ADS was characterized by recording its IR, \textsuperscript{1}H NMR, \textsuperscript{13}C NMR and mass spectral data and is given in Figures 2.17 to 2.20 (See next pages 96 - 100).

\begin{align*}
\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1} & \quad 3089, 1646, 1356, 1205; \\
\delta H(300 \text{ MHz; CDCl}_3; \text{Me}_4\text{Si}) & \quad 3.58 (4H, t, \text{-O-CH}_2\text{-CH}_2\text{-}), 3.88 (4H, t, 2 \times \text{SO-O-CH}_2\text{-CH}_2\text{-}), 4.36 (4H, m, 2 \times \text{-SO-O-CH}_2\text{-}), 5.21 (4H, dd, 2 \times \text{CH}=), 5.77 (2H, m, 2 \times \text{CH}=); \\
\delta C(300 \text{ MHz; CDCl}_3; \text{Me}_4\text{Si}) & \quad 62.6 (2 \times t), 64.2 (2 \times t), 70.85 (2 \times t), 120.5 (2 \times t), 133.3 (2 \times d), \text{m/z (TOF ES)} 337.0384 (\text{M}^+ + \text{Na}. \text{C}_{10}\text{H}_{16}\text{O}_{7}\text{S}_2 \text{ requires 337.0392})
\end{align*}
Figure 2.17: Infrared spectrum allyl diglycol sulphite.
Figure 2.18: $^1$H NMR spectrum of allyl diglycol sulphite.
Figure 2.19: $^{13}$C NMR spectrum of allyl diglycol sulphite.
Figure 2.20: HRMS of allyl diglycol sulphite.
2.6.7 Diethyleneglycol bis(allyl sulfonate):\(^{124,125,126}\)

**i) Synthesis of sodium allyl sulfonate:**- Allyl chloride (200 g, 2.61 mol) was added drop wise to a stirred solution of aqueous sodium sulphite (370.62 g, 2.62 mol) in a three neck flask provided with a reflux condenser and a thermometer. After completion of addition, the reaction mixture was stirred at 60 °C for 6 hr. Water was carefully removed by distillation and the solid obtained was recrystallized using 4:1 ethanol:water mixture. Sodium allyl sulfonate (263.52 g, 70 %) was obtained as a white solid. The IR spectrum is depicted in Figure 2.21 (See page 101). \(v_{\text{max}}(\text{KBr})/\text{cm}^{-1}\) 3095, 1639, 1371, 1165. The synthetic scheme is given below.

\[
\begin{align*}
\text{ Allyl chloride} & \quad \text{ Sodium sulphite} & \rightarrow & \quad \text{ Allyl sodium sulfonate} & \quad \text{ Sodium chloride}
\end{align*}
\]

Scheme 2.6: Synthesis of allyl sodium sulfonate.

**ii) Synthesis of Allyl chloro sulfonate:**- Sodium allyl sulfonate (100 g, 0.69 mol) was reacted with phosphorous oxy chloride (107.45 g, 0.7 mol) and the mixture was heated at 120 °C for 8 hr. The brown colored mixture was poured in ice water under vigorous stirring and extracted in 4 x 50 mL diethyl ether. The ether was carefully evaporated and the mixture was vacuum distilled to get chloro allyl sulfonate (65 g, 67 %) as a colorless liquid. The synthetic scheme is given below. The IR spectrum of the compound is shown in Figure 2.22 (See page 102). \(v_{\text{max}}(\text{KBr})/\text{cm}^{-1}\) 3086, 1641, 1220, 1205.

\[
\begin{align*}
\text{ Allyl sodium sulfonate} & \quad \text{ Phosohorous oxy chloride} & \rightarrow & \quad \text{ Allyl chloro sulfonate}
\end{align*}
\]

Scheme 2.7: Allyl chloro sulfonate synthesis.
Figure 2.21: Infrared spectrum of sodium allyl sulfonate.
Figure 2.22: Infrared spectrum of allyl sulfonyl chloride.
iii) **Diethylene glycol bis(allyl sulfonate):** Diethylene glycol (10 g, 0.094 mol) was cooled to 0 °C in a two neck flask having a thermometer pocket and dropping funnel. Chloro allyl sulfonate (26.7 g, 0.19 mol) was added to the flask and the mixture was stirred vigorously. Pyridine (15 g, 0.19 mol) was added drop by drop at such a rate that the temperature remained in the range of 0-5 °C. After this is complete, the mixture was stirred for further 1 hr. The product was suspended in 50 mL water and extracted with 3x50 mL of diethyl ether. The product obtained was purified by column chromatography using 3:7 v/v ethyl acetate/n-hexanes to afford DEAS (23.11 g, 78 %) as a white crystalline solid. The Scheme 2.8 depicts the reaction involved.

![Scheme 2.8: Synthesis of Diethylene glycol bis(allyl sulfonate)](image)

The structure of DEAS was characterized by recording its IR, $^1$H NMR, $^{13}$C NMR and HRMS data. Figures 2.23 to 2.26 (See page 104 - 107) give IR, PMR, CMR and HRMS spectra respectively, of DEAS monomer.

$\nu_{\text{max}}$(KBr)/cm$^{-1}$ 3089, 1641,1352, 1165; $\delta$(300 MHz; CDCl$_3$; Me$_4$Si) 3.7 (4H, t, 2 x SO$_2$-CH$_2$-),3.8 (4H, t, 2 x O-CH$_2$-), 4.3 (4H, t, 2 x SO$_2$-O-CH$_2$-), 5.4 (4H, dd, 2 x CH$_2$=), 5.9 (2H, m, 2 x CH=,); $\delta$(300 MHz; CDCl$_3$; Me$_4$Si) 54.9 (2 x t), 69.1 (2 x t), 69.5 (2 x t), 124.4 (2 x d), 124.72 (2 x t), m/z (TOF ES) 337.0378 (M$^+$ + Na. C$_{10}$H$_{18}$O$_7$S$_2$ requires 337.0392)
Figure 2.23: Infrared spectrum of diethylene glycol bis(allyl sulfonate).
Figure 2.24: $^1$H NMR spectrum of diethylene glycol bis(allyl sulfonate).
Figure 2.25: $^{13}$C NMR spectrum of diethylene glycol bis(allyl sulfonate).
Figure 2.26: HRMS of diethylene glycol bis(allyl sulfonate).
**2.6.8 Diethylene glycol bis(n-propyl sulfonate) (DEPS):**

DEAS (1 g, 3.2 mmol) monomer was dissolved in 20 mL ethyl acetate and 200 mg of 10% Pd/C catalyst was added to the reaction mixture. The mixture was hydrogenated at 3 Kg/cm² of hydrogen pressure using the hydrogenation apparatus for 40 hrs. The reaction mixture was filtered and concentrated to get 0.888 g of crude product. The product was finally purified by column chromatography using silica gel and 1:1 v/v ethyl acetate/n-hexanes mixture as eluent to afford DEPS (0.754 g, 74%) as a colorless liquid.

![Diagram](image)

**Scheme 2.9: DEPS monomer synthesis.**

The structure of DEPS was characterized by using its IR, ¹H NMR & ¹³C NMR spectral data (Figures 2.27 to 2.29, See page 109 - 111)

\[
\begin{align*}
\nu_{max}(\text{KBr})/\text{cm}^{-1} &\quad 1346, 1165, 935; \\
\delta H(300 \text{ MHz; CDCl}_3; \text{Me}_4\text{Si}) &\quad 1.1 (6H, p, 2 \times -\text{CH}_2\text{-CH}_3), 1.9 (4H, m, 2 \times -\text{CH}_2\text{-CH}_3), 3.1 (4H, p, 2 \times -\text{CH}_2\text{-SO}_2^-), 3.8 (4H, p, 2 \times -\text{O-CH}_2^-), 4.3 (4H, p, 2 \times -\text{SO}_2^-\text{-O-CH}_2^-); \\
\delta C(300 \text{ MHz; CDCl}_3; \text{Me}_4\text{Si}) &\quad 12.8 (2 \times q), 17.2 (2 \times t), 52.2 (2 \times t), 68.2 (2 \times t), 69.1 (2 \times t)
\end{align*}
\]
Figure 2.27: Infrared spectrum of diethylene glycol bis(n-propyl sulfonate) in ethyl acetate.
Figure 2.28: $^1$H NMR spectrum of diethylene glycol bis(n-propyl sulfonate).
Figure 2.29: $^{13}$C NMR spectrum of diethylene glycol bis(allyl sulfonate).
2.6.9 Pentaerythritol terakis(allyl carbonate): In a three neck flask cooled to 0 °C, Pentaerythritol (10 g, 0.073 mol) was suspended in 50 mL benzene containing pyridine (23.82 g, 0.302 mol) The flask was provided with a mechanical stirrer, a dropping funnel and a thermometer. Allyl chloroformate (36.35 g, 0.302 mol) was added drop by drop with vigorous stirring. The temperature was not allowed to rise above 5 °C. After complete addition of allyl chloroformate the mixture was stirred for 1hr at room temperature. The mixture was washed with 1 × 50 mL 2 N HCL, 3 × 50 mL of water and organic layer dried over anhy. Na₂SO₄. The solvent was removed under vacuum to afford 27.21 g of crude product. The product was purified by activated carbon treatment followed by column chromatography using 3:7 v/v ethyl acetate/n-hexanes mixture to get (26.13 g, 75 %) light yellow liquid. The structure of PETAC was characterized by its IR, PMR CMR and mass spectral data given in Figure 2.30 to 2.33 (page 113 - 116).

\[
\text{Pentaerythritol Allylchloroformate} \quad \text{Benzene} \quad \text{Pyridine} \quad \text{Pentaerythritol tetrakis(Allylcarbonate)}
\]

Scheme 2.10: Synthesis of PETAC monomer.

\[
\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1} \ 1751, 1371, 1244,986; \delta H(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si}) \ 4.18 (8H, s, 4 x -C-\text{CH}_2), 4.54(8H, t, 4 x -O-\text{CH}_2-\text{CH}=), 5.22 (4H, dd, 4 x -\text{CH}=-), 5.84(8H, m, 4 x \text{CH}_2=); \delta C(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si}) \ 43.9 (1 x C), 66.6 (4 x t), 70.2 (4 x t), 120.6(4 x t), 132.6 (4 x d), 155.8 (4 x s); m/z (TOF ES) 495.1476 (M⁺ + Na). \text{C}_{21}\text{H}_{28}\text{O}_{12} \text{ requires } 495.1478)
Figure 2.30: Infrared spectrum of Pentaerythritol tetrakis(allyl carbonate).
Figure 2.31: $^1$H spectrum of pentaerythritol tetrakis(allyl carbonate).
Figure 2.32: $^{13}$C NMR spectrum of pentaerythritol tetrakis(allyl carbonate).
Figure 2.33: Mass spectrum of pentaerythritol tetrakis(allyl carbonate).
2.6.10 Isopropylperoxydicarbonate: Isopropyl chloroformate (10 g, 0.082 mol) was taken in a two neck flask provided with a thermometer pocket and a magnetic stirrer. The flask was cooled using a cryostat and the temperature inside the flask was maintained at 2 °C. Na₂O₂ (3.28 g, 0.042 mol) prepared from aq. H₂O₂ and aq. NaOH was added drop by drop at such a rate that temperature inside the flask does not rise above 6 °C. After completion of addition, the mixture was stirred for further 1 hr at temperature between 5-10 °C. The product obtained was extracted in dichloromethane and washed with 2 x 20 mL ice cold water. The organic layer was dried over anhy. Na₂SO₄ and solvent evaporated under reduced pressure at a temperature below 20 °C. The product obtained was stored at temperature below 0 °C. The IPP initiator so obtained was analyzed by iodometry and used for polymerization without further purification. The IR spectrum of the compound is shown in Figure 2.34, page 118. v_max(KBr)/cm⁻¹ 2987, 1797, 1209,1095. The synthetic scheme is given below.

\[
\begin{align*}
H₂O₂ + 2NaOH & \rightarrow Na₂O₂ + H₂O \\
\text{2-} & \text{Cl} \text{-O} & \rightarrow \text{NaOONa} & \rightarrow \text{O-} \text{-O} \text{-O} \text{-} \text{Cl}
\end{align*}
\]

Isopropylperoxydicarbonate

Scheme 2.11: IPP initiator synthesis.

PRECAUTIONS:

1) Initiator should not be prepared in large quantities as it degrades violently.

2) Initiator should be stored always below 0 °C.

3) Rapid drying should be performed on anhy. Na₂SO₄.

4) Initiator should be analyzed before use.
Figure 2.34: Infrared spectrum of IPP initiator.
2.6.11 Pentaerythritol bis(allyl carbonate) bis(allyl sulfonate): The monomer was synthesized as a white solid product using multi step strategy. However the product is highly unstable and decomposes on storage. The synthetic is as discussed below.

**Pentaerythritol mono(benzal):**\(^{130}\) Pentaerythritol (50 g, 0.37 mol) was dissolved in 360 mL water containing 2 mL of concentrated HCl in a three neck flask provided with magnetic stirrer, a dropping funnel and a thermometer. Under vigorous stirring, benzaldehyde (40.83 mL, 0.37 mol) was added to the flask drop by drop. After complete addition, the mixture was stirred for 1 hr. The white precipitate obtained was filtered on a Buckner funnel and washed with alkaline cold water. The solid product obtained was refluxed in 80 mL toluene and filtered. The filtrate obtained was cooled at 0 °C to crystallize the product which was filtered and dried to obtain the pentaerythritol mono(benzal) (56.37 g, 68.45 %) as a white solid.

\[
\begin{align*}
\text{HO} & \quad \text{OH} & \quad \text{HO} & \quad \text{OH} \\
\text{HO} & \quad \text{OH} & \quad \text{Ph} & \quad \text{H}
\end{align*}
\]

Pentaerythritol  
Benzaldehyde  
Pentaerythritol mono(benzal)

Scheme 2.12: Pentaerythritol mono(benzal).

**Pentaerythritol mono(benzal) bis(allyl carbonate):**
Pentaerythritol mono(benzal) (25 g, 0.112 mol) was suspended in diallyl carbonate (159 g, 1.12 mol) in a three necked flask fitted with a distillation head, dry nitrogen inlet and a thermometer pocket. Nitrogen was bubbled and the reaction was heated to 60 °C using an oil bath. 1 g of KOH was added and the temperature was raised to 110 °C, when allyl alcohol distills out from the mixture. After about (12 g, 0.224 mol) of allyl alcohol was distilled and reaction
was allowed to cool. The mixture was taken in ether and washed with $3 \times 50$ mL distilled water. The organic layer was dried over anhy. $\text{Na}_2\text{SO}_4$. Ether was evaporated and the mixture was vacuum distilled to remove diallyl carbonate. The product remained in distillation flask as a light brown liquid which was used without further purification in next step. The synthetic scheme is given below.

Scheme 2.13: Synthesis of Pentaerythritol mono(benzal) bis(allyl carbonate).

**Pentaerythritol bis(allyl carbonate):** Pentaerythritol mono(benzal) bis(allyl carbonate) (20 g, 0.05 mol) was placed in a two neck flask provided with fractional distillation setup. 120 mL of 1:1 acetic acid:water mixture was added and the flask was heated to 120 °C. Benzaldehyde (5 g, 0.047 mol) was removed by azeotropic distillation. Finally, acetic acid and water was removed by vacuum distillation. Pentaerythritol bis(allyl carbonate) (11.32 g, 73 %) was obtained as a white solid.

Scheme 2.14: Synthesis of Pentaerythritol bis(allyl carbonate).

The IR spectra of the compound is shown in Figure 2.35, Page 122.
Pentaerythritol bis(allyl carbonate) bis(allyl sulfonate):

Recrystallised pentaerythritol bis(allyl carbonate) (5 g, 0.0164 mol) was cooled to 10 °C and pyridine (2.6 g, 0.0328 mol) was added along with 20 mL dichloromethane. Allyl sulfonyle chloride (4.6 g, 0.0328 mol) was added drop by drop and temperature maintained below 15 °C during the course of addition. The mixture was stirred for 1 hr at room temperature. The organic layer was washed with 1 × 20 mL of 2 N HCl and 3 × 20 mL distilled water. The organic layer was dried over anhy. Na$_2$SO$_4$ and solvent was removed under vacuum. The product was purified by silica gel column chromatography using 3:7 v/v ethyl acetate/n-hexanes mixture as a white solid. The IR spectrum of the product (Figure 2.36, Page 123) showed complete conversion of the starting. $v_{\text{max}}$(KBr)/cm$^{-1}$ 3086, 1751, 1647, 1246, 968. However, the PMR shows more peaks in addition to the product peaks (Figure 2.36, Page 124). Decomposition can be seen in the HRMS (Figure 2.38, Page 125) of the product which suggest formation of the following product from the M+H peak observed at m/z 307 by nucleophilic substitution reaction.
Figure 2.35: Infrared spectrum of Pentaerythritol bis(allyl carbonate).
Figure 2.36: Infrared spectrum of Pentaerythritol bis(allyl carbonate) bis(allyl sulfonate).
Figure 2.37: $^1$H NMR of Pentaerythritol bis(allyl carbonate) bis(allyl sulfonate).
Figure 2.38: HRMS of Pentaerythritol bis(allyl carbonate) bis(allyl sulfonate).
2.6.12 Pentaerythritol tetrakis(allylsulfonate)PETAS: The success of the PETAC monomer encouraged us to prepare the PETAS monomer as the polymer of the monomer would have had more vulnerable sulfonate group in addition to high crosslinks in the matrix. Pentaerythritol was reacted with allyl sulfonyl chloride in presence of base to get the desired monomer. The synthetic scheme proposed for the synthesis is as illustrated.

Scheme 2.15: Pentaerythritol tetrakis(allylsulphonate)PETAS.

Table 2.1 gives different reaction conditions tried to prepare the PETAS monomer. However, all the attempts in this direction failed. In some cases, no product was formed, whereas, in other cases, a tarry product material was obtained. The IR spectra of the tarry product is shown in figure 2.39, Page 128. $v_{\text{max}}$(KBr)/cm$^{-1}$ 1635, 1372, 1166, 948.

<table>
<thead>
<tr>
<th>Reaction condition</th>
<th>Base</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene reflux</td>
<td>Not added</td>
<td>No product</td>
</tr>
<tr>
<td>Neat</td>
<td>Not added</td>
<td>No product</td>
</tr>
<tr>
<td>RT, benzene</td>
<td>Pyridine</td>
<td>Black tarry product</td>
</tr>
<tr>
<td>0 °C, benzene</td>
<td>Pyridine</td>
<td>Black tarry product</td>
</tr>
<tr>
<td>0 °C, benzene</td>
<td>Triethyl amine</td>
<td>Black tarry product</td>
</tr>
<tr>
<td>0 °C, benzene</td>
<td>NaOH</td>
<td>No product</td>
</tr>
<tr>
<td>0 °C</td>
<td>aq. NaOH</td>
<td>No product</td>
</tr>
<tr>
<td>0 °C, Aliquat, DCM</td>
<td>NaOH</td>
<td>No product</td>
</tr>
</tbody>
</table>
Table 2.1: Reaction conditions used for synthesis of PETAS.

<table>
<thead>
<tr>
<th>Temperature, Solvent</th>
<th>Reactant</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 °C, Aliquat, DCM</td>
<td>Pyridine</td>
<td>Black tarry product</td>
</tr>
<tr>
<td>0 °C</td>
<td>aq. Na2CO₃</td>
<td>No product</td>
</tr>
<tr>
<td>0 °C, DCM</td>
<td>Pyridine</td>
<td>Black tarry product</td>
</tr>
<tr>
<td>0 °C, Dioxane</td>
<td>n-BuLi</td>
<td>No product</td>
</tr>
<tr>
<td>0 °C, Dioxane</td>
<td>NaH</td>
<td>No product</td>
</tr>
</tbody>
</table>

2.7 X-Ray Characterization of DEAS: It was observed that DEAS was solid and melted at 53 °C, whereas, its functional isomer ADS with same molecular formula of C₁₀H₁₈O₇S₂ was liquid. The single crystal X-ray studies were performed on the monomer which showed that the molecules are involved in several weak C-H...O interactions. The crystal structure of the title compound shows that the molecules are located with the ether oxygen atom (O₁) on a 2-fold axis with one half of the molecule constituting the asymmetric unit.

Figure 2.40: Crystal structure of DEAS showing the atom labeling scheme. Displacement ellipsoids are drawn at 30 % probability level. The O₁ atom is situated on a two-fold axis.

From the analysis of the structure of DEAS one finds that
Figure 2.39: Infrared spectrum of Pentaerythritol tetrakis(allyl sulfonate). (tarry product)
each molecule is hydrogen bonded to four symmetry related molecules with the aid of C-H...O interactions. These O...H contacts are shorter than the sum of their Van der Waals radii.\footnote{132}

![Diagram of molecular structure with hydrogen bonds](image)

Figure 2.41: A view of the surrounding showing it's linking to four symmetry related molecules.

2.8 FTIR spectra of various polymers: The FTIR spectra of polymers were recorded and are given in Figures 2.42 to 2.49 (See next pages 130 - 137).

2.9 Photomicrographs of nuclear tracks in various polymeric track detectors.
Photomicrographs of nuclear tracks (alphas from $^{252}$Cf or $^{239}$Pu and fission fragments from $^{252}$Cf) were recorded for various polymers prepared during this work. Some photomicrographs are given below. The experimental conditions are mentioned along with respective photomicrograph. (See next pages 138 - 142).
Figure 2.48: Infrared spectrum of PETAC homopolymer.
Figure 2.47: Infrared spectrum of DEAS:ADC 1:1 w/w copolymer.
Figure 2.46: Infrared spectrum of DEAS homopolymer.
Figure 2.45: Infrared spectrum of ADS:ADC 1:9 w/w copolymer.
Figure 2.44: Infrared spectrum of DAS:ADC 2:8 w/w copolymer.
Figure 2.43: Infrared spectrum of DAS homopolymer.
Figure 2.42: Infrared spectrum of CR-39™.
Figure 2.49: Infrared spectrum of PETAC:ADC 1:1 w/w copolymer.
DEAS:ADC 3:7 w/w: Alpha and fission fragment tracks. Exposed to $^{252}$Cf, 5 cm at 0.02 mbar, Optical zoom: 100X

DEAS:PETAC 3:7 w/w: Alpha and fission fragment tracks. Exposed to $^{252}$Cf, 5 cm at 0.02 mbar, Optical zoom: 400X
DEAS: ADC: PETAC 3:3:4 w/w/w: Alpha autoradiograph.
Exposed to $^{239}$Pu, 1 mm, Optical zoom: 400X

DEAS: ADC 3:7 w/w: Alpha autoradiograph.
Exposed to $^{239}$Pu, 1 mm, Optical zoom: 400X
DAC:ADC 1:1 w/w: Alpha and fission fragment tracks.
Exposed to $^{252}$Cf, 5 cm at 0.02 mbar, Optical zoom: 100X

DEAS:ADC 2:8 w/w: Alpha autoradiograph.
Exposed to $^{239}$Pu, 1 mm, Optical zoom: 400X
PETAC:ADC 4:6 w/w: Fission fragment tracks.
Exposed to $^{252}$Cf at 1 mm, Optical zoom: 400X

DEAS:PETAC 4:6 w/w: Alpha and fission fragment tracks.
Exposed to $^{252}$Cf, 5 cm at 0.02 mbar, Optical zoom: 100X
PETAC:ADC 1:1 w/w: Fission fragment tracks.
Exposed to $^{252}$Cf, 1 mm, Optical zoom: 100X

PETAC homopolymer: Alpha autoradiograph.
Exposed to $^{239}$Pu, 1 mm, Optical zoom: 400X