Since the research work was based on stereoregular polymers and the polymers were not available, attempts were made to synthesize stereoregular polyvinyl alcohol through the procedures reported in the literature. Correspondence to get monomers and stereoregular polyvinyl alcohol has been attached in Appendix I.

Vinyltrimethylsilylether (VTMSE) and t-butyl vinyl ether (tBVE) are the vinyl monomer from which stereospecific polyvinyl alcohol can be obtained after polymerization followed by hydrolysis. Since these monomers were not available, attempts were also made to synthesize these monomers.

It is reported that VTMSE monomer polymerises in presence of ethyl aluminium dichloride or stannic chloride as catalyst in different polar and non-polar solvents at -78°C under nitrogen. The polymer obtained from the method cited above is reported to be stereospecific. In toluene it gives isotactic while in dichloromethane it gives syndiotactic polymer. Moreover this is a unique vinyl ether which gives PVA simply by treating the cationic polymerizate with methanol. Stereoregularity of the resulting PVA can be regulated widely using suitable catalyst and solvent. tBVE monomer has been reported to polymerise in presence of
BF$_3$-etherate catalyst at $-78^\circ$C in toluene as solvent under nitrogen atmosphere. This leads to an isotactic polymer after hydrolysis$^{176,244}$.

Following routes were selected to synthesize monomers and polymerization of monomers to get stereospecific polyvinyl alcohol after hydrolysis.

**SYNTHESIS OF VTMSE MONOMER AND ITS POLYMERIZATION**

VTMSE monomer was synthesized through acetaldehyde and trimethyl chlorosilane in presence of hydrohalide accepter using Zinc chloride catalyst in n-pentane$^{241,242}$. The content was filtered and filtrate obtained was fractionally distilled in thermostatically controlled oil bath. Following three fractions were collected and analysed by NMR spectra in deuterated chloroform. Spectra of the three fractions are shown in Figure 22.

- **Fraction 1**: 70$^\circ$C to 72$^\circ$C
- **Fraction 2**: 72$^\circ$C to 75$^\circ$C
- **Fraction 3**: 76$^\circ$C to 105$^\circ$C

The different fractions obtained were contaminated with n-pentane. Triethyl amine hydrochloride obtained as by-product of the reaction weighed about 55 g.

The NMR spectra in Figure 22 show three peaks at $\delta$ 4.00, 4.30 and 6.25. These values agree well with the values of authentic sample of silyl ethers reported in the literature$^{189}$. 
FIG. 22: NMR SPECTRA OF THE VTMSE MONOMER FRACTIONS OBTAINED.
Thus it is evident from the spectra that vinyl trimethylsilyl ether is formed. It is noteworthy that the intensity of absorption of the vinylic proton is different in different fractions. The intensity of absorption is maximum in the Fraction 2 whereas in remaining fractions it is low. The difference in the intensity of absorption of the three fractions suggested that the content of VTMSE is maximum in the middle fraction.

**Polymerization**

Five ml VTMSE monomer was polymerized in dry toluene at -30° to -40°C as per method described in Chapter II. After completion of the reaction, methanol was added and the content was stirred to hydrolyse the silyl polymer. The precipitate of the polymers were not seen.

The content was evaporated under vacuum on flash evaporator. Blackish brown viscous material was obtained. It was dried under vacuum over anhydrous calcium chloride and weighed 2.830 g as Product A.

The product obtained was extracted with distilled water and filtered through 0.3 sintered funnel. A light yellow filtrate obtained was evaporated on flash evaporator. The product obtained was dried under vacuum and weighed 1.50 g as Product B. Product B is thick viscous liquid soluble in methanol. Products A and B were subjected to infrared analysis. The spectra are shown in Figure 23.
FIG. 23: INFRARED SPECTRA OF THE POLYMER FRACTIONS OBTAINED THROUGH POLYMERIZATION OF VTMSE MONOMER WITH EtAlCl₂ CATALYST AT -40°C (PRODUCT-A AND PRODUCT-B).
The characteristic infrared absorption of the Products A and B in the region 2900 cm\(^{-1}\) to 3400 cm\(^{-1}\) show the presence of -OH stretching. The absorption at 2400 cm\(^{-1}\) of -CH stretching, at 1430 cm\(^{-1}\) for -CH\(_2\) wagging and 1335 cm\(^{-1}\) for -CH\(_2\) bending are observed. The product turned brown during polymerization. This may be due to oxidation occurring during polymerization. A peak at 1620 cm\(^{-1}\) may be assigned to carboxylate ion (\(\text{COO}^-\)) formed by oxidation during polymerization. A shoulder at 1100 cm\(^{-1}\) to 1200 cm\(^{-1}\) is present as in the standard polyvinyl alcohol sample. In addition to this there is a sharp peak at 815 cm\(^{-1}\), but no absorption is observed at 849 cm\(^{-1}\) and 916 cm\(^{-1}\) i.e., in the stereospecific region.

Polymerization of VTMSE monomer was carried out similarly as mentioned above using BF\(_3\)-etherate as catalyst at -30\(^\circ\) to -40\(^\circ\)C. Methanol was added. The content was stirred to hydrolyse the silyl polymer. The precipitates of the polymer were not seen. The content was evaporated under vacuum. The viscous liquid obtained as Product C. It was dried under vacuum and analysed by infrared spectra by smearing the product on NaCl plate. Infrared spectrum is given in Figure 24.

Product C in Figure 24 shows absorption of -OH stretching and -CH stretching. A sharp absorption at 1370 cm\(^{-1}\) and 1430 cm\(^{-1}\) of -CH\(_2\) wagging and bending respectively are present. A shoulder at 1100 cm\(^{-1}\) is also present as observed
FIG. 24: INFRARED SPECTRA OF THE POLYMERS OBTAINED THROUGH POLYMERIZATION OF VTMSE MONOMER WITH BF$_3$-ETHERATE CATALYST AT 40°C (PRODUCT-C) AND WITH ETAICL$_2$ CATALYST AT 78°C (PRODUCT-D).
in the authentic polyvinyl alcohol sample. There is no absorption found in the stereospecific region.

Similarly polymerization experiments of VTMSE monomer were also carried out at -78°C using dry-ice + acetone mixture. Methanol was added at the end of the reaction to hydrolyse the silyl polymer. No precipitates were seen. The content was evaporated under vacuum and the solid obtained was dried under vacuum and weighed 0.120 g as Product D. It was subjected to infrared analysis. The spectrum is given in Figure 24.

Product D in Figure 24 shows different type of spectral trend. In the spectrum no -OH or -CH stretching absorption are observed. This spectrum is assumed to be that of the residue of the catalyst obtained after evaporation.

From the products obtained above it is concluded that the polymers obtained are of very low molecular weight and did not show any stereospecificity. Therefore, further characterization and study of the polymer obtained was discontinued.

SYNTHESIS OF t-BUTYL VINYL ETHER

Synthesis of 2-Chloroethyl Vinyl Ether for the Preparation of t-Butyl Vinyl Ether

2-chloroethyl vinyl ether was synthesized by transesterification of vinyl acetate with ethylene chlorohydrine at -30°C as per the method described in Chapter II. Unreacted
Vinyl acetate was removed by fractional distillation at 72°-73°C. Fraction distilling at 108°-110°C/760 mm was collected as 2-chloroethyl vinyl ether. About 25 ml liquid was obtained.

t-Butylvinyl ether was synthesized by refluxing 2-chloroethyl vinyl ether with t-butanol in the presence of mercuric acetate as catalyst. Fraction collected at 76°-78°C was washed twice with distilled water, dried over calcium chloride and fractionally distilled.

**Polymerization**

Polymerization of t-butylvinyl ether was carried out in toluene using BF₃-etherate as catalyst at -78°C. At the end of the reaction, methanol was added and the content was stirred. No polymer precipitates were observed. Hence the content was evaporated under vacuum. No polymer was observed indicating absence of any polymerization.

In one of the experiments for synthesis of 2-chloroethyl vinyl ether, a fractional distillation was carried out through 2-feet long fractionating column. It was observed that, because of long heating period during fractional distillation, the content gets polymerised and solution becomes thick. This product was characterised by IR-spectroscopy by casting a film of the polymer. Spectrum of the film is shown in the Figure 25. Spectrum of authentic polyvinyl acetate is also included. The trend of the spectrum
FIG. 25: INFRARED SPECTRA OF THE POLYMER OBTAINED DURING FRACTIONAL DISTILLATION OF THE VINYL ACETATE AND 2-CHLOR ETHYL VINYL ETHER MIXTURE.
resembles the authentic spectrum of polyvinyl acetate. In addition to this the viscous solution was giving very prompt sweet smell quite different from that of vinyl acetate, probably of vinyl ether. This observation shows that probably 2-chloroethylvinyl ether might not be getting co-polymerised with vinyl acetate.