

Polymerisation of Allyl 4-Methoxyphenyl Ether

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The monomer allyl 4-methoxyphenyl ether has been polymerised by the bulk polymerisation procedure in the presence of borontrifluoride dietherate. The polymer has been characterised by IR, UV and PMR spectral data. A probable mechanism is also suggested for the polymerisation.

We report in this paper the synthesis and characterisation of a new polymer using allyl 4-methoxyphenyl ether as the monomer. The utility of polymers derived from allylic compounds has been realised only recently. Some of these are resistant to acids, alkalis and heat.

Allyl 4-methoxyphenyl ether was prepared as follows: 4-Methoxyphenol (0.1ml) and allyl bromide (0.15 mol) were refluxed in acetone (100 ml) in the presence of anhydrous potassium carbonate for 10 hr, extracted with ether, the ether layer repeatedly washed with 10% NaOH, separated, dried over anhydrous sodium sulphate and the solvent removed by distillation. The purity of the monomer was tested by TLC; yield 47%.

The IR spectrum of monomer in KBr matrix exhibited peaks at 1025, 1110, 1170 and 1235 cm^{-1} indicating the presence of $\text{C}=\text{C}-\text{C}-\text{O}-\text{C}-$ group. Thus condensation has occurred at the phenolic OH group, resulting in the formation of an allyl ether. This was confirmed by the PMR spectrum of the monomer in CDCl_3 ; PMR (ppm): δ 3.83 (3H, $-\text{OCH}_3$), 4.25 (2H, $-\text{CH}_2-$), 5.1-5.4 (2H, $=\text{CH}_2$), 5.8 (1H, $-\text{CH}=-$) and 6.7 (4H, aromatic H). The UV spectrum of the monomer in dry ethanol exhibited absorption maxima at 213, 232, 298 and 337 nm.

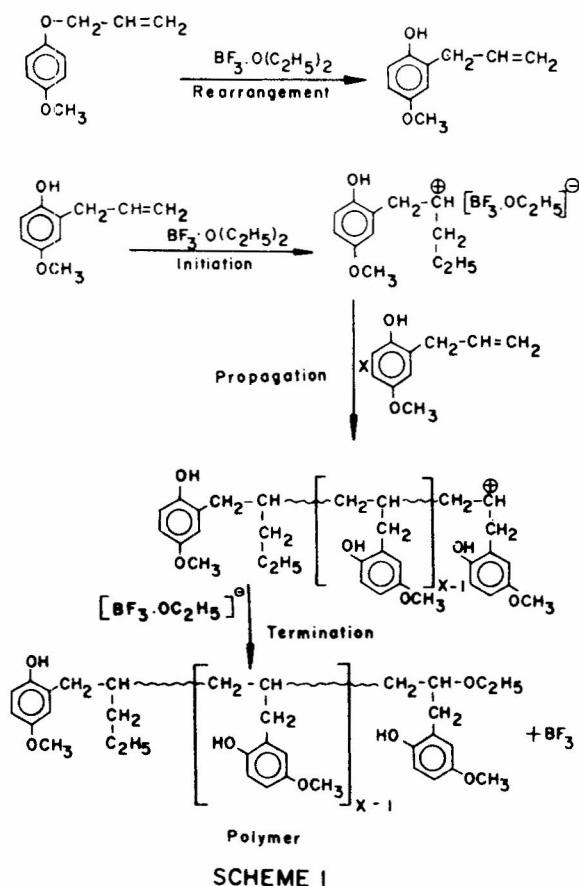
The polymer was obtained by the bulk polymerisation method. Allyl 4-methoxyphenyl ether was degassed by passing nitrogen. Borontrifluoride dietherate was added to it dropwise at 30°C, when a vigorous reaction took place. The contents were cooled and kept overnight. The dark viscous liquid obtained was dissolved in minimum amount of

acetone and poured into water, when a white solid was obtained. It was filtered, washed and dried *in vacuo* over P_2O_5 at 60° C for 15 hr (Yield 90%).

The following spectral data were obtained for the polymer: IR (KBr): 3400, 1650, 1510, 1370, 815 cm^{-1} ; PMR (CDCl_3): δ 1.2-1.5 (4H, $-\text{CH}_2-$), 2.05 (1H, $-\text{C}-\text{H}$), 3.8 (3H, OCH_3), 4.7 (1H, phenolic OH) and 6.6-6.8 (3H, aromatic H); UV (dry EtOH): 213, 232 and 298 nm.

The appearance of absorption at 3400cm^{-1} and the disappearance of monomer peaks at 1235, 1170 and 1025cm^{-1} in the IR spectrum of the polymer clearly indicate that the polymerisation has occurred. This is further supported by the presence of a signal at $\delta 4.7$ due to OH group in PMR and the absence of UV maximum at 337nm in the UV spectrum of the polymer (disappearance of olefinic double bond). The polymer is sparingly soluble in CCl_4 , ethanol and methanol, soluble in benzene and toluene and highly soluble in CHCl_3 , acetone and conc. H_2SO_4 .

It has been established that the polymerisation is preceded by Claisen rearrangement¹. The rearranged phenol undergoes polymerisation in the presence of



BF_3 as co-catalyst. The presence of an allyl group at the end of the growing chain has also been confirmed by tracer technique. Thus the following mechanism (Scheme 1) may be suggested for the polymerisation of this monomer. The molecular weight of the polymer as determined by Rast method using camphor ($K_f = 37.7$) comes out to be 1348 corresponding to the degree of polymerisation 8.2. The elemental analysis of the polymer gave the following results: Found: C, 72.9; H,

7.4. Calc: C, 73.2; H, 7.32%, in accordance with the assigned structure. Although the molecular weight is low, thermal studies indicate that the polymer is thermally stable upto 450°C and decomposes in the temperature range $470\text{--}520^\circ\text{C}$ without leaving any residue.

References

- 1 Hui K M & Yip L C, *J polym Sci*, **14** (1976) 2689.