

## Polymerisation of Allyl Phenyl Ether: a Polymerisation involving Intramolecular Rearrangement

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**Summary** Polymerisation of allyl phenyl ether involves intramolecular rearrangement in the propagation step.

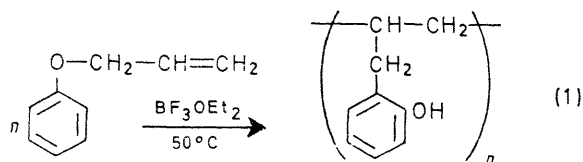
INTRAMOLECULAR rearrangement in simple molecules are well-studied and -documented. In comparison, there are few examples of intramolecular rearrangement in polymerisation in the literature and most of these have been found in cationic polymerisation. As a result of the occurrence of intramolecular rearrangement in the propagation step of the polymerisation, the repeating unit of the polymers formed is structurally different from the atomic arrangement in the monomer molecule. For this reason, the polymers formed in this way have been termed "phantom" polymers. The majority of the phantom polymers in cationic polymerisation involve hydride ion or methyl group shifts.<sup>1</sup> We now report a cationic phantom polymerisation involving an allyl group shift similar to the Claisen rearrangement of allyl phenyl ether to 2-allylphenol<sup>2</sup> but with the difference of a much lower temperature and a catalyst being used.

Allyl phenyl ether was polymerised in bulk under high vacuum at 50 °C using  $\text{BF}_3\text{OEt}_2$  as catalyst. As polymerisation proceeds, the allyl phenyl ether turns more and

more viscous until finally a hard glassy product is obtained. This product is soluble in methanol and precipitation from a methanol solution of the product in water yields a white fluffy polymer in almost quantitative yield (analysis correct for  $\text{C}_9\text{H}_{10}\text{O}$ ). The polymer has a density of  $1.21 \text{ g cm}^{-3}$  and m.p. 92–95 °C. Its molecular weight was found to be 1300 by a cryoscopic method. I.r. spectra of this polymer showed the absence of the allyl double bond and, unexpectedly, the presence of the phenolic OH group ( $3300\text{--}3400 \text{ cm}^{-1}$ ) and a 1,2-disubstituted benzene ring ( $755 \text{ cm}^{-1}$ ). The strong absorptions at  $700$  and  $750 \text{ cm}^{-1}$  in the i.r. spectrum of the monomer which are indicative of mono-substituted benzene ring have disappeared. When the spectra of the polymer were compared with that of poly-2-allylphenol ( $755, 1450, 1485, 1590, 1610, 2880\text{--}2960, 3350 \text{ cm}^{-1}$ )<sup>3</sup> they were found to have the same principal absorption bands. The spectra of the polymer were also very similar to that of poly-*o*-hydroxystyrene ( $1450, 1485, 1582, 1600, 2890, 3350 \text{ cm}^{-1}$ ).<sup>4</sup> Treatment of this polymer with benzoyl chloride in anhydrous pyridine gave a solid product. The i.r. spectrum of this product showed the presence of the benzoate ester group ( $1730 \text{ cm}^{-1}$ ) and the disappearance of the OH group. This confirms the presence

of the phenolic OH group in the polymer. Further confirmation was obtained by diazo-coupling. Addition of diazotised sulphanilic acid to a methanolic solution of poly(allyl phenyl ether), followed by sodium hydroxide solution, produced an intense red coloration.

These facts suggest that the polymerisation of allyl phenyl ether involves the rearrangement shown in reaction (1). The structure of the polymer is identical to that of poly-2-allylphenol (obtained using conc.  $\text{H}_2\text{SO}_4$  as catalyst) which was reported previously.<sup>3</sup> Poly-2-allylphenol also has a m.p. of 92–95 °C. The m.p. of a mixture of the two polymers in equal proportions was also 92–95 °C.



In order to investigate the possibility that allyl phenyl ether could have rearranged to 2-allylphenol prior to propagation, the polymerisation of the latter was studied

under identical conditions. It was found that the polymerisation was much slower, and the product, obtained in very low yield, was a gum. These features are in sharp contrast to the more rapid polymerisation of allyl phenyl ether which gave an almost quantitative yield of a solid polymer. It was also found that the polymerisation of 2-allylphenol with a mixture of  $\text{BF}_3\text{OEt}_2$  and a small quantity of allyl phenyl ether as catalyst was in no way different from that with  $\text{BF}_3\text{OEt}_2$  alone. This excludes the possibility that  $\text{BF}_3\text{OEt}_2$  reacts with allyl phenyl ether to form a more active catalytic species than  $\text{BF}_3\text{OEt}_2$  for 2-allylphenol. It appears that rearrangement prior to propagation is unlikely since the structure necessary for rearrangement is no longer present.<sup>2</sup> Furthermore, rearrangement after propagation would involve intramolecular arrangement of the  $\left( \begin{array}{c} -\text{CH}-\text{CH}_2- \\ | \\ \text{CH}_2 \\ | \end{array} \right)$

other such groups in the polymer molecule; this seems most unlikely. It is therefore concluded that rearrangement takes place in the propagation step.

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<sup>2</sup> D. S. Tarbell, *Org. Reactions*, 1949, 2, 4.

<sup>3</sup> K. M. Hui and L. C. Yip, *Chem. Comm.*, 1970, 402.

<sup>4</sup> M. Kato and H. Kamogawa, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1966, 4, 1773.