

THIOPHOSPHORYL FLUORIDE AND PHOSPHORYL FLUORIDE AS  
INITIATORS FOR THE POLYMERISATION OF TETRAHYDROFURAN

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SUMMARY

Thiophosphoryl fluoride and phosphoryl fluoride have been found to initiate the polymerisation of tetrahydrofuran. The living polymer formed has a high molecular weight of the order of a million and the density is found to be between 0.98 - 1.02 g/cc. A cationic mechanism for the polymerisation has been proposed.

INTRODUCTION

While investigating the chemistry of thiophosphoryl fluoride, it has been observed that it forms a 1:1 adduct with pyridine [1]. The coordination takes place at phosphorus of the thiophosphoryl fluoride. This acceptor property of the thiophosphoryl fluoride molecule shows it to be a good 'Lewis acid'. Lewis acids and their salts have been found to be good initiators for the polymerisation of tetrahydrofuran (THF) [2]. It was of interest, therefore, to see whether thiophosphoryl fluoride would also initiate the polymerisation

of THF. Preliminary experiments indicated that THF could easily be polymerised in the presence of thiophosphoryl fluoride in about 7 hours. Phosphoryl fluoride is also a good Lewis acid and THF is found to polymerise in its presence. However, the time required for complete polymerisation is about 70 hours, nearly ten times more than in the case of thiophosphoryl fluoride. The physical characteristics of this polymer are found to be very similar to those of the one obtained with the thiophosphoryl fluoride and THF system.

Such polymers are found to have high molecular weights. Formation and characterisation of these polymers are discussed in this paper.

#### EXPERIMENTAL

Thiophosphoryl fluoride is prepared and stored in a previously evacuated and dry glass globe [3]. In a similar manner, phosphoryl fluoride is prepared by fluorination of phosphoryl chloride using sodium fluoride as the fluorinating agent in boiling acetonitrile [4].

##### A. Polymerisation of THF using thiophosphoryl fluoride as initiator

Pure and dry THF (100-200 ml) is taken in a reaction tube (8" x 2") fitted with vacuum stop cocks and ground glass joints. The liquid is frozen with liquid nitrogen as coolant and the uncondensable gases are pumped out. About 100 mg of thiophosphoryl fluoride is then metered and frozen over the solidified THF. The reaction vessel is then allowed to attain room temperature (25°C) gradually. After about an hour the liquid becomes viscous and the viscosity increases rapidly. Within 7 hours the whole of THF sets into a hard transparent mass. Vacuum is released and polytetrahydrofuran (PTHF) is taken for investigations.

The polymer is found to swell in organic solvents (benzene, ethyl acetate, methyl ethyl ketone etc.) and dissolves with difficulty. For instance, it requires three days to prepare a 1% solution in benzene. The PTFE is precipitated in methanol using a benzene solution of PTFE and it is dried under vacuum. The m.p. of the PTFE is found to be around 56°C. The measurement is made using a polarising hot stage microscope.

Fibres and sheets can easily be drawn either from the melt or from the highly viscous (swelled PTFE) benzene solution. Such fibres and sheets are stable in air and are elastic like rubber.

The viscosity of PTFE in benzene solution is measured using an Ubbelohde viscometer at 30°C. The intrinsic viscosity is found to be 5.5. From this value, the molecular weight is calculated using the Mark-Houwink equation,  $[\eta] = K M^{\alpha}$  where  $K = 13.1 \times 10^{-4}$  and  $\alpha = 0.6$  [5]. The molecular weight  $\bar{M}_w$  is found to be  $1.109 \times 10^6$ .

The density of PTFE is measured with a specific gravity bottle using water. The value is found to vary between 0.9 and 1.02 g/cc.

The infrared spectrum of the polymer (in carbon tetrachloride) is recorded using a UR 10 Carl Zeiss spectrophotometer. The characteristic frequencies recorded correspond to those reported for PTFE [6]: 730, 100, 1100, 1200, 1400, 1500, 2940-60  $\text{cm}^{-1}$ .

The nmr spectrum of PTFE is recorded on a Varian NA 100 D nmr spectrometer and it corresponds to that reported [7].

The polymer disintegrates above 200°C. The gaseous products evolved, on hydrolysis, show the presence of sulphide, sulphite, thio-sulphate, phosphate and fluoride, indicating the association of thio-phosphoryl fluoride with the polymer. In addition, a considerable amount of monomer (50%) is obtained, the rest getting converted into a resinous material.

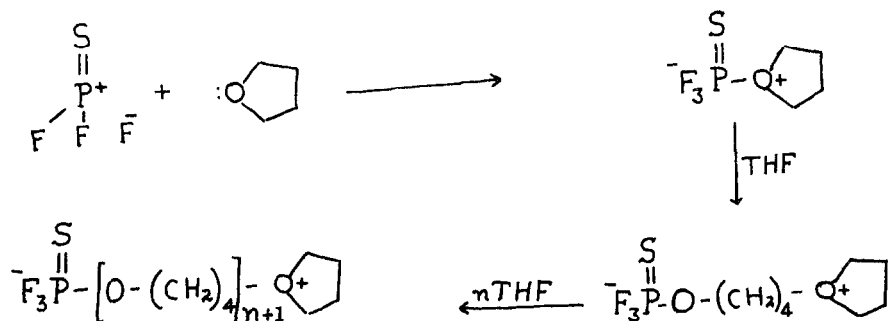
## B. Polymerisation of THF using phosphoryl fluoride as initiator

THF is polymerised with phosphoryl fluoride as initiator by employing a similar procedure to the one described in the earlier case.

The polymer obtained has the same characteristics and properties as that of PTHF obtained with thiophosphoryl fluoride as initiator. The molecular weight of the polymer is found to be of the order of a million ( $9.98 \times 10^5$ ).

### RESULTS AND DISCUSSION

It is known that phosphorus pentafluoride initiates the polymerisation of THF to yield a high molecular weight elastomer [2]. The mechanism of the process involves the formation of an oxonium ion [8]. It is interesting to point out that the rate of polymerisation of THF by thiophosphoryl fluoride is more than with phosphorus pentafluoride and phosphoryl fluoride. The formation of the oxonium ion can be pictured in the following way :



One of the canonical forms of thiophosphoryl fluoride is an ionic structure wherein the electron density is more concentrated at fluorine, with corresponding depletion at phosphorus [9], thus permit-

ting easier acceptance of electrons donated by the oxygen of TTF. The resulting oxonium ion gets attached to another molecule of TTF at either the 2 or 5 position and a new tertiary oxonium ion results exactly like the original, but one monomer unit larger. The chain is thus propagated and an elastomer is produced. As already mentioned, the polymerisation goes to completion in about 7 hours in the case of thiophosphoryl fluoride as initiator and 70 hours in the presence of phosphoryl fluoride as initiator. The rapid polymerisation of TTF in the presence of thiophosphoryl fluoride may be attributed to the larger difference of electronegativity between sulphur and fluorine compared with oxygen and fluorine, which helps phosphorus to accept electrons relatively more easily. The polymer formed is living, as it initiates the polymerisation of added TTF.

The molecular weight of the polymer formed is of the order of a million. This is similar to the polymer obtained when phosphorus pentafluoride is used as an initiator. It is observed that phosphorus trifluoride, phosphorus trichloride, phosphorus pentachloride, thiophosphoryl chloride and phosphoryl chloride do not function as initiators for the polymerisation of TTF. The fact that pentavalent phosphorus-fluorine compounds initiate the polymerisation of TTF can be attributed to the presence of the highly electronegative fluorine atoms which permits the easy accommodation of the electrons donated by oxygen of the TTF into the partially filled d orbitals of the pentavalent phosphorus.

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