ON THE PROPAGATING SPECIES IN TETRAHYDROFURAN-FLUOROSULPHONIC ACID POLYMERIZATION PROCESS

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Introduction

The use of sodium phenoxide as a capping reagent in the polymerization of four, five and seven membered cyclic ethers is a well known method for determining the concentration of active centres [1-3]. Recently, in the study of the kinetics of tetrahydrofuran (THF) polymertization, cationically initiated by FSO_3H and such esters as $CH_3OSO_2CF_3$, $C_2H_5OSO_2CF_3$, CH_3OSO_2F and $C_2H_5OSO_2F$; concentration of active centres were directly determined from proton NMR spectra [4-8]. Data derived from these investigations have led to the generally accepted view that there are two kinds of active species—macro–ion and macro-ester in the process of polymerization. Both species have been identified in the ^1H NMR spectrum [8-12]. In contrast to the ester derivatives, however, it was observed that some inconsistency existed in the assignment of the NMR signals of the active intermediates in THF-FOS_3H polymerization process [5-7].

The proton NMR spectra of the tetrahydrofuran polymerization in dichloromethane will be discussed, concentrating attention to characterize different species in the reaction mixture. This has been accomplished with the aid of model compounds. The observed chemical shifts of the active species are found to be dependent on the concentratiin ratio of the reactants and reaction time.

Experimental

Materials. Tetrahydrofuran (THF), Merck P.a., was dried on potassium at its boiling temperature by refluxing for a period of at least two days in a nitrogen atmosphere. After the removal of one-third by distillation, the middle fraction was collected from the deep blue coloured solution of THF in potassium and benzophenone.

Dichloromethane (CH_2Cl_2), Merck P.a., containing about 0.3 percent of ethanol was treated with calcium chloride and left overnight before filtration and subsequent drying on $LiAlH_4$ and purification by fractional distillation under nitrogen atmosphere.

Eplchlorohydrin (C_3H_5OCl), commercial grade, was purified by fractional distillation at 117°C at atmospheric pressure.

1-Propanol (C_3H_7OH), Merck P.a., was used from the fresh bottle without any further treatment.

Fluorosulphonic acid (FSO_3H) and boron trifluoroetherate ($C_4H_{10}OBF_3$), pure grade, obtained from Fluka were used without further purification.

Polymerization. The polymerization reaction was carried out in a round bottom flask with a three opening adopter under nitrogen atmopshere. The reactants were added in the following order: solvent, initiator and monomer. The solution was mixed thoroughly by constant stirring with the help of a magnetic stirrer. The temperature of the solution was kept at 0°C by dipping the flask in an ice-water bath. However, during initial addition of the reactants, the flask was maintained in a dry ice-acetone bath to avoid sudden change of temperature due to the exothermic nature of the reaction.

About 1.0 ml of the solution was then transferred into an NMR tube and the reaction was allowed to proceed at 0°C . The ^1H NMR spectrum was recorded with the aid of a Varian A-60 (60 MHz) spectrometer.

Result and Discussion

Assuming that the propagation occurs predominantly in the process of cationic polymertization of THF with FSO_3H in an analogous fashion as with ester derivatives [5,6,9], the propagation reactions can be presented as follows:

Thus, in addition to the starting materials, it is expected that α-methylene protons of tertiaryoxonium ion (TOI) and α-methylene protons of superacid ester (SAE) shown in equations (I) and (II) of the growing polymer chain and other species if any formed could be monitored by ^1H NMR spectrosocopy. However, this is likely, provided the concentration of each species is not very low and their life time is not considerably short in terms of NMR time and concentration scale.

A typical ^1H NMR spectrum of the reaction mixture of THF and FSO_3H in dichloromethane at 0°C

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TABLE 1. DEPENDENCE OF CHEMICAL SHIFTS OF DIFFERENT SPECIES ON TIME AND CONCENTRATION IN THE THF–FSO₃H POLYMERIZATION MIXTURE IN DICHLOROMETHANE AT 0°C.

Expt. No.	Time		A	B	C	D	E	H	J	G
	hr	min	(δ) ppm	(δ) ppm	(δ) ppm	(δ) ppm	(δ) ppm	(δ) ppm	(δ) ppm	(δ) ppm
MI	2	50	4·03	2·02	3·58	1·68	5·12	4·32	5·73	15·97
	20	25	3·85	1·90	3·43	1·61	4·92	4·27	5·52	13·94
	72	05	3·80	1·89	3·44	1·60	4·89	4·30	4·49	13·30
MII	2	35	4·02	2·00	3·58	1·67	5·12	4·30	5·73	15·83
	20	40	3·83	1·92	3·45	1·63	4·93	4·29	5·53	13·89
	72	20	3·80	1·89	3·45	1·62	4·89	4·32	5·50	13·23
MIII	2	30	3·95	1·95	3·57	1·67	5·20	4·29	5·73	15·79
	20	12	3·83	1·89	3·45	1·62	4·97	4·29	5·53	13·83
	71	55	4·79	1·88	3·44	1·62	4·93	4·33	5·52	13·20

[THF]= 7·31 mol 1⁻¹. Internal standard TMS. Concentration of FSO₃H in experiments MI, MII and MIII are 1·1, 0·90 and 0·60 mol 1⁻¹ respectively; and [CH₂Cl₂] are 5·24 5·50 and 5·70 mol 1⁻¹ respectively. [FSO₃H] mentioned above is the initial concentration.
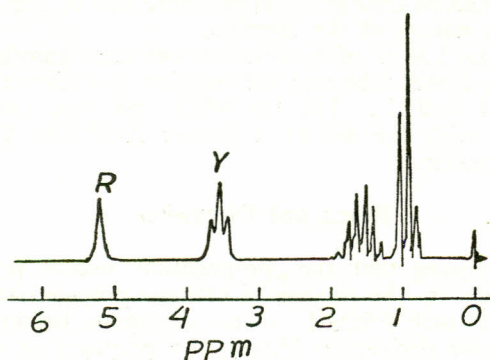
Fig. 1. ¹H NMR spectrum of the polymerization mixture of THF in dichloromethane after 20 hr. at 20°. FSO₃H is used as an initiator, TMS as an internal standard.
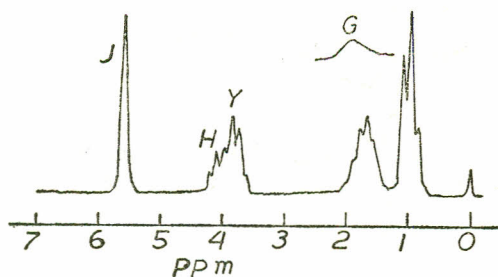
Fig. 2. ¹H NMR spectrum of triethyltetrafluoroborate in dichloromethane; TMS as an internal standard.

after 20 hr of reaction is shown in Fig. 1. This spectrum is indistinguishable to that of the spectrum reported by Pruckmayr and Wu[5]. Nevertheless, it is observed that the chemical shifts of all the species in the medium continuously changes the field (with refrence to the conventional internal standard TMS) significantly as the reaction proceeds. Chemical shifts of various species as a function of time and concentration are presented in Table 1. These results suggest that it is not possible to quote the chemical shifts of the species in the THF–FSO₃H system, unless reference is enumerated to the concentration of the reactants, solvent and reaction period. The reason for such a change in the observed chemical shifts is not clearly understood but may be the result of changes in the dielectric of the medium.

In Fig. 1, peaks A and B are due to α and β-methylene protons of tetrahydrofuran monomer, peaks C and D are due to α and β-methylene protons of the polymer. Assignment of these peaks are in agreement with the observed and reported ¹H NMR spectra of pure-THF and poly-THF. Assignment of peak E and the slowly developed peak, H, due to two traceable active intermediates in the polymerization mixture, has been disputed [5-7]. In order to assign these peaks correctly, the following compounds were prepared.

Meerwein salt (triethyloxonium tetrafluoroborate, $(C_2H_5)_3{}^+OBF_4{}^-$) was prepared by the interaction of epichlorohydrin and boron trifluoroetherate in dry ether medium[13]. The salt was then recovered carefully by adhering strictly with the precautions suggested in the literature. The purity of the compound was ascertained by the determination of the melting point (m.p.90–93°C) and subsqent ¹H NMR experiment. In an NMR tube 60 mg of the dry Meerwein salt was dissolved in 0.5 ml of dichloromethane under nitrogen aomposhere and an NMR spectrum was taken. Two signals as expected were observed, signal X a triplet for the methyl protons at 1.68 ppm and signal E for the α-mtehylene protons, resonate at a lower field, 4.8 ppm in the form of a quartet. The spectrum is shown in Fig. 2.

The superacid ester (III) was prepared by a simple condensation reaction, employing 1-propanol and FSO₃H. Figure 3 illustrates the ¹H NMR spectrum
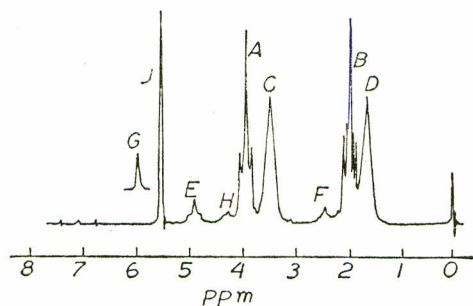
$$CH_3-CH_2-CH_2-OH + FSO_3H$$
$$\downarrow$$
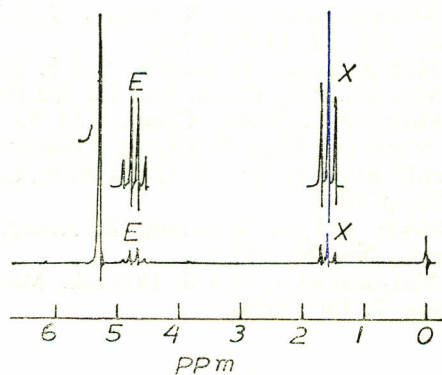$$CH_3-CH_2-CH_2-OSO_2F + H_2O$$
$$(III)$$
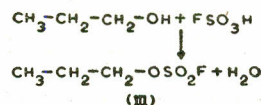
Fig. 3. (a)

Fig. 3. (b)

Fig. 3. (a) ¹H NMR spectrum of propanol (b) ¹H NMR spectrum of the reaction mixture of propanol and fluorosulphonic acid in dichloromethane (internal standard TMS).
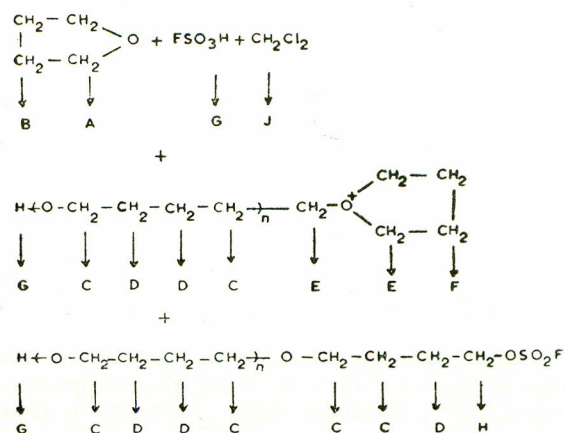
Scheme 1

TABLE 2. SULPHUR COMPOUNDS IN DISTILLATION FRACTIONS OF LIGHT ARABIAN AND KUWAIT CRUDE OIL.

Active species	Model compounds (δ) ppm	Reaction mixture (δ) ppm	Reaction mixture (δ) ppm
TOI	4·80	4·75	4·92
SAE	4·10	4·10	4·27
Reference	TMS	CH_2Cl_2	TMS

[THF]$=7\cdot3$ mol 1^{-1}, [FSO$_3$H]$=1\cdot1$ mol 1^{-1} and [CH_2Cl_2]$=5\cdot2$ mol 1^{-1}

of 1-propanol (3a) and the mixture of 1-propanol and FSO$_3$H (3b). A new growing peak H at 4.1 ppm can be seen very clearly in Fig. 3(b). This is as a result of the formation of superacid ester and the peak is due to the α-methylene protons of the ester chain. Preparation of superacid ester by this method was described by Meyer *et al.* [4].

Thus, from the analysis of the spectra of the model compounds, in Fig. 1, signals E and H can be assigned to the α-methylene protons of the propagating TOI and SAE species, respectively. In Scheme 1 assignment of ¹H NMR signals of various species in the polymerization mixture is described.

It has been demonstrated in Table 1 that the signals E and H resonate within the field of ≈ 0.25 ppm and ≈ 0.12 ppm under the present experimental condition in about 70 hr of reaction period. Consquently, an apparent deviation of 0.17 ppm and 0.12 ppm in up field direction for the signals E and H (when THM is an internal reference) from the corresponding signals of the model compounds does not invalidate the assignment. In addition, the chemical shifts presented in Table 1 were carefully examined. It is found, if the signals for the methylene protons of dichloromethane is taken as a reference instead of the conventional TMS peak, the observed chemical shifts of TOI and SAE (i.e., signals E and H in Fig. 1) after about 20 hr of reaction superimposes on the co-

rresponding bands of the model compounds (Table 2). The chemical shifts presented in Table 2 can be expressed relative to internal standard dichloromethane or TMS by using equation (IV).

$$\delta_{TMC} = \delta_{CH_2Cl_2} + 0.17 \qquad (IV)$$

Furthermore, by assuming the signals E and H for the secondary oxonium ion and tertiary oxonium ion respectivley, Penczek *et al.* [15] analyzed the kinetic data for the THF–FSO$_3$H polymerization process [5] and proposed that the assignment of the signals for the active intermediates in the work were not conclusive. Alternatively, these authors [15] claimed that when signals E and H were assigned to the α-methylene protons of TOI and α-methylene protons of SAE of the propagating chain, meaningful rate constants were obtained. It is, therefore, another evidence in support of the above assignments of the active species in the polymerization of THF, initiated cationically by FSO$_3$H. Assignments consistent to these results were also postulated by Saegusa *et al.* [6].

In the present system, no others pecies resulting from the possible transfer and termination reactions was observed in the ¹H NMR spectrum. The protonated monomer species (V) produced in the initiation reaction could not be traced at temperature as —50°C.

$$\text{(V)}$$
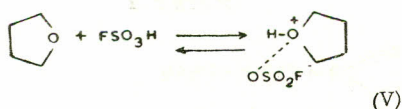
This observation is analogous to that of the finding of other authors [6,15]. Failure to observe protonated monomer (V) is attributed to the fast proton exchange reaction. Signals F, labelled in Fig. 1 could not be confirmed from these model compounds. But such a signal is most likely be due to the β-methylene protons of the propagating TOI species.

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