Notes

Fluorine-19 Nuclear Magnetic Resonance Studies on the Polymerization of Tetrahydrofuran by Superacid Esters[1]

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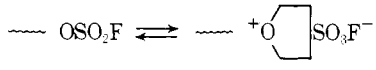
A number of reports have recently been published in which the polymerization of tetrahydrofuran was studied by proton nmr spectroscopy.[3-5] Detailed spectral assignments were given, but there is no agreement on the exact chemical shifts of some intermediates in the polymerization.[4,5] Some of our assignments have also been questioned.[4,6] It was correctly pointed out that secondary oxonium ions should not be observable separately under the given experimental conditions. In turn, an equilibrium between a macroester and a macroion was proposed,[6] at least for systems with no free protons.



Such an equilibrium has been proposed earlier by Smith and Hubin[7] for the polymerization of tetrahydrofuran catalyzed by trifluoromethyl sulfonic anhydride $(CF_3SO_2)_2O$ and pyrosulfuryl fluoride $(FSO_2)_2O$. More recently, however, no macroester was observed by proton nmr in the equilibrium polymerization mixture of tetrahydrofuran catalyzed by "superacid esters."[4] In view of these discrepancies we decided to utilize ^{19}F-nmr spectroscopy to examine the different fluorine species present in this polymerization mixture.

In the present investigation, the model compound for fluosulfate anion FSO_3^- was a solution of fluosulfonic acid in ether. The model for fluosulfate ester was ethyl fluosulfate. The ^{19}F spectra of these compounds were obtained in a highly polar solvent (CH_3NO_2) and a nonpolar solvent (CCl_4) on a Varian A 56/60 nmr spectrometer at ambient temperatures. The corresponding fluorine chemical shifts, measured from internal reference trichlorofluoromethane, are listed in Table I.

Addition of ethyl fluosulfate to THF–CH_3NO_2 (2:1 by weight) leads to a rapid transformation of the fluosulfate ester to FSO_3^- anion, as shown by a growing signal at 38.0 ppm. After 1 hr the mixture did not contain any fluosulfate ester in concentrations detectable by our instrument (Figure 1B). Addition of ethyl fluosulfate to tetrahydrofuran in a nonpolar solvent (66.6 wt % in CCl_4), however, leads to an appreciable amount of macroester, as shown by a slowly increasing signal at 34.5 ppm. In this system it is possible to distinguish between the fluosulfate of the macroester and ethyl fluosulfate, which absorbs at 35.1 ppm (Figure 1A).[8]

The low-field proton nmr spectrum in CCl_4 shows a quartet at 4.65 ppm, due to the methylene protons of ethyl fluosulfate, and a superimposed triplet centered at 4.62 ppm, due to the α-methylene protons of the macroester, measured with respect to internal TMS. The corresponding spectrum in CD_3NO_2 solution shows the quartet at 4.65 ppm and a signal at 4.8 ppm, which should be due to the methylene groups of the oxonium ion.

The oxonium ion has limited solubility in tetrahydrofuran and appears as a crystalline precipitate soon after addition of ethyl fluosulfate. This precipitate is insoluble in nonpolar solvents but dissolves readily in polar solvents such as nitromethane. A solution of this material in CD_3NO_2 shows a single fluorine absorption peak at 38.0 ppm and a proton signal at 4.8 ppm.

Similar results were obtained with triflate esters. Addition of ethyl triflate (CF_3SO_3Et) to tetrahydrofuran in

Table I
^{19}F-Nmr Assignments

Species	Solvent	^{19}F chemical shift[a]		
$EtOSO_2F$	(CCl_4)		34.8	
	(CH_3NO_2)		35.0	
$Et_2O^+H\,SO_3F^-$	(CCl_4)			38.8
	(CH_3NO_2)			38.6
$EtOSO_2F$–THF[b]	(CCl_4)	34.5	35.1	
	(CH_3NO_2)			38.0
$EtOSO_2CF_3$	(CCl_4)		−76.0	
	(CH_3NO_2)		−75.8	
$Et_2O^+H\,CF_3SO_3^-$	(CCl_4)			−79.0
	(CH_3NO_2)			−78.4
$EtOSO_2CF_3$–THF[b]	(CCl_4)	−75.7	−76.0	
	(CH_3NO_2)			−78.7

[a] Chemical shifts are given in ppm with respect to internal reference CCl_3F. Positive values indicate downfield shifts. [b] Polymerization mixture ester-tetrahydrofuran (1:10), 66.6 wt % solution, after 60 min polymerization time.

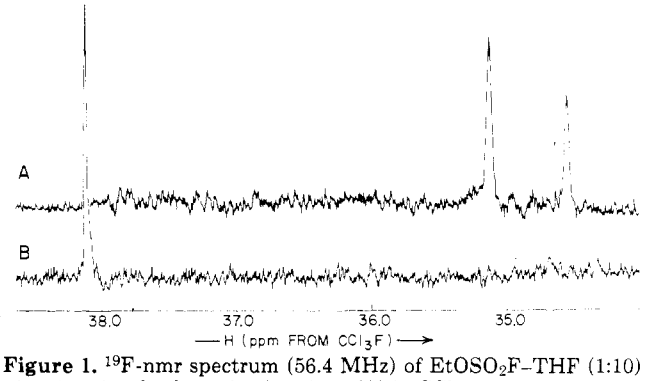


Figure 1. ^{19}F-nmr spectrum (56.4 MHz) of $EtOSO_2F$–THF (1:10) after 60 min of polymerization time: (A) in CCl_4 (66.6 wt %); (B) in CH_3NO_2 (66.6 wt %).

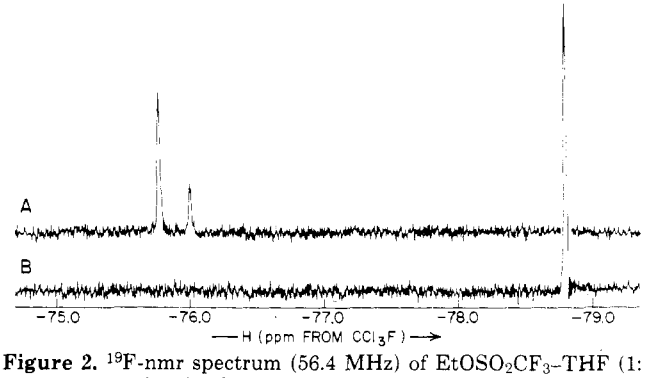


Figure 2. ^{19}F-nmr spectrum (56.4 MHz) of $EtOSO_2CF_3$–THF (1:10) after 60 min of polymerization time: (A) in CCl_4 (66.6 wt %); (B) in CH_3NO_2 (66.6 wt %).

CCl_4 (66.6 wt %) results in a trifluoromethyl macroester absorption at −75.7 ppm, while in polar medium (66.6 wt % in CH_3NO_2) a signal at −78.7 ppm due to triflate anion appears (Table I). These examples are further illustrated in Figure 2.

The macroester ⇌ macroion equilibrium in the polymerization of tetrahydrofuran catalyzed by "superacid" anhydrides and esters, proposed by Smith and Hubin[7] and Penczek,[5] as well as the dependence of such an equilibrium on solvent polarity can therefore be directly observed by ^{19}F-nmr. The polymerization of THF catalyzed by proton acids such as CF_3SO_3H and HSO_3F reported in our previous paper[3] is complicated by the possibility of secondary reactions.[4] A detailed analysis of this system has been made using fluorine nmr spectroscopy, and the results will be published elsewhere.

References and Notes

(1) After this manuscript had been submitted for approval by our company, a paper on a similar subject appeared: S. Kobayashi, H. Danda, and T. Saegusa, *Macromolecules*, **7**, 415 (1974). The authors reported ^{19}F and ^{1}H-nmr studies of THF polymerizations initiated by ethyl triflate.
(2) (a) Plastics Department; (b) Industrial Chemicals Department.
(3) G. Pruckmayr and T. K. Wu, *Macromolecules*, **6**, 33 (1973).
(4) S. Kobayashi, H. Danda, and T. Saegusa, *Bull. Chem. Soc. Jap.*, **46**, 3214 (1973).
(5) K. Matyjaszewski, P. Kubisa, and S. Penczek, *J. Polym. Sci.*, **12**, 1333 (1974).
(6) K. Matyjaszewski and S. Penczek, *Macromolecules*, **7**, 137 (1974).
(7) S. Smith and A. J. Hubin, *J. Macromol. Sci., Chem.*, **7**, 1399 (1973).
(8) The peak positions were identified by adding more ethyl fluosulfate to the nmr sample.

Microstructure of Poly(2,3-dimethyl-1,3-butadiene) Prepared by Butyllithium in Polar Solvent

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Recently, Yuki, *et al.*,[1] reported an extensive structural study on poly(2,3-dimethyl-1,3-butadiene) (PDMB) prepared by anionic polymerization under various conditions. Using 100-MHz nmr spectroscopy they showed that the 1,2 content of PDMB prepared by *n*-butyllithium in a polar solvent (tetrahydrofuran) depends strongly upon the polymerization temperature, behavior of which contrasts with both butadiene and isoprene polymerization. In fact, when the polymerization temperature was increased from −78 to 50° the microstructure varied gradually from 86 to 42 mol % of 1,2 units. They attributed this behavior to the steric hindrance involved in the 1,2 structure propagation. On the same basis they suggested that the polymers prepared above −30°, which contain nearly 50 mol % of 1,2 units, have alternating arrangements of 1,2 and 1,4 structures.

In a previous paper[2] devoted to the nmr analysis of highly 1,4-PDMP prepared in cyclohexane we have reported that the 220-MHz spectra of PDMB show features in both the methylene and methyl proton regions that are not apparent in spectra recorded at lower fields. In fact, from these spectra it has been possible to determine the distribution of the dyads and triads of the cis-1,4 and trans-1,4 units. With the hope that 220-MHz spectroscopy might also reveal interesting features for PDMB prepared in polar solvents, we have investigated the nmr spectra of PDMB prepared with *n*-butyllithium in pure tetrahydrofuran at −45 and 25° as well as those of PDMB prepared in cyclohexane in the presence of a small amount of tetrahydrofuran at 25°.

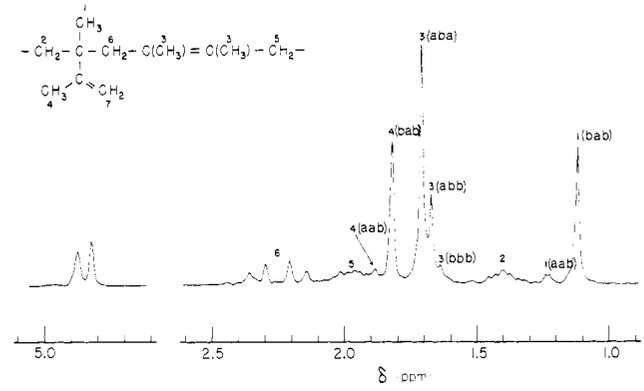

Figure 1. Nmr spectrum (220 MHz) of poly (2,3-dimethyl 1,3-butadiene) prepared at 25° in cyclohexane containing 1% v/v of tetrahydrofuran. Chlorobenzene solution at 100° with tetramethylsilane as reference.

Experimental Section

All preparations were carried out in sealed high-vacuum systems. 2,3-Dimethyl-1,3-butadiene of a purity of 99.9% (vapor-phase chromatography) was degassed on the vacuum line, submitted to a partial prepolymerization with *n*-BuLi, and distilled into a flask where it was stored over calcium hydride. Tetrahydrofuran was refluxed over sodium, fractionally distilled, degassed, and stored in a flask containing sodium–potassium alloy. Cyclohexane was purified by the usual method and distilled over *n*-BuLi before use. Polymerizations were carried out as follows.

Solvent (100 ml) and 15 ml of monomer were transferred to a flask which had been evacuated, degassed, and placed in a Dry Ice–acetone bath. Then 0.2 ml of a 1.6 *M* solution of *n*-BuLi in hexane (as received from Foote Mineral Co.) was added by syringe through a serum cap and the flask was sealed and immediately placed in a thermostat where the reaction was allowed to proceed for 7 days. The reaction mixture was killed by adding a small amount of methanol and the polymer was isolated by pouring the solution into methanol containing 0.03% of 2,6-di-*tert*-butyl-4-methoxyphenol.

The 220-MHz nmr spectra were measured at 100° with a Varian HR 220 spectrometer using chlorobenzene as solvent and tetramethylsilane as internal reference. Sample concentrations were close to 10%. The individual peak outlines were constructed by hand on expanded scale spectra. Peak areas were determined with a planimeter.

Results and Discussion

Figure 1 shows the spectrum of PDMB prepared at 25° in cyclohexane containing 1% v/v of tetrahydrofuran. A quite similar spectrum was obtained for PDMB prepared at the same temperature in pure tetrahydrofuran. Figure 2 shows the spectrum of PDMB prepared at −45° in pure tetrahydrofuran. As expected these two spectra reveal much more detail than those measured at 100 MHz.[1] The resonances of almost all groups of protons are strongly affected by the variation of the microstructure of the polymer. This makes the spectra capable of yielding useful information concerning the triad distribution of the 1,2 and 1,4 units. Evaluation of the 1,2 content from the olefinic proton intensities at 4.8–4.9 ppm yields 45 and 75% of 1,2 units in polymers prepared at 25 and −45°, respectively. The first result is in good agreement with that published by Yuki, *et al.*, but the later is slightly higher than that reported by these authors for the same system.

Peak assignments given in Figures 1 and 2 as well as the discrimination of triad sequences of the 1,2 and 1,4 units are based on the relative 1,2 content of the two polymers. For the sake of simplicity, the 1,2 and 1,4 structures are designated by the letters a and b, respectively. No other specification is given concerning the 1,4 structure because it is believed that one of the isomeric cis or trans forms is dominant in these polymers. This is evidenced by the sin-