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The Preparation and Chemistry of Dicationically Active Polymers of Tetrahydrofuran

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ABSTRACT

The anhydrides of the very strong acids, CF_3SO_3H and FSO_3H, polymerize tetrahydrofuran (THF) to give a living polyether having cationic activity at each chain end. The surprising fact that both chain ends are cationically active necessitates the postulation of a reaction mechanism wherein the YSO_3-ester end group ($Y = CF_3$ or F) formed as an intermediate in the polymerization generates an oxonium ion by a subsequent O-alkylation reaction involving either a THF molecule or a nearest neighbor ether group of the polymer chain.

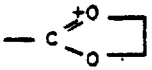
Kinetic studies of polymerizations involving $(CF_3SO_2)_2O$ and the bis-ester, $CF_3SO_3-C_4H_8-O_3SCF_3$, as initiators indicate that chain growth is much faster where an oxonium ion rather than an ester is the end group.

The chemistry of poly-THF dications is discussed. These are strong alkylating agents which make possible the facile preparation of unusual copolymers, block copolymers, and functionally terminated polymers.

INTRODUCTION

The subjects of the cationic polymerization of tetrahydrofuran (THF) and the conditions required to produce a living poly-THF having one cationically active end group per chain have been comprehensively reviewed [1]. In general, it had been shown that certain carbonium ion salts operated by abstracting a hydride ion from THF to give a cation capable of initiating polymerization. No termination occurred if the counteranion was stable with respect to the single propagating THF-oxonium ion [2-5]. Suitably stable counteranions included $SbCl_6^-$, PF_6^-, and ClO_4^-. Since hydride ion transfer, rather than carbonium ion addition to THF, constituted the initiation step, the use of dicarbonium ion salts was found unsuitable for preparing poly-THF dications [3].

Recently, Yamashita and co-workers reported the preparation of dicationically active polymers of THF by using 2,2'-octamethylene bis-1,3-dioxolenium perchlorate as the initiator [6, 7]. A noteworthy aspect of this work was the slow overall rate of polymerization, which was attributed both to the insolubility of the initiator salt in THF and the apparent stability of the dioxolenium ion,



with respect to nucleophilic attack by THF [6].

The present paper describes the preparation of poly-THF dications using as initiators appropriate derivatives of the very strong acids, trifluoromethanesulfonic acid (CF_3SO_3H) and fluorosulfuric acid (FSO_3H). Suitable derivatives for this purpose include trifluoromethanesulfonic anhydride, $(CF_3SO_2)_2O$, tetramethylene bis (trifluoromethanesulfonate), $CF_3SO_3C_4H_8O_3SCF_3$, and pyrosulfuryl fluoride, $(FSO_2)_2O$, the anhydride of FSO_3H. The chemistry of the polymeric dications is also discussed in this paper.

The chemistry of CF_3SO_3H and its derivatives has been described by many workers [8-11]. Briefly, it has been found that one of the most notable features of this chemistry is the unique activity of the alkyl trifluoromethanesulfonates (the so-called "triflates") in alkylation reactions. The powerful alkylation activity of the triflates has been attributed, at least in part, to the remarkable quality of the $CF_3SO_3^-$ leaving group.

The chemistry of $(FSO_2)_2O$ has also been discussed [12]. The latter reference mentions the polymerization of THF using $(FSO_2)_2O$ as initiator, but the discussion of the reaction is largely limited to the observation that this is the first nonprotic anhydride found to polymerize cyclic ethers. The present authors, however, had previously described the use of $(FSO_2)_2O$, as well as $(CF_3SO_2)_2O$, in the preparation of poly-THF dications in several issued patents, e.g., Ref. 13.

EXPERIMENTAL

THF. Anhydrous THF was used in all polymerizations. It was provided by distilling THF (Quaker Oats Co.) from a flask containing either $LiAlH_4$ powder or freshly prepared sodium ribbon.

$(CF_3SO_2)_2O$. This anhydride, bp 84°, $n_D^{25} = 1.3200$, was prepared by the dehydration of CF_3SO_3H (3M Co.) with excess P_2O_5 [14]. It was freshly distilled from P_2O_5 before use in polymerization reactions.

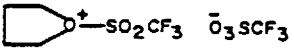
$(FSO_2)_2O$. Pyrosulfuryl fluoride, bp 51°, $n_D^{25} = 1.3205$, was prepared by the reaction of cyanuric chloride and FSO_3H [15].

$CH_3O_3SCF_3$. Methyl ester was prepared by refluxing a mixture of 100 g $Ba(CF_3SO_3)_2$ and 150 g dimethyl sulfate for 10 min and distilling the product. Fractionation of the distillate gave the methyl ester, bp 97°, $n_D^{25} = 1.3238$, in 90% yield.

$CF_3SO_3C_4H_8O_3SCF_3$. This alkylene bisester was prepared by adding 3.6 g of THF dropwise to a test tube containing 14.0 g of $(CF_3SO_2)_2O$ at -60° and allowing the mixture to warm to 0°. The product was dissolved in boiling CCl_4 and crystallized by cooling to 0°, washed with ice water, and then recrystallized from CCl_4. Yield was 8.4 g of white crystals, mp 36° C.

Analysis: Calculated for $C_6H_8F_6O_6S_2$: C, 20.3%; H, 2.3%; F, 32.2%. Found: C, 20.1%; H, 2.7%; F, 32.5%.

Fluorine NMR confirmed that the product was the indicated bisester. (Only one F-peak was observed, whereas two F-peaks would be expected for the salt which is isomeric with the bisester,



Caution: All of the initiator compounds mentioned herein are believed to be very toxic.

Polymerizations. These were carried out in stirred flasks by the addition of the indicated amount of initiator to anhydrous THF. Reactions were conducted under dry nitrogen atmospheres and temperatures were controlled with appropriate baths. In kinetic studies, measured aliquots of polymer solution were periodically removed and terminated by addition to THF solutions of excess LiBr. (A rapid termination occurs which involves the reaction of each active chain end to append a bromo-group and form the THF- and water-soluble lithium salt of the anion fragment of the initiator, e.g., LiO_3SCF_3.) The terminated polymers were dried, slurried in water and then treated with successive portions of cyclohexane to extract the polymers as quantitatively as possible from the water-soluble lithium salts. The cyclohexane solutions were combined, treated with anhydrous $MgSO_4$, centrifuged to clarify the solutions, and then dried of solvent. The polymer residues were weighed to get conversion results. Bromine content was analyzed in most cases and number-average molecular weight (M_n) was determined using the Hitachi 115 vapor phase osmometer. Molecular weight distribution was obtained for a few samples by gel permeation chromatography (Waters Associates).

The experimental conditions used to prepare the various derivativ of poly-THF dications are given separately in the discussion of the chemistry of the dications.

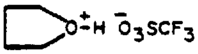
DISCUSSION OF RESULTS

Preparation of Poly-THF Dications

All of the reactions reported here were homogeneous in that the initiators were completely soluble in THF at the given reaction conditions.

Kinetic data are shown in Fig. 1 for the polymerization at 2° of bulk THF (12.3 moles/liter) using $(CF_3SO_2)_2O$ at concentration levels of 1.73 and 3.39×10^{-3} moles/liter. Comparative rate data ar shown for the use of a much higher concentration (0.596 mole/liter) of CF_3SO_3H as initiator.

Within experimental error, the polymerization rate is directly proportional to anhydride concentration and remains linear at least until THF depletion becomes appreciable. Polymerization of THF at 2° with CF_3SO_3H is very slow initially and the rate accelerates with time. (The initial polymerization rate is about one thousand times faster at 2° for anhydride than for acid at comparable initiator concentrations.) The rate relationships (which were also found to hold at temperatures of 14 and 25°) indicate that THF propagation is the rate-controlling step using anhydride initiation, while initiation is the important rate-controlling step in the case of acid initiation. (The latter point suggests a remarkable stability of the protonated oxonium salt,



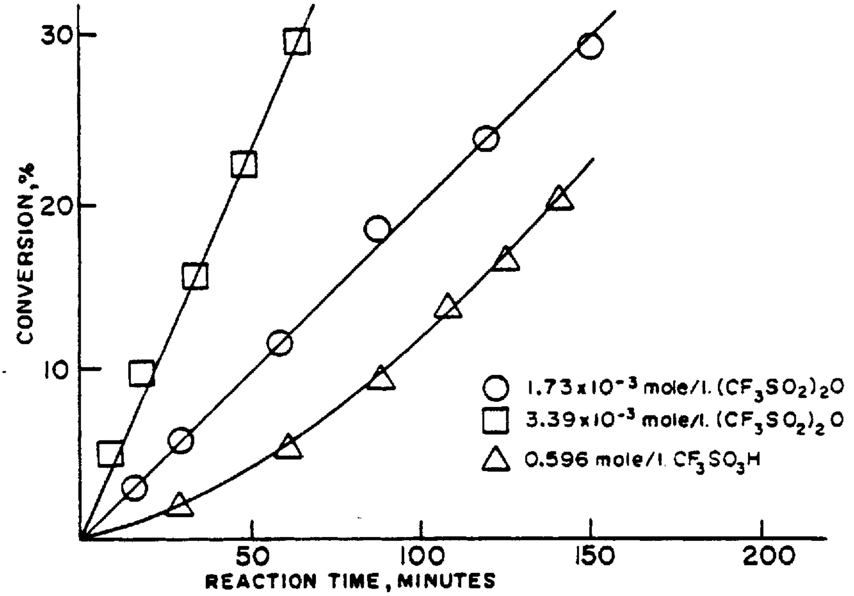


FIG. 1. THF polymerization rates at 2° C.

A study was made of the comparative polymerization rates and end group activities for THF polymerized at 35° in cyclohexane solutions using $(CF_3SO_2)_2O$ and $CH_3O_3SCF_3$ as initiators. As indicated above, all samples were quenched in lithium bromide solutions to append bromine to any chain end capable of sustaining polymerization and the polymer molecular weight (M_n) and bromine content were used to calculate the number of cationically active chain ends per molecule. The data are given in Table 1.

Despite some scatter in the M_n and bromine content data, it is clear that the anhydride causes the polymerization of THF to proceed in both directions of the linear chain, as reflected by the incorporation of two bromine atoms per molecule on quenching. Moreover, the activity of the end groups persists even after the equilibrium polymer concentration has been reached, corresponding to about 48% monomer conversion in this case. (The equilibrium nature of THF polymerization has been discussed [1]).

The methyl ester, on the other hand, gives a living poly-THF chain having a single active end group. The polymerization rate in this case, as might be expected, is about one-half the rate of polymerization proceeding from both ends.

TABLE 1. Polymerization Rates and End Group Activities of THF Polymerized at 35° in Cyclohexane, [THF] = 10.4 moles/liter

Initiator ([I] = 0.151 mole/liter)	Time (min)	Conversion (%)	M_n	Bromine	
				Weight (%)	No. per molecule
$(CF_3SO_2)_2O$	4	16.9	1560	10.8	2.11
	7	24.5	-	-	-
	15	38.0	3900	5.38	2.62
	25	45.1	-	-	-
	60	45.5	4190	4.45	2.33
	120	50.3	3840	4.48	2.16
	180	49.1	4210	4.38	2.11
$CH_3O_3SCF_3$	10	13.6	1340	6.55	1.09
	25	26.1	2830	3.51	1.24
	180	42.6	4340	1.86	1.01
	420	48.8	4170	2.00	1.04

Additional data of this nature are shown in Table 2 for the bulk polymerization of THF using $(CF_3SO_2)_2O$, $(FSO_2)_2O$, and the bisester, $CF_3SO_3C_4H_8O_3SCF_3$, as initiators.

It is seen that each of these initiators polymerizes THF to a living polymer which propagates at both chain ends. The bisester initiator gives a considerably lower initial polymerization rate than does either $(CF_3SO_2)_2O$ or $(FSO_2)_2O$ at comparable temperatures, but the rate accelerates with reaction time. This, of course, suggests that the initiation step is to some extent rate-controlling in the case of bisester initiation, whereas it is not with either of the anhydride initiators.

Polymerization Mechanism

The following mechanism is proposed to account for the observed results with the above initiators.

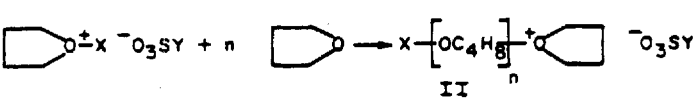
Initiation involves an O-alkylation of THF when esters are used, and O-sulfonation when anhydrides are used as initiators to generate an oxonium salt, as shown generically below:

I

(1)

where X = CH_3, FSO_2, CF_3SO_2, or $CF_3SO_3-C_4H_8$, and Y = F or CF_3.

Propagation involves the progressive nucleophilic attack of THF monomer at the α-carbon atom of the oxonium ion chain end, as indicated:



II

(2)

Although the initiators used here are novel and YSO_3^- has only now been determined to be a nonterminating anion, the initiation and propagation reactions shown above are consistent with the mechanism previously postulated for THF polymerization [1]. Where X = CH_3 (e.g., $CH_3O_3SCF_3$ as initiator), the previously established THF polymerization scheme accounts for the observed results. In this case the polymer bears a reactive cation at only one chain end and an unreactive methoxyl group at the other end.

Where X = FSO_2, CF_3SO_2, or $CF_3SO_3-C_4H_8$, it is necessary to invoke a further reaction to account for the cationic activity of both

TABLE 2. Polymerization Rates and End Group Activities of THF Polymerized in Bulk, [THF] = 12.3 moles/liter

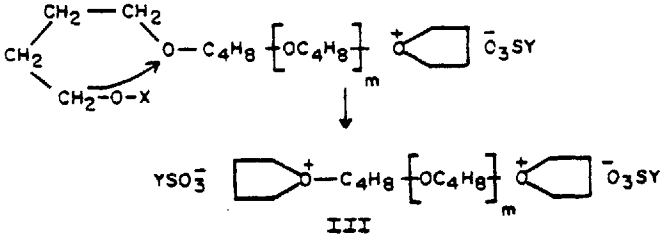
Initiator ([I] = 0.166 mole/liter)	Temp (°C)	Time (min)	Conversion (%)	M_n	Bromine	
					Weight (%)	No. per molecule
$(CF_3SO_2)_2O$	-10	5.2	5.7	525	29.03	1.91
		13.2	10.7	990	14.16	1.75
		26.3	18.0	1880	8.49	1.99
		41.2	27.3	2900	5.52	2.00
		60.3	38.5	3990	4.00	2.00
$(FSO_2)_2O$	5	7.3	14.0	940	17.38	2.04
		19.0	22.2	1550	11.29	2.19
		37.1	37.2	2240	8.10	2.27
		55.2	49.4	2640	6.59	2.17
$(FSO_2)_2O$	20	3.8	13.7	795	-	-
		12.2	25.8	1590	-	-
		20.0	39.3	1960	-	-
		28.2	45.3	2660	-	-
		40.0	53.7	2950	-	-
$CF_3SO_3C_4H_8O_3SCF_3$	5[a]	30.1[a]	15.3	3000	5.49	2.06
		61	33.9	4100	4.31	2.21
		90.2	55.8	5500	3.50	2.43

[a] This reaction was started at -10°, but conversion had reached only 8.3% after 40 min. The temperature was then raised to 5° and the times shown are the subsequent reaction times at 5°.

chain ends of the corresponding polymer. It is postulated that a second oxonium ion end group may be generated in either of two possible fashions.

a. The O-alkylation of a THF molecule by the ester chain end in a propagation reaction which is essentially analogous to the initiation reaction shown above in Eq. (1), where the initiating species is an ester (i.e., X = CH_3 or $CF_3SO_3{-}C_4H_8$).

b. The backbiting alkylation of a nearest-neighbor ether oxygen of the polymer chain by the ester to effect a ring-closure, as illustrated in



(3)

where X is FSO_2 or CF_3SO_2.

It is not possible to distinguish between reactions (a) and (b), but each seems to represent a feasible mechanism for the generation of the second oxonium ion in view of both the pronounced alkylating activity of these esters and their viability in initiating THF polymerization.

It is believed that the above reactions actually involve the equilibria:

$$\underset{\text{Dioxonium ion}}{\mathrm{III}} \rightleftharpoons \underset{\substack{\text{Monooxonium ion,}\\ \text{Monoester}}}{\mathrm{II}} \rightleftharpoons \text{Poly-THF-diester} \qquad (4)$$

Each of these forms appears to be capable of sustaining polymer growth at both ends, albeit at considerably different rates. The fact that $CF_3SO_3{-}C_4H_8{-}O_3SCF_3$, which is, of course, structurally analogous to the polymeric ester end group, shows a relatively low initiation rate for THF polymerization indicates that the oxonium ion is appreciably more reactive than the ester end group in the polymer propagation process. The relative equilibrium concentrations of the ester and oxonium ion end groups remain to be determined for these reactions. (It should be pointed out that the quenching reaction with

LiBr does not distinguish between oxonium ion and ester end groups. The bromination reaction is rapid and quantitative in each case.)

The molecular weight distribution of a poly-THF dibromide was determined for a sample which had been prepared by the LiBr termination of polymer made at 39% conversion using $(CF_3SO_2)_2O$ as initiator at -10°. The distribution, shown in Fig. 2, is very narrow ($M_w/M_n = 1.08$). This suggests that the equilibria of Eq. (4) are established very rapidly in this case. (Factors such as either a slow initiation reaction, a slow approach to equilibrium end group concentrations, or the occurrence of any termination reaction would, of course, each act independently to broaden the molecular weight distribution.)

If the proposed polymerization mechanism is correct, the following conditions should hold:

1. The polymerization reaction should be first order with respect to both THF and initiator concentrations. Such is the case for $(CF_3SO_2)_2O$, $CH_3O_3SCF_3$, and $(FSO_2)_2O$ initiations. The bisester, as mentioned above, gives more complex kinetics due to a slower initiation step. (The disparity between the initiation rates obtained with the methyl ester and the bisester is assumed to relate to the

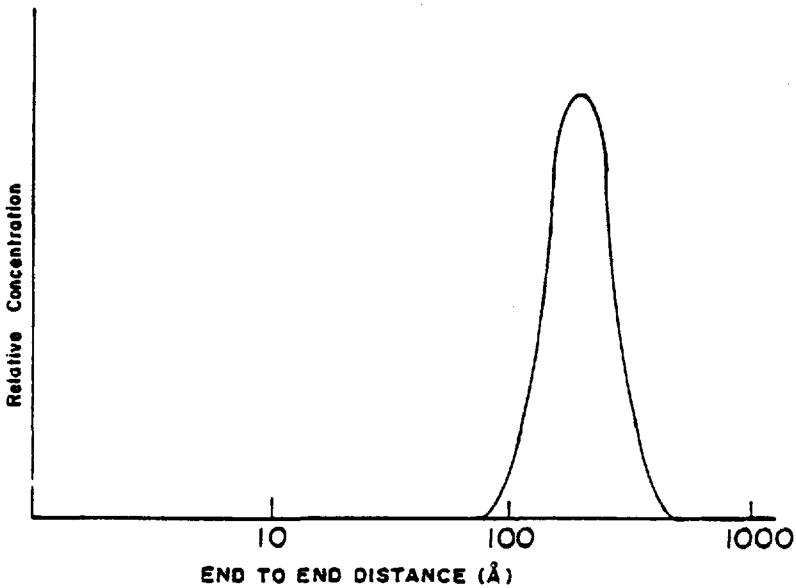


FIG. 2. Molecular weight distribution of poly-THF dibromide made at -10°C; $(CF_3SO_2)_2O$ as initiator.

generally greater rates of methylation as opposed to alkylations involving larger groups.)

2. The molecular weights of the polymer formed should be linear functions of polymer conversion at any given concentration of initiator. Figure 3 shows a plot of M_n vs percent conversion for data given in Table 2. Linear relationships are seen to be obtained in three separate reactions.

3. Each anhydride initiator molecule should furnish two poly-THF end groups, i.e., each mole of initiator should yield 1 mole of polymer. Curiously, $(FSO_2)_2O$ seems to conform more to expectations than $(CF_3SO_2)_2O$. The latter has an efficiency of only about 60% in this respect. (The two lines shown in Fig. 3 would coincide if both initiators had identical efficiencies in this respect.)

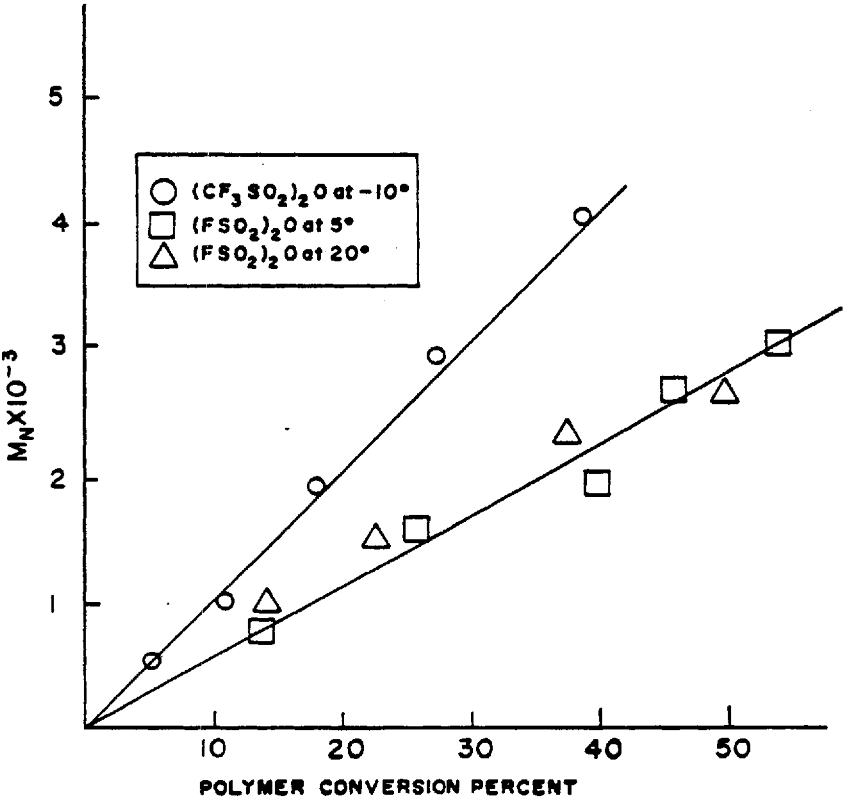


FIG. 3. Molecular weight as a function of degree of conversion of THF. [THF] = 12.3 moles/liter. [I] = 0.166 mole/liter.

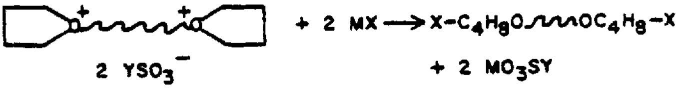
Chemistry of Poly-THF Dications

The poly-THF dications are effective polymerization initiators for various cyclic ethers, such as ethylene oxide and THF itself. A low molecular weight A-B-A block copolymer prepared by the room temperature addition of ethylene oxide to poly-THF dication was a very surface-active, water-soluble material which gave stable emulsions of benzene in water. Extremely high molecular weight poly-THF (> 500,000) is readily prepared either by single stage polymerization or by multistep additions of THF to polymeric dications.

Among the most interesting reactions of the poly-THF dications are the alkylations of anions (including polymeric anions) and of compounds containing two or more active hydrogens.

Alkylation of Simple Anions

The generic reaction of interest here is



(5)

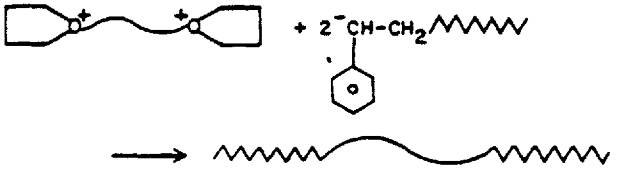
Suitable salts for this reaction include lithium bromide (discussed previously), sodium phenoxide, and potassium cyanate. (Saegusa and co-workers have used phenoxide quenching of poly-THF to determine the concentration of polymeric cations by subsequent determination of the UV absorption spectra of the phenoxylated polyether [16].) The cyanate salt reacts to yield poly-THF diisocyanate, a resin of especial interest, as illustrated in the following example.

Poly-THF dication was prepared by reacting 177 g THF and 16.7 g $(CF_3SO_2)_2O$ for 10 min at 50°. Twenty-eight grams of finely powdered potassium cyanate was added and the slurry was stirred for an additional 90 min at 50°. The product was taken up in 200 ml of cyclohexane and decanted from the insoluble salts after centrifugation. The dried, colorless product (45% yield based on THF monomer) showed a strong absorption band at 4.4 μ, typical of an isocyanate. Characterization gave isocyanate equivalent weight = 1140 (by dibutylamine titration), M_n = 2260 (1.97 NCO groups per molecule), and viscosity = 6300 cP. A noteworthy point is that the viscosity of this resin is considerably lower than that of a comparable molecular weight, conventional isocyanate resin which is prepared by capping a polyether diol by reaction with 2 moles of an organic diisocyanate. The higher viscosity of the latter resin is assumed to result from the intermolecular hydrogen-bonding of urethane groups.

The utilization in curing reactions of the poly-THF diisocyanates prepared in this fashion has been described [17].

Alkylation of Polymeric Anions

A three-segment block copolymer was prepared by the coupling of 2 moles of polystyrene anion with poly-THF dication:



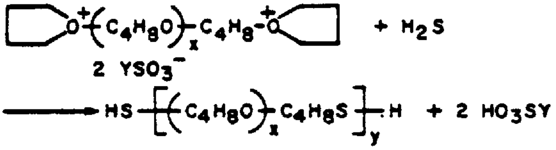
(6)

A living polystyrene monoanion was prepared by the dropwise addition over a 30-min period of 130 g pure styrene to a stirred solution of 0.555 g butyllithium (8.68 moles) in toluene. The reaction was continued under dry argon for an additional 30 min at 50°. A small aliquot sample of the solution was terminated by addition to methanol. The resulting styrene homopolymer of approximately 15,000 mol wt was found to have an inherent viscosity in benzene of 0.12 at 25°. The molecular weight distribution of this sample was found to be monodisperse (M_w/M_n = 1.09) with the end-to-end distance peak in THF solution occurring at 400 Å.

In a separate flask connected to the polystyrene reaction flask by a stopcock fitting, 1.22 g of $(CF_3SO_2)_2O$ (4.34 mmoles) was added to 21 g of THF under dry argon. The mixture was stirred for 10 min at 25° to produce a poly-THF dication of approximately 2000 mol. wt. The polystyrene monoanion solution was then drained into the stirred poly-THF dication solution. The red color of the living polystyrene dissipated rapidly and a slightly turbid solution resulted. The product was stripped in vacuum to give 149 g of a white powder. A sample of the product was Soxhlet extracted for 48 hr with methanol to remove any unreacted poly-THF. The block copolymer thus purified had an inherent viscosity in benzene of 0.23 and showed a monodisperse molecular weight distribution (M_w/M_n = 1.09) and a peak end-to-end distance value in THF solution of 800 Å.

Alkylation of Active H-Compounds

Poly-THF dication reacts with compounds containing active hydrogen atoms to displace protons and give the corresponding poly-THF-alkylated derivative of such compounds. When these compounds contain two or more active hydrogens, they can be reacted in stoichiometric proportion to yield polymers in which the chemical residue of the compound, from which the active hydrogens have been removed, appears as a recurring unit in the resulting chain-extended polymer. Thus, bubbling H_2S slowly into poly-THF dication solution gives a large increase in molecular weight and yields a linear polymer containing recurring thioether groups:



(7)

It has been of great interest to produce functionally terminated poly-THF samples by reacting the dication with large excesses of compounds containing active hydrogens. Because of the outstanding elastomers that can be prepared using epoxy resin curing reactions, the poly-THF diprimary amines produced by reaction of poly-THF dication with excess ammonia have been given considerable attention [18, 19]. The following example is illustrative of the manner in which the diamine may be prepared.

Forty-five grams of $(CF_3SO_2)_2O$ was added to 490 g of stirred THF and the reaction was conducted for 4 min at 25°. The viscous product was then poured into a stirred solution of 400 g NH_3 in 440 g THF maintained at -70°. The excess NH_3 was boiled off by allowing the solution to warm to 25°. The polymer was precipitated in water, washed repeatedly with aqueous NaOH and then water, and then finally vacuum-dried at 60°. The product (200 g yield) had an M_n value of 3350 and analysis gave an amine equivalent weight of 1620 by perchloric acid titration in glacial acetic acid (indicating 2.07 amine groups/molecule) and a nitrogen content of 0.904% (indicating 2.16 amine groups/molecule).

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