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Polymerization of Tetrahydrofuran Initiated by Isomeric 2,4,5-Trisubstituted 1,3-Dioxolan-2-ylium Salts. Mechanism of the Initiation

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ABSTRACT: The course of tetrahydrofuran (THF) polymerization carried out in the presence of isomeric 2,4,5-trisubstituted 1,3-dioxolan-2-ylium salts was investigated. A polymerization initiation mechanism was proposed for that system on the basis of results of end-group and ^1H NMR analyses. It was shown that the initiation reaction proceeds with the formation of two products (reaction Scheme III), a polymer having ester end groups being obtained. The influence of the dioxolenium cation structure on the polymerization reaction was also discussed.

Introduction

Stable carbenium and oxonium salts have recently found widespread use as cationic polymerization initiators.[1,2] Owing to the specific properties of these salts, their application has eliminated a number of difficulties encountered when using such conventional initiators as protonic acids, Lewis acids, aluminium alkyl compounds, etc.

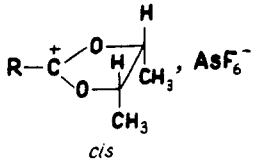
The 1,3-dioxolan-2-ylium salts also belong to the group of carbenium salt type initiators. The stable salts, derivatives of the trisubstituted dioxolane, have been recently used for initiating the polymerization of such heterocyclic monomers as 1,3-dioxolane[3] and trioxane.[4-6] Unsubstituted or monosubstituted dioxolenium salts have been also used to initiate the polymerization of tetrahydrofuran (THF).[7-11] The aim of the present paper is to discuss the effect of the structure of the isomeric 2,4,5-trisubstituted 1,3-dioxolan-2-ylium salts on the course of THF polymerization as well as to elucidate the mechanism of this reaction, especially its initiation step.

Experimental Section

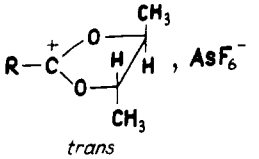
Monomer and Solvents. THF and THF-d_8 were purified by hours of long boiling over Na/K alloy in an atmosphere of dry nitrogen. The THF used in the polymerization was distilled over Na/K alloy directly before use.

Methylene chloride, CD_2Cl_2, and *n*-heptane were purified by conventional techniques used in cationic polymerization.

Initiators. The following trisubstituted isomeric 1,3-dioxolan-2-ylium salts were used as THF polymerization initiators.



cis



trans

R = { -CH3 (1); -CH2CH3 (2); -CH(CH3)2 (3); -C6H5 (4); -CH=CH-C6H5 (5) }

These salts were obtained by reacting a corresponding acetal with a triphenylmethylium salt, according to the method described previously.[12]

Table I
Viscosity-Average Molecular Weights of Polymers Obtained after 7 Days[a] from the Start of the Polymerization Reaction[b]

init	$\bar{M}_\eta$	init	$\bar{M}_\eta$
trans-**1**	18 600	*cis*-**4**	20 000
trans-**2**	18 700	*trans*-**4**	21 200
trans-**3**	19 100	*cis*-**5**	26 100
		trans-**5**	28 000

[a] The time required for equilibrium conversion in the polymerization initiated by *trans*-**5** initiator. [b] $[M]_0$ = 7.9 mol/L, $[I]_0$ = 1.8 × 10^{-2} mol/L, CH_2Cl_2 at 20 °C.

Table II
Theoretical and Experimental $\overline{DP}_n$ Values Obtained for Various Polymerization Times[a]

			$\overline{DP}_n$		
init	time, h	% conv	theor	UV	IR
trans-**4**	5	28	145	1702	
	10	35	181	1190	
	15	39	202	964	
	23	42	217	772	
	48	48	248	489	
cis-**5**	5	16	83	1560	1577
	10	26	134	1244	1250
	15	32	165	1140	1128
	23	37	191	956	953
	48	45	233	589	576

[a] $[M]_0$ = 9.3 mol/L, $[I]_0$ = 1.8 × 10^{-2} mol/L, CH_2Cl_2 at 20 °C.

Polymerization. The THF polymerization process was conducted in methylene chloride solution at 20 °C in the presence of the above-listed 1,3-dioxolan-2-ylium salts. The polymerization was terminated by adding to the system a methylene chloride solution of diethylamine. The polymer was precipitated with cold water, filtered off, and dried in vacuo to constant weight in order to determine the degree of conversion of the monomer.

Determination of Average Molecular Weights. The viscosity-average molecular weights were calculated from the Mark-Houwink relation:[13]

$$[\eta] = 2.98 \times 10^{-4} \bar{M}_\eta^{0.79}$$

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Table III
Theoretical and Experimental $\overline{DP}_n$ Values for Polymers Obtained in the Presence of Various 2,4,5-Trisubstituted 1,3-Dioxolan-2-ylium Salts after 7 Days from the Start of the Polymerization Reaction (Equilibrium State)[a]

	$\overline{DP}_n$		
init	theor	UV	IR
trans-1	178		176
cis-3	189		172
trans-3	178		191
trans-4	193	228	218
cis-5	189	277	290
trans-5	178	307	312

[a] $[M]_0$ = 7.9 mol/L, $[I]_0 = 1.8 \times 10^{-2}$ mol/L, CH_2Cl_2 at 20 °C.

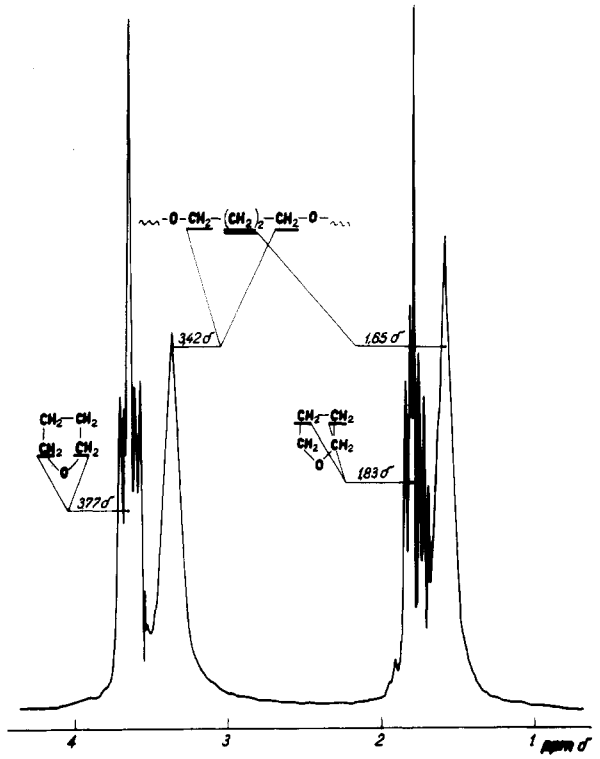


Figure 1. 100-MHz ^1H NMR spectrum of living poly(THF) recorded in CH_2Cl_2 at 20 °C ($[M]_0$ = 9.3 mol/L, $[M]_e$ = 4.3 mol/L, $[I]_0 = 1.8 \times 10^{-2}$ mol/L; initiator: *trans*-4·AsF_6^-).

The intrinsic viscosity $[\eta]$ was determined in benzene at 25 °C. The results are listed in Table I.

End-Group Determination. The end-group content of the polymer listed in Tables II and III was determined by UV spectroscopy (for compounds 4 and 5) and IR spectroscopy (for all compounds 1–5). The polymers were first purified by repeated dissolution in diethyl ether and precipitation with cold methanol until approximately constant DP_n values were obtained.

The UV spectra of the CH_2Cl_2 solutions of the polymers were recorded on a double-beam Specord UV–Vis Carl Zeiss Jena spectrometer, a quartz cell 1 cm thick being used. The DP_n(UV) values were calculated from the UV absorption data and the ϵ_{max} values found for the polymer samples studied, assuming each polymer chain to be terminated by one chromophoric group. For benzoic end groups (salt 4), $\epsilon_{max} = 1.16 \times 10^4$ L mol^{-1} cm^{-1} for λ_{max} = 230 nm was taken from the literature,[14] while for the cinnamic end groups (salt 5), $\epsilon_{max} = 2.2 \times 10^4$ L mol^{-1} cm^{-1} for λ_{max} = 278 nm was found experimentally.

The IR spectra of the CH_2Cl_2 solutions of the polymers were recorded on a double-beam UR-20 Carl Zeiss Jena spectrometer using NaCl and LiF prisms in the wavenumber range 4000–700 cm^{-1}. NaCl cells 1.02 mm thick were used for polymer solutions and cells 1.01 mm thick for the reference methylene chloride. The DP_n(IR) values were calculated based on the polymer carbonyl group IR absorption bands, using suitable calibration curves and assuming that each chain is terminated by one carbonyl group.

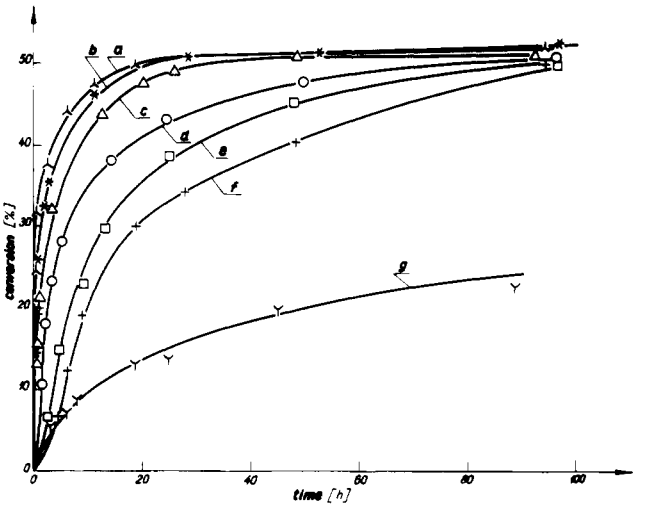


Figure 2. Polymerization initiated by 1,3-dioxolan-2-ylium hexafluoroarsenates and $Ph_3C^+AsF_6^-$ ($[M]_0$ = 9.3 mol/L, $[I]_0 = 1.8 \times 10^{-2}$ mol/L, CH_2Cl_2, 20 °C): (a), *cis*-1; (b), *cis*-3; (c), *trans*-3; (d), *trans*-4; (e), *cis*-5; (f), *trans*-5; (g) $Ph_3C^+AsF_6^-$.

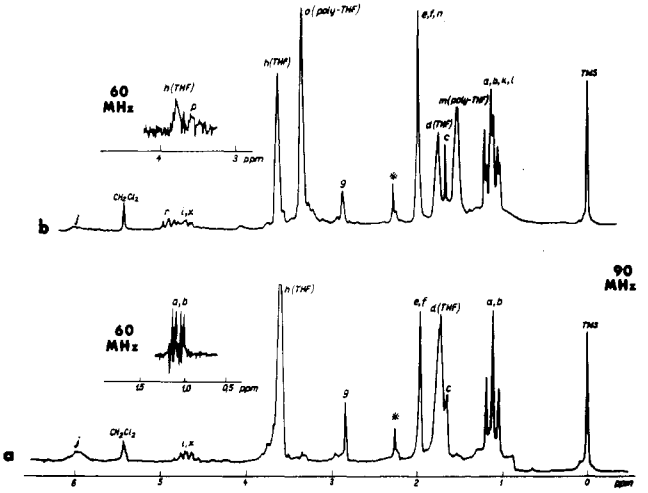


Figure 3. 90-MHz ^1H NMR spectrum of the THF/*cis*-1 reaction mixture recorded after (a) several minutes and (b) 32 h from the start of the reaction ($[M]_0$ = 9.3 mol/L, $[I]_0 = 1.8 \times 10^{-2}$ mol/L, CD_2Cl_2, 20 °C). The 60-MHz spectra were recorded for $[M]_0$ = 1.8 mol/L and $[I]_0$ = 0.13 mol/L (CD_2Cl_2, 20 °C).

Kinetic Measurements and Reaction Mechanism Studies. ^1H NMR Measurements. Polymerization kinetics was monitored by ^1H NMR spectroscopy, the reaction being run directly in the NMR sample tubes. The ^1H NMR spectra were recorded at 20 °C on a JEOL JNM-C-60 H or a Varian XL-100 spectrometer.

Changes in the intensities of the bands corresponding to the protons of the CH_2 groups neighboring the oxygen atom present in both monomer and polymer (Figure 1) were determined and conversion was calculated as a function of reaction time.

The corresponding conversions of the monomer to the polymer are shown in Figure 2 for polymerizations run in the presence of various isomeric 2,4,5-trisubstituted 1,3-dioxolan-2-ylium salts.

^1H NMR spectroscopy was also used for investigating the initiation reaction. Measurements were conducted under model conditions ($[I]_0$ = 0.13 mol/L, $[M]_0$ = 1.8 mol/L, CD_2Cl_2, 20 °C) using a JEOL JNM-C-60-H spectrometer and under polymerization conditions ($[I]_0 = 1.8 \times 10^{-2}$ mol/L, $[M]_0$ = 9.3 mol/L, CD_2Cl_2, 20 °C) using a Bruker FT WH-90 pulse spectrometer.

Typical ^1H NMR spectra of a reaction mixture, recorded after initiation of the reaction and 32 h after initiation, are shown in Figure 3. The assignment of signals present in the ^1H NMR spectra shown is given in Tables IV and V. Upon examination of the changes in the intensity of those signals it was observed that the drop in intensity of signals due to the initiator corresponds to the increase in intensity of signals assigned to individual

Table IV
Identification of Signals Present in the ^1H NMR Spectrum (Figure 3a) of the Reaction Mixture THF-*cis*-1 Recorded after Several Minutes from the Start of the Reaction

desig[a] of signal in spectrum (Figure 3a)	δ	type of signal
a	1.1	doublet
b	1.14	doublet
c	1.75	multiplet
d	1.83	multiplet
e, f	1.97	broadened singlet
g	2.84	singlet
h	3.77	multiplet
i, x	4.7	two superimposed quartets
j	5.95	multiplet

[a] The designation of signals given in this table is the same as that given in the following:

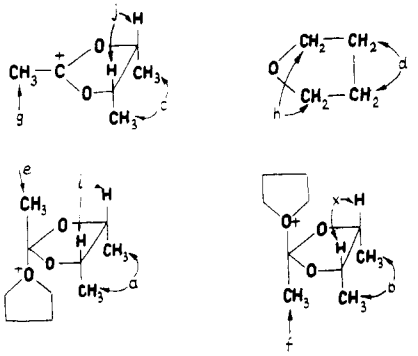
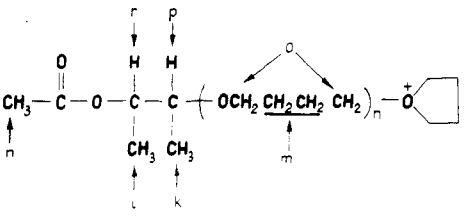


Table V
Identification of Signals Present in the ^1H NMR Spectrum (Figure 3b) of the Reaction Mixture THF-*cis*-1 Recorded after 32 h from the Start of the Polymerization Reaction

design[a] of signals in spectrum (Figure 3b)	δ	type of signal
k	1.1	doublet
l	1.14	doublet
m	1.65	multiplet
n	1.97	broadened singlet
o	3.42	multiplet
p	3.6	multiplet
r	4.9	multiplet

[a] The designation of signals given in this table is the same as that given in the following:

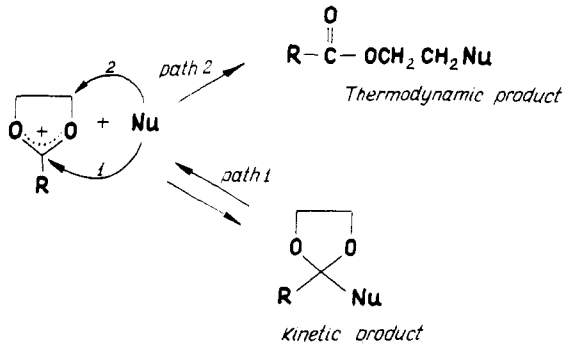


products. The signal intensity ratios of the products (e + f):(a + b) and (e + f + n):(a + b + k + l) were found to be 1:2 and remain constant throughout the reaction.

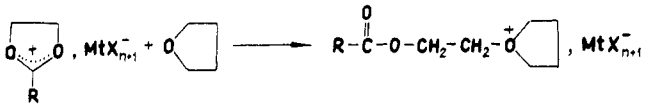
Results and Discussion

1. Influence of Structure of the 2,4,5-Trisubstituted 1,3-Dioxolan-2-ylium Salts on the Course of THF Polymerization and Molecular Weights of the Polymers Obtained. The time conversion curves in Figure 2 illustrate the course of THF polymerization carried out under the same reaction conditions in the presence of various 2,4,5-trisubstituted, 1,3-dioxolan-2-ylium salts and, for comparison, in the presence of a triphenylmethylium salt, a conventional cationic polymerization initiator. On comparison of the curves it may be seen that the rates of THF polymerization initiated by 2,4,5-trisubstituted 1,3-dioxolan-2-ylium salts are higher than those of polymerizations initiated by the corresponding triphenylmethylium salt having the same counterion, e.g., AsF_6^-.

Scheme I



Scheme II



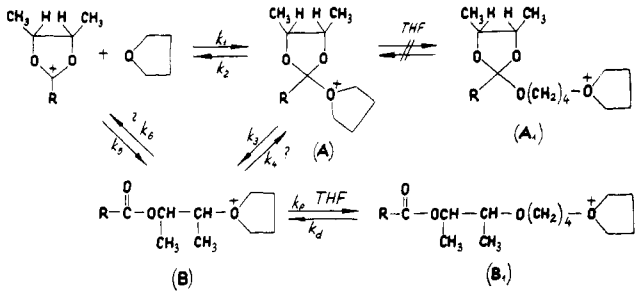
The THF polymerization rate however was found to depend on the dioxolenium cation structure. Salts with alkyl substituents at C-2 in the cation ring (1 and 3) are more active initiators than the C-2 aromatic substituted salts (4 and 5).

Slight differences between the catalytic activity of individual salts with alkyl substituents (1 and 3) were also observed. Replacement of the methyl substituent at C-2 of the cation ring (salt 1) by the bulkier alkyl substituent (salt 3) was found to result in reduction of the catalytic activity of the initiator. However, for each pair of isomers, the catalytic activity of the salt with the cis configuration was always greater than that of the corresponding trans isomer (Figure 2).

Differences in the catalytic activity of the individual salts investigated are also reflected in the values of the viscosity-average molecular weights of the obtained polymers. It follows from the data listed in Table I that products of polymerization reactions initiated by salts with alkyl substituents at C-2 (1–3) possess lower molecular weights than those of polymers obtained in the presence of aromatic substituted salts (4 and 5). In a polymerization process initiated by a salt with the cis configuration, polymer molecular weight was found to be lower than that of a polymer obtained using as an initiator a salt with the trans configuration (Table I).

2. Mechanism of Initiation. A number of THF polymerization initiation mechanisms are found in the literature for processes initiated by various stable organic salts. We believe that the mechanism of THF polymerization initiation by 2,4,5-trisubstituted 1,3-dioxolan-2-ylium salts may differ from those postulated for conventional initiators, as dioxolenium salts are known to exhibit certain specific properties. These salts have been, for instance, found to exhibit an ambident reactivity in reactions with nucleophiles.[15] A nucleophilic attack may proceed on C-2 yielding the so-called "kinetic product" as well as on C-4 and C-5 whereby the so-called "thermodynamic product" is formed (Scheme I). In the published works on the polymerization of THF initiated by dioxolenium salts,[7-11] it was postulated that attack of the monomer occurs on C-4 or C-5, and the thermodynamic

Scheme III



product formed acts as the active center in further chain propagation as shown in Scheme II. However, results of our NMR studies of the initiation step of THF polymerization carried out in the presence of 2,4,5-trisubstituted 1,3-dioxolan-2-ylium salts indicated clearly that its course was more complex than that hitherto postulated.[7-11] Formation of two different initiation products was found to occur, as confirmed by the values of the chemical shifts, the shape of the signals recorded in the ^1H NMR spectra (Figure 3), and changes of the intensities of the respective ^1H NMR signals during the reaction. One of these is formed rapidly at the beginning of the reaction (product A in Scheme III, corresponding to the kinetic product; signals a, b, e, f, i, and x in Figure 3a), while the formation of the second one is much slower (product B_1 in Scheme III, corresponding to the thermodynamic product; signals l, k, n, m, o, p, and r in Figure 3b). According to these data the initiation step in the polymerization of THF initiated by 2,4,5-trisubstituted 1,3-dioxolan-2-ylium salts may be therefore represented as shown in Scheme III.

Product A is formed as a result of a fast reversible reaction involving an addition of the monomer molecule to C-2 of the dioxolenium cation ring. Intermediate product A is then converted into ester B, which reacts with other monomer molecules to give the macroester B_1. Ester B may be, however, also formed as a result of a direct reaction of the dioxolenium salt with the monomer, which would proceed with opening of the dioxolenium ring due to attack of a THF molecule at C-4 or C-5. The initiation mechanism proposed in Scheme III was confirmed by polymer end-group determination results (Tables II and III).

The presence of ester groups in the polymer, which are the only end groups coming from the initiator (product B_1), makes it also possible to eliminate the mechanism of polymer chain growth with formation of structure A_1. The lack of acetal end groups can result from a steric hindrance in product A, which decreases the probability of nucleophilic attack of the next THF molecule on C-2 or C-5 in the cyclic oxonium ion A. The same effect can be caused by a probable delocalization of the positive charge, which decreases the reactivity of product A.

The data showing the contents of end groups in polymer (Tables II and III (UV and IR measurements)), similar to the ^1H NMR data, indicate that the formation of B_1 is slow.

Polymer samples obtained after relatively short reaction times (5–18 h) contained a smaller amount of end groups coming from the initiator than expected, taking into account the theoretical DP_n values (Table II). The data listed in Table III reveal that complete incorporation of the initiator into the polymers occurs only after a long period of time. The time required for completion of that process depends on the structure of the dioxolenium cation. It is shorter for more active initiators carrying an aliphatic substituent at C-2 than for initiators bearing aromatic substituents at C-2. The proposed course of the initiation reaction (Scheme III) is in good agreement with earlier work concerning the mechanism of model reactions of dioxolenium salts with various nucleophiles.[15-19] The course of such model reactions was shown to depend on the nature of the nucleophiles. In the case of strong nucleophiles (RO^- and CN^-),[15] attack on C-2 of the dioxolenium cation takes place. Weak nucleophiles (Cl^-, Br^-, and I^-) were demonstrated to attack C-4 or C-5 of the dioxolenium cation. Compounds with a moderate nucleophilic nature, e.g., H_2O or ROH, were shown[15,17-19] to form with dioxolenium salts the kinetic products, which may be subsequently transformed into the more stable thermodynamic ones (Scheme III). Bearing in mind that the basicity of THF ($pK_a = 2.08$) is close to the basicities of ROH and H_2O ($pK_a = 2.0$ and 1.74, respectively), it may be seen, that its reaction with 2,4,5-trisubstituted 1,3-dioxolan-2-ylium salts proceeds in a similar manner as the reaction of the latter with H_2O or ROH.

Conclusion

2,4,5-Trisubstituted 1,3-dioxolan-2-ylium salts may be used as effective initiators for THF polymerization. The kind and configuration of dioxolenium cation substituents influence significantly the rate of the polymerization. The initiator structure was shown to control the rate of the initiation step, which in turn determines the overall polymerization rate.

The initiation process involves a fast formation of a kinetic product, which is then slowly converted into a thermodynamic product whose ester group is present in the polymer (Scheme III).

Experimental results obtained in this work make it possible to correct, in conjunction with the results of model reactions[15-19] the hitherto available literature data[7-11] concerning the mechanism of initiation of THF polymerization carried out in the presence of initiators of the dioxolenium salt type.

Registry No. *trans*-1, 97171-56-7; *trans*-2, 97171-58-9; *trans*-3, 75425-35-3; *cis*-4, 75425-41-1; *trans*-4, 75425-36-4; *cis*-5, 75425-42-2; *trans*-5, 75425-37-5; THF, 109-99-9.

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