Cationic Polymerization of Cyclic Ethers Initiated by Macromolecular Dioxolenium Perchlorate

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ABSTRACT: Cationic polymerization of tetrahydrofuran (THF) with 2-methyl-1,3-dioxoleum perchlorate proceeded as a living system without chain transfer and termination, and the initiation reaction was shown to be the bonding mechanism. Poly-THF with terminal dioxolenium perchlorate group was synthesized from poly(tetramethylene glycol) by stepwise reaction with adipoyl chloride, ethylene bromohydrin, and silver perchlorate. The quantitative formation of macromolecular dioxolenium salt was proved from the polymerization behavior of the THF. Polymerization of 3,3-bischloromethyloxetane by the initiator yielded block copolymer, and no chain-transfer reaction except the termination reaction was observed. Polymerization of 7-oxabicyclo[2.2.1]heptane by the initiator yielded homopolymer as well as block copolymer, and a significant amount of chain transfer reaction was observed. Polymerizatian of dioxolane and tetraoxane by the initiator yielded little block copolymer, demonstrating the different mechanism of the initiation reaction in the case of cyclic formals.

KEY WORDS Block Copolymer / Cationic Polymerization / Tetrahydrofuran / Ring-Opening Polymerization /

In recent years, several active catalysts have been reported for the cationic polymerization of tetrahydrofuran (THF), which was shown to proceed with little termination or chain transfer.[1] Several publications have reported to prepare block copolymers by using the living nature of the cationic polymerization of THF.[2–5] Polymerization of THF and other cyclic ethers by macromolecular initiators can provide an interesting procedure for the synthesis of block copolymers consisting of well characterized sequences. Although polymers having terminal groups such as acyl halide or epoxide can initiate the polymerization of THF in the presence of Lewis acid, some transfer or termination reaction occurs leading to block copolymers[6] with insufficient sequence. A 2-substituted dioxolenium group with perchlorate gegen-anion was shown to initiate the polymerization of THF by the bonding mechanism and practically no transfer or termination reaction was observed in the polymerization of THF.[7] In this paper poly-THF with dioxolenium perchlorate end-groups was prepared and the polymerization of THF and other cyclic ethers by the macromolecular initiator was studied in a high vacuum system.

EXPERIMENTAL

Materials

Commercial THF was rectified over metallic sodium sealed in an ampoule after distillation from a green-colored solution of sodium naphthalene in a high vacuum system. 3,3-Bischloromethyloxetane was prepared according to Campbell,[8] and rectified over calcium hydride and distilled. 7-Oxabicyclo[2.2.1]heptane was prepared according to Campbell,[9] and distilled from a solution of sodium naphthalene in a vacuum system. Commercial tetraoxane was recrystalized from dichloromethane. Commercial 1,3-dioxolane was distilled from a solution of sodium naphthalene in a vacuum system.

Dichloroethane, nitromethane, and pyridine were dried with calcium hydride and distilled into ampoules in a vacuum system. Adipoyl chloride and ethylene bromohydrin were prepared by the usual procedure, and commercial

silver perchlorate was used with dehydrarion in a vacuum system.

Poly(tetramethylene glycol) (PTG 2000) and poly(ethylene glycol) (PEG 1000) were used after freeze-drying the benzene solution of the commercial products.

Preparation of Macromolecular Dioxolenium Perchlorate

To the freeze-dried PTG 2000 in a flask was added solvent, the stoichiometric amount of pyridine and excess adipoyl chloride from a break seal in a vacuum system. After 12-hr stirring at room temperature, excess ethylene bromohydrin was added and stirred for 12 hours. The reaction product was poured into water, extracted with dichloromethane and precipitated by pouring into *n*-hexane. The prepolymer I was further purified by reprecipitation with dichloromethane—*n*-hexane and with THF—water, and freeze-dried from benzene solution. The purity of the prepolymer I was checked by bromine analysis, molecular weight by vapor pressure osmometer, and number of ester groups per polymer chain using IR spectra.[7]

Macromolecular initiator solution containing terminal dioxolenium perchlorate group was obtained in a vacuum system by filtering the reaction product of the prepolymer I with excess silver perchlorate in nitromethane at 0°C for three hours. The weight of the precipitated silver bromide was more than 95 percent of the calculated value.

Chain extension was carried out by stirring PTG 2000 or PEG 1000 with the stoichiometric amount of adipoyl chloride in dichloroethane at room temperature in the presence of pyridine. After end-capping with excess adipoyl chloride and ethylene bromohydrin, the prepolymer was precipitated by *n*-hexane. Three days were required to complete the reaction. The freeze-dried prepolymer was converted to the macromolecular initiator by the same procedure.

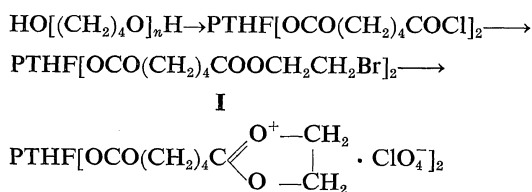*Polymerization Procedure and Characterization*

Polymerization was carried out by adding a measured amount of monomer in a break-seal to the nitromethane solution of macromolecular initiator, and stirred at 0°C. The polymer was precipitated with methanol or ethyl ether, and freeze-dried from benzene solution. The frac-

tionation experiment was carried out at room temperature by dissolving in chloroform. Each fraction was characterized by its NMR spectrum. Comonomer content in the block copolymer was determined by elementary analysis and NMR. $\overline{M}_n$ was measured by vapor pressure osmometer or membrane osmometer in benzene or chloroform solution.

RESULTS AND DISCUSSION

Polymerization of THF by Poly-THF Dioxolenium Perchlorate

Poly-THF with terminal dioxolenium perchlorate groups was prepared according to the following equation.

$$HO[(CH_2)_4O]_nH \rightarrow PTHF[OCO(CH_2)_4COCl]_2 \longrightarrow$$
$$PTHF[OCO(CH_2)_4COOCH_2CH_2Br]_2 \longrightarrow$$

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$$PTHF[OCO(CH_2)_4C\overset{O^+-CH_2}{\underset{O\ -CH_2}{\diagdown}}\cdot ClO_4^-]_2$$

PTG 2000 reacted with adipoyl chloride and ethylene bromohydrin. The prepolymer I was precipitated and the freeze-dried prepolymer I was analyzed as shown in Table I. The prepolymer I reacted with silver perchlorate in nitromethane. The precipitated silver bromide

Table I. Preparation of prepolymer I from PTHF
$$BrCH_2CH_2OCO(CH_2)_4CO[O(CH_2)_4]_{27.6}-$$
$$OCO(CH_2)_4COOCH_2CH_2Br$$

Exptl no.	1	2	3	4
Reagents				
PTG 2000, 10^{-3} mol	10.2	2.94	2.17	5.10
Adipoyl chloride, 10^{-3} mol	27.1	9.02	5.96	12.5
Ethylene bromohydrin, 10^{-3} mol	32.1	10.08	7.04	13.1
Solvent, m*l*	THF 60	THF 20	EDC 20	EDC 50
Pyridine, m*l*	—	1.5	1.0	—
Prepolymer				
M_n, obsd[a]	—	2510	—	1900
Number of ester groups per polymer chain	3.66	4.19	3.93	3.56

[a] The calculated molecular weight from PTG 2000 is 2470.

was weighed to show the completion of the reaction. Although the dioxolenium group shows specific absorption in UV spectrum (λ_{max} 220 mμ, ε 26.3 l/mol cm) and in IR spectrum (ν_{co} 1730 cm^{-1}) resembling ethyl acetate, quantitative determination of the end groups is not easy because of their low optical density.

To determine the purity of the end groups by an indirect method, the polymerization of THF with poly-THF-dioxolenium perchlorate solution was carried out in nitromethane at 0°C. The results are shown in Table II. The agreement of the observed $\overline{M}_n$ with the calculated value from conversion assuming the formation

of living polymer is fairly good. The number of ester groups per polymer chain analyzed from IR spectra[7] is nearly four after the polymerization as shown in Table II, and agrees with the value for the prepolymer I in Table I. From these results, the formation of macromolecular dioxolenium salt at both ends of PTHF could be substantiated.

Polymerization of Cyclic Ethers and Formals by Poly-THF—Dioxolenium Salt

The polymerization of cyclic ethers and formals by PTHF dioxolenium perchlorate was carried out at 0°C in nitromethane to provide clarification on the presence of termination or transfer reactions. The results are shown in Table III. In the polymerization of 3,3-bis-chloromethyloxetane (BCMO), block copolymer soluble in chloroform having the expected molecular weight was formed and the homopolymer of BCMO insoluble in chloroform was not observed. The block copolymer showed a crystalline band of BCMO at 700, 860, and 890 cm^{-1} and the formation of ABA block could be suggested. The polymerization of BCMO by dioxolenium salt seems to involve the initiation by bonding and the living nature of the propagation without chain transfer. The spectra of the block copolymer are shown in Figure 1. However, the yield was low even after a prolonged time and the polymerization

Table II. Polymerization of THF by PTHF dioxolenium salt

Exptl no.	4-1	2-1
Prepolymer I, 10^{-4} mol	9.63	11.63
CH$_3$NO$_2$, ml	4.57	9.05
THF, 10^{-2} mol	6.10	12.08
Polymerization time, hr	12	15
Polymer, g	2.99	5.82
Conversion of THF, %	26.4	21.8
$\overline{M}_n$, obsd	3400	3500
$\overline{M}_n$, calcd[a]	3100	3700
Number of ester groups per polymer chain	3.86	3.70

[a] From conversion.

Table III. Polymerization of cyclic ethers and formals by PTHF dioxolenium salt

Exptl no.	4-2	4-3	2-2	4-4	3-1
Comonomer	BCMO	OBH	OBH	TEX	DOL
PTG initiator, 10^{-4} mol	9.95	9.37	10.40	10.05	5.04
Comonomer, 10^{-2} mol	2.99	4.45	6.67	3.17	10.9
CH$_3$NO$_2$, ml	8.10	4.36	6.98	21.9	10.0
Polymerization time, hr	14.5	0.67	24	0.17	1
Block copolymer, g[a]	2.99	1.06	5.61	—	1.65[b]
MeOH-soluble polymer, g	0.185	0.143	0.05	1.80	
CHCl$_3$-insoluble polymer, g	0	1.52	2.21	1.03	2.09[c]
Conversion of comonomer, %	25.6	21.6	46.0		38.2
Block copolymer					
$\overline{M}_n$, obsd	3500	1500	2650		2600
$\overline{M}_n$, calcd	3100	—	—		—
Comonomer content, mol%	43.0	—	21.6		29.7

[a] MeOH-insoluble and CHCl$_3$-soluble part.

[b] Soluble in hot petroleum ether.

[c] Insoluble in hot petroleum ether and soluble in CHCl$_3$ and benzene; DOL homopolymer.

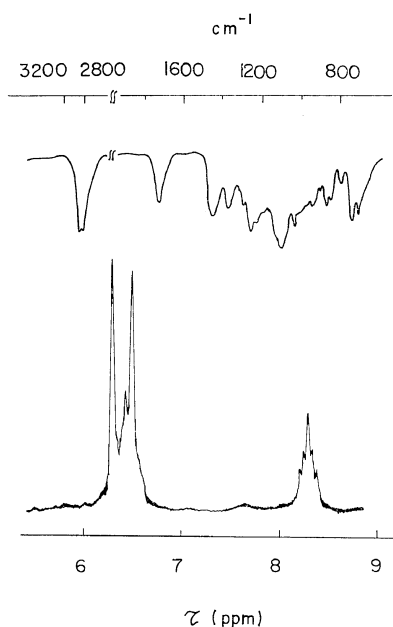**Figure 1.** IR and NMR spectra of BCMO—THF—BCMO block copolymer.

Figure 2. IR and NMR spectra of OBH—THF—OBH block copolymer.

of BCMO by a low concentration of initiator (10^{-5} mol) to reach high molecular weight block copolymer stopped at low conversion of BCMO after several days, showing the importance of the termination reaction.[10] In the polymerization of 7-oxabicyclo[2.2.1]heptane (OBH), block copolymer soluble in chloroform and homopolymer of OBH insoluble in chloroform was formed. The decrease of molecular weight suggested the occurrence of some chain-cleavage reaction due to reactive OBH cation. The spectra of the block copolymer are shown in Figure 2. Thus, although the dioxolenium salt can initiate the polymerization of OBH by bonding, considerable chain-transfer reaction to monomer seems unavoidable at the propagation step. In the polymerization of tetraoxane (TEX), the formation of block copolymer could not be detected, thus showing the mechanism of the initiation reaction was different and indicating the occurrence of chain transfer at the initiation step. This is also true for the polymerization of 1,3-dioxolane (DOL). The formation of the homopolymer of DOL suggested the presence of a chain-transfer reaction at the propagation step. Also the presence of
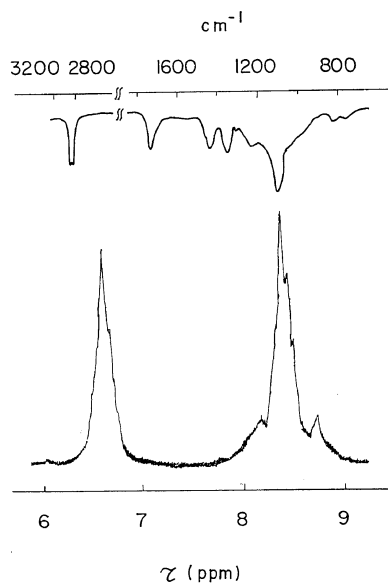
THF homopolymer suggested that the initiation reaction by bonding was not complete. These results are in agreement with the authors' previous results[11] on attempted copolymerization of THF and DOL, where the presence of homopolymer mixture lead to the idea that the oxonium ion initiates the polymerization of DOL by proton transfer.

Further experiments to prepare block copolymers having longer sequences of each segment were carried out. PTG 2000 reacted first with equimolar amounts of adipoyl chloride for chain

Table IV. Preparation of BCMO—EO—BCMO block copolymer

Exptl no.		5	6
PEG initiator, 10^{-5} mol		6.14	8.91
BCMO monomer, 10^{-2} mol		5.10	7.87
Solvent CH_3NO_2, ml		9.50	15.97
Polymerization time, hr		24	30
Polymerization temperature, °C		0	−20
Block copolymer, g		1.74	2.12
Conversion of BCMO, %		4.9	5.1
$\overline{M}_n$, obsd		26,000	31,000
$\overline{M}_n$, calcd		28,000	29,000
BCMO content, mol%		3.4	5.2

extension, and after treating with excess adipoyl chloride, the bromoethyl ester end-group was introduced. The molecular weight of the prepolymer reached 69000. However, its low solubility in nitromethane disturbed the formation of dioxolenium salt. On the other hand PEG 1000 was successfully chain-extended to a molecular weight of 22000. Polymerization of BCMO by this macromolecular initiator prepared in nitromethane is shown in Table IV. Again, the significant termination reaction of BCMO prevented the incorporation of higher BCMO content in the block copolymer even at $-20°C$.

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