

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

MECHANISM AND KINETICS FOR HOMO- AND
COPOLYMERIZATION OF CYCLIC ACETALS

BY

NA LU

A dissertation submitted to the Graduate Faculty
in Chemistry in partial fulfillment of the
requirements for the degree of Doctor of
Philosophy, The City University of New York

1996

UMI Number: 9618082

UMI Microform 9618082
Copyright 1996, by UMI Company. All rights reserved.
This microform edition is protected against unauthorized
copying under Title 17, United States Code.

UMI
300 North Zeeb Road
Ann Arbor, MI 48103

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

Jan. 28, 1996

Date

han-shi yang

Chair of Examining Committee

25-Jan-1996

Date

Hyun C. Kim

Co-Chair of Examining Committee

Jan. 26, 1996

Date

Robert R. E.

Executive Officer

Prof. David Locke

Prof. Carol Steiner

Supervisory Committee

The City University of New York

Abstract

MECHANISM AND KINETICS FOR HOMO- AND COPOLYMERIZATION OF CYCLIC ACETALS

by

Na Lu

Advisers: Professor Nan-Loh Yang and Dr. George L. Collins

Bulk homo- and copolymerization of trioxane and dioxolane initiated with boron trifluoride etherate was studied through the application of ^1H and ^{13}C NMR. The results confirmed that trioxane homopolymerization is characterized by an "induction period", during which steady state concentrations of formaldehyde and tetraoxane are built up. Rapid propagation will not occur until the concentration of these two generated "monomeric" species reach their maximum. The formation of tetraoxane in trioxane polymerization is understood through insertion of formaldehyde into monomer trioxane. In contrast to polymerization of trioxane, polymerization of dioxolane involves an equilibrium of polymer and monomer only, without generation of formaldehyde and any other small cyclic compounds.

It was concluded that water acts as coinitiator and

inactivator in both dioxolane and trioxane polymerizations. Time-conversion curves for both polymerization systems display a similar feature. That is, for the polymerization system with high water concentration, consumption of monomers is faster initially and then levels off. For the system with a low concentration of water, the initial rate of polymerization is slower but propagation increases rapidly. For trioxane polymerization, ^1H NMR spectra show that significant levels of formaldehyde cannot be formed and polymerization cannot proceed when the water content is undetectable by NMR. There is no direct evidence to exclude direct initiation in dioxolane polymerization. But from the concentration of propagation species measured through the ion-trapping method, it seems that direct initiation through self-ionization also occurs together with a cointiation mechanism. The different behavior for trioxane and dioxolane polymerization may be attributed to the fact that trioxane is a weaker base and has a stable six-member ring structure.

Formaldehyde plays an important role in copolymerization of trioxane and other cyclic acetals. Again, trioxane is not directly incorporated into the copolymer chain before formaldehyde reaches its steady state concentration. Instead, trioxane decomposes into formaldehyde. The insertion of formaldehyde into dioxolane leads to formation of trioxepane. This generated trioxepane is able to participate in copolymerization, leading to a

shift in the equilibrium of propagation $\rightleftharpoons$ depropagation to the direction of generation of more trioxepane. These processes occur repeatedly until a stable microstructure of copolymer is formed. Of course, occurrence of transacetalization during copolymerization of cyclic acetals may also contribute to sequence redistribution of microstructure.

*This thesis is dedicated to my farther, Nian-Gong Lu, in
memory of his love and encouragement.*

Acknowledgments

I would like to take this opportunity to thank Dr. Nan-Loh Yang and Dr. George Collins for their guidance, encouragement and help throughout my research work. Thanks also to Dr. David Locke and Dr. Carol steiner, who gave valuable comments on this work. I would like to express my appreciation to Dr. George Odian, Dr. Ruth Stark and Dr. Howard Haubenstein who have taught me during my graduate study.

The support of Hoechst Celanese for this work is gratefully acknowledged.

A special thank is given to Mr. Tai Park for his guidance in using NMRi software in sun SPARCstation and Mr. Kenneth Ao for his help in writing computer programs for kinetic models. There are many others in our laboratory who has provided helpful discussions and suggestions.

I am indebted to my friends, Wei Yang and Xia Zhao, they have offered me support and residence so that I can finally finish writing my thesis. I am very much impressed with their kindness and friendship.

TABLE OF CONTENTS**Introduction**

1. Initiation	1
2. Propagation	2
3. Chain transfer	3
4. Formation of cyclic compounds	3
5. References	5

**Part 1 The mechanism and kinetics of bulk polymerization
of dioxolane**

1.1 Introduction	8
1.2 Experimental	11
1.3 Equilibrium constants for initiation and propagation steps	13
1.4 ^1H NMR spectra of polymerization processes and mechanistic scheme for propagation steps.....	23
1.5 The concentration of propagation species and propagation rate constant.....	31
1.6 Initial rate of polymerization versus the concentrations of water and initiator	44
1.7 Mechanism and kinetic model for polymerization of dioxolane	55
1.8 Conclusions	62

1.9 References	65
----------------------	----

Part 2 Initial processes in the bulk polymerization of trioxane

2.1 Introduction	67
2.2 Experimental	70
2.3 ^1H NMR spectra for initial processes of trioxane polymerization	73
2.4 Kinetic curves for the polymerization of trioxane from GC determination	79
2.5 The effect of water on the "induction period" of trioxane polymerization	84
2.6 The effect of addition tetraoxane on the "induction period" of polymerization of trioxane	87
2.7 Mechanistic schemes for the polymerization of trioxane	93
2.8 Conclusions	96
2.9 References	99

Part 3 Microstructure analyses for the copolymers of trioxane and other cyclic acetals

3.1 Introduction	101
3.2 Experimental	104
3.3 ^1H NMR spectra of the copolymerization of	

dioxolane with trioxane	105
3.4 Microstructure analysis and ^{13}C NMR spectra for copolymer of dioxolane with trioxane	113
3.5 Copolymerization of dioxolane with trioxane through sequential monomer addition	128
3.6 Copolymerization of dioxolane with tetraoxane	137
3.7 Homopolymerization of trioxepane	144
3.8 Conclusions	151
3.9 References	153
Appendix	154
References	160

LIST OF FIGURES

Part 1

1-1 ^1H NMR spectrum of a mixture of OEt_2 / BF_3OEt_2 in chloroform solvent	15
1-2 Calibration curve for mole ratio of OEt_2 / BF_3OEt_2 versus chemical shift in CDCl_3	17
1-3 ^1H NMR spectra of the mixtures of BF_3OEt_2 / H_2O in chloroform solvent	18
1-4 Temperature dependence of the equilibrium monomer concentrations in bulk dioxolane polymerization initiated with BF_3OEt_2	21
1-5 ^1H NMR spectra as function of time for bulk dioxolane polymerization initiated with BF_3OEt_2 at 22°C	24
1-6 ^1H NMR spectra for bulk dioxolane polymerization initiated with BF_3OEt_2 at 22°C	26
1-7 ^{13}C NMR and DEPT NMR spectra for bulk polymerization of dioxolane initiated with BF_3OEt_2 at 22°C	27
1-8 ^1H NMR spectrum for bulk polymerization of dioxolane with addition of D_2O and initiated with BF_3OEt_2 at 22°C	28
1-9 ^{31}P NMR spectra for bulk dioxolane polymerization system initiated with BF_3OEt_2 and terminated by triphenylphosphine at 22°C	33
1-10 ^{31}P NMR spectra of model compounds	35

1-11	The change of monomer and propagation species concentrations versus time for bulk polymerization of dioxolane initiated with BF_3OEt_2 at 22°C	36
1-12	The relation of monomer concentration and propagation species in bulk polymerization of dioxolane initiated with BF_3OEt_2 at 22°C	40
1-13	The consumption of monomer versus time for bulk dioxolane polymerization systems with different water and BF_3OEt_2 concentrations at 22°C	48
1-14	The dependence of initial rate on water concentration in bulk dioxolane polymerization initiated with BF_3OEt_2 at 22°C	52

Part 2

2-1	^1H NMR spectra as a function of time for bulk polymerization of trioxane initiated by BF_3OEt_2 at 63°C	74
2-2	^1H NMR spectra as a function of time for bulk polymerization of trioxane initiated BF_3OEt_2 at 63°C	76
2-3	Kinetic profiles for each component during the course of trioxane polymerization initiated by BF_3OEt_2 at 63°C	78
2-4	Calibration curves for integral ratios of TOX / THF and TEOX / THF from GC spectra versus weight	

ratios of TOX / THF and TEOX / THF	80
2-5 Kinetic curves for bulk trioxane polymerization from GC determination	82
2-6 The change of maximum formaldehyde concentration versus water for bulk polymerization of trioxane initiated by BF_3OEt_2 at 63°C	88
2-7 ^1H NMR spectra as a function of time for bulk polymerization of trioxane initiated by BF_3OEt_2 at 63°C	90
2-8 ^1H NMR spectra as a function of time for bulk polymerization of trioxane with addition of tetraoxane initiated by BF_3OEt_2 at 63°C	91
2-9 The effect of addition tetraoxane on the time for formation of insoluble polyoxymethylene in bulk trioxane polymerization initiated by BF_3OEt_2 at 63°C	92

Part 3

3-1 ^1H NMR spectra as a function of time for bulk copolymerization of trioxane with dioxolane initiated by BF_3OEt_2 at 63°C	106
3-2 ^1H NMR spectra as a function of time for bulk copolymerization of trioxane with dioxolane initiated by BF_3OEt_2 at 63°C	109
3-3 ^1H NMR spectra as a function of time for bulk copolymerization of trioxane with dioxolane	

	initiated by BF_3OEt_2 at 63°C	110
3-4	A illustration of curve fitting to the overlapping peaks in copolymerization of Trioxane / dioxolane initiated by BF_3OEt_2 at 63°C	114
3-5	The average sequence length of formal units and mole fraction of triad sequences versus conversion for the copolymerization of trioxane / dioxolane initiated by BF_3OEt_2 at 63°C	117
3-6	Kinetic curves for each component of trioxane / dioxolane copolymerization initiated by BF_3OEt_2 at 63°C	119
3-7	^{13}C NMR spectra as a function of time for bulk copolymerization of trioxane with dioxolane initiated by BF_3OEt_2 at 63°C	125
3-8	Heteronuclear Shift Correlated 2D NMR spectrum for bulk trioxane and dioxolane copolymer mixture in DMSO solvent	126
3-9	^{13}C NMR spectra for bulk copolymerization of trioxane / dioxolane through sequential monomer addition at 63°C	129
3-10	The average sequence length of formal units and mole fraction of triad sequences vs. conversion for trioxane / dioxolane copolymerization through sequential monomer addition at 63°C	131
3-11	^{13}C NMR spectra for bulk trioxane /dioxolane copolymerization through addition of living homopolymer of dioxolane into molten trioxane at	

63°C	136
3-12 ^1H NMR spectra as a function of time for bulk copolymerization of tetraoxane with dioxolane initiated by BF_3OEt_2 at 65°C	139
3-13 ^{13}C NMR spectra as a function of time for bulk copolymerization of tetraoxane with dioxolane initiated by BF_3OEt_2 at 70°C	140
3-14 The average sequence length of formal units and mole fraction of triad sequences vs. conversion for tetraoxane / dioxolane copolymerization initiated by BF_3OEt_2 at 63°C	142
3-15 ^1H NMR spectra as a function of time for bulk homopolymerization of trioxepane initiated with BF_3OEt_2 at 63°C	145
3-16 ^{13}C NMR spectra as a function of time for bulk homopolymerization of trioxepane initiated with BF_3OEt_2 at 63°C	146
3-17 The average sequence length of formal units and mole fraction of triad sequences vs. conversion for bulk homopolymerization of trioxepane initiated by BF_3OEt_2 at 63°C	149

LIST OF TABLES

Part 1

1-1 The equilibrium constants for water / boron trifluoride etherate at 22°C	20
1-2 The thermodynamic parameters for bulk dioxolane polymerization	22
1-3 The propagation rate constants for bulk polymerization of dioxolane initiated with BF_3OEt_2 at 22°C	43
1-4 The propagation rate constants for polymerization of dioxolane	44
1-5 The estimated deviation in integral of NMR peaks	45
1-6 The initial rate and water concentration for bulk polymerization of dioxolane initiated with BF_3OEt_2 at 22°C	51
1-7 Rate constants derived from kinetic model	60

Part 2

2-1 The effect of water on the "induction period" for bulk trioxane polymerization initiated by BF_3OEt_2 at 63°C	85
---	----

INTRODUCTION

Polymerization of cyclic acetals to form linear polymer is well known. Among these polymer systems, the homo- and copolymerizations of trioxane and dioxolane have been investigated in detail. Trioxane homo- and copolymers have been produced on a commercial scale. Most concern has been for the mechanism of initiation, propagation and the formation of cyclic compounds during polymerization (1 - 7).

1. Initiation

The mechanism of initiation, especially with BF_3OEt_2 as initiator, is still obscure partly because very low concentration of water can make a substantial contribution to initiation by cocatalyst. On the other hand, the study on initiation of cyclic acetal polymerization with Lewis acids as initiator was limited to the characterization of active species. Two mechanisms, direct initiation and initiation through a cointiation have been proposed (8, 9). A generally accepted mechanism for direct initiation involves a self-ionization of the complex formed between BF_3 and cyclic acetals, followed by reaction with monomer. Cointiation mechanism involves the initiation by BF_3OEt_2 requiring the presence of a proton donor such as water.

Water reacts with BF_3OEt_2 to form an initiator-coinitiator complex (such as $\text{H}^+\text{BF}_3\text{OH}^-$) which then proceeds to donate a proton to monomer, thus, to initiate propagation.

2. Propagation

There have been two major controversies in the mechanism of propagation. Plesch and Westermann (10) concluded that poly(1,3-dioxolane) and poly(1,3-dioxepane) are exclusively cyclic based on studies of the end groups by IR and ^1H NMR analyses. Hence, they assumed that growth proceeds by ring expansion. Jaacks suggested that the growing chains are linear and the formation of cyclic oligomer was through a back-biting reaction (11). Penczek stated that living poly(dioxolane) can be either mostly (almost exclusively) cyclic or mostly linear, depending on the starting concentrations of monomer and initiator (6, 12).

Analysis of the structure of propagation species has also been attempted (13 - 16). The growing species can not be directly detected in most polymerization systems. Both oxonium and alkoxy-carbenium ions were usually considered as growing species because of the stabilizing effect of the α -oxygen atom of the ions. However, this stabilization may be insufficient to render the alkoxy-carbocations as the propagation species in preference to the oxonium ion. Studies of model systems have revealed that propagation is predominately through oxonium ions (15).

3. Chain transfer

Chain transfer to polymer, i.e. transacetalization, is defined as an exchange of alkoxymethylnium cation between different oxygen atoms along the polymer backbone. These reactions may proceed as an intra- or intermolecular process leading to formation of macrocycles or redistribution of polymer segments (7, 17). The reactions are facilitated because of the higher basicity of oxygen atoms in the polymer chain. Sequence redistribution of copolymer microstructure is often observed in copolymerizations of cyclic acetals, this phenomenon was usually considered as a result of transacetalization (18). In addition, propagation $\rightleftharpoons$ depropagation equilibria may become important in some copolymerization of cyclic acetals so that copolymer composition is no longer determined by the reactivity of the monomers (19).

4. Formation of cyclic compounds

Another important question concerns the mechanism of the formation of cyclic compounds during the homo- and copolymerization of cyclic acetals (20 - 23). This phenomenon was rationalized through a back-biting mechanism (20). However, an insertion mechanism has been proposed for the formation of trioxepane in the copolymerization of

trioxane and dioxolane (21). Collins, et al. (23) suggested a mechanism for the formation of dioxolane from the insertion of formaldehyde into ethylene oxide in the copolymerization of trioxane / ethylene oxide. Further insertion of a second molecular formaldehyde yields a trioxepane in this copolymerization system.

In the present investigation, bulk homo- and copolymerizations of trioxane and dioxolane initiated with boron trifluoride etherate were studied using ^1H and ^{13}C NMR. Mechanistic scheme and kinetic model of initiation and propagation for dioxolane homopolymerization were developed based on the NMR observation and fundamental consideration. In the case of homopolymerization of trioxane, we have observed the formation of formaldehyde and tetraoxane during the "induction period". The kinetic and mechanistic relations for these generated "monomeric species" were examined. In addition, the effect of water concentration on the rate of polymerization was studied systematically for both homopolymerization of trioxane and dioxolane. The role played by water on the initiation and retardation of polymerization has been discussed. Although a complete mechanistic scheme and kinetic model are not available for copolymerization due to its complication, we have focused on seeking reasonable mechanisms to explain the microstructure rearrangement and formation of cyclic compounds.

5. References

1. J. Masamoto, "Modern Polyacetals" *Prog. Polym. Sci.*, **18**, 1 (1993).
2. G. Odian, "Ring-Opening polymerization" in *Principles of Polymerization*, 3rd ed, Wiley-Interscience, New York, (1991), chap. 7.
3. S. Penczek and P. Kubisa, "Cationic Ring-opening Polymerization: Acetals", in *Comprehensive Polymer Science*, **Vol. 3**, G. C. Eastmond, A. Ledwith, S. Russo, and P. Sigwalt, Eds., Pergamon Press, London, (1989), chap. 49.
4. S. Penczek, P. Kubisa and K. Matyjaszewski, "Cationic ring-opening polymerization, Part II, Synthetic Application", *Adv. Polym. Sci.* **68/69**, 118 (1985).
5. R. C. Schulz, W. Hellermann and J. Nienburg, "Cyclic Compounds Containing Two or More Oxygen Atoms in the Ring" in *Ring-Opening Polymerization*, Vol. 1, K. J. Ivin and T. Saegusa, Eds., Elsevier, London, (1984), chap. 6.
6. R. Szymanski, P. Kubisa and S. Penczek, *Macromolecules*, **16**, 1000 (1983).
7. S. Penczek, P. Kubisa and K. Matyjaszewski, "Cationic ring-opening polymerization, vol. I, Mechanisms", in *Adv. Polym. Sci.* **37**, 1 (1980).
8. V. Jaacks and W. Kern, *Makromol. Chem.*, **62**(1), 1963.
9. G. L. Collins, R. K. Green, F. M. Berardinelli and W.

- V. Garruto, *J. Polym. Sci., Pol. Lett.* **17**, 667 (1979).
10. P. H. Plesch and P. H. Westermann, *J. Polym. Sci. Part C*, **16(7)**, 3837 (1968).
11. K. Boehlke and V. Jaacks, *Makromol. Chem.*, **145**, 219 (1971).
12. P. Kubisa and S. Penczek, *Makromol. Chem.*, **180**, 1821 (1979).
13. B. Xu, C. P. Lillya and J. C. W. Chien, *Macromolecules*, **20**, 1445 (1987).
14. V. A. Ponomarenko, E. L. Berman, A. M. Sakharov and Z. N. Nysenko, *Eur. Polym. J.*, **17**, 1111 (1981).
15. P. M. Lahti, C. P. Lillya and J. C. W. Chien, *Macromolecules*, **23**, 1214 (1990).
16. J. C. W. Chien, Y-G. Cheun and C. P. Lillya, *Macromolecules*, **21**, 870 (1988).
17. P. Colombo, S. Custro and P. Radici, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 681 (1980).
18. P. Dreyfuss and M. P. Dreyfuss "Cationic Ring-opening Polymerization: copolymerization," in *Comprehensive Polymer Science*, **Vol. 3**, G. C. Eastmond, A. Ledwith, S. Russo, and P. Sigwalt, Eds., Pergamon Press, London, (1989), chap 53.
19. Y. Yamashita "Random and Block copolymers by Ring Opening Polymerization". *Adv. Polym. Sci.*, **28**, 1 (1978).
20. T. Miki, T. Higashimura, K. Hayashi and S. Okamura, *J.*

- Polym. Sci., Polym. Lett.*, **5**, 65 (1967).
21. G. Mngoli and F. Furlanetto, *Markromol. Chem.*, **176**, 143, (1975).
22. T. Iwaisako, J. Masamoto, K. Yoshida, etc., *ACS, Polym. Preprints*, **30 (1)**, 241 (1989).
23. G. L. Collins, R. K. Greene, F. M. Beradinelle and W. H. Ray, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1597 (1981).

Part 1

THE MECHANISM AND KINETICS OF BULK POLYMERIZATION OF DIOXOLANE

1.1 Introduction

Although there have not been significant technical applications of dioxolane polymer, polymerization of dioxolane has been studied in detail (1 to 6). This system provides a suitable model for a thorough study of the initiation, kinetic, mechanism and thermodynamics of ring-opening polymerization.

Studies of the mechanism of initiation have been carried out in a number of dioxolane polymerization systems (7 - 9). For instance, the kinetics of polymerization of dioxolane initiated with $(\text{C}_6\text{H}_5)_3\text{C}^\oplus\text{SbF}_6^\ominus$ were studied dilatometrically (8). The polymerization is characterized by an induction period. Addition of water and $(\text{C}_6\text{H}_5)_3\text{CCl}_3$ caused the induction period to increase. The mechanism of initiation was suggested through the formation of a dioxolonium ion, which is a product of hydride transfer from an α -methylene group of dioxolane to $(\text{C}_6\text{H}_5)_3\text{C}^\oplus$. The prolonged induction period upon addition of water and $(\text{C}_6\text{H}_5)_3\text{CCl}_3$ was ascribed to the reactions of these two reagents with the dioxonium ion. Propagation rate constant

for the polymerization system was also calculated by assuming that concentration of propagation species equals to initiator concentration. Polymerization of dioxolane initiated with $\text{C}_6\text{H}_5\text{CO}^\oplus\text{SbF}_6^\ominus$ was also reported to proceed by an induction period (9). It was suggested that $\text{C}_6\text{H}_5\text{CO}^\oplus\text{SbF}_6^\ominus$ initiates polymerization by a direct addition mechanism. However, for the polymerization of dioxolane initiated with BF_3OEt_2 , whether the polymerization occurs through direct initiation or initiated by coinitiation is not clear.

Determination of active species has been a subject of much investigation (10 - 13). Polymerization of dioxolane initiated with $\text{CH}_3\text{OSO}_2\text{F}$ was investigated in both chloroform-d (CDCl_3) and nitromethane-d₃ (CD_3NO_2) solvents (12). The propagation species in the system was directly determined by ^1H and ^{13}C NMR spectra. It was found that polymerization of dioxolane initiated with $\text{CH}_3\text{OSO}_2\text{F}$ involves only ester growing species ($-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{OSO}_2\text{F}$) in CDCl_3 solution, while it contains both oxycarbenium ion ($-\text{OCH}_2\text{CH}_2\text{OCH}_2^\oplus\text{OSO}_2\text{F}^\ominus$) and ester species in CD_3NO_2 solution. Kinetic analysis of the polymerization in CDCl_3 gave the rate constant of propagation. Publications addressing the dioxolane- BF_3OEt_2 polymerization system have not been found. However, propagation species of polymerization of cyclic ethers initiated with boron trifluoride have been detected using ^{19}F NMR (13). It was stated that initiation by BF_3 yields an active center of zwitterionic nature ($\text{BF}_3\text{O}^\ominus\sim\sim\sim^\oplus$) under the experimental conditions. When cyclic

ether was added to a system containing only hydrated forms of BF_3 initiator, the polymerization proceeds through a new types of active center ($\text{HO} \sim \sim \sim \sim \text{BF}_3\text{OH}^\ominus$). Thus, initiation of polymerization of cyclic ether by BF_3 seems to be either through direct self-ionization mechanism or coininitiation mechanism (i.e., water acts as coininitiator) depending on experimental conditions.

Numerous kinetic studies have been carried out (14 - 17). The rate constants derived from different researchers are difficult to compare since the conditions and experimental methods employed varied greatly. In addition, there have been few studies on bulk polymerization. Most of the previous work was carried out in solution.

In this chapter, the bulk cationic polymerization of dioxolane initiated with BF_3OEt_2 was investigated by means of ^1H NMR spectroscopy. A mechanistic scheme and kinetic model have been developed based on known chemistry and experimental observations. A kinetic model was applied to experimental results to extract initiation and propagation rate constants using non-linear least-square fitting to the curve obtained by numerical integration of the kinetic expressions. A computer program was written for this curve fitting. For the first time, the quantitative relationship between the initial rate of polymerization and water concentration in this system was derived.

1.2 Experimental

All the materials in the experiments were obtained from Aldrich Co. The monomer dioxolane (DOL) was distilled under dry nitrogen from potassium metal to remove inhibitor and water with benzophenone as an indicator. When the solution turned to blue color, the fraction with b.p. 74°C at atmospheric pressure was collected in a closed three-neck flask, then transferred under N₂ into a NMR tube through a connecting needle inserted through a fitted rubber septum. All the apparatus were flame dried and then flushed with dry nitrogen gas before use. The water content in monomer was controlled by addition of the desired amount of water using microsyringes and determined at once by ¹H NMR or Karl-Fisher methods. The difference between two measurements is usually less than 15 % with ¹H NMR giving slightly higher results. Initiator boron trifluoride ethyl etherate (BF₃OEt₂), boron trifluoride dihydrate (BF₃·2H₂O) and terminator triphenyl-phosphine { (C₆H₅)₃P } are of reagent grade purity and were used without further purification.

The course of polymerization was observed *in situ* using an IBM WP-200 SY FT NMR operated at 200 MHz for ¹H. The NMR tube was flamed to remove the absorbed moisture before use. About 0.5g (nearest to 0.1 mg) of monomer and the desired amounts of initiator were injected rapidly into the tube and the contents were mixed vigorously with a

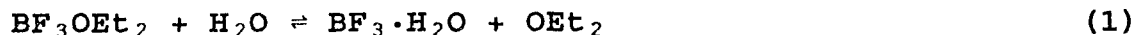
Vortexgenie. The sample tube was immediately placed in NMR probe kept at 22°C. Timing of the polymerization began at the moment of injection of the initiator into the monomer. Sixteen FID were collected at different reaction times as polymerization processed using an automated pulse program.

The concentration of propagation species was determined by the ion-trapping method (17) based on the conversion of the less stable cations to stable phosphonium ions which can be observed readily by ^{31}P NMR. The dioxolane polymer samples were prepared in bulk at 22°C with BF_3OEt_2 as the initiator. The polymerizations were quenched with a 15%-25% solution of triphenylphosphine in CDCl_3 at various reaction times. After adding the quenching solution, the mixture was stirred for about 10 min. A set of samples were collected at different reaction times until the conversion reached 40%-50%. These samples were measured by ^{31}P and ^1H NMR. The ^{31}P NMR spectra were obtained on the same instrument as ^1H NMR operating at 81.026 MHz. A 85% H_3PO_4 sample was used as an external reference and sufficient numbers of FID were accumulated in order to give adequate signal-to-noise ratio for quantitative data collection.

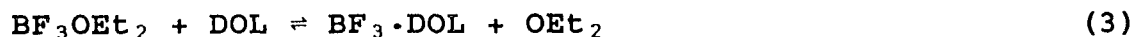
The equilibrium monomer concentrations at different temperatures were obtained by measuring the residual monomer in polymerization samples from the ^1H NMR spectra. The polymerization was carried out under controlled temperatures overnight to ensure the reaction equilibria.

1.3 Equilibrium constants for initiation and propagation steps

As observed in ^1H NMR spectra of bulk polymerization of DOL initiated with BF_3OEt_2 under the influence of a trace amount of water, water was consumed and ether was released from the complex immediately after the addition of boron trifluoride etherate. In addition, ether was also partially released in the system containing almost exclusively DOL and BF_3OEt_2 . Thus equilibria were developed between the Lewis acid (BF_3OEt_2) and both bases (DOL and H_2O) at the moment when they were in contact with each other. Two hydrates $\text{BF}_3\text{H}_2\text{O}$ and $\text{BF}_3(\text{H}_2\text{O})_2$ are expected to be produced when BF_3OEt_2 reacts with H_2O (18). The equilibria are expressed as

$$K_1$$


$$K_2$$


$$K_3$$


The equilibrium constant for the reaction of BF_3OEt_2 / DOL cannot be derived directly from this system because of propagation to form polymer. However, the equilibrium constants for the reactions between BF_3OEt_2 and H_2O can be estimated using ^1H NMR to monitor the reaction between

BF_3OEt_2 and water.

Based on the assumption that release of one mole of ether from BF_3OEt_2 will generate one mole of $\text{BF}_3\text{H}_2\text{O}$, the equilibrium constants are given by

$$K_1 = \frac{[\text{BF}_3\text{H}_2\text{O}][\text{OEt}_2]}{[\text{BF}_3\text{OEt}_2][\text{H}_2\text{O}]}$$

$$= [\text{OEt}_2]^2 / \{ ([\text{BF}_3\text{OEt}_2]_0 - [\text{OEt}_2]) ([\text{H}_2\text{O}]_0 - [\text{OEt}_2]) \} \quad (4)$$

$$K = K_1 \cdot K_2 = \frac{[\text{BF}_3\text{H}_2\text{O}][\text{OEt}_2]}{[\text{BF}_3\text{OEt}_2][\text{H}_2\text{O}]^2}$$

$$= [\text{OEt}_2]^2 / \{ ([\text{BF}_3\text{OEt}_2]_0 - [\text{OEt}_2]) ([\text{H}_2\text{O}]_0 - [\text{OEt}_2])^2 \} \quad (5)$$

Here, $[\text{BF}_3\text{OEt}_2]_0$ and $[\text{H}_2\text{O}]_0$ are the initial concentrations of boron trifluoride etherate and water. $[\text{OEt}_2]$ is the free ether concentration at equilibrium. The equilibrium constants can be calculated only if the concentration of free ether at equilibrium is determined.

The method used to determine the concentration of free ether was based on time-average chemical shift for species involved. We prepared a series of mixtures by dissolving known amounts of ether and BF_3OEt_2 into CDCl_3 and analyzing the mixtures using ^1H NMR. Fig. 1-1 shows a typical NMR spectrum of the mixtures. The broadening of the peak at 3.8 ppm is due to the fast exchange between the free ether and the bond ether in the BF_3OEt_2 complex. This peak shifts from 3.45 ppm toward 4.25 ppm with chemical shift depending on the ratio of free ether to bond ether in BF_3OEt_2 complex. The chemical shifts versus the ratios of $[\text{OEt}_2] / [\text{BF}_3\text{OEt}_2]$ were plotted to construct a calibration curve

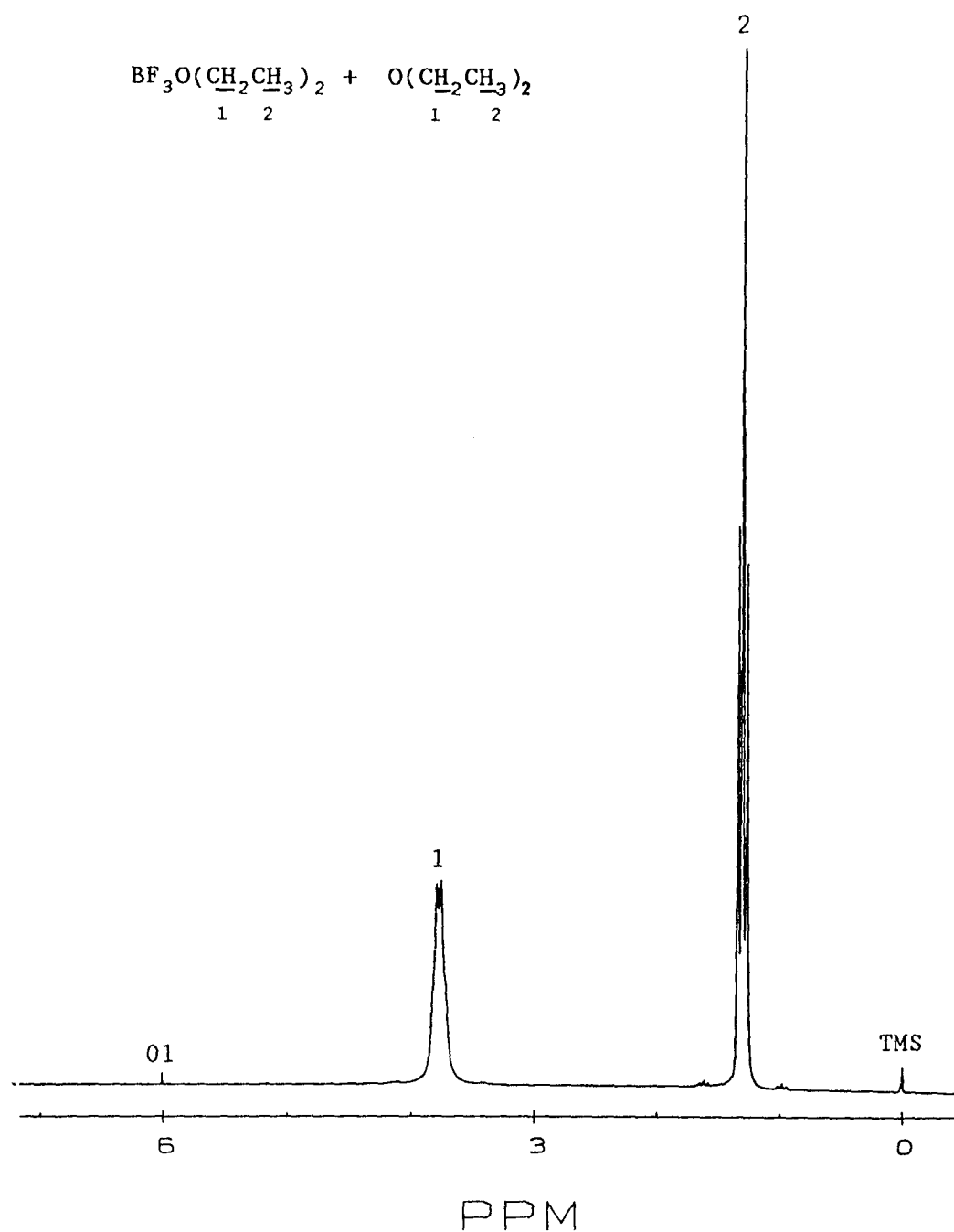
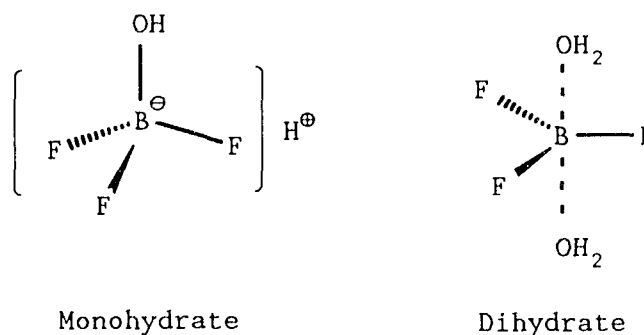


Fig.1-1 ^1H NMR spectrum of a mixture of OEt_2 / BF_3OEt_2 in chloroform solvent. $\text{BF}_3\text{OEt}_2:\text{OEt}_2=1.5:1$ (mole ratio).

(Fig. 1-2).

Fig. 1-3 represents the ^1H NMR spectra of mixtures with various ratios of BF_3OEt_2 and H_2O . In addition to two peaks due to ether, there are two peaks located at 7.3-8.7 ppm and 10.0-10.5 ppm. These two peaks may be due to the two protons in monohydrate ($\text{H}^+\text{BF}_3\text{OH}^-$). They merge into one broad peak when the ratio of $\text{H}_2\text{O} / \text{BF}_3\text{OEt}_2$ reaches 2. The NMR spectrum of $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ complex also displays a broad peak at the same location. This may be attributed to the formation of a symmetric structure in the dihydrate. This NMR observation may also imply that monohydrate is highly ionized in solution and should be considered as hydroxy-trifluoroboric acid ($\text{H}^+\text{BF}_3\text{OH}^-$). But the dihydrate should not be considered as ionized compound (i.e., $\text{H}_3^+\text{OBF}_3\text{OH}^-$).



Nevertheless, the concentration of free ether in the equilibrium system can be calculated from its chemical shift in Fig. 1-3 and the calibration curve (Fig. 1-2). Then the equilibrium constants can be determined by substituting the concentration of free ether into equations 4 and 5 (Table 1-1). Actually, the concentration of monohydrate was determined directly from the integral area

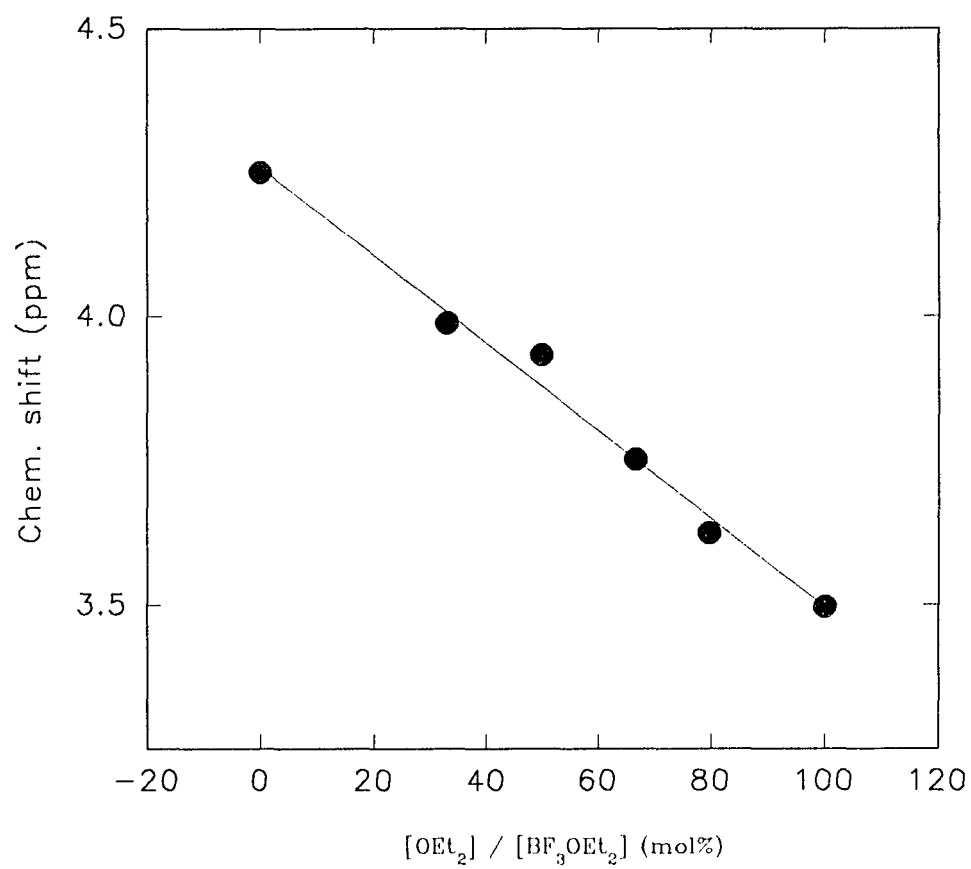


Fig. 1-2 Calibration curve for mole ratio of free ether and BF_3OEt_2 versus chemical shift in CDCl_3

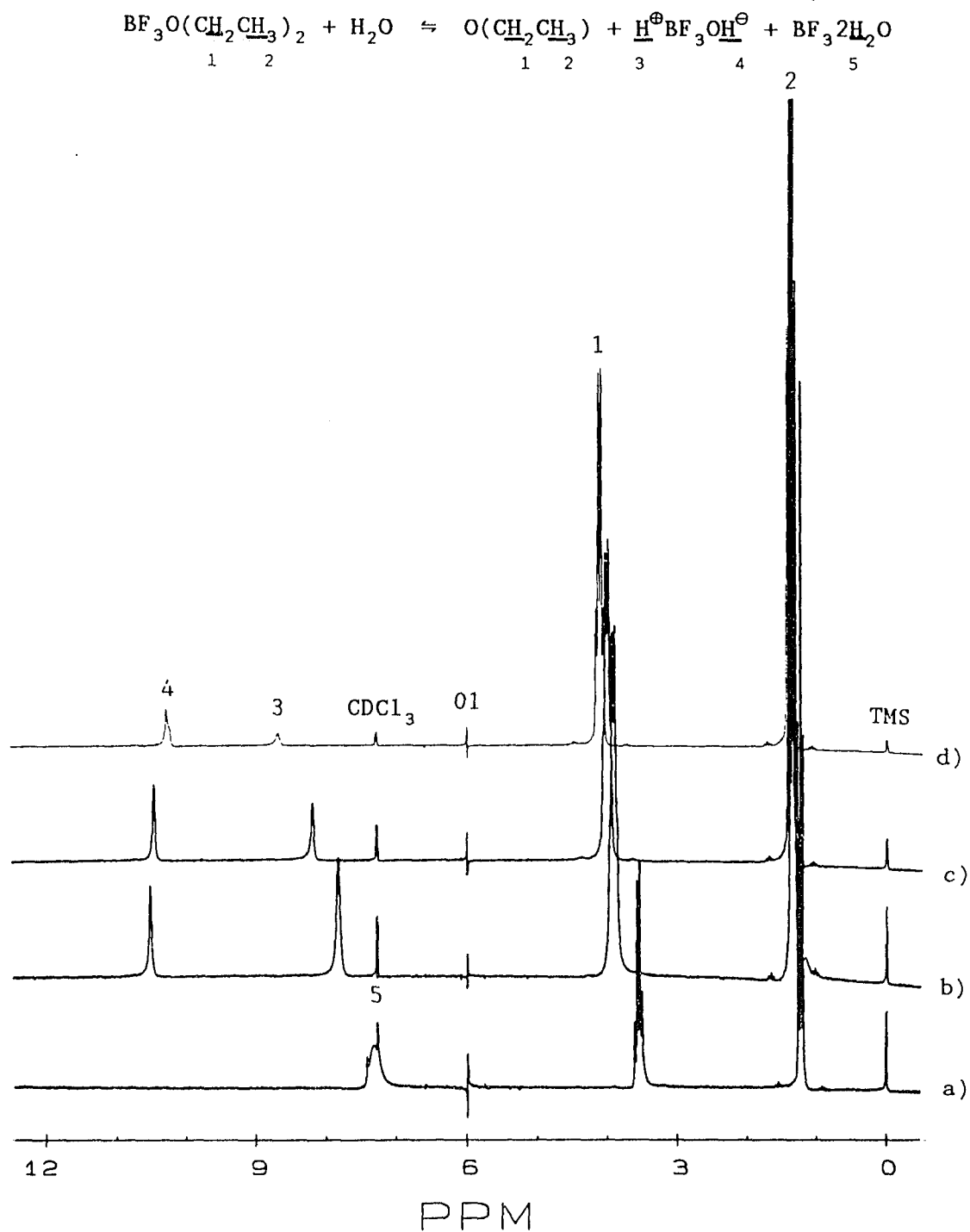


Fig.1-3 ^1H NMR spectra of the mixtures of BF_3OEt_2 / H_2O in CDCl_3 . Mole ratio of BF_3OEt_2 : H_2O are: a) 1:2, b) 1:1, c) 2:1, d) 4:1.

of the two peaks at 7.3-8.7 ppm and 10.0-10.5 ppm in Fig. 1-3. The results are close to the concentration of free ether. The equilibrium constants listed in Table 1-1 suggest that formation of dihydrate ($\text{BF}_3\cdot 2\text{H}_2\text{O}$) is favored over formation of monohydrate ($\text{BF}_3\cdot \text{H}_2\text{O}$) complex. This result is in accordance with the previous assertion that the dihydrate is more stable as compared with the monohydrate (19). The derived equilibrium constants were used in our kinetic model. These parameters were used only as approximate values for our model because the equilibrium constants are also dependent on the reaction medium.

The propagation steps in ring opening polymerization are also considered as reversible. The equilibrium constant is defined as the ratio of the rate of propagation, k_p , to that of depropagation, k_{-p} . Because the rate of propagation is equal to the rate of depropagation at equilibrium, the equilibrium constant can be calculated by the reciprocal monomer concentration at equilibrium $[\text{M}]_e$. The measurement of $[\text{M}]_e$ at different temperatures should yield the enthalpy and entropy of polymerization

$$k_p [\text{M}^+] [\text{M}]_e = k_{-p} [\text{M}^+] \quad (6)$$

$$K = k_p/k_{-p} = 1/[\text{M}]_e \quad (7)$$

$$\ln[\text{M}]_e = \Delta H_p/(RT) - \Delta S_p/R \quad (8)$$

In Fig. 1-4, $\ln[\text{M}]_e$ is plotting against the reciprocal of polymerization temperature. The enthalpy and entropy for

TABLE 1-1
The equilibrium constants for $\text{H}_2\text{O}/\text{BF}_3\text{OEt}_2$ at 22°C

$[\text{H}_2\text{O}]/$ $[\text{BF}_3\text{OEt}_2]$	Chem Shift (ppm)	$[\text{OEt}_2]$ (mol%)	K
1.00	3.88	49.8	0.98
1.89	3.71	72.0	1.58
1.37	3.78	62.8	1.43
0.92	3.87	51.0	1.28
1.04	3.83	56.2	1.51
0.78	3.90	47.6	1.41
0.50	3.98	36.6	1.52
0.36	4.06	26.2	0.93
$K_1(\text{ave}) = 1.29$			
2.37	3.54	94.2	7.54
2.05	3.58	89.0	5.39
2.02	3.57	90.3	6.79
$K_2(\text{ave}) = K/K_1 = 5.10$			

the bulk polymerization of dioxolane were found to be -32 kJ/mole and -91.6 J/mole $^\circ\text{K}$ from the slope and intercept of the straight line.

In fact, the thermodynamic parameters of dioxolane have been investigated by a number of authors. Table 1-2 presents some previously published data. For bulk polymerization, $[\text{M}]_e$ should have only one unique value at a given temperature. The variations of the thermodynamic parameters obtained by different researchers may be due to

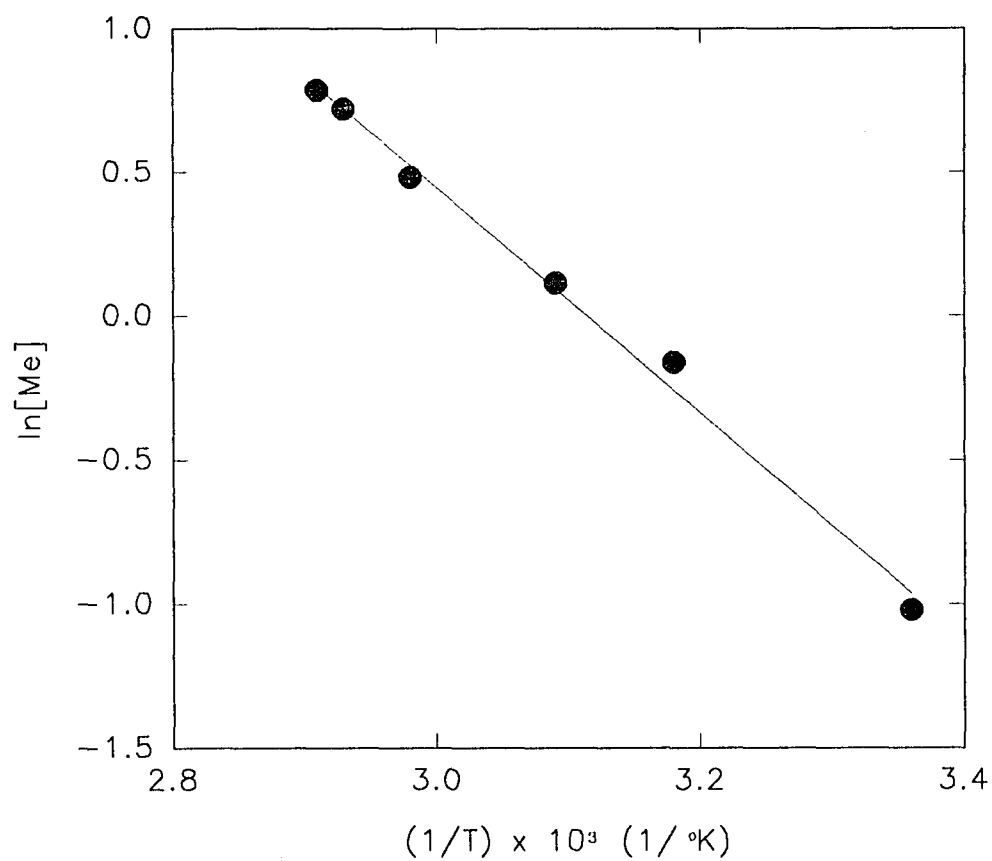


Fig. 1-4 Temperature dependence of the equilibrium monomer concentration in bulk polymerization of dioxolane $[\text{BF}_3\text{OEt}_2] = 0.024 \text{ mol/l}$.

TABLE 1-2

The thermodynamic parameters for bulk polymerization of dioxolane

phase transition	$-\Delta H_p$ kJ/mole	$-\Delta S_p$ J/mole $^{\circ}$ K	K at 25 $^{\circ}$ C
lc	23.0	62.7	5.7
lc	24	76	1.7
lc	15	37	5.0
lc	17.5	48	3.6
lc*	32.5	91.6	8.2

* These data were obtained from our experimental results.

different methods used. For example, the value of $\Delta H = -24$ kJ/mol and $\Delta S = -76$ J/mol $^{\circ}$ K were obtained using a semi-empirical calculation (20). This method relies on the known ΔH and ΔS values determined experimentally for the given class of monomer, and relates structural and electronic features of these monomers to the known thermodynamic parameters. The equilibrium constant corresponding to this method is far different from the others. All other thermodynamic parameters were derived using thermodynamic approach (21 - 23), i.e., one allows the polymerization to reach equilibrium at a series of temperatures and determines $[M]_e$ for the equilibrium system. The equilibrium constant obtained for our work based on *in situ* observation of $[M]_e$ is higher than the results from other investigators. The deviation among the measurements could

be due to: 1) whether a true equilibrium is established, a decrease in monomer concentration may only indicate that the plateau is of kinetic origin; 2) variations in the methods of determining the equilibrium monomer concentration, e.g., by gravimetry, dilatometry, gas chromatography or NMR.

1.4 ^1H NMR spectra of polymerization processes and mechanistic scheme for propagation steps

^1H NMR spectra for DOL homopolymerization processes were carefully examined (Fig. 1-5). Similar to polymerization of TOX, the peak due to water (2.38-2.44 ppm) disappears and ether is released from BF_3OEt_2 complex immediately after addition of BF_3OEt_2 . A small triplet which is believed from hydroxy end group is detected at 4.31 ppm. Only four peaks due to the unreacted DOL monomer and DOL homopolymer sequences MEM and EME are observed during the polymerization processes. The observation indicates the polymerization is an equilibrium involving polymer and monomer only, without generation of any small cyclic compounds. For trioxane polymerization, the formation of tetraoxane is due to the insertion of formaldehyde into the monomers trioxane (24). Here, it is understandable that no small cyclic compounds such as trioxepane can be generated since no formaldehyde can be formed in this system. However, the existence of large

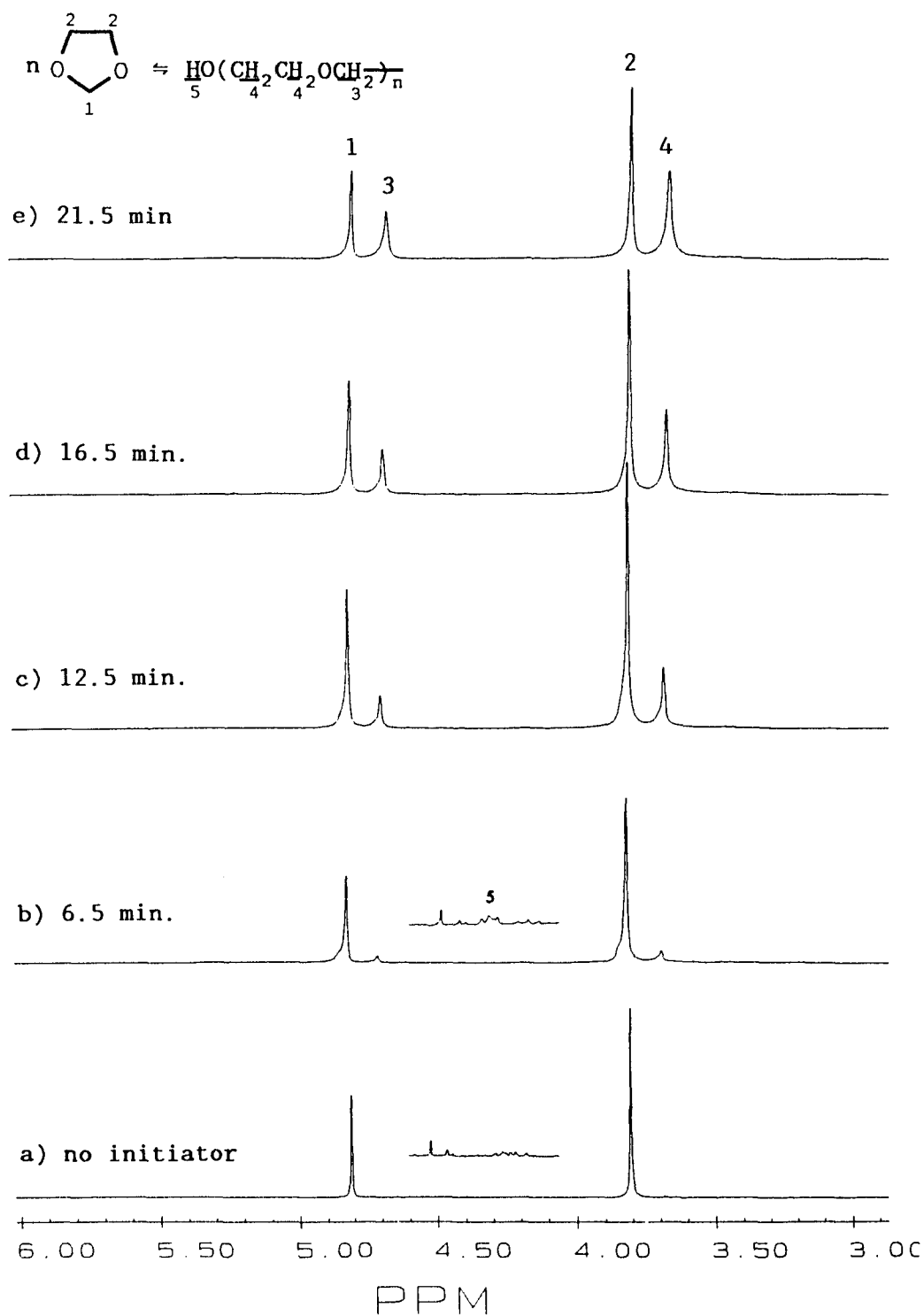


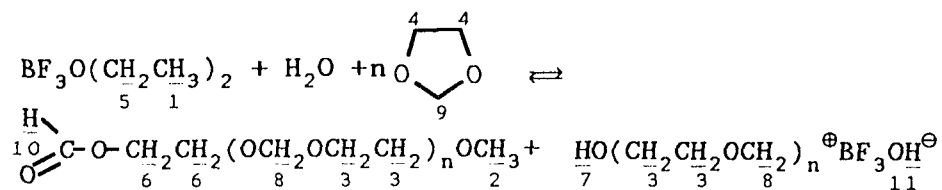
Fig.1-5 ^1H NMR spectra as a function of time for bulk dioxolane polymerization initiated by BF_3OEt_2 at 22°C . $[\text{BF}_3\text{OEt}_2] = 0.10 \text{ mol/l}$; $[\text{H}_2\text{O}] = 0.011 \text{ mol/l}$.

cyclic oligomers can not be excluded because ^1H NMR absorption is unable to distinguish between linear sequence and large cyclic oligomer.

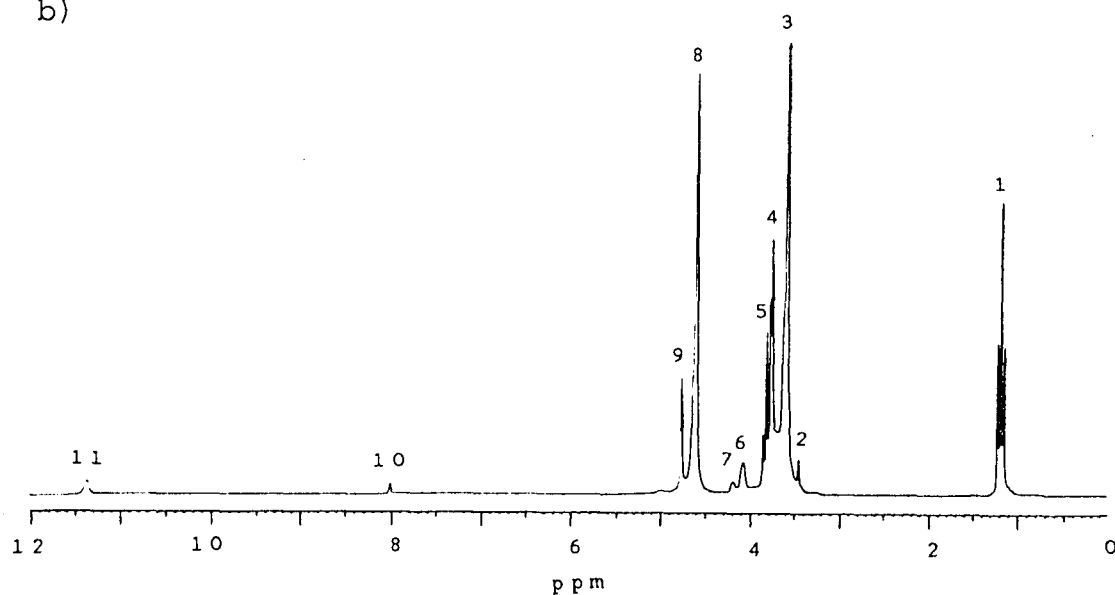
In addition to hydroxy end group, formate and methoxy end groups were detected for higher concentration of initiator (Fig. 1-6a). These end group absorption peaks, increasing with water (Fig. 1-6b), reflect a decrease in molecular weight with water concentration. The assignment of ^1H and ^{13}C spectra is indicated in Fig. 1-6 and Fig. 1-7a. A DEPT (Distortionless Enhancement by Polarization Transfer) NMR spectrum confirms the assignment (Fig. 1-7b). When D_2O was used in place of H_2O in the polymerization system, all the peaks due to end groups disappeared except the peak at 4.1 ppm which is assigned to the protons neighbored to the formate end group (Fig. 1-8).

The disappearance of hydroxy end group peak is expected because hydroxy end group is formed either through water acting as coinitiator or through chain transfer to water. The formation of formate and methoxy end groups is usually considered as a result of hydride-ion transfer reactions (25) (reaction scheme I). The disappearance of the formate peak may be caused by the formate hydrogen can exchange with D_2O . But the disappearance of the methoxy end group is difficult to explain. This peak sometimes overlaps partly with released ether from BF_3OEt_2 .

The peaks at 8.0 and 11.2-11.6 ppm were first suspected to be due to oxonium and alkoxycarbenium ions, but DEPT and



b)



a)

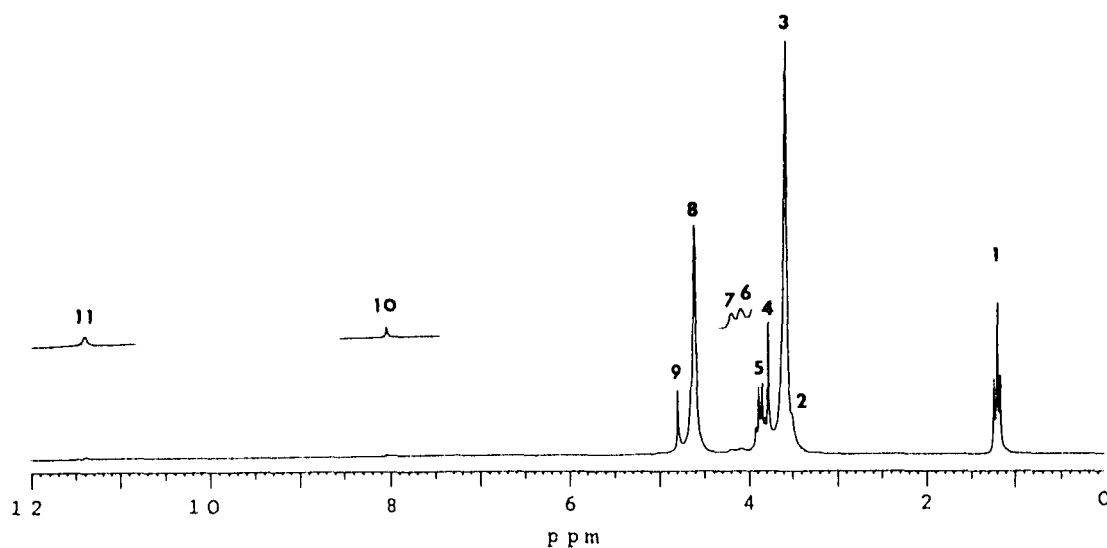


Fig.1-6 ^1H NMR spectra for bulk dioxolane polymerization initiated by BF_3OEt_2 at 22°C . a) $[\text{BF}_3\text{OEt}_2] = 1.4 \text{ mol/l}$; $[\text{H}_2\text{O}] \approx 0.025 \text{ mol/l}$, b) Same sample recorded after 4 days later.

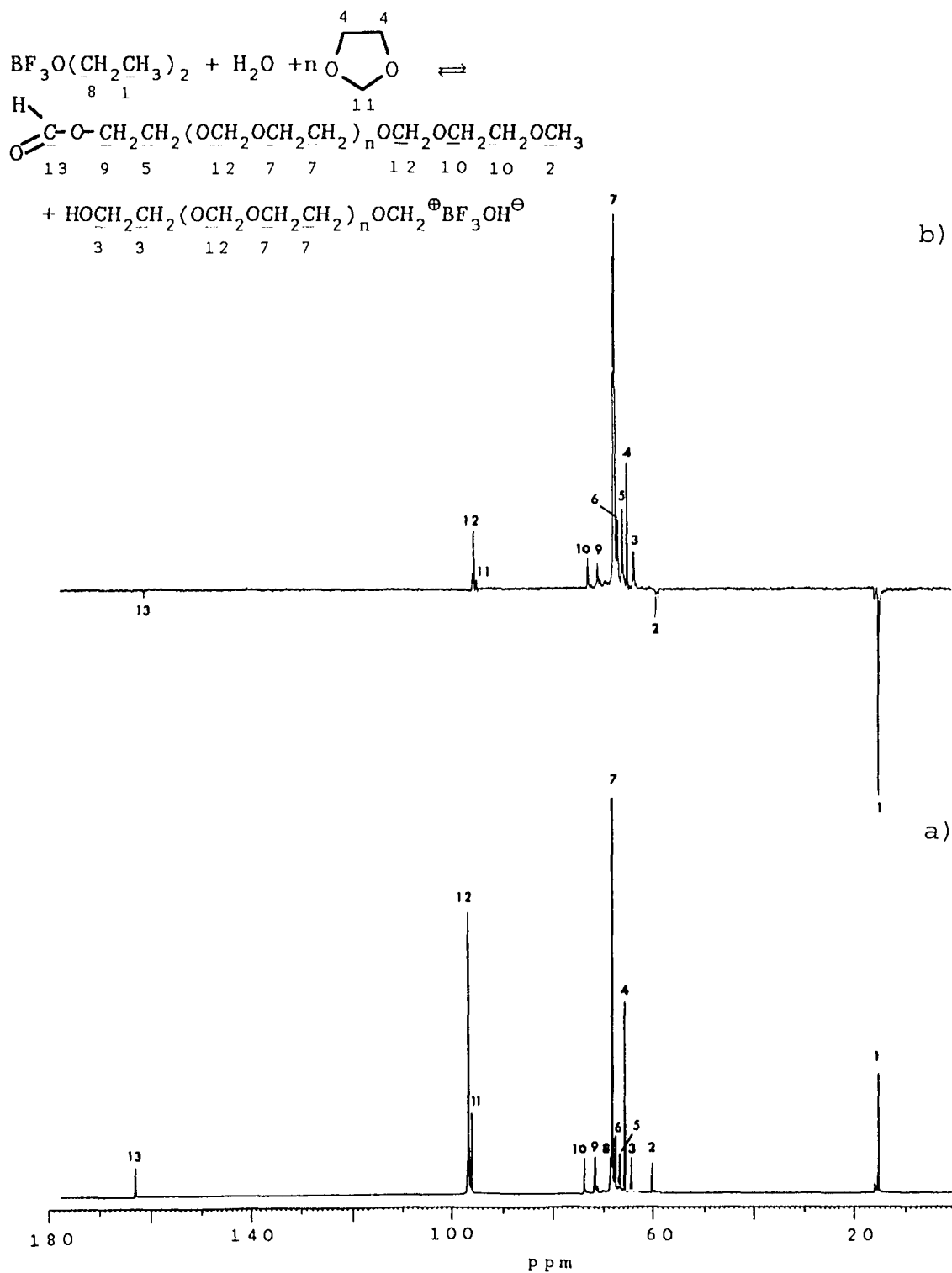


Fig.1-7 ^{13}C NMR and DEPT NMR spectra for bulk dioxolane polymerization initiated by BF_3OEt_2 at 22°C . a) Same sample as in Fig.1-6b, b) $[\text{BF}_3\text{OEt}_2] = 1.1 \text{ mol/l}$; $[\text{H}_2\text{O}] \approx 0.1 \text{ mol/l}$.

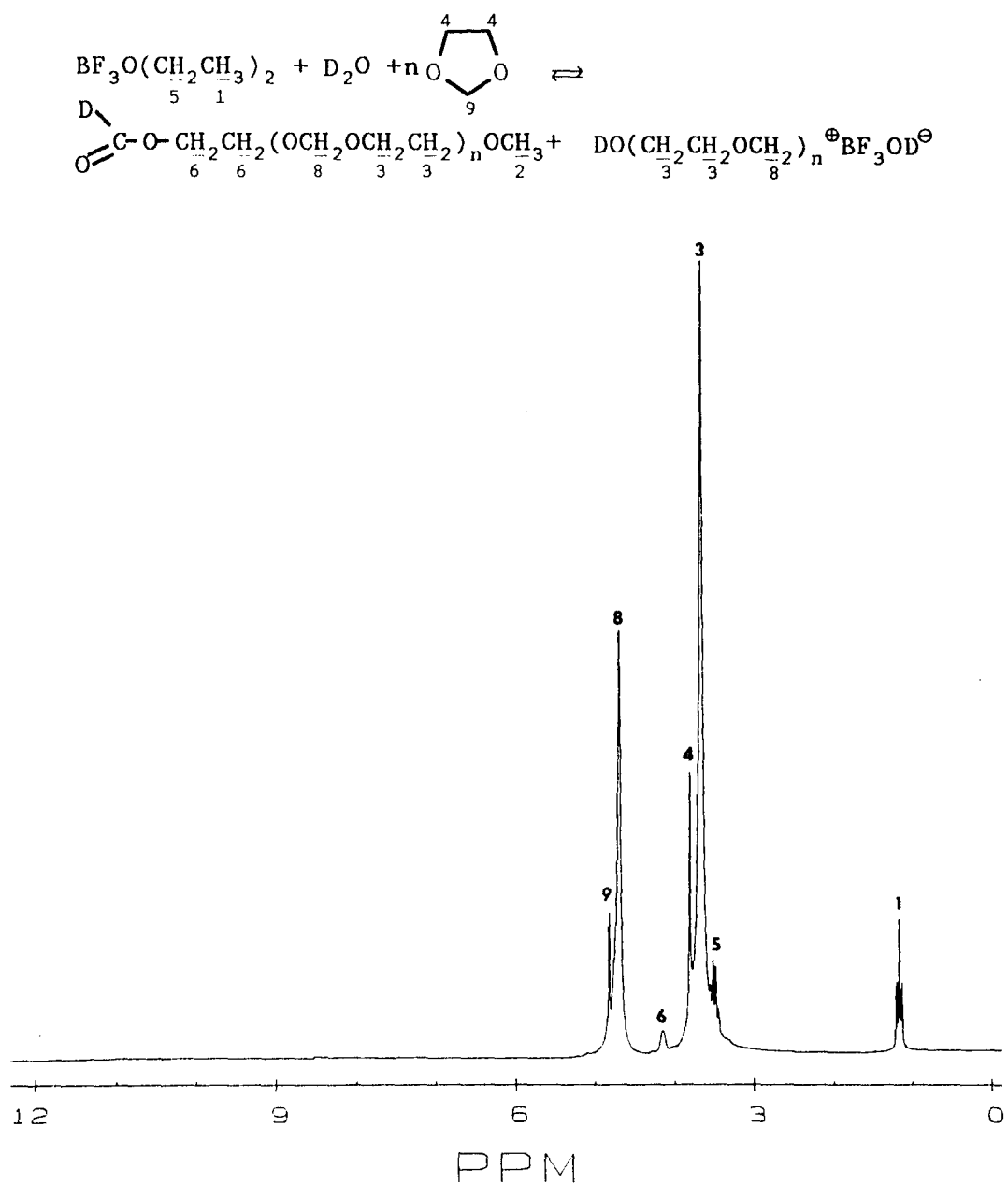
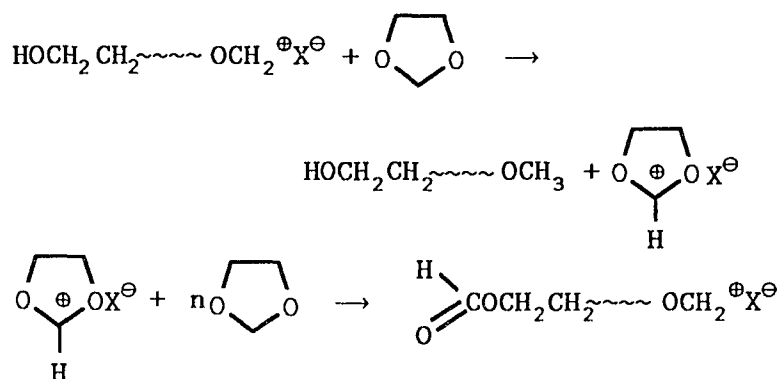


Fig.1-8 ^1H NMR spectrum for bulk dioxolane polymerization with addition of D_2O and initiated with BF_3OEt_2 at 22°C .
 $[\text{BF}_3\text{OEt}_2] = 2.1 \text{ mol/l}$; $[\text{D}_2\text{O}] = 0.32 \text{ mol/l}$.



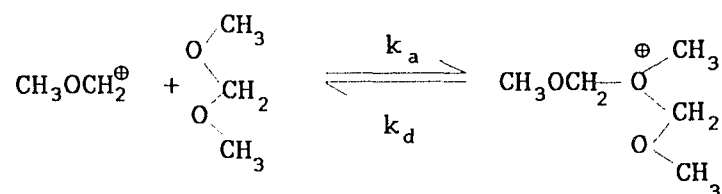
(Reaction scheme I)

spectra from D₂O system cannot support this assignment. The peak at 8.0 ppm is assigned to formate end group based on the comparison of its chemical shift with a model compound. In addition, this peak disappears in D₂O spectrum and appears inverted in DEPT spectrum. The broad peak at 11.2-11.6 ppm may be due to the proton of water bond to boron trifluoride. The evidence for this assignment is: 1) no corresponding peak can be found in the ¹³C NMR spectrum; 2) a ¹H NMR spectrum for BF₃OEt₂ and H₂O dissolved in CDCl₃ shows a peak at 10.0-10.5 ppm (see Fig. 1-3).

From ¹H NMR spectra for both high and low initiator concentrations under the present experimental conditions, no small cyclic compounds were detected, but end groups were observed. Hence, a ring-expansion mechanism as the only propagation step for this polymerization system seems unlikely.

As mentioned in the introduction, both oxonium and alkoxy-carbenium ions were usually considered as growing species which can add to another monomer molecule for propagation. However, an attempt to detect the growing

species directly by ^1H NMR was not successful even at high concentration of initiator. One possible explanation may be the fast equilibrium between alkoxy-carbenium and oxonium ions. Penczek et al. (10) studied the equilibrium as shown in reaction scheme II. The association and dissociation constants (k_a , k_d) at -70°C are 2×10^6 l/mol sec and 6.7×10^2 l/mol sec. At such a low temperature, this exchange rate is sufficiently slow to permit the observation of both cations separately by 60 MHz ^1H NMR.



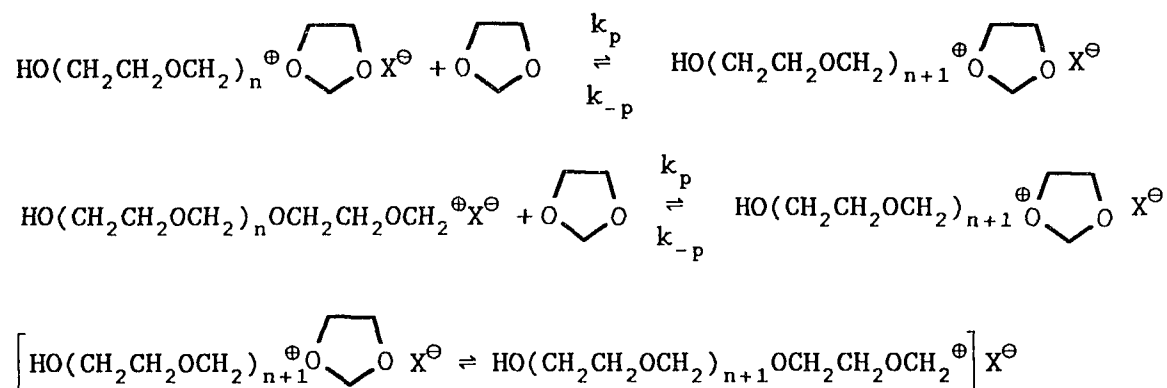
(Reaction scheme II)

Based on previous research work and our experimental observations, we assumed that a linear growth mechanism plays an important role in the propagation steps and the propagation species consist of both alkoxy-carbenium and oxonium ions although a small proportion may exist in the form of alkoxy-carbocation. A mechanistic scheme for the propagation is shown in reaction scheme III.

1.5 Concentration of propagation species and propagation rate constant

Concentrations of active species were determined by the ion-trapping method. This technique is based on the

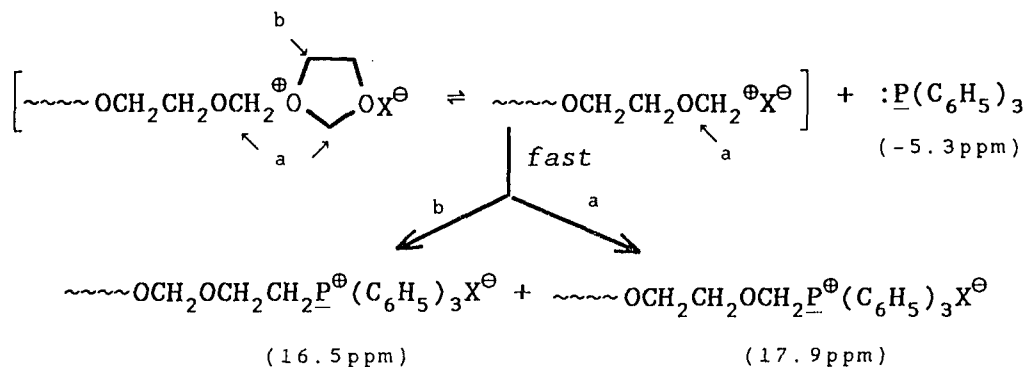
Propagation steps



(Reaction scheme III)

reaction of oxonium ion and aloxycarbocation with triphenylphosphine (reaction scheme IV), and subsequent determination of the product concentration by ^{31}P NMR. The rate for this reaction is expected to be much faster than that of propagation. Thus, the trapping can be considered as instantaneous when compared with propagation. The reaction is considered to be very efficient since the maximum concentration of propagation species determined by this method is close to the added initiator concentration. Although no information about the structure of propagation species can be provided by this ion-trapping method, it is an efficient method to determine the total concentration of active species.

Fig. 1-9 displays ^{31}P NMR spectra corresponding to different quenching times for a polymerization system with 6.2×10^{-2} mole/l of BF_3OEt_2 and about 1.0×10^{-2} mole/l of water. The spectra were recorded after the quenched polymer



(Reaction scheme IV)

mixtures were kept at room temperature for about 24 hrs. The peak at -5.3 ppm was assigned to unreacted free phosphine. The double peak at 17.9 and 16.5 ppm is most likely due to the two different phosphonium salts $-\text{OCH}_2\text{P}^\oplus(\text{C}_6\text{H}_5)_3$ and $-\text{OCH}_2\text{CH}_2\text{P}^\oplus(\text{C}_6\text{H}_5)_3$ (see reaction scheme IV). Based on the intensity of these two peaks (Fig. 1-9), the formation of $-\text{OCH}_2\text{P}^\oplus(\text{C}_6\text{H}_5)_3$ species is considerably more favored than the formation of $-\text{OCH}_2\text{CH}_2\text{P}^\oplus(\text{C}_6\text{H}_5)_3$. This result is expected since $-\text{OCH}_2\text{P}^\oplus(\text{C}_6\text{H}_5)_3$ is more stable. The signal close to 29.2 ppm was also assigned to $-\text{OCH}_2\text{CH}_2\text{P}^\oplus(\text{C}_6\text{H}_5)_3$ ion by other researchers (17). This assignment is unlikely to be correct, because the difference in chemical shifts between $-\text{OCH}_2\text{P}^\oplus(\text{C}_6\text{H}_5)_3$ and $-\text{OCH}_2\text{CH}_2\text{P}^\oplus(\text{C}_6\text{H}_5)_3$ should not be so large. Furthermore, the calculated concentration of propagation species based on this assignment would be greater than the concentration of added initiator. A ^{31}P NMR spectrum of mixture of DOL monomer and triphenylphosphine shows a peak with the same chemical shift (29.2 ppm, Fig. 1-10). Hence, this peak was

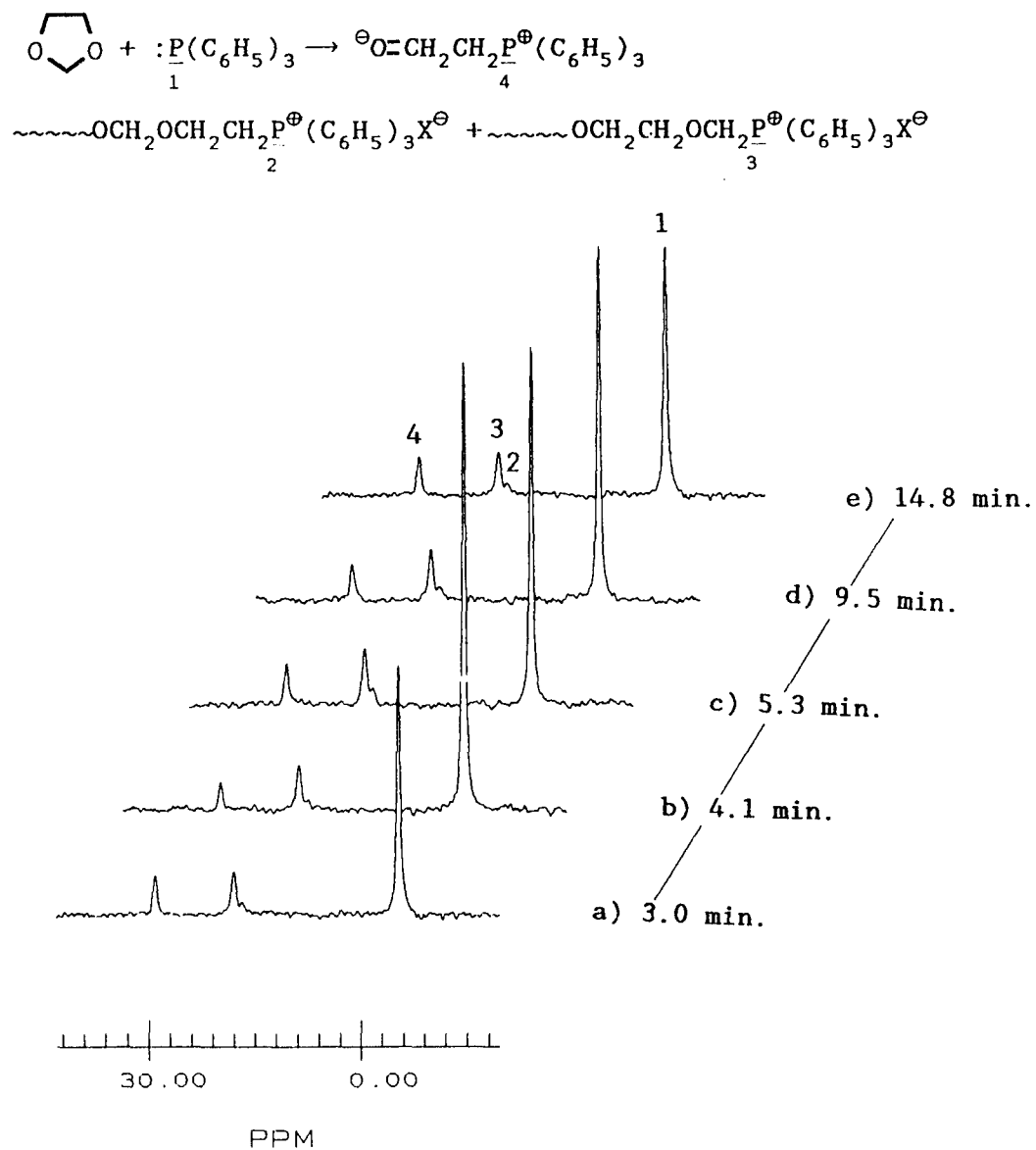


Fig.1-9 ^{31}P NMR spectra for bulk dioxolane polymerization system initiated with BF_3OEt_2 and terminated by triphenylphosphine at 22°C . $[\text{BF}_3\text{OEt}_2]=0.062 \text{ mol/l}$; $[\text{H}_2\text{O}]=0.010 \text{ mol/l}$; $[(\text{C}_6\text{H}_5)_3\text{P}]=0.3 \sim 0.4 \text{ mol/l}$. ^{31}P NMR spectra in CDCl_3 .

assigned to a product of the reaction of DOL monomer with triphenylphosphine. Since the rate of this reaction is much slower than that of the trapping reaction, this peak was not observed in the spectra recorded shortly after addition of $(C_6H_5)_3P$.

The concentration of the propagation species was determined from the initial concentration of triphenylphosphine and the relative integration fraction of the ^{31}P NMR peaks. Fig. 1-11 illustrates the time dependence of monomer and propagation species in the bulk polymerization of dioxolane at $22^\circ C$. The concentration of dioxolane was measured from ^1H NMR spectra using the same samples prepared for ^{31}P NMR measurement. The concentration of propagation species grew to slight maximum and reached a constant value. The maximum concentration of propagation species is close to the initiator concentration. A similar time curve of propagation species was also observed in the DOL - CH_3OSO_2F polymerization system (12).

Based on the developed propagation mechanism of DOL polymerization, the rate of propagation is given by equations 9 and 10 Where $[M]$ and $[M]_e$ are the instantaneous

$$\frac{d[M]}{dt} = -k_p[P^+][M] + k_{-p}[P^+] = -k_p[P^+]\{[M] - [M]_e\} \quad (9)$$

$$\ln \frac{[M]_0 - [M]_e}{[M] - [M]_e} = k_p \int_0^t [P^+] dt \quad (10)$$

and equilibrium monomer concentrations, and $\int_0^t [P^+] dt$ was obtained by Simpson graphical integration. A plot of the

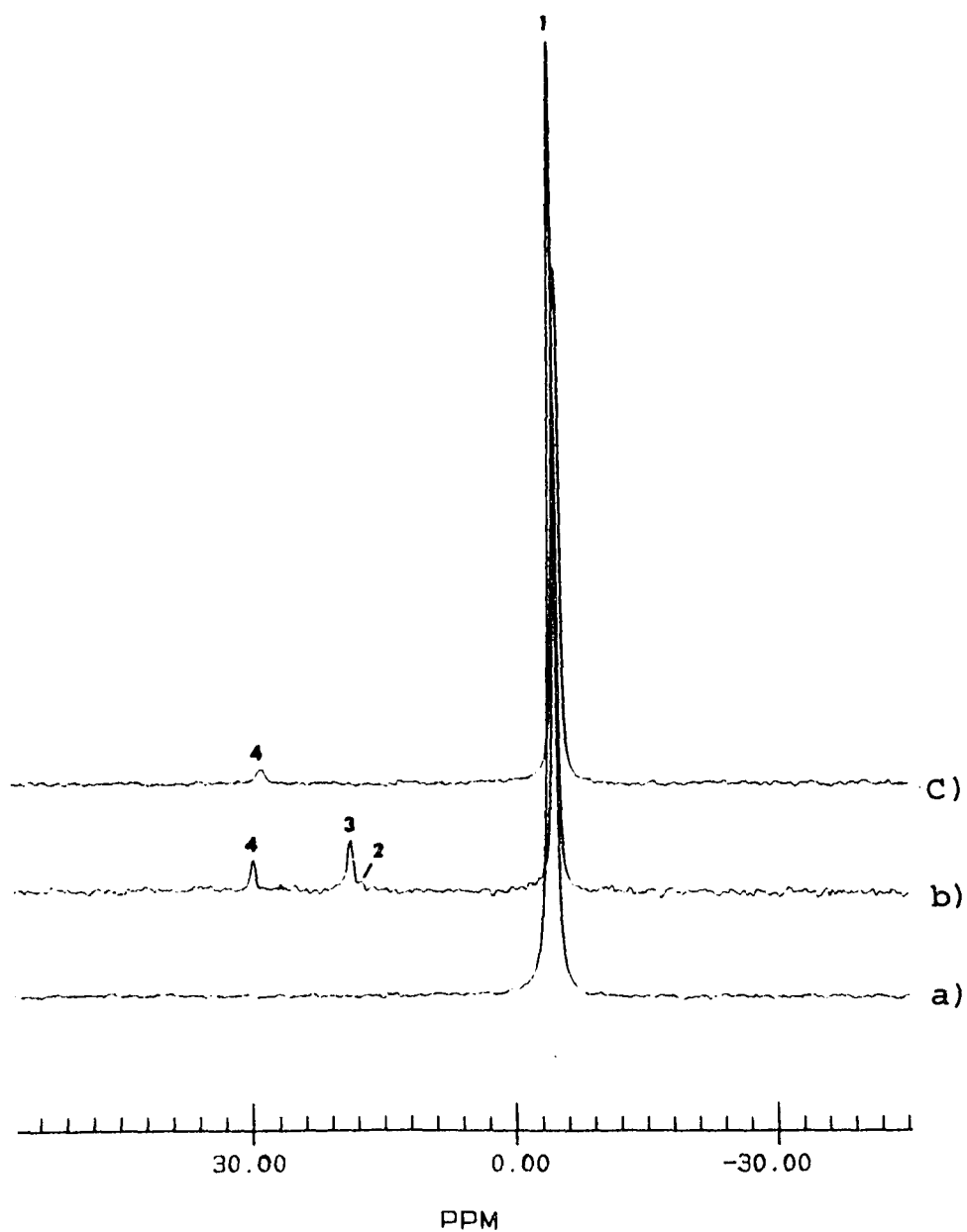
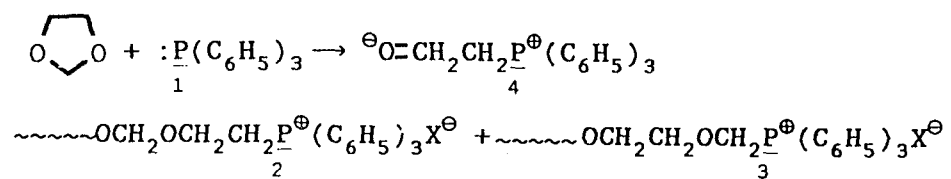


Fig.1-10 ^{31}P NMR spectra of model compounds. a) BF_3OEt_2 and $(\text{C}_6\text{H}_5)_3\text{P}$ in CDCl_3 , b) spectrum (a) in Fig. 1-9, c) dioxolane and $(\text{C}_6\text{H}_5)_3\text{P}$ in CDCl_3 .

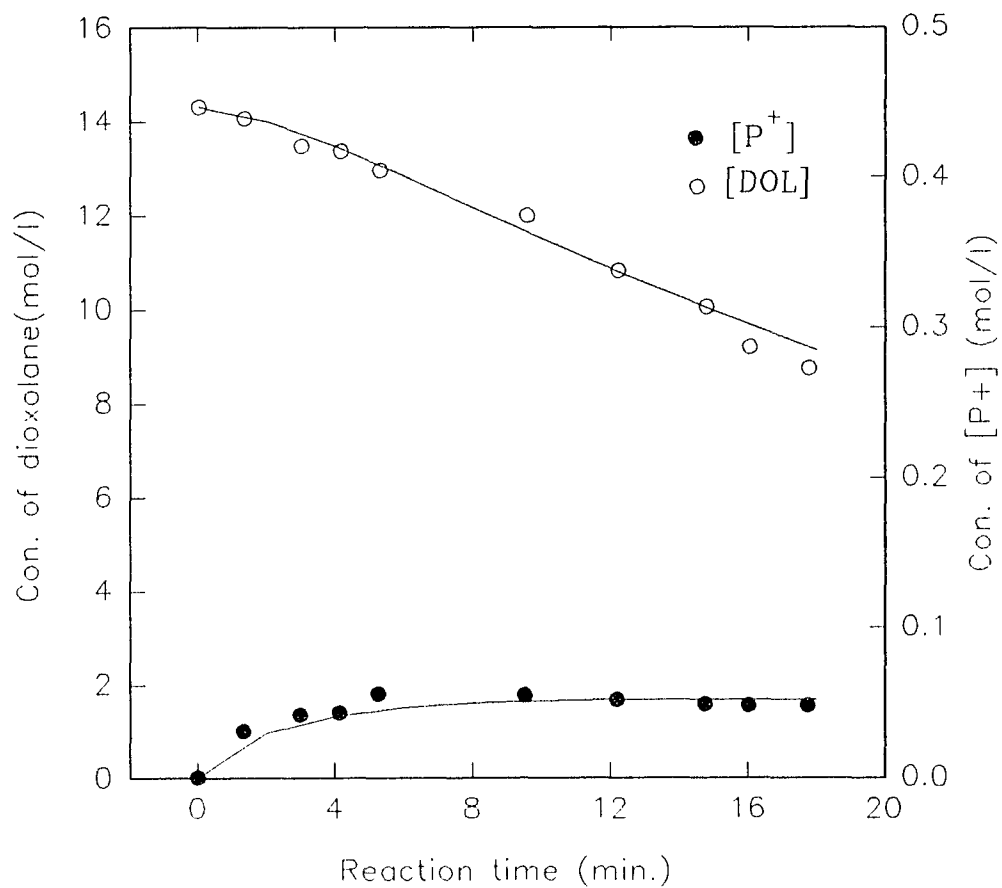


Fig. 1-11a The change of monomer and propagation species concentrations versus time for bulk polymerization of dioxolane initiated with BF_3OEt_2 at 22°C . $[\text{BF}_3\text{OEt}_2] = 0.062 \text{ mol/l}$; $[\text{H}_2\text{O}] = 0.010 \text{ mol/l}$. Symbols stand for experimental data and lines are calculated value from kinetic model.

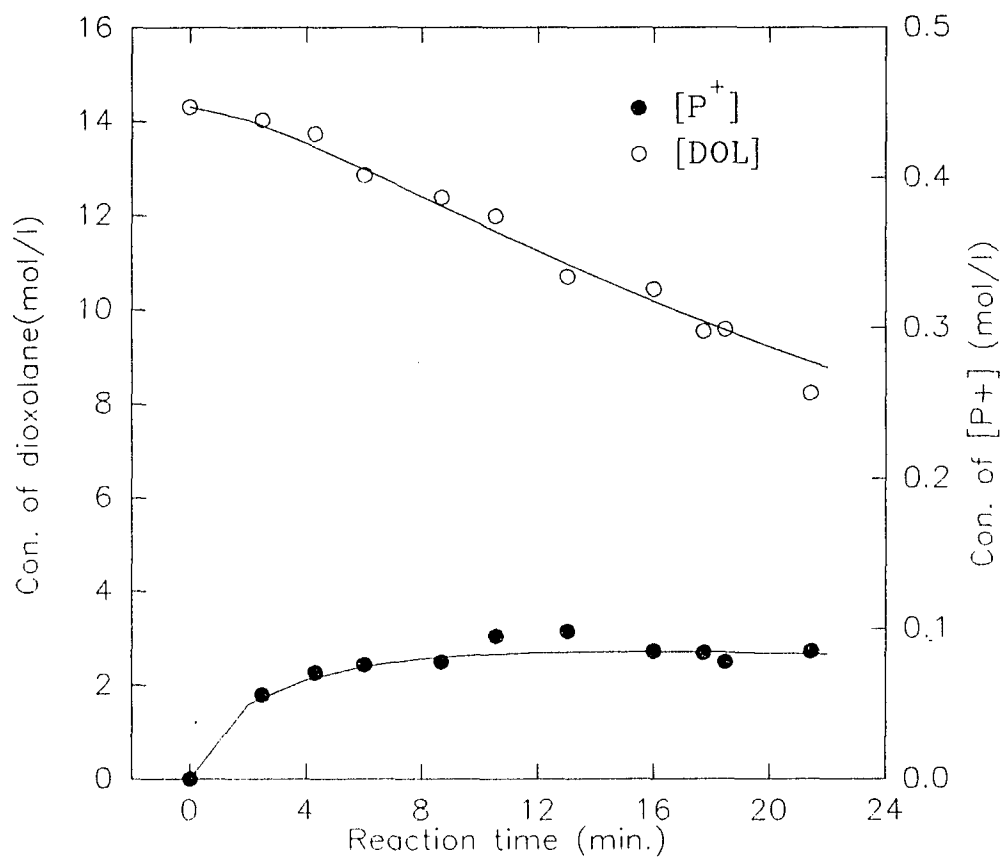


Fig. 1-11b The change of monomer and propagation species concentrations versus time for bulk polymerization of dioxolane initiated with BF_3OEt_2 at 22°C . $[\text{BF}_3\text{OEt}_2] = 0.11 \text{ mol/l}$; $[\text{H}_2\text{O}] = 0.030 \text{ mol/l}$. Symbols stand for experimental data and lines are calculated value from kinetic model.

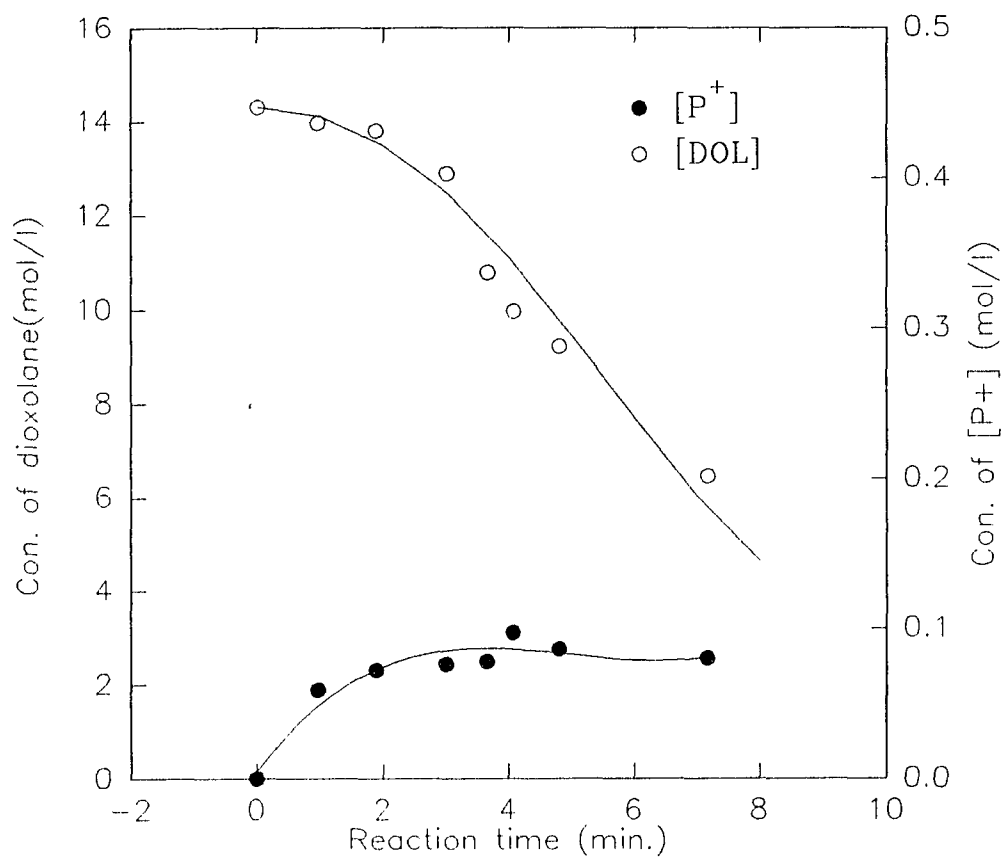


Fig. 1-11c The change of monomer and propagation species concentrations versus time for bulk polymerization of dioxolane initiated with BF_3OEt_2 at 22°C . $[\text{BF}_3\text{OEt}_2] = 0.10 \text{ mol/l}$; $[\text{H}_2\text{O}] = 0.010 \text{ mol/l}$. Symbols stand for experimental data.

left side term in equation 10 versus $\int_0^t [P^+] dt$ should give a straight line with slope k_p . Fig. 1-12 represents the plots in accordance with equation 10 for three systems with different concentrations of initiator and water. Fig. 1-12a and 1-12b display a fair first-order relation except a few data points at later stage. However, deviation from a straight line is found for the system with $[BF_3OEt_2]=0.10$ mol/l and $[H_2O]\approx 0.010$ mol/l (Fig. 1-12c). The non-linear relation implies that k_p does not remain constant during the conversion. This observation can be attributed to the temperature rise of the reaction mixture with conversion in the bulk polymerization system. This was confirmed by direct measurement of the temperature of reaction mixture versus conversion. Temperature change is dependent on the rate of polymerization. The faster of the polymerization rate, the faster the observed increase in the temperature of reaction mixture. For the polymerization systems presented in Fig. 1-12a and 1-12b, only about 40% of conversion was obtained after ca. 20 minutes of reaction time. Such a low polymerization rate leads to an insignificant change in temperature before 35% of conversion. After 35% conversion, the polymerization systems start to display a slight deviation from a straight line, indicating a slight change in propagation rate constant at this point. A different behavior was observed for the fast polymerization system (Fig. 1-12c). About 55% of conversion is reached within 7 minutes of polymerization time. A significant temperature

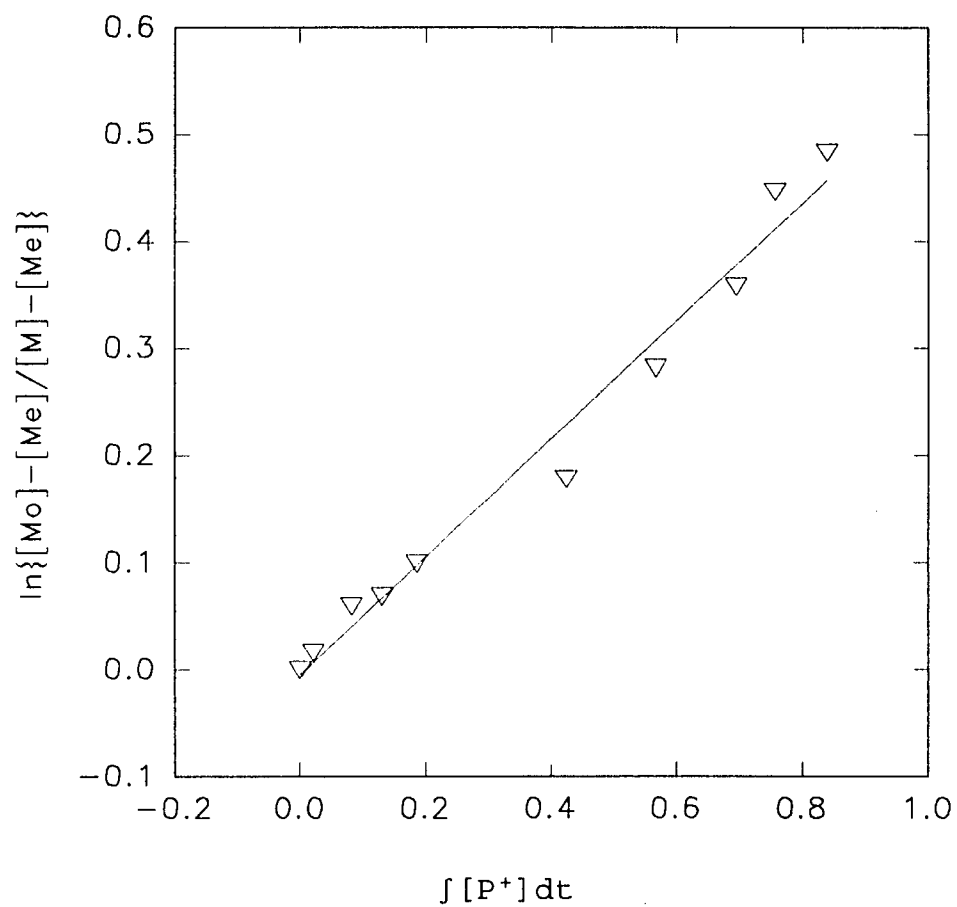


Fig. 1-12a The relation of monomer concentration and propagation species for bulk polymerization of dioxolane initiated with BF_3OEt_2 at 22°C . $[\text{BF}_3\text{OEt}_2] = 0.062 \text{ mol/l}$; $[\text{H}_2\text{O}] = 0.010 \text{ mol/l}$.

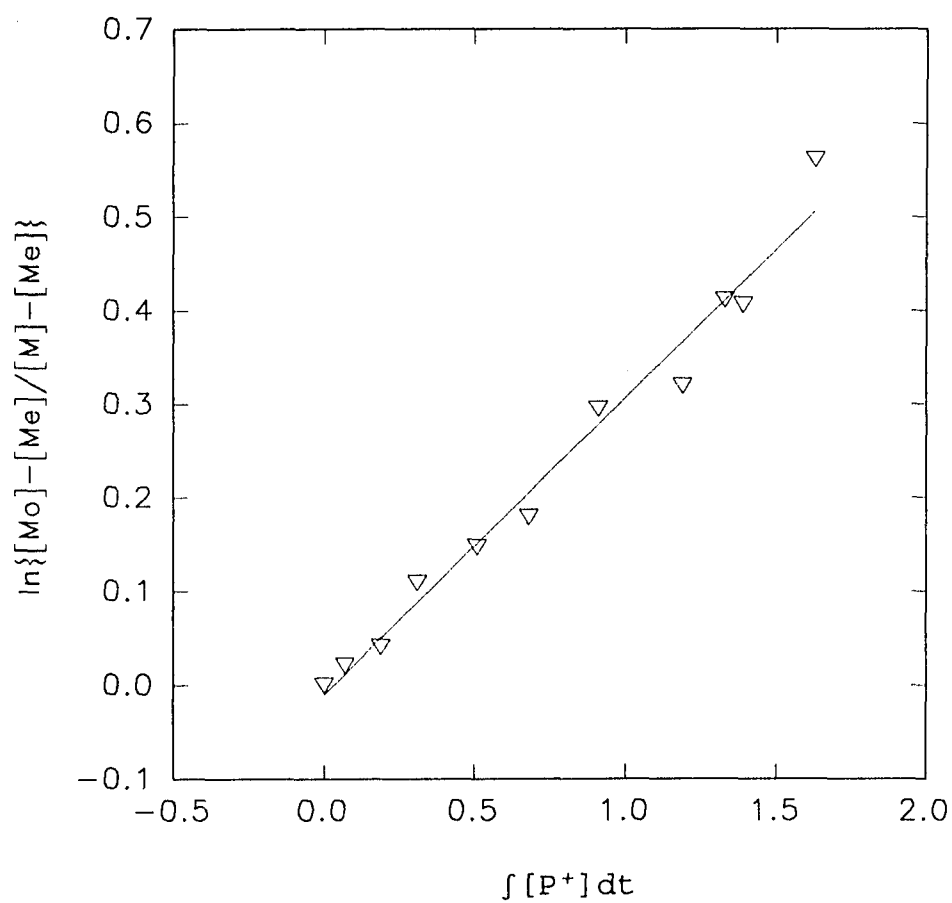


Fig. 1-12b The relation of monomer concentration and propagation species for bulk polymerization of dioxolane initiated with BF_3OEt_2 at 22°C . $[\text{BF}_3\text{OEt}_2] = 0.11 \text{ mol/l}$; $[\text{H}_2\text{O}] = 0.030 \text{ mol/l}$.

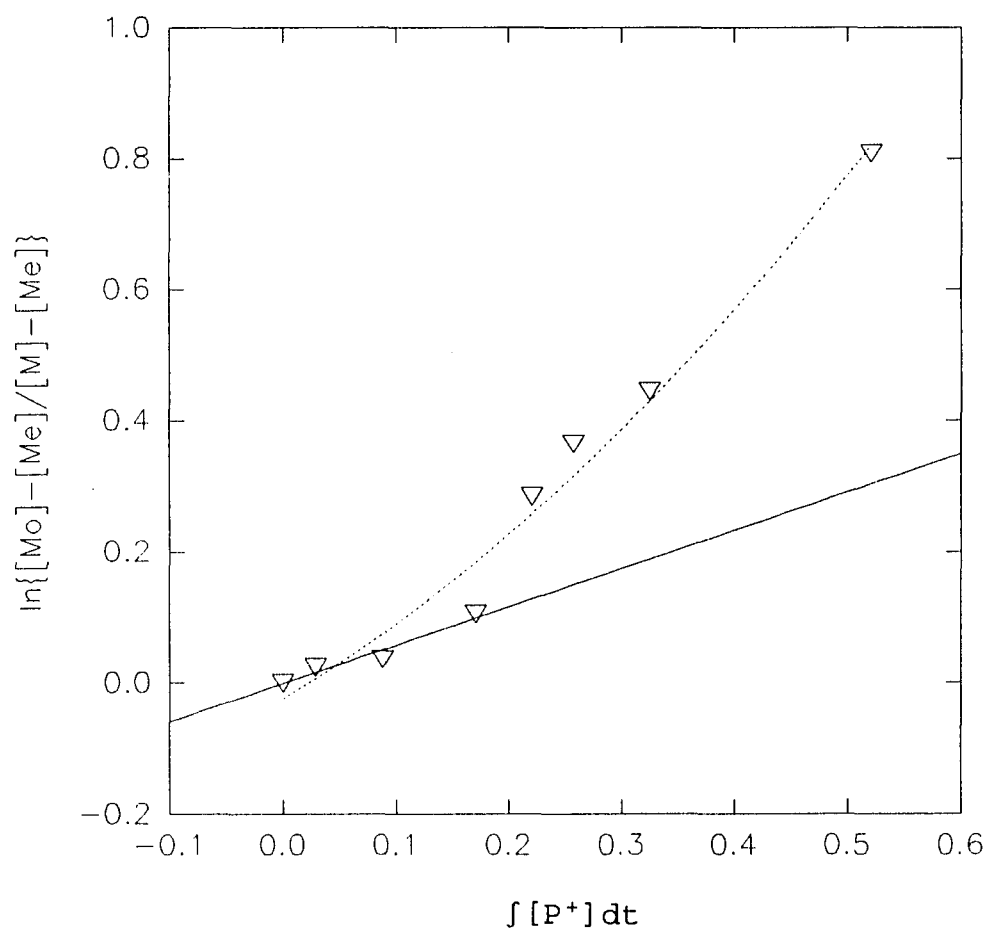


Fig. 1-12c The relation of monomer concentration and propagation species for bulk polymerization of dioxolane initiated with BF_3OEt_2 at 22°C . $[\text{BF}_3\text{OEt}_2] = 0.10 \text{ mol/l}$; $[\text{H}_2\text{O}] = 0.010 \text{ mol/l}$.

change starts at only about 10% of conversion. In this case, the relation corresponding to equation 10 displays a nonlinear feature.

Because of the temperature effect, we determined the propagation rate constant from the initial slope (less than 10% of conversion, Fig. 1-12c). Thus we obtained an "initial propagation rate constant". The temperature change is not significant in the system with slow rate of polymerization (Fig. 1-12a,b); we simply calculated the propagation rate constant from the slope of the entire straight lines for these system. The results are listed in Table 1-3.

TABLE 1-3

The Propagation rate constants for bulk polymerization of dioxolane initiated with BF_3OEt_2 at 22°C

DATA	PDL826	PDL906	PDL118
BF_3OEt_2 (mol/l)	0.062	0.10	0.11
H_2O (mol/l)	0.010	0.010	0.030
$k_p \times 10^3$ (l/mol.sec)	9.2	9.7	5.3

The rate constants listed in Table 1-3 indicate that good reproducibility was not achieved between the systems with high and low water concentrations. This suggests that the propagation rate constant may be affected by the water

concentration (see discussion later). Also, the error in measuring the concentrations of propagation species and monomer may also contribute to this poor reproducibility.

The average propagation rate constant for bulk polymerization of DOL initiated with BF_3OEt_2 at low concentration of water is listed in Table 1-4 together with

TABLE 1-4

The propagation rate constants for dioxolane polymerization

TEMP. °C	INITIATOR	SOLVENT	k_p (1/mol. sec.)	REF.
-5	$\text{CH}_3\text{OSO}_2\text{F}$	CDCl_3	1.3×10^{-2}	12
0	$\text{C}_6\text{H}_5\text{CO}^+\text{SbF}_6^-$	CH_2Cl_2	25 ± 5	15
-	BF_3OEt_2	-	6.8×10^{-2}	14
22	BF_3OEt_2	bulk	9.4×10^{-3}	obs.

three reported values for the polymerization of DOL under different conditions. Direct comparison of these data is difficult, because initiator and solvent varied.

Furthermore, polymerizations are carried out under bulk or solution conditions. Due to different methods used, errors peculiar to these methods occurred. A relatively low value of k_p for BF_3OEt_2 -DOL polymerization was also obtained by other researchers. The slow polymerization of the BF_3OEt_2 -DOL system under the effect of electric field was ascribed to the polymerization mostly by ion pairs(14). The propagation rate constant derived from our experimental data should be considered as initial propagation rate constant at 22°C.

1.6 The initial rate of polymerization versus the concentrations of water and initiator

To study the effect of water and initiator on the rate of polymerization, the course of polymerization was investigated systematically using ^1H NMR. The instantaneous monomer concentration was calculated from the initial monomer concentration $[\text{M}]_0$ and the integrated fraction of peak area. Average standard deviation for the integration was estimated to be within 5% - 7% (Table 1-5).

The trace amount water was determined from its NMR peak at 2.38-2.44 ppm. The accuracy of the measurement was checked by the Karl-Fisher method (the instrument was calibrated using saturated cyclohexane solvent as standard water content=0.01%), or by adding a known amount of water into the NMR tube and determining its concentration. The error for this NMR measurement was estimated to be within 15 %-20%.

Independent polymerization experiments showed that the reaction is very sensitive to the water present in the system and the reproducibility of the time-conversion curve is poor probably due to the difficulty in controlling the exact water concentration.

Monomer concentration was plotted versus time for four different initiator concentrations with controlled water levels at $6.0 - 8.0 \times 10^{-3}$ mole/l (Fig. 1-13a). The

TABLE 1-5

The estimated deviation in integral of NMR peaks

TIME (min)	$[M]_1$ (M/L)	$[M]_2$ (M/L)	$[M]_{ave}$ (M/L)
0	14.25	14.25	14.25
4.8	12.75	13.04	12.90
6.3	12.61	12.84	12.73
7.9	12.40	12.43	12.42
9.8	12.27	12.34	12.31
11.8	12.17	12.30	12.24
14.8	11.97	12.05	12.01
17.8	11.89	11.97	11.93
22.8	11.66	11.53	11.60
29.8	11.34	11.34	11.34
38.8	10.87	10.99	10.93

$[BF_3OEt_2] = 0.15 \text{ mol/l}$, $[H_2O] = 0.080 \text{ mol/l}$.

same plots corresponding to four different water contents at two initiator concentrations (0.10 mole/l and 0.15 mole/l) are shown in Fig. 1-13b and Fig. 1-13c. We noticed

different shapes in the monomer consumption-time curves between the systems with high and low water levels. For the systems with high water level, monomer was consumed rapidly at the initial stage and then almost leveled off. On the other hand the consumption of monomer starts slowly but increases quickly in the system with less water. This observation gives an important message, which is, water acts as both coinitiator and inactivator in dioxolane polymerization.

The initial rate R_0 of each polymerization was evaluated from the instantaneous differential of time-conversion curve. This time-conversion curve was obtained by fitting a third order polynomial equation to experimental observations. The method of "differential plot" was also used to calculate initial rate of polymerization, which is described as follows. Assuming that x is the fractional conversion and substituting $[M] = [M]_0 (1 - X)$ into equation 10, we have

$$\begin{aligned} d[M]/dt &= -k_p [P^+] \{ [M] - ([M]_0 X + [M]_e) \} \\ &= R_0 + k_p [P^+] \{ [M]_0 X + [M]_e \} \end{aligned} \quad (11)$$

Plots correspond to equation 11 give R_0 as the intercept when $[P^+]$ is approximated by the concentration of initiator. The initial rates of DOL polymerization R_0 calculated from both methods are listed in Table 1-6. The R_0 values derived from the two methods are slightly

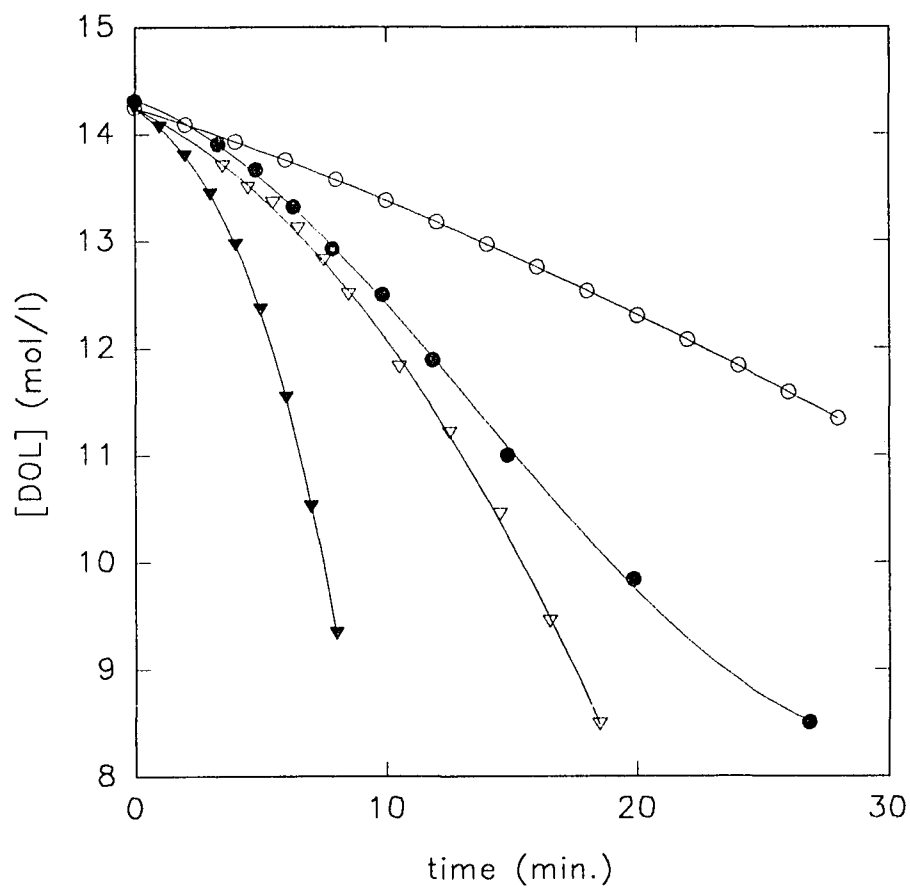


Fig. 1-13a The consumption of monomer versus time for bulk dioxolane polymerization systems with different levels of BF_3OEt_2 at 22°C . $[\text{H}_2\text{O}] = 6 - 8 \times 10^3 \text{ mol/l}$
 $\circ$ $[\text{BF}_3\text{OEt}_2] = 0.050 \text{ mol/l}$; $\bullet$ $[\text{BF}_3\text{OEt}_2] = 0.063 \text{ mol/l}$;
 ∇ $[\text{BF}_3\text{OEt}_2] = 0.088 \text{ mol/l}$; $\blacktriangledown$ $[\text{BF}_3\text{OEt}_2] = 0.150 \text{ mol/l}$.

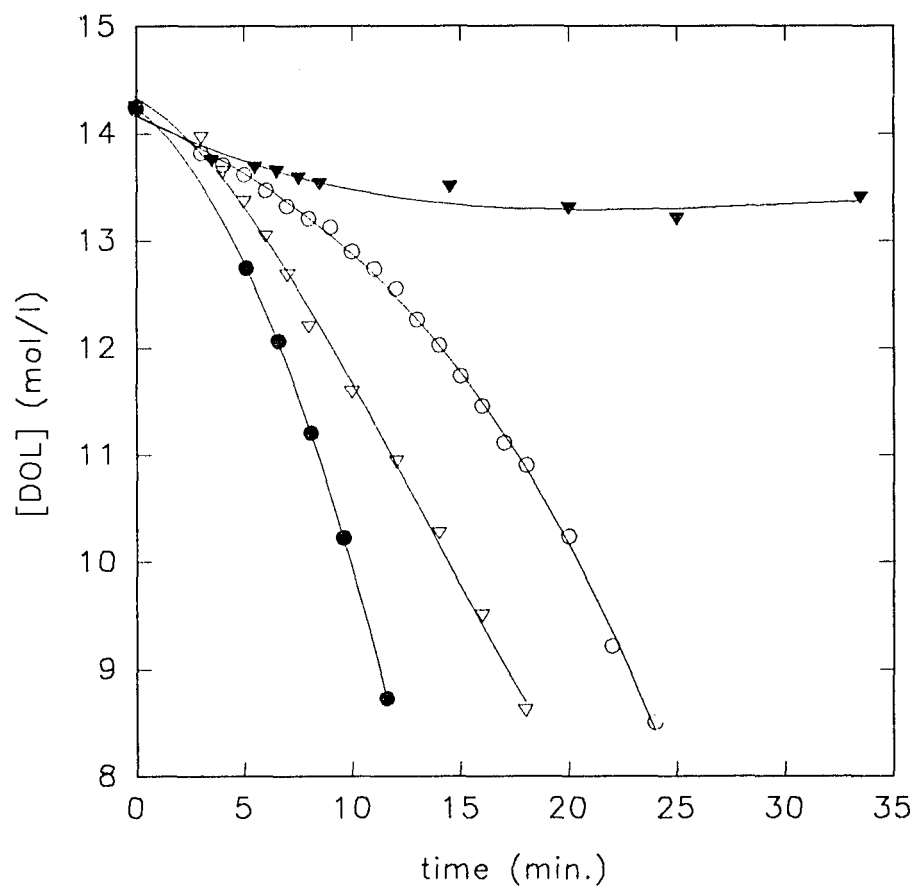


Fig. 1-13b The consumption of monomer versus time for bulk dioxolane polymerization systems with different levels of H_2O at 22°C . $[\text{BF}_3\text{OEt}_2] = 0.10 \text{ mol/l}$.
 ○ $[\text{H}_2\text{O}] = 0.009 \text{ mol/l}$; ● $[\text{H}_2\text{O}] = 0.012 \text{ mol/l}$;
 ▽ $[\text{H}_2\text{O}] = 0.021 \text{ mol/l}$; ▼ $[\text{H}_2\text{O}] = 0.110 \text{ mol/l}$.

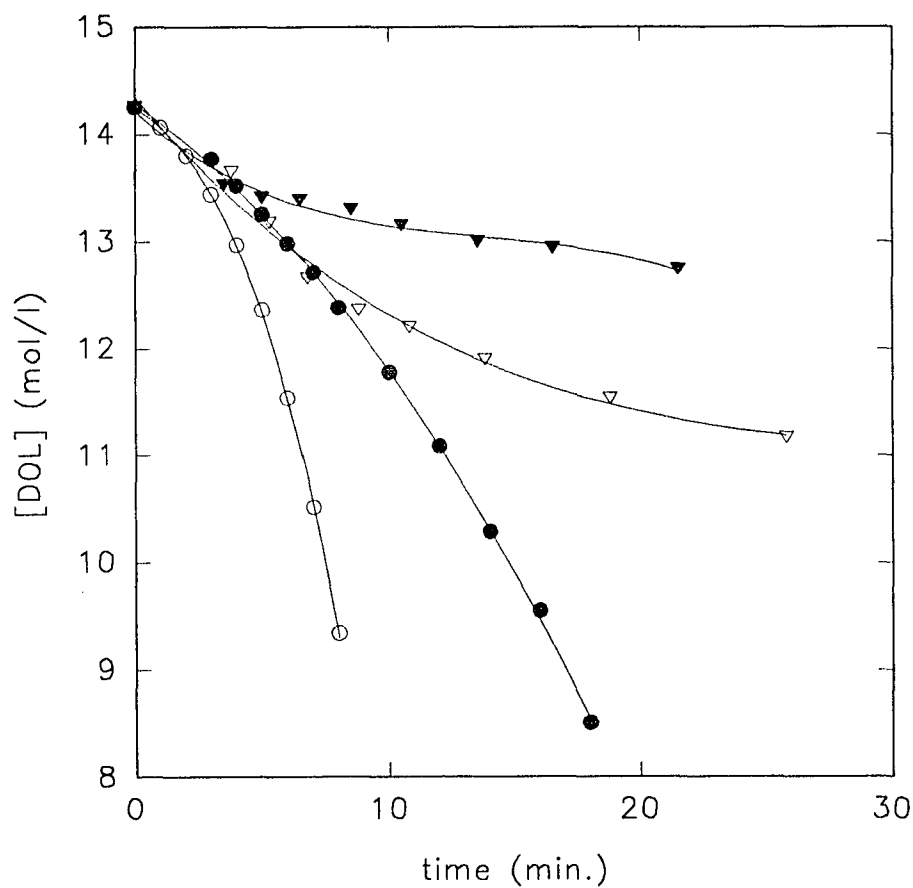


Fig. 1-13c The consumption of monomer versus time for bulk dioxolane polymerization systems with different levels of H_2O at 22°C . $[\text{BF}_3\text{OEt}_2] = 0.15 \text{ mol/l}$.
 $\circ$ $[\text{H}_2\text{O}] = 0.009 \text{ mol/l}$; $\bullet$ $[\text{H}_2\text{O}] = 0.038 \text{ mol/l}$;
 ∇ $[\text{H}_2\text{O}] = 0.102 \text{ mol/l}$; $\blacktriangledown$ $[\text{H}_2\text{O}] = 0.123 \text{ mol/l}$.

different, in both cases, the results give a well-defined maximum between the relation of R_o and water concentration.

TABLE 1-6a

The initial rate and water concentration for DOL polymerization initiated with BF_3OEt_2 at 22°C

Data	$[\text{H}_2\text{O}] \times 10^3$ (mol/l)	$R_o^{(a)}$ (M/min)	$R_o^{(b)}$ (M/min)
PDL401	2.5	0.028	0.165
PDL402	2.5	0.019	0.033
PDL728	8.0	0.110	0.150
PDL717	25	0.291	0.435
PDL718	30	0.214	0.250
PDL625	38	0.226	0.195
PDL514	79	0.136	0.122
PDL513	80	0.086	0.099
PDL511	102	0.146	0.168
PDL512	123	0.074	0.090
$[\text{BF}_3\text{OEt}_2] = 0.15 \text{ mol/l}$			

In Fig. 1-14, the initial rate R_o is shown as a function of water concentration for two different initiator concentrations. Although the data are scattered due to the error in measurement of water concentration, it

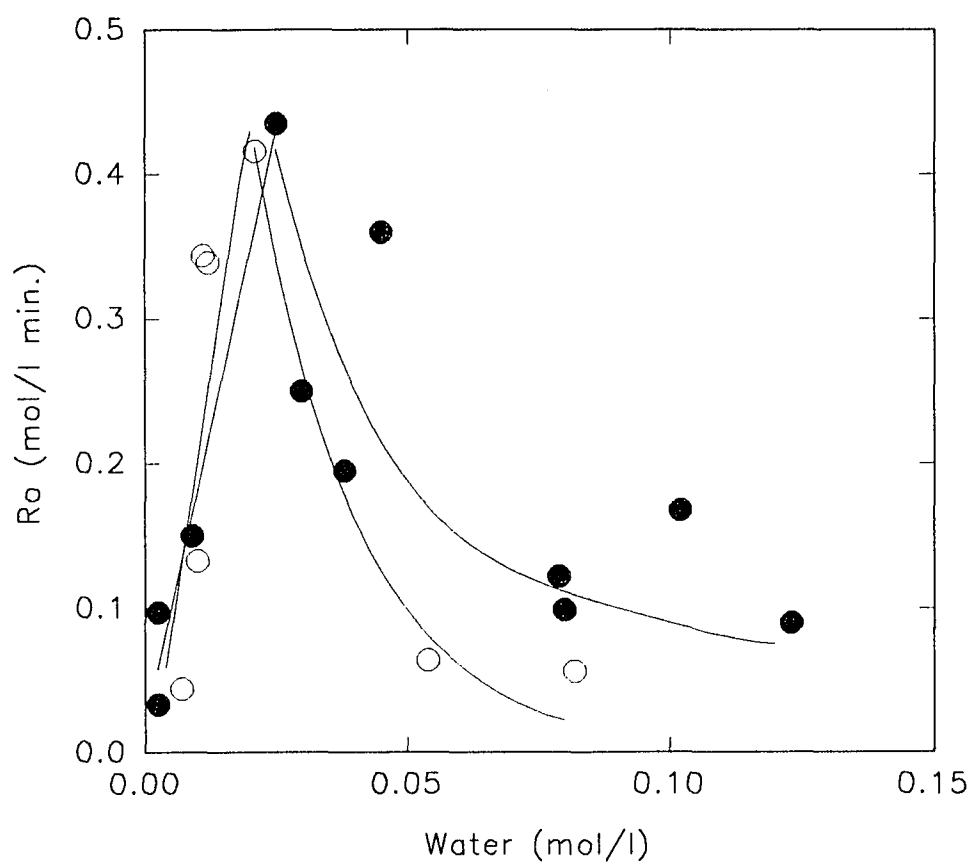


Fig. 1-14 The dependence of initial rate on concentration of water in bulk dioxolane polymerization initiated by BF_3OEt_2 at $22^\circ C$. ○ $[BF_3OEt_2] = 0.10$ mol/l; ● $[BF_3OEt_2] = 0.15$ mol/l.

Table 1-6b

The initial rate and water concentration for DOL polymerization
initiated with BF_3OEt_2 at 22°C

Data	$[\text{H}_2\text{O}] \times 10^3$ (mol/l)	$R_o^{(a)}$ (M/min)	$R_o^{(b)}$ (M/min)
PDL617	7.0	0.096	0.044
PDL809	10	0.165	0.133
PDL812	11	0.333	0.344
PDL403	12	0.289	0.339
PDL730	21	0.334	0.416
PDL719	54	0.055	0.064
PDL616	82	0.048	0.056
$[\text{BF}_3\text{OEt}_2] = 0.10 \text{ mol/l}$			

(a). Data was determined from "differential plot"

(b). Data was determined from "instantaneous differential" of
time - conversion curve.

can be seen clearly that initial rate of polymerization tends to increase with water and reaches a maximum at a ratio of $[\text{H}_2\text{O}] / [\text{BF}_3\text{OEt}_2] \approx 0.2$. As water concentration continues to increase, R_o decreases sharply then level off. In addition, ^1H NMR spectra showed that water was consumed immediately after addition of BF_3OEt_2 . All the experimental data suggest that under influence of water, polymerization occurs through a coinitiation mechanism. Water should be

considered as cocatalyst which can increase the rate of polymerization. But excess water in system can decrease the rate of polymerization. The decrease in rate at higher water concentration is usually ascribed to inactivation of the coinitiator by water, e.g., formation of boron trifluoride dihydrate which is too inactive to protonate DOL. A polymerization experiment of DOL initiated with $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ gives clear evidence of the inefficiency of initiation by dihydrate. With $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ at 0.15 mol/l and water under 6.3×10^{-4} mol/l, the initial rate of this polymerization is 0.0023 M/min and only about 5% of conversion was obtained after 180 minutes of polymerization time, a much lower rate than that of the polymerization initiated with BF_3OEt_2 .

Many polymerizations exhibit a maximum polymerization rate at certain ratio of initiator to coinitiator. For instance, a study on the cocatalyst effect of water on polymerization system of BF_3OEt_2 - styrene showed that maximum polymerization rate occurs at ratio $[\text{H}_2\text{O}]/[\text{BF}_3\text{OEt}_2] \approx 0.1 - 0.5$ depending on the initial monomer concentration (26). The effect of the concentration of water on the polymerization system BF_3OEt_2 -trioxane was studied at fixed concentrations of initiator and monomer (27). The initial rate of polymerization reaches a maximum at $[\text{H}_2\text{O}]/[\text{BF}_3\text{OEt}_2] \approx 0.5$ in n-hexane. Therefore, the author concluded that water is necessary as a cocatalyst for the polymerization in non-polar solvent. On the other hand, in nitrobenzene

the rate of polymerization is not affected by water concentration within the given range of water. Hence, initiation of polymerization in polar solvent was considered to occur through a self-ionization process.

The maximum rate was usually observed at quite low ratio of $[H_2O]/[initiator]$. Because the basicity of most monomer is far less than that of water. The optimum ratio of initiator to coinitiator varies considerably depending on the initiator, coinitiator, monomer, solvent and temperature, because these factors affect the balance between the competing process of initiation and inactivation.

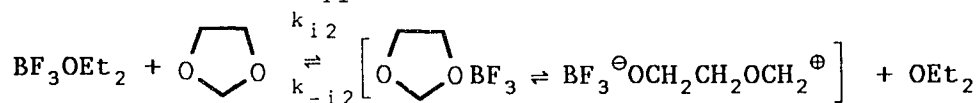
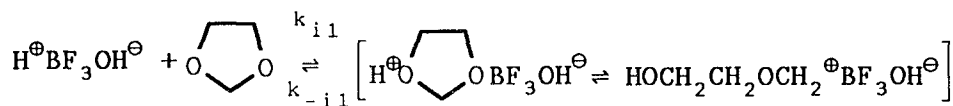
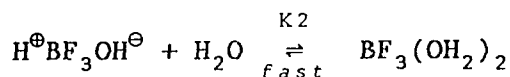
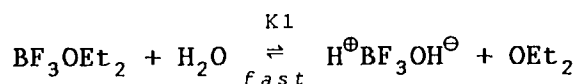
1.7 The mechanism and kinetic model for polymerization of dioxolane

Based on our experimental observations and fundamental considerations, a mechanism was developed as shown in reaction scheme V.

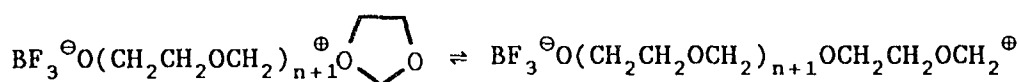
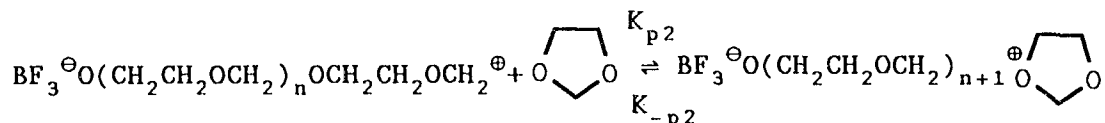
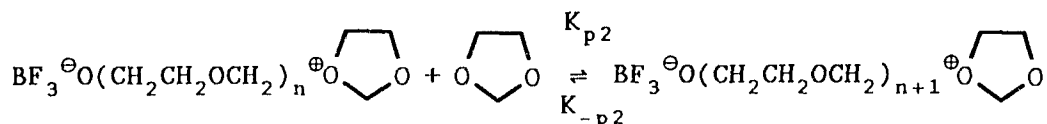
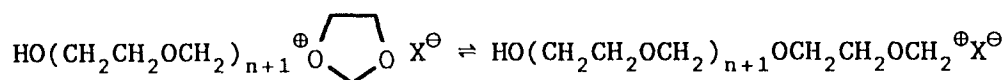
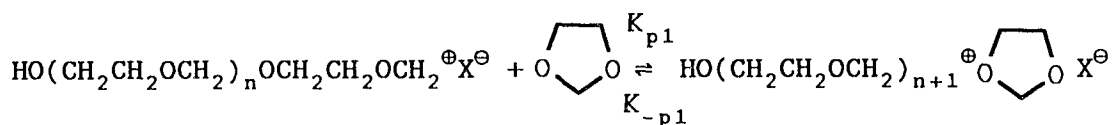
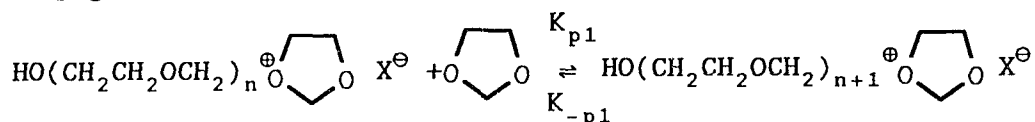
Chain transfers to water and monomer have not been included in this mechanism, because the chain transfer reactions do not affect the rate of polymerization but change only the molecular weight of polymer.

In this mechanism, we assumed that both direct initiation through self-ionization of $BF_3 \cdot DOL$ complex and coinitiation through formation of monohydrate of boron trifluoride ($[H^+BF_3OH^-]$) can occur, but dihydrate ($BF_3 \cdot 2H_2O$)

Initiation steps



Propagation steps



(Reaction scheme V)

cannot initiate polymerization of dioxolane. The experimental evidence for these assertions is: 1) water acts as coinitiator which increases initial rate of

polymerization, but excess water in the system retards the rate of polymerization; 2) polymerization of DOL initiated with $\text{BF}_3(\text{H}_2\text{O})_2$ shows no significant polymerization conversion within 3 hrs of observation time. In addition, the ^1H NMR spectra of $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ displays only one peak at ca. 7.2 ppm, suggesting that dihydrate should have a symmetric structure and may not be considered as hydroxonium hydroxytrifluoroborate ($\text{H}_3^+\text{OBF}_3\text{OH}^-$); 3) there is no direct evidence for direct initiation since a polymerization system with complete exclusion of water is not available. But in our experimental systems, water concentration was always much less than the concentration of BF_3OEt_2 . This means that the maximum concentration of propagation species should not be greater than water concentration if monohydrate $\text{H}^\oplus\text{BFOH}^\ominus$ is considered as the only initiation species. The concentration of the propagation species determined by the ion-trapping method is close to the concentration of BF_3OEt_2 . This result suggests that direct initiation should also occur together with coininitiation mechanism.

Because water is a much stronger base than DOL, we further specify that the forward reactions of first two steps in reaction scheme V are very rapid as compared with initiation and propagation steps. Under these circumstances, the concentration of monohydrate $[\text{H}^+\text{BF}_3\text{OH}^-]$, which is not measurable, is related to $[\text{BF}_3\text{OEt}_2]$ and $[\text{H}_2\text{O}]$ by equilibrium constants

$$K_1 = [\text{H}^+\text{BF}_3\text{OH}^-]^2 / \{[\text{BF}_3\text{OEt}_2][\text{H}_2\text{O}]\} \quad (12)$$

$$K_2 = [\text{BF}_3\cdot 2\text{H}_2\text{O}] / \{[\text{H}^+\text{BF}_3\text{OH}^-][\text{H}_2\text{O}]\} \quad (13)$$

From a material balance, we have

$$[\text{BF}_3\text{OEt}_2] + [\text{H}^+\text{BF}_3\text{OH}^-] + [\text{BF}_3\cdot 2\text{H}_2\text{O}] = [\text{BF}_3\text{OEt}_2]_0 \quad (14)$$

$$[\text{H}_2\text{O}] + [\text{H}^+\text{BF}_3\text{OH}^-] + 2[\text{BF}_3\cdot 2\text{H}_2\text{O}] = [\text{H}_2\text{O}]_0 \quad (15)$$

By solving equations 12 - 15, we can express the concentrations of $[\text{H}^+\text{BF}_3\text{OH}^-]$ and $[\text{BF}_3\text{OEt}_2]$ in terms of equilibrium constants (K_1 , K_2), initial water and boron trifluoride etherate concentrations ($[\text{BF}_3\text{OEt}_2]_0$ and $[\text{H}_2\text{O}]_0$).

The rate for the propagation and initiation steps is expressed in equations 16 and 17. In the equations, $[M]$ and

$$\begin{aligned} \frac{d[M]}{dt} &= -k_{p1}[P_1^+][M] - k_{p2}[P_2^+][M] + k_{-p1}[P_1^+] + k_{-p2}[P_2^+] \\ &= -k_p[P^+][M] + k_{-p}[P^+] \end{aligned} \quad (16)$$

$$\begin{aligned} \frac{d[P^+]}{dt} &= \frac{d[P_1^+]}{dt} + \frac{d[P_2^+]}{dt} \\ &= k_{i1}[\text{H}^+\text{BF}_3\text{OH}^-][M] - k_{-i1}[P_1^+] + k_{i2}[\text{BF}_3\text{OEt}_2][M] - k_{-i2}[P_2^+]^2 \end{aligned} \quad (17)$$

$[P^+]$ represent the concentration of monomer DOL and the total concentration of propagation species. $[P^+]$ is equal to the sum of two different propagation species $[P_1^+]$ and $[P_2^+]$. The two constants k_p and k_{-p} are defined as

apparent propagation and depropagation rate constants

$$k_p = \{k_{p1}[P_1^+] + k_{p2}[P_2^+]\} / [P^+] \quad (18)$$

$$k_{-p} = \{k_{-p1}[P_1^+] + k_{-p2}[P_2^+]\} / [P^+] \quad (19)$$

Since these kinetic equations are too complicate to express in integrated form, we calculated the concentration of each species by Euler Method, i.e., by numerical integration of the differential equations. A detailed description of the method is in the Appendix. The rate constants for each step can be extracted by fitting the calculated concentration to the experimental data using non-linear least square procedure. The resulting parameters of the best fit are given in Table 1-7.

Fair reproducibility between two sets of data has been achieved for the initiation rate constants. Although the absolute value for each individual initiation constant may need to be confirmed by another methods, the interrelationship among these initiation rate constants is taken as representative. It should be mentioned that we have used the equilibrium constants of BF_3OEt_2 / H_2O derived from $CDCl_3$ solvent in our kinetic model. This would affect the accuracy of the quantitative relations among these initiation rate constants. Nevertheless, relation of the parameters is reasonable. For instance, $k_{i1} / k_{i2} \approx 10$ from Table 1-7, which means that the initiation through coinitiator monohydrate of boron trifluoride $[H^+BF_3OH^-]$ is

TABLE 1-7

Rate constants derived from kinetic model

DATA	PDL826	PDL118	ave.
$[\text{BF}_3\text{OEt}_2](\text{M/L})$	062	0.11	
$[\text{H}_2\text{O}](\text{M/L})$	010	0.030	
$k_{i1} \times 10^3$ (l/mol sec)	4.2	3.3	3.8
$k_{-i1} \times 10^3$ (l/mol sec)	5.8	6.7	6.3
$k_{i2} \times 10^3$ (l/mol sec)	0.3	0.3	0.3
$k_{-i2} \times 10^3$ (l/mol sec)	13	11	12
$k_p \times 10^3$ (l/mol sec)	9.3	5.3	
E^*	0.086	0.052	

$$^* E = \left[\frac{\sum_i^n \left(\frac{y_e - y_c}{y_e} \right)^2 + \sum_i^n \left(\frac{z_e - z_c}{z_c} \right)^2}{n} \right]^{1/2}$$

much faster than that of the direct initiation through self-ionization of BF_3DOL complex. In addition, the formation of BF_3DOL is unfavorable as seen by comparing the k_{i2} and k_{-i2} values. This result is expected since DOL is weaker base than ether.

The propagation rate constant derived from this kinetic model is about the same as the one from the slope

in Fig. 1-12. Both methods show significantly different propagation rate constants for the polymerization systems with low and high levels of water. A higher propagation rate constant seems to correspond to lower water concentration in the polymerization system. The reason may be because the propagation rate constant here represents the apparent rate constant (see equations 18 and 19). It is a function of each individual propagation rate constant corresponding to two propagation species and also a function of the concentrations of these two propagation species. It is expected that propagation through a zwitterion ($\text{BF}_3^\ominus\text{OCH}_2\text{CH}_2\sim\sim\sim\text{OCH}_2^\oplus$) is much faster than that of ion pair ($\text{HOCH}_2\text{CH}_2\sim\sim\sim\text{OCH}_2^\oplus\text{BF}_3\text{OH}^\ominus$). The system with lower water should contain fewer ion pair propagation species, which is from monohydrate ($\text{H}^+\text{BF}_3\text{OH}^-$) initiation species. Hence it is not surprising that a higher propagation rate corresponds to a lower water concentration.

As compared with coinitiation through formation of monohydrate ($\text{H}^+\text{BF}_3\text{OH}^-$) and its propagation, direct initiation through self-ionization is slower, but its propagation is much faster. This result is consistent with the observed kinetic curves. Experimental kinetic curves show that polymerization occurs faster initially but levels off for the system with higher water concentration, while the system with lower water concentration displays a slower initial rate of polymerization but monomer consumption

increases rapidly.

The parameters derived from the kinetic model were used to predict the concentrations of monomer and propagation species during the polymerization. The calculated concentrations are plotted in Fig. 1-11 together with experimental data for comparison. These figures show good agreement between the predicted concentrations and experimental data.

1.8 Conclusions

From the NMR spectra of the polymerization system and end group analysis in both higher and lower initiator concentrations, linear growth process may be considered to play an important role in propagation steps for bulk homopolymerization of dioxolane. It is certain that no formaldehyde is generated in this system, hence, no trioxepane or other small cyclic compounds formed from the insertion of formaldehyde can be observed in this system. But the existence of large cyclic oligomer cannot be excluded since NMR cannot distinguish larger cyclic oligomers from linear polymers.

Although the propagation species are not detectable directly from ^1H NMR spectra even at very high concentrations of initiator, the total concentration of propagation species was determined by the ion-trapping method. The apparent propagation rate constant was

calculated once the concentrations of monomer and propagation species were determined. The results indicate that change in temperature of bulk polymerization becomes more noticeable as the polymerization rate increases. Thus, the propagation rate constant is not a constant during conversion. In addition, the apparent propagation rate constant seems to be affected by the water concentration in the polymerization system. This is understandable because there are two propagation species due to direct initiation and coininitiation, water level affects the ratio of these two propagation species.

We have observed from ^1H NMR spectra that water was consumed at once after addition of BF_3OEt_2 . Quantitative analyses of initial rate of polymerization at different water concentrations have shown that maximum rate can be achieved at ratio $\alpha = [\text{H}_2\text{O}]/[\text{BF}_3\text{OEt}_2] = 0.2 - 0.25$, giving evidence that water should be considered as both coinitiator and inactivator. There is no direct evidence to exclude the direct initiation mechanism. The maximum concentration of propagation species is close to the initiator concentration. This result suggests that direct initiation through the self-ionization mechanism may also occur in addition to the coininitiation through monohydrate of boron trifluoride. The results from the kinetic model suggest that initiation of the polymerization through the coininitiation mechanism (i.e., $[\text{H}^+\text{BF}_3\text{OH}^-]$) is much more effective as compared to direct initiation. But propagation

species from this monohydrate is less active and its propagation is slower. The suggestion is supported by experimental observations. Time-conversion curves show that monomer consumption is faster initially but polymerization proceeds slowly for the system with higher water concentration.

The actual reactions involved in this polymerization system must be much more complicated than that described here via mechanism and kinetic model. However, the mechanism scheme and kinetic model presented here describe the major events in the polymerization processes.

1.9 References

1. J. M. Williams, H. R. Schulten and N. E. Vanderborgh,
Polymer, **33**, 4630 (1992)
2. L. C. Reibel, C. P. Durand and E. Franta, *Can. J. Chem.*, **63**, 264 (1985).
3. R. Alamo, J. G. Fatou and J. G. Guzman, *Polymer*, **23**, 379 (1982).
4. P. Archambault and R. E. Prud'Homme, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 35 (1980).
5. S. Bywater and D. J. Worsfold, *Can. J. Chem.*, **55**, 85 (1977).
6. L. L. Ivanova, N. A. Grebennikova, G. P. Sokolova, L. A. Pudina and N. S. Enikolopyan, *Vysokomol. Soyed.* **A18 (8)**, 1824 (1976).
7. Y. Yamashita, M. Okada and M. Kasahara, *Makromol. Chem.*, **117**, 256 (1968)
8. O. A. Plechova, V. V Ivanov, etc., *Vysokomol. Soyed.* **A15 (1)**, 14 (1973).
9. Z. N. Nysenko, E. L. Berman, E. B. Ludvig and J. Ponomarenko, *J. Macromol Sci.- Chem.*, **A10(6)**, 1093 (1976).
10. R. Szymanski and S. Penczek, *Makromol. Chem.*, **183**, 1588 (1982).
11. S. Penczek and R. Szymanski, *Polym. J.*, **12(9)**, 617 (1980).
12. Y. Yokoyama, M. Okada and H. Sumitomo, *Polym. J.*, **11**

- (5), 365 (1979).
13. T. V. Grinevich, A. N. Shupik, G. V. Korovina and S. G. Entelis, *Eur. Polym. J.*, **17**, 1107 (1981).
 14. A. T. Ponomarenko, V. G. Shevchenko and N. S. Enikolopov, *J. Macromol. Sci.-Chem.*, **A11(1)**, 195 (1977).
 15. P. Kubisa, *J. Macromol. Sci.-Chem.*, **A11(12)**, 2247 (1977).
 16. A. Stolarczyk, P. Kubisa and S. Penczek, *J. Macromol. Sci.-Chem.*, **A11(11)**, 2047 (1977).
 17. K. Brzezinska; ect, *Makromol. Chem.*, **178**, 2491 (1977).
 18. D. Mootz and M. Steffen, *Acta Cryst.* **B37**, 1110 (1981).
 19. N. M. Greenwood and R. L. Martin, *J. Chem. Soc.*, 1915 (1951).
 20. L. A. Kharitonova, G. V. Rahova, A. A. Shagingan and N. S. Enikolopyan, *Vysokomol. Soedin.*, **A9**, 2586 (1967).
 21. R. Binet and J. Leonard, *Polymer*, **14**, 355 (1973).
 22. W. K. Busfield, R. M. Lee and D. Merigold, *Makromol. Chem.*, **156**, 183 (1972).
 23. L. I. Kuzab, M. A. Markevitch, AI. AI. Berlin and N. S. Enikolopyan, *Vysokomol. Soedin.*, **A10**, 2007 (1968).
 24. N. Lu, G. L. Collins and N. L. Yang, *Makromol. Chem., Macromol. Symp.*, **42/43**, 425 (1991).
 25. See reference 4 in "introduction".
 26. P. Giusti; F. Andruzzi; P. Cerrai and L. Possanzini, *Makromol. Chem.*, **136**, 97 (1970).
 27. See reference 1 in part 2.

Part 2

INITIAL PROCESSES IN BULK POLYMERIZATION OF TRIOXANE

2.1 Introduction

Because of the generation of formaldehyde during trioxane polymerization, the cationic polymerization is much more complicated than dioxolane polymerization. The study of this system was limited to the initial stage due to precipitation of crystalline polyoxymethylene which is insoluble in bulk monomer. A number of papers (1 - 10) have been published to describe the phenomena in the trioxane polymerization. Yet little is known as to the elementary reactions involved.

At first, the initiation process and the chemical nature of the growing chain ends were the topic of study by several investigators, often with inconsistent results. Kern and Jaacks (11) studied the solution polymerization of trioxane initiated with BF_3 in dichloromethane (CH_2Cl_2) and concluded that the addition of a coinitiator was neither necessary nor useful for this polymerization. They assumed that boron trifluoride forms a rather stable complex with trioxane. This complex is able to initiate propagation through a self-ionization mechanism. Collins, et al. (12) studied bulk polymerization

of trioxane initiated with $\text{BF}_3\text{O}(\text{Bu})_2$ at 70°C . They found that the lower overall rate was associated with lower initial water concentration as determined by an electrochemical Karl-Fisher device. The molten monomer remained clear for two days showing no evidence of insoluble polyoxymethylene formation for the system without water. However, upon addition of water in concentration comparable to that of BF_3 complex, the polymerization of trioxane starts. Hence, they concluded that the initiation of trioxane by $\text{BF}_3\text{O}(\text{Bu})_2$ in the presence of water occurs by rapid hydrolysis of BF_3 to form protonic acids which protonate trioxane. In the absence of water no initiation occurs because trioxane is not basic enough to form a complex with $\text{BF}_3\text{O}(\text{Bu})_2$. The same conclusion was reported earlier for solution polymerization of trioxane in cyclohexane (13).

Polymerization of trioxane has been characterized by the occurrence of an "induction period". The roles played by water as well as the formation of formaldehyde and cyclic formals during the "induction period" have been studied. It has been proposed by Kern and Jaacks (14) that the "induction period" is due to the build up of equilibrium formaldehyde concentration. They found that addition of formaldehyde at the beginning of polymerization leads to a considerable shortening of the induction period. Studies by Miki, et al (15), however, did not confirm this. Instead, they observed that a certain amount of tetraoxane

is produced in the polymerization of trioxane in dichloroethane before the formation of methanol-insoluble polymer. Addition of tetraoxane to the polymerization system of trioxane shortens the "induction period" for the formation of methanol insoluble polymer. Thus, it was concluded that the "induction period" is due to formation of tetraoxane but not formaldehyde. In addition, the mechanism of formation of tetraoxane was attributed to a "back-biting" reaction of growing chain end with depolymerization (16). Penczek has summarized the previous research work in his review article (17), and pointed out that the formation of polymer may require that the equilibrium concentration of any "monomeric" species in equilibrium with polymer is reached first. He explained these phenomena from a thermodynamic point of view, i.e., the polymer formed initially from trioxane is thermodynamic unstable with respect to formaldehyde and tetraoxane because their concentrations are below $[M]_e$. Thus, the polymer will undergo depropagation to formaldehyde and tetraoxane and this process will continue until the equilibrium concentrations of these "monomeric" species are reached. Consequently, at this stage trioxane will be consumed but polymer will not be formed. Moreover, Wegner (18) suggested that the need to complete nucleation of crystal growth may also lead to an induction period in trioxane polymerization.

In the present investigation, the dependences of

the "induction period" of trioxane polymerization on the concentration of water, generation of formaldehyde and the addition of tetraoxane, were systematically studied. The initial processes of trioxane polymerization were followed through the application of ^1H NMR spectroscopy. The kinetic and mechanistic relationship for these compounds was examined. The NMR method has the advantage of direct, *in situ*, simultaneous observation of all species, including water and formaldehyde without disturbing the processes involved. This method has been limited to the initial stage. Once the polymerization mixture becomes turbid, the NMR spectra lose their resolution. Gas chromatography (GC) was also used as a complementary method to monitor the kinetic profiles of various species. The application of ^1H NMR to study of bulk trioxane polymerization was attempted previously (19). In that study, however, conclusions on the polymerization mechanism were drawn based on erroneous chemical shift assignment. We report here our recent studies, leading to the development of a more detailed mechanistic scheme for the initial process.

2.2 Experimental

Monomer trioxane (TOX) was distilled under the protection of dry nitrogen at 104°C from sodium metal using benzophenone as an indicator to remove water. Tetraoxane (TEOX) was obtained from Polyscience Inc.

Water content in the polymerization system was determined by the Karl-Fisher method or from ^1H NMR spectra. The course of polymerization was observed in a similar way as described in the polymerization of DOL. The polymerization was carried out at 63°C , the melting point of TOX. For the purpose of observing the initial stage of polymerization, the concentration of BF_3OEt_2 was controlled at about 10^{-4} - 10^{-5} mole/l. Such a small amount of initiator was added as diluted ether solution for accurate control of its concentration.

Water in the monomer TOX was measured using the Karl-Fisher method just before addition of BF_3OEt_2 . The samples used for GC measurement were prepared as follows: About 0.3 - 0.4 g (to nearest 0.1 mg) of reaction mixture was withdrawn using a hot syringe at different reaction times and added to THF solvent (ca. 2.0 g, to nearest 0.1 mg) containing a small amount of triethylene amine. The solutions were stirred and centrifuged for about 5 minutes, then the precipitated polymer was dried under ambient conditions overnight and dried again in a vacuum oven kept at 50°C overnight. The dried polymer was weighed and its concentration was determined by comparing its weight with total sample weight. The supernatant was used for GC analysis for the concentrations of TOX and TEOX.

The GC instrument used for this analysis was HP 5880A with a flame ionization detector. Oven temperature was controlled using a single temperature program. The detailed

GC conditions were listed as follows:

Column: 6 ft x 1/8 in

Stationary phase: 100% dimethyl polysilaxane

Carrier gas: Helium

Flow rates: He = 20 ml/min, H₂ = 32 ml/min,

air = 430 ml/min

Sample size: 0.8 - 1.0 μ l

Injector temperature: 200°C

Detector temperature: 350°C

Oven temperature: Initial value 35°C

Initial time 7 min.

Temp. programming rate 8.5°C/min

Final value 65°C

Final time 10 min.

To determine the effects of water and addition TEOX on the time for formation of insoluble polyoxymethylene, trioxane polymerization was carried under the condition at which temperature and initiator were kept constant. For a sets of tubes which contained a known amount of TOX, the water level was controlled by adding a desired amount of water to TOX using microsyringes. The accurate concentration of water was measured by the Karl-Fisher method just before the addition of BF₃OEt₂. We started to time the reaction at the moment of addition the initiator and stopped to record the time at the moment of the polymer

mixture become turbid or solid.

2.3 ^1H NMR spectra for initial processes of trioxane polymerization

^1H NMR spectrum obtained for the polymerization system consisting of dry distilled TOX (H_2O undetectable by NMR) with about 0.06 mol/l BF_3OEt_2 shows only TOX absorption located at 5.11 ppm. A formaldehyde peak (9.63 ppm) is barely discernible only at very high instrument sensitivity. The intensity of this TOX peak remains unchanged with time, giving evidence that at very low water content a significant level of formaldehyde cannot be formed and polymerization cannot proceed.

At a higher level of water content (0.016 mol/l based on NMR absorption at 2.14 ppm) homopolymerization was observed. At a low level (9.5×10^{-4} mol/l) of initiator concentration, the kinetic process can be monitored readily (Fig. 2-1). Before the addition of initiator, only absorptions due to TOX, H_2O and trace amount of soluble oligomer (4.87 ppm) are present (Fig. 2-1a). Immediately after the injection of BF_3OEt_2 , the disappearance of H_2O is accompanied by the appearance of formaldehyde. The ethyl ether molecule is also shown to be released from the BF_3OEt_2 complex (Fig. 2-1b). TEOX is formed subsequent to the appearance of formaldehyde (Fig. 2-1b,c d). The signal at 5.02 ppm is assigned to TEOX based on a comparison with

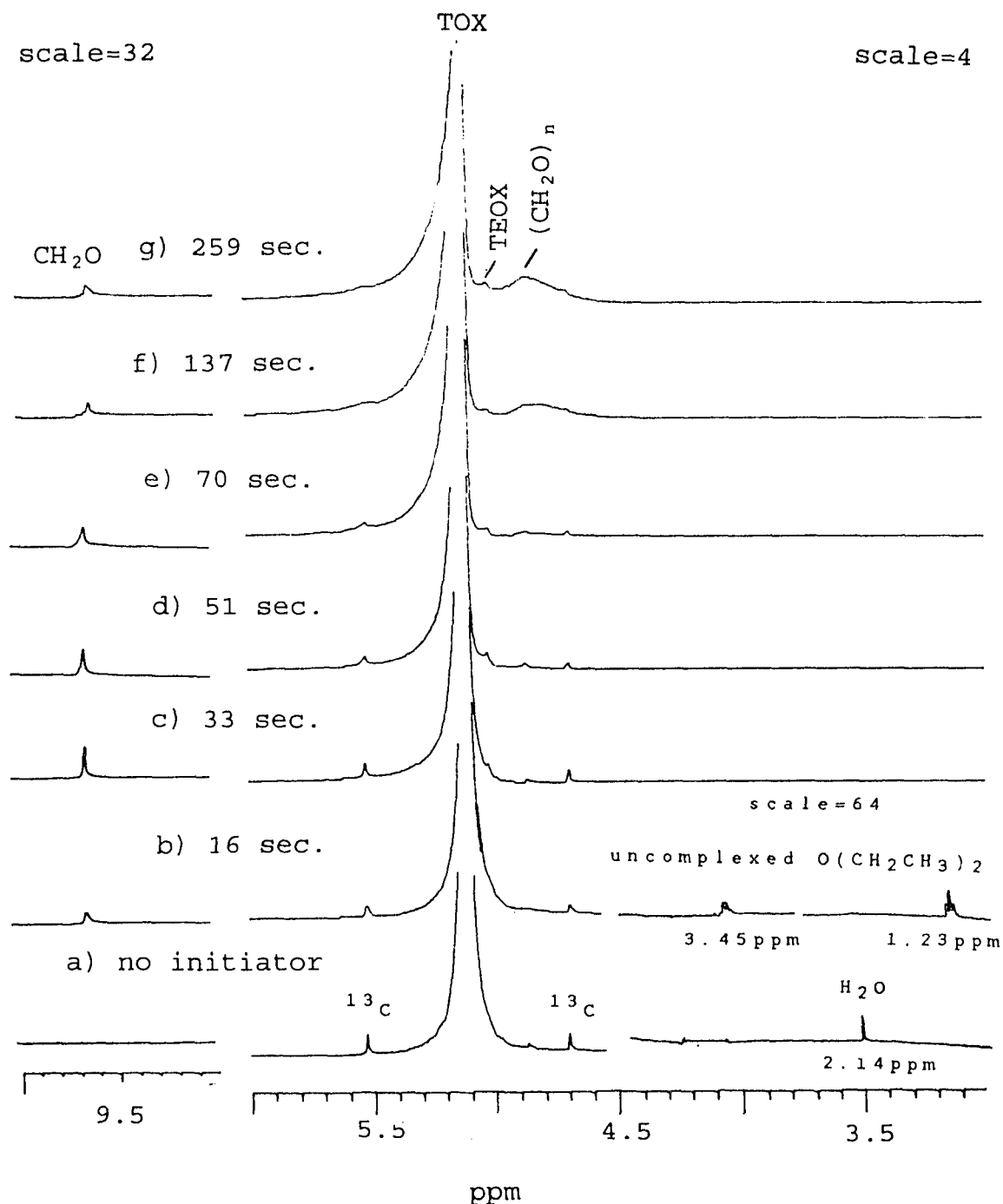


Fig.2-1 ¹H NMR spectra as a function of time for bulk polymerization of trioxane initiated with BF₃OEt₂ at 63°C. [BF₃OEt₂]=9.5 × 10⁻⁴ mol/l; [H₂O]=0.016 mol/l.

the spectrum of a mixture consisting of TOX and TEOX. The absorption located at 4.87 ppm is assigned to the growing TOX homopolymer $(\text{CH}_2\text{O})_n$, i.e., MMM sequence. This peak becomes broader with time due to crystallization of the polymer and heterogeneity of the reaction mixture. The broadening of the formaldehyde absorption peak with time is most likely due to the presence of some fraction of formaldehyde in the proximity of the polymer particle surface.

For a system with a much higher water level, 0.049 mol/l (Fig. 2-2), no significant level of formaldehyde is observed until most of water is consumed (Fig. 2-2a,b,c). After about 10 minutes of reaction time, all water disappears and significant level of formaldehyde appears with the first observation of the growth of TEOX (Fig. 2-2d). MMM sequence begins to appear by about 13 minutes (Fig. 2-2e). The result indicates that water also retards the rate of polymerization.

Fig. 2-1 and Fig. 2-2 show clearly that TEOX was formed after the appearance of formaldehyde and before significant growth of the MMM sequence was detected. Hence, formal back-biting by a growing chain with significant chain length to give TEOX is unlikely. An insertion process involving the addition of formaldehyde to TOX to form TEOX seems more plausible. A kinetic insertion could involve a rapid process wherein ring-opening or partial ring-opening of TOX followed by the addition of CH_2O and immediate

scale=32

scale=4

scale=32

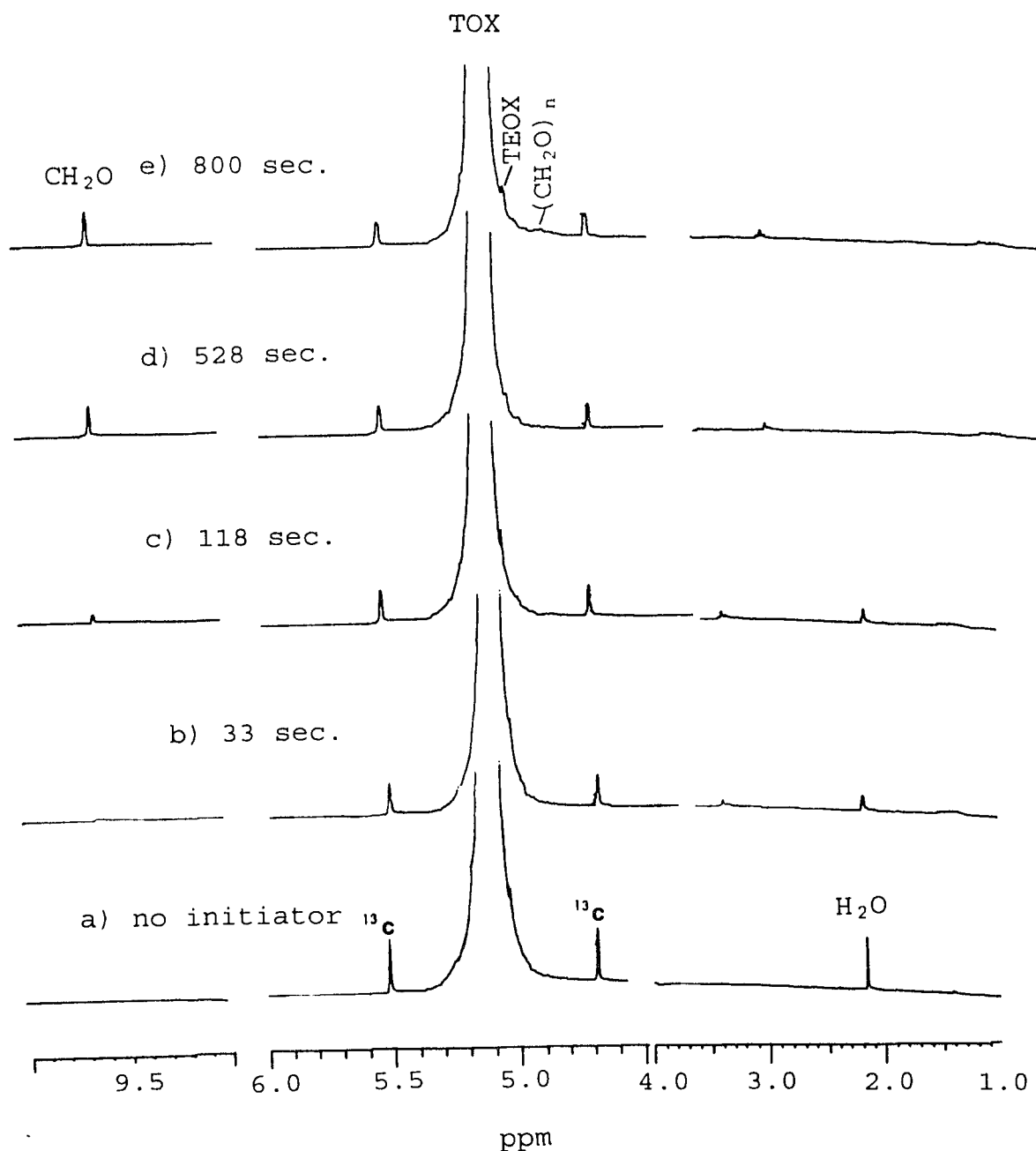
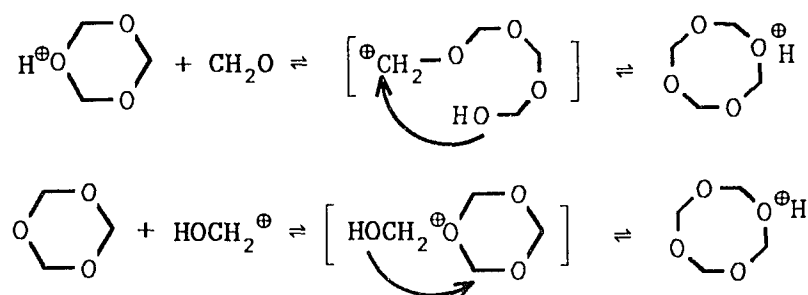


Fig.2-2 ¹H NMR spectra as a function of time for bulk polymerization of trioxane initiated with BF₃OEt₂ at 63°C. [BF₃OEt₂]=6.5 × 10⁻⁴ mol/l; [H₂O]=0.049 mol/l.

closure. A speculative process of this type reaction is suggested below (reaction scheme I);



(Reaction scheme I)

The kinetic profiles for the change of formaldehyde concentration together with the formation of polymer sequence and TEOX are shown in Fig. 2-3. These kinetic profiles show two characteristics: 1) there is an "induction period" during which formaldehyde reaches a maximum followed by the maximum of TEOX, but polymer growth is not significant; and 2) initial rapid polymerization begins only after formaldehyde passes its maximum and TEOX grows to a significant concentration.

The steady state concentration of formaldehyde for the system depicted in Fig. 2-3 is about 4×10^{-2} mol/l, comparable to a value of 6×10^{-2} mol/l found from the solution polymerization of TOX in dichloroethane at 30°C (11). From the kinetic point of view, what has historically been viewed as an equilibrium concentration of formaldehyde must be properly considered as a steady state concentration which reflects the overall kinetic behavior of the reaction

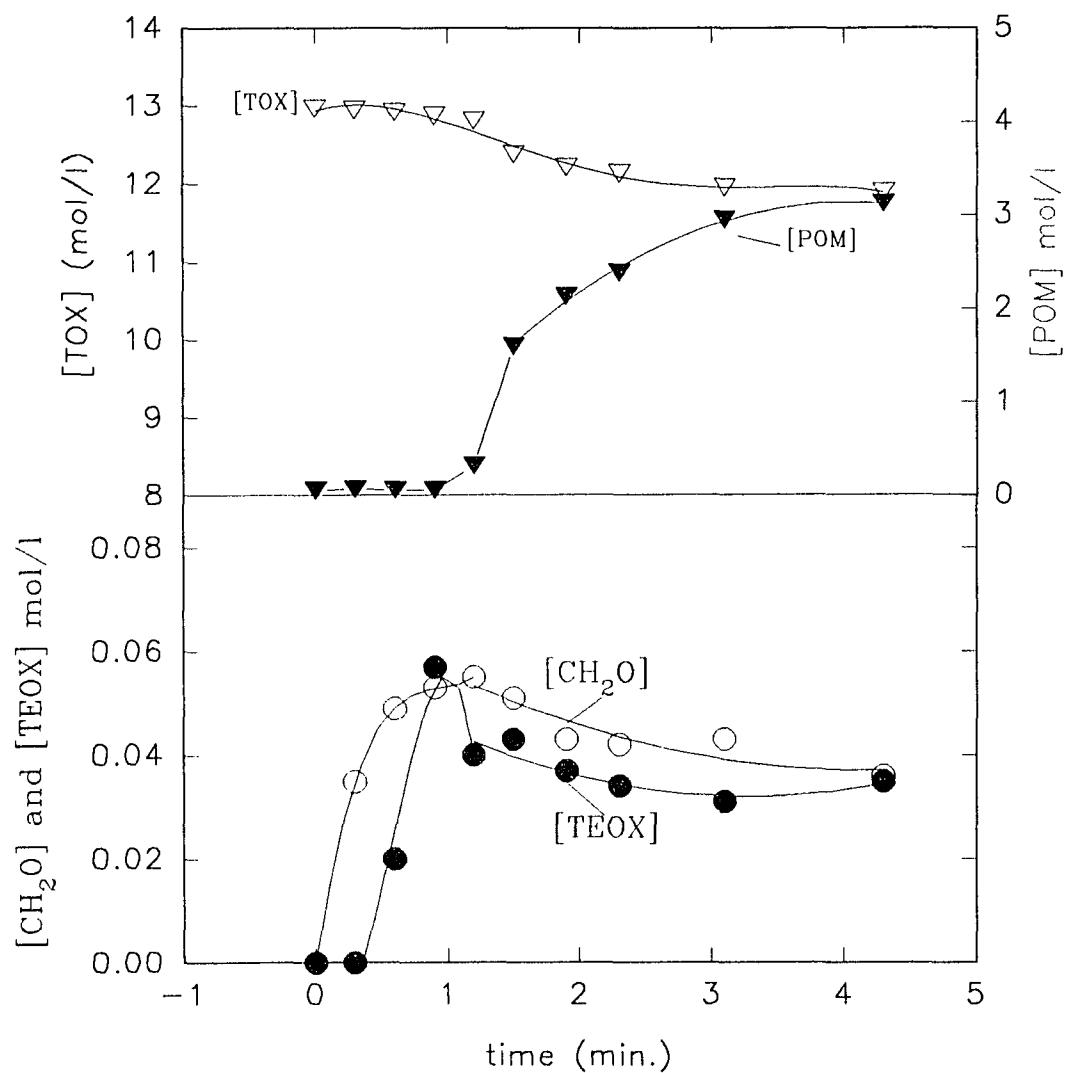


Fig. 2-3 Kinetic profiles for each component during the course of trioxane polymerization initiated with BF_3OEt_2 at 63°C (data was obtained from NMR spectra). $[\text{BF}_3\text{OEt}_2] = 9.5 \times 10^{-4} \text{ mol/l}$, $[\text{H}_2\text{O}] = 0.016 \text{ mol/l}$.

system. The decrease from the maxima of formaldehyde and TEOX concentrations reflects an increase in their rate of consumption as a consequence of an increase in overall rate of polymerization that occurs with the onset of heterogeneous polymerization.

2.4 Kinetic curves for the polymerization of trioxane from GC determination

The use of NMR to observe the polymerization processes of TOX has been limited to the initial stage. In addition to the complication of precipitation of polymer, line broadening of the polyoxymethylene (POM) peak and the overlap of the TOX and TEOX peaks may affect the accuracy of the quantitative measurement. These disadvantages can be overcome using GC to monitor the polymerization processes.

The internal standard method was used to determine quantitatively the concentrations of TOX and TEOX. Sets of standard samples were injected and GC traces were obtained. The peak area ratios of TOX and TEOX to the internal standard THF in GC traces are plotted against the weight ratios of TOX/THF and TEOX/THF to construct calibration curves (Fig. 2-4). Thus, the actual weight of TOX and TEOX in polymerization mixtures is calculated from known weight of THF and the calibration curves. The concentrations of TOX and TEOX were obtained by comparing its weight with total sample weight.

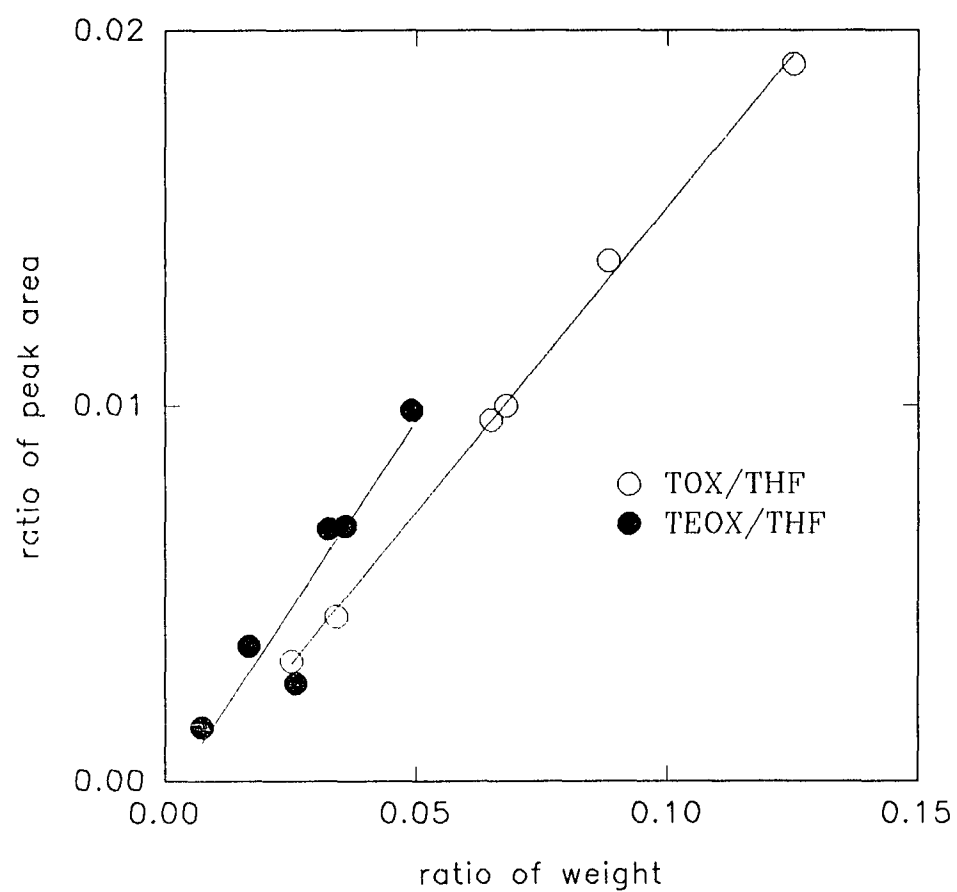


Fig. 2-4 Calibration curves for peak area ratios of TOX/THF and TEOX/THF from GC chromatograms versus weight ratios of TOX/THF and TEOX/THF.

Fig. 2-5 shows the kinetic curves corresponding to two different water contents and the same initiator concentration. The kinetic profile of formaldehyde can not be measured by GC method. As compared with the kinetic curves obtained from NMR spectra, again the polymerization is characterized by an "induction period"; rapid growth of polyoxymethylene will not occur until TEOX reaches its steady state concentration. Similar to DOL polymerization, we see different features of the monomer consumption curve between the two systems. For the system with low levels of water (Fig. 2-5a), almost no monomer was consumed before 4.0 minutes of reaction time. But the consumption of monomer and the formation of polyoxymethylene increase rapidly once the polymerization starts. On the other hand, the initial rate of consumption monomer for the system with higher water content (Fig. 2-5b) is faster, but the decrease in monomer concentration slows down and almost levels off with polymerization time. This result indicates strongly that water acts as both coinitiator and inactivator for TOX polymerization initiated by BF_3OEt_2 . The initial rate of polymerization is slow for the system with low water concentration, because there is not much water available to form $\text{H}^+\text{BF}_3\text{OH}^-$ which is believed to be the actual initiation species. For water content at a higher level, the initiation of polymerization is fast with water as coinitiator, but the strong retardation effect by water becomes important. As a result, the polymer

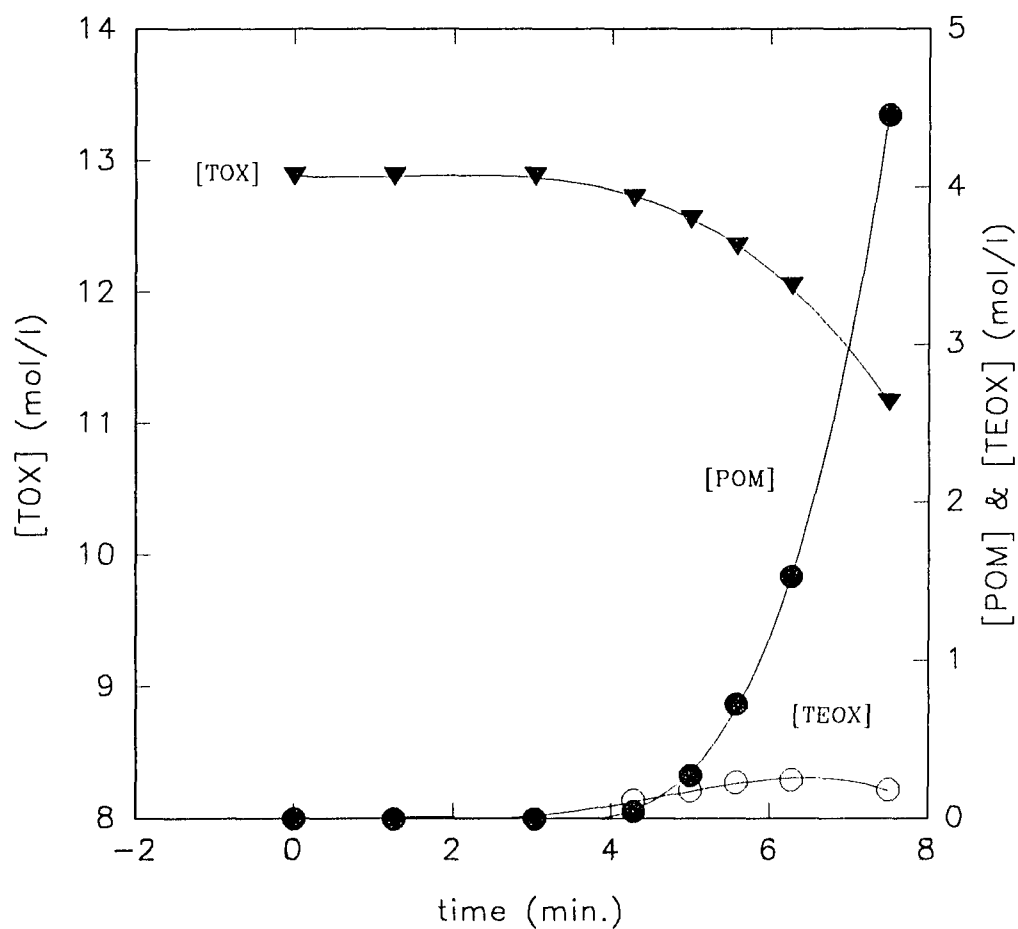


Fig. 2-5a Kinetic curves for bulk polymerization of trioxane₅ initiated with BF_3OEt_2 at 63°C . $[\text{BF}_3\text{OEt}_2]=8.2 \times 10^{-5}$ mol/l; $[\text{H}_2\text{O}]=0.0070$ mol/l. Data was obtained from GC peak area ratios.

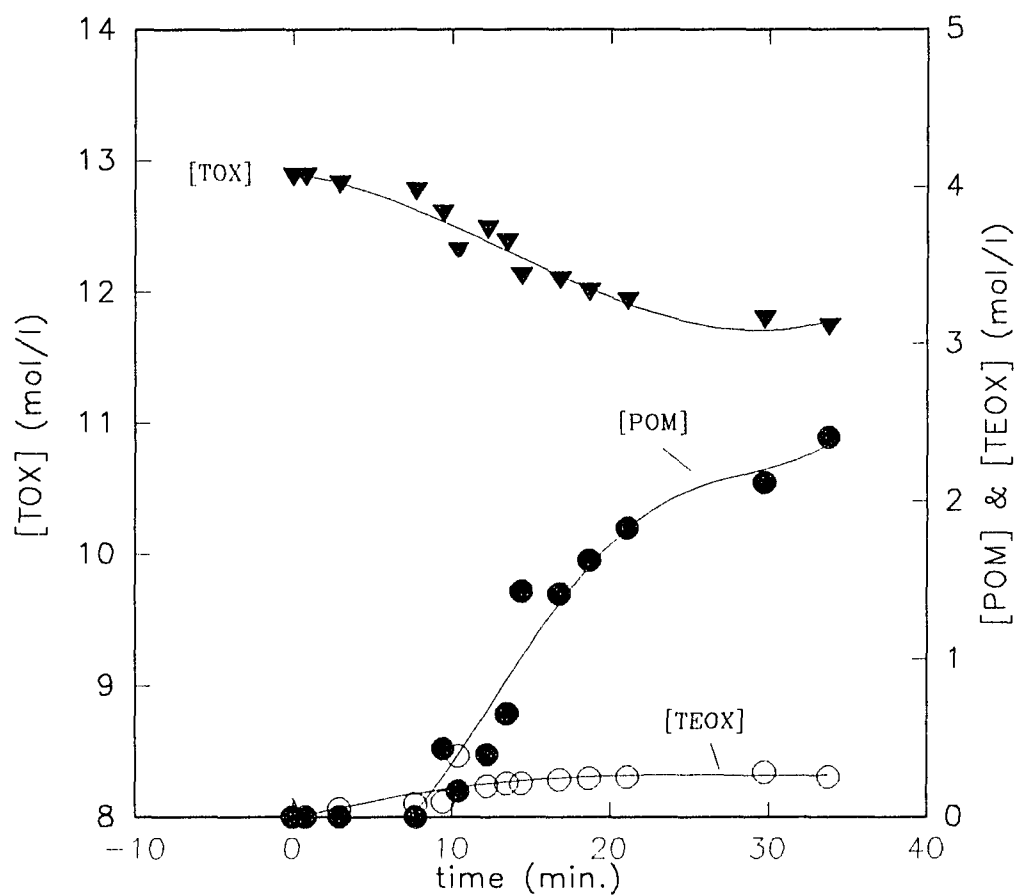


Fig. 2-5b Kinetic curves for bulk polymerization of trioxane₅ initiated with BF_3OEt_2 at 63°C . $[\text{BF}_3\text{OEt}_2]=8.2 \times 10^{-5}$ mol/l; $[\text{H}_2\text{O}]=0.019$ mol/l. Data was obtained from GC peak area ratios.

conversion over an extended polymerization time is lower for high water content.

2.5 The effect of water on the "induction period" of trioxane polymerization

Both ^1H NMR spectra and kinetic curves from GC measurements indicate that water has dramatic effect on the polymerization of TOX.

The relationship between of water content and "induction period", i.e., the time required for the appearance of solidification for TOX polymerization, was investigated systematically. The results are listed in Table 2-1. In spite of the scattering of the data, all three sets of experiments show that the time for the polymer mixture to become solid tends to increase with water for constant concentration of BF_3OEt_2 . The "induction period" is only prolonged slightly with water when water is below $4 - 6 \times 10^{-3}$ mol/l; above this concentration, the polymerization rate decreases dramatically.

The results in Table 2-1 reflect the retardation of the polymerization rate when water in the system reaches a certain concentration. This seems to contradict the assertion of that water is needed as coinitiator for the polymerization of TOX. The reasons that we did not observe a minimum in the time for formation of insoluble polymer may include the following: 1) in the polymerization systems

TABLE 2-1

The effect of water on the "induction period" of trioxane polymerization initiated with BF_3OEt_2 at 63°C .

TOX (g)	BF_3OEt_2 (ul)	$[\text{BF}_3\text{OEt}_2]$ $\text{mol/l} \times 10^{+4}$	H_2O (ppm)	$[\text{H}_2\text{O}]$ $\text{mol/l} \times 10^{+3}$	time ^(a) (sec.)
10.57	10.4	1.86	21	1.19	7
8.75	8.6	1.85	22	1.21	6
12.23	12.0	1.85	23	1.29	18
8.64	8.3	1.85	24	1.36	14
8.11	8.0	1.86	25	1.40	3
8.08	7.9	1.84	26	1.43	18
12.53	12.3	1.85	30	1.64	4
10.02	10.0	1.88	33	1.81	20
8.96	8.8	1.85	41	2.28	9
9.77	9.6	1.85	80	4.44	22
9.72	9.6	1.86	110	6.09	12
11.33	11.2	1.86	113	6.27	16
9.08	8.9	1.85	128	7.11	39
10.96	10.8	1.86	140	7.77	43
10.98	10.8	1.86	226	12.6	45
9.36	9.2	1.85	264	14.7	125
$[\text{BF}_3\text{OEt}_2]^{(b)} = 1.9 \times 10^{-4} \text{ mol/l, temp} = 64^\circ\text{C}$					
11.93	24.5	1.94	32	1.76	50
9.38	19.2	1.93	44	2.42	60
9.91	20.4	1.94	50	2.78	74
10.48	21.5	1.93	63	3.51	109
9.98	20.5	1.94	138	7.69	106
10.13	20.8	1.94	88	4.87	115
11.06	22.7	1.94	149	8.30	109
11.76	24.2	1.94	109	6.07	126
$[\text{BF}_3\text{OEt}_2]^{(c)} = 1.9 \times 10^{-4} \text{ mol/l, temp} = 64^\circ\text{C}$					
11.90	13.0	2.06	30	1.67	13
9.79	10.7	2.06	63	3.50	26
7.76	8.5	2.07	73	4.06	36
9.13	10.0	2.07	120	6.67	40
7.29	8.0	2.07	144	8.00	290
$[\text{BF}_3\text{OEt}_2]^{(d)} = 2.1 \times 10^{-4} \text{ mol/l, temp} = 79^\circ\text{C}$					

(a) The time for polymer mixture become solid.

(b) BF_3OEt_2 was dilute in ether by 50 times

(c) BF_3OEt_2 was dilute in ether by 100 times.

(d) BF_3OEt_2 was dilute in ether by 50 times.

studied, the water concentration is about $1.2 - 15 \times 10^{-3}$ mol/l, which is still much higher than the concentration of BF_3OEt_2 (mole ratio of $[\text{H}_2\text{O}] / [\text{BF}_3\text{OEt}_2] \approx 6 - 75$). The maximum initial rate of dioxolane polymerization was found a mole ratio of $[\text{H}_2\text{O}] / [\text{BF}_3\text{OEt}_2]$ of ca. 0.2 (see Section 1.6 in part 1). TOX is a weaker base than DOL, so it is not surprising that we did not observe a decrease in time for solidification of the polymer mixtures within the range of water concentration observed. For the polymerization system with high level of water, kinetic curves show that the initial rate of monomer consumption is fast but this rate slows down and almost levels off as polymerization proceeds. In other words, water acting as a coinitiator; it only accelerates the initiation of polymerization. It also acts as an inactivator which retards the polymerization strongly. As a result, we only expect an increase in initial rate of polymerization when water concentration increases. The time for formation of insoluble polymer may not reflect the initial rate of polymerization.

The retardation of the polymerization rate by water may again be related to the generation of the dihydrate complex of boron trifluoride ($\text{BF}_3\cdot 2\text{H}_2\text{O}$), which is considered too inactive to initiate the polymerization. In the presence of a considerable amount of water, the preferred reaction for $\text{H}^+\text{BF}_3\text{OH}^-$ is probably not addition to TOX but reaction with water to form $\text{BF}_3\cdot 2\text{H}_2\text{O}$, since water is a

stronger base than TOX.

Since formaldehyde controls the generation of polymer, the effect of water on the polymerization rate is also reflected through the relationship between the generation of formaldehyde and water concentration. ^1H NMR spectrum shows that no significant formaldehyde can be generated, hence no polymerization can proceed for the system with undetectable amount of water. While for the system with higher water level, formaldehyde is produced slowly, leading to a delay in generation of the polymer. Fig. 2-6 presents a plot of the of maximum concentration of formaldehyde with water content for each individual system. As water content increases, the maximum concentration of formaldehyde increases initially and then decreases. The increase in generation of formaldehyde with water concentration is probably due to the increase of concentration of protonated trioxane. But excess water may cause hydrolysis of molecular formaldehyde (i.e., formation of $\text{CH}_2(\text{OH})_2$); thus we observed a decrease in formaldehyde concentration decrease as water content increases.

2.6 The influence of addition of tetraoxane on the "induction period" of trioxane polymerization

In addition to formaldehyde, TEOX also plays an important role in the induction period of polymerization. From kinetic curves, the initial rapid polymerization

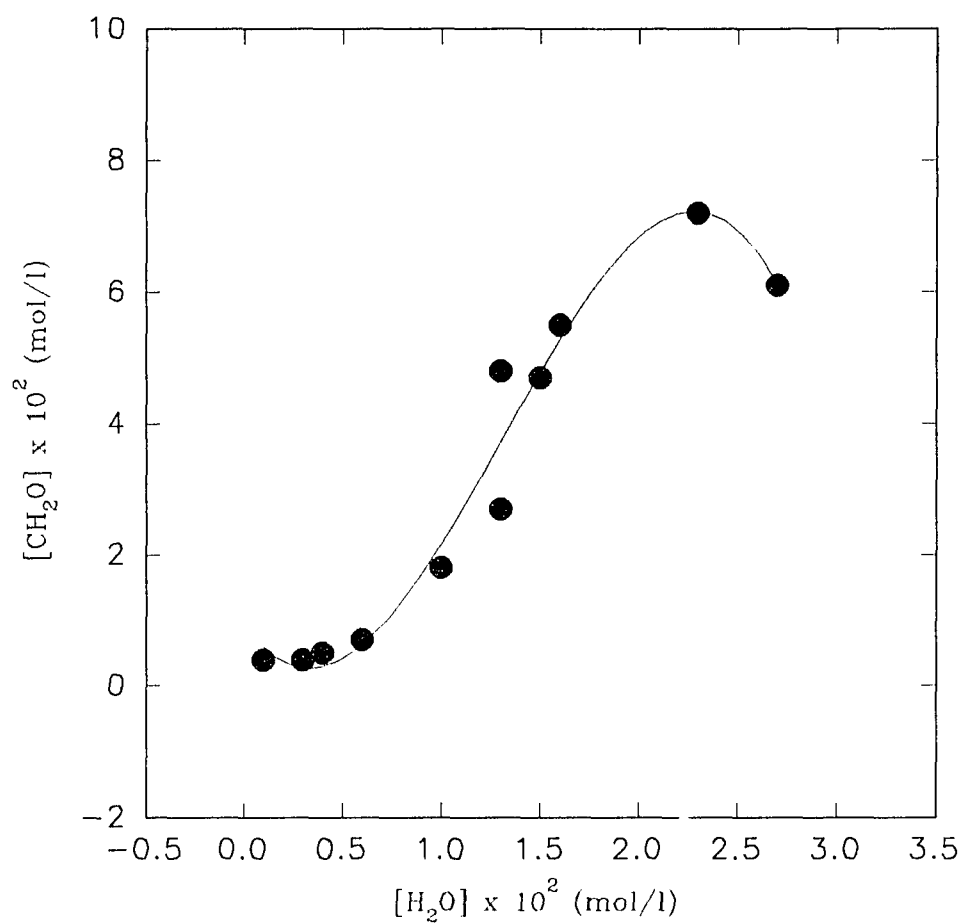


Fig. 2-6 The change of maximum concentration of formaldehyde versus water for bulk polymerization of trioxane initiated with BF_3OEt_2 at 63°C . $[\text{BF}_3\text{OEt}_2] = 9.5 \times 10^{-4} \text{ mol/l}$.

begins only after formaldehyde passes its maximum and TEOX grows to a significant concentration. Therefore, addition of TEOX into the polymerization system may shorten the "induction period". ^1H NMR spectra corresponding to the systems with and without addition of TEOX confirm this suggestion (Fig. 2-7, 2-8). For polymerization initiated by 7.0×10^{-4} mol/l of BF_3OEt_2 without addition of TEOX, formaldehyde and TEOX grow slowly; no significant growth of polymer sequence occurs during 5.5 minutes of observation time (Fig. 2-7). For the system with 0.02 mol/l of TEOX added, formaldehyde and TEOX increase much faster even the initiator concentration is low (4.7×10^{-4} mole/l), and polymer sequence starts to grow significantly at about 0.5 minutes of observation time (Fig. 2-8). The concentration of TEOX in this system can reach 0.09 mol/l, which is twice as that in the system without added TEOX. Moreover, pentaosane is also detected at 4.98 ppm per reported NMR assignment (20), indicating that insertion of formaldehyde into TEOX also takes place at high concentrations of TEOX.

Fig. 2-9 illustrates the effect of addition TEOX on the "induction period" of trioxane polymerization. The time for polymerization mixture to become turbid and solid decreases linearly as added concentration increases for constant water and initiator concentrations. These experimental data further confirm that the induction period for the formation of polymer is due to the requirement critical concentrations of formaldehyde and TEOX.

scale=32

scale=4

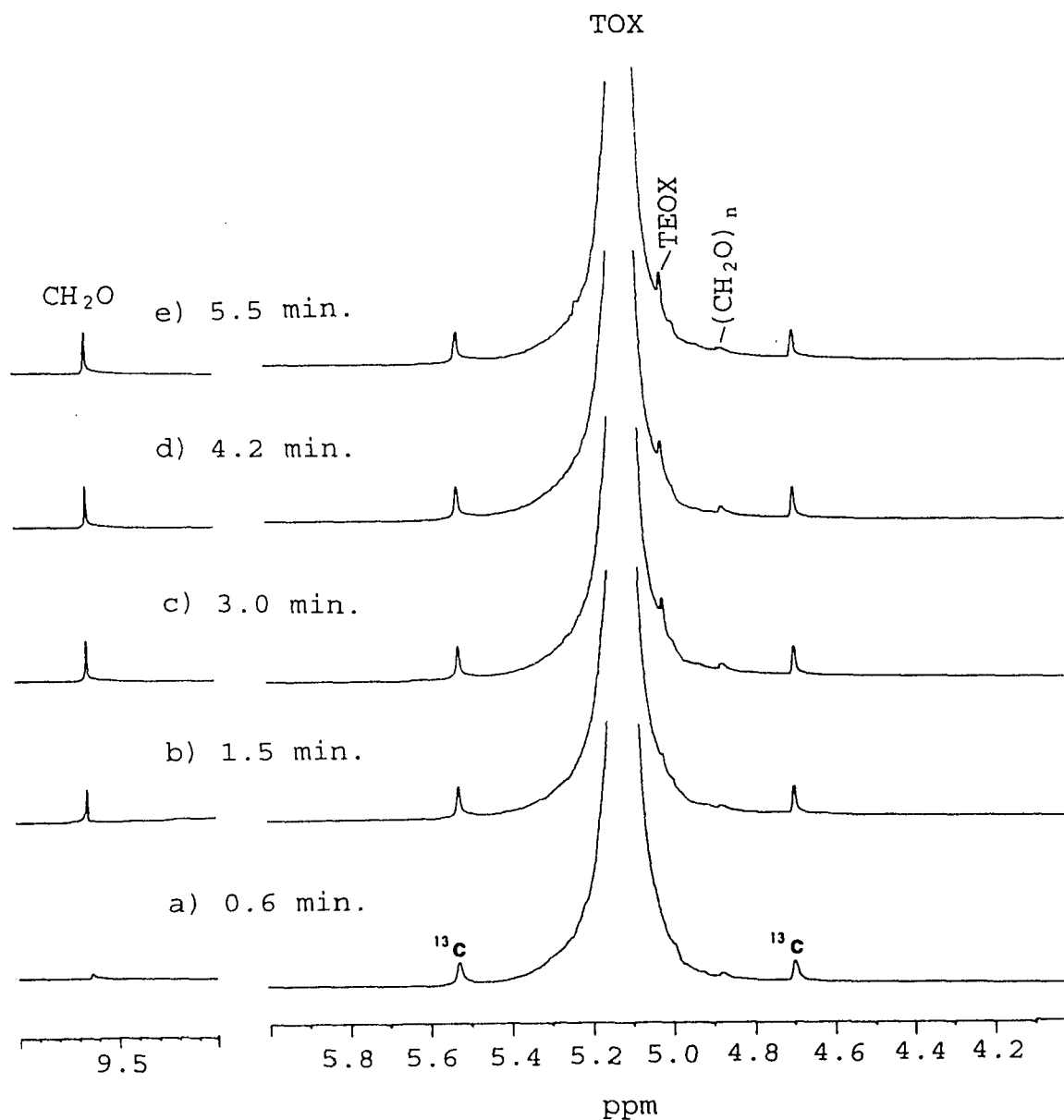


Fig.2-7 ^1H NMR spectra as a function of time for bulk polymerization of trioxane initiated with BF_3OEt_2 at 63°C . $[\text{BF}_3\text{OEt}_2] = 7.0 \times 10^{-4} \text{ mol/l}$.

scale=32

scale=4

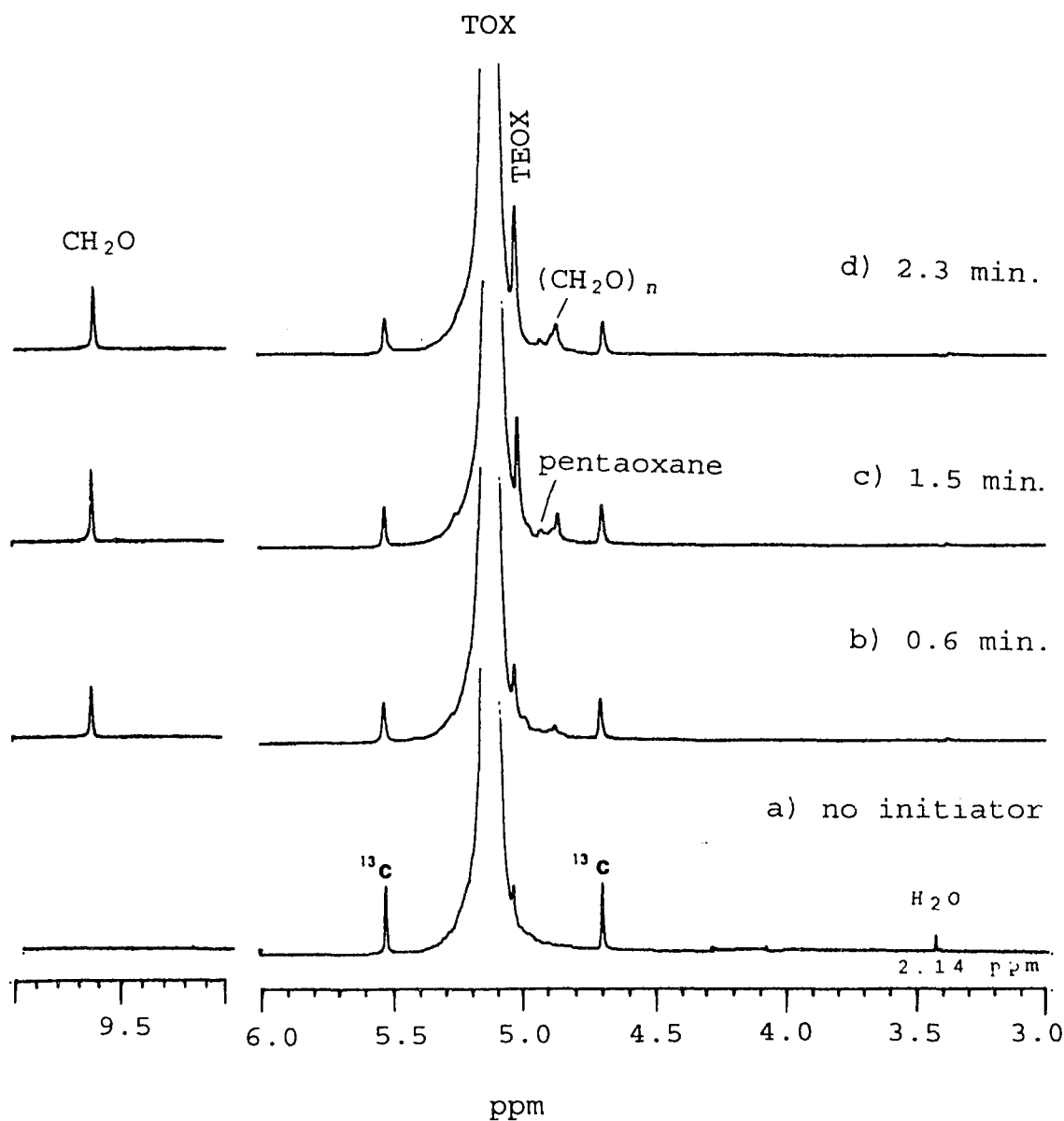


Fig.2-8 ¹H NMR spectra as a function of time for bulk polymerization of trioxane with addition of tetraoxane at 63°C. [BF₃OEt₂] = 4.7 x 10⁻⁴ mol/l. [TEOX]₀ = 0.02 mol/l.

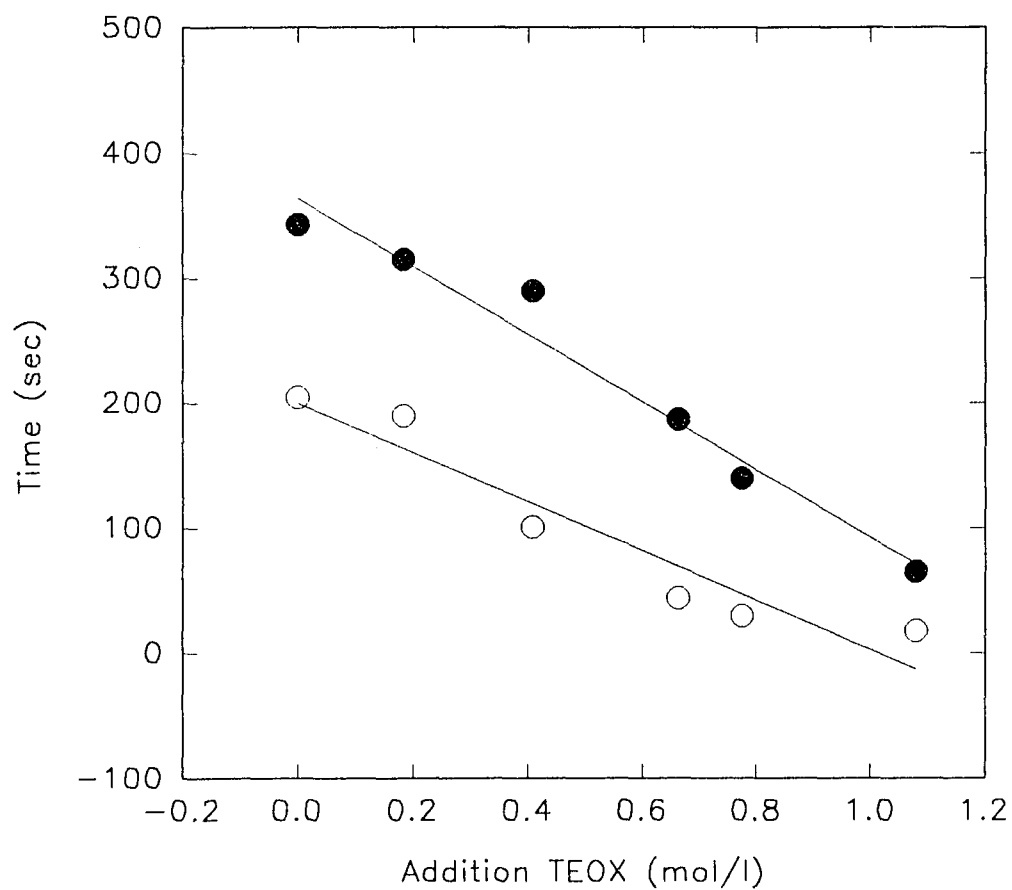


Fig. 2-9 The effect of addition of TEOX on the times for bulk polymerization of trioxane becoming solid (●) and turbid (○). Temp.=64°C. $[\text{BF}_3\text{OEt}_2]=8.4 \times 10^{-5} \text{ mol/l}$. $[\text{H}_2\text{O}]=1.0\text{--}1.2 \times 10^{-3} \text{ mol/l}$.

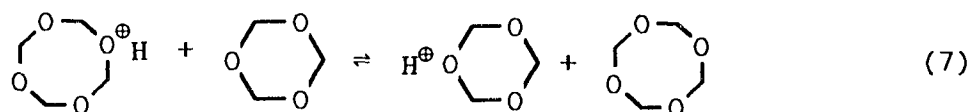
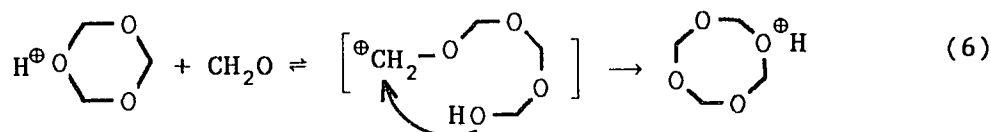
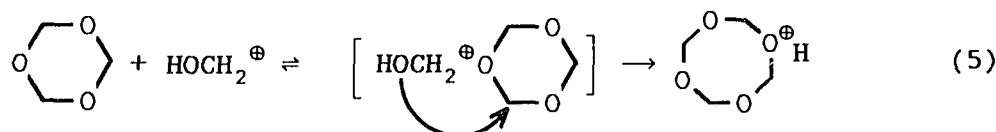
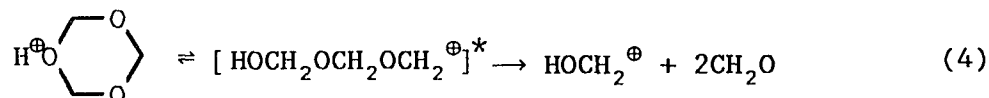
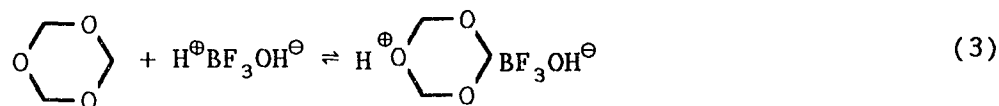
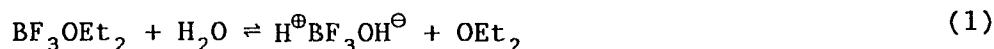
2.7 Mechanistic schemes for the polymerization of trioxane

The kinetic profiles of various species during the course of polymerization as monitored *in situ* by ^1H NMR provide data for the articulation of component behavior in kinetic and mechanistic terms. The initial steps involved in TOX homopolymerization can be summarized with scheme II (reactions 1 - 10):

The initial event is the conversion of the Lewis acid to a Bronsted acid by reaction of BF_3OEt_2 with water (reactions 1 and 2). The Bronsted acid acts as a strong electrophile which can attack TOX, resulting in the generation of formaldehyde (reactions 3 and 4). The rapid rearrangement of TOX-cyclic oxonium to form TEOX is kinetically equivalent to an insertion process, i.e., kinetic insertion (reactions 5 and 6). Formaldehyde and TEOX each pass through their maxima, reflecting dynamic balance between their generation (reactions 4, 5 and 6) and their consumption in both homogeneous and heterogeneous polymerization (reactions 6 and 9).

Initially all components are soluble, hence solution remains clear. The historical designation, "induction period", can now be understood in these terms. Because the system is initially far from equilibrium, the intermediate decomposition of the oxocarbenium is favored, and a build-up in formaldehyde is observed. As formaldehyde

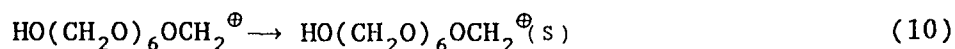
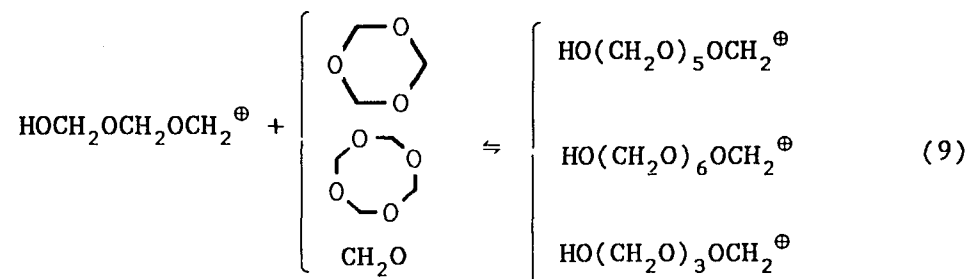
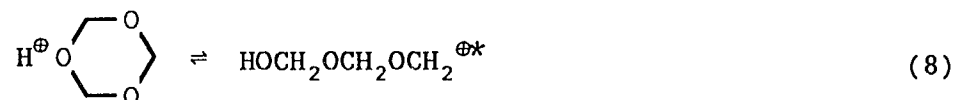
Initial steps for TOX homopolymerization



*Initially far from equilibrium.

concentration increases, the short oxymethylene active sites are transformed from fleeting intermediates to kinetically viable species (reaction 8). The termination of the induction period occurs when the first insoluble component, crystalline polyoxymethylene (POM), is formed (reaction 10). Crystalline POM can only be formed when oxymethylene segments of sufficient length are generated (6 - 8 units). The enthalpy of crystallization enhances

End of induction period



*At higher formaldehyde concentration, oxymethylene active site dose not decompose as rapidly.

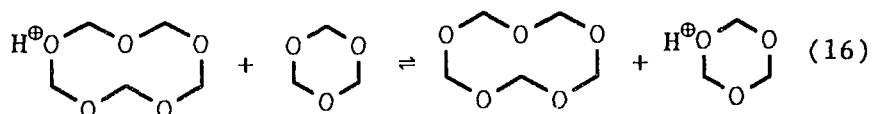
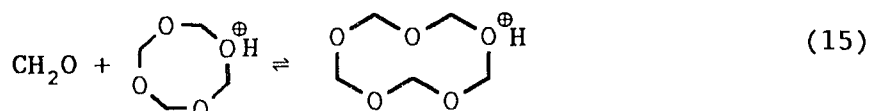
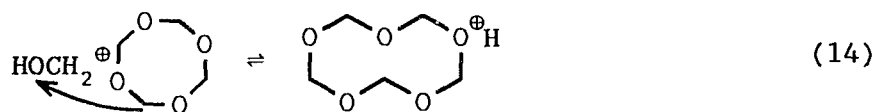
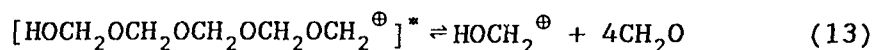
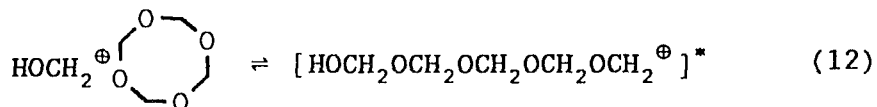
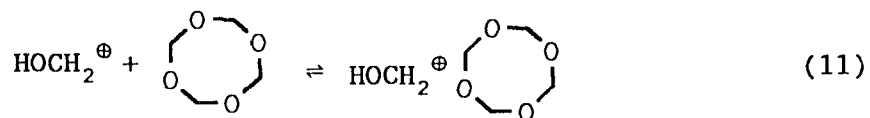
(Reaction scheme II)

substantially the driving force for crystalline polymer formation. The appearance of crystalline polymer results in an increase in the rate of consumption of formaldehyde and TEOX, leading to the occurrence of maxima in the concentration profiles. Steady state concentrations of formaldehyde and TEOX are reached which balance the generation and consumption of these components.

The role of TEOX can be expressed by scheme III (reactions 11 - 19):

TEOX does not play a critical role in the mechanistic path to crystalline polymer. It can, however, influence the kinetics. At high concentrations, TEOX can shorten the induction period by providing longer oxymethylene segments. Initially, formaldehyde generation is faster on an

Initial steps for high level of TEOX



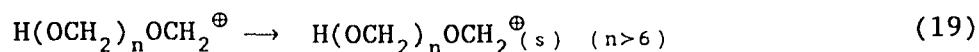
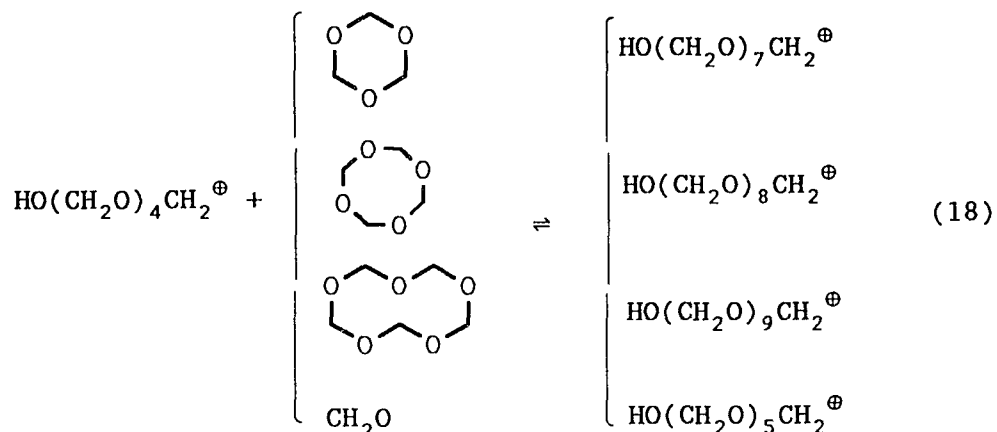
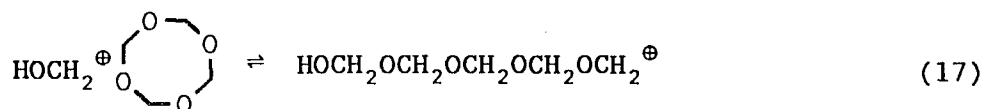
*Initially far from equilibrium

equivalent per event basis (reaction 13). At the end of induction period, opening TEOX allows the oxymethylene chain to reach the critical length sooner (reaction 18).

2.8 Conclusions

Based on the data from the present ^1H NMR study and other experimental observations, the following conclusions can be drawn. Water is involved in the polymerization of TOX not only as coinitiator but also as inactivator. The initial phase of TOX reaction, historically described as the "induction period", has a kinetic rather than a thermodynamic origin. Depending on conditions, formaldehyde

End of induction period



(Reaction scheme III)

can reach a kinetic steady state but not an equilibrium concentration. The generation of cyclic acetals occurs by a process that is kinetically equivalent to insertion rather than by back-biting. The increase in formaldehyde concentration during the "induction period" controls the transformation of oxymethylene active sites from kinetically short-lived intermediates to kinetically viable elements of the mechanistic scheme, which are capable of growth. The termination of the "induction period" is brought on by the growth of oxymethylene segments of lengths sufficient to crystallize. In contrast to polymerization of TOX, there are no formaldehyde or other small cyclic compounds formed in DOL polymerization, and

the propagation of DOL monomer into polymer does not need to build up a certain concentration of any other "monomeric" species.

2.9 References

1. S. Okamura, T Higashimura and T. Miki, " *Cationic Polymerization of Trioxane in Solution*", *Prog. Polym. Sci.*, **3**, 97 (1972)
2. M. Hasegawa, K. Yamamoto, T. Shiwaku and T. Hashimoto, *Macromolecules*, **23**, 2629 (1990).
3. M. Bednarek, et al., *Makromol. Chem.*, **190(5)**, 929 (1989).
4. J. Stasinski and G. Dmowska, *Makromol. Chem., Rapid Commun.* **8 (11)**, 535 (1987).
5. M. N. Chandrashekhara, D. Desai and M. Chanda, *Eur. Polym. J.*, **21(9)**, 933 (1985).
6. G. L. Collins, N. Lu and N. L. Yang, *ACS, Polym. Mat. Sci. Eng. Preprints*, **61**, 700 (1989).
7. P. S. Raman and V. Mahadevan, *Makromol. Chem.*, **178**, 1367 (1977).
8. K. Weissermel, E. Fischer, K. Gutweiler, H. D. Hermann and H. Cherdron, *Angew. Chem. Internat. Edit., Eng.* **6(6)**, 526 (1967)
9. L. Leese and M. W. Baumber, *Polymer*, **6(5)**, 269 (1965).
10. M. Kucera, E. Hladky and K. Majerova, *J. Polym. Sci., Polym. Symp.*, **16**, 257 (1966).
11. V. Jaacks and W. Kern, *Makromol. Chem.*, **62**, 1 (1963).
12. See reference 9 in "introduction".
13. M. Iguchi, *British Polym. J.*, **5**, 195 (1973).
14. W. Kern and V. Jaacks, *J. Polym. Sci.*, **48**, 399 (1960).

15. T. Miki, T. Higashimura, S. Okamura, *J. Polym. Sci.*, **A5**, 2997 (1967).
16. See reference 20 in "introduction".
17. See reference 4 in " introduction".
18. G. Wegner, et al., *Makromol. Chem.*, **181**, 1763 (1980)
19. C. S. Hsia Chen, *J. Polym. Sci., Polym. Chem. Ed.* **14**, 143 (1976).
20. Von K. H. Burg, H. D. Hermann and H. Rehling, *Makromol. Chem.*, **111**, 181 (1968).

Part 3

MICROSTRUCTURE ANALYSES FOR THE COPOLYMERS OF TRIOXANE AND OTHER CYCLIC ACETALS

3.1 Introduction

Cationic copolymerizations of trioxane with dioxolane and other cyclic acetals have been extensively studied (1 - 10). The resulting copolymers exhibit improved stability due to the stabilizing effect of the comonomer units in stopping stepwise elimination of formaldehyde.

The copolymerizations of trioxane with dioxolane and other cyclic acetals cannot be described by the usual Mayo-Lewis equations due to the following reasons: 1) cleavage of formaldehyde from cationic chain ends or protonated trioxane. The generated formaldehyde can react with trioxane and dioxolane giving tetraoxane and trioxepane, which in turn can participate in the copolymerization. Thus the copolymerization of trioxane and dioxolane is actually a five component copolymerization. 2) all the steps involved in the initiation and propagation are reversible and should be considered as equilibria. Due to these complications, a complete kinetic model to describe the copolymerization has not yet been available. However, the analyses of polymer chain microstructure can

provide significant information regarding the nature of propagation and depropagation processes.

One of the important features of copolymerization of cyclic acetals is a statistical redistribution of the monomer units during the copolymerizations. Thus, the copolymer final sequence is independent of the reactivity of the monomers and the rate of the propagation steps. For example, in copolymerizations of trioxane / dioxolane and trioxane / ethylene oxide, dioxolane and ethylene oxide are initially consumed much faster than trioxane because of their higher basicity. It has been found that ethylene oxide is nearly completely consumed before trioxane consumption starts (3). However, both dioxolane and ethylene oxide monomer units distribution in the final polymer is close to random placement. Further evidence for this redistribution is derived from the attempted preparation of a block copolymer through a sequential monomer addition method. However, an almost random copolymer of dioxolane / dioxepane was obtained through this method (11). Similar results were also observed in our present investigation for trioxane / dioxolane copolymer system.

The mechanism for the sequence redistribution, i.e., rearrangement of microstructure in copolymerization of cyclic acetals, was attributed to propagation $\rightleftharpoons$ depropagation and transacetalization. In 1982, Penczek and his coworkers attempted to prepare a block copolymer of

dioxolane / dioxepane by addition of dioxolane into living bifunctional poly-(dioxepane). An almost random copolymer resulted (11). They considered that less than 10% of the monomer is at equilibrium with a living polymer at the end of the first stage. This small amount of monomer may participate in copolymerization, but it should not play an important role in randomization during second stage of copolymerization. Transacetalization was believed to take place in the system. Since at no stage of reaction could pure block copolymer be isolated, they concluded that the rate of transacetalization had to be at least comparable to the rate of propagation.

Jaacks (12) studied the cationic copolymerization of trioxane and dioxolane in dichloroethane with SnCl_4 as initiator. He found that at first dioxolane was consumed much faster than trioxane and a soluble copolymer with over 50% dioxolane content was formed. After 50% conversion, a second type of copolymer began to form, which contained most of crystallized trioxane homopolymer (98%). As the conversion increased, soluble copolymer depolymerized into dioxolane and formaldehyde. Then, the dioxolane was incorporated gradually into crystalline polymer, leading to a crystalline copolymer with random distribution.

A study of the effect of conversion upon the microstructure of the copolymer of trioxane and dioxolane showed that the fraction of formal units in copolymer increased with conversion (13). Even after equilibrium

conversion had apparently been established the microstructure appeared to slowly rearrange to longer polyoxymethylene sequence. The author explained that this rearrangement resulted mainly from an inter-chain transacetalization reaction. It was also concluded that dioxolane is kinetically more reactive than trioxane.

In this aspect of the research work, we used ^1H and ^{13}C NMR to monitor the copolymerization processes for trioxane /dioxolane, tetraoxane/dioxolane and homopolymerization of trioxepane systems. NMR spectra give direct information about the change of triad and pentad sequences versus conversion. In order to obtain direct evidence for the sequence redistribution, copolymerization of trioxane / dioxolane through sequential monomer addition was also observed using both ^1H and ^{13}C NMR. The mole fraction of triad sequences based on ^1H NMR data was examined using the a Bernoullian random statistic model. From the change of these sequence fractions versus conversion and fundamental considerations, we attempted to develop a consistent mechanism to describe the redistribution of polymer sequences and the formation of cyclic compounds.

3.2 Experimental

Monomers trioxane (TOX) and dioxolane (DOL) were purified as described in "Part I" and "Part II". Tetraoxane (TEOX) was used without purification. The synthesis of

trioxepane (TOP) can be described as follows: About 9.0 g of paraformaldehyde was added into a flask which contained 27 ml DOL and 500 ml chloroform and one drop sulfuric acid was added as catalyst. The reaction mixture was refluxed overnight at 55°C, and then filtered to remove unreacted paraformaldehyde. About 2 g of K_2CO_3 was added into the filtrate to remove water and H_2SO_4 . After removal of K_2CO_3 by filtration, the solution was evaporated to remove chloroform solvent. The crude product was distilled from $LiAlH_4$. Two fractions were collected. The first fraction, DOL, was obtained at 38 torr and 28°C; the second fraction, TOP, was collected at 18 torr and 35 - 36°C. The purity of the final product, TOP, was over 99% based on NMR measurement; only a trace amount of TOX was left in the product.

The course of copolymerization was monitored by both ^1H and ^{13}C NMR using a procedure described in "Part 1". Forty FID's were collected for each spectrum using an automated pulse program at different reaction times as polymerization progressed.

3.3 ^1H NMR spectra of the copolymerization of dioxolane with trioxane

Observation of copolymerization processes for different TOX to DOL mole ratios provided important mechanistic information. Fig. 3-1 shows the ^1H NMR spectra accompanying

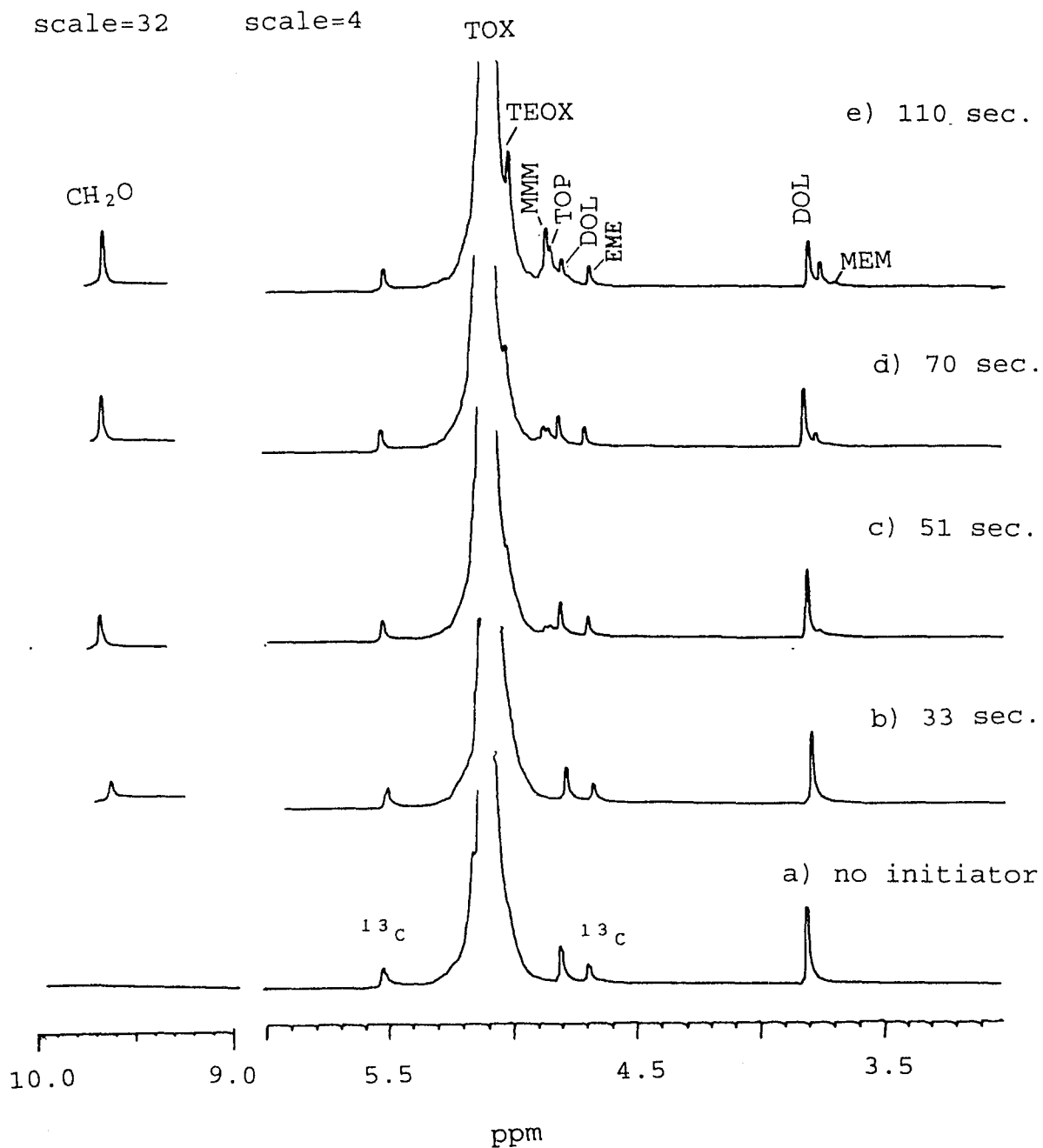


Fig.3-1 ¹H NMR spectra as a function of time for bulk copolymerization of trioxane with dioxolane initiated by BF₃OEt₂ at 63°C. [BF₃OEt₂]=0.042 mol%, TOX:DOL=13:1.0 (mole ratio).

the process of copolymerization of TOX with DOL (mole ratio of TOX / DOL = 13:1) at 63°C with 5.2×10^{-3} mol/l of BF_3OEt_2 as initiator. Only three peaks due to TOX and DOL monomers (5.11, 4.80, 3.81 ppm) are present (Fig. 3-1a) before the addition of initiator. Once BF_3OEt_2 was added into the reaction system, formaldehyde peaks appear (Fig. 3-1b) followed by the absorptions due to TEOX (5.02 ppm), TOP (4.85, 3.76 ppm) and polymer triad sequence MMM ($-\text{OCH}_2\text{OCH}_2\text{OCH}_2-$, 4.87 ppm) (Fig. 3-1c,d). The MEM ($-\text{OCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2-$, 3.69 ppm) and EME ($-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{CH}_2-$, 4.69 ppm) sequences due to DOL homopolymer are observed only after 110 seconds of reaction time (Fig. 3-1e). Even though DOL ($\text{PK}_b = 7.5$) is a stronger base than TOX ($\text{PK}_b = 10$) (14), the much higher initial concentration of TOX in this system leads to an appreciable concentration of protonated TOX which decomposes into formaldehyde (Fig. 3-1b). The reactive formaldehyde molecules can be inserted into protonated TOX and DOL to give TEOX and TOP (Fig. 3-1c). The concentration of generated formaldehyde and TEOX increased rapidly. The MMM sequence appears only when formaldehyde and TEOX are present close to their steady state concentrations. On the other hand, most of protonated DOL reacts with formaldehyde to give TOP at early stage, i.e., the insertion of formaldehyde into protonated DOL is favored over propagation of protonated DOL when TOP concentration is low. DOL homopolymer sequences, MEM and EME, are not found until the insertion reactions reache

their steady states (Fig. 3-1e).

When the mole ratio of TOX / DOL is decreased to 2:1 (Fig. 3-2), the absorption due to formaldehyde and TOP appear immediately after addition of initiator (Fig. 3-2b). Even as the concentrations of formaldehyde and TOP increase, none of the polymer sequences are observed (Fig. 3-2c). This strongly suggests that the process of forming long growing polymer chain first and then back-biting to give cyclic compound is not likely. Unlike the system with high TOX / DOL mole ratio, polymer sequences MEM and EME are found (fig. 3-2d) before MMM sequence which only begins to grow when formaldehyde and TEOX reach their steady state concentrations (Fig. 3-2e). In general, DOL is incorporated into polymer chain prior to TOX due to its higher basicity. When both DOL and TOX concentrations in monomer feed is about the same, more protonated DOL will be generated. The insertion of formaldehyde to DOL is thus favored. As a result, more formaldehyde will be consumed. Here DOL acts to consume formaldehyde. The slow increase of formaldehyde leads to the delayed appearance of MMM sequence.

This suggestion can be supported by the experiment with further reduction of TOX / DOL mole ratio to 0.3:1 (Fig. 3-3). In this system, the initiator protonated mostly DOL which has a higher concentration and basicity. In other words, protonated TOX is at a much lower concentration and hence formaldehyde cannot be generated rapidly at the early stage. Because of the lower formaldehyde concentration,

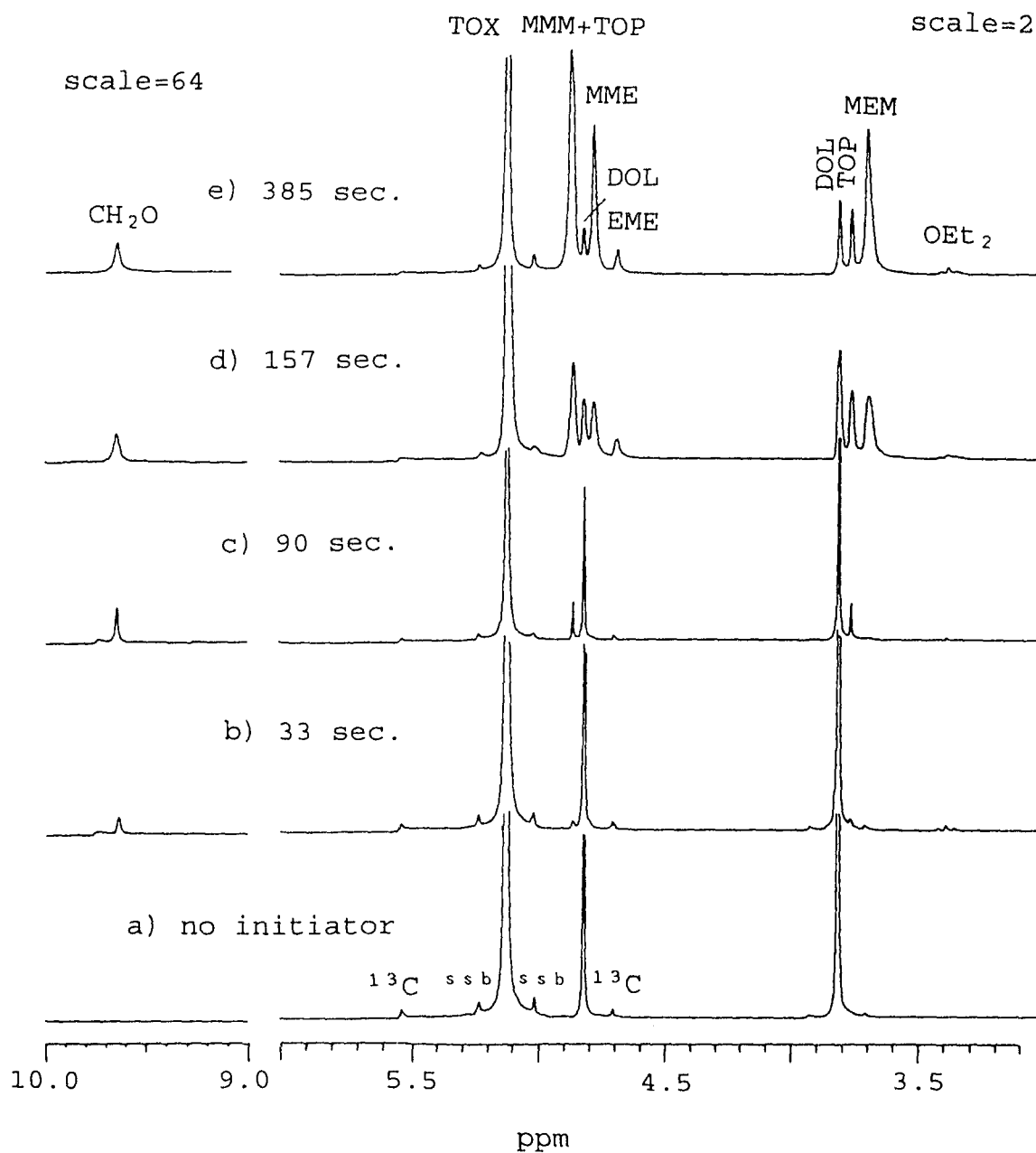


Fig.3-2 ¹H NMR spectra as a function of time for bulk copolymerization of trioxane with dioxolane initiated by BF₃OEt₂ at 63°C. [BF₃OEt₂]=0.028 mol%, TOX:DOL=2.0:1.0 (mole ratio).

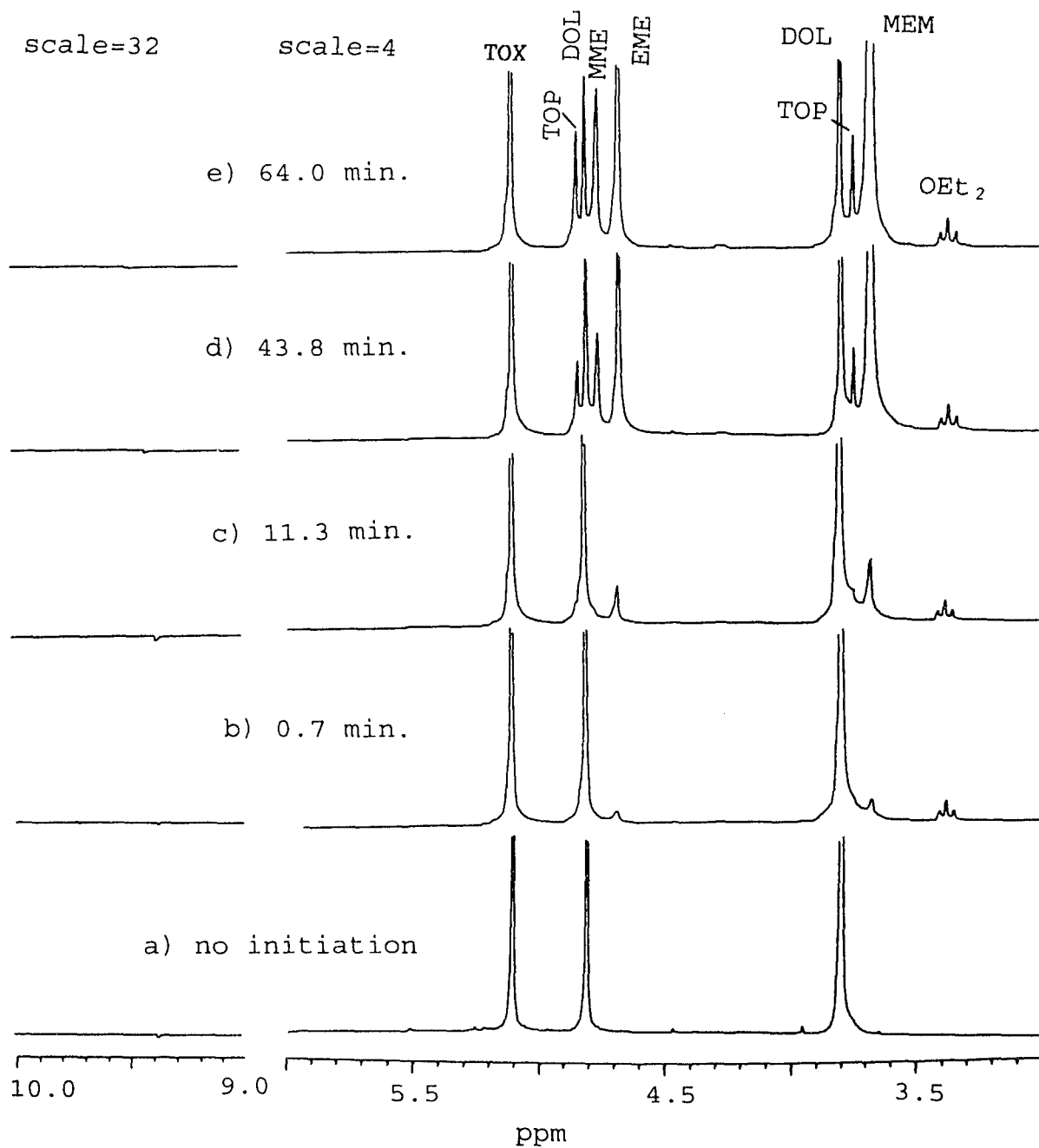


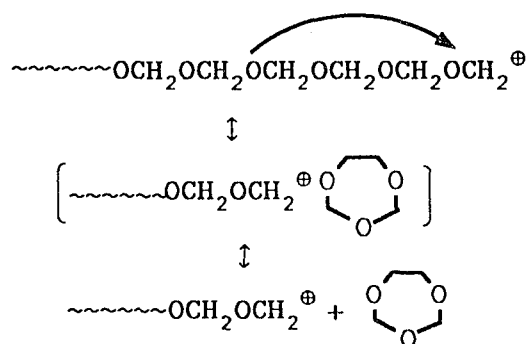
Fig.3-3 ¹H NMR spectra as a function of time for bulk copolymerization of trioxane with dioxolane initiated by BF₃OEt₂ at 63°C. [BF₃OEt₂]=0.105 mol%, TOX:DOL=0.3:1.0 (mole ratio).

protonated DOL reaction with formaldehyde to give TOP was suppressed, and reaction with another DOL monomer to give MEM and EME sequences becomes favored (Fig. 3-3b,c). TOP and copolymer sequence MME increase rapidly between 11.3 and 43.8 minutes (Fig. 3-3d). But formaldehyde is still undetectable probably because it is consumed immediately in the insertion reaction once it is generated. The high concentration of protonated DOL makes free formaldehyde unavailable in the system. Hence, no TEOX and MMM sequence are observed even after one hour of reaction time (Fig. 3-3e).

In summary, in homopolymerization of TOX, "induction period" terminates when crystallized MMM segments form. In copolymerization with DOL, however, the ethylene group interrupts crystal registry; hence, the soluble MMM sequence remains in solution longer. Increasing DOL concentration extends the "induction period" because formaldehyde is consumed by DOL in the cyclic acetals generation, leading to delay in generation of MMM sequence. This result provides further evidence that rapid propagation of TOX into MMM sequence will not occur until the system builds up the necessary concentration of formaldehyde.

Formation of TOP is always favored over propagation when formaldehyde is initially present in copolymerization system. Formal back-biting involves the intramolecular reaction of the linear active site with its own chain, and

can actually be considered as a depropagation process through the equilibrium between the alkoxycarbenium and oxonium (see reaction scheme I). TOX cannot be directly



(Reaction Scheme I)

incorporated into polymer chain before formaldehyde and TEOX reach certain concentration levels. Hence, the formation of TEOX and TOP in the copolymer system is not likely through the formation of polymer chains first, and then the depropagation of polymer chain ends to give these cyclic compounds. Instead, the formation of TEOX and TOP is most likely due to a process that is kinetically equivalent to direct insertion of formaldehyde into TOX and DOL. Experimental results also support this contention: 1) our NMR spectra indicate that significant levels of cyclic acetals such as TEOX and TOP are formed in homo- and copolymerization before polymeric sequences can be detected. In the copolymerization of TOX and ethylene oxide, DOL is also reported to be initially generated (3). 2) no TOP or other small cyclic compounds were found in homopolymerization of DOL when no formaldehyde was generated in this polymerization system.

3.4 Microstructure analysis and ^{13}C NMR spectra of the copolymerization of dioxolane with trioxane

Peak area of the signals in ^1H NMR spectra during the course of polymerization was obtained to determine the change of the concentration of the corresponding polymer sequences and unreacted monomers. The quantitative measurement of the overlapping peaks can be resolved using curve fitting. A combination of Lorentzian and Gaussian functions was chosen as lineshape for the fitting as illustrated in Fig. 3-4. NMR spectra of several standard samples which contain known amounts of TOX, DOL, TEOX and TOP showed that the integral accuracy after curve fitting is within 5% for most of the peaks.

The mole fraction of various triad sequences $F\{ \}$ based on total number mole of all the triads is given by following relations

$$F(\text{MMM}) = k S_{\text{MMM}} \quad (1)$$

$$F(\text{MME}) = k S_{\text{MME}} \quad (2)$$

$$F(\text{EME}) = k S_{\text{EME}} \quad (3)$$

$$F(\text{MEM}) = k/2 S_{\text{MEM}} \quad (4)$$

$$k (S_{\text{MMM}} + S_{\text{MME}} + S_{\text{EME}} + S_{\text{MEM}} / 2) = 1 \quad (5)$$

Where S_{MMM} , S_{MME} , S_{EME} and S_{MEM} are the corresponding peak areas, and k is a normalization constant.

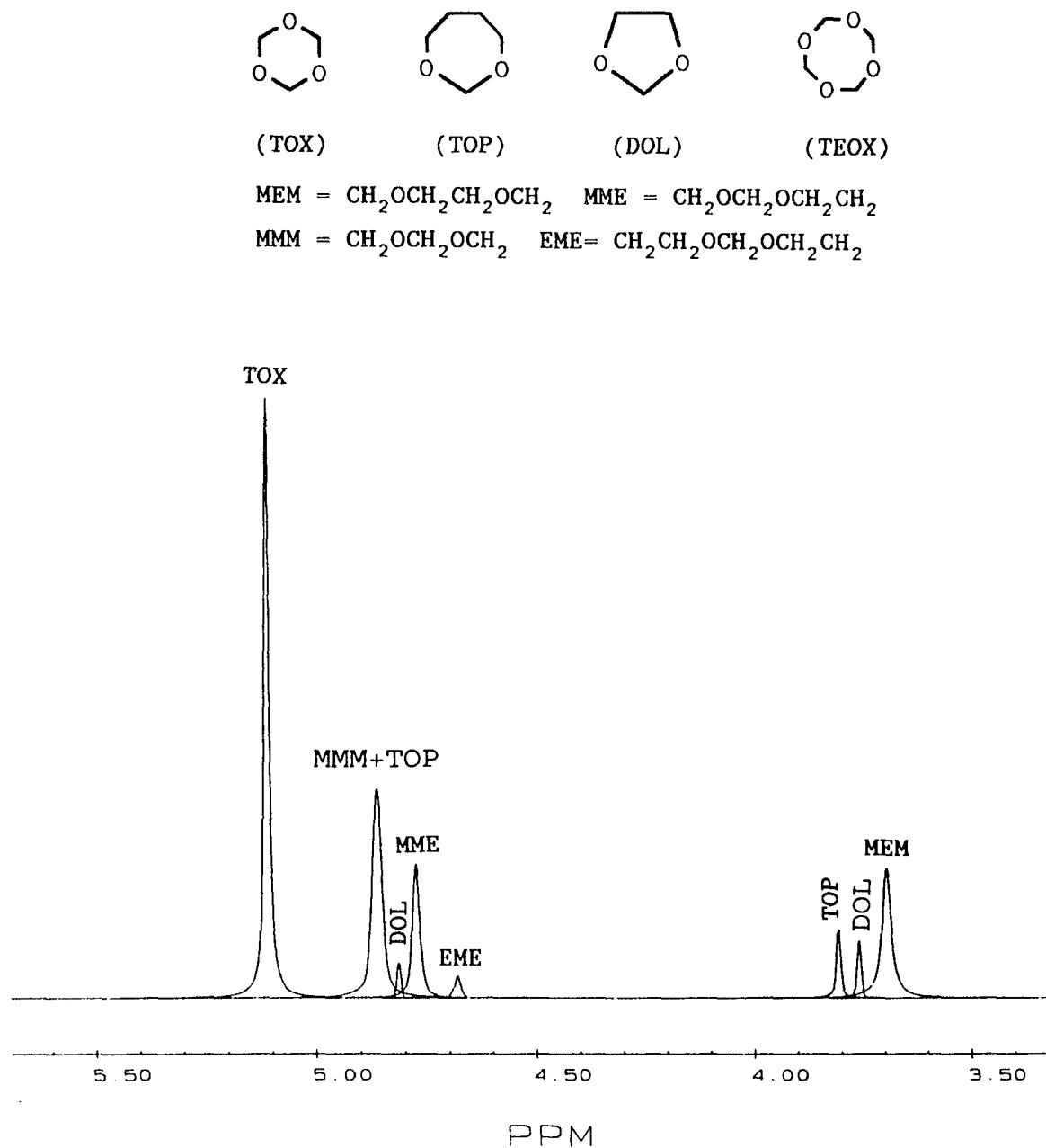


Fig.3-4 A illustration of curve fitting of the overlapping peaks in copolymerization of trioxane / dioxolane initiated by BF_3OEt_2 at 63°C . $[\text{BF}_3\text{OEt}_2]=0.030$ mol%, TOX:DOL=2.0:1.0 (mole ratio).

The number average sequence length of formal and ethylene oxide units, denoted by L_M and L_E can be expressed in terms of simple measurable sequences (15)

$$L_M = \{F(MMM) + F(MME) + F(EME)\} / \{F(MME)/2 + F(EME)\} \quad (6)$$

$$L_E = \{F(MEM) + F(EEM) + F(EEE)\} / \{F(EEM) + F(MEM)\} \quad (7)$$

No signals corresponding to MEE and EEE sequences can be detected for both ^1H and ^{13}C NMR spectra. Thus the sequence length, L_E , is always equal to one for the copolymer. We have focused on the change of average sequence length L_M during the course of copolymerization.

A Bernoullian statistic model describes a perfectly random distribution of two or more types of monomer units in the copolymer chain. The copolymer microstructure was examined for Bernoullian behavior in order to measure its departure from random statistics. According to Bernoullian statistic model, the triad sequences of comonomer units $P\{\}$ can be calculated based on conditional probabilities of $P(M)$ and $P(E)$

$$P(MMM) = [P(M)]^3 \quad (8)$$

$$P(MME) = 2[P(M)]^2[P(E)] \quad (9)$$

$$P(EME) = [P(M)][P(E)]^2 \quad (10)$$

$$P(MEM) = [P(M)]^2[P(E)] \quad (11)$$

Here the conditional probabilities $P(M)$ and $P(E)$

represent the probabilities of finding either M and E units within the polymer chains, therefore they correspond to the M and E mole fractions observed for the copolymers, i.e.,

$$P(M) = F(MMM) + F(MME) + F(EME) \quad (12)$$

$$P(E) = F(MEM) \quad (13)$$

The examination was performed through the comparison of complete sets of experimentally observed comonomer mole fraction $F\{ \}$ with those calculated from individual unit mole fraction $P\{ \}$. The change of average sequence length of L_M together with the change of mole fractions of triad sequences during the copolymerization of TOX / DOL with two different monomer feed ratios are plotted against conversion (Fig. 3-5). In these figures, symbols and lines stand for the mole fraction of triad sequences observed from NMR data $F\{ \}$ and calculated from Bernoullian model $P\{ \}$ respectively. Fig.3-6 presents quantitatively the concentration profile of various species for the same copolymerization systems. All the concentrations are expressed in terms of mole %, i.e., the number moles of the species divided by the total number moles of various species in the copolymer mixture.

Fig. 3-5a and Fig. 3-6a correspond to the copolymer system with 1:4 of TOX / DOL monomer feed ratio. Before 15 minutes reaction time (i.e., 10% polymer conversion), the rate of consumption of DOL is about 25 times faster than

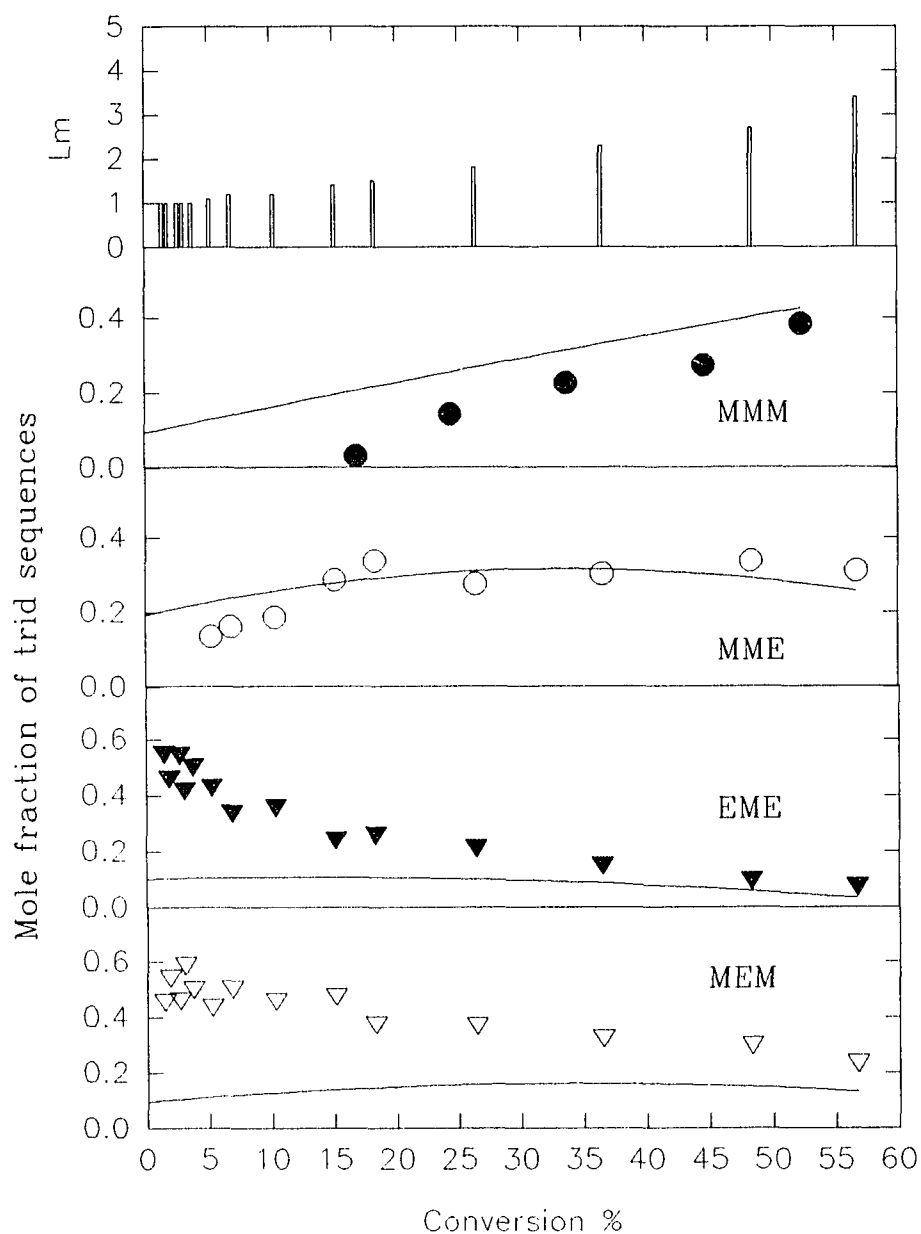


Fig.3-5a The average sequence length of formal units and mole fraction of triad sequences versus conversion for trioxane / dioxolane copolymerization at 63°C. $[BF_3OEt_2]=0.028$ mol/l, TOX:DOL=1.4:1 (mole ratio). Symbols stand for NMR observed data $F\{\}$ and lines are calculated from Bernoullian statistical model $P\{\}$.

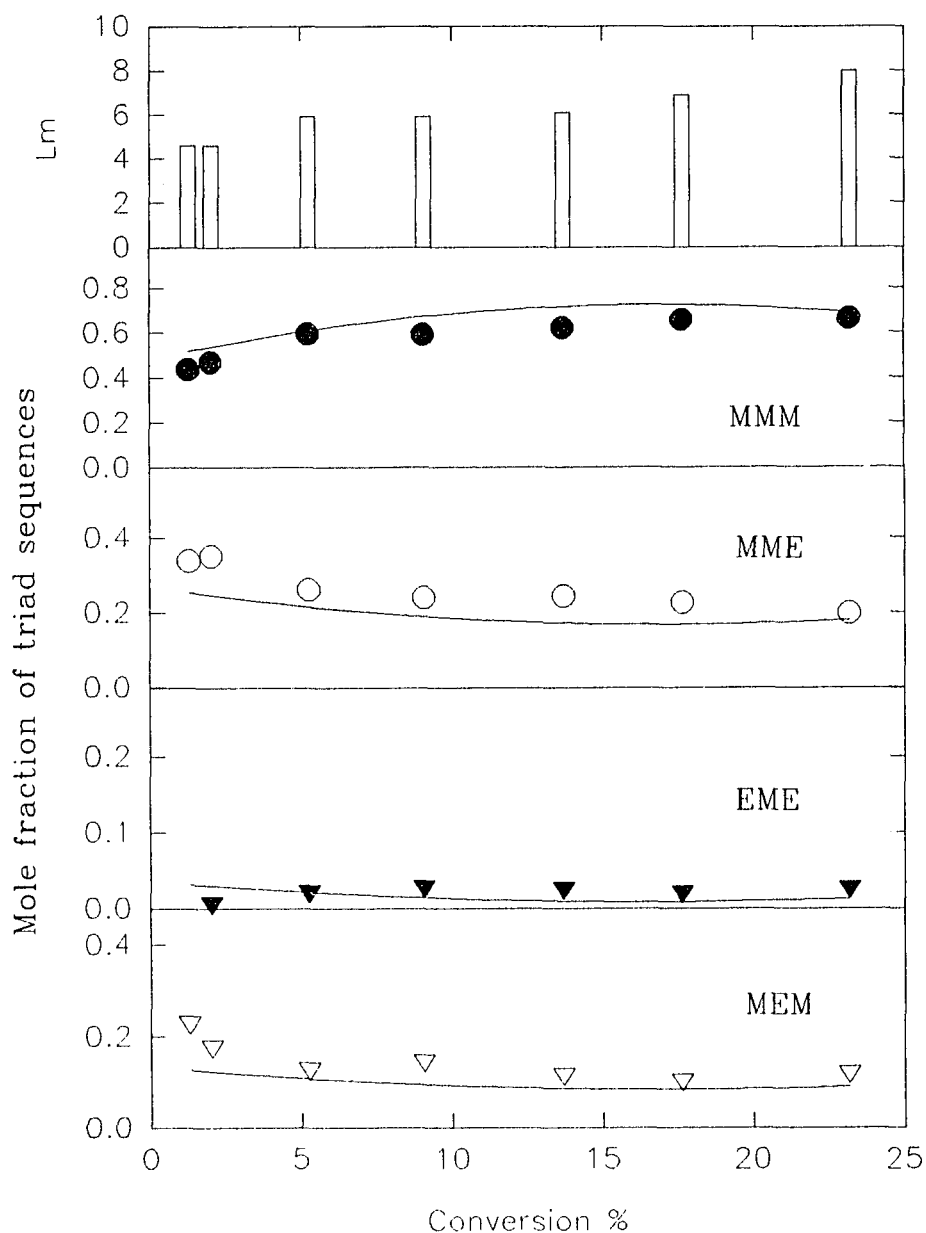


Fig. 3-5b The average sequence length of formal units and mole fraction of triad sequences versus conversion for trioxane / dioxolane copolymerization at 63°C. $[\text{BF}_3\text{OEt}_2]=0.006$ mol%, TOX:DOL=6.3:1 (mole ratio). Symbols stand for NMR observed data $F\{\}$ and lines are calculated from Bernoullian statistical model $P\{\}$.

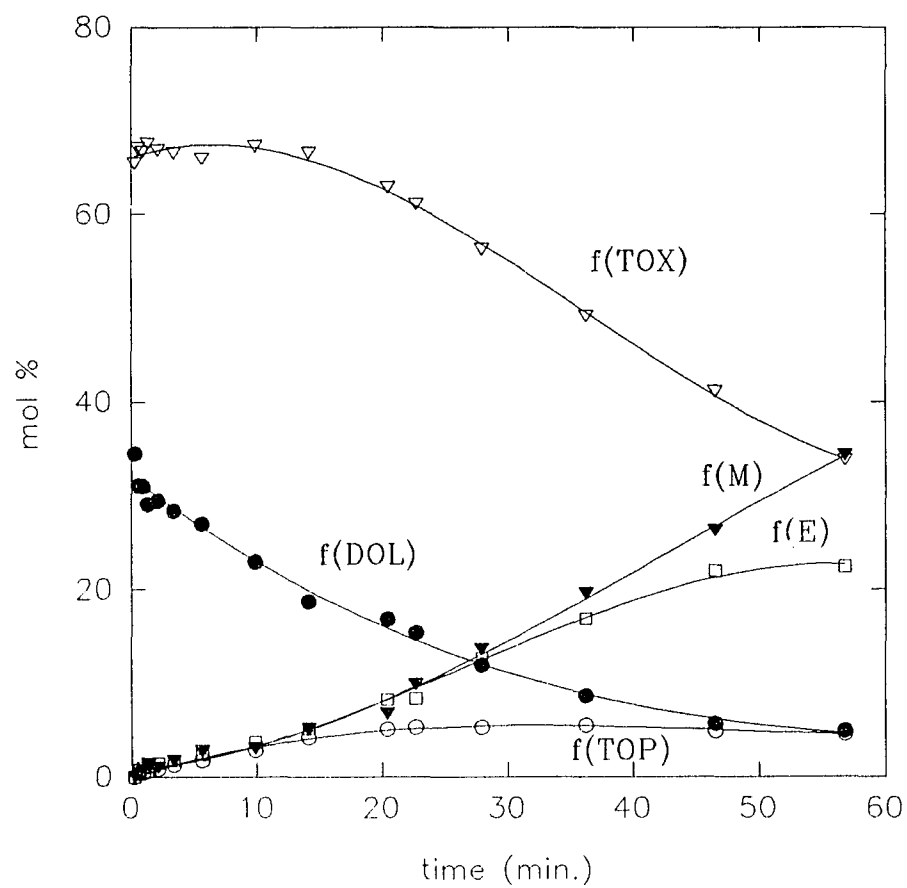


Fig. 3-6a Kinetic curves of each component for trioxane / dioxolane copolymerization at 63 C. $[\text{BF}_3\text{OEt}_2]=0.028$ mol%. TOX:DOL=1.4:1.0 (mole ratio).

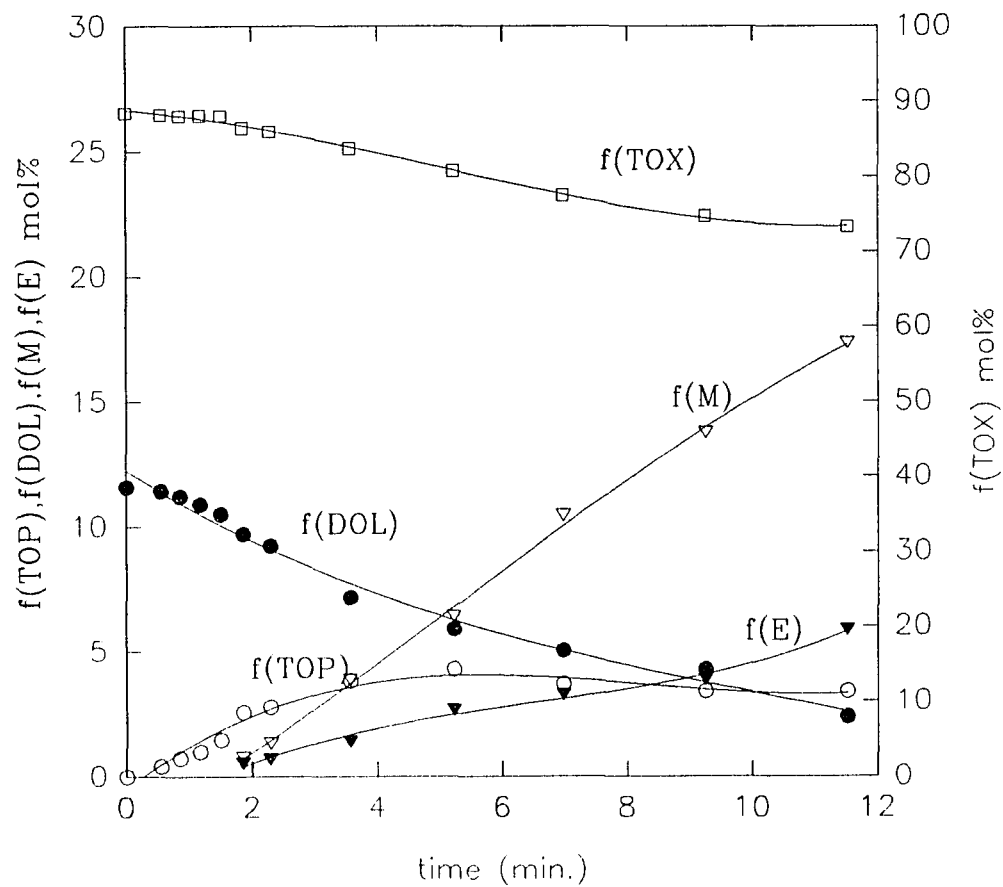


Fig. 3-6b Kinetic curves of each component for trioxane / dioxolane copolymerization at 63°C. $[\text{BF}_3\text{OEt}_2] = 0.006$ mol%. TOX:DOL=6.3:1 (mole ratio).

that of TOX. The copolymer composition consists almost exclusively of DOL homopolymer sequences (MEM and EME). The sequence length L_M is close to one indicating an alternating arrangement of M and E units in the polymer chain. The sum of the increases in TOP and polymer sequences is about the same as the decrease in DOL. Hence, apparently the consumption of DOL leads to the formation of TOP and polymer sequences of MEM and EME. TOX has not been incorporated into copolymer chains and small amount of TOX was consumed to give formaldehyde. The rate of generation of TOP is as fast as the rate of formation of polymer chain. TOP concentration is more than 4.0 mol% at 15 minutes of reaction time. Thus the small amount of MME sequence is most likely due to the incorporation of TOP into the polymer chain. After 15 minutes of polymerization time (i.e., above 10% conversion), TOX monomer starts to decrease dramatically and a rapid increase in formal units takes place. The rate of consumption of TOX is about twice as fast as that of DOL. Furthermore it is about the same magnitude as the rate of generation of formal units. This implies that formal units come mainly from incorporation of TOX into the copolymer chain. The concentration of TOP stays at a constant value at this stage, suggesting that an steady state concentration has been built up between the consumption and generation of TOP.

The microstructure of the copolymer changes gradually from an alternating nature to longer polyoxymethylene

sequence, i.e., an increase in triad MMM sequence. The average sequence length L_M reached greater than three units within the time of observation. A comparison of the mole fraction of triad sequences obtained from NMR data and of that calculated from the Bernoullian model indicates a decrease in the departure of copolymer microstructure from the Bernoullian behavior as copolymerization proceeds, i.e., the microstructure of copolymer tends toward random placement as conversion increases. At 55% conversion, the copolymer chains contain about 40% triad MMM unit, 30% triad MME sequence and 30% of DOL homopolymer MEM and EME sequences. An almost random distribution of M and E units among the polymer chain was achieved.

Fig.3-5b and Fig.3-6b represent the change of microstructure and kinetic profiles vs. conversion for the copolymerization with 6.3:1 of TOX/DOL monomer feed ratio. Before 2 minutes of reaction (about 5% conversion), no polymer sequences but only TOP was generated. The rate of monomer DOL consumption was three times faster than the rate of monomer TOX consumption and was about the same as the increase in TOP. So it is clear that the consumption of both monomers DOL and TOX are used in the formation of TOP. Polymer sequences begin to form at about 2 minutes of reaction time. The kinetic profiles showed a similar relation to the TOX/DOL copolymerization with a 1.4:1 monomer feed ratio at this stage. That is, rate of consumption of TOX is also about twice as fast as that of

DOL, and it is about the same magnitude as the rate of generation of formal units. Furthermore, the concentration of TOP stays at a constant value. However, the change of microstructure vs. conversion displays a significant difference compared with the copolymerization system with 1.4:1 of TOX/DOL monomer feed ratio. The homopolymer of DOL is no longer generated initially. Instead, the copolymer chains consist of almost 50% triad MMM sequence. The initial microstructure is only slightly different from that expected by random statistics and is slightly richer in MME and MEM sequences. The sequence distribution of triad units shows a perfect fit to the Bernoullian statistic model only at 5% conversion. After 5% conversion, the microstructure of copolymer does not show significant change within the time of observation. The slight increase in average sequence length of L_M probably is a result of a slight increase in mole fraction of formal units versus conversion.

Combining the results from both kinetic curves and the microstructure analysis, one can conclude that DOL monomer is kinetically more reactive than TOX monomer. Hence, if the initial concentrations of TOX and DOL are about the same, copolymer composition should be richer in DOL monomer unit initially, i.e., the sequence distribution of the initially formed copolymer is far from random statistics. As copolymerization proceeds, TOX begins to incorporate into copolymer chains. But TOX does not show any tendency

to form a block copolymer with the first-formed DOL polymer. Instead, the formal and ethylene oxide units tend to distribute along the copolymer chain statistically as conversion increases. Increasing TOX in monomer feed shortens the time for the randomization process to occur. An almost random distribution and fair amount of formal unit in the copolymer chains can be achieved at the beginning of conversion for systems with high TOX feed. This is understandable because the copolymer composition is not only dependent on its monomer reactivity but also on the initial concentration in the monomer feed.

^{13}C NMR spectra with pentad sequences resolved were used to monitor TOX/DOL copolymerization processes to give more detail information about the microstructure of the copolymer (Fig. 3-7). Our assignment of the peaks based on Heteronuclear Shift Correlated 2D NMR spectrum of the copolymerization mixture (Fig. 3-8) and theoretical calculation (16) support literature results (17). From Fig. 3-8, peaks (3), (2,13), (4,10) are related to monomers TOX, DOL and generated TOP respectively. The peaks located at 88 - 95 ppm correspond to the six possible M- centered pentads without E-E connection. They are found in three groups: signals(1), (5,6) and (7,8,9) corresponding to the three triad centered EME, EMM and MMM, signals 12 and 13 are related to the E-centered pentads MMEMM and EMEME.

The TOX / DOL feed ratio is 1.3:1 in Fig. 3-7. Again, the formation of TOP is the first event after addition of

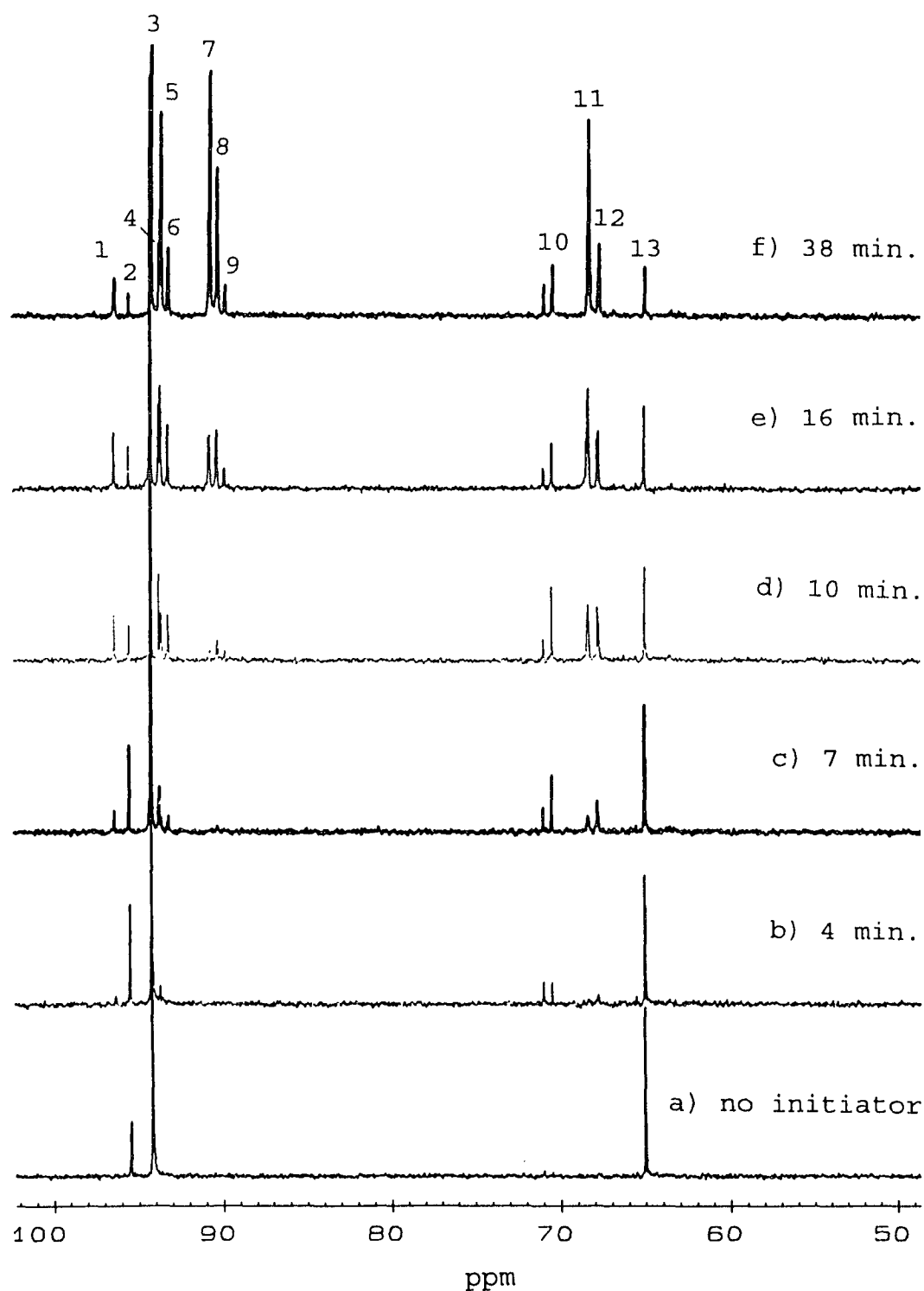


Fig.3-7 ^{13}C NMR spectra as a function of time for bulk trioxane / dioxolane copolymerization initiated by BF_3OEt_2 at 63°C . $[\text{BF}_3\text{OEt}_2] = 0.035 \text{ mol\%}$, $\text{TOX:DOL} = 1.3:1.0$ (mole ratio). (1) = MEMEM, (2,13) = DOL (3) = TOX, (4,10) = TOP, (5) = MMMEM, (6) = EMMEM, (7) = MMMMM (8) = EMMMM, (9) = EMMME, (11) = MMEMM, (12) = EMEME.

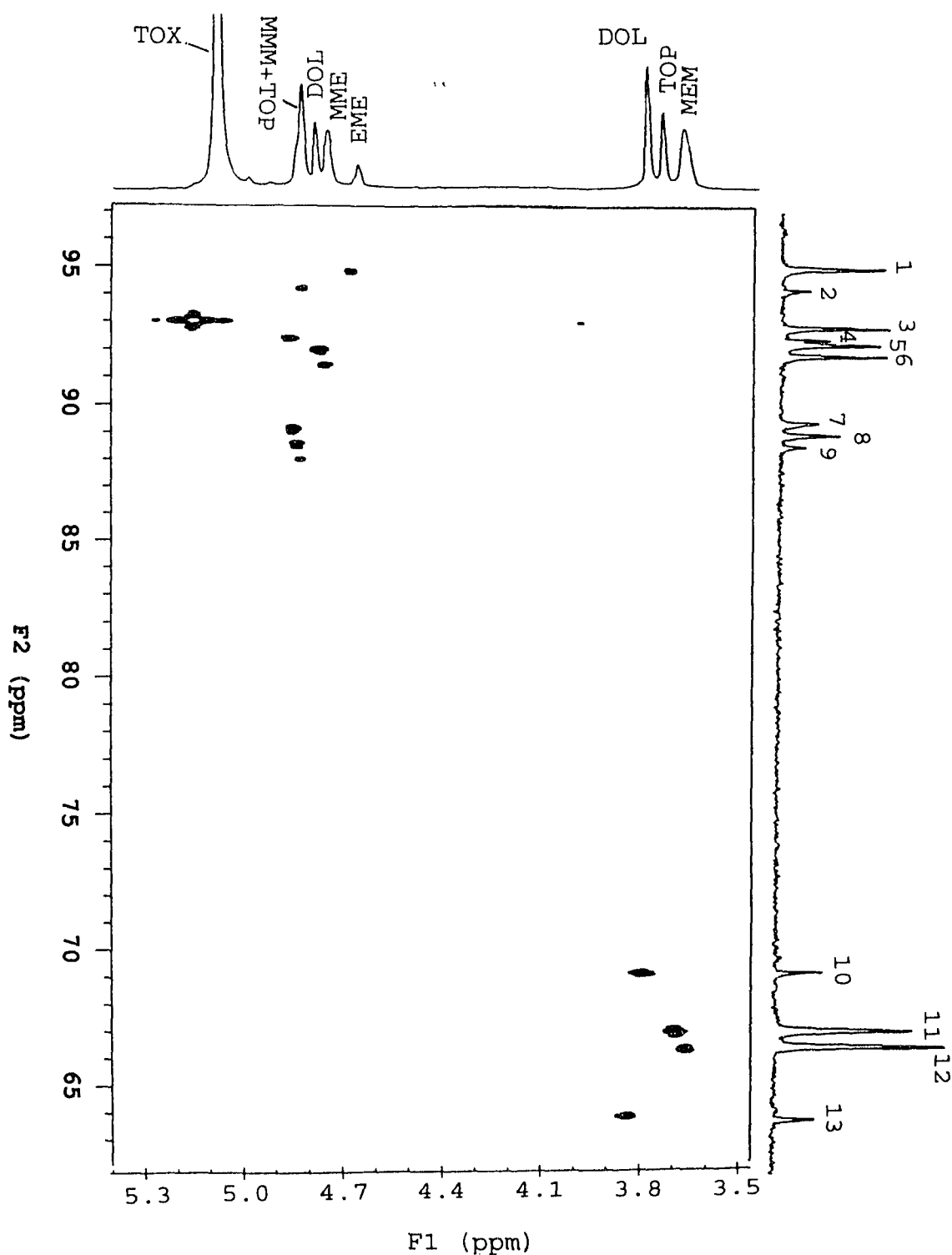


Fig.3-8 Heteronuclear Shift Correlated 2D NMR spectrum for bulk TOX/DOL copolymer mixture in DMSO solvent. $[\text{BF}_3\text{OEt}_2]=0.048$ mol%, TOX:DOL=1.8:1.0 (mole ratio). (1)=MEMEM, (2, 13)=DOL, (3)=TOX, (4, 10)=TOP, (5)=MMMEM, (6)=EMMEM, (7)=MMMMM, (8)=EMMMM, (9)=EMMME, (11)=MMEMM, (12)=EMEME.

initiator (Fig. 3-7b), followed by the appearance of the signals of MEMEM, EMMEM, MMEMM and EMEME, indicating that DOL and the generated TOP are incorporated into copolymer chain. Longer polyoxymethylene (i.e., $(\text{CH}_2\text{O})_n$, $n > 3$) cannot be detected probably because TOX acts only as a source of formaldehyde at this stage (Fig. 3-7c). As conversion increases, TOX begins to be incorporated into polymer chain, ^{13}C NMR (Fig. 3-7d) shows that the signals for longer polyoxymethylene sequences (MMMMM, EMMMM) grow rapidly.

Based on the average sequence length, L_M , calculated from ^1H NMR spectra, one can conclude that the microstructure of copolymer continues to show longer polyoxymethylene sequence as more and more TOX is consumed. ^{13}C NMR spectra for the copolymerization process show clearly that the sequences with two successive formal units appear first followed by the ones with three, four and five formal units. The longer the polymerization time, the larger the signals for longer polyoxymethylene units (MMMMM and MMMME).

From the statistical calculation, we have concluded that microstructure of copolymer tends toward random distribution gradually from an alternating arrangement. In addition, no block copolymer was found at any stage of copolymerization. ^{13}C NMR spectra give consistent observations, since the increase in polyoxymethylene sequence length is gradual and the signals of copolymer

units (MMMM, EMMM) are present in a significant proportion.

3.5 Copolymerization of dioxolane with trioxane through sequential monomer addition

In order to gain more information about the randomization process in copolymerization of cyclic acetals, we attempted to synthesize a block copolymer (TOX - block - DOL) through sequential monomer addition. The copolymerization can be divided into two stages: the first stage is defined as the formation of homopolymer of DOL; and the second stage starts from the addition of the second monomer, TOX. The process of the sequence redistribution for the second stage was monitored using ^{13}C NMR spectra (Fig. 3-9). Homopolymerization of DOL was first carried out at 63°C ; after 30 minute reaction time, the conversion reached about 75% (Fig. 3-9b), and monomer TOX was added into the polymerization mixture. In addition to the five peaks due to TOX monomer (94.1 ppm), DOL monomer (95.5 ppm, 65.5 ppm) and homopolymer of DOL (MEMEM, 96.5 ppm, MEMEM, 67.8 ppm), the peak due to TOP starts to emerge (Fig. 3-9c). If block copolymer was formed, the NMR spectra should have consisted of larger signals of MMMMM and MMMME due to the long polyoxymethylene block and signals of MEMEM and EMEME due to the DOL homopolymer block. Instead, we observed an increase in the signals for TOP followed by

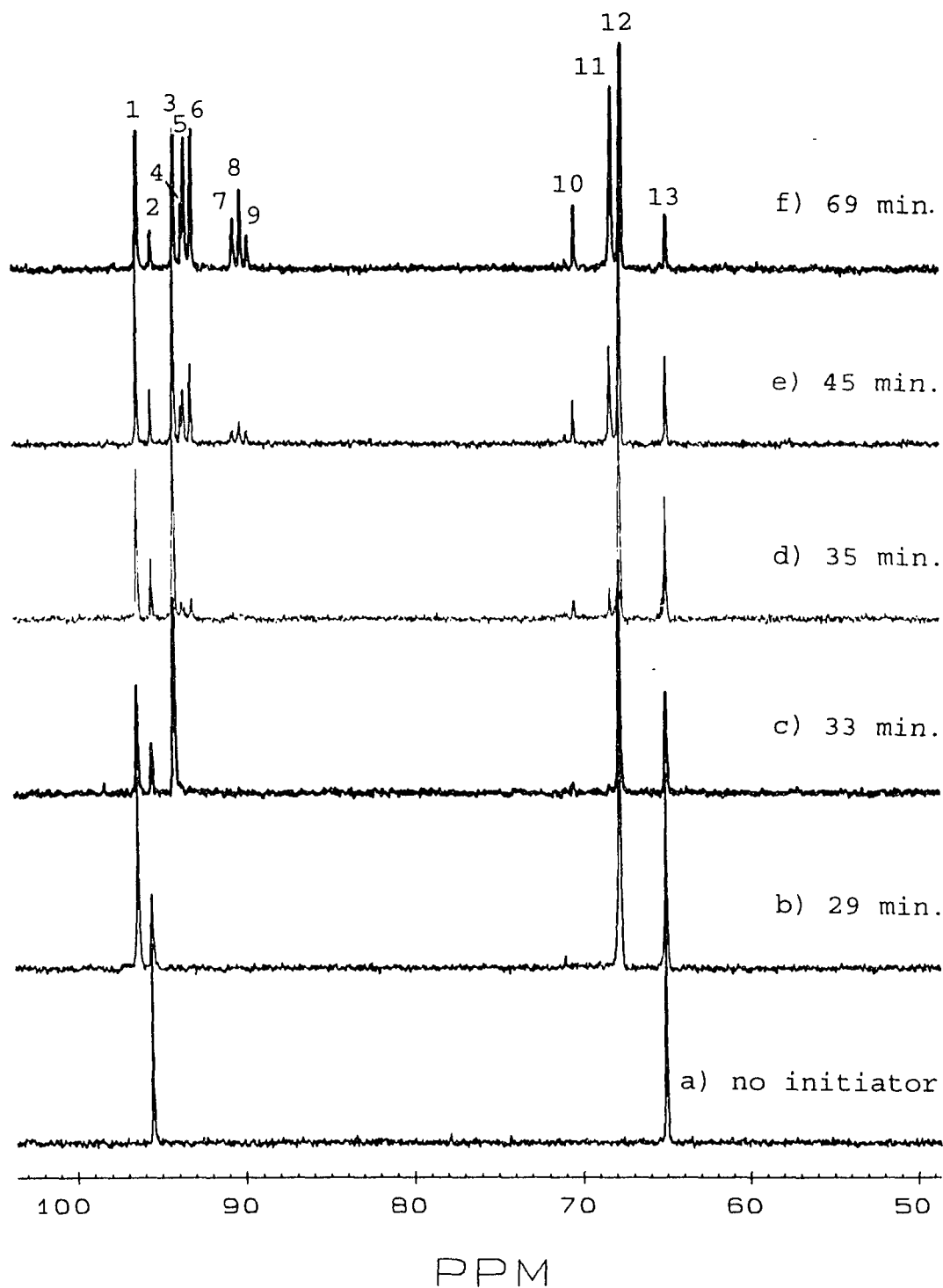


Fig.3-9 ^{13}C NMR spectra for bulk copolymerization of TOX/DOL through sequential monomer addition at 63°C .
 $[\text{BF}_3\text{OEt}_2]=0.078$ mol%, TOX:DOL=0.5:1.0 (mole ratio).
 (1)=MEMEM, (2,13)=DOL, (3)=TOX, (4,10)=TOP,
 (5)=MMMME, (6)=EMMEM, (7)=MMMMM, (8)=EMMMM,
 (9)=EMMME, (11)=MMEEM, (12)=EMEEM.

copolymer sequences with two successive formal units EMMEM and MMEMM (Fig. 3-9d). This implies that at this point TOX has not been incorporated into polymer chain directly, but decomposed into formaldehyde, which reacted with DOL giving TOP. The copolymer sequences EMMEM and MMEMM are most likely from the incorporation of TOP into the polymer chain. As polymerization time increases, TOP and copolymer sequences continue to increase and the signals for longer formal units MMMMM, EMMMMM and EMMME begin to appear, indicating TOX monomer starts to play a more direct role (Fig. 3-9e).

Fig. 3-10 presents the average sequence length of formal units, mole fraction of triad sequences and mole % of TOP (based on total number mole of each component in polymerization mixture) versus reaction time for the same copolymerization system. Before addition of TOX (about 30 minutes), polymer chains contain only homopolymer of DOL sequences MEM and EME. As the second monomer TOX was added into the homopolymerization mixture, TOP increases rapidly to about 3 mol% accompanied by an increase in MME sequence. The change of microstructure of copolymer versus conversion displays a similar tendency to the system of TOX / DOL copolymerization. An almost random statistical arrangement of M and E units along the copolymer chain was found within the time observed.

Combining ^{13}C NMR observations and the result from microstructure analysis, mechanistic schemes for the

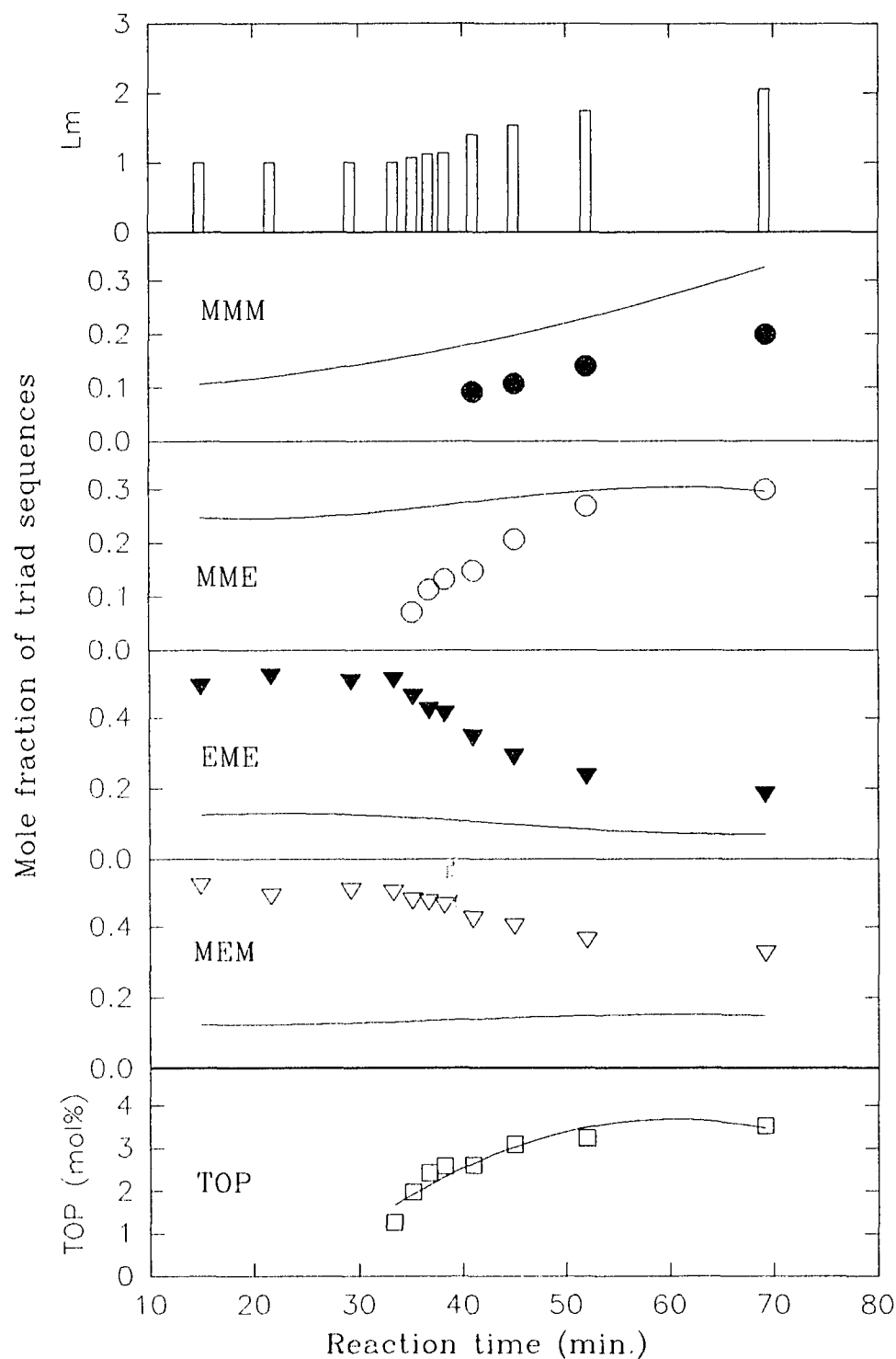
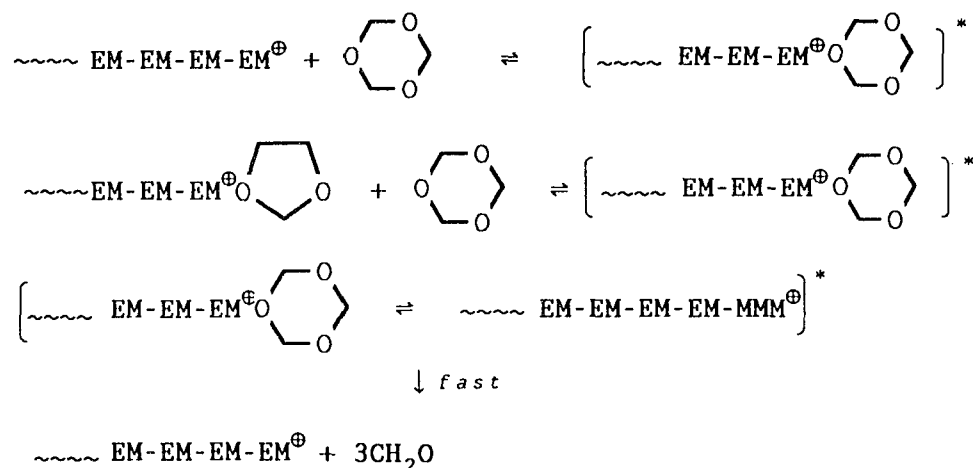


Fig. 3-10 Average sequence length of formal units, mole fraction of triad sequences and TOP versus time for TOX/DOL copolymerization through sequential monomer addition at 63°C. $[\text{BF}_3\text{OEt}_2] = 0.078\text{mol}\%$; TOX:DOL = 0.5:1 (mole ratio). Symbols stand for NMR observed data and lines are calculated from Bernoullian statistical model.

sequence redistribution in copolymerization of TOX / DOL through sequential monomer addition were suggested as follows:

1) A block copolymer is not formed when TOX was added into homopolymerization mixture of DOL. The reason is similar to the case of TOX homopolymerization, that is, the propagation of TOX into polyoxymethylene sequence cannot proceed before formaldehyde reaches its steady state concentration. Thus TOX does not directly propagate from the living polymer chain ends formed at first stage, instead, it decomposes into formaldehyde (reaction scheme II).

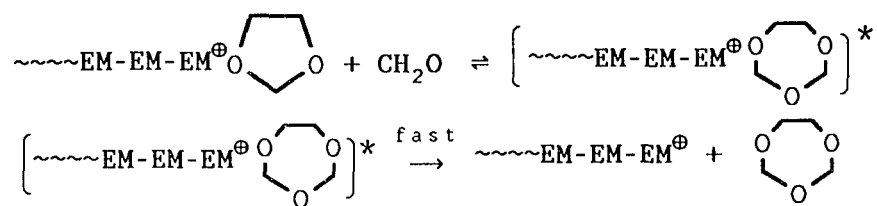


* When formaldehyde concentration is zero the forward reaction is much favor.

(Reaction scheme II)

2) The insertion of formaldehyde into the DOL leads to the generation of TOP and the signal for TOP begins to emerge (reaction scheme III, Fig. 3-9c).

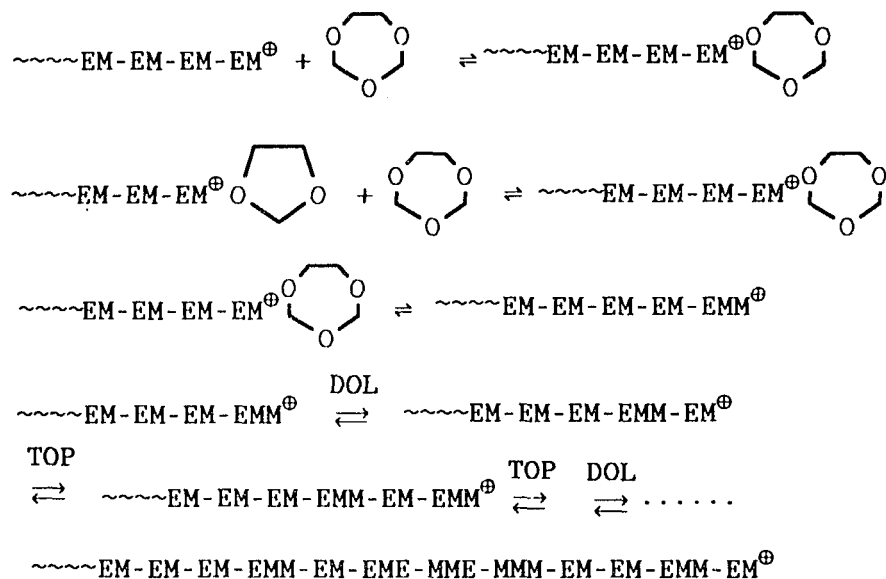
3) Once TOP concentration increases to a certain level,



* When trioxepane concentration is zero the forward reaction is much favor.

(Reaction scheme III)

it starts to participate in copolymerization together with the monomer DOL left at first stage. Thus polymer chains no longer consist of only an alternating arrangement of M and E units. The signals corresponding to two successive formal units such as EMMEM and MMEMM begin to emerge (reaction scheme IV, Fig. 3-9d).

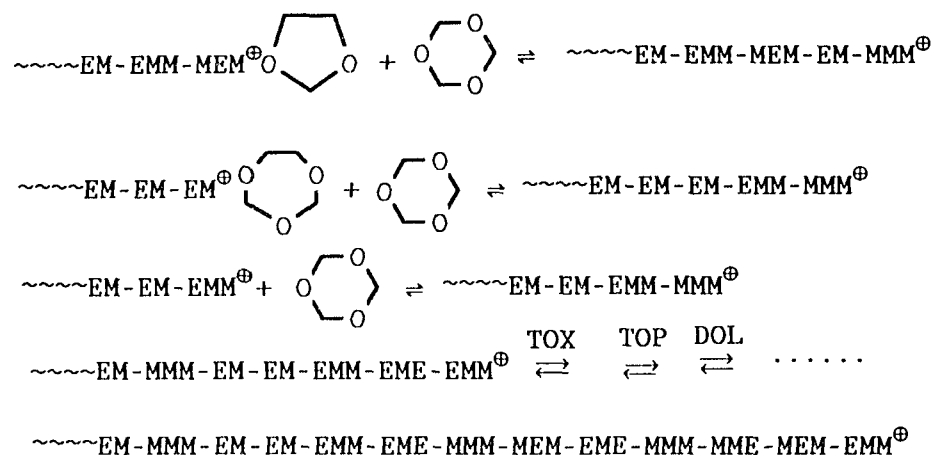


(Reaction scheme IV)

4) As TOP continues to be incorporated into polymer chain, a steady state is established between its consumption and its formation. The formation of TOP (at

reaction scheme III) is accompanied by depolymerization of poly(DOL) formed in the first stage. Fig. 3-10 shows that TOP concentration stays at a constant value and mole fractions of DOL polymer sequences MEM and EME decrease. This process occurs repeatedly so that the E and M units of the originally formed DOL polymer are redistributed.

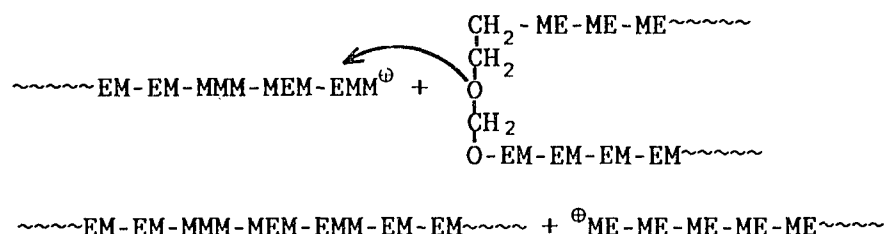
5) As copolymerization continues, more formaldehyde is generated and reaches its steady state concentration. Then, TOX is ready to be incorporated into polymer chain giving longer polyoxymethylene sequences such as MMMMM, MMMME and EMMMM (reaction scheme V, Fig. 3-9e). Microstructure of copolymer tends to develop toward a Bernoullian statistical distribution (Fig. 3-10).



(Reaction scheme V)

6) Transacetalization can also contribute to redistribute the M and E units in the originally formed DOL polymer (reaction scheme VI). Average sequence length of formal units increases gradually versus conversion, because the net effect of transacetalization is separation of ethylene oxide unit along the copolymer chain as far as

possible. In other words it supports the survival of a longer polyoxymethylene sequence.



(Reaction scheme VI)

In the above copolymerization system (Fig. 3-9), the DOL monomer concentration was about 25% before second monomer TOX was added. This raises a question of the mechanism for the formation of almost random copolymer. Is the randomization through the suggested mechanism, or just a simple result of considerably higher monomer DOL concentration left at the first stage? The following experiment, with close to zero DOL concentration, gives a direct evidence to further confirm the suggested mechanism. A living polymer of DOL with close to 100% conversion was added into molten TOX monomer kept at 63°C. This living polymer of DOL can initiate the polymerization of TOX leading to a copolymer. A series of samples from the polymerization mixture were withdrawn at different reaction times for NMR analysis in CDCl₃ solvent. Fig. 3-11 shows the ¹³C NMR spectra for the copolymerization process. Three peaks due to TOX monomer (94.1 ppm) and DOL polymer sequences MEMEM (96.1 ppm) and EMEME (67.5 ppm) were immediately observed after the poly(DOL) had been dissolved in molten TOX monomer (Fig. 3-11a). The close to 100%

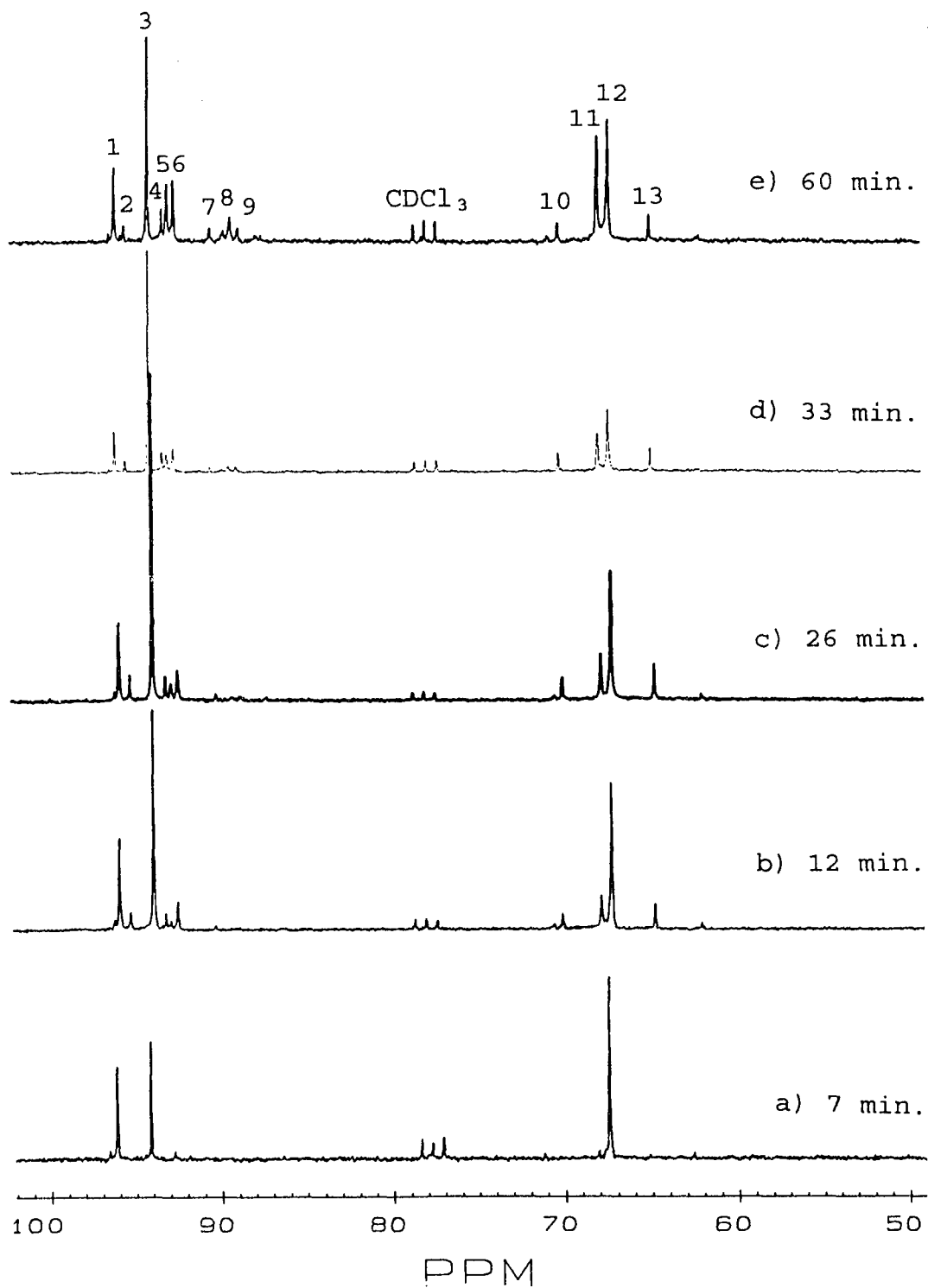


Fig.3-11 ^{13}C NMR spectra for bulk TOX/DOL copolymerization through addition of living homopolymer of dioxolane into molten trioxane at 63°C , $[\text{BF}_3\text{OEt}_2]=0.12$ mol% (based on dioxolane monomer), TOX:DOL $\approx$ 1:1 (mole ratio). Solvent for NMR spectrum: CDCl_3 . (1)=MEMEM, (2)=DOL, (3)=TOX, (4)=TOP, (5)=MMMME, (6)=EMMEM, (7)=MMMMM, (8)=EMMMM, (13)=DOL, (9)=EMMME, (10)=TOP, (11)=MMEEM, (12)=EMEME.

conversion of monomer DOL into polymer at the first stage was confirmed by the absence of NMR peaks due to DOL monomer. After about 12 minutes of reaction time, the signals for DOL monomer together with TOP and copolymer sequences EMMEM and MMEMM appear (Fig. 3-11b). Here the appearance of monomer DOL is probably due to the temperature increase of this system when poly(DOL) was dissolved into molten TOX at 63°C. Similar to the process in Fig. 3-9, copolymer sequences EMMEM, MMEMM and MMMEM continue to increase and longer polyoxymethylene units MMMMM, EMMMM and EMMME start to appear (Fig. 3-11c, d). Finally, the copolymer chains contain more and more longer polyoxymethylene units (Fig. 3-11e).

For the copolymer formed through the addition of living poly(DOL) into molten monomer TOX, the results from microstructure analysis showed that copolymer tends toward a random statistical distribution accompanied by a gradual increase in sequence length of polyoxymethylene during the second stage of copolymerization. The concentrations of TOP and DOL increase slightly first and then level off, reflecting steady states between the rate of consumption and the rate of generation of these two monomers.

3.6 Copolymerization of dioxolane with tetraoxane

The course of copolymerization of TEOX with DOL can be monitored directly by NMR only at low content of TEOX in

the monomer feed. At higher TEOX concentration, the very rapid polymerization of TEOX to long polyoxymethylene chain leads to a heterogeneous reaction mixture.

Fig. 3-12 shows the ^1H NMR spectra for the bulk copolymerization of TEOX / DOL at 65°C . The mole ratio of TEOX / DOL in the feed is 0.4:1 and initiator concentration is 0.028 mol%. In contrast to the copolymerization of TOX with DOL, we observed that almost all TEOX was consumed and that the MMM sequence grew very rapidly at the beginning of polymerization (Fig. 3-12b). This result is consistent with the previously reported results (18), i.e., TEOX is far more reactive than DOL from both kinetic and thermodynamic points of view. A significant amount of formaldehyde, TOX and TOP were also found during the copolymerization (Fig, 3-12b). As conversion increased, triad MMM sequence decreased accompanied by an increase in copolymer sequence (MME) and poly(DOL) sequences (EME, MEM) (Fig. 3-12b,c,d).

Fig. 3-13 represents the ^{13}C NMR spectra for the bulk copolymerization of TEOX and DOL at 70°C . The samples were obtained by withdrawing the copolymer mixture at different reaction times, and then added to the NMR tubes with a trace amount of triethylene amine in CDCl_3 solvent. During polymerization the appearance of polymer mixture changed gradually from a turbid solution to a transparent gel as conversion increased. From the ^{13}C NMR spectra of Fig 3-13a, no signal corresponding to TOEX monomer could be detected at about 24 seconds of reaction time. The copolymer chains

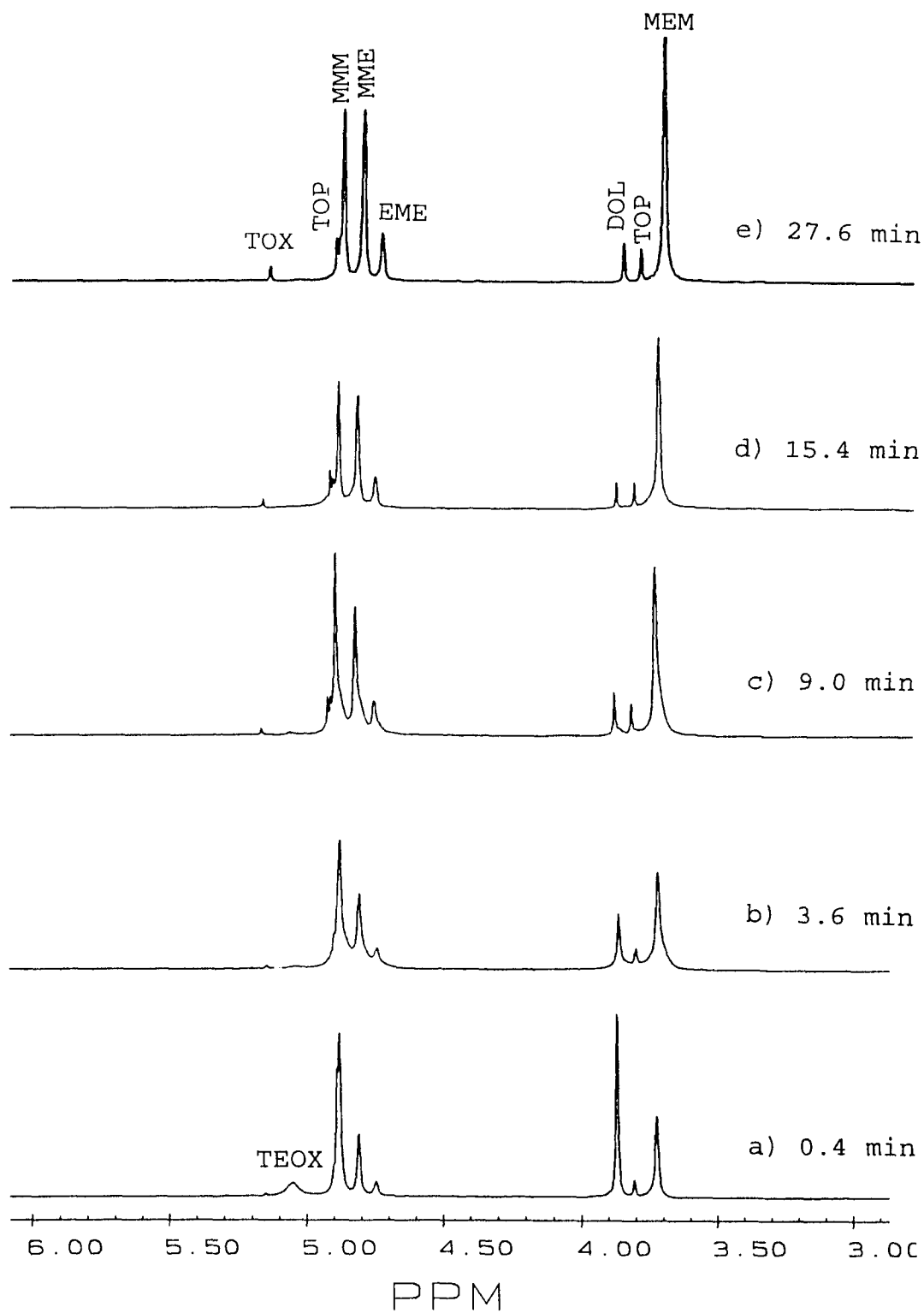


Fig.3-12 ^1H NMR spectra as a function of time for bulk copolymerization of tetraoxane with dioxolane initiated by BF_3OEt_2 at 65°C . $[\text{BF}_3\text{OEt}_2]=0.028$ mol%, $\text{TEOX:DOL}=0.4:1.0$ (mole ratio).

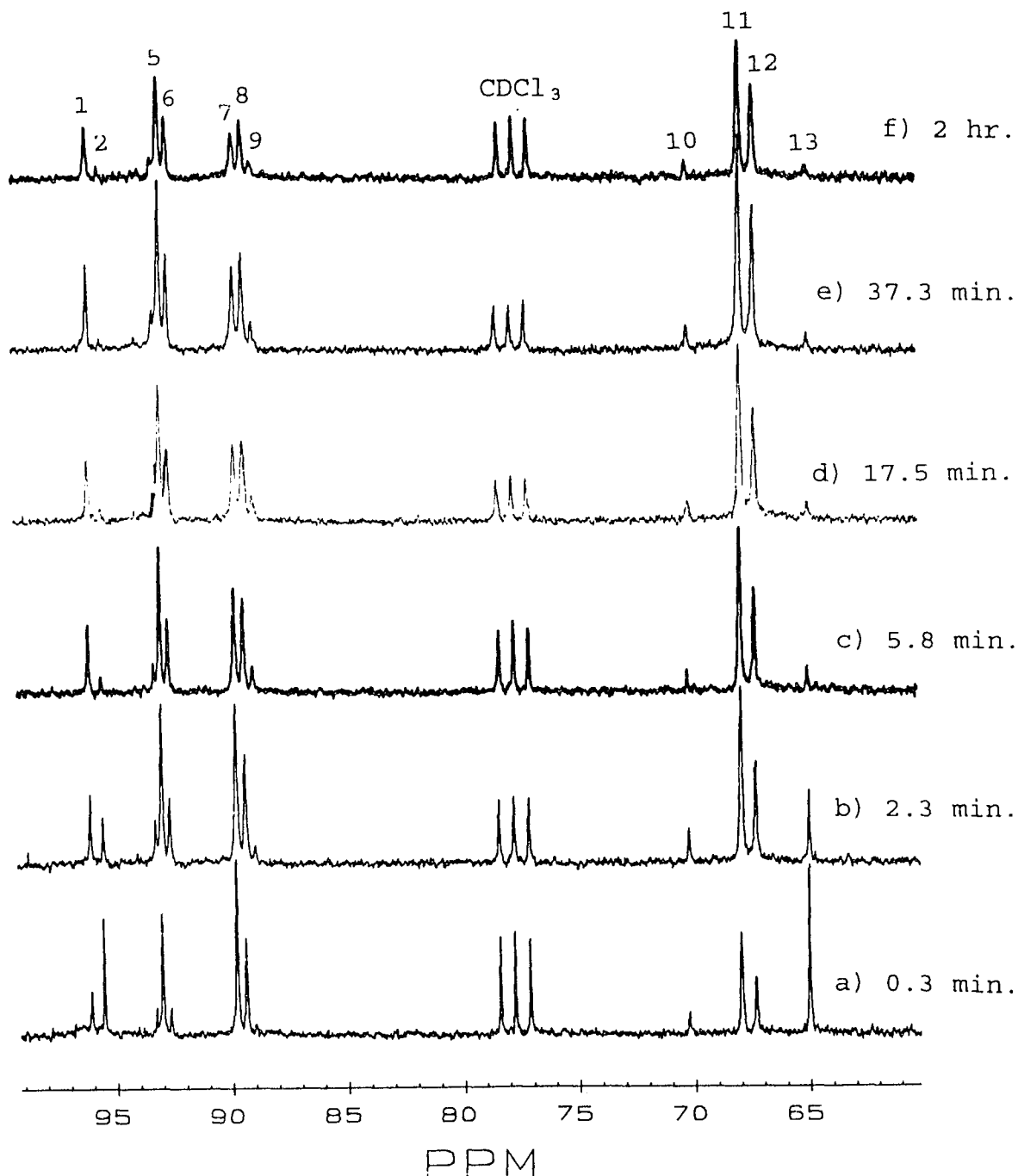


Fig.3-13 ^{13}C NMR spectra as a function of time for bulk copolymerization of tetraoxane / dioxolane with BF_3OEt_2 at 70°C . $[\text{BF}_3\text{OEt}_2]=0.028$ mol%, $\text{TEOX:DOL}=0.4:1.0$ (mole ratio). Solvent for NMR spectrum: CDCl_3 . (1)=MEMEM, (2)=DOL, (3)=TOX, (4)=TOP, (5)=MMMMM, (6)=EMMEM, (7)=MMMMM, (8)=EMMMM, (13)=DOL, (9)=EMMME, (10)=TOP, (11)=MMEMM, (12)=EMEME.

contained a large proportion of long polyoxymethylene sequences (such as MMMMM and MMMME) and small amount of MEMEM and EME ME sequences due to DOL monomer unit. The signals of longer polyoxymethylene sequences such as MMMMM and MMMME became smaller with conversion, and peaks of copolymer units (MMMEM, EMMEM, MMEMM) and homopolymer of DOL (MEMEM, EME ME) increased gradually (Fig. 3-13c, d).

Fig. 3-14 represents the change of copolymer microstructure and average sequence length of formal units as a function of conversion. In contrast to the copolymerization of TOX and DOL, the mole fraction of formal units as well as its average sequence length decrease with conversion. The mole fraction of MME, MEM and EME sequences due to TOP and DOL increase slightly with polymerization time. This is understandable, since the fast consumption of TEOX leads to polymer chains rich in polyoxymethylene, a longer sequence length of this unit is expected at the early stage of polymerization. As reaction continues, less reactive DOL starts to be incorporated and distributed statistically along the polymer chains. As a result, the longer polyoxymethylene sequence is interrupted as more and more DOL units are incorporated into polymer chains. A fairly random statistical arrangement of M and E units along the copolymer chain can be achieved at about 20% of conversion. As conversion increases, the microstructure of the copolymer continues to show a tendency toward a random distribution. The polymerization

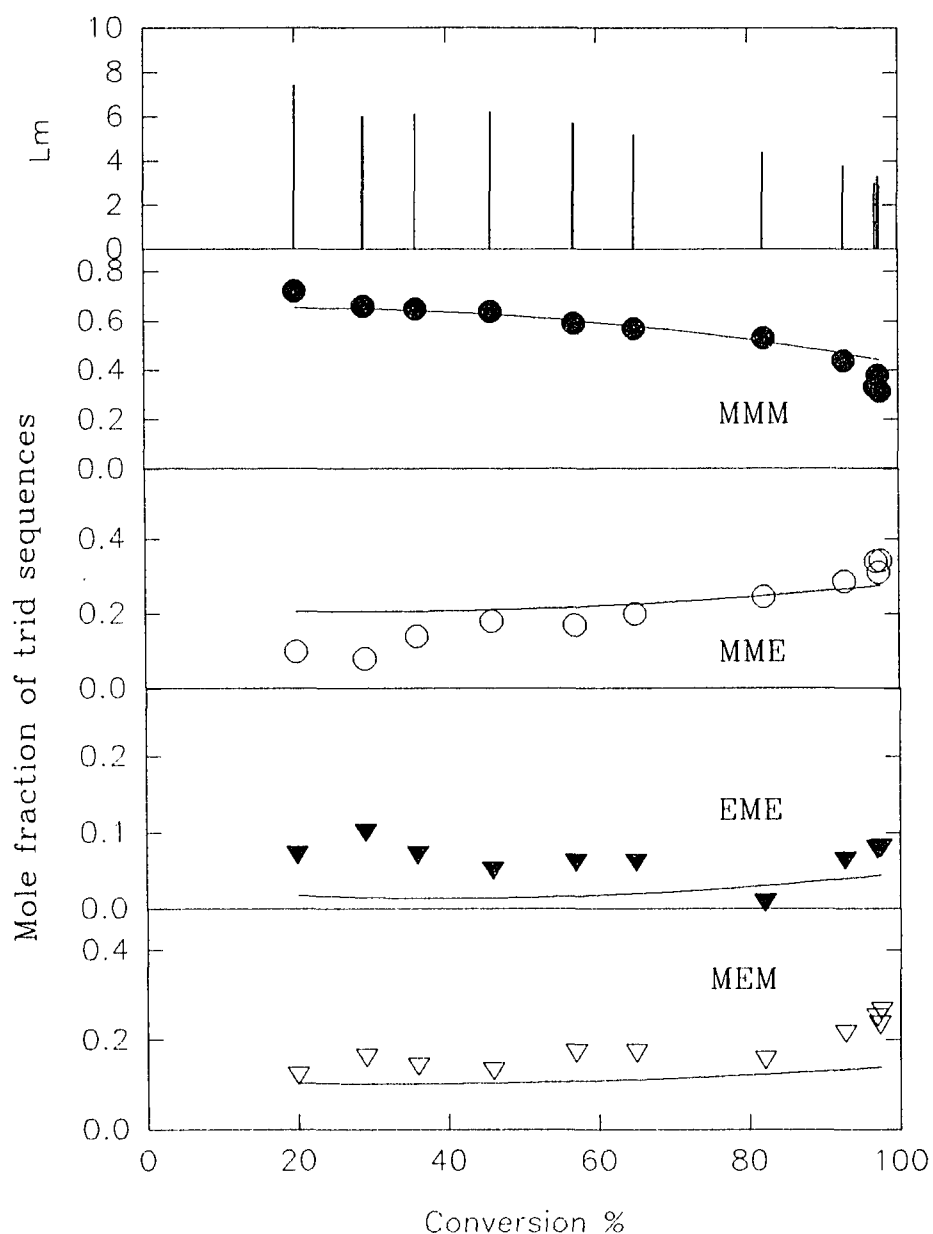


Fig.3-14 The average sequence length of formal units and mole fraction of triad sequences versus conversion for trioxane / dioxolane copolymerization at 63°C. $[BF_3OEt_2]=0.028$ mol/l, TEOX:DOL=0.4:1 (mole ratio). Symbols stand for NMR observed data $F\{\}$ and lines are calculated from Bernoullian statistical model $P\{\}$.

reaches equilibrium at about 97% of conversion. The reaction system was monitored for about 2 hours. The mole fractions of various sequences and average sequence length, L_M , do not show significant change after equilibrium conversion.

On the whole, it appears that the copolymerization of TEOX and DOL is very different from the copolymerization of TOX / DOL. In the latter system, DOL is initially consumed faster than TOX, yielding a copolymer with higher dioxolane content. In the case of TEOX / DOL copolymerization, TEOX is kinetically more reactive than DOL and is consumed at a much faster rate, leading to a copolymer with most of polyoxymethylene units at early stage of conversion. In both cases, however, randomization occurs gradually as the second monomer begins to be incorporated into the polymer chain.

Since we have observed that the conversion of longer polyoxymethylene into a shorter arrangement is accompanied by the generation of formaldehyde, TOX and TOP, it is reasonable to assume that the randomization process occurred mainly through the formation of formaldehyde and TOX from decomposition of polymer chains, and through the generation of TOP from insertion of formaldehyde into monomer DOL. On the other hand, the generated formaldehyde, TOX and TOP are consumed due to their incorporation into copolymer chains. This consumption shifts the equilibria to the direction of generation of more formaldehyde, TOX

and TOP. Eventually, a copolymer chain with random microstructure will be formed.

3.7 Homopolymerization of trioxepane

In both copolymerizations of TOX / DOL and TEOX / DOL, TOP was generated and participated in randomization of the copolymerization processes. Therefore, it is of interest to study the microstructure of homopolymerization TOP. Fig. 3-15 is the ^1H NMR spectra of homopolymerization of TOP initiated with ca. 0.20 mol% of BF_3OEt_2 at 63°C . A trace amount of TOX and formaldehyde exist in the monomer before adding initiator (Fig. 3-15a). Regular homopolymer sequences (MME, 4.78 ppm, MEM, 3.69 ppm) and formaldehyde grow immediately after the addition of initiator (Fig. 3-15b). But this regular sequence was disrupted at about 5 minutes as we observed the appearance of EME sequence in Fig. 3-15c. At the same time, the peak of formaldehyde continued to increase and DOL began to form (fig. 3-15d,e).

Because the peak of triad MMM sequence overlaps with the peak of TOP monomer, it is difficult to determine the existence of the longer polyoxymethylene in the homopolymer from ^1H NMR spectra. ^{13}C NMR spectra were used to monitor the homopolymerization process of TOP (Fig. 3-16). The polymer chains contain mostly regular homopolymer TOP sequences (EMMEM, MMEMM) and a small amount of DOL monomeric units (MEMEM, EMEME) at the early stage of

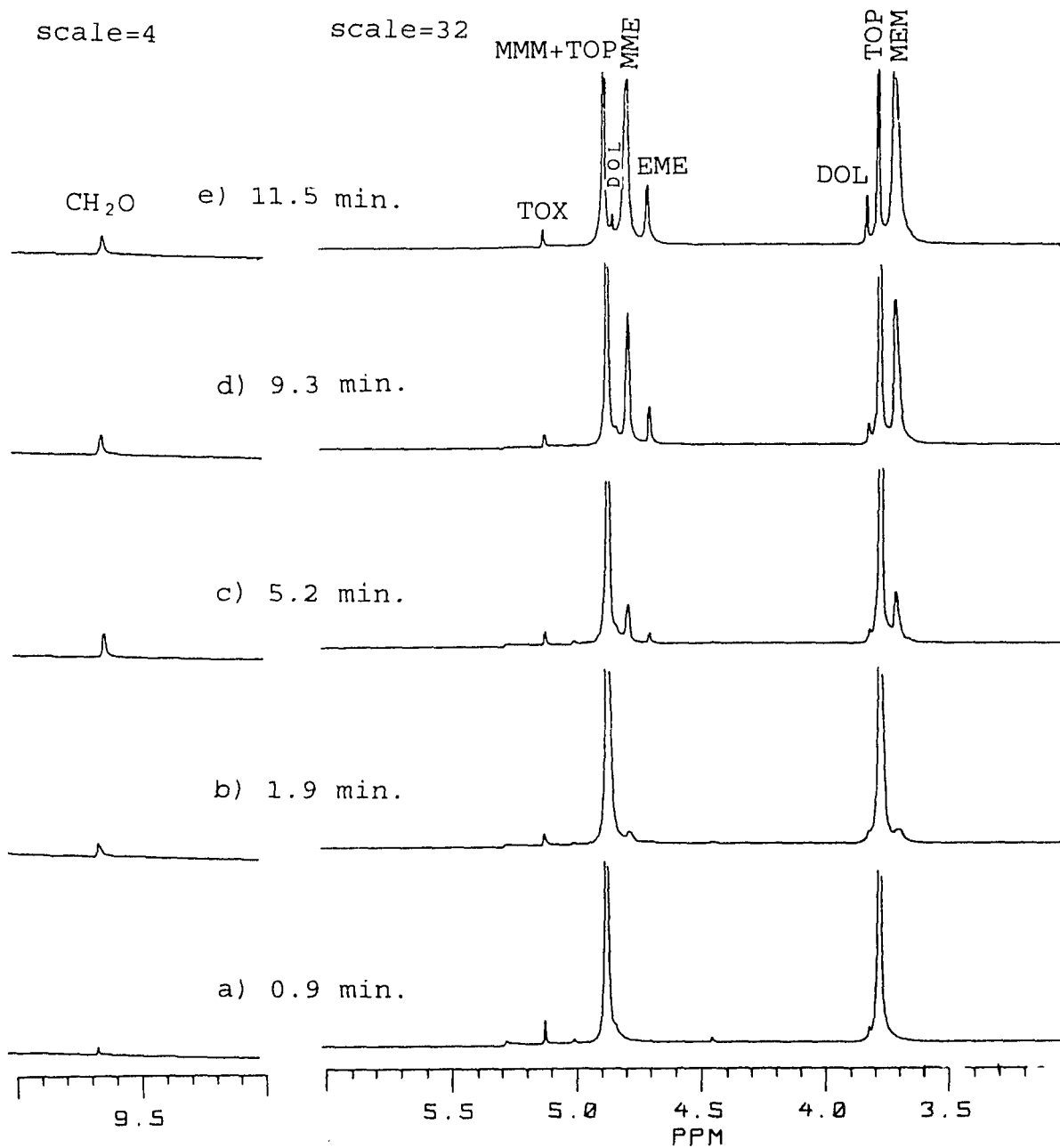


Fig.3-15 ¹H NMR spectra as a function of time for bulk homopolymerization of trioxepane initiated by BF₃OEt₂ at 63°C. [BF₃OEt₂]=0.20 mol%.

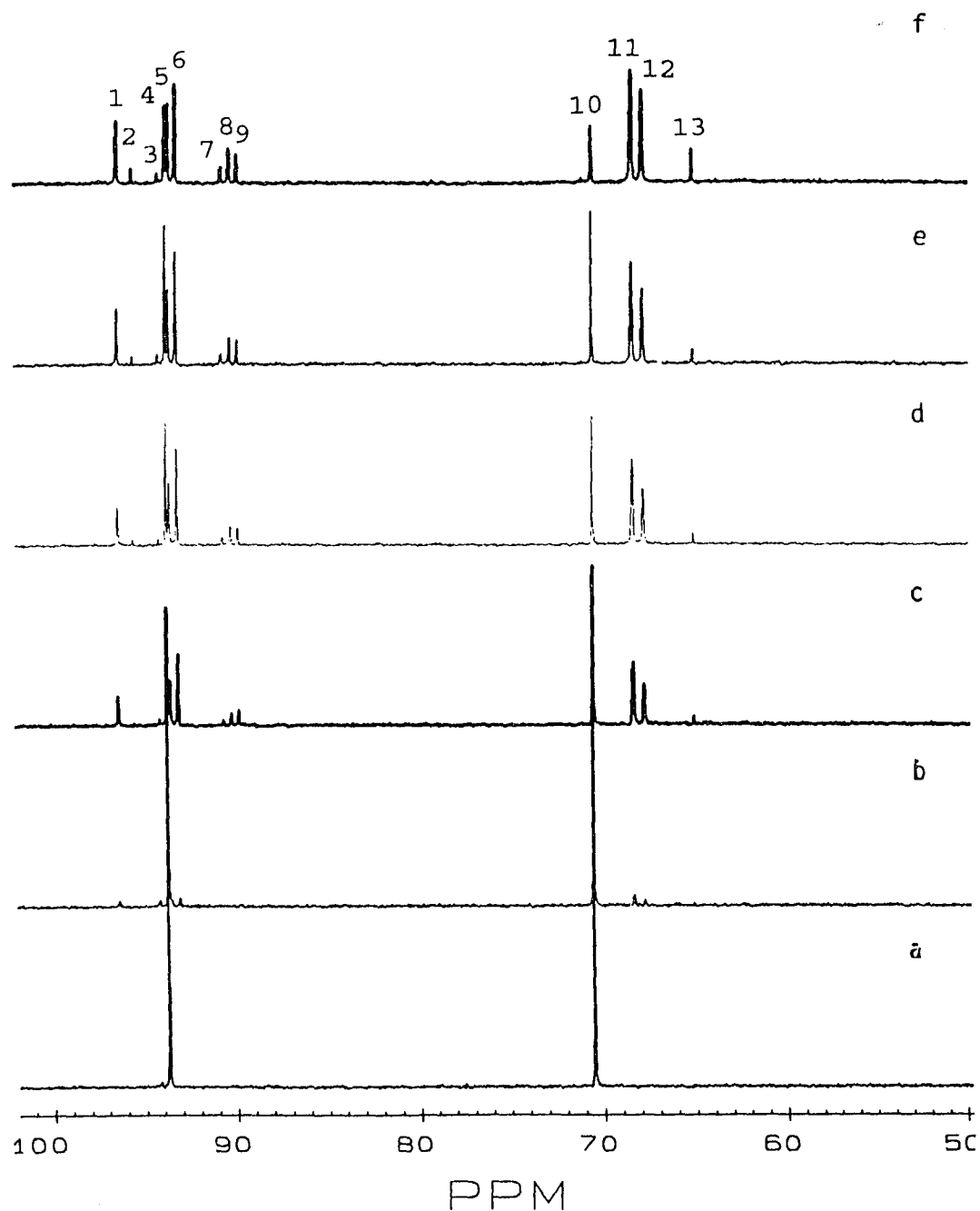


Fig.3-16 ^{13}C NMR spectra for bulk homopolymerization of trioxepane with BF_3OEt_2 at 63°C (reaction time is not available). $[\text{BF}_3\text{OEt}_2]=0.11$ mol%. (1)=MEMEM, (2)=DOL, (3)=TOX, (4)=TOP, (5)=MMMEM, (6)=EMMEM, (7)=MMMMM, (8)=EMMMM, (9)=EMMME, (10)=TOP, (11)=MMEMM, (12)=EMEME, (13)=DOL.

conversion (Fig. 3-16b). The peaks corresponding to the longer polyoxymethylene (MMMMM, EMMMM and EMMME) appear together with the generation of DOL monomer (Fig. 3-16c). These peaks continue to grow as conversion increases, indicating that the microstructure tends to rearrange to longer polyoxymethylene sequence (Fig. 3-16d, e).

The analysis of microstructure (Fig. 3-17) showed that the average sequence length, L_M for homopolymerization of TOP is kept at about two units throughout the observed conversion (about 80% of polymer conversion). This result is expected because the mole ratio of M and E units in copolymer composition is equal to two. The appearance of longer polyoxymethylene sequences (e.g., MMMMM and MMMME) should be accompanied by the formation of isolated formal unit (MEMEM) so that the copolymer composition will not change. In fact, we did observe that the mole fraction of the EME sequence increased slightly with conversion. Mole fraction of MMM sequence was about 15% which is still much less than the mole fraction calculated from the Bernoullian random statistical model. The copolymer chains contain essentially a large proportion of regular sequence (MME and EME). Although the mole fraction of the MME sequence decreased with conversion, indicating a tendency toward to random distribution, a completely random microstructure could not be reached within the observed conversion.

The repeating polymer sequence (-MME-MME-) could not be achieved in TOP homopolymerization. The reason for this

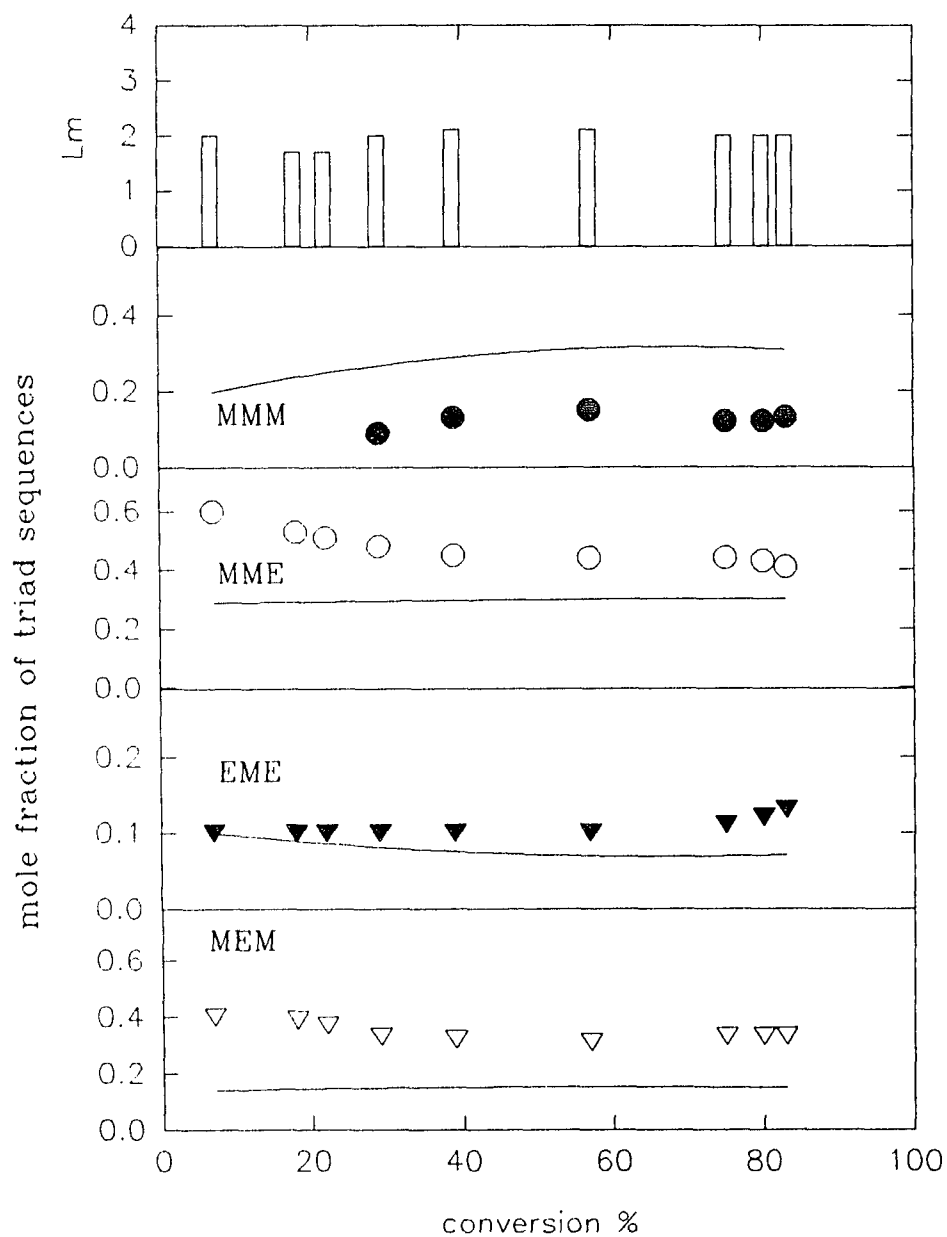
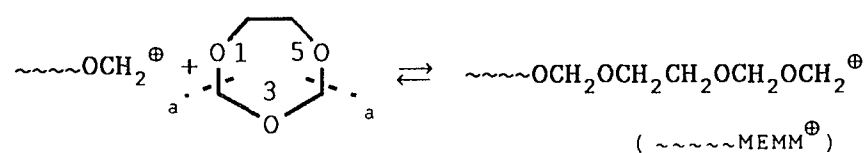


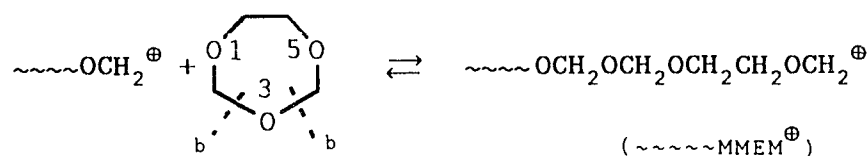
Fig.3-17 The average sequence length of formal units and mole fraction of triad sequences vs. conversion for bulk homopolymerization of trioxepane with BF_3OEt_2 at 63°C . $[\text{BF}_3\text{OEt}_2]=0.20$ mol%. Symbols stand for NMR observed data $F\{ \}$ and lines are calculated from Bernoullian statistical model $P\{ \}$.

observation was attributed to the two possible propagation mechanisms (19): 1) an attack of an active group ($--OCH_2^\oplus$) on O^1 or O^5 followed by opening of the oxonium to give the EMM sequence (reaction scheme VII),



(Reaction scheme VII)

2) an attack of $--OCH_2^\oplus$ on O^3 followed by ring-opening to yields MEM sequence (reaction scheme VIII).



(Reaction scheme VIII)

If propagation proceeded always by route (VII) or always by route (VIII), the resulting polymer would be regular (i.e., $--EMM-EMM-EMM--$ or $--MEM-MEM-MEM--$). A change of the ring-opening mechanism would lead to different triad sequences. Reaction VII followed by reaction VIII yields MMM triad; or the vice-versa gives EME triad. But this explanation cannot account for the existence of the longer polyoxymethylene sequences (such as MMMMM etc.).

Our ^1H and ^{13}C NMR spectra for the polymerization process of TOP give detailed information about the sequence redistribution. The regular polymer sequence $-EMM-$, which was formed initially from TOP, was first disrupted by

cleavage of some formaldehyde. At this point, polymer chains contain mostly MME sequence and small amount of EME units (Fig.3-15c and Fig. 3-16b). At the same time, more formaldehyde and DOL were generated from TOP monomer (Fig. 3-15d, and Fig. 3-16c). Once formaldehyde reaches a certain concentration, it can be incorporated into the polymer chain giving some triad formal sequence such as EMMME, MMMEM and even a small amount of EMMMM and MMMMM (Fig. 3-16d). Thus, the equilibrium $TOP \rightleftharpoons DOL + CH_2O$ will continuously shift to the right as more and more formaldehyde is incorporated into polymer chains. As a result we observed an increase in the signals of longer sequences of polyoxymethylene (MMMMM, EMMMM and EMMME). At the same time, more and more DOL was released from polymer chain (Fig. 3-16e, f). TOX also shows a slight increase with conversion. This monomer may also participate in the polymerization and contribute to the formation of longer polyoxymethylene sequences.

In summary, NMR spectra show the sequence redistribution is accompanied by the generation of formaldehyde, DOL and TOX, which can be incorporated into the polymer chains. Actually the homopolymerization should be considered as copolymerization. This probably is the reason that a regular homopolymer sequence has not be obtained in this apparent homopolymerization.

3.8 Conclusions

Dependent on their concentrations and basicity, monomers TEOX, TOX and DOL are consumed and incorporated into polymer chains at much different rate during their copolymerizations. The initial microstructure resulting from different polymerization systems varies. For example, TEOX / DOL copolymer gives a long polyoxymethylene arrangement at the beginning; while a polymer chain containing almost exclusively a DOL sequence is initially observed at TOX / DOL copolymer; with homopolymerization of TOP, a regular structure of two M and one E units was generated at first, but this regular sequence was disrupted as conversion increased. In all cases (copolymer TEOX / DOL, TOX / DOL, homopolymer TOP), the E unit tends to be distributed along the polymer chain statistically as conversion increases. Furthermore, at no stage of polymerization can block copolymers be detected even though we tried to add living homopolymer of DOL into TOX monomer. The driving force for the sequence rearrangement into random microstructure is attributed mainly to the formation of a thermodynamically stable structure. The occurrence of chain transfer by transacetalization cannot be doubted during redistribution of copolymer sequence. But the polymer backbone must be cleaved repeatedly before a random distribution can result. In addition, the rate of this transacetalization also needs to be fast since at no stage

of reaction time can pure block copolymer be isolated. Based on this consideration, the effect of propagation $\rightleftharpoons$ depropagation equilibrium on the redistribution of acetal sequences should be more important. Our NMR observations give direct evidence that this sequence redistribution is accomplished through a series of propagation $\rightleftharpoons$ depropagation equilibrium processes. The presence of formaldehyde in the polymerization system causes the generation of new monomeric species other than the original monomers. For instance, TOP was formed in TOX / DOL and TEOX / DOL copolymers; and DOL is generated in TOP homopolymer. Once these generated monomers reach their steady state concentrations, they are able to participate in the copolymerization. As a result, the consumption of these generated monomers will shift the equilibrium between propagation $\rightleftharpoons$ depropagation continually to the direction of decomposition of more and more of these new monomeric species. This process continues until finally a thermodynamically stable structure has been formed.

3.9 References

1. J. Masamoto, T. Iwaisako, K. Yoshida, etc., *Makromol. Chem., Macromol. Sym.*, **42/43**, (1991).
2. M. Gibas and Z. Jedlinski, *Macromolecules*, **14**, 1012 (1981).
3. C. H. Chen and A. Di Edwardo, *Adv. in Chem. Series A*, **91**, 359 (1969).
4. T. Ogawa, W. Ishitobi and K. Jinta., *J. Appl. Polym. Sci.*, **38**, 87 (1989).
5. P. Kubisa, S. Penczek and K. Brzezinsk, et al., *Cationic Polym. Relat. Processes*, 395 (1984).
6. D. Fleisher, R. C. Schulz, *Makromol. Chem.*, **176**, 677 (1975).
7. K. Burg, H. Schlaf and H. Cherdron, *Makromol. Chem.*, **116**, 203 (1968).
8. S. Penczek, et al., *Makromol. Chem.*, **116**, 1031 (1968).
9. K. Burg, H. Schlaf and H. Cherdron, *Makromol. Chem.*, **145**, 247 (1971).
10. N. L. Yang, R. Pesce, J. Wang, A. Auerbach and J. Paul, *Polym. Mater. Sci. Eng.* **58**, 873 (1988).
11. W. Chwialkowska, P. Kubisa and S. Penczek, *Makromol. Chem.*, **183**, 753 (1982).
12. V. Jaacks, *Adv. Chem. Series A*, **91**, 371 (1969).
13. Y. Yamashita, T. Asakura, M. Okada, *Makromol. Chem.*, **129**, 1 (1969).
14. See reference 9 in "Introduction".

15. J. C. Randall, *Polymer Sequence Determination*, Chap. 4, Academic Press, New York, 1977.
16. D. W. Brown, *J. Chem. Ed.*, **62** 209 (1985).
17. D. Fleischer and R. C. Schulz, *Makromol. Chem.*, Suppl. **1**, 235, (1975).
18. Y. Yamashita, T. Inoue, G. Hattori and K. Ito, *Makromol. Chem.*, **151**, 91 (1972).
19. See reference 5 in "Introduction".

APPENDIX

This chapter describes the method for deriving rate constants from time - conversion kinetic curves for systems in which the rate laws cannot be integrated in closed form. The method can basically be divided into two parts. First, the theoretical concentration of each species in the reactions will be calculated by numerical integration of the rate law based on Euler's method (1). These calculated concentrations will be used to fit the experimental observations, then the "best fit" parameters, i.e., the rate constants can be derived using a nonlinear least-square method. The detailed description is illustrated through the examples.

For a simple first order reaction such as



the integrated form of the rate law can be obtained easily,

$$[A] = [A_0] \text{EXP}(-kt) \quad (2)$$

here, $[A_0]$ is the initial concentration of component A. By determining experimentally the concentration $[A]$ at different reaction times t , and substituting into the equation 2, one can obtain the rate constant k easily. But for a two step reaction such as



the differential rate laws for the successive steps are:

$$dA/dt = -k_1 [A] \quad (5)$$

$$dB/dt = k_1 [A] - k_2 [B] \quad (6)$$

$$dC/dt = k_2 [B] \quad (7)$$

the integrated form of the reactions are far more complicated

$$[A] = \frac{k_1 [A_0]}{k_1 + k_{-1}} \left\{ \frac{k_{-1}}{k_1} + \exp[-(k_1 + k_{-1})t] \right\} \quad (8)$$

$$[B] = \frac{k_1 [A_0]}{k_1 + k_{-1}} \left\{ 1 - \exp[-(k_1 + k_{-1})t] \right\} \quad (9)$$

Generally speaking, when polymerization processes contain a number of single steps, it is difficult to express the rate laws of the reactions into an integrated form. But one can solve the equations by numerical integration of the rate laws, i.e., by Euler's method. For example, in equations 5 to 7, the concentration of each component at any moment of reaction time ($t + \Delta t$) can be approached by

$$[C]_{t+\Delta t} = [C]_t + (dC/dt)_t \Delta t \quad (10)$$

or more closely by

$$[C]_{t+\Delta t} = [C]_t + (dC/dt)_{ave} \Delta t \quad (11)$$

$$(dC/dt)_{ave} = 1/2 \{ (dC/dt)_t + (dC/dt)_{\Delta t} \} \quad (12)$$

if we know only the initial concentration $[C]_t$ at time t , we can calculate the final concentration $[C]_{t+\Delta t}$ at time $t + \Delta t$. For a defined time step, the final concentration can be used as a new initial concentration to find out the new final concentration. By repeating this process, we can calculate the concentration profiles for each component. The approximate values will be closer to the true values through the adjustment of the iteration number and the time step interval.

The next step uses a non-linear least square method to extract the "best parameters". This method requires the derivatives for $(C_{obs} - C_{cal})^2$ with respect to each of the parameter. C_{obs} is the observed concentration and C_{cal} is the calculated concentration from Euler's method. For example, in equations 5 to 7, we assume two initial estimates for the parameters k_1^0 and k_2^0 , input them into the equations, and the calculated concentration (C_{cal}) for each component can be found by numerical integration from the differential equations. Then one parameter is changed by a small amount, and inputted into the equations again to determine another set of $(C_{obs} - C_{cal})$. This procedure has to be repeated for each parameter many times until a minimum $(C_{obs} - C_{cal})^2$ is achieved. The set of parameters corresponding to the minimum is defined as the "best

parameters".

The least-square fitting was carried using the Marquardt-algorithin (2) to give an improved value through the adjustment of iteration number. A computer program has been written to perform this calculation and curve fitting.

This method allows one to extract each individual rate constant from a complicated system. One general problem is that it requires specification of more parameters than it can be defined by the observed curve. For any set of data, there is very limited number of parameters which can be determined by fitting an equation to the data. For example, an exponential curve is specified by three parameters and data distributed about an exponential curve allows determination of three parameters but no more. As we mentioned above, polymerization processes usually contain a number of single steps. In the models for DOL polymerization, numerical calculation requires that one specifies not less than 10 quantitatively. Although we have done some thermodynamic studies and made some reasonable assumptions so that we only need to extract five parameters from the kinetic model. However, the experimental data imply a curve which is not sufficiently complicated to define five parameters. Three or four parameters give a fairly good fit. As a result, for some parameters which are not well determined by the data, the "best parameters" from least square curve fitting may not be unique. In this case,

the reliability of the rate constants from this method need to be confirmed by another method.

References

1. S. C. Chapra and R. P. Canale, "*Numerical Methods For Engineers*", Chap. 16, McGraw-Hill Book Company, 1985.
2. J. P. Guthrie, *Can. J. Chem.*, **60**, 765 (1982).

References

Introduction

1. J. Masamoto, "Modern Polyacetals" *Prog. Polym. Sci.*, **18**, 1 (1993).
2. G. Odian, "Ring-Opening polymerization" in *Principles of Polymerization*, 3rd ed, Wiley-Interscience, New York, (1991), chap. 7.
3. S. Penczek and P. Kubisa, "Cationic Ring-opening Polymerization: Acetals", in *Comprehensive Polymer Science*, Vol. 3, G. C. Eastmond, A. Ledwith, S. Russo, and P. Sigwalt, Eds., Pergamon Press, London, (1989), chap. 49.
4. S. Penczek, P. Kubisa and K. Matyjaszewski, "Cationic ring-opening polymerization, Part II, Synthetic Application", *Adv. Polym. Sci.* 68/69, 118 (1985).
5. R. C. Schulz, W. Hellermann and J. Nienburg, "Cyclic Compounds Containing Two or More Oxygen Atoms in the Ring" in *Ring-Opening Polymerization*, Vol. 1, K. J. Ivin and T. Saegusa, Eds., Elsevier, London, (1984), chap. 6.
6. R. Szymanski, P. Kubisa and S. Penczek, *Macromolecules*, **16**, 1000 (1983).
7. S. Penczek, P. Kubisa and K. Matyjaszewski, "Cationic ring-opening polymerization, vol. I, Mechanisms", in *Adv. Polym. Sci.* **37**, 1 (1980).

8. V. Jaacks and W. Kern, *Makromol. Chem.*, **62**(1), 1963.
9. G. L. Collins, R. K. Green, F. M. Berardinelli and W. V. Garruto, *J. Polym. Sci., Pol. Lett.* **17**, 667 (1979).
10. P. H. Plesch and P. H. Westermann, *J. Polym. Sci. Part C*, **16**(7), 3837 (1968).
11. K. Boehlke and V. Jaacks, *Makromol. Chem.*, **145**, 219 (1971).
12. P. Kubisa and S. Penczek, *Makromol. Chem.*, **180**, 1821 (1979).
13. B. Xu, C. P. Lillya and J. C. W. Chien, *Macromolecules*, **20**, 1445 (1987).
14. V. A. Ponomarenko, E. L. Berman, A. M. Sakharov and Z. N. Nysenko, *Eur. Polym. J.*, **17**, 1111 (1981).
15. P. M. Lahti, C. P. Lillya and J. C. W. Chien, *Macromolecules*, **23**, 1214 (1990).
16. J. C. W. Chien, Y-G. Cheun and C. P. Lillya, *Macromolecules*, **21**, 870 (1988).
17. P. Colombo, S. Custro and P. Radici, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 681 (1980).
18. P. Dreyfuss and M. P. Dreyfuss "Cationic Ring-opening Polymerization: copolymerization," in *Comprehensive Polymer Science*, Vol. 3, G. C. Eastmond, A. Ledwith, S. Russo, and P. Sigwalt, Eds., Pergamon Press, London, (1989), chap 53.
19. Y. Yamashita "Random and Block copolymers by Ring Opening Polymerization". *Adv. Polym. Sci.*, **28**, 1

(1978).

20. T. Miki, T. Higashimura, K. Hayashi and S. Okamura, *J. Polym. Sci., Polym. Lett.*, **5**, 65 (1967).
21. G. Mngoli and F. Furlanetto, *Makromol. Chem.*, **176**, 143, (1975).
22. T. Iwaisako, J. Masamoto, K. Yoshida, etc., *ACS, Polym. Preprints*, **30 (1)**, 241 (1989).
23. G. L. Collins, R. K. Greene, F. M. Beradinelle and W. H. Ray, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1597 (1981).

Part 1

1. J. M. Williams, H. R. Schulten and N. E. Vanderborgh, *Polymer*, **33**, 4630 (1992)
2. L. C. Reibel, C. P. Durand and E. Franta, *Can. J. Chem.*, **63**, 264 (1985).
3. R. Alamo, J. G. Fatou and J. G. Guzman, *Polymer*, **23**, 379 (1982).
4. P. Archambault and R. E. Prud'Homme, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 35 (1980).
5. S. Bywater and D. J. Worsfold, *Can. J. Chem.*, **55**, 85 (1977).
6. L. L. Ivanova, N. A. Grebennikova, G. P. Sokolova, L. A. Pudina and N. S. Enikolopyan, *Vysokomol. Soyed.* **A18 (8)**, 1824 (1976).
7. Y. Yamashita, M. Okada and M. Kasahara, *Makromol. Chem.*,

- 117, 256 (1968)
8. O. A. Plechova, V. V Ivanov, etc., *Vysokomol. Soyed.* **A15** (1), 14 (1973).
9. Z. N. Nysenko, E. L. Berman, E. B. Ludvig and J. Ponomarenko, *J. Macromol Sci.- Chem.*, **A10(6)**, 1093 (1976).
10. R. Szymanski and S. Penczek, *Makromol. Chem.*, **183**, 1588 (1982).
11. S. Penczek and R. Szymanski, *Polym. J.*, **12(9)**, 617 (1980).
12. Y. Yokoyama, M. Okada and H. Sumitomo, *Polym. J.*, **11** (5), 365 (1979).
13. T. V. Grinevich, A. N. Shupik, G. V. Korovina and S. G. Entelis, *Eur. Polym. J.*, **17**, 1107 (1981).
14. A. T. Ponomarenko, V. G. Shevchenko and N. S. Enikolopov, *J. Macromol. Sci.-Chem.*, **A11(1)**, 195 (1977).
15. P. Kubisa, *J. Macromol. Sci.-Chem.*, **A11(12)**, 2247 (1977).
16. A. Stolarczyk, P. Kubisa and S. Penczek, *J. Macromol. Sci.-Chem.*, **A11(11)**, 2047 (1977).
17. K. Brzezinska; ect, *Makromol. Chem.*, **178**, 2491 (1977).
18. D. Mootz and M. Steffen, *Acta Cryst.* **B37**, 1110 (1981).
19. N. M. Greenwood and R. L. Martin, *J. Chem. Soc.*, 1915 (1951).
20. L. A. Kharitonova, G. V. Rahova, A. A. Shagingan and N. S. Enikolopyan, *Vysokomol. Soedin.*, **A9**, 2586 (1967).

21. R. Binet and J. Leonard, *Polymer*, **14**, 355 (1973).
22. W. K. Busfield, R. M. Lee and D. Merigold, *Makromol. Chem.*, **156**, 183 (1972).
23. L. I. Kuzab, M. A. Markevitch, AI. AI. Berlin and N. S. Enikolopyan, *Vysokomol. Soedin.*, **A10**, 2007 (1968).
24. N. Lu, G. L. Collins and N. L. Yang, *Makromol. Chem., Macromol. Symp.*, **42/43**, 425 (1991).
25. See reference 4 in "introduction".
26. P. Giusti; F. Andruzzi; P. Cerrai and L. Possanzini, *Makromol. Chem.*, **136**, 97 (1970).
27. See reference 1 in part 2.

Part 2

1. S. Okamura, T Higashimura and T. Miki, " *Cationic Polymerization of Trioxane in Solution*", *Prog. Polym. Sci.*, **3**, 97 (1972)
2. M. Hasegawa, K. Yamamoto, T. Shiwaku and T. Hashimoto, *Macromolecules*, **23**, 2629 (1990).
3. M. Bednarek, et al., *Makromol. Chem.*, **190(5)**, 929 (1989).
4. J. Stasinski and G. Dmowska, *Makromol. Chem., Rapid Commun.* **8 (11)**, 535 (1987).
5. M. N. Chandrashekara, D. Desai and M. Chanda, *Eur. Polym. J.*, **21(9)**, 933 (1985).
6. G. L. Collins, N. Lu and N. L. Yang, *ACS, Polym. Mat. Sci. Eng. Preprints*, **61**, 700 (1989).

7. P. S. Raman and V. Mahadevan, *Makromol. Chem.*, **178**, 1367 (1977).
8. K. Weissermel, E. Fischer, K. Gutweiler, H. D. Hermann and H. Cherdron, *Angew. Chem. Internat. Edit.*, Eng. **6(6)**, 526 (1967)
9. L. Leese and M. W. Baumber, *Polymer*, **6(5)**, 269 (1965).
10. M. Kucera, E. Hladky and K. Majerova, *J. Polym. Sci., Polym. Symp.*, **16**, 257 (1966).
11. V. Jaacks and W. Kern, *Makromol. Chem.*, **62**, 1 (1963).
12. See reference 9 in "introduction".
13. M. Iguchi, *British Polym. J.*, **5**, 195 (1973).
14. W. Kern and V. Jaacks, *J. Polym. Sci.*, **48**, 399 (1960).
15. T. Miki, T. Higashimura, S. Okamura, *J. Polym. Sci.*, **A5**, 2997 (1967).
16. See reference 20 in "introduction".
17. See reference 4 in "introduction".
18. G. Wegner, et al., *Makromol. Chem.*, **181**, 1763 (1980)
19. C. S. Hsia Chen, *J. Polym. Sci., Polym. Chem. Ed.* **14**, 143 (1976).
20. Von K. H. Burg, H. D. Hermann and H. Rehling, *Makromol. Chem.*, **111**, 181 (1968)

Part 3

1. J. Masamoto, T. Iwaisako, K. Yoshida, etc., *Makromol. Chem., Macromol. Sym.*, **42/43**, (1991).
2. M. Gibas and Z. Jedlinski, *Macromolecules*, **14**, 1012

- (1981).
3. C. H. Chen and A. Di Edwardo, *Adv. in Chem. Series A*, **91**, 359 (1969).
 4. T. Ogawa, W. Ishitobi and K. Jinta., *J. Appl. Polym. Sci.*, **38**, 87 (1989).
 5. P. Kubisa, S. Penczek and K. Brzezinski, et al., *Cationic Polym. Relat. Processes*, 395 (1984).
 6. D. Fleisher, R. C. Schulz, *Makromol. Chem.*, **176**, 677 (1975).
 7. K. Burg, H. Schlaf and H. Cherdron, *Makromol. Chem.*, **116**, 203 (1968).
 8. S. Penczek, et al., *Makromol. Chem.*, **116**, 1031 (1968).
 9. K. Burg, H. Schlaf and H. Cherdron, *Makromol. Chem.*, **145**, 247 (1971).
 10. N. L. Yang, R. Pesce, J. Wang, A. Auerbach and J. Paul, *Polym. Mater. Sci. Eng.* **58**, 873 (1988).
 11. W. Chwialkowska, P. Kubisa and S. Penczek, *Makromol. Chem.*, **183**, 753 (1982).
 12. V. Jaacks, *Adv. Chem. Series A*, **91**, 371 (1969).
 13. Y. Yamashita, T. Asakura, M. Okada, *Makromol. Chem.*, **129**, 1 (1969).
 14. See reference 9 in "Introduction".
 15. J. C. Randall, *Polymer Sequence Determination*, Chap. 4, Academic Press, New York, 1977.
 16. D. W. Brown, *J. Chem. Ed.*, **62** 209 (1985).
 17. D. Fleischer and R. C. Schulz, *Makromol. Chem., Suppl.* **1**, 235, (1975).

18. Y. Yamashita, T. Inoue, G. Hattori and K. Ito,
Makromol. Chem., **151**, 91 (1972).
19. See reference 5 in "Introduction".

Appendix

1. S. C. Chapra and R. P. Canale, "*Numerical Methods For Engineers*", Chap. 16, McGraw-Hill Book Company, 1985.
2. J. P. Guthrie, *Can. J. Chem.*, **60**, 765 (1982).