

AD-A120 199

SRI INTERNATIONAL MENLO PARK CA
SYNTHESIS OF ENERGETIC POLYMERS.(U)
SEP 82 G E MANSER, D L ROSS

F/8 7/3

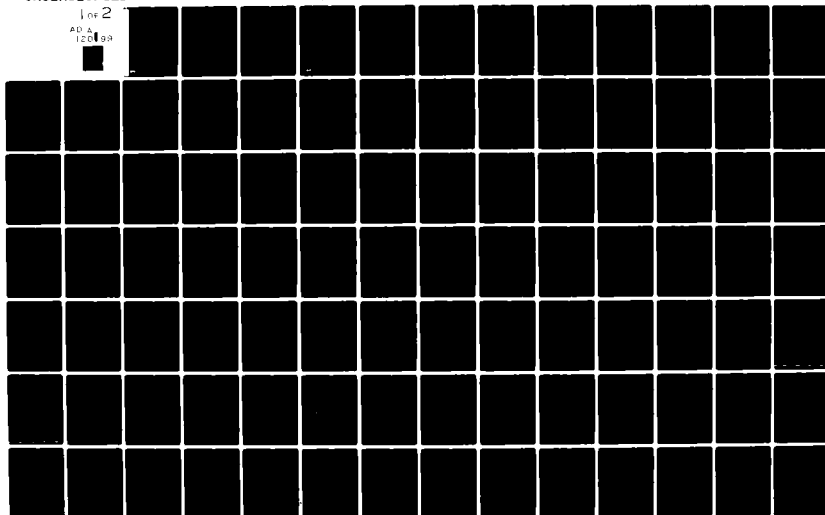
N00014-79-C-0525

UNCLASSIFIED

NL

1 of 2

AD-A
120 199



AD A120199

1 (B)
**SYNTHESIS OF
ENERGETIC POLYMERS**

Final Report
15 July 1979 to 14 September 1982

September 15, 1982

By: G. E. Manser and D. L. Ross

Prepared for:

OFFICE OF NAVAL RESEARCH
800 N. Quincy Street
Arlington, Virginia 22217

Attention: Dr. Richard S. Miller
Code 473

Contract No. N00014-79-C-0525; NR093-063

SRI Project PYU 8627

Approved for public release; distribution unlimited.

Reproduction in whole or in part is permitted
for any purpose of the United States Government.

SRI International
333 Ravenswood Avenue
Menlo Park, California 94025
(415) 326-6200
TWX: 910-373-2046
Telex: 334 486



DTIC FILE COPY

82 10 12 007

A

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER	2. GOVT ACCESSION NO. <i>AD-1120199</i>	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) Synthesis of Energetic Polymers		5. TYPE OF REPORT & PERIOD COVERED Final 15 July 1979 to 14 July 1982	
7. AUTHOR(s) G. E. Manser and D. L. Ross		6. PERFORMING ORG. REPORT NUMBER Final PYU-8627	
9. PERFORMING ORGANIZATION NAME AND ADDRESS SRI International 333 Ravenswood Avenue Menlo Park, CA 94025		8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0525; NR093-063	
11. CONTROLLING OFFICE NAME AND ADDRESS Dr. R. S. Miller Office of Naval Research, Code 473 Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS N/A	
14. MONITORING AGENCY NAME & ADDRESS (if diff. from Controlling Office) N/A		12. REPORT DATE 15 September 1982	
		13. NO. OF PAGES 102	
		15. SECURITY CLASS. (of this report) UNCLASSIFIED	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this report) Approved for public release; distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) energetic polymers energetic monomers nitro oxetanes azido oxetanes nitro tetrahydrofurans azido tetrahydrofurans cationic polymerization reactivity ratios copolymerization. gumstocks binders			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The objective of this work was to investigate energetic polyether glycol prepolymers for cast-cured propellants and explosives. We investigated the synthesis of several energetic cyclic ether monomers and methods for their polymerization. To optimize the physical properties of the polymers, we examined the relationship of monomer structures to polymerization ability. This information was then used to select monomer pairs that would produce random copolymers,			

DD FORM 1473
1 JAN 73
EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19. KEY WORDS (Continued)

20 ABSTRACT (Continued)

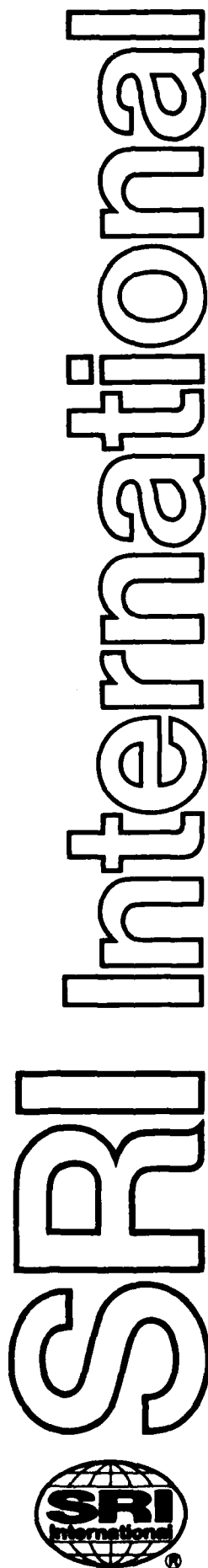
materials that have a very low degree of crystallinity. This low crystallinity is reflected in the superior elastomeric properties and plasticizer retention of the polymers examined. Preliminary evaluation of the polyether glycols and cured gum stocks indicate that binders can be produced that will add considerable energy content to propellant formulations. Ten polymers were investigated; one of these, the BAMO/THF copolymer, has been produced in multipound quantities and actual propellant formulation and testing is being conducted in various laboratories.

Accession	✓
Index	
File	
Class	
Subject	
Author	
Editor	
Reviewer	
Appr	
Spec	
Dist	
Pub	
Other	
A	



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)



SYNTHESIS OF ENERGETIC POLYMERS

Final Report
15 July 1979 to 14 September 1982

September 15, 1982

By: G. E. Manser and D. L. Ross

Prepared for:

**OFFICE OF NAVAL RESEARCH
800 N. Quincy Street
Arlington, Virginia 22217**

**Attention: Dr. Richard S. Miller
Code 473**

Contract No. N00014-79-C-0525; NR093-063

SRI Project PYU 8627

Approved by:

**M. E. Hill, Laboratory Director
Chemistry Laboratory**

**G. R. Abrahamson, Vice President
Physical Sciences Division**

CONTENTS

LIST OF FIGURES	3
LIST OF TABLES	4
ACKNOWLEDGEMENTS	5
I INTRODUCTION AND BACKGROUND	6
II DISCUSSION	8
Monomer Synthesis	8
Oxetanes	8
Tetrahydrofurans	14
Polymer Synthesis	17
Homopolymerization	18
Copolymerization	19
Scale-Up of BAMO/THF Copolymer	21
Gumstock Preparation and Testing of 50/50 mol%	
BAMO/THF Polymer	22
Monomer Reactivity	23
Polymer Evaluation	25
III CONCLUSIONS AND RECOMMENDATIONS	43
IV EXPERIMENTAL DETAILS	45
Monomer Synthesis Procedures	45
Dimethyl 2-(2,2-dinitropropyl)-1,4-butanedioate.....	45
2-(2,2-Dinitropropyl)-1,4-butanediol	45
3-(2,2-Dinitropropyl) Tetrahydrofuran (3-DNP THF)	45
3,3-Bis(cyanomethyl)oxetane	46
Oxetane 3,3-Diacetic acid	46
3-Methyl-3-(Potassium 2,2-Dinitroethoxymethyl)oxetane	47
3-Methyl-3-(2-fluoro-2,2-dinitroethoxymethyl)oxetane (FOE)	47
3,4-Bis(hydroxymethyl)tetrahydrofuran	
Bis(p-toluenesulfonate)	47
3,4-Bis(azidomethyl)tetrahydrofuran	48
2-Hydroxymethyltetrahydrofuran p-Toluenesulfonate	49
2-Azidomethyltetrahydrofuran	49
3-Hydroxymethyltetrahydrofuran p-Toluenesulfonate	49
3-Azidomethyltetrahydrofuran	49
3-Methyl-3-(p-toluenesulphoxymethyl)oxetane	49
3-Azidomethyl-3-methyloxetane	50

Polymerization Procedures	50
Materials	50
Typical Solution Polymerization Procedure	50
Functionality Determination	51
REFERENCES	53
PUBLICATIONS, PATENTS, AND PRESENTATIONS	55
DISTRIBUTION LIST	56
APPENDICES	
A THE CONTROLLED CATIONIC POLYMERIZATION OF CYCLIC ETHERS	63
B COPOLYMERIZATION OF 3,3-BIS(AZIDOMETHYL) OXETANE WITH TETRAHYDROFURAN	75
C A NEW POLYMERIZATION TECHNIQUE FOR PREPARING LOW MOLECULAR WEIGHT POLYETHER GLYCOLS	86
D BAMO/THF COPOLYMER: A CANDIDATE ENERGETIC POLYETHER GLYCOL	96

FIGURES

1	Effect of Monomer Ratio on the Melting Point Transition Temperature of BAMO/THF Copolymer	20
2	BASIC Reactivity Ratio Program	26
3	Instantaneous BAMO/THF Copolymer Composition Curve	28
4	Instantaneous BAMO/AZOX Copolymer Composition Curve	29
5	Instantaneous BAMO/AMMO Copolymer Composition Curve	30
6	360 MHz NMR Spectrum of 1,4-Butanediol	34
7	360 MHz NMR Spectrum of 1,4-Butanediol/Boron Trifluoride Complex ..	35
8	360 MHz NMR Spectrum of 2-(2,2-Dinitropropyl)-1,4-butanediol	36
9	Methylene Chloride Solution Infrared Spectrum of 2-(2,2-Dinitropropyl)-1,4-butanediol	37
10	90 MHz NMR Spectrum of 2-(2,2-Dinitropropyl)-1,4-butanediol and 13 Mole% Eu(FOD) ₃ Shift Reagent	38
11	MHz NMR Spectrum of 2-(2,2-Dinitropropyl)-1,4-butanediol/ Boron Trifluoride Complex	39
12	90 MHz NMR Spectrum of 3,3-Dimethyloxetane	41
13	90 MHz NMR Spectrum of 2-(2,2-Dinitropropyl)-1,4-butanediol Initiated Polymerization of 3,3-Dimethyloxetane	42

Appendix A

1	First- and Second-Order Plot of Polymerization of BAMO to 94% Conversion	70
2	First-Order Plot of Polymerization of BAMO to 74% Conversion ...	71

Appendix B

1	Eta Versus Xi Plot for BAMO/THF	82
2	Instantaneous Composition Curve of BAMO-THF Copolymer as a Function of the Monomer Charge	84

Appendix C

1	GPC of FOE Polymerization	89
2	GPC of 50/50 mol% BAMO/THF Copolymer	93

TABLES

1	Properties of FOE	10
2	Properties of 3-DNP THF	15
3	Properties of BAMO/THF Copolymers	19
4	Reactivity Ratios for Monomer Pairs	24
5	Density and Heat of Formation of Experimental Polymer Systems	31

Appendix A

1	Effect of Diol Catalyst Ratio on Polyol Molecular Weight	68
2	Controlled Polymerization of 3-(2,2-Dinitropropoxymethyl)- 3-Methyloxetane, Oxether-1	68

Appendix B

1	Polymer Properties of BAMO/THF	79
2	η and ξ Parameters	81

Appendix C

1	Polymerization Runs for FOE	88
2	Controlled Polymerization of Oxether-1	90
3	Effect of Diol/Catalyst Ratio on Polyol Molecular Weight	91
4	Effect of BAMO/THF Monomer Ratio on Physical Properties	92

ACKNOWLEDGMENTS

We wish to acknowledge the efforts of the following SRI personnel who contributed to this work: Ronald Chiarello, David Cotts, John Guimont, Deborah Scott, Scott Selover, Robert Simon, Steven Staats, and Donald Rogers.

We also wish to acknowledge the valuable suggestions and encouragement of Dr. P. A. Miller, Project Consultant, and Dr. R. S. Miller, ONR Project Monitor. This work has been aided considerably by the valuable communications between the project staff and following investigators: Dr. M. Frankel, Rocketdyne, Dr. K. Baum, Fluorochem, Inc., Dr. M. Farber, Space Sciences, Inc., and Dr. R. Reed, NWC, China Lake.

I INTRODUCTION AND BACKGROUND

The objective of the research described here was to investigate energetic polymers for use in cast-curable, heat and shock resistant explosives and propellants. The general approach was to prepare energetic polyether glycols by the cationic polymerization of energetic cyclic ethers. To achieve the objectives we investigated the synthesis of energetic oxetanes and tetrahydrofurans. Energy is derived from the introduction of azido, nitro, and nitrato groups into already formed cyclic ether structures, or energetic precursors that are cyclized. We investigated the polymerization of the synthesized monomers to produce polyether glycols of predetermined molecular weight and functionality. The effect of monomer structure on the polymerization ability was examined to select monomer pairs that would produce polymers having the requisite properties. As a result of this research, we synthesized and evaluated ten new energetic polymers.

Much of the research described here on the synthesis and polymerization of energetic oxetanes and tetrahydrofurans was first proposed to AFRPL in 1975^{1a} and later to AFOSR in 1976^{1b}. The rationale was to synthesize cyclic ether monomers, containing pendant energetic groups, and to develop methods for the cationic polymerization of the synthesized monomers to produce energetic, difunctional, cast-curable homopolymers and copolymers. The resultant polymers, we reasoned, should possess increased energy and chemical and physical properties over current materials. Subsequently, and as a result of a formal proposal to AFRPL in 1978^{1c}, work began under Contract F04611-78-C-0051^{1d}. During the course of the research a great deal of understanding had been gained on the preparation of energetic polymers.

The research of others in the synthesis of energetic polymers has also contributed to this understanding. Included is the work of Dr. Milton Frankel of Rocketdyne and his valuable research on azido polymers, and Dr. Kurt Baum of Fluorochem, who in 1976 proposed^{1e} and subsequently

synthesized monomers in which energetic groups are attached directly to the oxetane ring.

As the Air Force work progressed, it became apparent that additional effort was needed to unravel many of the problems encountered in monomer synthesis and polymerization. Consequently, the current contract with ONR was initiated in 1979 to fulfill this need. This research concerned general approaches to energetic monomer synthesis and an investigation of the problems encountered in the polymerization of 4- and 5-membered cyclic ethers. Thus, with the combined support of ONR and AFRPL, the efforts of the two research teams resulted in significant advances in the field of energetic polymers as described below.

II DISCUSSION

The research program was conducted in three phases:

1. Synthesis of monomers
2. Synthesis of polymers
3. Evaluation of polymers

The target properties of the polymers investigated during this program were:

Low temperature properties (-65°C)
Superior elastomeric properties
Thermal and chemical stability
Chemical and physical compatibility
Processibility
Reproducibility
Difunctionality
Energetic
Broad applicability

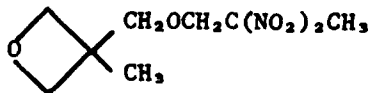
Monomer Synthesis

In this phase of the program we investigated general synthetic routes to energetic oxetanes and tetrahydrofurans as the few that were known involved diverse and difficult synthesis routes. Therefore, we investigated the synthesis of these classes of monomers by routes that could be used later to prepare other monomers as needed.

Oxetanes

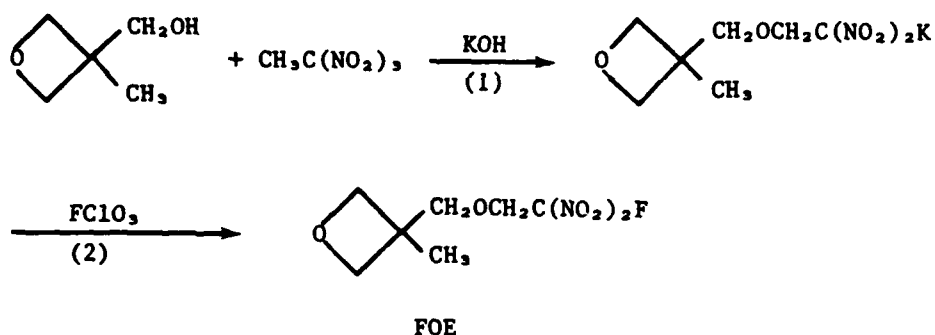
3-Methyl-3-(2-fluoro-2,2-dinitroethoxymethyl)oxetane (FOE)

One of the monomers under investigation for AFRPL was oxether-1¹

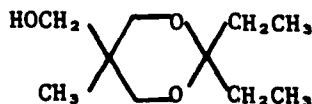


Oxether-1

Oxether-1 polymerizes readily and its synthesis has already been established. Because the presence of fluorine was not acceptable at the time for Air Force applications, it was reasonable in this case, to modify the route to Oxether-1 to provide the fluorinated analog, FOE. The presence of fluorine not only resulted in a more dense material than Oxether-1, but also increased the oxygen balance. FOE was prepared as shown in equations (1) and (2).

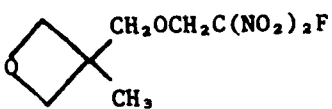


The starting oxetane alcohol was prepared from tris(hydroxymethyl)ethane and diethyl carbonate by formation and pyrolysis of the intermediate cyclic carbonate.



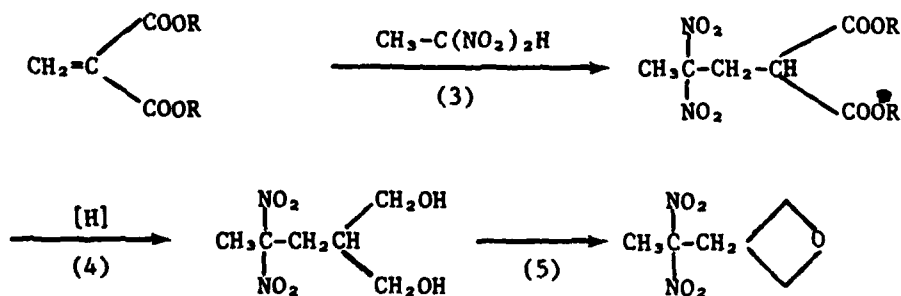
The potassium salt, equation (1), was prepared by the same dinitroethylation procedure used for Oxether-1¹, and the fluorination with perchloryl fluoride, equation (2), was based on a published procedure.² The overall yield of the two reactions is 17%; however, reaction conditions have not been optimized. Alternative methods of fluorination were not been investigated. The properties of FOE are shown in Table 1.

Table 1
PROPERTIES OF FOE

Structure	
Molecular Formula	C ₇ H ₁₁ FN ₂ O ₆
Formula Weight	238.2
Density (g/cm ³)	1.365
ΔH _f (gas) kcal/mol, est.	-183

3-(2,2-Dinitropropyl)oxetane

The first of two general synthetic routes to nitroalkyl-substituted oxetanes is shown in equations (3) to (5). The first target monomer was 3-(2,2-dinitropropyl)oxetane, but many other monomers could be prepared by replacing dinitroethane with any of several other 1,1-dinitroalkanes.



Methylene diethylmalonate was prepared in high yield by the method of Bachmann and Tanner³ and purified by vacuum distillation. Reaction with dinitroethane in the presence of triethyl amine, equation (3), as described by Kloetzel,⁴ was found to produce diethyl 2-(2,2-dinitropropyl)diethyl malonate in almost quantitative yield.

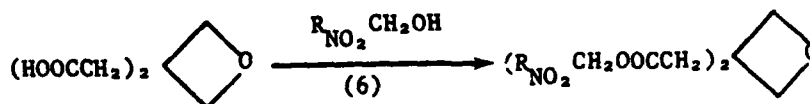
An extensive study of the chemical reduction of this ester was then undertaken. Lithium borohydride in THF from ambient temperature to reflux was found to have little effect; even sodium borohydride-aluminum chloride in diglyme, which is considered to be a very effective reducing agent for esters in the presence of nitro groups, was ineffective to 75°C. Diborane, under increasingly vigorous conditions, also had no effect. A possible cause of failure of this reduction is the keto-enol tautomerism, which malonate esters are known to undergo.

A method of Olah^{8,9} and Tse Lok Ho,¹⁰ involving transesterification by hexamethyldisilane followed by hydrolysis with ice water, was used, but on work-up no identifiable product was isolated.

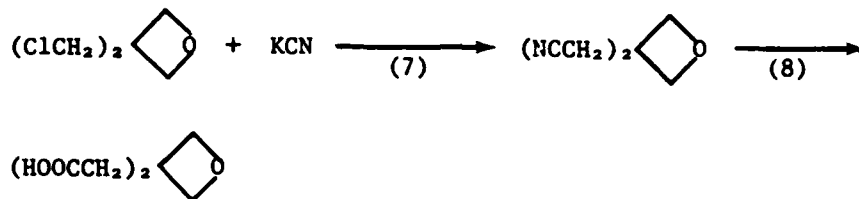
Because the literature suggested that the methyl ester might be hydrolyzed more readily than the ethyl ester, the hydrolysis procedures were repeated using the dimethyl ester; only decarboxylated product was obtained. In a final effort to obtain the diol, we attempted to convert the ester to the amide and then hydrolyze the amide. Although diethylmalonate is readily converted to the amide in liquid ammonia using a catalytic amount of ammonium chloride,¹¹ the reaction of diethyl 2-(2,2-dinitropropyl)malonate with ammonia gave only degradation products.

Oxetane 3,3-Diacetic Acid

The second general route to energetic oxetanes that we investigated required synthesis of oxetane 3,3-diacetic acid as an intermediate for esterification with energetic alcohols, equation (6).



Initial investigation of the synthesis of oxetane diacetic acid was based on the reported procedure¹² shown in equations (7) and (8).



Conversion of bis(chloromethyl)oxetane to the bis-nitrile, equation (7), proceeded in good yield, but the reported hydrolysis of the nitrile to the diacid with barium hydroxide did not occur as described.* Therefore, we investigated a second method¹³ using potassium hydroxide and hydrogen peroxide. Oxetane diacetic acid was isolated from the hydrolysis reaction mixture only with great difficulty because of the high solubility of the free acid in water. During the work-up a significant amount (relative to the free acid) of the anhydride was also obtained.

The preferred procedure for esterification, equation (6), involves the use of dicyclohexylcarbodiimide (DCC), but the acid tended to form anhydride. Therefore, we attempted to prepare the bis(fluorodinitroethyl) ester by a procedure reported¹⁴ for esterification of malonic acid with fluorodinitroethanol in trifluoroacetic acid. None of the desired product was detected.

Investigation of the polymerization of oxetane esters under our Air Force contract revealed that polymerization with boron trifluoride proceeds slowly and in low conversion compared with other substituted oxetanes. Because oxetane diacetic acid did not esterify readily and the ester may not polymerize well, further work on esters was abandoned.

Bis(azidomethyl)oxetane (BAMO)

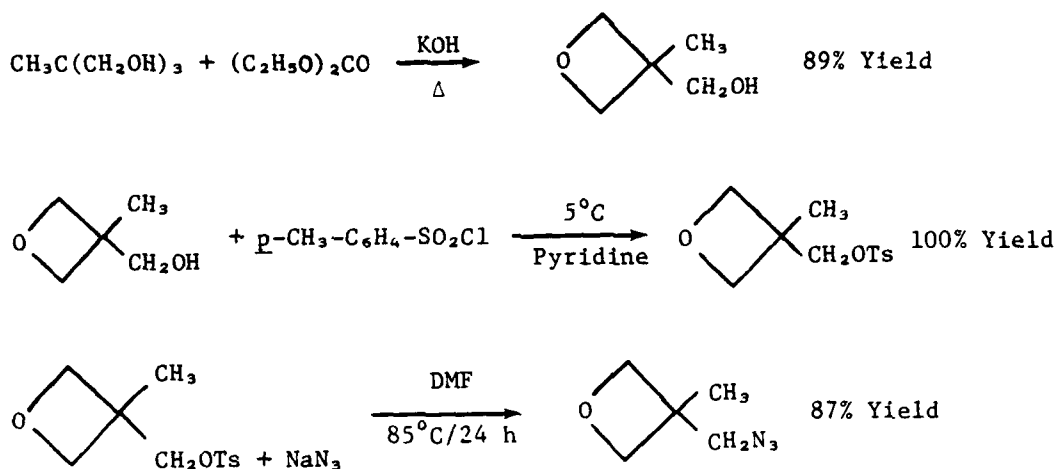
The synthesis of BAMO as reported by Carpenter¹⁵ by the reaction of sodium azide with bis(chloromethyl)oxetane in DMSO at 90°C. (Caution: the monomer should not be distilled, as on one occasion a detonation occurred.) We have found that column chromatography using methylene

*The hydrolysis was based on the abstract of a Belgian journal as given by Chemical Abstracts.

chloride on silica gel produces a monomer of sufficient purity for polymerization.

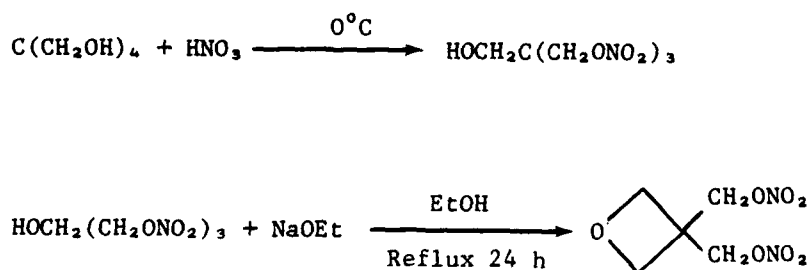
3-Azidomethyl-3-methyloxetane (AMMO)

AMMO was best prepared by the route shown below. A total of 300 g was prepared in an overall yield, after purification by column chromatography, of 78% at better than 99.8% purity.



Bis(nitratomethyl)oxetane (BNMO)

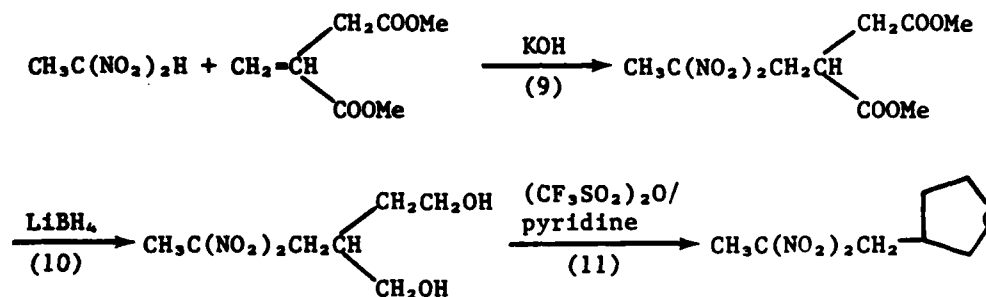
BNMO was prepared by the reaction scheme as shown below:



Pentaerythritol trinitrate was prepared in moderate yield by reaction of pentaerythritol with 60% nitric acid at 0°C.¹⁷ Ring closure was effected by reaction of the nitrate ester with sodium ethoxide.¹⁶ The overall yield of 25% can be expected to be improved by further investigation.

Tetrahydrofurans

The general route for synthesis of energetic tetrahydrofurans, equations (9) to (11), parallels the route used for synthesis of oxetanes.



Synthesis of substituted tetrahydrofurans is described extensively in the literature and several alternative methods for ring closure are available. Although nitroalkyl-substituted tetrahydrofurans can be prepared more easily than oxetanes, we restricted our investigation to one route because of anticipated polymerization difficulties. Only 3-methyl and 2-methyl tetrahydrofuran have been polymerized and then only with great difficulty.

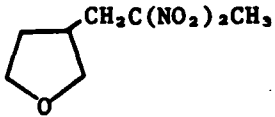
3-(2,2-Dinitropropyl) Tetrahydrofuran (3-DNP THF)

Addition of dinitroethane to dimethyl itaconate, equation (9), was successfully performed using potassium hydroxide as a catalyst, and reduction of the ester with lithium borohydride, equation (10), yielded the diol. The ring closure, equation (11), using trifluoromethane sulfonic anhydride and pyridine, yielded 3-(2,2-dinitropropyl) tetrahydrofuran which

is a colorless oil. Details of the procedure are given in section IV, Experimental Details, and the properties of 3-DNP THF are given in Table 2.

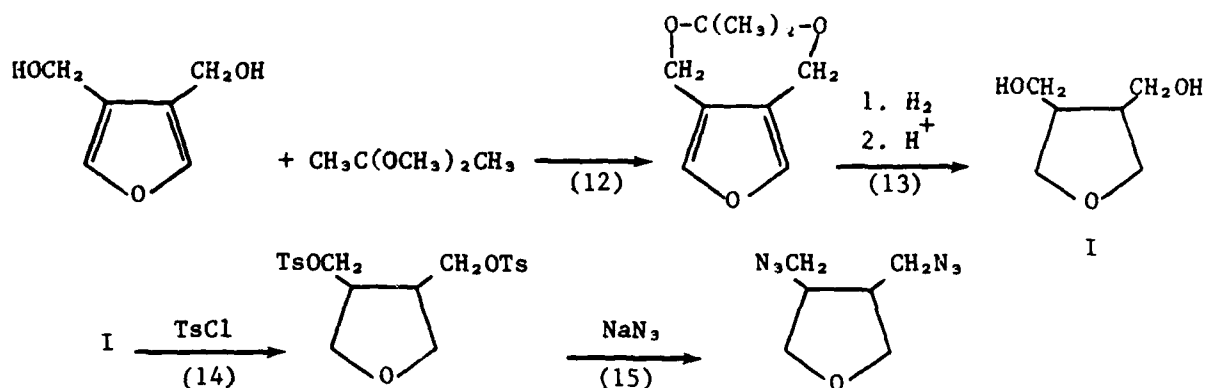
Table 2

PROPERTIES OF 3-DNP THF

Structure	
Molecular Formula	C ₇ H ₁₁ N ₂ O ₅
Formula Weight	204.2
Density (g/cm ³)	1.305
ΔH _f (gas) kcal/mol, est.	-111.65

3,4-Bis(azidomethyl) Tetrahydrofuran

3,4-Bis(azidomethyl) THF was prepared by the following sequence of reactions.

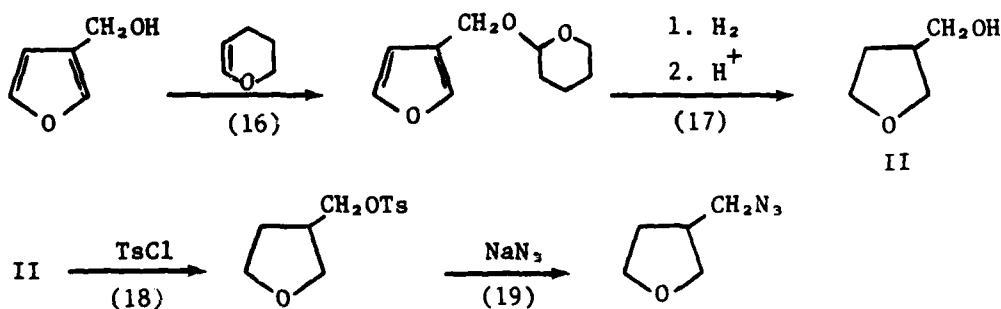


Equations (12) through (14) are described by Gatos.¹⁸ The replacement of the tosyl groups with azido groups, equation (15), was accomplished in dimethyl sulfoxide (DMSO). The desired product distilled at 81°C (0.01 Torr) to give a clear colorless liquid in 80% yield (based on the tosylate).

Attempts to prepare 3,4-bis(azidomethyl) tetrahydrofuran via reaction of sodium azide with bis(chloromethyl) tetrahydrofuran were not successful.

3-Azidomethyl Tetrahydrofuran

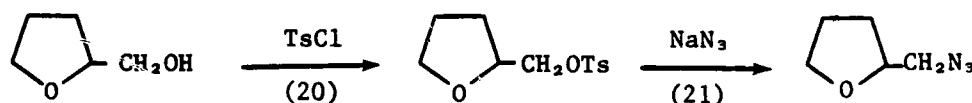
The preparation of 3-azidomethyl tetrahydrofuran, equations (16)-(19), follows that of the bis(azidomethyl) tetrahydrofuran.



The reactions shown in equations (16) through (18) were successfully completed and the products characterized. The azide displacement, equation (19), was attempted using DMSO as the solvent; a clear, colorless liquid was isolated, bp 72°C/15 Torr. Analysis of the product indicated a stable complex composed of 2 parts 3-azidomethyl tetrahydrofuran and 1 part DMSO. The complex appears to be thermally stable as demonstrated by a single peak in the GC analysis (injector temperature 250°C). Other reaction solvents need to be investigated to avoid the formation of a complex. However, rather than experiment with 3-azidomethyl THF in searching for an appropriate solvent we chose to examine 2-azidomethyl tetrahydrofuran.

2-Azidomethyl Tetrahydrofuran

Our reasons for using the 2-azidomethyl tetrahydrofuran are: (a) 2-azidomethyl tetrahydrofuran is easily prepared from the inexpensive tetrahydrofurfuryl alcohol, equations (20) and (21); (b) we were interested in determining if 2-substituted THF's can be copolymerized; and (c) DMSO may not form a complex with the 2-azidomethyl THF.



2-Azidomethyl THF was prepared from the tosylate in DMSO, as shown in equation (20) and (21). Unfortunately, a stable, distillable 1:1 complex of 2-azidomethyl THF and DMSO was obtained. It is interesting to note that 3,4-bis(azidomethyl) THF does not form a DMSO complex whereas 3-azidomethyl THF forms a 2:1 DMSO complex.

Polymer Synthesis

The major effort of polymer synthesis concerned the development of new polymerization techniques that can be used to control the physical properties of polymers derived from oxetanes and tetrahydrofurans.

Our experience as well as published data show that the polymerization of oxetanes is difficult to control because of high monomer reactivity. We found that the published¹⁹⁻²² techniques used to lower molecular weights had little effect. These included use of dilute solutions, high catalyst loading, water as a cocatalyst, high temperatures, and quenching at low polymer yields. High molecular weights are obtained if a small number of initiating species is formed during polymerization. However, since our objective was to achieve relative low molecular weights (2000 to 4000), our research was concerned with increasing the number of initiating species. We found that the molecular weight is limited by the ratio of monomer units to initiating species: when the catalyst (boron trifluoride in most cases) is added to an oxetane and alkanediol mixture, the catalyst preferentially reacts with the diol to form an "adduct" that initiates polymerization. Because the resultant molecular weight is inversely proportional to the adduct concentration, we have therefore demonstrated an accurate technique to vary and predict molecular weight by varying the number of initiating species.

Homopolymerization

Polymerizations were conducted using various ratios of oxetane to diol. Initially we used 3-methyl-3-(2-fluoro-2,2-dinitroethoxymethyl)oxetane (FOE) as the oxetane monomer and 2-(2,2-dinitropropyl)butane-1,4-diol as the diol. In three polymerizations the molecular weights of the resultant polymers were the same as the sum of the molecular weights of the oxetane and diol stoichiometry. The polymers were obtained in >90 wt% conversion, based on monomer, and had very narrow molecular weight distributions.

To rapidly explore a system that could possibly meet the Navy's short term goals, we concentrated on developing a polyol based on 3,3-bis(azidomethyl)oxetane (BAMO) because it is readily prepared in large quantities. BAMO polymerizations were conducted to produce a range of molecular weights for determining the relationship of melting point to molecular weight. The polyol derived from BAMO of molecular weight 3000 melts at 78°C. By varying the molecular weight from 1500 to 6500 little change in melting

point was observed (76° to 80°C). Considering the technique now used for cast-cured systems, the melting points of these polyols are at the upper practical limit.

Copolymerization

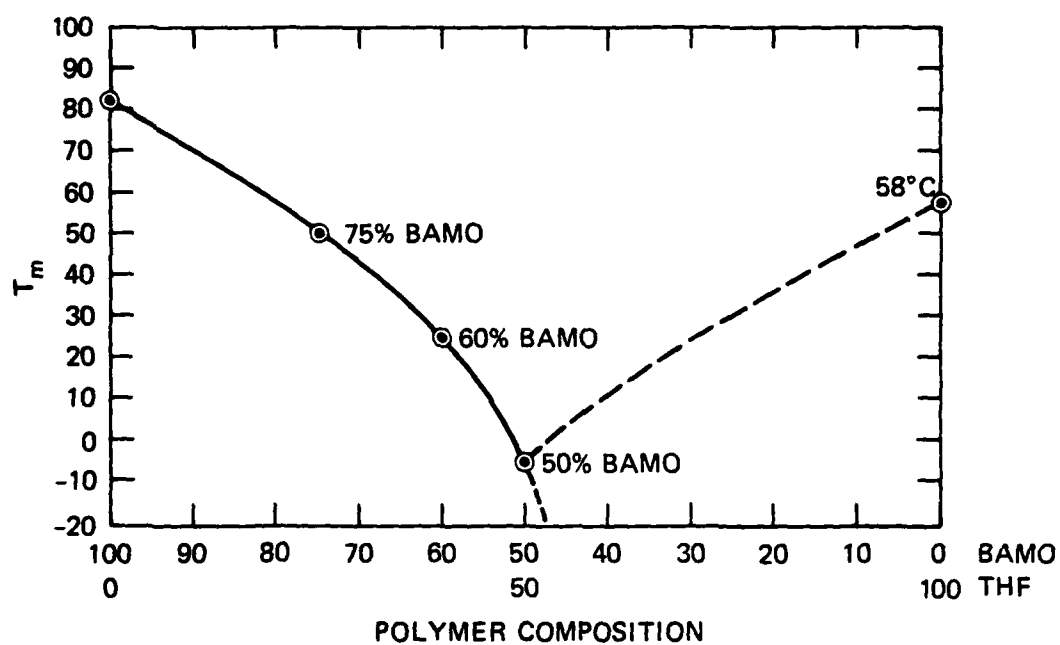
Because the melting point of poly-BAMO could not be lowered by molecular weight control, we shifted our research to the copolymerization of BAMO. Much of the literature states that the physical properties of macromolecules depend on the crystallinity of the system, and the symmetry of the repeating units. Also it has been demonstrated by many other investigators that a homopolymer tends to be more crystalline than a copolymer containing dissimilar monomers. This lower crystallinity lowers the melting point and glass transition temperature and increases the overall flexibility of the polymers.

With the foregoing in mind, we conducted copolymerizations of BAMO with THF. The two systems, namely 75/25 and 50/50 mole% BAMO/THF, show a dramatic lowering of melting point as shown in Figure 1. Physical properties are compared in Table 3.

Table 3
PROPERTIES OF BAMO/THF COPOLYMERS

<u>Polyol, BAMO/THF (mole %)</u>	<u>Molecular Weight (Mw)</u>	<u>Melting Point (°C)</u>	<u>Density (g/cc)</u>	<u>ΔHf est. (kcal/100 g)</u>	<u>f</u>
100/0	6500	78	1.3	+60	1.92
75/25	6900	50	1.24	+42	2.0
60/40	6200	25	1.27	+28	2.0
50/50	7300	<0	1.18	+17	2.0

At a molecular weight of 6900 the 75/25 system had a melting point of 50°C, whereas the 50/50 system was a flowable oil at room temperature. The 75/25 mol% BAMO/THF is comparable in melting point to PEG 4000 (mp 55°C). Although THF is a nonenergetic monomer, the calculated heats of formation of the copolymers are still favorable. The functionalities of the copolymers were almost the theoretical value of 2.0.



SA-8627-13A

FIGURE 1 EFFECT OF MONOMER RATIO ON THE MELTING POINT
TRANSITION TEMPERATURE OF BAMO/THF COPOLYMER

Scale-Up of BAMO/THF Copolymer

The 50/50 mol% BAMO/THF polymer was selected for scale-up and subsequent formulation to a cured gumstock. As stated previously, the copolymer is a mobile oil at ambient temperature and its viscosity is relatively low compared with polymers with higher BAMO content. Viscosity was troublesome on a small scale, but stirring became easier as the batch size increased.

Polymerization temperature is considered the most important parameter for high monomer conversion. It is known²³ that the conversion of THF to polymer is 89% at 0°C, 72% at 30°C and 0% at the ceiling temperature of 85°C. Although our initial work was conducted at -20°C, we found that -5°C produces identical material. As a bonus, the polymerization viscosity is lowered somewhat at the higher temperature. Consequently, we examined four methods of polymer preparation at -5°C.

First we prepared the initiator by reaction of butanediol with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in THF. We then added BAMO to the THF solution over a 15-min period. A rapid uptake of BAMO and THF was observed over the first hour at which point the rate of THF uptake decreased. After 5 h 75% BAMO and 55% THF had been converted. After 20 h BAMO had reached a steady state of 98% conversion whereas THF reached a steady state of 85% after 38 h. Based on the amount of monomers remaining, the final polymer composition was calculated to be 56% BAMO/44% THF.

Due to the difference in reactivity of THF and BAMO one could expect that the head of the polymer chain would be rich in BAMO and the tail rich in THF; however, during the middle 60% of the polymerization time a 1:1 monomer uptake was observed.

A second method of preparation was examined to achieve a more random copolymer: BAMO was added dropwise to the THF initiator solution over the entire run of 42 h. In this case nearly 3 h passed before BAMO was in high enough concentration to take part in the polymerization, whereas 30% of the THF had polymerized. However, once BAMO began to polymerize the ratio of monomer uptake was 1:1. This rate of uptake continued for 23 h at which time the THF level decreased and BAMO homopolymerization predominated. After 45 h, a steady state was achieved, indicating a final 87% THF and 96%

BAMO uptake. The resultant polymer was similar to that obtained when BAMO and THF were added simultaneously, that is, a head rich in BAMO and a tail rich in THF. It should be noted that because THF was in excess during most of the run, the polymerization viscosity was relatively low until the final 2 h when the viscosity approached that observed in the previous run.

A third method, namely solution polymerization, was examined in an attempt to reduce the polymerization viscosity. It is well-known²⁴ that oxetanes readily polymerize in solution, whereas tetrahydrofuran polymerization is hindered. THF homopolymerization to 90% conversion is attained in bulk, but only a 27% conversion is achieved at room temperature in a 60% dichloromethane solution. However, the use of nitromethane is reported²⁴ to effect higher conversions. Consequently a BAMO/THF copolymerization was run in nitromethane. Analysis showed that the polymerization had achieved a steady state of 98% conversion of BAMO and 52% of THF after 24 h. We concluded that solution copolymerization of BAMO/THF will require further investigation if the need arises.

A fourth method of polymerization was examined in which all monomers and catalysts were stirred at -5°C for 3 min and then allowed to polymerize for 40 h without further stirring. After quenching, the resulting polymer was found to be identical in all respects to those obtained previously. As this method of polymerization alleviates the problems of stirring increasingly viscous material it is the method of choice for scale-up.

Gumstock Preparation and Testing of 50/50 mol % BAMO/THF Polymer

Gumstocks were prepared from bulk-polymerized 50/50 BAMO/THF polymers. The polymer was mixed with trimethylolethane to achieve the required crosslink density and then mixed with one equivalent of tolylene diisocyanate, which is the amount required to give an infinite network. After a 24 h at 65°C the samples were subjected to various tests.

The stress/strain curve, obtained by Instron measurement, gave a value of 115 psi at 425% elongation at a crosslink density of 10%. An average of 89,000 molecular weight between crosslinks was determined by swelling experiments. A Rheovibron study showed a classical E' curve for an elastomer from -80°C to room temperature and the E'' curve showed a single deflection at -54°C corresponding to the glass transition temperature.

Differential scanning calorimetry showed a flat trace until the onset of an exotherm starting at 210°C and maximizing at 254°C. Samples of polymer and gumstocks have been distributed to other investigators for further studies.

Monomer Reactivity

At this point in the program we had developed technology enabling us to prepare a variety of energetic monomers and then to controllably polymerize them. As previously stated, it is required that any candidate polymer be energetic, liquid at or below 50°C, and isocyanate curable. Due to the number of possible combinations of homopolymers and copolymers it was necessary to select monomer pairs that would give the best physical properties when used to prepare polyetherglycols. That is, apart from the energy content, information was needed on each monomer so as to produce homo- and copolymers with the lowest stereoregularity.

To ensure polymers of low stereoregularity it is necessary to match the ability of each monomer to take part in chain extension on a competitive basis. If reactivity is not matched, then a relatively well ordered block copolymer, rather than one with random distribution, would result.

We measured the reactivity ratios of monomer pairs. Not only did we expect to match reactivity ratios for preparing superior polymers, but the knowledge gained about the effect of substitution on the polymerization will aid in selecting new monomers. If we found that placing an energetic group in certain positions in the monomer reduces its ability to polymerize, then similar structures should be avoided.

The methods in the literature for determining reactivity ratios require that the polymer be analyzed for comonomer content. These data are collected for a series of initial monomer charges and the reactivity ratio is mathematically derived. The errors in polymer analysis can be considerable and therefore the resultant data can be only indicative of the reactivity ratio. Because our intent was to generate precise data, we considered other methods of measuring monomer uptake. As we have shown, using diol-initiating polymerization, we observe no cyclic oligomer production during propagation, so we chose to use "monomer remaining" techniques to measure monomer uptake. This method is as follows.

A series of polymerizations are conducted at various monomer ratios. At a point during the polymerization, a sample is removed and quenched in wet solvent. By introducing an internal standard, we can determine the unreacted comonomer content by GC. It is therefore assumed that the decrease in monomer content of this sample compared with the initial charge reflects the monomer content of the polymer.

These data are then used to determine the reactivity of the monomer pair. The calculation of reactivity ratio is derived from a series of rate equations that can be quite complicated. Their derivation is beyond the scope of this report. Nevertheless the literature is very helpful and many investigators^{25,26,27} have derived simplified methods of data handling. Although these methods are called "approximation methods", we have found that the results are very reproducible and closely reflect the polymerization ability of the monomers under investigation.

To handle the considerable amount of data required, to calculate the reactivity ratios, and to run least squares plots and generate instantaneous polymerization curves, a basic program was written and the data processed on an Apple II 48K computer. The program used is presented Figure 2.

The reactivity ratios measured for a series of azido monomers are given in Table 4.

Table 4
REACTIVITY RATIOS FOR MONOMER PAIRS

<u>Monomer Pair</u>	<u>Reactivity Ratio</u>	<u>Correlation Coefficient</u>
BAMO	1.73 ± 0.24	0.96
THF	0.44 ± 0.17	
BAMO	1.62 ± 0.35	0.99
AZOX	0.47 ± 0.07	
BAMO	1.01 ± 0.11	0.99
AMMO	1.34 ± 0.07	

Based on these data we generated the instantaneous polymerization curves shown in Figures 3 through 5. These data clearly show that the copolymer derived from BAMO/AMMO follows the ideal copolymer composition curve: the polymer composition reflects the monomer charge. Because both monomers have nearly equal reactivity, monomer insertion is completely random and controlled only by the concentration of the monomers in the initial monomer charge.

Although BAMO/AZOX and BAMO/THF do not follow the ideal polymer composition curve, deviation is not significant. As long as there is not a large excess of BAMO in the initial charge, a reasonably random composition can be expected. Note also that the reactivity ratio of THF and AZOX are almost equal and that an ideal copolymer would result from this system. We have not determined the AZOX/THF value at this time because the polymer derived from this monomer pair would be less energetic than BAMO/THF.

From these data the structure/polymerizability aspect can also be determined. For azido-substituted oxetanes the position of the azido group in the molecule dramatically affects its ability to polymerize. By placing the azido group on the gamma carbon (BAMO and AMMO), we produced a monomer that is readily polymerized. Very little difference in rate is observed when either one or two azido groups are placed in this position. But placing the azido group on the beta carbon (AZOX) reduces the ability to polymerize by nearly an order of magnitude. It may be assumed that if the substitution is placed on the alpha carbon then the monomer will be unpolymerizable.

Polymer Evaluation

During the course of this research we investigated ten new polymer systems:

Poly(BAMO)
Poly(AZOZ)
Poly(AMMO)
Poly(BAMO/THF)
Poly(BAMO/AMMO)

Poly(BAMO/AZOX)
Poly(BAMO/BNMO)
Poly(AZOZ/AMMO)
Poly(AZOX/THF)
Poly(AMMO/THF)

```

5 DIM E(7,7),F(7,7),G(7,7),H(7,7),K(7,7),O(7,7),P(7,7),T(7,7)
10 PRINT "STANDARDIZATION CALCULATION---"
15 PRINT "INPUT THE NUMBER OF GC SHOTS"
20 INPUT N1
25 PRINT "INPUT THE WEIGHT OF STANDARD"
30 INPUT WS
35 PRINT "INPUT THE WEIGHT OF MONOMER 1"
40 INPUT W1
45 PRINT "INPUT THE WEIGHT OF MONOMER 2"
50 INPUT W2
55 FOR I = 1 TO N1
60 PRINT "INPUT THE AREA OF STANDARD IN GC SHOT 'I"
65 INPUT A(I)
70 A = A + A(I)
75 PRINT "INPUT THE AREA OF MONOMER 1 IN GC SHOT 'I"
80 INPUT B(I)
85 B = B + B(I)
90 PRINT "INPUT THE AREA OF MONOMER 2 IN GC SHOT 'I"
95 INPUT C(I)
100 C = C + C(I)
110 NEXT I
120 R1 = B / A * WS / W1
125 R2 = C / A * WS / W2
130 PRINT "REACTIVITY RATIO CALCULATION---"
135 PRINT "INPUT THE NUMBER OF RUNS AT DIFFERENT"
140 PRINT "INITIAL MONOMER CONCENTRATIONS"
145 INPUT N4
150 PRINT "INPUT THE NUMBER OF SAMPLES TAKEN"
155 PRINT "PER RUN"
160 INPUT N3
165 PRINT "INPUT THE NUMBER OF GC SHOTS"
170 PRINT "PER SAMPLE"
175 INPUT N2
180 PRINT "INPUT THE MOL. WT. OF MONOMER 1"
185 INPUT W3
190 PRINT "INPUT THE MOL. WT. OF MONOMER 2"
195 INPUT W4
196 Y2 = - 9999999
197 Y3 = 9999999
200 FOR I4 = 1 TO N4
205 PRINT "*****"
210 PRINT "* ANALYSIS FOR RUN 'I4' *"
215 PRINT "*****"
220 PRINT "INPUT THE WEIGHT OF SOLVENT+CATALYST"
225 PRINT "IN RUN 'I4"
235 INPUT Y0
240 PRINT "INPUT THE WEIGHT OF MONOMER 1"
245 PRINT "IN RUN 'I4"
250 INPUT W5
255 PRINT "INPUT THE WEIGHT OF MONOMER 2"
260 PRINT "IN RUN 'I4"
265 INPUT W6
270 FOR I3 = 1 TO N3
275 PRINT "FOR RUN 'I4' SAMPLE 'I3"
280 PRINT "INPUT THE WEIGHT OF SAMPLE TAKEN"
290 INPUT W7
295 PRINT "INPUT THE WEIGHT OF STANDARD ADDED"
300 INPUT W8
305 A = 0
310 B = 0
315 C = 0
320 FOR I2 = 1 TO N2
325 PRINT "INPUT THE AREA OF STANDARD"
330 PRINT "IN GC SHOT 'I2"
335 INPUT A(I2)
336 A = A + A(I2)
340 PRINT "INPUT THE AREA OF MONOMER 1"
345 PRINT "IN GC SHOT 'I2"
350 INPUT B(I2)
351 B = B + B(I2)
355 PRINT "INPUT THE AREA OF MONOMER 2"
365 PRINT "IN GC SHOT 'I2"
370 INPUT C(I2)
375 C = C + C(I2)
376 NEXT I2
380 W9 = (B * W8 * ((Y0 + W5 + W6) - W7)) / (A * R1 * W7)
385 M1 = W5 / W3

```

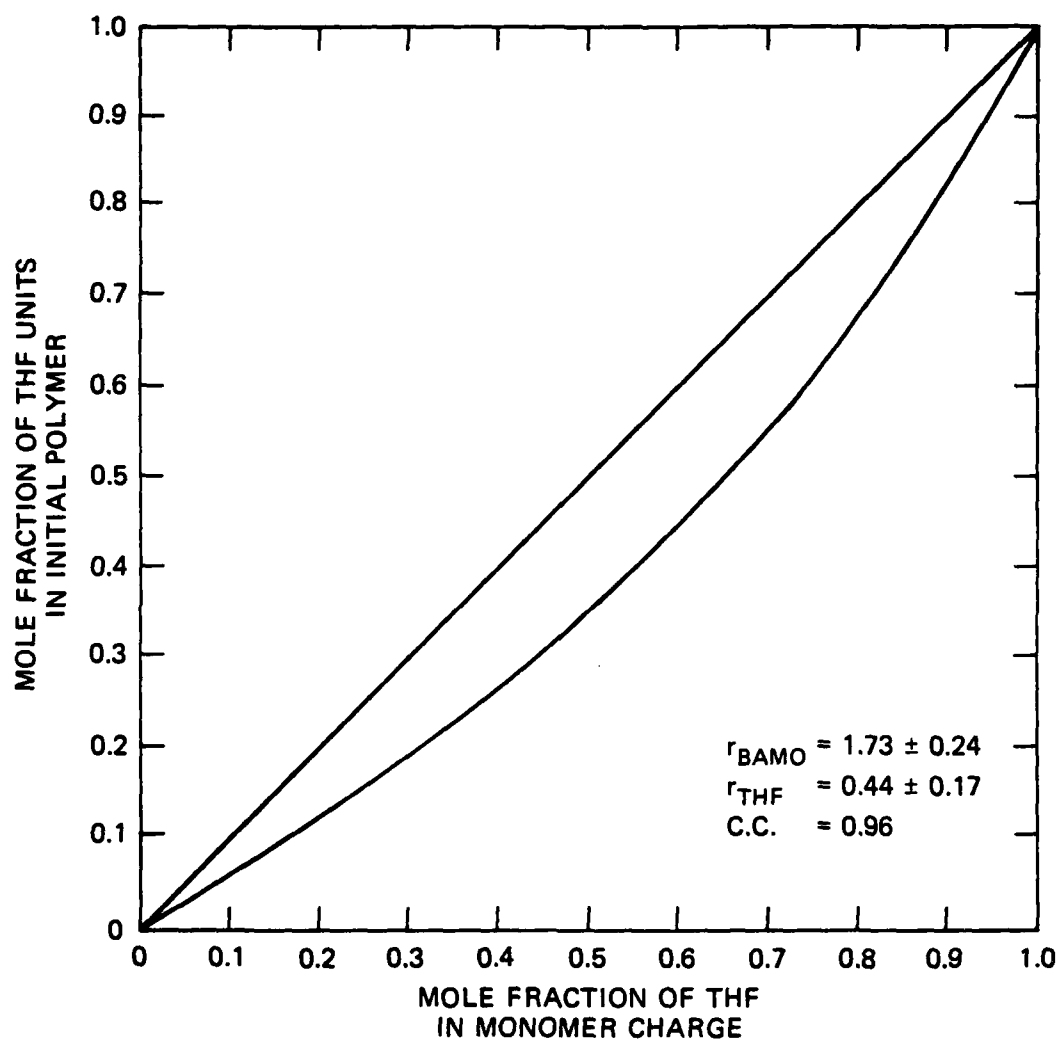
FIGURE 2 APPLE BASIC REACTIVITY RATIO PROGRAM

```

390 M2 = W6 / W4
400 W0 = (C * W8 * ((Y0 + W5 + W6) - W7)) / (A * R2 * W7)
405 M3 = W9 / W3
410 M4 = W0 / W4
415 M5 = M1 - M3
420 M6 = M2 - M4
425 E(I4,I3) = M1 / (M1 + M2)
430 F(I4,I3) = M2 / (M1 + M2)
435 G(I4,I3) = M5 / (M5 + M6)
440 H(I4,I3) = M6 / (M5 + M6)
445 K(I4,I3) = (M6 + M5) / (M1 + M2)
450 PRINT "RUN 'I4'---SAMPLE 'I3"
455 PRINT "IN. MOLEX A", "IN. MOLEX B"
460 PRINT E(I4,I3), F(I4,I3)
475 PRINT "MOLEX A IN POLY", "MOLEX B INPOLY"
480 PRINT G(I4,I3), H(I4,I3)
485 PRINT "PERCENT CONVERSION"
490 PRINT K(I4,I3)
500 X = E(I4,I3) / F(I4,I3)
505 Y = G(I4,I3) / H(I4,I3)
510 L2 = K(I4,I3) * (1 + X) / (1 + Y)
515 L1 = L2 * Y / X
520 Z = (LOG (1 - L1)) / (LOG (1 - L2))
525 O(I4,I3) = Y / (Z * Z)
530 P(I4,I3) = (Y - 1) / Z
535 IF O(I4,I3) < Y2 GOTO 545
540 Y2 = O(I4,I3)
545 IF O(I4,I3) > Y3 GOTO 555
550 Y3 = O(I4,I3)
555 NEXT I3
560 NEXT I4
565 AA = SQR ((Y2 * Y3))
570 FOR I4 = 1 TO N4
575 FOR I3 = 1 TO N3
580 Q(I4,I3) = O(I4,I3) / (AA + O(I4,I3))
585 T(I4,I3) = P(I4,I3) / (AA + O(I4,I3))
590 OX = OX + Q(I4,I3)
600 OY = OY + T(I4,I3)
605 XS = XS + (Q(I4,I3) ^ 2)
610 YS = YS + (T(I4,I3) ^ 2)
615 XY = XY + (T(I4,I3) * Q(I4,I3))
620 NEXT I3
625 NEXT I4
630 A = N4 * N3
635 SL = ((A * XY) - (OX * OY)) / ((A * XS) - (OX ^ 2))
640 IN = (OY - (SL * OX)) / A
645 RR = (((A * XY) - (OX * OY)) ^ 2) / (((A * XS) - (OX ^ 2)) * ((A * YS) - (OY ^ 2)))
650 PRINT "CORRELATION COEFFICIENT=" SQR (RR)
655 R4 = - (IN * AA)
660 R3 = SL + IN
665 PRINT "R1=R3, R2=R4"
670 DD = (A * XS) - (OX ^ 2)
675 SE = SQR ((A * YS) - (OY ^ 2) - ((SL ^ 2) * DD)) / SQR ((A - 2) * A)
680 SS = SE * (SQR ((A / DD)))
685 SI = SE * SQR ((XS / DD))
690 D1 = SQR ((SI ^ 2) + (SS ^ 2))
700 D2 = SQR (((- AA * SI) ^ 2))
705 PRINT "DEV. IN R1=", "DEV. IN R2="
710 PRINT "+/-" D1, "+/-" D2
720 PRINT "CALCULATED COMPOSITION CURVE"
725 PRINT "*****"
730 PRINT "IN. MOLE IN. MOLE FIN. MOLE FIN. MOLE"
735 PRINT "FRAC. A FRAC. B FRAC. A FRAC. B"
740 PRINT "*****"
745 FOR F1 = .05 TO .95 STEP .05
750 F2 = 1 - F1
755 C1 = ((R3 * (F1 ^ 2)) + (F1 * F2)) / ((R3 * (F1 ^ 2)) + (2 * F1 * F2) + (R4 * (F2 ^ 2)))
760 C2 = 1 - C1
765 F1 = INT (1000000 * F1 + .5) / 1000000
770 F2 = INT (1000000 * F2 + .5) / 1000000
775 C1 = INT (1000000 * C1 + .5) / 1000000
780 C2 = INT (1000000 * C2 + .5) / 1000000
785 PRINT F1 TAB( 11) F2 TAB( 21) C1 TAB( 32) C2
790 NEXT F1
795 END

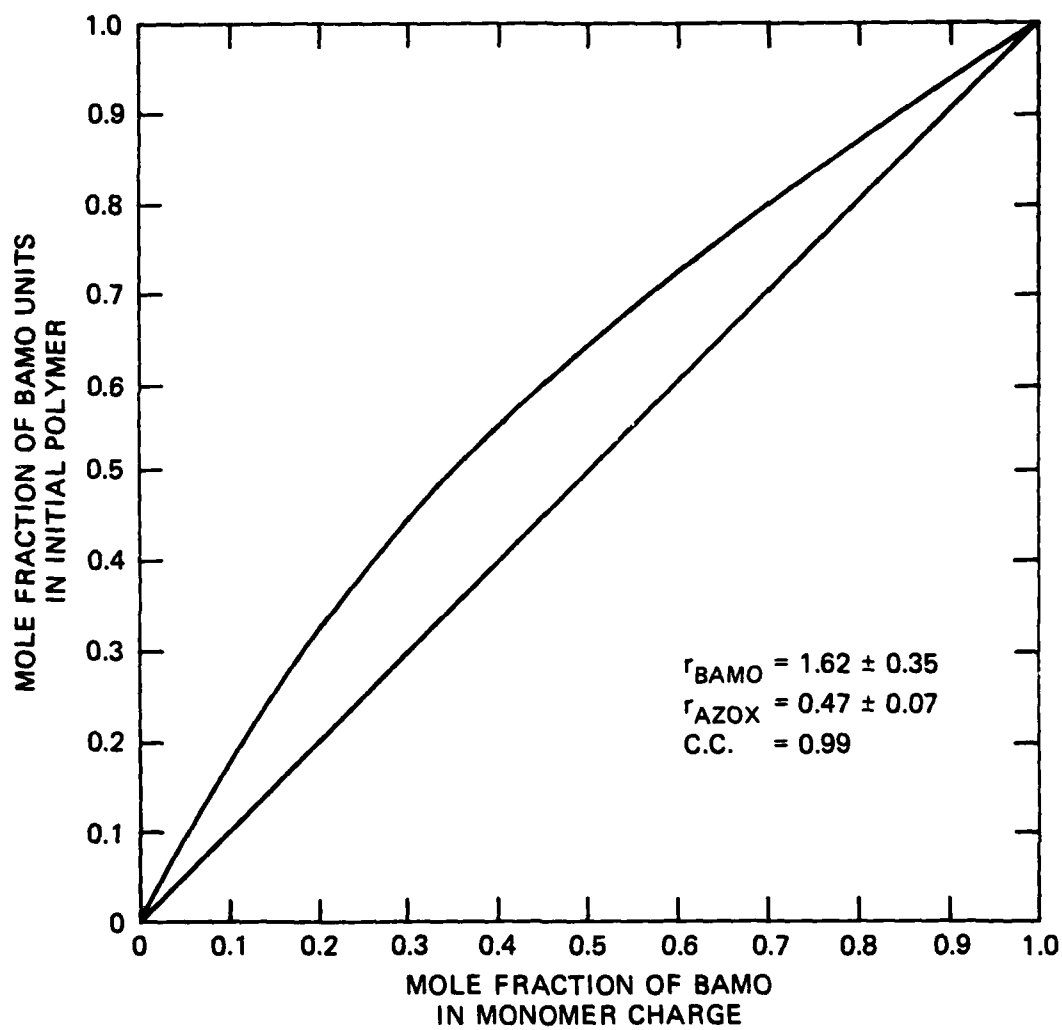
```

APPLE BASIC REACTIVITY RATIO PROGRAM (Concluded)



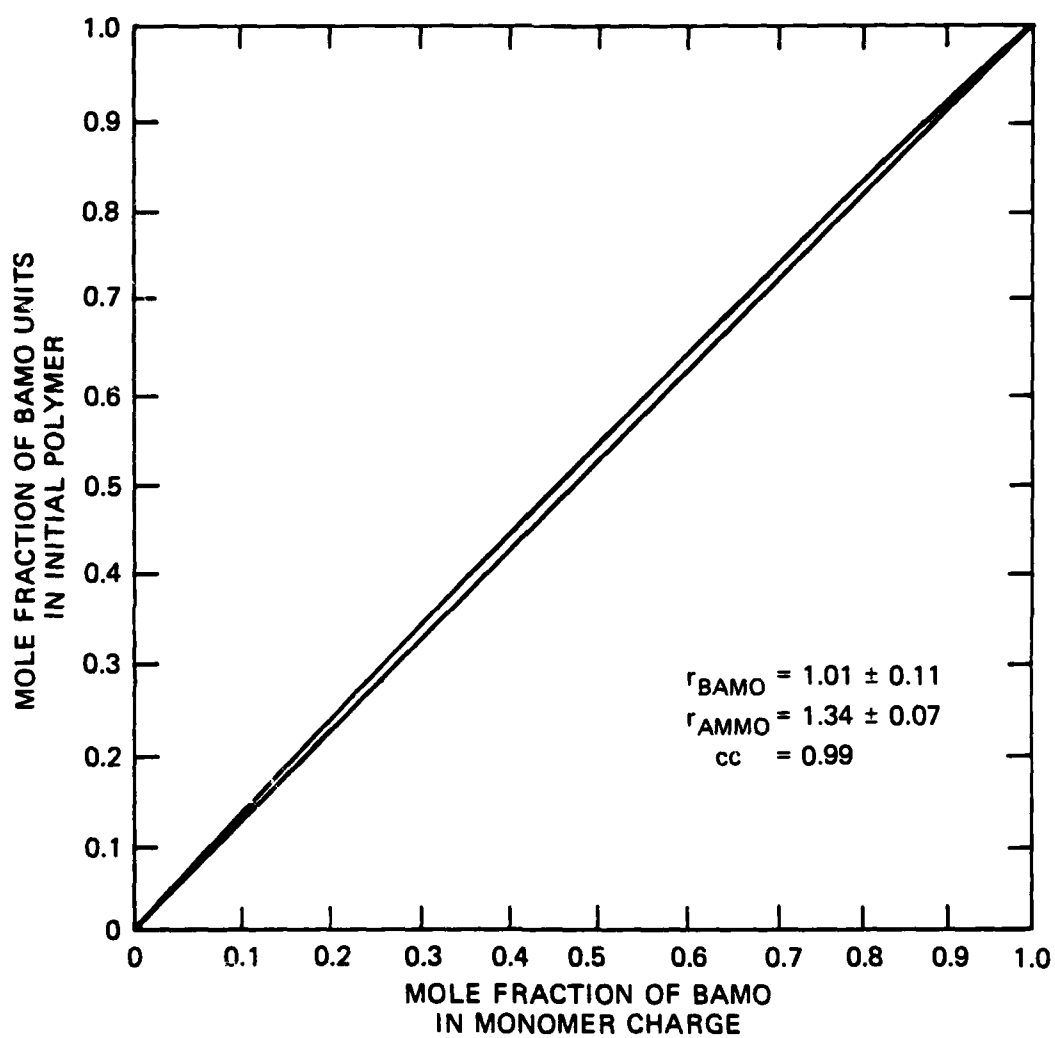
JA-323525-4

FIGURE 3 INSTANTANEOUS BAMO/THF COPOLYMER COMPOSITION CURVE



JA-323525-6

FIGURE 4 INSTANTANEOUS BAMO/AZOX COPOLYMER COMPOSITION CURVE



JA-323525-3

FIGURE 5 INSTANTANEOUS BAMO/AMMO COPOLYMER COMPOSITION CURVE

These polymers have been prepared and preliminary characterizations are complete. Samples have been submitted to various investigators for further evaluation.

The density and heats of formation presented in Table 5 were measured by Dr. R. Reed and Dr. M. Chan at NWC/China Lake. A more detailed and complete report will be presented by them at a later date. Additional data will become available as these systems are evaluated in formulations at various laboratories.

Table 5
DENSITY AND HEAT OF FORMATION OF
EXPERIMENTAL POLYMER SYSTEMS*

<u>Polymer System</u>	<u>ΔH_f Repeating Unit (Cal/g)</u>	<u>ΔH_f Corrected (Cal/g)</u>	<u>Density (g/cc)</u>
PEG	-1058	-	1.18
BAMO/THF (50/50)	211	168	1.19
BAMO/AMMO (50/50)	244	190	1.25
AZOX	286	192	1.34
BAMO/AZOX (50/50)	318	263	1.33

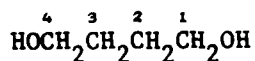
* Gumstocks were prepared using the Biuret trimer or hexamethylene diisocyanate (N-100) at a NCO/O ratio of unity. The catalyst was DBTDL.

We have demonstrated that the use of a diol to initiate the polymerization of cyclic ethers enables us to control the molecular weight of the resultant polymer. During the initial stages of our work with diol initiation we were only concerned with controlling molecular weight. Later we postulated that if the mechanism were better understood other property modifications might be achieved.

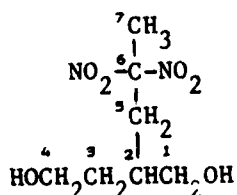
To better understand the role of the BF_3 /diol initiator used to control the molecular weight of polymers produced via cationic polymerization of cyclic ethers, we investigated the nature of the preinitiator. The preinitiator, formed by adding two equivalents of BF_3 to a substituted 1,4-butanediol, provides more control of polymerization than previously possible. However, the diol-based preinitiators only promote reaction at one of the two hydroxyl functions. The purpose of this structural investigation was to determine what differences exist between these two functional groups that could explain the different reactivity. Information derived from this study may aid in the design of a preinitiator that would initiate polymerization at both ends of the diol. This would allow the composition of the polymer to be better controlled and provide additional flexibility in polymer synthesis.

Our investigation used a variety of spectroscopic methods, the most useful being proton nuclear magnetic resonance spectroscopy (NMR). A carbon-13 NMR study was attempted, but the low solubility of the preinitiators prevented meaningful spectra from being obtained in a reasonable time. NMR spectra were obtained using either a Varian EM-390 spectrometer operating at 90 MHz or a Bruker HXS-360 Fourier transform NMR operating at 360 MHz.

The results of this study, while still preliminary, have displayed some interesting features. We investigated the BF_3 complexes of 1,4-butanediol (BDO) and 2-(2,2-dinitropropyl)-1,4-butanediol (DNPBDO).



1,4-Butanediol



2-(2,2-Dinitropropyl)-1,4-butanediol

The BF_3 was added to the diols both as the gas and as the etherate. In each case a mole ratio of two BF_3 to one diol was used. In several cases the preinitiator was added to a single equivalent of 3,3-dimethyloxetane to form the actual initiator species.

The proton NMR of 1,4-butanediol (BDO) displayed the expected AA'XX' type spectrum Figure 6, but when BF_3 was added the resolution of the spectrum was lost, Figure 7. This was likely caused by a restriction of free rotation of the molecule. This would imply that there was some conformation preferred in the complex. The nature of this conformation was not obvious by inspection of the spectrum.

Substitution at the 2-position of 1,4-butanediol results in an asymmetric center in the molecule. Thus the spectrum of 2-(2,2-dinitropropyl)-1,4-butanediol was quite complicated, even at 360 MHz, Figure 8. Several of the proton coupling constants were apparent from inspection of the spectrum. First-order approximations of the coupling constants revealed some aspects of the solution conformation of the molecule. In several cases it appeared that there was a difference between the two hydroxyl functions in the molecule. Infrared spectroscopy of a solution of DNPBDO revealed that one hydroxyl was hydrogen bonded while one was not, Figure 9. This was also seen in the proton NMR spectrum, Figure 10. Whether the C-1 or C-4 hydroxyl was involved in this hydrogen bond could not be determined. Further, the electron donating group could not be identified.

A conformational model based on dihedral angles derived from coupling constants allowed a number of hydrogen bonds to exist. It is important to note that the proton spectrum represents the time-averaged conformation. It is possible that there were several different species in solution that are rapidly interconverting. An attempt to determine which hydroxyl was more strongly hydrogen bonded was made using a shift reagent; however, the results were ambiguous.

Adding BF_3 to the diol in deuterated solvent solution again broadened the proton NMR signals, Figure 11. The only coupling constants apparent in the spectrum were from the methine proton at C-2 to the methylene protons of the dinitropropyl side chain at C-5. The couplings were the same in the complex as in the starting diol. If there is a hydrogen bond to a nitro

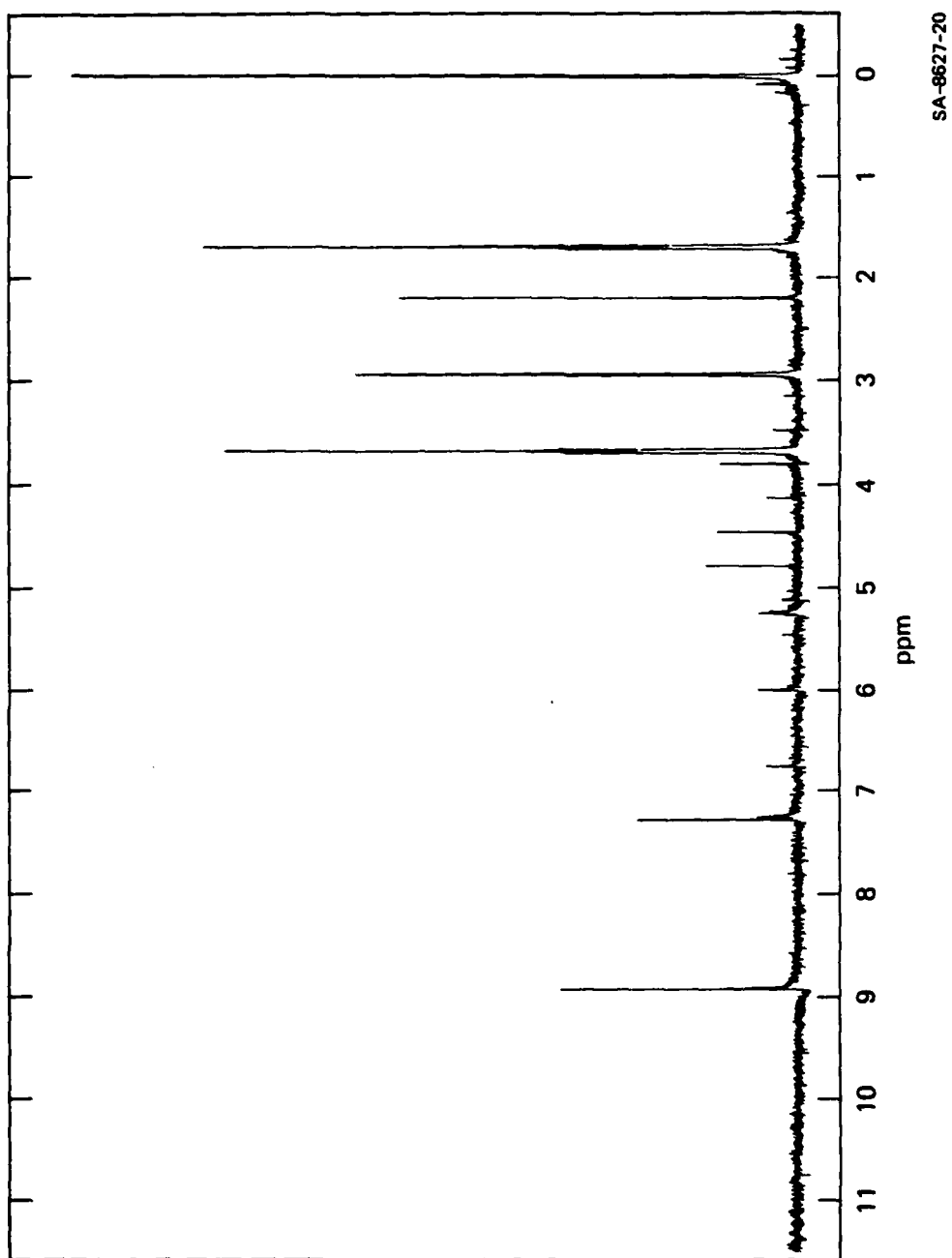
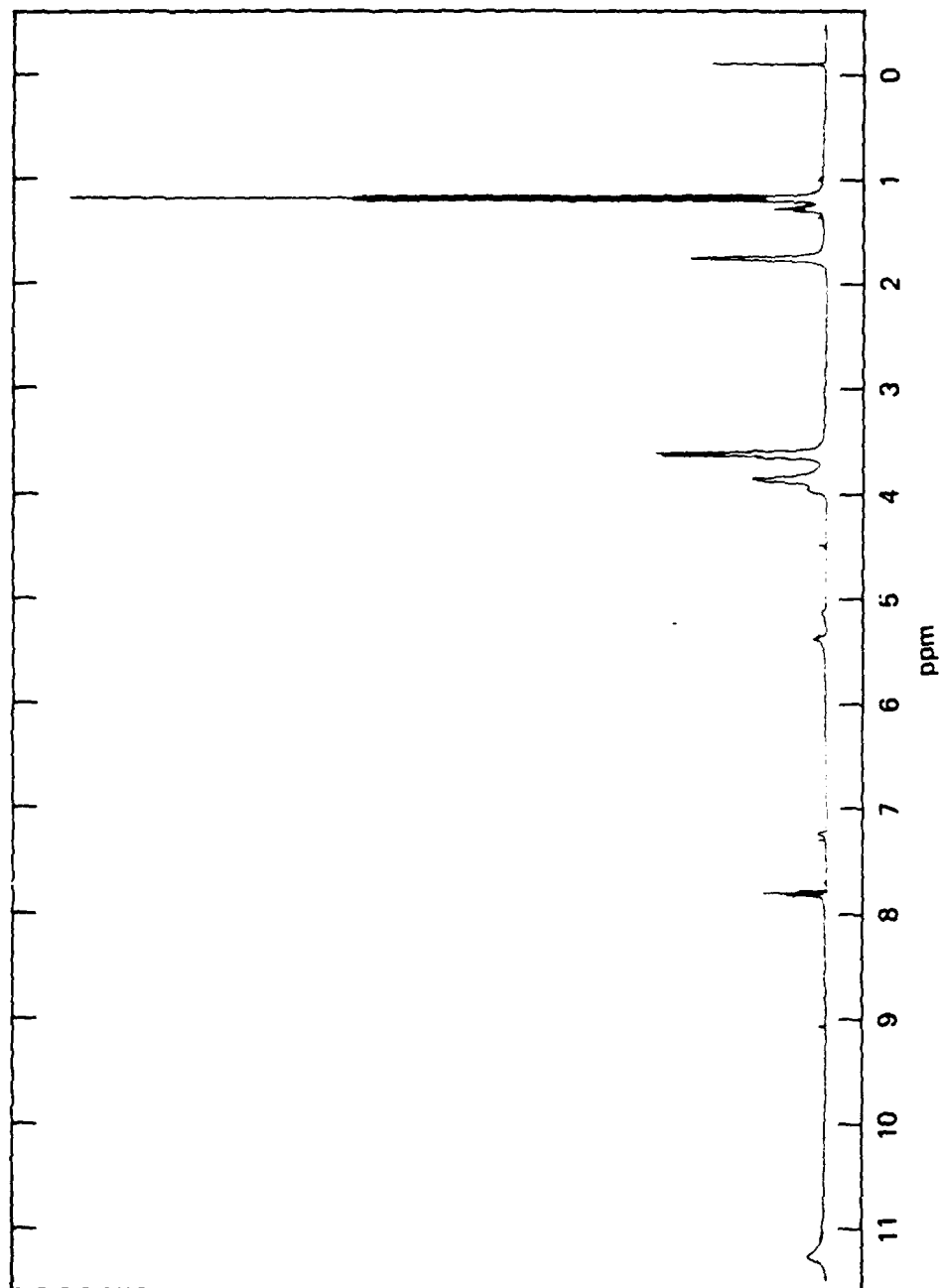
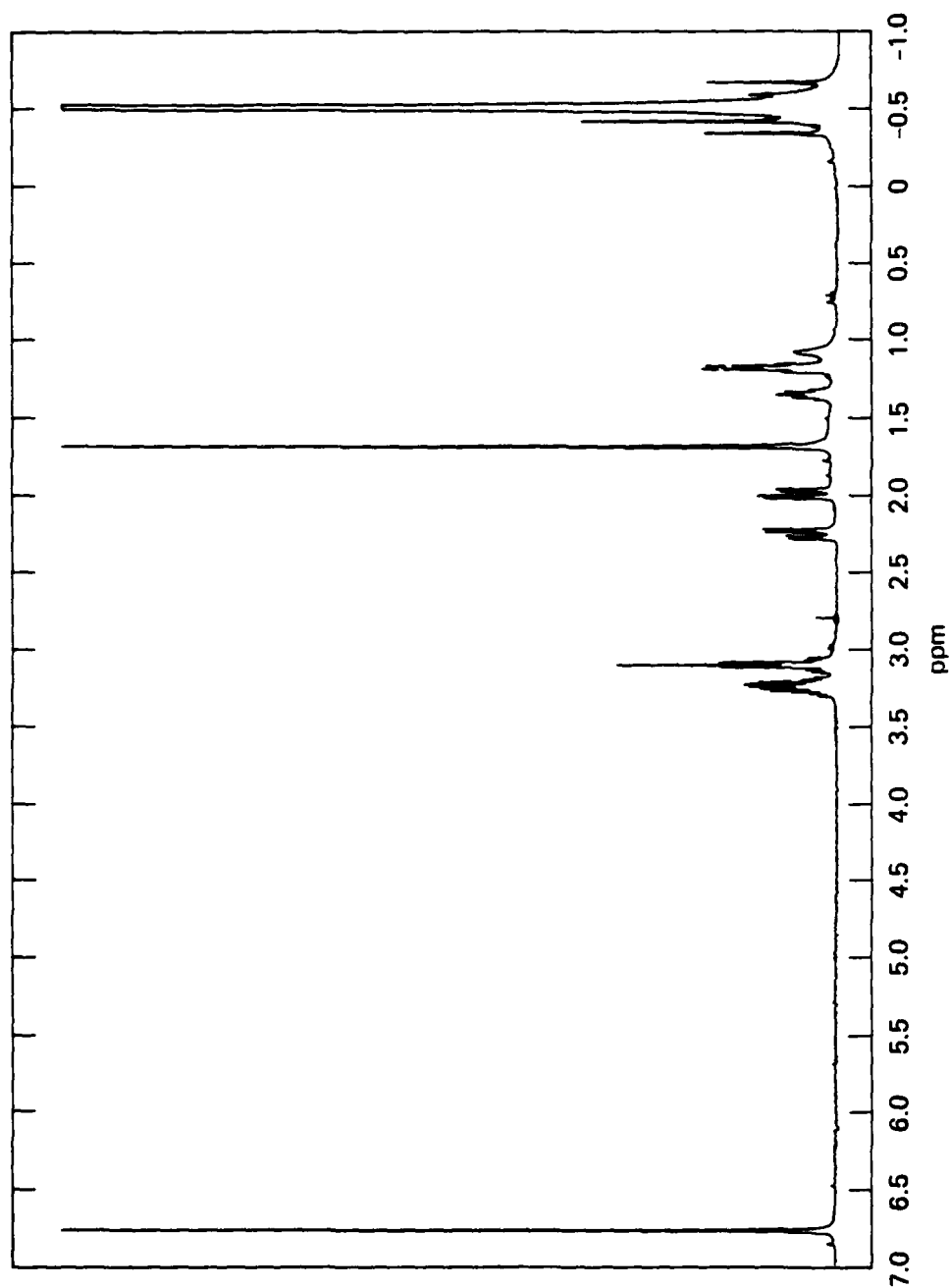


FIGURE 6 360-MHz NMR SPECTRUM OF 1,4-BUTANEDIOL



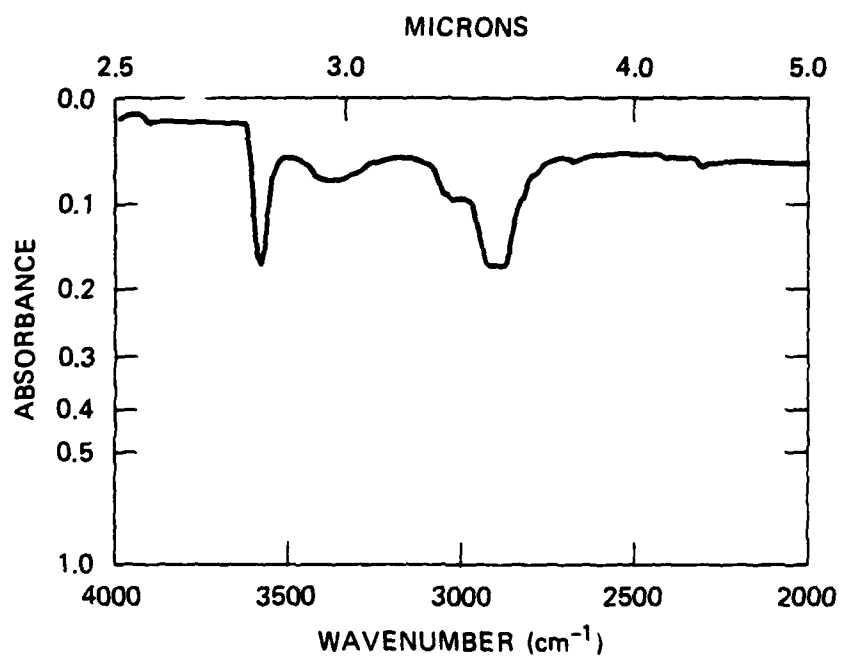
SA-8627-21

FIGURE 7 360-MHz NMR SPECTRUM OF 1,4-BUTANE DIOL/BORON TRIFLUORIDE COMPLEX



SA-8627-22

FIGURE 8 360-MHz NMR SPECTRUM OF 2-(2,2-DINITROPROPYL)-1,4-BUTANEDIOL



SA-8627-23

FIGURE 9 METHYLENE CHLORIDE SOLUTION INFRARED SPECTRUM
OF 2-(2,2-DINITROPROPYL)-1,4-BUTANEDIOL

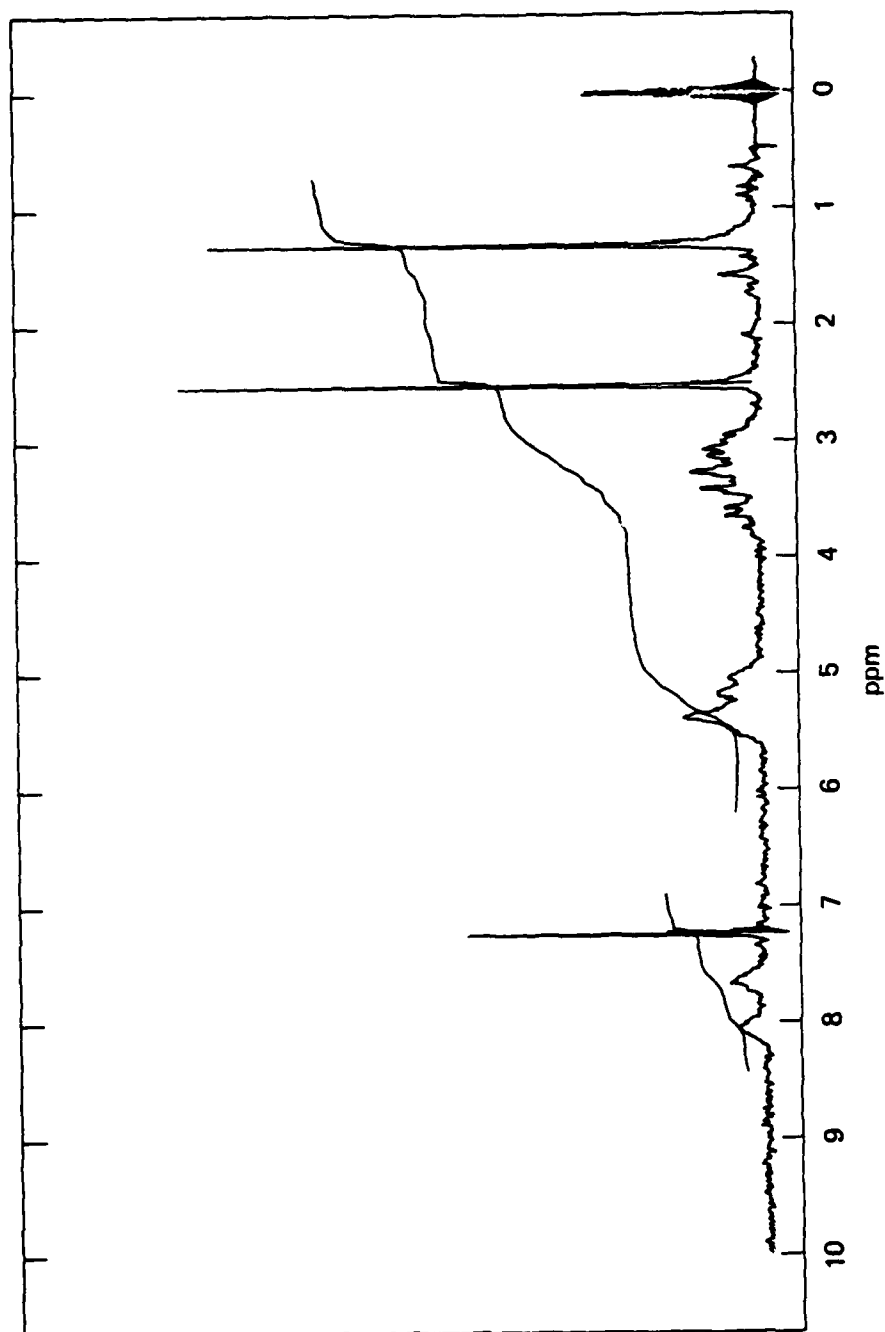
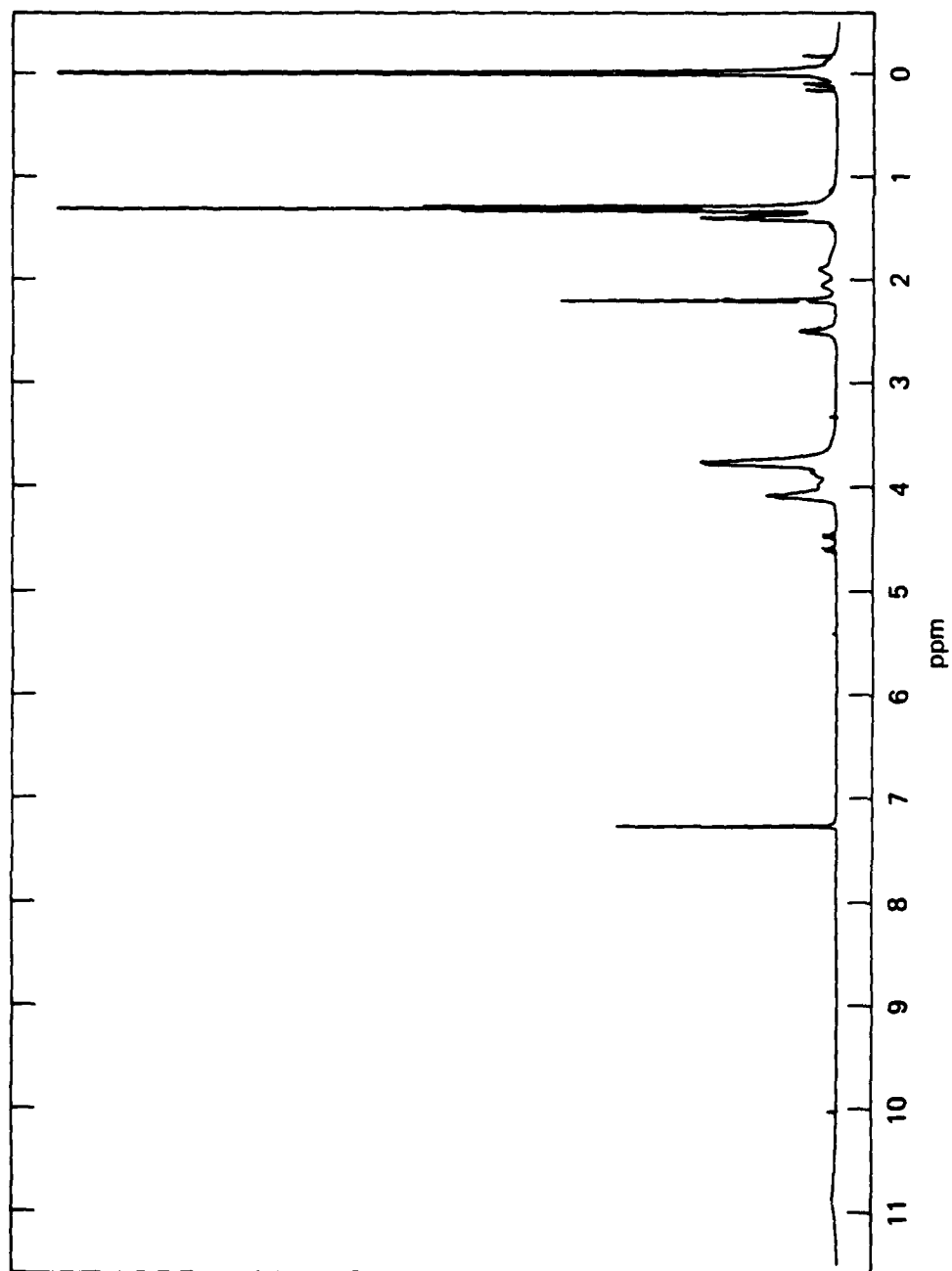


FIGURE 10 90-MHz NMR SPECTRA OF 2-(2,2-DINITROPROPYL)-1,4-BUTANEDIOL AND 13 mole% Eu(FOD)₃
SHIFT REAGENT

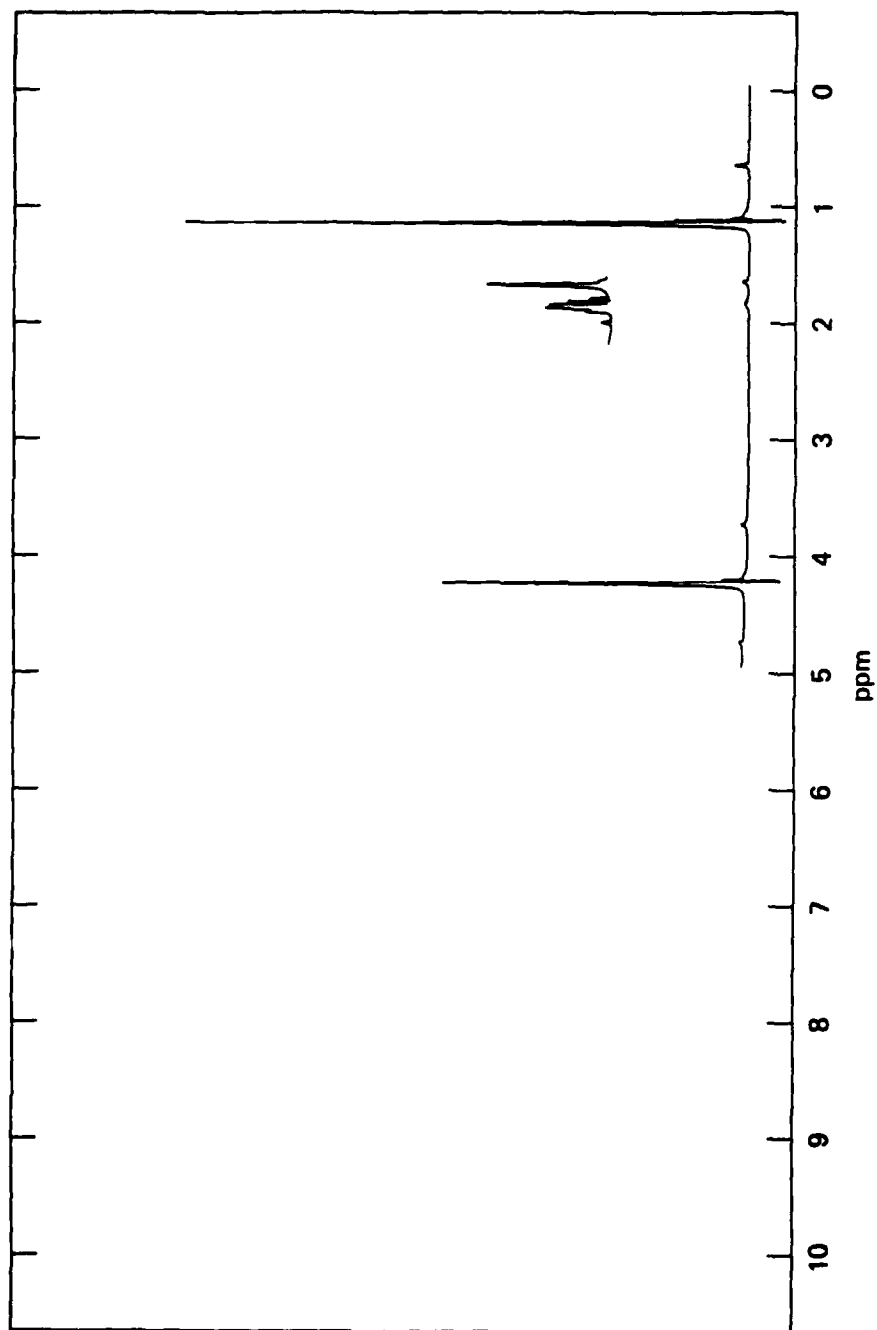


SA-8627-25

FIGURE 11 360-MHz NMR SPECTRA OF 2-(2,2-DINITROPROPYL)-1,4-BUTANEDIOL/BORON TRIFLUORIDE COMPLEX

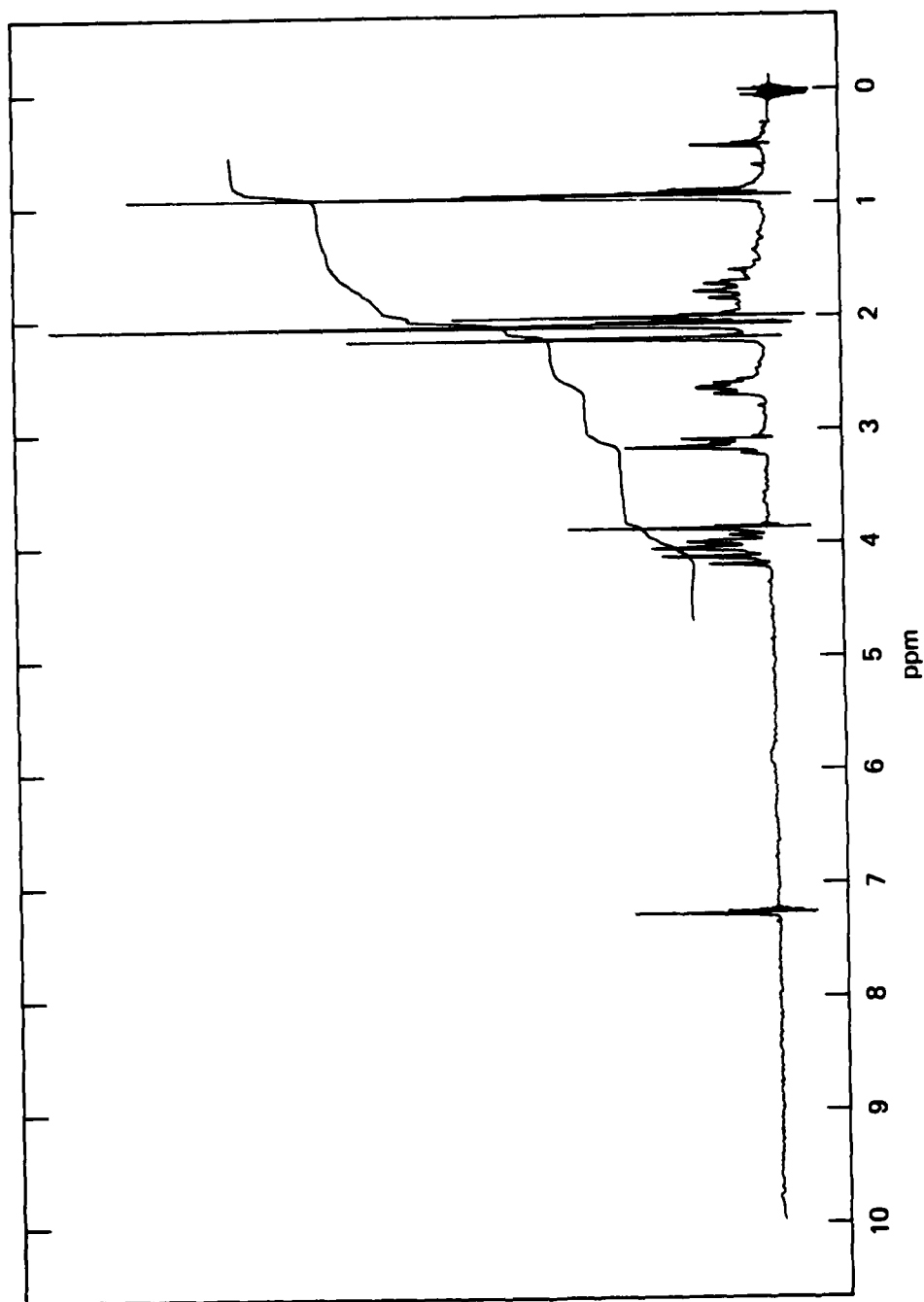
group in the diol, then the bond in the complex. In each case the protons of the hydroxyl-bearing methylenes (C-1 and C-4) were shifted down field as the electron density around the oxygen decreased. This shift seemed to be roughly equal for each diol, and supports the belief that the BF_3 complexes with each hydroxyl group. Further, it appears that the hydroxyl hydrogen remains bonded to the oxygen in the complex. This observation contradicts currently accepted mechanisms that require the protons to be free to initiate the polymerization.

An alternative mechanism would involve the SN-2 attack of a hydroxyl of the preinitiator on the 2-position of the oxetane. The fact that a diol molecule is incorporated in the head of the polymer supports this theory. If this mechanism is correct, it should be observable by proton NMR spectroscopy. Thus one equivalent of 3,3-dimethyloxetane was added to one equivalent of preinitiator. NMR spectra of the resulting solution indicated the presence of the proposed initiator. The oxetane signals disappeared and a set of more complicated signals appeared, Figure 12 and 13.



SA-8627-26

FIGURE 12 90-MHz NMR SPECTRA OF 3,3-DIMETHYLOXETANE



SA-8827-27

FIGURE 13 90-MHz NMR SPECTRA OF 2-(2,2-DINITROPROPYL)-1,4-BUTANEDIOL INITIATED POLYMERIZATION OF 3,3-DIMETHYLOXETANE

III CONCLUSIONS AND RECOMMENDATIONS

We have demonstrated that energetic polyether glycols can be prepared that appear to meet the requirements for use in high energy propellant formulations. We have prepared a series of energetic cyclic ether monomers that readily undergo cationic polymerization to form hydroxyl-terminated polymers and have shown that these materials are isocyanate curable.

The cured polymers exhibit the desired stability and elastomeric properties. Because of the low degree of crystallinity of these polymers, we observe a substantial increase in plasticizer miscibility and retention, and glass transition temperatures as low as -60°C . Because of the relative ease of synthesis of the monomers we have concentrated on azido polymers to obtain the required energy content.

We have developed a polymerization technique that produces polymers of preselected molecular weight and difunctionality. We also examined the relationship between monomer structure and polymerizability to provide a rationale for new monomer synthesis. This information was also used to select monomer pairs for copolymerization to produce completely random copolymers.

During the last year of this contract we transferred the technology to Rocketdyne, Canoga Park, CA for scale-up of the BAMO/THF polymer system. As a result of Rocketdyne's efforts other organizations have received multipound quantities of the polymer for evaluation.

We make the following recommendations:

- (1) Other polymer systems should be scaled-up for evaluation. Although BAMO/THF can be considered energetic, the THF content detracts from the total energy of the polymer. We have developed polymers based on copolymerization of two azido monomers and we therefore recommend that BAMO/AMMO and BAMO/AZOX be scaled-up and evaluated in propellant formulations.
- (2) We have not optimized the monomer ratios in any of the polymer systems, but have shown that monomer ratios in the monomer charge are reflected in the final polymer. We

therefore recommend that optimum monomer ratios be investigated with respect to energy content and elastomeric properties.

- (3) The main stumbling block has been the lack of known chemistry of introducing energetic groups into acid-sensitive molecules. We highly recommend that nonacidic nitration and nonacidic nitramine synthesis be investigated. When this chemistry has been developed many new materials may be available for new polymer systems.

IV EXPERIMENTAL DETAILS

Monomer Synthesis Procedures

The experimental procedures reported below are either new synthetic reactions that are not reported in the literature or are significantly modified versions of known reactions. All other experiments reported in the text duplicate published procedures.

Dimethyl 2-(2,2-Dinitropropyl)-1,4-butanedioate

A mixture of 155 g (1.3 mol) 1,1-dinitroethane, 205 g (1.3 mol) dimethyl itaconate, 20 ml 20% aqueous sodium hydroxide, 250 mL water, and 500 mL methanol was refluxed for 5 days. The reaction mixture was cooled, and the lower organic phase was separated. The aqueous phase was extracted with 500 mL of methylene chloride; this was combined with the organic phase, washed with 5% sodium bicarbonate, dried over magnesium sulfate, and evaporated. The product was 267 g of a dark oil 75% yield that crystallized on standing. This product was used without further purification. ^1NMR (CDCl_3) δ 2.2 (2, CH_3CNO_2), 2.75 (d, $J = 7$ Hz), 3.2 (m, CH), 3.7 (s, CH_3O), 3.75 (d, CH_2CNO_2 $J = 7$ Hz).

2-(2,2-Dinitropropyl)-1,4-butanediol

A solution of 32 g (0.12 mol) of dimethyl 2-(2,2-dinitropropyl)-1,4-butanedioate in 400 mL THF was added to a mixture of 7 g (0.32 mol) of lithium borohydride in 700 mL THF at 23°C over a period of 1 h. The reaction mixture was stirred for an hour at 25°C, and 50 mL of water was added cautiously. The mixture was reduced to 100 mL volume on a rotary evaporator and then diluted to 200 mL with water. This solution was extracted with ether to give 20 g crude product in 75% yield. This product was used without further purification. $^1\text{H NMR}$ (CDCl_3) δ 1.7 (m, CH_2C), 2.2 (s, CH_3), 2.6 (m, CH), 3.7 (m, CH_2OH , CH_2NO_2).

3-(2,2-Dinitropropyl)tetrahydrofuran (3-DNP THF)

A solution of 25.4 g (0.09 mol) trifluoromethane sulfonic acid in 400 mL ether was added to a mixture of 20 g (0.09 mol) of 2-(2,2-dinitropropyl)-1,4-butanediol, 7.1 g (0.09 mol) pyridine, and 500 mL ether at 25°C

over a period of 1 h. After it was stirred an additional hour at 24°C, the ether solution was decanted, washed with 5% sodium bicarbonate, and dried with magnesium sulfate. The ether solution was evaporated, and the crude product was chromatographed on silica gel with methylene chloride as eluent to give 3.4 g pure product in 19% yield. ^1NMR (CDCl_3) δ 2.15 (s, CH_3), 2.64 (d, CH_2CNO_2 , $J = 6$ Hz), 3.3 (m, CH_2CH), 3.8 (m, CH_2OCH_2). Elemental anal. calcd. for $\text{C}_7\text{H}_{12}\text{N}_2\text{O}_5$: C, 41.17; H, 5.88; N, 13.72. Found: C, 41.09; H, 6.00; N, 13.64.

3,3-Bis(cyanomethyl)oxetane

To 50 g bis(chloromethyl)oxetane (0.323 mol) dissolved in 200 mL ethyl alcohol was added 34 g sodium cyanide (0.694 mol), and the resulting suspension was heated to reflux for 18 h. Filtration of the deep-red solution yielded 40 g (0.69 mol) sodium chloride. Further purification of the required product was found to lead to decomposition; hence, the ethyl alcohol was carefully removed and the viscous product was stored under nitrogen at 0°C until used.

Oxetane 3,3-Diacetic Acid

In 200 mL 30% potassium hydroxide was dissolved 36.2 g bis(cyanomethyl)oxetane. Then with vigorous stirring, 72 mL of 30% hydrogen peroxide was added dropwise at a rate so that the temperature did not exceed 60°C. After complete addition the reactor was purged with nitrogen and the reactants were warmed to 75°C. A strong evolution of ammonia gas was detected, but this ceased after 16 h. The clear orange solution was then cooled to room temperature and extracted with 200 mL diethyl ether. The aqueous solution was held at 20°C and acidified to pH 2.0 with concentrated hydrochloric acid. The resultant solution was then continuously extracted with ether for 2 weeks. The ether extract was evaporated to dryness, yielding 5.1 g of a viscous oil. From this product was recovered 3.7 g of white solid, which was shown to be the cyclic anhydride by elemental analysis, and titration against base showed that the oil was the required oxetane 3,3-diacetic acid. Anhydride anal. calcd. for $\text{C}_7\text{H}_8\text{O}_4$: C, 53.85; H, 5.12. Found: C, 53.41; H, 5.21. Acid anal. calcd. for $\text{C}_7\text{H}_{10}\text{O}_5$: C, 48.27; H, 5.24. Found: C, 48.01; H, 5.57.

3-Methyl-3-(potassium 2,2-dinitroethoxymethyl)oxetane

Potassium hydroxide (6.6 g; 0.1 mol) was dissolved in 30 g 3-methyl-3-hydroxymethyloxetane by stirring at 50°C for 18 h. This solution was cooled and mixed with 100 mL ether to facilitate stirring. To this mixture was added a solution of 8.25 g (0.05 mol) of trinitroethane in 50 mL ether at 25°C over a period 1 h. The reaction mixture was refluxed for 2 h, cooled, and filtered. The filtered salt was washed with ether and dried under vacuum. The salt was used in the subsequent fluorination without purification.

3-Methyl-3-(2-fluoro-2,2-dinitroethoxymethyl)oxetane (FOE)

A mixture of 6.33 g (0.025 mol) of 3-methyl-3-(potassium 2,2-dinitroethoxymethyl)oxetane in 70 mL methanol was placed in a flask fitted with a gas inlet over the liquid surface and dry ice/acetone condenser. The flask was purged with nitrogen, and perchloryl fluoride was added at a rate that maintained a slow reflux for 2 h. After 70 mL of water was added to the flask, the mixture was extracted with methylene chloride. The methylene chloride solution was dried and evaporated, leaving a crude product. Chromatography on silica gel with methylene chloride showed that the product was 1.0 g of pure FOE in 17% yield. ^1H NMR (CDCl_3) δ 1.28 (s, CH_3), 3.77 (s, CH_2O), 4.41 (s, CH_2 ring), 4.65 (d, CH_2F , $J = 17$ Hz).

3,4-Bis(hydroxymethyl)tetrahydrofuran Bis(p-toluenesulfonate)

A solution of 38 g (0.02 mol) of p-toluenesulfonyl chloride in 50 mL of pyridine was added to a solution of 7.8 g (0.06 mol) 3,4-bis(hydroxymethyl)tetrahydrofuran in 100 mL of pyridine over a period of 15 min at 10°-20°C. The reaction mixture was stirred at ambient temperature for 18 h and then poured into 500 mL of ice water. The aqueous solution was decanted from the gummy residue, which was then dissolved in methylene chloride. The methylene chloride solution was dried with magnesium sulfate and evaporated, leaving 8.5 g (32% yield) of product which was used without further purification.

3,4-Bis(azidomethyl)tetrahydrofuran

A mixture of 8.5 g (19.3 mmol) of 3,4-bis(hydroxymethyl)-tetrahydrofuran bis(p-toluenesulfonate), 7 g (107 mmol) of sodium azide, and 50 mL of DMSO was stirred at 65°C for 18 h. The reaction mixture was cooled and poured into 200 mL of water, which was then extracted with methylene chloride. The methylene chloride solution was dried over magnesium sulfate and evaporated. The product was distilled at 81°C/0.01 torr to yield 2.9 g product (82% yield). ir: 2060 cm^{-1} (s, N_3), 1260 (m, COC). NMR (CDCl_3): δ 2.5 (m, CHCH), 3.4 (d, CH_2OCH_2 , $J_{\text{Hz}} = 7$), 3.8 (m, CH_2N_3). Elemental analysis calculated for $\text{C}_6\text{H}_{10}\text{N}_6\text{O}$: C, 39.56; H, 5.53; N, 46.13. Found: C, 39.54; H, 5.47; N, 44.80.

2-Hydroxymethyltetrahydrofuran p-Toluenesulfonate

A solution of 304 g (1.6 mol) of p-toluenesulfonyl chloride in 400 mL of pyridine was added to a solution of 96 g (0.94 mol) of 2-hydroxymethyltetrahydrofuran in 400 mL of pyridine over a period of 1 h at 10°-20°C. The reaction was stirred at ambient temperature for 4 h and then poured into 3 L of water. The oil that separated was washed repeatedly with water until it crystallized to a fine powder, which was filtered and dried in vacuum to yield 214 g of product (89% yield).

2-AzidomethylTetrahydrofuran

A mixture of 102 g (0.4 mol) of 2-hydroxymethyltetrahydrofuran p-toluenesulfonate (0.8 mol), sodium azide, and 300 mL of ethylene glycol was stirred at 80°C for 18 h. The reaction mixture was cooled and poured into 2 L of water, and the product was extracted with three 300 mL portions of methylene chloride. The methylene chloride solution was dried over magnesium sulfate and evaporated leaving 47 g of crude product, which was distilled at 54°/4 torr to yield 35.6 g (70%) pure product. ir: 2110 (s, N_3), 1090 cm^{-1} (m, COC). NMR (CDCl_3): δ 1.9 (m, CH_2CH_2), 3.3 (m, CH_2N_3), 3.9 (m, CH_2CH) Elemental analysis calculated for $\text{C}_5\text{H}_9\text{N}_3\text{O}$: C, 47.23; H, 7.13; N, 33.06.

3-Hydroxymethyltetrahydrofuran p-Toluenesulfonate

A solution of 15.25 g (0.08 mol) p-toluenesulfonyl chloride in 13 mL pyridine was added to a solution of 8.0 g (0.08 mol) 3-hydroxymethyltetrahydrofuran in 10 mL pyridine dropwise at 10°C. The reaction mixture was stirred at 0°-5°C for 18 h and then at ambient temperature for 24 h. It was then poured into ice water and stirred 30 min. The water was decanted from the organic phase, which was dissolved in ether, washed with water, and dried over magnesium sulfate. The ether was evaporated leaving 10.6 g (52% yield) of product, which was used without further purification.

3-Azidomethyltetrahydrofuran

A mixture of 10.6 g (0.041 mol) of 3-hydroxymethyltetrahydrofuran p-toluenesulfonate, 2.7 g (0.04 mol) sodium azide, and 50 mL DMSO was stirred at 65°C for 18 h. The reaction mixture was cooled to ambient temperature and poured into 200 mL water. The aqueous solution was extracted with three 50-mL portions of methylene chloride, and the methylene chloride solution was dried over magnesium sulfate and evaporated leaving 4.1 g of crude product. The product was distilled at 69°/15 torr to yield 3.1 g pure product (99.9% based on GC analysis). The product appeared to be 2:1 complex of 3-azidomethyl THF and DMSO. Both the NMR and elemental analyses supported this conclusion. ir: 2070 cm^{-1} (s, N_3), 1275 (m, S=O), 1055 (s, COC). NMR (CDCl_3): δ 1.9 (m, CH_2CH), 2.6 (s, CH_3), 3.3 (d, CH_2N_3 , $J_{\text{Hz}} = 8$), 3.8 (m, CH_2OCH_2). Elemental analysis calculated for $\text{C}_{12}\text{H}_{24}\text{N}_6\text{OS}$: C, 43.36; H, 7.28; N, 25.28. Found: C, 43.78; H, 7.15; N, 24.46.

3-Methyl-3-(p-toluenesulphoxymethyl)oxetane

90 g of 3-hydroxymethyl-3-methyl oxetane (0.88 mol) was dissolved in 71 g of pyridine (0.9 mol) in a 2000-mL roundbottom flask. The flask was then cooled to -5°C and, with vigorous stirring, 172 g of p-toluene sulphonyl chloride (0.9 mol) in 71 g of pyridine (0.9 mol) was added slowly. The rate of addition was maintained so that the contents of the flask were kept below 0°C. Upon complete addition, the solution temperature was held at -5°C for 30 min, then allowed to come to room temperature and held there for 2 h. The contents of the flask were then quenched by pouring into 3000 mL of ice water. The resultant solid was

filtered off, washed twice with ice water, and dried overnight under high vacuum. The required product was obtained in 100% yield, 224 g, and no further purification was necessary.

3-Azidomethyl-3-methyloxetane

200 g of 3-methyl-3-(p-toluenesulphoxymethyl)oxetane (0.78 mol), and 56 g of sodium azide (0.86 mol) were suspended in 500 ml of dimethyl formamide in a 2000-ml roundbottom flask. The reactants were heated to 85°C for 5 h and then allowed to cool to room temperature overnight. The contents of the flask were poured into 1000 mL of water and the solution extracted twice with 500 mL portions of methylene chloride. The combined extractions were washed with 500 mL of water and then dried over magnesium sulfate. The residue was first concentrated and then fractionated by passing it down an alumina column, and eluting it with methylene chloride. By this method 86 g of the required product was obtained, in 87% yield.

Polymerization Procedures

Materials

Burdick and Jackson UV grade THF and methylene chloride were used as received and stored over molecular sieves. Commercial grade boron trifluoride etherate was freshly distilled in vacuo before use. 1,4-Butanediol was distilled from calcium hydride and stored over molecular sieves. Monomers were freshly distilled from calcium hydride before use. All glassware was flame dried and swept with dry nitrogen immediately preceding the introduction of reactants. During polymerizations the reactants were maintained under a dry nitrogen atmosphere.

Typical Solution Polymerization Procedure

A flame-dried resin flask was charged with the calculated weight of diol as a 50 wt/wt% solution in methylene chloride. The solution was cooled to 0°C, and the desired amount of boron trifluoride etherate was added dropwise. After the solution was stirred 1 h the desired amount of monomer was added as a 20% w/w solution in methylene chloride over a 10-min period. After the solution was stirred for 24 h, the solution was quenched

with a volume of saturated aqueous sodium chloride solution equal to the volume of catalyst used. The organic layer was separated, washed with an equal volume of 10% aqueous sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. The organic fraction was then added to a vigorously stirred 10-fold volume excess of methanol. The resulting insoluble residue was separated and dried to constant weight under high vacuum at ambient temperature.

Typical Bulk Polymerization Procedure

A flame-dried resin flask was charged with the calculated weight of monomer and diol. The flask was then cooled down to the temperature selected for the polymerization, usually below -5°C . The calculated amount of boron trifluoride etherate was then added and the mixture stirred vigorously for 30 min. At this point the stirring may be stopped, but the cooling must be maintained during the entire polymerization.

When the polymerization reached a steady state, an equal volume of methylene chloride was added to dissolve the polymer mass, and a volume of saturated aqueous sodium chloride was added to quench the reaction. The organic layer was separated, washed with an equal volume of 10% aqueous sodium bicarbonate solution, and then dried over anhydrous magnesium sulfate. The resultant solution was added to a vigorously stirred 10-fold volume excess of methanol. The insoluble residue was separated and dried to constant weight under high vacuum at ambient temperature.

Functionality Determination

The polyol (1 g) was heated for 15 min at 95°C with 2 mL of a 2:1 mixture of pyridine and acetic anhydride. The resulting solution was then added to 50 mL of water and the mixture titrated with 0.1N sodium hydroxide. The titer of the polyol solution was compared with the titer of a blank containing no polyol. The difference between the blank solution and the polyol sample solution was used to calculate the hydroxyl functionality of the polymer.

Alternatively 1 g of the polyol was heated with an excess of trimethylsilyl chloride for 1 h. The mixture was then heated overnight under moderate vacuum to remove the volatile trimethyl silyl ether formed

by any water present in the sample. The residue was dissolved in deuterated chloroform (without TMS standard). The silylated end group content was then determined by NMR using benzene as the internal reference. The functionality of the polyol could be calculated from the number average molecular weight and the end-group content.

Molecular Weight Determination

All molecular weights were determined using a Waters gel permeation chromatograph equipped with a differential refractive index detector and a Data Module 730. The column set consisted of seven microstyragel columns (two 100 Å, two 500 Å, two 1000 Å, and one 10000 Å) connected in series. The eluting solvent was tetrahydrofuran. The system was calibrated with polypropylene glycol standards of molecular weight 800, 1200, 2000, and 4000. Molecular weight determinations were confirmed using a Chromatix KMX6 light-scattering analyzer.

REFERENCES

- 1a. D. L. Ross, E. Sincich, and J. M. Guimont, "Nitropolymers for Smokeless Propellants," SRI-International Research Brief, 19 December 1975, submitted to Air Force Rocket Propulsion Laboratory.
- b. D. L. Ross, E. Sincich, and J. M. Guimont, "Nitropolymers for Smokeless Propellants," SRI-International Research Brief, 13 July 1976, submitted to Air Force Office of Scientific Research.
- c. E. Sincich and D. L. Ross, "Nitropolymers for Smokeless Propellants," SRI-International Proposal PYU 78-053, 2 March 1978.
- d. "Nitro Ingredient Feasibility Demonstration," SRI-International, AFRPL Contract No. F04611-78-C-0051.
- e. Naval Research Reviews, Vol. XXXIII, No. 2, Office of Naval Research, Spring 1981, p. 28.
2. E. F. Witucki et al., J. Org. Chem., 37 152 (1972).
3. G. B. Bachmann and H. A. Tanner, J. Org. Chem., 4, 493 (1939).
4. M. C. Kloetzel, J. Am. Chem. Soc., 70, 3571 (1948).
5. M. C. Kloetzel, J. Am. Chem. Soc., 69, 2271 (1947).
6. P. Magee and M. C. Kloetzel, J. Org. Chem., 19, 168 (1953).
7. E. Brittan and E. Monroe, U.S. Pat. 2,373,011 (1945).
8. G. Olah, J. Org. Chem. 45, 1251 (1979).
9. G. Olah, Angew. Chem. Int. Ed., 18, 012 (1979).
10. Tse Lok Ho, Syn. Comm., 9 (4), 233 (1979).
11. C. Slabulsky, Nat. Acad. Sci. Proc., 23, 611 (1937).
12. O. F. Govaert and P. Cornand, Mededel Koninkl, Vlaam. Acad. Wetenschad Belg., Kl. Wetenschap., 16 (14) (1954).
13. D. Hartley, J. Am. Chem. Soc., 34, 4722 (1962).
14. R. E. Cochoy and R. R. McGuire, J. Org. Chem., 37 (19), 3041 (1972).

15. W. Carpenter, U.S. Pat. 3,138,609 (1964).
16. A. T. Camp et al., J. Am. Chem. Soc., 77, 751 (1955).
17. D. E. Erlick et al., J. Am. Chem. Soc., 76, 1374 (1954).
18. G. C. Gatos, U.S. Pat. 3,855,237 (1974).
19. H. Meervein, D. Delfs, and H. Morshel, Angew. Chem., 72, 927 (1960).
20. R. Chaing and J. Rhodes, Polymer Letters, 1, 643 (1969).
21. J. Hellman, Die Angwert Makromol. Chem., 74, 105 (1978).
22. S. Smith and A. J. Hubin, British Pat. 1,120,304 (1968).
23. L. A. Dickinson, J. Polym. Sci., 58, 857 (1962).
24. Encyclopedia of Polymer Technology, 9, 668-701 (1980).
25. T. Kelen and F. Tudos, J. Macromol. Sci.-Chem., A9(1), 1-27 (1975).
26. J. P. Kennedy, T. Kelen, and F. Tudos, J. Polym. Sci., 13, 2277-2289 (1975).
27. T. Kelen, F. Tudos, B. Turcsanyi, and J. P. Kennedy, J. Polym. Sci., 15, 3047-3074 (1977).

PATENTS, PUBLICATIONS, AND PRESENTATIONS

The following patent applications were submitted during the report period:

No. 262935, "Cationic Polymerization," (May 12, 1981)

No. 379354, "Energetic Copolymers and Method of Making Same," (May 18, 1982).

The following publications were submitted during the report period:

"The Controlled Cationic Polymerization of Cyclic Ethers," Journal of Polymer Sciences (September 1981).

"Copolymerization of 3,3-Bis(azidomethyl)oxetanes and Tetrahydrofuran," Journal of Polymer Sciences (September 1981).

"Recent Advances in the Synthesis of Azido Polymer Glycols," (abstract) 1982 JANNAF Propulsion Meeting (February 20, 1982).

"Determination of Reactivity Ratios of Comonomer Pairs," (abstract) 1982 JANNAF Propulsion Meeting (February 20, 1982).

The following presentations were made during the report period:

"A Technique for Preparing Low Molecular Weight Polyether Glycols," 1981 JANNAF Propulsion Meeting, New Orleans, LA (May 26, 1981).

"BAMO/THF Copolymer: A Candidate Energetic Polyether Glycol," 1981 Symposium on the Chemistry of Synthesis and Characterization of Energetic Monomers and Polymers, the Johns Hopkins University, Laurel, Maryland (July 21, 1981).

"Recent Advances in the Synthesis of Azido Polyether Glycols," Energetic Polymer Workshop, Chestertown, Maryland (August 17, 1982).

DISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. L.V. Schmidt Assistant Secretary of the Navy (R,E, and S) Room 5E 731 Pentagon Washington, D.C. 20350	1	Dr. F. Roberto Code AFRPL MKPA Edwards AFB, CA 93523	1
Dr. A.L. Slafkosky Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1	Dr. L.H. Caveny Air Force Office of Scientific Research Directorate of Aerospace Sciences Bolling Air Force Base Washington, D.C. 20332	1
Dr. Richard S. Miller Office of Naval Research Code 413 Arlington, VA 22217	10	Mr. Donald L. Ball Air Force Office of Scientific Research Directorate of Chemical Sciences Bolling Air Force Base Washington, D.C. 20332	1
Mr. David Siegel Office of Naval Research Code 260 Arlington, VA 22217	1	Dr. John S. Wilkes, Jr. FJSRL/NC USAF Academy, CO 80840	1
Dr. R.J. Marcus Office of Naval Research Western Office 1030 East Green Street Pasadena, CA 91106	1	Dr. R.L. Lou Aerojet Strategic Propulsion Co. P.O. Box 15699C Sacramento, CA 95813	1
Dr. Larry Peebles Office of Naval Research East Central Regional Office 666 Summer Street, Bldg. 114-D Boston, MA 02210	1	Dr. V.J. Keenan Anal-Syn Lab Inc. P.O. Box 547 Paoli, PA 19301	1
Dr. Phillip A. Miller Office of Naval Research San Francisco Area Office One Hallidie Plaza, Suite 601 San Francisco, CA 94102	1	Dr. Philip Howe Army Ballistic Research Labs ARRADCOM Code DRDAR-BLT Aberdeen Proving Ground, MD 21005	1
Mr. Otto K. Heiney AFATL - DLDL Elgin AFB, FL 32542	1	Mr. L.A. Watermeier Army Ballistic Research Labs ARRADCOM Code DRDAR-BLI Aberdeen Proving Ground, MD 21005	1
Mr. R. Geisler ATTN: MKP/MS24 AFRPL Edwards AFB, CA 93523	1	Dr. W.W. Wharton Attn: DRSMI-RKL Commander U.S. Army Missile Command Redstone Arsenal, AL 35898	1

DISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. R.G. Rhoades Commander Army Missile Command DRSMI-R Redstone Arsenal, AL 35898	1	Dr. E.H. Debutts Hercules Inc. Baccus Works P.O. Box 98 Magna, UT 84044	1
Dr. W.D. Stephens Atlantic Research Corp. Pine Ridge Plant 7511 Wellington Rd. Gainesville, VA 22065	1	Dr. James H. Thacher Hercules Inc. Magna Baccus Works P.O. Box 98 Magna, UT 84044	1
Dr. A.W. Barrows Ballistic Research Laboratory USA ARRADCOM DRDAR-BLP Aberdeen Proving Ground, MD 21005	1	Mr. Theodore M. Gilliland Johns Hopkins University APL Chemical Propulsion Info. Agency Johns Hopkins Road Laurel, MD 20810	1
Dr. C.M. Frey Chemical Systems Division P.O. Box 358 Sunnyvale, CA 94086	1	Dr. R. McGuire Lawrence Livermore Laboratory University of California Code L-324 Livermore, CA 94550	1
Professor F. Rodriguez Cornell University School of Chemical Engineering Olin Hall, Ithaca, N.Y. 14853	1	Dr. Jack Linsk Lockheed Missiles & Space Co. P.O. Box 504 Code Org. 83-10, Bldg. 154 Sunnyvale, CA 94088	1
Defense Technical Information Center DTIC-DDA-2 Cameron Station Alexandria, VA 22314	12	Dr. B.G. Craig Los Alamos National Lab P.O. Box 1663 NSP/DOD, MS-245 Los Alamos, NM 87545	1
Dr. Rocco C. Musso Hercules Aerospace Division Hercules Incorporated Alleghany Ballistic Lab P.O. Box 210 Washington, D.C. 21502	1	Dr. R.L. Rabie WX-2, MS-952 Los Alamos National Lab. P.O. Box 1663 Los Alamos NM 37545	1
Dr. Ronald L. Simmons Hercules Inc. Eglin AFATL/DLGL Eglin AFB, FL 32542	1	Dr. R. Rogers, WX-2 Los Alamos Scientific Lab. P.O. Box 1663 Los Alamos, NM 87545	1

DISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Mr. R. Brown Naval Air Systems Command Code 330 Washington, D.C. 20361	1	Dr. J. Schnur Naval Research Lab. Code 6510 Washington, D.C. 20375	1
Dr. H. Rosenwasser Naval Air Systems Command AIR-310C Washington, D.C. 20360	1	Mr. R. Beauregard Naval Sea Systems Command SEA 64E Washington, D.C. 20362	1
Mr. B. Sobers Naval Air Systems Command Code 03P25 Washington, D.C. 20360	1	Mr. G. Edwards Naval Sea Systems Command Code 62R3 Washington, D.C. 20362	1
Dr. L.R. Rothstein Assistant Director Naval Explosives Dev. Engineering Dept. Naval Weapons Station Yorktown, VA 23691	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, PA 19112	1
Dr. Lionel Dickinson Naval Explosive Ordnance Disposal Tech. Center Code D Indian Head, MD 20640	1	Dr. H.G. Adolph Naval Surface Weapons Center Code R11 White Oak Silver Spring, MD 20910	1
Mr. C.L. Adams Naval Ordnance Station Code PM4 Indian Head, MD 20640	1	Dr. T.D. Austin Naval Surface Weapons Center Code R16 Indian Head, MD 20640	1
Mr. S. Mitchell Naval Ordnance Station Code 5253 Indian Head, MD 20640	1	Dr. T. Hall Code R-11 Naval Surface Weapons Center White Oak Laboratory Silver Spring, MD 20910	1
Dr. William Tolles Dean of Research Naval Postgraduate School Monterey, CA 93940	1	Mr. G.L. Mackenzie Naval Surface Weapons Center Code R101 Indian Head, MD 20640	1
Naval Research Lab. Code 6100 Washington, D.C. 20375	1	Dr. K.F. Mueller Naval Surface Weapons Center Code R11 White Oak Silver Spring, MD 20910	1

DISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Mr. J. Murrin Naval Sea Systems Command Code 62R2 Washington, D.C. 20362	1	Dr. A. Nielsen Naval Weapons Center Code 385 China Lake, CA 93555	1
Dr. D.J. Pastine Naval Surface Weapons Center Code R04 White Oak Silver Spring, MD 20910	1	Dr. R. Reed, Jr. Naval Weapons Center Code 388 China Lake, CA 93555	1
Mr. L. Roslund Naval Surface Weapons Center Code R122 White Oak, Silver Spring MD 20910	1	Dr. L. Smith Naval Weapons Center Code 3205 China Lake, CA 93555	1
Mr. M. Stosz Naval Surface Weapons Center Code R121 White Oak Silver Spring, MD 20910	1	Dr. B. Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1
Dr. E. Zimmet Naval Surface Weapons Center Code R13 White Oak Silver Spring, MD 20910	1	Dr. A. Faulstich Chief of Naval Technology MAT Code 0716 Washington, D.C. 20360	1
Dr. D. R. Derr Naval Weapons Center Code 388 China Lake, CA 93555	1	LCDR J. Walker Chief of Naval Material Office of Naval Technology MAT, Code 0712 Washington, D.C. 20360	1
Mr. Lee N. Gilbert Naval Weapons Center Code 3205 China Lake, CA 93555	1	Mr. Joe McCartney Naval Ocean Systems Center San Diego, CA 92152	1
Dr. E. Martin Naval Weapons Center Code 3858 China Lake, CA 93555	1	Dr. S. Yamamoto Marine Sciences Division Naval Ocean Systems Center San Diego, CA 91232	1
Mr. R. McCarten Naval Weapons Center Code 3272 China Lake, CA 93555	1	Dr. G. Bosmajian Applied Chemistry Division Naval Ship Research & Development Center Annapolis, MD 21401	1
		Dr. H. Shuey Rohn and Haas Company Huntsville, Alabama 35801	1

DISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. J.F. Kincaid Strategic Systems Project Office Department of the Navy Room 901 Washington, D.C. 20376	1	Dr. C.W. Vriesen Thiokol Elkton Division P.O. Box 241 Elkton, MD 21921	1
Strategic Systems Project Office Propulsion Unit Code SP2731 Department of the Navy Washington, D.C. 20376	1	Dr. J.C. Hinshaw Thiokol Wasatch Division P.O. Box 524 Brigham City, Utah 84302	1
Mr. E.L. Throckmorton Strategic Systems Project Office Department of the Navy Room 1048 Washington, D.C. 20376	1	U.S. Army Research Office Chemical & Biological Sciences Division P.O. Box 12211 Research Triangle Park NC 27709	1
Dr. D.A. Flanigan Thiokol Huntsville Division Huntsville, Alabama 35807	1	Dr. R.F. Walker USA ARRADCOM DRDAR-LCE Dover, NJ 07801	1
Mr. G.F. Mangum Thiokol Corporation Huntsville Division Huntsville, Alabama 35807	1	Dr. T. Sinden Munitions Directorate Propellants and Explosives Defence Equipment Staff British Embassy 3100 Massachusetts Ave. Washington, D.C. 20008	1
Mr. E.S. Sutton Thiokol Corporation Elkton Division P.O. Box 241 Elkton, MD 21921	1	Capt. S. Shackelford AFRPL/LKLR Edwards AFB, CA 93523	1
Dr. G. Thompson Thiokol Wasatch Division MS 240 P.O. Box 524 Brigham City, UT 84302	1	Dr. Merrill K. King Atlantic Research Corp. 5390 Cherokee Avenue Alexandria, VA 22314	1
Dr. T.F. Davidson Technical Director Thiokol Corporation Government Systems Group P.O. Box 9253 Ogden, Utah 84409	1	Dr. W. Wharton Army Missile Command DRSMI-RK Redstone Arsenal, AL 35898	1
		Dr. David C. Sayles Ballistic Missile Defense Advanced Technology Center P.O. Box 1500 Huntsville, AL 35807	1

DISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. Kurt Baum Fluorochem, Inc. 680 South Ayon Ave. Azusa, CA 91702	1	Dr. R. Atkins Naval Weapons Center Code 3852 China Lake, CA 93555	1
Professor J. H. Boyer Univ. of Illinois Dept. of Chemistry Box 4348 Chicago, Illinois 60680	1	Dr. May L. Chan Naval Weapons Center Code 3244 China Lake, CA 93555	1
Dr. Joyce J. Kaufman The Johns Hopkins University Department of Chemistry Baltimore, MD 21218	1	Dr. T. B. Joyner Naval Weapons Center Code 3264 China Lake, CA 93555	1
Dr. C. Coon Lawrence Livermore Lab. University of California P.O. Box 808 Livermore, CA 94550	1	Dr. R. A. Rhein Naval Weapons Center Code 3244 China Lake, CA 93555	1
Professor J. C. Chien University of Massachusetts Department of Chemistry Amherst, MA 03003	1	Dr. B. David Halpern Polysciences, Inc. Paul Valley Industrial Park Warrington, PA 18976	1
Professor P. Lillya University of Massachusetts Department of Chemistry Amherst, MA 03003	1	Dr. Karl O. Christe Rockwell International 6633 Canoga Avenue Canoga Park, CA 91304	1
Prof. Richard A. Reinhardt Naval Postgraduate School Physics & Chemistry Department Monterey, CA 93940	1	Dr. M. B. Frankel Rockwell International Rocketdyne Division 6633 Canoga Avenue Canoga Park, CA 91304	1
Dr. J. Karle Naval Research Laboratory Code 6030 Washington, D.C. 20375	1	Dr. D. L. Ross SRI International 333 Ravenswood Avenue Menlo Park, CA 94025	1
Dr. M. J. Kamlet Naval Surface Weapons Center Code R11 White Oak, Silver Spring, MD 20910	1	Mr. Ed van Ribbink Space Ordnance Systems 25977 San Canyon Road Canyon Country, CA 91351	1

DISTRIBUTION LIST

	<u>No. Copies</u>	<u>No. Copies</u>
Mr. M. Baron SP 27314 Strategic Systems Project Office Department of the Navy Washington, D.C. 20376	1	
Dr. J. Hinshaw Thiokol/Wasatch Div. P.O. Box 524 Brigham City, Utah 84302	1	

Appendix A

THE CONTROLLED CATIONIC POLYMERIZATION OF CYCLIC ETHERS

To be submitted to the Journal of Polymer Sciences

THE CONTROLLED CATIONIC POLYMERIZATION OF CYCLIC ETHERS

G. E. Manser, S. J. Staats, and R. L. Simon
SRI International
Menlo Park, California 94025

SYNOPSIS

We have demonstrated that cationic polymerization of cyclic ethers can be controlled to give polyethers of predetermined molecular weight by adjusting the stoichiometry of initiator and monomer. The initiator is a complex of an alkanediol and a Lewis acid. The polymer molecular weights achieved are proportional to the sum of the molecular weights of the initiator diol and the monomer. The resulting polymers have a narrow polydispersity and a functionality of 2.

INTRODUCTION

The cationic polymerization of cyclic ethers to produce polyether glycols has been extensively investigated during the past fifteen years. Aside from the polymers derived from epoxides, poly(tetrahydrofuran) is the most widely produced polyether glycol of commercial interest. These polyethers are used as prepolymers in the preparation of polyurethanes. This application requires low molecular weights (2000 to 4000) and a hydroxy functionality of 2.

The objective of our research is to prepare energetic polyether glycols for formulation into energetic polyurethane binders for propellants and explosives. We have focused our research on the cationic polymerization of substituted oxetanes, and tetrahydrofuran, with the aim of preparing polyether glycols with molecular weights between 2000 and 4000, narrow polydispersities, and functionalities of 2.

The methods reported in the literature¹⁻³ for producing low molecular weight oligomers from cyclic ethers include using high catalyst loadings, high polymerization temperature, and cocatalysts. These techniques produce lower molecular weights by increasing the frequency of termination steps. In our hands these techniques produced a lower molecular weight, but also gave decreased monomer conversion, a decrease in functionality, and a marked increase in the formation of cyclic oligomers. The decreased monomer conversion required the separation of monomer from polymer, preventing practical scale-up, and polydispersities of greater than two were commonly observed in products produced by these methods.

We felt that a more satisfactory approach would be to choose an initiator that would produce a reaction mixture that was reasonably free of transfer and termination reactions. This would permit an increase in the initiator concentration and allow the molecular weight of the product to be controlled only by the amount of monomer available.

A review of the literature on stable BF_3 -initiator complexes⁴⁻⁸ indicated that the use of 1,4-butanediol did decrease the cyclic oligomer content of the product mixture. Cyclic oligomer formation is the most obvious termination reaction competing with the desired polymerization. Hammond's work¹⁰ suggested that the molecular weight was affected by the quantity of diol used, but his work did not address the distinction between conversion and diol content. In Hammond's work the catalyst and diol were only used in catalytic amounts (less than 2 mole %).

EXPERIMENTAL

All reagents and solvents were rigorously dried and freshly distilled before use. Polymerizations were conducted under a dry nitrogen atmosphere.

Polymerization Procedure. A flame dried resin flask was charged with the calculated weight of diol as a 50% w/w solution in methylene chloride. The solution was cooled to 0°C, and the desired amount of boron trifluoride etherate added dropwise. After stirring 1 hour the calculated amount of monomer was added as a 20% w/w solution in methylene chloride over 10 minutes. After stirring 24 hours, the solution was quenched with a

volume of saturated aqueous sodium chloride solution equal to the volume of catalyst used. The organic layer was separated, washed with an equal volume of 10% aqueous sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. The organic fraction was then added to a vigorously stirred 10 fold volume excess of methanol. The resulting insoluble residue was separated and dried to constant weight under high vacuum at ambient temperature.

The disappearance of monomer was monitored using a Varian 1400 gas chromatograph equipped with a glass column packed with 10% OV-101 on chrom Q, with n-decane as an internal standard. Rates of polymerization were calculated using the assumption that all monomer consumed was converted to polymer.

Molecular Weight Determination. All molecular weights were determined using a Waters gel permeation chromatograph equipped with a differential refractive index detector and a Data Module 730. The column set consisted of seven microstyragel columns (two 100Å, two 500Å, two 10³Å, and one 10⁴Å) connected in series; the eluting solvent was tetrahydrofuran. The system was calibrated with polypropylene glycol standards of molecular weight 800, 1200, 2000, and 4000. Molecular weight determinations were confirmed using a Chromatrix KMX6 light scattering analyzer.

Functionality Determination. The polyol (1 g) was heated for 15 minutes at 95°C with 2 ml of a 2:1 mixture of pyridine and acetic anhydride. The resulting solution was then added to 50 ml water, and the mixture titrated with 0.1N sodium hydroxide. The titer of the polyol solution was then compared with the titer of a blank solution containing no polyol. The difference in titer between the sample and blank was used to calculate the hydroxy functionality of the polymer.

RESULTS AND DISCUSSION

Our initial experiments with oxetanes indicated that the rate of reaction of boron trifluoride etherate and butanediol was rapid, and even in the presence of monomer formed a boron trifluoride-diol complex. We therefore preformed a 2 to 1 boron trifluoride-butanediol complex and used this to initiate the polymerization of 3, 3-bis(azidomethyl)oxetane, a monomer of considerable interest to our program. We observed that polymerization of a mixture of 1 mole boron trifluoride-butanediol complex and 16 moles of monomer, if allowed to go to completion, gave a polymer of molecular weight 2800 and a polydispersity of 1.1. The observed molecular weight was, within experimental error, equal to the sum of the molecular weights of 1 mole butanediol and 16 mole monomer (2778).

The results of experiments on the effect of diol to catalyst ratio on the polyol molecular weight are shown in Table 1. The desired molecular weights were produced when a 2/1 ratio of boron trifluoride etherate to butane diol was used. A ratio of 1/1 does not give an effective initiator, while a 3/1 ratio gives an uncontrolled polymerization forming a high molecular weight polymer, apparently due to the presence of uncomplexed catalyst. The structure of the boron trifluoride-diol complex is now being examined and will be described in a later paper.

In order to achieve a polymer with a high energy content we examined the polymerization of 3-(2,2-dinitropropoxymethyl)-3-methyloxetane. In this case we used a nitroalkanediol, 2-(2,2-dinitropropyl)-1,4-butane diol, as the initiating diol. The results of these experiments are shown in Table 2. In all cases the molecular weight of the product as determined by GPC was in agreement with the expected molecular weight. For example, the molecular weight of a polyol containing four units of monomer and 1 unit of diol is 1157. The observed molecular weight in this case was 1200. In these reactions the monomer conversion was greater than 95%, and the polydispersity was 1.1. NMR analysis of these products showed that the diol had been incorporated with the theoretical amount of monomer.

Table 1

EFFECT OF DIOL/CATALYST RATIO ON POLYOL MOLECULAR WEIGHT

Reactant Mole Ratio			Observed $\bar{M}_w^*$
BAMO	BDO	BF_3	
16	2	1	No polymerization
16	1	1	No polymerization
16	1	2	2800
16	1	2.5	2800
16	1	3	3700
16	1	4	5000

* Calculated molecular weight 2778.

Table 2

 CONTROLLED POLYMERIZATION OF
 3-(2,2-DINITROPROPOXY METHYL)-3-METHYL OXETANE

Mole Ratio Oxetane/diol	Observed $\bar{M}_w$	Calculated $\bar{M}_w$
4/1	1200	1157
6/1	1600	1625
8/1	2000	2093

To determine if the diol was incorporated in the head of the polymer chain (a monocation), or in the middle (a dication), we conducted the following experiment. One mole of diol complex was used to initiate the polymerization of six moles of oxetane and the living cation quenched with excess diol. If a dication had been generated, then the polymer would contain six units of monomer and 3 units of diol (molecular weight 2067). If a monocation was formed then six units of monomer would be combined with two units of diol to give a molecular weight of 1846. The observed molecular weight was 1800, indicating agreement with Hammonds observation⁹ that a monocation is involved.

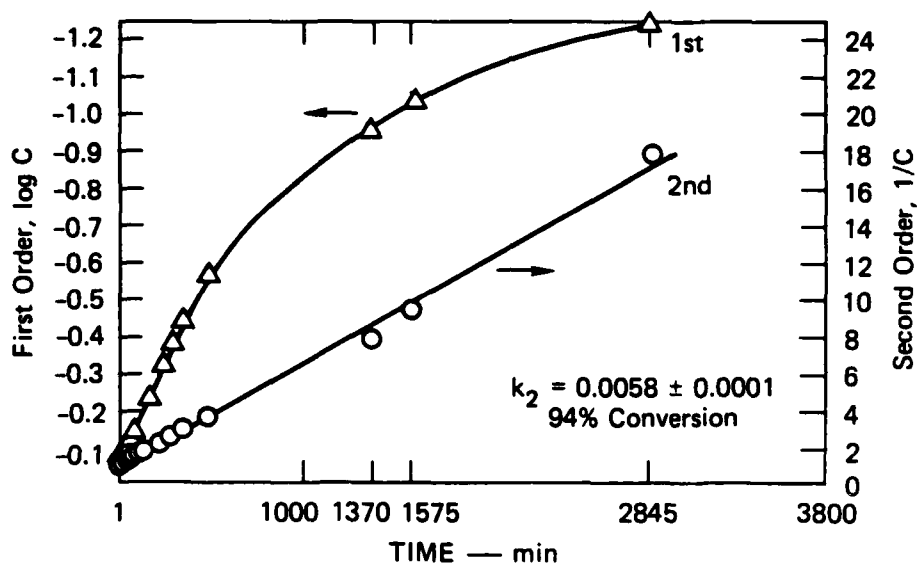
Analysis of the functionality of all polymers described in this paper showed that a theoretical value of 2 was obtained, indicating that a high degree of control of the polymerization had been achieved.

GENERAL KINETICS OF POLYMERIZATION

We examined the rate of polymerization of BAMO in an effort to elucidate the mechanism of polymerization.

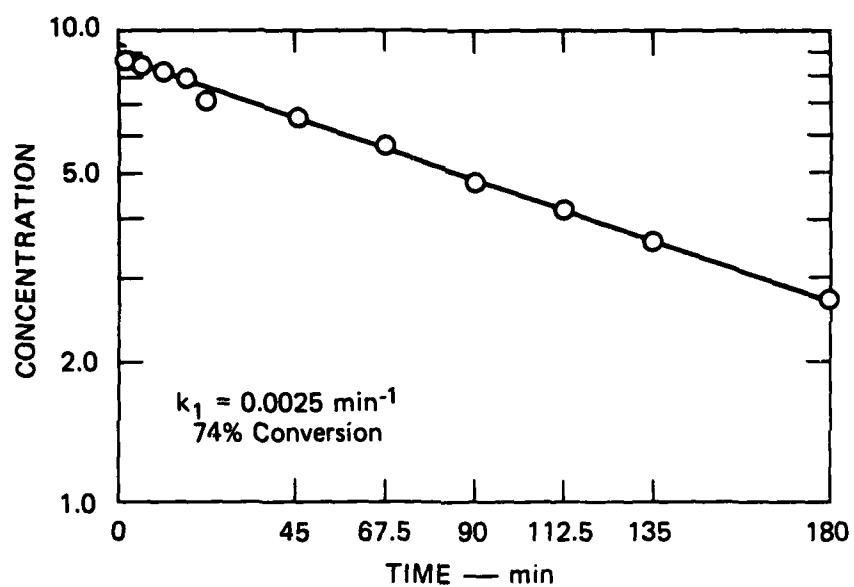
Our investigation began by determining the rate of polymerization of BAMO using the stoichiometry which gives molecular weight control, namely, a 20%wt/wt solution of BAMO (0.06 mol), 1,4-butanediol (BDO) (0.003 mol), and boron trifluoride etherate (0.006 mol) in methylene chloride. The reaction temperature was kept at 19°C during the entire polymerization. At time zero, BAMO was added to a solution of BDO, boron trifluoride etherate, and methylene chloride. The reaction was quenched after 47 hours giving a 94% conversion. The data obtained were plotted as both first and second order reactions with respect to monomer concentration, Figure 1. The graph indicates that the reaction is second order over the 94% conversion. However, if the data are plotted up to 74% conversion the reaction appears to follow first order kinetics, Figure 2.

Rose¹⁰ reports that the concentration of the cocatalyst in the polymerization affects the rate and order of the reaction. That is, the reaction changes from first to second order as the cocatalyst concentration increases. As a result of this, the rate of monomer uptake is described



SA-8627-16

FIGURE 1 FIRST AND SECOND ORDER PLOT OF POLYMERIZATION OF BAMO TO 94% CONVERSION



SA-8627-17

FIGURE 2 FIRST ORDER PLOT OF POLYMERIZATION OF BAMO
TO 74% CONVERSION

by the following equation, provided the cocatalyst concentration does not exceed a limiting value:

$$-d[M]/dt = \text{const.} \times [M] [BF_3] [\text{cocatalyst}]$$

where $[M]$ = monomer concentration. However, when the cocatalyst concentration exceeds the limiting value the rate expression becomes:

$$-d[M]/dt = \text{const.} \times [BF_3 \cdot M] [M]^2$$

The rate values quoted in Rose's paper¹⁰ represent conversions between 70 to 80%. However, our data show that the polymerization appears to follow first order kinetics up to 74% conversion and then changes at higher conversion. Because Rose does not report conversions as high as 94% we are not sure if his system displays the same phenomenon.

CONCLUSIONS

We have demonstrated that polyether glycols of varying, pre-determined molecular weights can be prepared by varying the stoichiometry of reactants. The molecular weight is controlled by an initiator composed of a 1/2 mole ratio of a diol and $BF_3 \cdot Et_2O$. The polymers are obtained in high yield, with low polydispersity, minimal cyclic oligomers contamination and with the desired functionality. Initial examination of the kinetics of the polymerization suggests a complex system that cannot be elucidated at this time.

ACKNOWLEDGEMENTS

This work was supported in part by the Office of Naval Research under Contract N00014-79-C-0525.

REFERENCES

1. H. Meerwein, D. Delfs, and H. Morschel, *Angew. Chem.*, 72 927 (1960).
2. M. P. Dreyfus and P. Dreyfus, *J. Polym. Sci. Part A-1*, 4 2179 (1966).
3. P. Dreyfus, *J. Macromol. Sci.-Chem* A7(7) 1361 (1973).
4. L. A. Dickinson, *J. Polym. Sci.* 58, 857 (1962).
5. W. J. Murbach and A. Adicoff, *Ind. Eng. Chem.* 52, 772 (1960).
6. L. P. Blanchard, J. Singh, and M. D. Baijal, *Can. J. Chem.* 44, 2679 (1966).
7. M. D. Baijal and L. P. Blanchard, *Macromol Chem.*, Kyoto-Tokyo 1966 (*J. Polym. Sci., C*, 23) I. Sakurada and S. Okamura, Eds. Interscience, New York 1968, p. 157.
8. G. A. Latremouille, G. T. Merrall, and A. M. Eastman, *J. Amer. Chem. Soc.* 82, 120 (1960).
9. J. M. Hammond, J. F. Hooper, and W.G.D. Robertson, *J. Polym. Sci. Part A-1*, 9, 265 (1971).
10. J. B. Rose, *J. Chem. Soc.* (1956) 542-546.

Appendix B

COPOLYMERIZATION OF 3,3-BIS(AZIDOMETHYL) OXETANE WITH TETRAHYDROFURAN

To be submitted to the Journal of Polymer Sciences

COPOLYMERIZATION OF 3,3-BIS(AZIDOMETHYL) OXETANE WITH TETRAHYDROFURAN

G. E. Manser, R. L. Simon, and S. J. Staats
SRI International
Menlo Park, California 94025

SYNOPSIS

The objective of the work was to synthesize energetic prepolymers for use in the formation of elastomeric binders for use in propellant and explosive compositions. The copolymerization of 3,3-bis(azidomethyl) oxetane (BAMO) with tetrahydrofuran (THF), using boron trifluoride etherate/1,4-butanediol complex as initiator was studied as a function of the ratio of BAMO to THF. The 50/50 mole percent oligomer was converted to a gumstock by reaction with trimethylolethane and tolylene diisocyanate. The tensile strength (engineering) of the gumstock at break of 7.93×10^6 dyne/cm² (115 psi) was obtained at an elongation of 425%. The monomer reactivity ratios, r_1 (THF) = 0.44 ± 0.17 and r_2 (BAMO) = 1.73 ± 0.24 , were determined by the Kelen-Tudos method.

INTRODUCTION

Low molecular weight (2000 to 4000) hydroxy-terminated polymers are required to form elastomeric binders for use in propellant and explosive formulations. The ideal prepolymer would be an inexpensive, stable, amorphous, flexible material with a glass transition temperature (T_g) below -60°C and a positive heat of formation. Polyethylene and polypropylene glycols are among the oligomers currently used in binder formation. Although these polyether glycols have many of the necessary properties, such as good chemical and thermal stability, high degree of flexibility and low T_g , they have a negative heat of formation. Consequently they detract from the overall energy of the formulation.

The successful synthesis of a prepolymer with a positive heat of formation that also possesses the necessary mechanical properties would represent a significant advance.

EXPERIMENTAL

Materials. Burdick and Jackson UV grade THF was dried by storing over 4A molecular sieve. Commercial grade boron trifluoride etherate was freshly distilled in vacuo prior to use. 1,4-butanediol was distilled from calcium hydride and stored over 4A molecular sieve.

3,3-Bis(azidomethyl)oxetane (BAMO) was prepared by heating a solution of one mole 3,3-bis(chloromethyl)oxetane and two moles sodium azide in dimethylformamide at 80°C for 18 hours. After cooling, the precipitated sodium chloride was removed by filtration and the filtrate vacuum distilled to give 130 g (80% yield) of BAMO, bp 78°C/0.2 Torr. CAUTION: Allowing the hot pot residue to contact air resulted in a violent detonation. Frankel has reported the purification of BAMO by column chromatography (methylene chloride, basic alumina)³, which is the method of choice.

Polymerization Procedure. The copolymerizations were run in a jacketed 100-ml glass resin flask equipped with a mechanical stirrer. In each case 0.25 moles of monomer, 0.025 moles BF_3 etherate, and 0.0125 moles butanediol were used. The THF, butanediol, and BF_3 etherate were combined and stirred for 30 minutes. The reaction mixture was then cooled to -5°C and the BAMO added. After stirring for 48 hours, the reaction was quenched with saturated aqueous sodium chloride. The crude polymer was separated, dissolved in a minimum volume of methylene chloride and reprecipitated by addition of a tenfold volume of methanol. The reprecipitated polymer was isolated by decanting the methanol and drying in vacuo.

Molecular Weight Determination. Number average and weight average molecular weights of poly-BAMO/THF were determined using a Waters gel-permeation chromatograph equipped with four microstyragel columns (100 Å, 500 Å, 10^3 Å, 10^4 Å), a differential refractive index detector, and a Data Module 730. The columns were calibrated with polypropylene glycol standards of molecular weight 800, 1200, 2000, and 4000.

Measurements of Reactivity Ratios. The reactivity ratios of THF and BAMO were determined by the Kelen-Tudos method.⁴ The disappearance of monomer was monitored by gas chromatography, using a glass column packed with 10% OV-101 on Chrom Q. Samples were periodically removed from the reaction mixture and quenched by dissolution in wet methylene chloride. At the end of the reaction the copolymer was isolated and purified as described above and characterized by its NMR spectrum and elemental analysis.

RESULTS AND DISCUSSION

The objective of the work described here was to develop a binder system that would not detract from the overall energy of the formulation. To this end we examined the synthesis of polyether glycols with positive heats of formation. One approach would be the cationic polymerization of azido or nitro-substituted oxetanes. However, earlier investigations have shown that homopolymers prepared from substituted oxetanes have unacceptably high T_g values.¹ One approach to lowering the T_g values of these materials would be to interrupt the symmetry of the polymer by copolymerization of dissimilar monomers. Therefore, we investigated the copolymerization of oxetanes with tetrahydrofuran (THF). We chose THF because it forms a polyether, is known to copolymerize with oxetane,² and should impart a low T_g to the copolymer. We have found that 3,3-bis(azidomethyl)oxetane (BAMO) is a promising oxetane monomer for binder applications. Therefore, we investigated the copolymerization of BAMO with THF.

The copolymerization of BAMO and THF was accomplished as described in the experimental section. To determine the effect of THF incorporation on the physical properties of the copolymer, a series of copolymerizations was run in which the initial ratio of BAMO to THF was varied. The properties of the polymers obtained from these copolymerizations are shown in Table 1.

Table 1
POLYMER PROPERTIES OF BAMO/THF

Mole Fraction of Monomer Charge		Mp	Density	Functionality	Molecular Weight
BAMO	THF	°C	g/cc	-OH/molecule	$\bar{M}_w$
1.00	0	78	1.30	1.9	6500
0.75	0.25	50	1.24	2.0	6900
0.60	0.40	25	1.27	2.0	6200
0.50	0.50	<0	1.18	2.0	7300

The copolymerization of BAMO and THF yields low molecular weight oligomers with melting points lower than that of the BAMO homopolymer. The 50/50 mole % copolymer is a mobile oil at ambient temperature, and its viscosity is relatively low compared to polymers of higher BAMO content. The 50/50 copolymer had the best overall physical properties for a binder application.

A gumstock was prepared from the 50/50 copolymer by mixing with trimethylolethane to achieve the required crosslink density of 10% and then condensed with one equivalent of tolylene diisocyanate. The sample was cured for 24 hours at 65°C.

The room temperature stress/strain curve of the 50/50 copolymer gumstock obtained at a strain rate of 0.02 in/min, gave an engineering stress at break of 7.93×10^6 dyne/cm² (115 psi). Elongations of up to 425% were observed. Equilibrium swelling measurements in THF gave an average molecular weight between crosslinks of about 89,000. Dynamic tensile moduli measurements at 110 hz indicated that the T_g of the gumstock was -56°C. Differential scanning calorimetry (20°C/min) showed only a single exotherm that began at 210°C and reached a maximum at 254°C.

To better characterize the copolymer composition and polymerization mechanism, the reactivity ratios of BAMO and THF were determined using the Kelen and Tudos (KT) improved linear graphic method.³ The KT method is an approximation that does not integrate the differential copolymerization equation (1).

$$\frac{dm_1}{dm_2} = \frac{m_1}{m_2} \frac{1 + r_1 m_1/m_2}{R_2 + m_1/m_2} \quad (1)$$

Because of this, the method is strictly valid only at very low conversions. However, the extended KT method has a conversion compensation factor that allows it to be used with high conversions. We used this compensation factor because the rates of cationic polymerizations are very high, and stopping the reaction at sufficiently low conversion is often impossible.

The KT equation (equation 2) is derived from equation 1 by a series

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \quad (2)$$

of assumptions that are beyond the scope of this paper. Eta and Xi are calculated from experimental data as shown in Scheme 1, r_1 and r_2 are the reactivity ratios, and alpha is an arbitrary constant. In Scheme 1, ζ_1 and ζ_2 are the partial molar monomer conversions, dm_1/dm_2 is the experimentally determined average copolymer composition, and alpha is an arbitrary constant that uniformly distributes the experimental points between 0 and 1.

Scheme 1

$$\xi = \frac{F}{\alpha + F}, \quad \eta = \frac{G}{\alpha + F}$$

where

$$F = \frac{dm_1/dm_2}{\log(1-\zeta_1)} \cdot \frac{1}{\log(1-\zeta_2)}, \quad G = \frac{dm_1/dm_2 - 1}{\log(1-\zeta_1)} \cdot \frac{1}{\log(1-\zeta_2)}$$

and

$$\alpha = (F_{\max}/F_{\min})^{1/2}$$

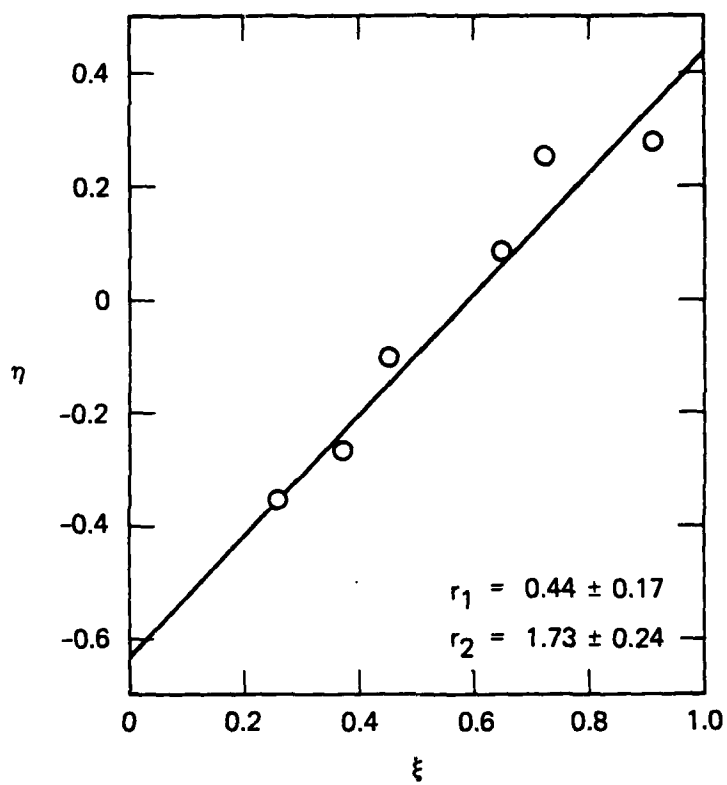
If a plot of η versus X_1 is linear, then the copolymerization is binary, and the slope of the plot is equal to $r_1 - r_2/\alpha$ and the y intercept equal to $-r_2/\alpha$. Since α is an arbitrary constant selected by the experimenter, r_1 and r_2 can then be calculated.

Table 2 shows the averaged η and X_1 values obtained from a series of copolymerizations of BAMO and THF. Since a plot of η versus X_1 for this series is linear (Figure 1), the BAMO/THF copolymerization system is binary. The calculated reactivity ratios are r_1 (THF) = 0.44 ± 0.17 and r_2 (BAMO) = 1.73 ± 0.24 .

Table 2

η and ξ PARAMETERS
 $\alpha = 2.79$

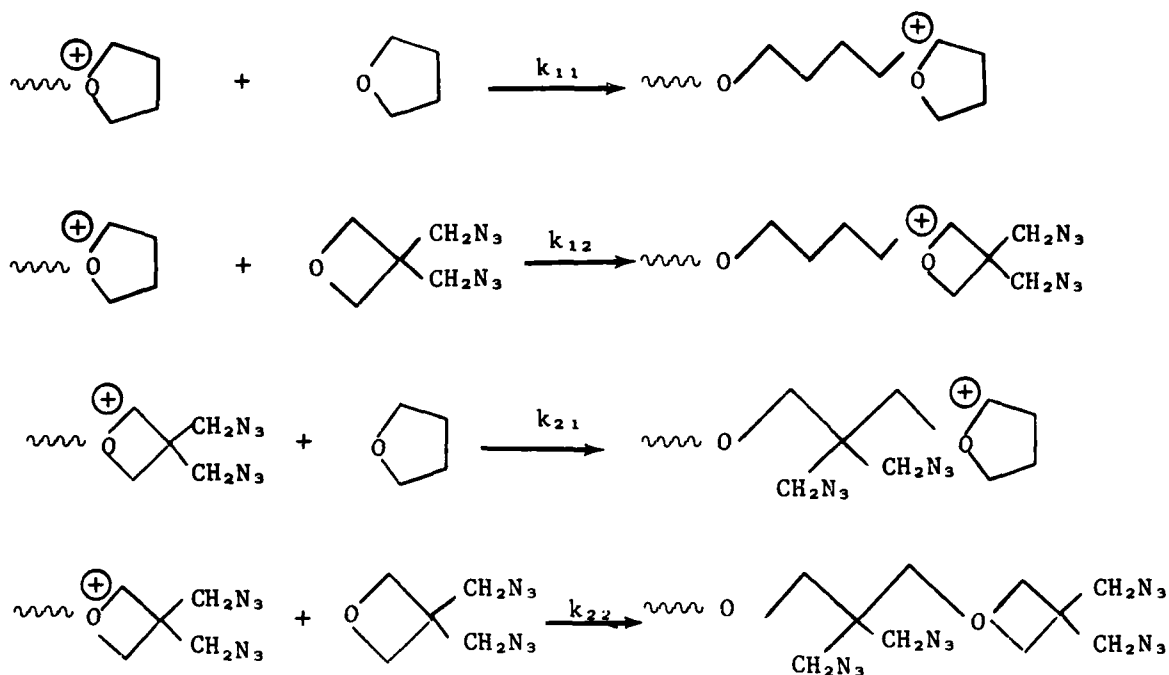
<u>Mole fraction of THF/BAMO in Charge</u>	<u>Mole fraction of THF/BAMO in Copolymer</u>	<u>ξ</u>	<u>η</u>
0.90/0.10	0.78/0.22	0.90 ± 0.02	0.25 ± 0.07
0.80/0.20	0.70/0.03	0.72 ± 0.05	0.25 ± 0.08
0.70/0.30	0.56/0.44	0.65 ± 0.07	0.08 ± 0.09
0.50/0.50	0.39/0.61	0.43 ± 0.04	-0.13 ± 0.02
0.40/0.60	0.28/0.72	0.38 ± 0.02	-0.27 ± 0.02
0.30/0.70	0.24/0.76	0.29 ± 0.02	-0.33 ± 0.03



SA-8627-18

FIGURE 1 Eta VERSUS Xi PLOT FOR BAMO/THF ($\alpha = 2.786$)

The reactions involved in the cationic copolymerization of THF with BAMO are shown in Scheme 2. The following relationships between the rate



Scheme 2

constants of these reactions can be derived from the monomer reactivity ratios:

1. $k_{11}/k_{12} = 0.44$
2. $k_{22}/k_{21} = 1.73$

The rate of reaction of THF oxonium ion with THF monomer is less than half the rate of reaction of THF oxonium ion with BAMO monomer. Similarly, the rate of reaction of BAMO oxonium ion with BAMO monomer is 1.75 times faster than the rate of reaction of BAMO oxonium ion with THF monomer. Because of this difference in monomer reactivity ratios, BAMO/THF copolymers are not totally random.

The instantaneous polymer composition as a function of monomer feed can be plotted when the reactivity ratios of the monomers in the copolymerization are known. Figure 2 shows such a plot for BAMO/THF, where the abscissa is the mole fraction of THF in the monomer charge (f_1) and the ordinate is the mole fraction of THF in the initial polymer formed.

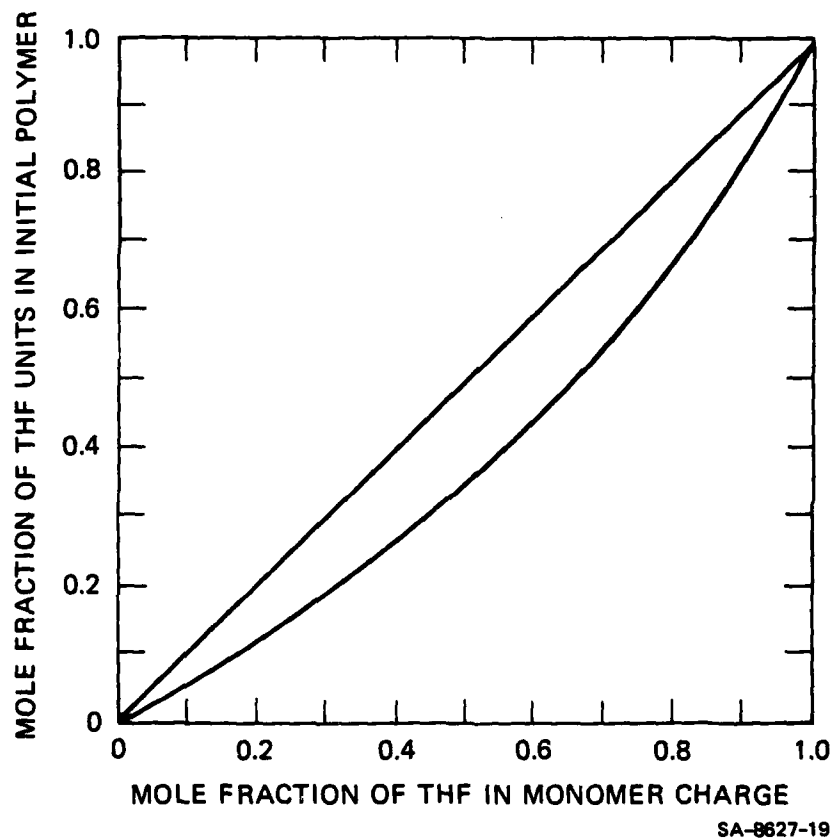


FIGURE 2 INSTANTANEOUS COMPOSITION OF BAMO/THF COPOLYMER AS A FUNCTION OF THF MONOMER CHARGE

The plot indicates that the BAMO/THF system can form polymers containing a significant concentration of each monomer over a considerable range of monomer mixtures. This degree of incorporation of THF and BAMO in the copolymer makes possible the preparation of well defined copolymers with respect to composition and molecular weight that have both a low degree of crystallinity and low glass transition temperatures.

CONCLUSIONS

Cationic copolymerization of BAMO and THF with a BF_3 etherate butane diol complex produces hydroxy terminated polyethers whose average molecular weight is a function of the mole ratio of initiator complex to monomer. The physical properties of BAMO/THF copolymers can be varied by changing the ratio of BAMO to THF in the monomer feed. Low melting (less than 0°C) high energy hydroxy terminated prepolymers for use in binder applications may be prepared by this method. Reactivity ratios generated by the Kelen-Tudos method indicate that the copolymerization of BAMO and THF proceeds by a binary mechanism.

ACKNOWLEDGMENT

Work supported by the Office of Naval Research under Contract No. N00014-79-C-0525.

REFERENCES

1. G. E. Manser, R. L. Simon, S. J. Staats, The Controlled Cationic Polymerization of Cyclic Ethers.
2. Encyclopedia of Polymer Technology, 9, 668-701, published 1980.
3. M. B. Frankel, Rockwell International, Rocketdyne Division, private communication.
4. (a) T. Kelen and F. Tudos, J. Macromol. Sci.-Chem., A9 (1), pp. 1-27 (1975). (b) J. P. Kennedy, T. Kelen, F. Tudos, J. Polymer Sci., 13, 2277-2289 (1975). (c) T. Kelen, F. Tudos, B. Turcsanyi, and J. P. Kennedy, J. Polymer Sci., 15 3047-3074 (1977).

Appendix C

A NEW POLYMERIZATION TECHNIQUE
FOR PREPARING LOW MOLECULAR WEIGHT POLYETHER GLYCOLS

Presented at the 1981 JANNAF Propulsion Meeting May 27, 1981

A NEW POLYMERIZATION TECHNIQUE
FOR PREPARING LOW MOLECULAR WEIGHT POLYETHER GLYCOLS*

G. E. Manser, J. Guimont, and D. L. Ross
SRI International
Menlo Park, California

Presented at the 1981 JANNAF Propulsion Meeting
New Orleans, Louisiana, 27th May 1981

ABSTRACT

We have demonstrated that exact and predetermined molecular weight polyols derived from the cationic polymerization of cyclic ethers can be obtained by using stoichiometric quantities of diol to monomer. The final molecular weight achieved is proportional to the stoichiometric addition of the molecular weights of the diol and cyclic ether. We have further demonstrated that liquid polyols are produced when a monomer that gives a crystalline homopolymer, is copolymerized with tetrahydrofuran. In both studies the polyols were found to have theoretical functionalities of 2 and minimal cyclic oligomer content.

INTRODUCTION AND BACKGROUND

The overall objective of our research was to produce energetic polyols from cyclic ethers that incorporated the following properties:

- Molecular weight control
- Reproducible molecular weight
- No cyclic oligomer contamination
- Hydroxy functionality of 2.0
- Low polydispersity (1.1 to 1.2)
- Liquid at $\leq 50^{\circ}\text{C}$
- Glass transition temperature less than -60°C .

In an effort to produce low molecular weight polyols (2000-4000), the polymerization of 3-(2-fluoro-2,2-dinitroethoxymethyl)-3-methyl oxetane (FOE) using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as the catalyst was conducted. The results of this work are given in Table I.

Run 1 was used as a starting point for catalyst loading to obtain relatively low molecular weight products. Methods investigated to lower the molecular weight further included increasing the catalyst loading, using water as a co-catalyst, and raising the polymerization temperature. All these parameters effectively increase the competing termination reactions. Only Run 3, using an equal amount of catalyst to water, had a noticeable effect on decreasing the polyol molecular weight. However, it also had a detrimental effect on polymer yield. Almost 80% of the monomer was recovered. Except for this run, the molecular weights recorded were in the range of 5000 to 6000. The GPC data also showed a major contaminant, which was identified as the FOE cyclic tetramer. A typical GPC trace is shown in Figure 1.

*This work was supported by the Office of Naval Research Contract N00014-79-C-0525.

Approved for public release; distribution unlimited.

Table I. POLYMERIZATION RUNS FOR FOE

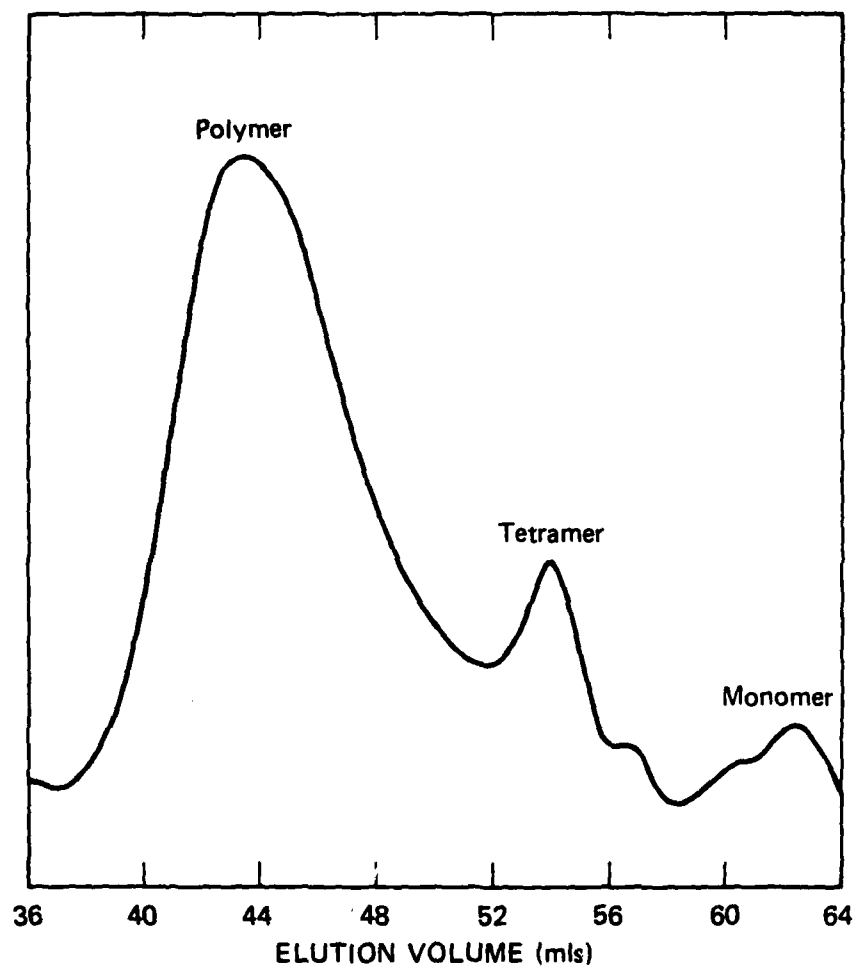
Run	Temperature (°C)	Reactants (parts by weight)			GPC Analysis ^a		Molecular Weight	
		Monomer	BF ₃ ·Et ₂ O	H ₂ O	Polymer Elution Volume (ml)	% Yield ^b	M _n (000)	M _w (000) Q ^d
1 ^c	20	100	3	0	42	92.3	3.126	6.662 2.13
2	20	100	20	0	43	83.0	--	5.4 --
3	20	100	10	10	52	14.8	--	1.3 --
4	20	100	10	1	43.5	82.0	--	5.0 --
5	40	100	10	1	43.8	87.6	--	4.4 --

^a Analyzed using a Waters Associates GPC with THF on microstyragel columns (two 100 Å, two 500 Å, one 10⁻³ Å, one 10⁻⁴ Å, one 10⁻⁵ Å).

^b The balance of recovered material was unreacted monomer (elution volume: 61.5 ml).

^c Analysis by Chromatix KMX6 light scattering analyzer attached to the effluent. All other molecular weights determined by comparison to polypropyleneglycol standards.

^d Polydispersity, $Q = \frac{M_w}{M_n}$



SA-8627-2

FIGURE 1 GPC OF FOE POLYMERIZATION

We concluded that the methods used in the above study would not produce polyols in high yield or in the molecular weight range desired. Furthermore without additional research the state of the art of cationic polymerization of cyclic ethers was inadequate¹⁻⁴ to permit the synthesis of polyols with the requisite properties.

High molecular weight polymers are obtained if a small number of initiating species is formed during the initial stage of polymerization. Since the objective of this research was to produce low molecular weight oligomers, we postulated that increasing the number of initiating species would limit the molecular weight of the final polyol. That is, the molecular weight would be determined by the ratio of initiator to monomer.

RESULTS AND DISCUSSION

The reported use of catalytic amounts of diols as co-catalysts with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ has been studied³⁻⁹ extensively. Inclusion of the diol in the polymer was observed in many cases. Hammond et al.¹⁰ noted that lower molecular weights were obtained at low conversion when the diol loading was increased from 0.08 to 1.65 mol%.

We postulated that the reactivity ratio of the cyclic ether to diol would favor preferential reaction of the diol with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to form a complex. If this complex could initiate cationic polymerization, then a large number of initiator species could be generated. The molecular weight of the polyol would then be directly proportional to the direct addition of the stoichiometric molecular weights of the diol and monomer.

HOMOPOLYMERIZATION

To test the hypothesis a series of polymerizations using 3-(2,2-dinitropropoxymethyl)-3-methyl oxetane (oxether-1) and 2-(2,2-dinitropropyl)-1,4-butanediol (DNPBDO) were conducted, as shown in Table II. In all cases

Table II. CONTROLLED POLYMERIZATION OF OXETHER-1

Mol Ratio Oxether-1/DNPBDO ¹	Observed M.W. $\bar{M}_w$ (000)	Calculated M.W. $\bar{M}_w$ (000)
4:1	1.2	1.157
6:1	1.6	1.625
8:1	2.0	2.093

¹6% $\text{BF}_3 \cdot \text{Et}_2\text{O}$ based on monomer

the molecular weight observed by GPC analysis was consistent with the calculated molecular weight. For example, four moles of oxether-1 and one mole of DNPBDO gives a calculated molecular weight of 1157. The observed molecular weight of the polyol was 1200. Two other oxetane monomers, 3,3-bis(azidomethyl) oxetane (BAMO) and FOE, and a second diol, 1,4-butanediol (BDO) were examined under the same conditions, and similar results were obtained.

A study was then initiated to determine the range of catalyst to diol ratios that may be used. The model system studied was BAMO and BDO. The effect of varying the mole ratio of BDO to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at a constant monomer ratio is shown in Table III. The results indicate that the preferred diol/catalyst

Table III. EFFECT OF DIOL/CATALYST RATIO
ON POLYOL MOLECULAR WEIGHT

BAMO	Reactant Mole Ratio		Observed* $\bar{M}_w$ (000)
	BDO	$\text{BF}_3 \cdot \text{Et}_2\text{O}$	
16	2	1	No polymerization
16	1	1	No polymerization
16	1	1.5	2.8
16	1	2	2.8
16	1	3	3.7
16	1	4	5.0

* Calculated molecular weight = 2778.

ratio is 1/2. It is interesting to note that a ratio of 1/1 does not initiate polymerization, and a ratio greater than 1/3 suggests that uncombined catalyst is present and initiates a competing, uncontrolled polymerization.

Because of its importance to the ongoing energetic polymer research program, BAMO was selected as the preferred monomer to investigate the effect of molecular weight on physical properties. A series of polyols was prepared with molecular weights ranging from 2000 to 6000. We found that the melting point was not affected by changing the molecular weight. For example, a molecular weight of 6000 gave a melting point of -78°C whereas molecular weight 2000 gave a melting point of -76°C . The functionality of these polyols was found to have a theoretical value of 2. As our objective was to produce a liquid polyol at room temperature, we concluded that this could not be met by homopolymerization of BAMO.

The physical properties of polyols are dependent on the crystallinity of the macromolecule, which in turn is a function of the symmetry of the macromole or repeating unit (monomer). Therefore, a homopolymer will tend to be more crystalline than a copolymer containing dissimilar monomers. Thus, lowering of crystallinity will reduce the melting point and T_g of the system. Because BAMO would not yield a liquid polyol, we investigated its copolymerization.

COPOLYMERIZATION

To demonstrate the effect of lower crystallinity on melting point, we conducted a series of copolymerizations of BAMO and tetrahydrofuran (THF).

The results of our investigation of three copolymer systems compared to poly-BAMO are given in Table IV. The results show the effect of the lowering

Table IV. EFFECT OF BAMO/THF MONOMER RATIO
ON PHYSICAL PROPERTIES

Polyol BAMO/THF mol %	Molecular Weight $\bar{M}_w$	Melting Point, °C	Density, g/cc	ΔH_f kcal/100g ¹ , est	Functionality
100/-	6500	78	1.3	+60	1.92
75/25	6900	50	1.245	+42	1.96
60/40	6300	25	1.21	+28	1.95
50/50	7300	-5	1.180	+17	1.99

of melting point by incorporating THF as a comonomer. A melting point of 50°C for the 75/25 mol% BAMO/THF is comparable to PEG 4000 (m.p. 55°C), a widely used polyol which is processible. Furthermore, the BAMO/THF polyol has the added improvement of increased energy content over PEG. A GPC trace of a 50/50 mol% BAMO/THF polyol is shown in Figure 2.

Work is now underway to prepare gum stocks from these polyols for subsequent physical testing. Preliminary DSC data show good thermal stability with an exotherm onset at 200° with a peak at 250°C.

CONCLUSIONS

We have demonstrated that polyether glycols of varying, predetermined molecular weights can be prepared by varying the stoichiometry of reactants. Molecular weight is controlled by generation of an initiating species from a complex derived from a diol and $\text{BF}_3 \cdot \text{Et}_2\text{O}$. The polyols are prepared in high yield, low polydispersity, theoretical functionality, and contain minimum cyclic oligomer.

A monomer (BAMO) which gives a crystalline homopolymer was copolymerized with tetrahydrofuran to produce low melting polyols that can be processed at ambient temperature into highly elastomeric, cured gum stocks.

EXPERIMENTAL

HOMOPOLYMERIZATION

To a flame dried resin flask was added a known weight of cyclic ether as a 20% w/w solution in dried methylene chloride. A calculated weight of the diol was then introduced and the solution stirred at room temperature for 10 minutes. A calculated weight of freshly distilled $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was then added and the reaction ran for 6 hours. The polymerization was quenched with a volume of saturated aqueous sodium chloride solution equal to the volume of

AD-A120 199

SRI INTERNATIONAL MENLO PARK CA
SYNTHESIS OF ENERGETIC POLYMERS.(U)
SEP 82 6 E MANSER, D L ROSS

F/6 7/3

UNCLASSIFIED

N00014-79-C-0525
NL

2 of 2

AD-A
120 199



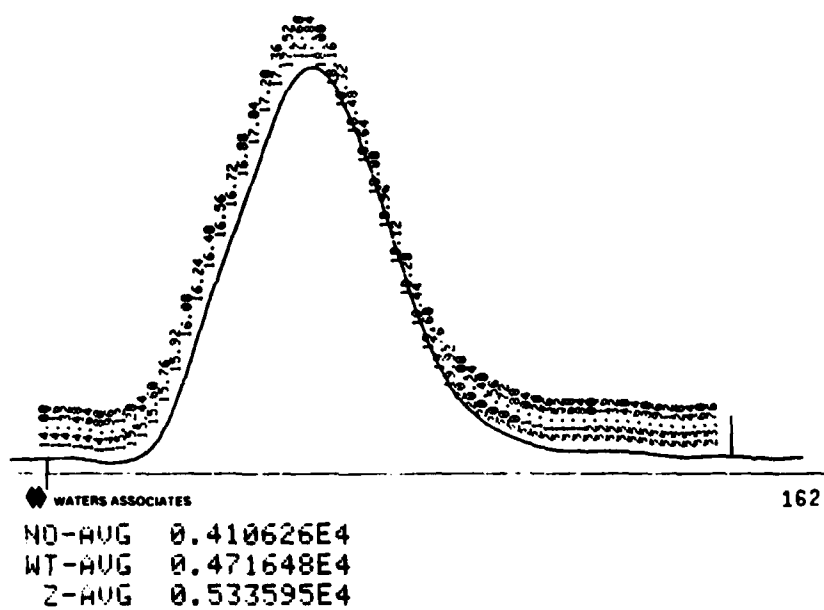
END

DATE

FILED

11-82

DTIC



DISPERSITY 0.114860E1

SA-8627-3

FIGURE 2 GPC OF 50/50 mol% BAMO/THF COPOLYMER

catalyst added. The organic layer was removed, washed with 10% sodium bicarbonate solution and dried over magnesium sulfate.

COPOLYMERIZATION

To a flame dried resin flask was added a known weight of tetrahydrofuran under a nitrogen atmosphere. A calculated weight of diol and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was then added. After 10 minutes mixing the solution was cooled to -5°C and the temperature was maintained at -5°C until the polymerization was quenched. The comonomer was then introduced to the flask and the polymerization allowed to run for 18 hours. An equal volume of dried methylene chloride was added to the flask, and after dissolution of the polymer was observed it was quenched with a volume of a saturated aqueous sodium chloride equal to the volume of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ used. The polymer solution was then warmed to room temperature, and the organic layer removed. The organic layer was then washed with 10% sodium bicarbonate solution and dried over magnesium sulfate.

POLYMER PURIFICATION

The methylene chloride solution of polymer was added slowly to a vigorously stirred ten-volume excess of anhydrous methanol. The insoluble residue was removed and dried on a high vacuum line at room temperature.

MOLECULAR WEIGHT DETERMINATION

All molecular weights were determined by gel permeation chromatography. The column set consisted of seven microstyragel columns (two 100 Å two 500 Å, one 10^3 Å one 10^4 Å, and one 10^5 Å), and the solvent used was tetrahydrofuran. The system was calibrated with molecular weight 800, 1200, 2000, and 4000 polypropylene glycol standards. The data from the refractive index detector was processed by a Waters Associates Data Module 730. Molecular weights determined in this manner were confirmed using a Chromatix KMX6 light scattering analyzer.

FUNCTIONALITY

The polyol (1 g) was treated with 2 ml of a standard acetylating agent (66 ml pyridine/33 ml acetic anhydride) for 15 minutes at 95°C . Each analysis was then compared with a blank by titrating with 0.1 N sodium hydroxide. The difference in titrant between the sample and the blank was used to calculate the hydroxyl equivalent weight of the polyol.

REFERENCES

1. H. Meervein, D. Delfs and H. Morshel, *Angew. Chem.* 72, 927 (1960).
2. R. Chaing and J. Rhodes, *Polymer Letters*, 1, 643 (1969).
3. H. Hellman, *Die Angwert, Makromol. Chem.*, 74, 105 (1978).
4. S. Smith and A. J. Hubin, *British Patent* 1,120,304 (1968).
5. L. A. Dickinson, *J. Polym. Sci.*, 58, 857 (1962).

6. W. J. Murbach and A. Adicoff, Ind. Eng. Chem., 62, 772 (1960).
7. L. P. Blanchard, J. Singh and M. D. Baijal, Can. J. Chem., 44, 2679 (1966).
8. J. B. Rose, J. Chem. Soc. 542-547 (1956).
9. G. A. Latremouille, G. T. Merrall and A. M. Eastman, J. Amer. Chem. Soc., 82, 120 (1960).
10. J. M. Hammond, J. F. Hooper and W. G. P. Robertson, J. Polm. Sci., 9, 265 (1971).

Appendix D

BAMO/THF COPOLYMER: A CANDIDATE ENERGETIC POLYETHER GLYCOL

Presented at the Symposium on the Chemistry of the Synthesis and
Characterization of Energetic Monomers and Prepolymers, July 21, 1981

BAMO/THF COPOLYMER: A CANDIDATE ENERGETIC POLYETHER GLYCOL

Gerald E. Manser
SRI International
Menlo Park, CA 94025

Presented at

Symposium on the Chemistry of the Synthesis and
Characterization of Energetic Monomers and Prepolymers

The Johns Hopkins University
Applied Physics Laboratory
Laurel, MD 20810

21 July 1981

We have demonstrated that exact and predetermined molecular weight polyols derived from the cationic polymerization of cyclic ethers can be obtained by using stoichiometric quantities of diol to monomer. The final molecular weight achieved is proportional to the stoichiometric addition of the molecular weights of the diol and cyclic ether. We have further demonstrated that liquid polyols are produced when a monomer that gives a crystalline homopolymer, is copolymerized with tetrahydrofuran. In both studies the polyols were found to have theoretical functionalities of 2 and minimal cyclic oligomer content.

The overall objective of our research is to polymerize cyclic ethers to produce energetic polyols with the following characteristics:

- Molecular weight control
- Reproducible molecular weight
- No cyclic oligomer contamination
- Hydroxy functionality of 2.0
- Low polydispersity (1.1 to 1.2)
- Liquid at $\leq 50^{\circ}\text{C}$
- Glass transition temperature less than -60°C .

An extensive investigation of the homopolymerization of 3,3-bis(azidomethyl)oxetane [BAMO] showed conclusively that the resultant polymer melting range was relatively independent of molecular weight. Over the molecular weight range of interest (1200

to 6500) the melting range of BAMO polyols was $78 \pm 4^\circ\text{C}$, which is considered marginal for processing by standard nonsolvent techniques. Also, to obtain polymers with glass transition temperature $< -40^\circ\text{C}$, we found it necessary to copolymerize BAMO with a dissimilar monomer to provide less "crystalline materials." Consequently, we conducted a series of copolymerizations of BAMO and tetrahydrofuran [THF] and found a dramatic lowering of the melting range; the minimum was -5°C obtained with a 50/50 mole ratio of monomers.

The aforementioned system was examined for the rate of monomer uptake. After 20 hours BAMO had achieved a steady state of 98% conversion, whereas THF required 38 hours to reach 85% conversion. The reactivity ratios of BAMO and THF were found to be 1.40 and 0.31, respectively. A molecular weight of 4,000 was used for this co-polymerization study; a polydispersity of 1.1 and a functionality of 2.0 was observed on analysis of all polymers. Gumstocks were then prepared from the 50/50 BAMO/THF polymer by curing with tolylene diisocyanate, and the crosslink density was controlled by adding the required amount of trimethylol ethane.

The stress/strain curve, obtained by Instron analysis, gave a value of 115 psi at 425% elongation. An average of 89,000 molecular weight units between crosslinks was determined by swelling experiments. A Rheovibron study showed a classical E' curve for an elastomer and the E'' curve showed a single glass transition temperature of -54°C . The $\tan \delta$ plot produced a value of over 1.5 from -60 to -30°C indicating a surprising ability to absorb a large amount of energy at this low temperature. Differential scanning calorimetry showed a flat trace until onset of an exotherm at 210°C , maximizing at 254°C .

At this point of our investigation it appears that a copolymer of BAMO/THF is a viable candidate system that provides good low temperature and elastomeric properties and thermal stability over the projected operating temperature.

In order to achieve a polymer containing a higher energy content over BAMO/THF, we have begun to examine the copolymerization of BAMO with other azido monomers. Two candidate comonomers, namely 3-azidomethyl tetrahydrofuran (AMTHF) and 3-azido oxetane (AO) are available for this study. The synthesis of AMTHF has been completed by us, and AO was prepared by Dr. K. Baum at Fluorochem. Preliminary data on a copolymer obtained from 50/50 mol% BAMO/AO indicate that a liquid polymer is produced at a molecular weight of 3,000. This particular system is being scaled up so that gumstocks may be produced for testing.

We wish to acknowledge the following SRI personnel who contributed to the effort described here: Robert L. Simon, Steven J. Staats, John M. Guimont, David B. Cotts, and Donald L. Ross. We also wish to acknowledge the valuable suggestions of Dr. R. S. Miller, the project monitor. This research was supported by the Office of Naval Research, Contract N00014-79-C-0525.

