

20000731247

ENERGETIC THERMOPLASTIC ELASTOMERS

Final Report

December 1982

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

Prepared for:

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

Contract No. N00014-82-K-0045  
SRI Project PYU 3928

Approved for public release, distribution unlimited.  
Reproduction in whole or in part is permitted for  
any purpose of the United States Government.

Reproduced From  
Best Available Copy

DTIC  
ELECTRONIC  
JAN 04 1983

E

333 Ravenswood Ave. • Menlo Park, CA 94025  
(415) 859-6200 • TWX: 910-373-2046 • Telex: 334 486

007

AC A 122909

# SRI International

# SRI



DTIC FILE COPY

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A 22907	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) Energetic Thermoplastic Elastomers		5. TYPE OF REPORT & PERIOD COVERED Final 15 Nov 81 to 14 Nov 82	
7. AUTHOR(s) G. E. Manser and D. L. Ross		6. PERFORMING ORG. REPORT NUMBER Final PYU-3928	
8. PERFORMING ORGANIZATION NAME AND ADDRESS SRI International 333 Ravenswood Ave. Menlo Park, CA 94025		8. CONTRACT OR GRANT NUMBER(s) N00014-82-K-0045	
9. CONTROLLING OFFICE NAME AND ADDRESS Dr. R. S. Miller, Code 473 Office of Naval Research Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
14. MONITORING AGENCY NAME & ADDRESS (if diff. from Controlling Office)		12. REPORT DATE 15 Dec 82	13. NO. OF PAGES 33
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) Thermoplastic elastomers                      Bis(ethoxymethyl)oxetane Block copolymers                                      Bis(azidomethyl)oxetane Solid gun propellant binders                      Butoxymethyl-methyloxetane Poly(ethylene glycol)                                      Tetrahydrofuran			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The objective of the research was to investigate the synthesis and polymerization of energetic and nonenergetic monomers to provide thermoplastic elastomers for use as binders in solid gun propellants and cast-cured explosives. The polymer systems investigated were designed to meet the requirements of the Navy's LOVA (low vulnerability ammunition) program.  During the first year's work we examined five polymer systems based on polymers of oxetanes, tetrahydrofuran, and polyethylene glycol. We demonstrated			

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19. KEY WORDS (Continued)

20 ABSTRACT (Continued)

that block polymers of these polyetherglycols can be synthesized and that they exhibit the desired thermoplastic, elastomeric behavior. Poly-bis(ethoxymethyl)oxetane (BEMO) and poly-bis(azidomethyl)oxetane (BAMO) are crystalline homopolymers having the required melting point transition temperatures for a thermoplastic elastomer that is processable at 90°C. Both polymers are candidate crystalline blocks. The three elastomeric blocks investigated were polyethyleneglycol (PEG), copoly-bis(azidomethyl)oxetane/tetrahydrofuran (BAMO/THF), and copoly-3-butoxymethyl-3-methyloxetane/tetrahydrofuran (BMMO/THF). Each of these polymers meets the requirements for the elastomeric block.

One di-block and one tri-block polymer were produced by block-linking using the bis chloroformate technique. Initial characterization of the polymer systems shows that they have the properties required of thermoplastic elastomers for extrudable gun propellants and are expected to meet the requirements for LOVA gun propellant binders.

Accession For	
NTIS GOMI	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	



## CONTENTS

ACKNOWLEDGMENTS .....	2
I INTRODUCTION AND BACKGROUND .....	3
II DISCUSSION .....	5
Monomer Synthesis .....	5
Polymer Synthesis .....	6
Block Formation .....	8
III CONCLUSIONS .....	15
IV EXPERIMENTAL DETAILS .....	17
Monomer Synthesis Procedures .....	17
3,3-Bis(ethoxymethyl)oxetane .....	17
3-Butoxymethyl-3-methyloxetane .....	17
Polymerization Procedures (Block Synthesis) .....	
Materials .....	18
Typical Solution Polymerization Procedure (BAMO; BEMO) .....	18
Typical Bulk Polymerization Procedure (BMMO/THF) .....	18
Block Linking Technique .....	19
Functionality Determination .....	19
Molecular Weight Determination .....	20
Molecular Weight by Determination (Preliminary) .....	20
Differential Refractive Index Determination .....	20
Glass Transition Temperature Determination .....	21
REFERENCES .....	22
V PUBLICATIONS AND PRESENTATIONS .....	23

#### ACKNOWLEDGMENTS

We wish to acknowledge the efforts of the following SRI personnel who contributed to this work: Ronald Chiarello, David Cotts, Deborah Scott, and Robert Simon.

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 was aided considerably by the valuable suggestions of Professor L. H. Sperling of Lehigh University, Bethlehem, Pennsylvania.

## I INTRODUCTION AND BACKGROUND

Navy gun propellant requirements have continually stressed the need for reduced gun barrel erosion and increased gun propellant performance. However, a new goal has been established by the need to reduce the vulnerability of munitions to unscheduled initiation. Additional requirements are high impetus and low flame temperature. Current operational gun propellants are highly vulnerable to initiation by high velocity, hot metal fragments resulting from spalling. Highly energetic propellants produce intense fires, which increase the likelihood of propagating to other charges in the magazines.

The Navy's concern over the vulnerability of current gun propellants and TNT-based-melt cast explosives to unscheduled initiation has resulted in the LOVA programs and the development of rubbery cast-cured explosives. Nitramine propellants and explosives containing inert binders in place of the conventional nitrocellulose (NC) or TNT offer the opportunity for reduced vulnerability. Tests of several LOVA candidate systems<sup>1</sup> [e.g., cellulose acetate (CA/RDX), cellulose acetate-butyrate (CAB/RDX), and polyurethane (PU/RDX)] have shown significant reduction in vulnerability when compared with NC/RDX systems. Formulations containing Kraton<sup>2</sup> and RDX were also tested and found to have a vulnerability to initiation by fragments or fire between that of NC/RDX and the above experimental systems. However, there are significant advantages to using a thermoplastic, elastomeric binder like Kraton, over CA, CAB, and PU: a thermoplastic binder can be more easily and safely processed than conventional binders, and the elastomeric properties of the binder permit the binder to absorb part of the impact energy, thus reducing overall shock sensitivity.

It has been reported<sup>3</sup> that some propellant binders (e.g., polyether-based polyurethanes) decompose endothermically when contacted by hot fragments. It is postulated that endothermic decomposition of such binders protects the energetic solid portion of the formulation from initiation,

thereby reducing the vulnerability of the gun propellant. Therefore, if we could introduce into the binder a polymer block that decomposes endothermically, we could produce a superior binder that should fulfil the requirements of the Navy's LOVA program.

Under contract with the Office of Naval Research<sup>4</sup> SRI developed a polymerization technique that permits synthesis of polyether glycols of predetermined molecular weight and functionality. We demonstrated that oxetanes and tetrahydrofurans (THFs) can be reproducibly homo- and copolymerized to give a wide range of physical properties. Consequently, we proposed to apply this new polymerization technique to prepare polyether-based thermoplastic elastomers.

By definition, a thermoplastic elastomer is a block copolymer containing distinct hard (glassy) or crystalline and soft (rubbery) segments. A triblock configuration (A-B-A), in which the "A" blocks are hard glassy or crystalline segments and the "B" blocks are rubbery segments has the optimum thermoplastic, elastomeric properties. Block copolymers of this type are rubbery, physically cross-linked, highly elastic materials at temperatures below the glass transition temperature ( $T_g$ ) of the hard glassy or crystalline component. This dual behavior results from the association of A-segment hard domains at temperatures below the softening point of the A component.<sup>5</sup>

## II DISCUSSION

The deficiencies of current gun propellant binders and the processing constraints of cast-cured explosive binders may be overcome by using thermoplastic elastomers. Also, the vulnerability of propellants to jet and spall detonation may be reduced by using thermoplastic, elastomeric materials that will depolymerize endothermally. Furthermore, incorporating energetic groups into the binders should permit the use of a lower solids loading, thus decreasing the sensitivity without sacrificing energy.

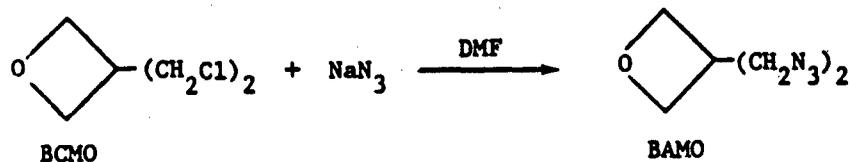
New materials synthesized during this research program were required to meet the following standards:

- (1) Be chemically stable from  $-40^{\circ}$  to  $60^{\circ}\text{C}$ .
- (2) Have a melting transition temperature  $T_m$  for the glassy block of  $80^{\circ}$  to  $90^{\circ}\text{C}$ .
- (3) Have a  $T_g$  for the rubbery block below  $-40^{\circ}\text{C}$ .
- (4) Be compatible with RDX and HMX.
- (5) Retain mechanical integrity when filled with solid explosive up to 80 wt%.
- (6) Exhibit endothermic depolymerization at temperatures above  $100^{\circ}\text{C}$ .

### Monomer Synthesis

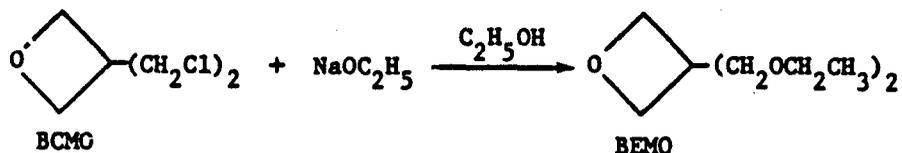
Two monomers were identified that would produce polymers having the requisite properties for the crystalline or glassy blocks of the proposed thermoplastics.

Our previous experience with bis(azidomethyl)oxetane (BAMO) showed that it was potentially the ideal energetic candidate for this application. When polymerized to a molecular weight of 4000 it has a  $T_m$  of  $82^{\circ}\text{C}$ . BAMO is readily prepared by reacting sodium azide with bis(chloromethyl)oxetane (BCMO).<sup>6</sup>



We found that if BCMO is purified by distillation before use, the product BAMO requires only one pass through an alumina column in chloroform to obtain monomer sufficiently pure for polymerization.

The second monomer prepared was bis(ethoxymethyl)oxetane (BEMO). BEMO is also prepared from bis(chloromethyl)oxetane by reaction with sodium ethoxide.<sup>7</sup>



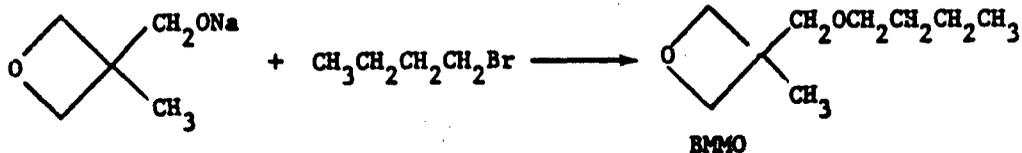
Similarly, if BCMO is purified before etherification a simple flash distillation from calcium hydride produces polymerizable grade BEMO.

### Polymer Synthesis

For the elastomeric block of the thermoplastics we investigated three candidate polymers.

Poly(ethylene glycol) (PEG) was selected to demonstrate the principle of the proposed approach. Although PEG is somewhat crystalline, we felt it was sufficiently elastomeric for a center block and for demonstration of the concept.

The second polymer investigated was a copolymer of THF and 3-butoxymethyl-3-methyloxetane (BMMO). To reduce the crystallinity to poly(THF), BMMO was incorporated to impart internal plasticization of poly(THF). BMMO was prepared by treating butyl bromide with the sodium salt of 3-hydroxymethyl-3-methyloxetane.<sup>8</sup>



The resulting BMO was distilled from calcium hydride before use.

The third polymer investigated was a copolymer of BAMO and THF, which was proposed as an energetic center block in the thermoplastics.

To evaluate each polymer as candidate glassy or elastomeric blocks, we first synthesized each polyetherglycol block by the polymerization method developed earlier at SRI.<sup>4</sup>

Molecular weights of 6000 to 8000 were required to produce the glassy blocks. Therefore, poly(BAMO) and poly(BEMO) were synthesized within this molecular weight range. Each polymer was characterized with respect to molecular weight, polydispersity, glass transition temperature, and melting transition temperature. These results are given below.

<u>Polymer</u>	<u>MW</u>	<u>Q</u>	<u>T<sub>g</sub> (°C)</u>	<u>T<sub>m</sub> (°C)</u>
BAMO	7800	1.2	-32	88
BEMO	8000	1.2	-6	84

The data show that both polymers melt within the desired range. Also the glass transition temperature indicates that both polymers would not be glassy at ambient temperature, but the crystalline nature of each would fulfill the requirements for the formation of crystalline domains within a thermoplastic.

The elastomer blocks synthesized and evaluated were poly(ethylene glycol), copoly(BMO/THF) and copoly (BAMO/THF). Ethylene oxide was polymerized to a molecular weight of 20,000 a value selected to exhibit phase separation in the final thermoplastic. Phase separation was demonstrated when a heated mixture of poly(BAMO) and poly(ethylene glycol) separated into two distinct phases on cooling.

Two alternative elastomeric blocks were synthesized by the copolymerizing of THF with BMMO and with BAMO. The objective here was to take advantage of the elastomeric properties of poly(THF), but to reduce its crystallinity by copolymerization with a second monomer and thus reduce the stereoregularity of the polymer backbone. We had demonstrated earlier that copolymerizing THF and BAMO produces a flowable liquid polyol, that when cured to an infinite network has good low temperature properties.<sup>4</sup>

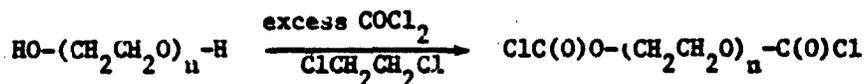
The copolymer of THF and BMMO incorporates the butoxymethyl side group of BMMO to disrupt the chain folding, and the crystallinity of poly(THF). A series of poly(THF/BMMO) polymers was therefore prepared to determine the minimum concentration of BMMO required to produce a noncrystalline polymer.

A detailed characterization of each material synthesized is described.

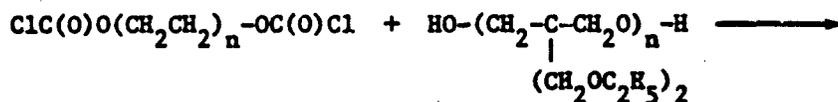
#### Block Formation

To characterize a thermoplastic block copolymer, we had to characterize each polymer block separately and also as part of the final block polymer. Before efforts were expended to copolymerize the candidate crystalline and elastomeric blocks, we elected to use diblock linking to provide material for evaluation. Results of the evaluation of the diblock and triblock polymers prepared in this manner would indicate whether the properties of the block polymers are within the desired range. For this study poly(BEMO) and poly(ethylene glycol) were used.

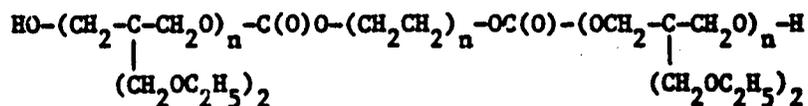
The polymer blocks were linked by reacting of the bis-chloroformate of the center block, PEG, with one or two equivalents of the end block, poly(BEMO), as shown below.<sup>9</sup>



PEG



Poly(BEMO)



BEMO-PEG-BEMO Triblock

The properties determined for the five homopolymers investigated are summarized in Table 1. The densities and refractive indices were each determined with Dale-Gladstone plots of polymer  $dn/dc$  in various solvents. The  $dn/dc$ 's show the expected linear dependence on solvent refractive index and are necessary for the measurement of  $M_w$  and polydispersity. They will also be used later in the analysis of the composition and true weight average molecular weight ( $M_w^*$ ), of copolymers.

Reasonably good agreement is obtained between the measured molecular weights ( $M_w$ ) and those calculated with the Mark-Houwink coefficients  $K$  and  $a$ . The significance of these numbers is illustrated in the gross discrepancies between the true molecular weight and that calculated from size exclusion chromatography (SEC) with polystyrene standards. The latter assumes that all polymers in every solvent can be characterized by the same  $K$  and  $a$  values, a widespread but completely incorrect assumption. The values for BEMO and BAMO reflect the high degree of steric hinderance to crankshaft rotations due to the pendant groups. The substitution of the stiff, polar azoxy group for the ethoxy group results in lower solubility and a decrease in the second virial coefficient  $A_2$ .

The characterization data for copoly(THF-BMBO) (Table 2) demonstrate the importance of accurate molecular weight characterization. The apparent

$M_w$  obtained by light scattering is always greater than the true weight average  $M_w^*$  and varies, with solvent refractive index, from 3430 to infinity

for the 20:80 THF:BMO composition. Analysis of the dependence of  $M_w^*$  on  $n$  indicates the following:

- o  $M_w$  measured in acetone is essentially identical to  $M_w^*$ .
- o The average distribution of THF and BMO repeating units is essentially random, but the exact distribution of segments within a given molecule varies with the  $M_w$  of the molecule.

Analysis of the copolymer composition, based on the well-known additive relationship between weight fraction and homopolymer refractive index, i.e.,  $dn/dc = \sum_i w_i^2 (dn/dc)_i$ , indicates that the actual composition is not identical to that of the initial monomer ratio. This observation and the molecular weight dependence of the segment distribution is very consistent with what one would expect from a slow polymerization reaction.

The block copolymers investigated were prepared in two reactions. The first produced a mixture of AB diblock plus excess B block and the second produced predominantly ABA triblock (Table 3). The excess B block (PEG) resulted because an incorrect molecular weight of 6,000, obtained with a polystyrene calibrated SEC, was used instead of the correct light-scattering molecular weight of 16,000.

Some of the problems encountered in interpreting the apparent weight average molecular weight obtained from copolymers are obviated in these measurements. If scattering is measured in a solvent for which the  $dn/dc$  of one block is very much smaller than the other, then it is essentially invisible. Therefore measurements in benzene, in which the PEG block is almost invisible, yielded the molecular weight of the BMO blocks in a given molecule. That is, the observed molecular weight of an AB diblock is identical to that of the A homoblock and one half of that of an ABA triblock. Thus the BMO homoblock and the methanol-insoluble fraction of the first block copolymer preparation have the same apparent  $M_w$ . The  $dn/dc$  and  $A_2$  each decrease because they are sensitive to the presence of the PEG

block. The apparent  $M_w$  for the AB diblock in THF is much higher as would be expected from the previous discussion of the apparent  $M_w$  and the solvent refractive index.

The methanol precipitation did not completely fractionate the PEG homoblock from the AB diblock as indicated by SEC-LALS (low angle light scattering) techniques. However, enough separated to demonstrate the presence of excess PEG. Both the light-scattering molecular weight and the  $T_g$  by differential scanning calorimetry (DSC) indicated that the soluble fraction was PEG. DSC measurements in the diblock showed distinct  $T_g$ s of  $-63^\circ$  and  $-3^\circ\text{C}$ , indicating that the  $M_w$  of the two blocks are sufficiently high for phase separation to occur.

Similar considerations apply to the analysis of the ABA triblock polymer. SEC-LALS indicates a single narrow distribution product with a  $M_w$  of 32,000, roughly equal to two BEMO blocks. The observed  $dn/dc$  and  $A_2$  are also consistent with what would be expected from an ABA triblock.

Table 1  
HOMOPOLYMER PROPERTIES

	Polymer				
	PEG	BEMO	BMMO	THF	BAMO
$\bar{n}$	1.485	1.460	1.408	1.407	--
$\rho$ (g/mL)	0.879	0.741	--	0.88	--
$M_w$ (dalton $\times 10^{-4}$ )	2.0	1.66	--	--	4.0
$M_w/M_n$	1.4	1.5	--	--	1.8
$A_2$ (dalton $\text{cm}^3/\text{g}^2$ $\times 10^3$ )	--	1.25	--	--	0.91
$M_w:M_n \times 10^{-4}$ (Polystyrene/THF calibration)	--	5.32: 3.27	--	--	5.53: 2.56
$dn/dc \times 10^2$ (mL/g)					
THF	9.8	5.4	-0.126	6.25	9.93
Benzene	-1.4	-4.75	--	--	--
Cymene	-0.4	-3.06	--	--	--
$\text{CCl}_4$	2.76	-0.76	--	--	--
$[\eta]$ (THF, dL/g)	--	0.54	--	--	0.14
$K, a$ (THF)	--	1.58 $\times$ $10^{-3}$ , 0.6	--	--	4.78 $\times$ $10^{-5}$ 1.08
$T_g$ ( $^{\circ}\text{C}$ )	-84	-8	--	--	--

Table 2

## RANDOM COPOLYMER PROPERTIES OF COPOLY (THF-BMMO)

<u>Solvent</u>	<u><math>dn/dc \times 10^2</math> (mL/g)</u>	<u><math>M_w^* \times 10^4</math></u>	<u><math>dn/dc \times 10^2</math> (mL/g)</u>	<u><math>M_w^*</math></u>
Benzene	-2.84	>25.4	--	--
CH <sub>2</sub> Cl <sub>2</sub>	4.09	0.44	--	--
Acetone	10.6	0.343	9.85	0.615
Hexane	8.87	1.0	--	--
CHCl <sub>3</sub>	2.0	1.44	--	--
p-Fluorotoluene	<0.1	"	--	--
CCl <sub>4</sub>	1.05	1.67	--	--
Composition THF:BMMO		20:80	27:73	

Table 3  
BLOCK COPOLYMER<sup>a</sup> PROPERTIES

Solvent	AB + B Preparation		ABA Preparation
	MeOH Soluble	MeOH Insoluble	MeOH Insoluble
BENZENE			
$M_w$ (dalton $\times 10^{-4}$ )	--	1.54	3.2
$A_2$ (dalton $\text{cm}^3/\text{g}^2$ $\times 10^3$ )	--	0.70	0.55
$dn/dc$ (mL/g $\times 10^2$ )	--	-4.43	-3.83
THF			
$M_w$ (dalton $\times 10^{-4}$ )	2.0	$10^5$	--
$A_2$ (dalton $\text{cm}^3/\text{g}^2$ $\times 10^3$ )	--	--	--
$dn/dc$ (mL/g $\times 10^2$ )	9.80	5.02	--
$M_w/M_n$	1.4	bimodal distribution	1.4
$T_g$ ( $^{\circ}\text{C}$ )	-5.1	-65, -3	--

<sup>a</sup>A block: poly(BEMO).  
B block: poly(ethylene glycol).

### III CONCLUSIONS

We have demonstrated that block polymers based on crystalline and rubbery segmented polyethers can be synthesized and that they show the properties required for thermoplastic elastomers.

To aid in synthesizing and characterizing these new materials, we used differential refractive index techniques to distinguish between mixtures of homopolymers, random copolymers, and block polymers.

Results for the random copolymers indicate the following:

- o Random copolymers without blockiness were obtained.
- o Reasonably high molecular weights were obtained, e.g., molecular weights above the point at which the glass transition temperature depends on the molecular weight.
- o Random copolymerization reduced the glass transition temperature substantially, indicating that block copolymers containing the random copolymer as the soft block will have the desired thermoplastic elastomer characteristics.
- o Intrinsic viscosity-molecular weight relationship indicates a high degree of steric hindrance by pendant azoxy groups to rotation about the carbon backbone, leading to a highly expanded coil in solution.

Characterization of homopolymers provided the following information:

- o Absolute molecular weights, scattering factors in different solvents, polydispersity data, and solvent interaction parameters.
- o The  $n$  and  $m$ , required for balanced stoichiometry in the block copolymer condensation, e.g.,  $2(A)_m + (B)_n = (A)_n(B)_m(A)_n$ .

Finally, the methods developed for block copolymer characterization allowed us to accomplish the following:

- o Unambiguously differentiate between starting materials (homopolymers  $A_n$  and  $B_m$ ) and the desired block copolymers ( $A_n B_m A_n$ ).

- o Demonstrate that the minimum required molecular weight necessary for phase separation was realized, and that phase separation occurred.

## 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 modified procedures of known reactions. All other experiments reported in the text duplicate published procedures.

#### 3,3-Bis(ethoxymethyl)oxetane

93 g (4 mol) of sodium was dissolved in 600 mL of ethanol. With vigorous stirring, 155 g (1 mol) of 3,3-bis(chloromethyl)oxetane was added over a 30-min period. The reaction flask was then heated to 80°C for 15 h and then cooled in an ice bath. The resultant white solid was filtered and the filtrate washed twice with an equal volume of water. The water-insoluble product was dried over magnesium sulfate and then vacuum distilled. The fraction boiling at 83-85°C at 10 torr yielded pure product, representing an 87% yield. Characterization was confirmed by NMR and IR analysis.

#### 3-Butoxymethyl-3-methyloxetane

102 g (1 mol) of 3-hydroxymethyl-3-methyloxetane was dissolved in 300 mL of 2-butanone. To this solution was added with vigorous stirring 35 g (0.9 g-atm) of potassium the solution was warmed to 45°C to aid dissolution. When a clear solution had been obtained, a solution of 221 g (1.2 mol) of 1-iodobutane in 100 mL of 2-butanone was added over a 5-min period. The resulting solution was then heated to reflux for 24 h. The mixture was cooled and quenched with 100 mL water and extracted with methylene chloride. The organic phase was dried over magnesium sulfate, evaporated to constant weight and the reaction products were isolated by open column chromatography using alumina and methylene chloride. The major fraction proved to be the required product representing a 37% yield. The structure was confirmed by NMR and IR analysis.

## Polymerization Procedures, Block Synthesis

### 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 before use. 1,4-Butanediol was distilled under reduced pressure 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 before the introducing reactants. During polymerizations the reactants were maintained under a dry nitrogen atmosphere.

### Typical Solution Polymerization Procedure (BAMO; BEMO)

A flame-dried resin flask was charged with the calculated weight of diol as a 50 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 wt% 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 (BMMO/THF)

A flame-dried resin flask was charged with the calculated weight of monomer and butanediol. The flask was then cooled 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.

### Block Linking Technique

#### Preparation of Poly(ethylene glycol)bis-chloroformate

In a flame-dried flask under a nitrogen atmosphere 20 g of poly(ethylene glycol) was dissolved in 100 mL of dry dichloroethane (dried over calcium hydride). The solution was cooled to  $-10^{\circ}\text{C}$  and then a 5 mol excess (0.005 mol) of phosgene was introduced. The temperature was maintained at  $-10^{\circ}\text{C}$  for 2 h, then allowed to come to ambient temperature overnight. Most of the excess phosgene was removed by passing a stream of dry nitrogen through the solution; the remainder was removed at reduced pressure. The product was used without further purification.

#### Block Polymer Preparation

To the poly(ethylene glycol)bis-chloroformate was added a solution of 14 g (0.002 mol) of 7,000 molecular weight poly(BEMO) in 50 mL of dry dichloroethane followed by 1 mL of analytical grade pyridine. The resulting solution was heated to  $50^{\circ}\text{C}$  overnight, cooled, quenched with water, and extracted with methylene chloride. Further isolation was achieved by precipitation from methanol.

#### Functionality Determination

The polymer (1 g) was heated for 15 min at  $95^{\circ}\text{C}$  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 0.1 N 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 hexamethyl disilazane for 1 h. The mixture was then heated overnight under moderate vacuum to remove the volatile trimethylsilyl 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 determined by NMR using benzene on 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 (Preliminary)

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 THF. The system was calibrated with polypropylene glycol standards of molecular weight 800, 1200, 2000, and 4000. Molecular weights determinations were confirmed using a Chromatix KMX6 light-scattering analyzer.

#### Molecular Weight by Light Scattering

Light scattering measurements of the weight average molecular weight ( $M_w^*$ ) and the second virial coefficient ( $A_2$ ) were made on solutions filtered through 0.2 µm filters with a LALS photometer (Chromatix KMX-6). Combined SEC-LALS were made with two independent commercial systems and the data were analyzed with a dedicated minicomputer (Chromatix, DP-1).

#### Differential Refractive Index Determination

The differential refractive index ( $dn/dc$ ) was obtained with a refractometer (Brice-Phoenix) modified for operation at 6328 Å. The

instrument was calibrated with two systems for which the  $dn/dc$  is well known, e.g., polystyrene:toluene and  $KCl:H_2O$ .

Glass Transition Temperature Determination

The glass transition temperature ( $T_g$ ) was determined both by DSC, (Du Pont 940) and by measurement of the temperature dependence of the dynamic tensile modulus ( $E^*$ , Rheovibron DVD-II) at 110 Hz.

## REFERENCES

1. "Propulsion Review: Solid Propellant Motor and Gun Propulsion Research and Exploratory Development Programs Sponsored by the Naval Sea Systems Command," Naval Weapons Center, China Lake, CA (July-September 1980), pp. 69-75, and (October-December 1980), pp. 61-68.
2. Kraton is a thermoplastic elastomer produced by block copolymerization of polystyrene and polybutadiene and manufactured by the Shell Chemical Company.
3. Gun Propellant Workshop, Naval Ordnance Station, Indian Head, MD, February 11, 1981.
4. G. E. Manser and D. L. Ross, "Synthesis of Energetic Polymers," SRI International, Final Report, 15 September 1982. ONR Contract No. N0014-79-C-0525.
5. J. A. Manson and L. H. Sperling, Polymer Blends and Composites (Plenum Press, New York, 1976), pp. 127-129.
6. W. Carpenter, U.S. Patent 3,138,609 (1964).
7. A. C. Farthing, J. Chem. Soc. 3648 (1955).
8. D. A. Levins, G. E. Manser, and D. L. Ross, "Nitro Ingredient Feasibility Demonstration," SRI International, Final Report, AFRPL-TR-82-065, October 1982.
9. S. H. Merrill, J. Polym. Sci., 55, 343 (1961).

## V PUBLICATIONS AND PRESENTATIONS

The following presentation was made during this reporting period

"Novel Polyether Block Copolymers," Energetic Polymer Workshop, Chestertown, Maryland (August 17, 1982)

The following abstract was submitted and accepted for the AIChE meeting in Los Angeles, CA, November 18, 1982:

"Viscoelastic Behavior of Block Copolymers Based on Polyethers," joint paper with L. H. Sperling et al., Lehigh University.

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/DL0L Eglin AFB, FL 32542	1	Dr. R. Rogers 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 O3P25 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. Doua 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 247 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 Odgen, 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>	
1	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

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	