21 June 1983

Office of Naval Research
800 North Quincy Street
Arlington, VA 22217

ATTENTION: Dr. R. S. Miller; Code 432

SUBJECT: Quarterly Letter No. 2: "High Energy Binders"
Contract N00014-82-C-0800; NR659-792
Thiokol Project: JM101

Dear Dr. Miller

During this reporting period, we have continued our research effort in the areas of monomer synthesis, including non-energetic monomers for the thermoplastic elastomers, polymer synthesis, and polymer characterization. We also initiated the determination of reactivity ratios of new monomers and the thermal depolymerization/decomposition of polyethers by thermogravimetric analysis.

Two new monomers were synthesized during this reporting period for use in imparting internal plasticization to poly(THF). The first, 3-octoxymethyl-3-methyl-oxetane (OMMO) was readily prepared in high yield by the reaction of octyl bromide on the sodium salt of 3-hydroxymethyl-3-methyloxetane in dioxane. The second monomer, bis(methoxyethoxy methyl)oxetane (BMEMO) was prepared by the action of bis(chloromethyl)oxetane on the sodium salt of methoxyethanol in excess methoxyethanol. Both monomers were isolated at >99% purity by vacuum distillation from sodium hydride.

The polymer synthesis effort was divided between preparing simple low molecular weight energetic polyether glycols and relatively high copolymers for the thermoplastic elastomers. During the early part of this reporting period, we prepared two 100-gram batches of poly[bis(azidomethyl)oxetane/bis(nitratomethyl)oxetane] (BAMO/BNMO) and poly(nitratomethyl-methyloxetane) (NMMO). Both materials were divided into three batches for evaluation by ourselves and outside investigators. Samples of each of these polymers (25 grams) were shipped to Dr. R. Reed at China Lake and Dr. C. Gotzheimer at Indian Head. Their individual results will be transmitted to you at the completion of their investigation. We submitted the remaining material to vacuum thermal stability and Taliani testing at our facility. Both polymers were evaluated against nitroglycerine (NG) and TMETN, with and without stabilizer (MNA). Initial results clearly show that both polymers are as stable or more stable than TMETN depending on the test and significantly more thermally stable than NG. Each polymer showed oven stability up to 130°C at which time self-heating occurred to fire at 208°C. This property is reflected by TMETN. Comparison of the two polymers shows that BAMO/BNMO is slightly more thermally stable than NMMO. In view of these encouraging results, we have scaled up poly(NMMO) to a one-pound quantity for formulation evaluation.
In order to develop thermoplastic elastomer with highly elastomeric properties, we have synthesized two new polymers based on poly(THF) using OMMO and BMEMO as comonomers. If our reasoning is correct, then a dramatic drop in viscosity should be noted over such polymers as THF/BMMO and THF/BEMO. Therefore, two polymers were prepared: poly(THF/OMMO) and poly(THF/BMEMO) with a molecular weight of 20,000. Both polymers were found to have very low viscosity upon isolation and visually can be called internally plasticized. As time permits, each will be incorporated into a thermoplastic elastomer with poly(BEMO) as the crystalline block.

During the previous reporting period, we identified the components of our first-generation thermoplastic elastomer. Poly(BEMO) was elected as the crystalline block and the copolymer poly(THF/BMMO) as the rubbery block. Theoretical calculations lead us to synthesized specific block sizes for phase separation. During this reporting period, we have prepared six distinct block copolymers varying block size and block configuration. Block sizes for poly(BEMO) were 12,000 and 20,000 and poly(THF/BMMO) 20,000 and 35,000. Block configurations of ABA and (AB)\text{n} were used for the above combinations of polymers. Blocks were linked via carbonated coupling employing phosgene in pyridine at 0°C. Initial results indicate that 20,000 BEMO produces too large a crystalline domain causing the material to be chesy under stress. 35,000 poly(THF/BMMO) with 12,000 poly(BEMO) in an (AB)\text{n} configuration appears to give very promising material. This polymer was extremely tough, 6,000 psi; Young's modulus $T_{\text{m}}$ -50°C, and $T_{\text{g}}$ 82°C. To show its thermoplastic property, it was processed ten times by melt casting at 100°C and cooling to room temperature. Each time, the polymer was observed to retain its physical properties. Samples of these polymers, as polymer crumbs and melt cast sheets, have been supplied to Professor Sperling at Lehigh University for his evaluation of physical properties and morphology.

The reactivity ratio of nitratomethyl-methyoxetane and bis(azidomethyl)oxetane was determined by our previously described method. The data was handled by a Hewlett-Packard 9825A computer. The Apple II program used for our previous work on the azido polymers was adapted to the H/P. The program and results are enclosed with this report and clearly show that copolymerization of azido and nitrato oxetanes will produce random insertion of each monomer.

$$
\begin{align*}
R_1 \text{ BAMO} &= 0.9346 \pm 0.1081 \\
R_2 \text{ AMMO} &= 1.1130 \pm 0.1683 \\
R_1 \text{ NMMO} &= 1.8909 \pm 0.1653 \\
R_2 \text{ BAMO} &= 2.4386 \pm 0.1427
\end{align*}
$$

Further monomer pairs will be examined during the next reporting period including nonenergetic cyclic ethers to enable the best copolymers to be synthesized for the thermoplastic elastomers.

To compliment the work being pursued at Lehigh University and Space Sciences, we have examined the thermal properties (depolymerization/decomposition) of polymer (BEMO) by thermogravimetric analysis (TGA). The TGA was calibrated using oxalic acid, the standard procedure. At 2°C/min a satisfactory calibration curve was observed for this standard. At heating rates greater than 2°C/mm, the dehydration overlapped the decomposition portion of the curve. Poly(BEMO) was then analyzed.
at 0.5, 2, 5, and 10°C/min in air and under nitrogen. It was immediately apparent that the analysis was extremely atmosphere dependent. The nitrogen atmosphere increased the "initial" temperature. The "initial" temperature is when the balance can first detect a change in mass. Repeated scans in nitrogen revealed initial temperatures between 205°C and 216°C. This inconsistency cannot be explained at this time but may be due to atmosphere loss on some runs.

Isothermal TGA curves were obtained at 125, 150, 175, 200, and 225°C under nitrogen. The lower temperature curves were straight lines for the mass versus time plots; however, the slope changed during the scan. The higher temperature scans were not straight lines and suggested that the order of the reaction changed with temperature. A more detailed report will be submitted when the completed data are assimilated. A DSC curve was obtained at 10°C/min with the sample in a large volume cell under air. An exotherm was observed at a significantly lower temperature (135°C) than by any of the "initial" temperatures observed by TGA (167°C).

During this reporting period, a presentation was given at the ONR Workshop held at the University of Massachusetts, April 5-6, 1983; and two abstracts were submitted for the upcoming JANNAF Propulsion Meeting.

1. "Novel Polyether Thermoplastic Elastomers for LOVA"

2. "Nitrate Ester Polyether Prepolymers"


Sincerely,

Gerald E. Mauser
Associate Scientist
Propellant Research Department

GEM/1w

Attachment
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60: ent "",C[I,J,I];wrt 16.2,E#;prt "IN GC SHOT",I,C[I,J,I],""
62: next K
63: S=I(I)+M(I)+N(I)-R(I,J)/r1AR(I,J)+r23
64: M(I)/r11+r24
65: N(I)/r12+r25
66: S=I(I)+M(I)+N(I)-R(I,J)/r2AR(I,J)+r26
67: r23+r11+r48
68: r26+r12+r49
69: r24+r48+r50
70: r25+r49+r51
71: r24/(r24+r25)+E[I,J]
72: r25/(r24+r25)+F[I,J]
73: r50/(r50+r51)+G[I,J]
74: r51/(r50+r51)+H[I,J]
75: (r50+r51)/(r24+r25)+k[I,J]
76: fx=6;wrt 16.1
77: prt "IN. MOLE% A",E[I,J],"
78: prt "IN. MOLE% B",F[I,J],"
79: prt "MOLE% A IN POLY",G[I,J],"
80: prt "MOLE% B IN POLY",H[I,J],"
81: prt ": CONVERSION",K[I,J],"
83: G[I,J]=H[I,J]+Y
84: K[I,J]=1+X/(1+Y)+r27
85: Yr27/X+r28
86: log(1-r28)/log(1-r27)+Z
87: Y-Z2+0[I,J]
88: (Y-1)/Z+P[I,J]
89: if 0[I,J]<r13;gto +2
90: 0[I,J]+r13
91: if 0[I,J]>r14;gto +2
92: 0[I,J]=r14
93: next J
94: if f1g5;gto "CHANGES"
95: next I
96: if f1g4;gto "CHANGES"
97: ent "CHANGES?",I;f1g13=0;gsb "CHANGES"
98: r(r13r14)+r29
99: for I=1 to r8
100: for J=1 to r9
101: 0[I,J]<r29+0[I,J]=Q[I,J]
102: P[I,J]<r29+0[I,J]=T[I,J]
103: r30+Q[I,J]+r30
104: r31+T[I,J]+r31
105: r32+Q[I,J]+r32
106: r33+T[I,J]+r33
107: r34+T[I,J]=Q[I,J]+r34
108: next J
109: next I
110: r89+A
111: (Ar34-r30r31)/(r32r30+r32r30)+r35
112: (r31-r35r30)/A+r36
113: (r34-A-r30r31)/2/(r32r30r32)+r37
114: prt "CORR COEF",r37
115: r36r29+r4
116: r35r36+r3
117: prt "R1="r3,"R2="r4
118: Ar32-r30+r36
119: r(r33A-r31r32-r30r352)/r(rA-2A)+r39
120: r39r(A-r30)+r40
121: r39r(r32r30)+r41
122: r41r(r32r30)+r42
123: r(r29r41)+r43
124: prt "DEV IN R1="r4
125: prt "DEV IN R2="r4
rcf I+1,r12
trak 0;ret

"LIMITS": cfg 3
if r57-r56>=10;1;r57=r57;1;r56=r56;cfg 3
(int(10-r56)-1)/10+r52

if r56(10;10;+rcf(10-r56)-1)/10+r52;int(10-r52);10+r54

0+r53;1+W

"INT": for I=5 to 9
if rcf(10-r54-r52)/I=0; (r54-r52)/I+r53
next I

if r53=0;1.W+r(53+W)+r(53+W);-1.W+W;gto "INT"

if r53<.5; r54-r55; r55-r55; r55-r54; if r57-r54; r54+r53=r54

if r55>-.5; r54+r55; r55+r54; r55-r54; if r56<r52; r52-r53+r52

if flg3; 10r52=r52; 10r53=r53; 10r54=r54

ret

"ETA-XI": wrt 705, "IP140, 3025, 6550, 7920"
scl 0,1,r52,r54; wrt 705, "NL2"; wrt 705, "VS"; csize 1.5, 1.5

xax r52, 1, 0, 1; fxd 1; for I=0 to 1 by .1
plt I; r52, 1; cplt .-2, -1; lbl I
next I

yax 0, r53, 52, r54, 1; csize 2, 1.5

wrt 705, "TL0,2"; xax r54, .1, 0, 1; yax 1, -r53, r54, r52

plt .5, r52, 1; cplt .-1, -2; lbl "Xi"

"Eta VS Xi PLOT FOR "[C];A#C"[len(C)+1]

"/"+C# [len(C)+1]; B#C"[len(C)+1]

plt 2.5, 1.5; plt .5, r54, 1; cplt -[len(C)+2, 2]; lbl C#

csize 1.5, 1.5; fxd 3; plt 1, r52, 1; cplt 0, 2; lbl "ALPHA=",[r29

ret

"SYMB": plt Q1I, JJ+.0075, T1I, J1, 1

for L=0 to 360 by 20

plt Q1I, JJ+.0075cos(L), T1I, J1+.0075(r54-r52)sin(L), 2
next L

plt Q1I, J1, T1I, J1, 1

ret

"CHANGES":

ent "CHANGE INITIAL PARAMETERS?", I; if flg13=0; sfg 2; 4; gto "INIT"
cfg 4

ent "CHANGE PARAMETERS FOR A RUN?", I; if flg13; ret

sfg 5, 2; ent "RUN #?", I; gto "ANAL"
cfg 5; ret

+31446
INSTANTANEOUS COMPOSITION CURVE
OF BAMO/AMMO COPOLYMER

MOLE FRACTION OF BAMO UNITS
IN INITIAL POLYMER

MOLE FRACTION OF BAMO UNITS
IN INITIAL POLYMER

R1 BAMO = 0.9348 +/- 0.1981
R2 AMMO = 1.1138 +/- 0.1683
CC = 0.9942

MOLE FRACTION OF BAMO IN MONOMER CHARGE

MOLE FRACTION OF AMMO IN MONOMER CHARGE
Eta VS Xi PLOT FOR BAMO/AMMO

\[\text{ALPHA} = 0.468\]
INSTANTANEOUS COMPOSITION CURVE
OF NMMO/BAMO COPOLYMER

MOLE FRACTION OF NMMO UNITS
IN INITIAL POLYMER

MOLE FRACTION OF NMMO IN MONOMER CHARGE

MOLE FRACTION OF BAMO UNITS
IN INITIAL POLYMER

MOLE FRACTION OF BAMO IN MONOMER CHARGE

R1 NMMO = 1.8929 ± 0.1653
R2 BAMO = 2.4386 ± 0.1427
CC = 0.9978
Eta VS Xi PLOT FOR NMMO/BAMO

Eta

Xi

ALPHA = 1.000