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ENERGETIC AZIDO COMPOUNDS

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20. ABSTRACT (Continued)

50/50 mol % BAMO/THF copolymer. Emphasis on the program was therefore concentrated on optimizing the preparation of this copolymer so that it would be suitable for scaleup.

A safe and reproducible process was demonstrated for the production of high-purity BAMO (99+%), at the 8- to 12-pound level in a 5-gallon Pfaudler reactor, with average yields of 80%. Five runs were conducted which yielded a total of 48.77 pounds of BAMO.

A safe and reproducible process was also developed for the production of the BAMO/THF copolymer at the 15- to 26-pound level in a 5-gallon Pfaudler reactor, and yields of 84 to 88% were obtained. Three runs were carried out which gave a total production amount of 59.9 pounds of the copolymer. The properties of the copolymers were quite comparable in terms of M_w (3833-4022), M_n (2541-2578), f (2.07-2.13), and Eq. Wt. (1210-1323). The production procedures used for BAMO and the BAMO/THF copolymer are described in the appendices.

Explosive classification tests were conducted on the BAMO/THF copolymer and a 30% solution of BAMO/THF in methylene chloride. A shipping classification of "Flammable Liquid, N.O.S." was assigned to the BAMO/THF copolymer in a 30% methylene chloride solution.

Shipment of the 59.9 pounds of the BAMO/THF copolymer was made to 17 laboratories designated by the scientific officer.

FOREWORD

The research reported herein was supported by the Office of Naval Research, Power Programs, Code 473, with Dr. R. S. Miller as the scientific officer. This report covers the period 1 May 1980 through 30 November 1981. The program was directed by Dr. M. B. Frankel. The scientific work was carried out by Dr. M. B. Frankel, E. R. Wilson, R. L. Kistner, and D. O. Woolery of Rocketdyne, and Dr. C. Hamermesh and C. McArthur of the Science Center (all of Rockwell International). Dr. L. R. Grant of Rocketdyne served as the program manager.



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GLOSSARY

BAMO	3,3-bis(azidomethyl) oxetane
BCMO	3,3-bis(chloromethyl) oxetane
BDO	1,4-butanediol
DMF	Dimethylformamide
Eq. Wt.	Equivalent weight
f	Functionality
GC	Gas chromatography
GPC	Gel permeation chromatography
M_n	Number average molecular weight
M_w	Weight average molecular weight
T_g	Glass transition temperature
THF	Tetrahydrofuran
TMP	Trimethylpropane

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INTRODUCTION

The objective of this program was to synthesize and evaluate energetic azide prepolymers for potential use in advanced solid and gun propellants, and explosives. The energetic azide compound used for these studies was 3,3-bis(azidomethyl) oxetane (BAMO). The prepolymer's property goals included, but were not limited to, the following:

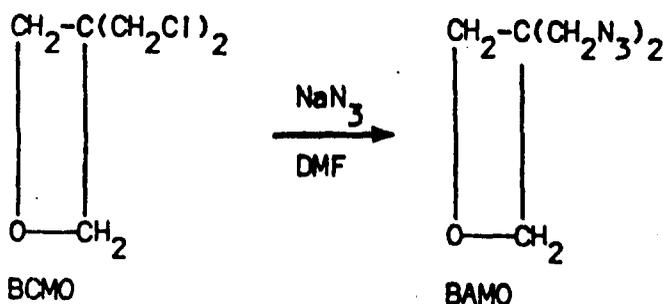
1. A molecular weight range of 2000 to 4000
2. A narrow molecular weight range
3. A hydroxyl functionality of two or greater
4. A liquid or low-melting polymer that was soluble in plasticizers.

The program consisted of three phases: (1) laboratory synthesis and characterization of BAMO and its homopolymer, (2) scaleup studies on BAMO and its conversion to a copolymer with tetrahydrofuran (THF), and (3) shipment of samples of the copolymer to various laboratories for evaluation. The results of the copolymerization efforts are first discussed, after which the homopolymerization studies are described.

TECHNICAL DISCUSSION

SYNTHESIS OF BAMO

During the first year of the program, a facile synthesis of 3,3-bis(azidomethyl) oxetane (BAMO) was developed (Ref. 1). This consisted of treating 3,3-bis(chloromethyl) oxetane (BCMO) with sodium azide in dimethylformamide (DMF) medium at 85 C for 2 hours:



The BCMO was purified by distillation prior to its use, and the material was recovered in 99+ % purity based on gas chromatography (GC) analyses. The BAMO was also purified by distillation in the earlier work to give material in a purity of 99+ %. Because of the potential hazard involved in the distillation of such an energetic compound (estimated $\Delta H_f = +102$ kcal/mole), a much safer and simpler purification procedure was developed. This simply consisted of passing a methylene chloride solution of the BAMO through a basic alumina column. High purity (99+ %) BAMO was obtained from this simple operation and in overall yields exceeding 90%. Several pounds of high-purity BAMO were prepared by this process for the laboratory polymerization studies.

An alternate process for converting BCMO to BAMO in aqueous medium was also developed using a phase transfer catalyst (methyl tricaprilylammonium chloride). This procedure has the potential advantage of being more economical since it eliminates the use of the organic solvent. In a single run, BAMO of 98% purity was prepared in a yield of 75%.

BAMO Scaleup

For the production of the BAMO/THF copolymer, large quantities of BAMO were needed. The requisite amounts of BAMO were successfully prepared as described below.

The BCMO, which was purchased from Hercules, Inc., had a purity of about 75+ %. Consequently, a rigorous purification of this material was required before it could be converted to BAMO. For this purpose, a 40-plate Oldershaw fractionating column was purchased and installed. Operating at a 15/1 reflux ratio and at 140 °/110 mm, BCMO was routinely produced with a purity of 99+ %. Approximately 60 pounds of high-purity BCMO were prepared in this manner.

A 5-gallon, glass-lined Pfaudler reactor was modified for scaling up the BAMO preparation to the 8- to 12-pound level. Based on the laboratory preparative studies, detailed certification procedures were written and approved by the Rocketdyne Safety Committee. Six scaled-up runs were carried out to give a total of 48.77 pounds of BAMO with a purity of 99+ %, and in an average yield of 80%. The results are summarized below.

<u>Run No.</u>	<u>Yield</u>		<u>Purity,*</u> <u>%</u>
	<u>Pounds</u>	<u>%</u>	
5-1	8.41	77.9	99+
5-2	8.86	80.7	99+
5-3	8.80	80.4	99+
5-4	11.79	82.3	99+
5-5	10.91	76.2	99+

*Analyses were performed by GC analysis. The procedure that was utilized for the BAMO production is delineated in detail in Appendix A.

SYNTHESIS AND CHARACTERIZATION OF THE COPOLYMER OF 3,3-bis(AZIDOMETHYL)
OXETANE AND TETRAHYDROFURAN

Previous homopolymerization studies conducted on 3,3-bis(azidomethyl) oxetane (BAMO) under varying experimental conditions invariably yielded a solid polymer which melted at temperatures >70 C (Ref. 1). Additional studies conducted during this report period gave similar results which are described in a subsequent section of this report.

The melting points of polyols, for example, are dependent on the crystallinity of the molecule (excluding molecular weight effects) which, in turn is a function of the symmetry of the macromolecule or repeating unit (monomer). Therefore, a homopolymer of BAMO, because of its symmetry, would tend to be more crystalline than a copolymer containing dissimilar monomers. By following this approach, copolymers of BAMO might therefore be obtained which possess lower melting points and glass transition temperatures (T_g) than exhibited by the homopolymer.

Research studies conducted at the Stanford Research Institute (SRI) demonstrated that the melting points of the BAMO polyols could be lowered by the copolymerization of BAMO with THF. They found that a melting point as low as -5 C could be obtained for a 50/50 mol % BAMO/THF copolymer (Ref. 2).

The SRI studies also showed that by use of a 2/1 molar ratio of boron trifluoride diethyletherate ($\text{BF}_3 \cdot \text{OEt}_2$) and an alkanediol, it was possible to control the initiator/monomer ratio to obtain a polyol of predetermined molecular weight and narrow polydispersity. The resulting polymer unit molecular weight was equal to the stoichiometric addition of the molecular weights of the diol and monomer. The functionality of the polymer was that theoretically predicted (2) with minimal cyclic oligomer contamination. While several copolymers of BAMO and THF were investigated by SRI, the material chosen for study at Rocketdyne for eventual scaleup was the one containing equal molar amounts of BAMO and THF. For the preparation of this copolymer, SRI utilized

a recipe consisting of BAMO:THF:1,4-butanediol (BDO): $\text{BF}_3 \cdot \text{OEt}_2$ in the molar amounts of 10:10:1:2, respectively. These relative molar amounts served as the basis for the laboratory and scaleup copolymer studies next described.

Laboratory Studies

Small-scale laboratory studies were first carried out on the preparation of the 50/50 mol % BAMO/THF copolymer using the SRI process. The objectives of this work were to verify the process and to determine the optimum reaction conditions for scaleup. The polymerization studies were performed in a jacketed round-bottom flask, equipped with a mechanical stirrer, which was thermostatted to the desired temperature by circulation of externally cooled isopropanol.

The SRI bulk copolymerization procedure consisted of first preparing the initiator by addition of $\text{BF}_3 \cdot \text{OEt}_2$ to a solution of BDO in THF, followed by addition of the BAMO. In the first three small-scale runs (Table 1), the effect of temperature on the polymerization rate was evaluated. The polymerizations were run at -20 (Run 1), -5 (Run 2), and 20 C (Run 3), and the disappearance of monomer, both BAMO and THF, was followed by GC analyses. For a quantitative conversion of both monomers, 48 hours were required at -20 C and 24 hours at -5 and 20 C. The equivalent weights of the polymers were 1940, 1510, and 1370 at -20, -5, and 20 C, respectively, which indicated that the lower temperatures favored higher molecular weight. Low glass transition temperatures were obtained for these copolymers (-35 to -49 C).

The principal experimental problem encountered in these runs was that associated with mechanically stirring the reaction mixture which became extremely viscous after several hours of reaction time. This was a particularly troublesome feature at the reaction temperature of -20 C. Consequently, no additional polymerization studies were conducted at this temperature.

TABLE 1. SUMMARY OF SMALL-SCALE BAMO/THF COPOLYMERIZATION STUDIES

Run	THF, GRAMS (MOLES)	BDO, GRAMS (MOLES)	BF ₃ ·OEt ₂ , GRAMS (MOLES)	BAMO, GRAMS (MOLES)	REACTION TEMPERATURE, C	REACTION TIME HOURS	EQUIVALENT WEIGHT	T _g ,C	REMARKS
1	8.8 (0.12)	1.09 (0.012)	3.4 (0.024)	20 (0.12)	-20	48	1940	-49	MECHANICAL STIRRING WAS PERFORMED THROUGHOUT REACTION TIME.
2	17.6 (0.24)	2.16 (0.024)	6.8 (0.048)	40 (0.24)	-5	20	1510	-35	MECHANICAL STIRRING WAS PERFORMED THROUGHOUT REACTION TIME.
3	17.6 (0.24)	2.16 (0.024)	6.8 (0.048)	40 (0.24)	20	24	1370	-48	MECHANICAL STIRRING WAS PERFORMED THROUGHOUT REACTION TIME.
4	31.1 (0.43)	3.85 (0.043)	11.85 (0.084)	72 (0.43)	20	22	1340	-	MECHANICAL STIRRING WAS PERFORMED THROUGHOUT REACTION TIME.
5	172 (2.38)	21.6 (0.24)	68 (0.43)	400 (2.38)	-5	48	-	-	STATIC POLYMERIZATION AFTER INITIALLY STIRRING FOR 8 HOURS.
6	172 (2.38)	21.6 (0.24)	68 (0.48)	400 (2.38)	20	17	-	-	MECHANICAL STIRRING WAS PERFORMED THROUGHOUT REACTION TIME.
7	86 (1.19)	10.7 (0.12)	34 (0.24)	200 (1.19)	-5	68	1230	-	STATIC POLYMERIZATION AFTER INITIALLY STIRRING FOR 8 HOURS.

The run size was scaled up from 0.12 mole to 2.38 moles for runs 4 through 7, and the experiments were conducted at temperatures of -5 and 20 C. During these runs, the effect of initially stirring the reaction mixture for 8 hours was investigated followed by allowing the polymerization to proceed to completion under static conditions. Based on periodic sampling and GC analyses of the reaction mixture, the reaction was completed after a longer reaction time, as is shown in Table 1.

One additional procedural modification was made for run 7. For this experiment, only one quarter of the THF normally used was added to the BDO/BF₃·OEt₂ solution. The remaining THF was mixed with the BAMO before its addition. This procedural change was considered to be important for scaleup operations because it would minimize the handling of large quantities of neat BAMO. Except for the time required for completion of the reaction, no adverse effects were noted as a result of this modification.

At the time these studies were being conducted, spurious molecular weight results for the copolymer were being obtained by the gel permeation chromatographic (GPC) technique. Since SRI had previously shown the materials to be difunctional, the hydroxyl equivalent weights were used to establish the molecular weight vs temperature of polymerization relationship. Also, since SRI had reported that better gumstock properties were obtained from the -5 vs 20 C prepared material, a reaction temperature of -5 C was chosen for the scaleup studies.

Scaleup Studies

A 5-gallon, jacketed, glass-lined Pfaulder reactor was utilized for the BAMO/THF copolymer production runs. Based on the laboratory-size experiments, detailed operational procedures were written and approved by the Rocketdyne Safety Committee. Three production-size runs were then carried out which gave a total amount of 59.9 pounds of the copolymer. The yields of the copolymer after purification ranged from 84 to 88%.

The reaction conditions employed for the three RAMO/THF copolymer production runs and the analyses for the purified products are summarized in Table 2. A detailed description of the reaction and copolymer workup procedure is given in Appendix B.

The larger-scale polymerizations were carried out nominally at -5°C and for reaction times of 64 to 85 hours. The reaction mixture was stirred for an additional hour after the monomer had been added, and the reaction was then allowed to proceed statically for the remainder of the reaction time.

Runs 5-1 and 5-3 (Table 2) were conducted in an identical manner, i.e., one quarter of the THF was used in the initiator solution and the remainder was added as a solution with BAMO. All of the THF was combined with the BDO and $\text{BF}_3 \cdot \text{OEt}_2$ in the reactor for run 5-2. During run 5-1, exotherms were recorded on addition of the BAMO/THF solution. This observation was believed due to the volume of THF, BDO and $\text{BF}_3 \cdot \text{OEt}_2$ initially in the reactor, which was insufficient to obtain optimum stirring and thus good heat exchange between the reaction mixture and the cooled reactor walls. In an attempt to correct this matter, the addition scheme given above for run 5-2 was employed.

There was a definite difference in the viscosities of the products obtained from runs 5-1 and 5-3 vs run 5-2. Copolymers 5-1 and 5-3 were flowable, viscous liquids at ambient temperature, whereas, copolymer 5-2 was much more viscous and would not flow at ambient temperature. These results indicated that the addition of the mixed monomers to the initiator solution is the preferred technique because it appears to give a more random distribution of the monomers in the polymer chain, which results in a less crystalline copolymer.

Characterization Studies

The properties measured on the copolymer products, summarized in Table 2, were quite comparable in terms of M_w , M_n , f , and Eq. Wt. (equivalent weight). The molecular weight determinations were made by SRI using a Waters gel permeation

TABLE 2. SUMMARY OF REACTION CONDITIONS, YIELDS AND ANALYSES OF THE SCALED-UP BAMO/THF COPOLYMER

RUN NO.	REACTANTS				REACTION TIME AND TEMPERATURE, C	YIELD, POUNDS (%)	ANALYSES						MOLE % BAMO BASED ON N ANALYSIS	
	BAMO, POUNDS (MOLES)	THF, POUNDS (MOLES)	BDO, POUNDS (MOLES)	BF ₃ ·DEI ₂ , POUNDS (MOLES)			M _w	M _n	f	EQ. WT.	C	H		N
5-1	13.99 (37.76)	6.0 (37.76)	0.75 (3.78)	2.36 (7.55)	64 HOURS AT -1	18 (86.8)	3833	2541	2.10	1260	44.08	6.60	36.18	52.87
5-2	20.2 (54.59)	8.67 (54.59)	1.08 (5.45)	3.41 (10.91)	35 HOURS AT -5	26.4 (88.1)	4022	2578	2.13	1210	41.14	6.57	35.33	50.79
5-3	12.35 (33.4)	5.31 (33.4)	0.66 (3.34)	2.0 ^a (6.68)	66 HOURS AT -5	15.5 (84.5)	3962	2542	2.07	1323	43.00	6.57	36.58	53.88

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 10³ Å and one 10⁴ 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. The GPC curves for BAMO/THF 5-1, 5-2, and 5-3 are shown in Fig. 1 through 3.

The functionalities were determined by SRI using an NMR technique developed at Fluorochem (Ref. 3). The hydroxyl equivalent weights were measured at Rocketdyne using a method recently developed by the Chemical Branch of the Air Force Rocket Propulsion Laboratory (Ref. 4). The elemental analyses were performed by Elek Microanalytical Laboratory and Galbraith Laboratory.

CLASSIFICATION TESTS ON BAMO/THF COPOLYMER

The program required that quantities of the BAMO/THF copolymer be shipped to various laboratories for evaluation. To do so, a shipping classification was required. Explosive classification tests were conducted on the BAMO/THF copolymer and a 30% solution of the copolymer in methylene chloride. The standard tests were carried out as described in Technical Bulletin TB700-2. Based on the test results, a shipping classification of "Flammable Liquid, N.O.S." was assigned to the BAMO/THF copolymer in a 30% methylene chloride solution. The details of the testing and the Navy correspondence are given in Appendix C.

SHIPMENT OF BAMO/THF COPOLYMERS

A summary of the BAMO/THF copolymer shipments made under this contract is given in Appendix D.

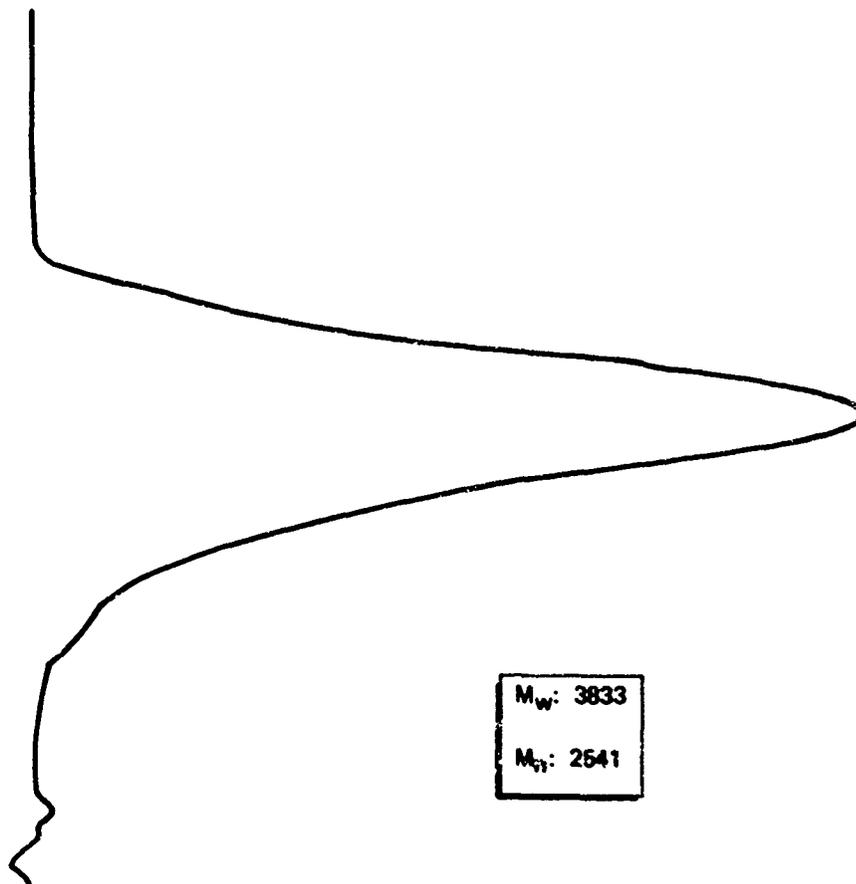


Figure 1. GPC of BAMO/THF 5-1

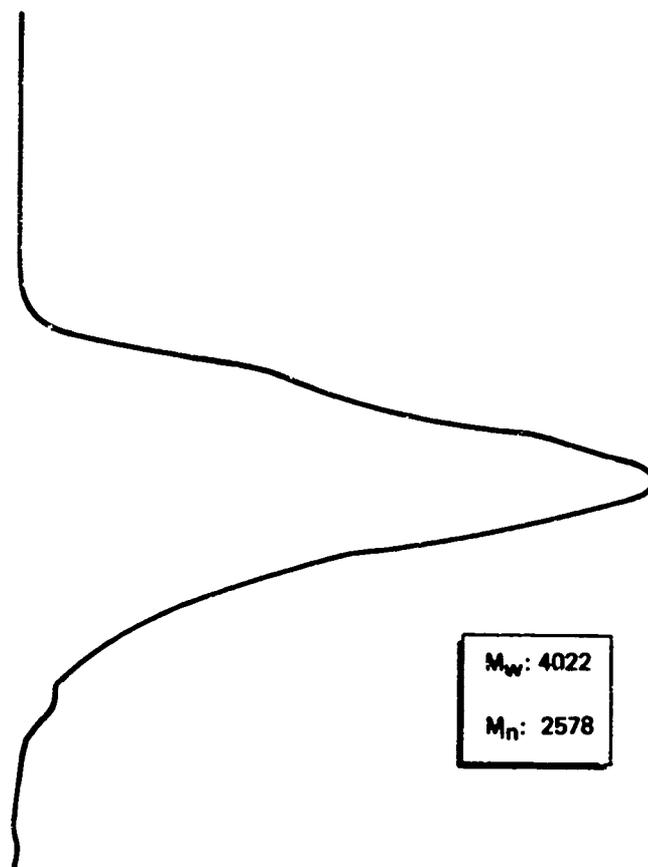


Figure 2. GPC of BAMO/THF 5-2

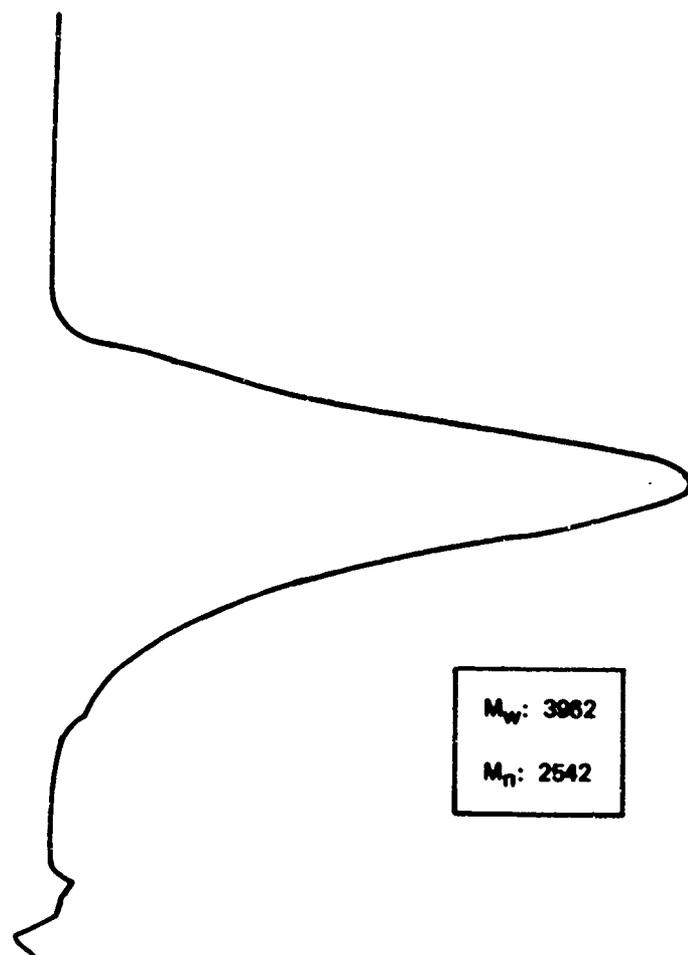
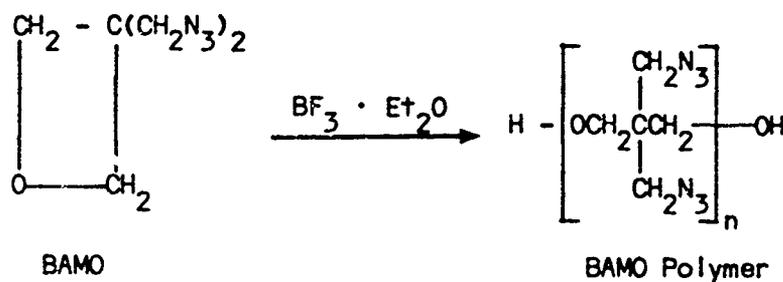


Figure 3. GPC of BAMO/THF 5-3

HOMOPOLYMERIZATION OF BAMO

Since BAMO could be prepared readily in a simple one-step reaction from a commercially available starting material, the polymerization studies in the current program were limited to this one energetic monomer. It was quickly established that BAMO monomer was readily polymerized using a $\text{BF}_3 \cdot \text{OEt}_2$ catalyst via a standard cationic polymerization technique for cyclic ethers. The problem was to control the molecular weight of the polymer produced, maintain a narrow molecular weight distribution, and obtain a polymer functionality of two or greater.

The polymerization of BAMO is illustrated below:



The polymerization parameters examined in this study were:

1. Solvent system
2. Reaction stoichiometry, i.e., the relative concentration of monomer, catalyst, and chain initiator
3. Type of chain initiator
4. Reaction time
5. Reaction temperature

For the purposes of analysis and discussion, the experiments are grouped according to the chain initiator employed.

Water as the Initiating Species

The initial polymerization experiments used water as the chain initiator. Selection of a suitable solvent medium for polymerization was the first priority. Halogenated solvents (carbon tetrachloride, chloroform, and methylene chloride) as well as nitromethane were examined. Polymerization occurred in all these media. In both carbon tetrachloride and nitromethane, the polymer precipitated during the reaction. Because of the broad molecular weight distribution of the polymer obtained, carbon tetrachloride and nitromethane were rejected for further study. In both methylene chloride and chloroform, polymers were obtained which did not precipitate from the reaction medium. These polymers were in the desired 2000 to 3000 molecular weight range, but had low functionality (1.7) and melting points of 75 C. This points up a fundamental difficulty in the system using water as a chain initiator. For this reason, replacement of water by polyhydric alcohols, such as glycerol, trimethylpropane, and ethylene glycol was investigated.

Glycerol as the Initiating Species

Influence of Solvent and Glycerol Concentration. The influence of solvent in the glycerol system was examined in runs 101A and 102 (Table 3). A narrower polymer distribution was obtained in methylene chloride (run 101A) than in chloroform (run 102). Runs 101A, 105, and 106 in methylene chloride determined the influence of changes in glycerol concentration on the molecular weight of the BAMO polymer obtained. Regardless of the amount of added glycerol, the polymer obtained had essentially the same molecular weight, and were solids with melting points of 75 to 78 C. A possible explanation of this result lies in the observation that in all the glycerol-containing reactions, the bulk of the glycerol was insoluble in the methylene chloride. Thus, the actual concentration of glycerol available in the solvent medium was far lower than that added, and was essentially at the saturation concentration. A more efficient means for molecular weight control in this system is via the $\text{BF}_3 \cdot \text{Et}_2\text{O}$ catalyst concentration. In run 107, where the catalyst amount is twice that of run 101A, the molecular weight was substantially reduced.

TABLE 3. POLYMERIZATION OF 3,3-bis (AZIDOMETHYL) OXETANE IN THE PRESENCE OF GLYCEROL

RUN NO.	OXETANE, MOLE	BF ₃ ETHERATE, MOLE	GLYCEROL, MOLE	SOLVENT (VOLUME, ml)	TEMPERATURE, C	REACTION TIME, HOURS	M _w	M _n	f
101	0.006	0.003	0.0045	CH ₂ Cl ₂ (5)	RT	3	**	**	
102	0.006	0.003	0.0045	CH ₂ Cl ₂ (5)	RT	3	**	**	
105	0.006	0.003	0.0025	CH ₂ Cl ₂ (5)	RT	3	**	**	
106	0.006	0.003	0.006	CH ₂ Cl ₂ (5)	RT	3	**	**	
101A	0.006	0.003	0.0045	CH ₂ Cl ₂ (5)	RT	3	3200	2670	
107	0.006	0.006	0.0045	CH ₂ Cl ₂ (5)	RT	3	2713	2372	2.1
101A-10X	0.06	0.03	0.045	CH ₂ Cl ₂ (50)	RT	3	2920	2237	2.5
107-10X	0.06	0.06	0.045	CH ₂ Cl ₂ (50)	RT	3	2037	1651	
108	0.006	0.006	0.0045	CH ₂ Cl ₂ (5)	24*	3	**	**	
109	0.006	0.006	0.0045	CH ₂ Cl ₂ (5)	24*	3	2376	1646	
110	0.006	0.006	0.0045	CH ₂ Cl ₂ (5)	40	3	2168	1547	
112	0.006	0.006	0.0045	CH ₂ Cl ₂ (5)	RT	1	2048	1293	
113	0.005	0.006	0.0045	CH ₂ Cl ₂ (5)	RT	2	**	**	
115	0.006	0.006	0.0045	CH ₂ Cl ₂ (5)	RT	3	**	**	
116	0.006	0.006	0.0045	CH ₂ Cl ₂ (5)	40	3	2141	1534	
117	0.006	0.006	0.0045	CHCl ₃ (5)	62	1	**	**	
118	0.006	0.006	0.0045	C ₂ H ₄ Cl ₂ (5)	84	1	**	**	
119	0.03	0.03	0.02	CH ₂ Cl ₂ (25)	RT	1	2055	1336	
120	0.03	0.03	0.02	CH ₂ Cl ₂ (25)	40	1	1689	1264	
121	0.03	0.03	0.02	CH ₂ Cl ₂ (10)	RT	1	1793	1310	
123	0.03	0.03	0.02	CH ₂ Cl ₂ (25)	40	3	1618	1271	
132	0.03	0.015	0.02	CH ₂ Cl ₂ (25)	40	3	2160	1650	2.0
139	0.20	0.10	0.13	CH ₂ Cl ₂ (175)	40	3	1790	1400	2.6

*-TEMPERATURE MAINTAINED WITH COOLING BATH.

**THE GPC CURVES FOR THE PRODUCTS WERE BROAD, AND MOLECULAR WEIGHTS WERE NOT CALCULATED FOR THESE SAMPLES. VISUAL INSPECTION OF THE CURVES WAS USED TO INDICATE MOLECULAR WEIGHT TRENDS VS REACTION CONDITIONS.

Having established that a polymer in the desired molecular weight range with a narrow molecular weight distribution could be obtained in this system, the typical 1-gram reaction was scaled up to the 10-gram level to provide sufficient polymer to determine functionality and curing behavior (runs 101A-10X and 107-10X). During this reaction, a significant polymerization exotherm was observed for the first time (the temperature rose approximately 15 C). This resulted in a change in the molecular weight distribution, a slight reduction in molecular weight, and GPC analyses indicated the presence of a fraction with an approximate degree of polymerization of 4. This product may have resulted either from the influence of the exotherm or may be evidence for the presence of a tetramer, which has been reported for other oxetane polymers.

Reaction Temperature. The initial experiments were run at room temperature without heating or cooling. When the polymerization exotherm was controlled by external cooling (run 108), high molecular weight species ($>7000 M_w$) were obtained which were absent in the uncontrolled experiments (e.g., run 107). These high molecular weight species have a deleterious effect on the polymer's dispersity. Runs 110 and 116 investigated the polymerization at the reflux temperature (40 C) of methylene chloride. With all other polymerization conditions constant, polymerization at the higher temperature produced a polymer of slightly lower average molecular weight and narrower dispersity. The dispersity was narrowest when all reactants were at the reflux temperature of CH_2Cl_2 before addition of the monomer was initiated (run 116).

Polymer Conversion vs Reaction Temperature. A set of three experiments at room temperature (runs 112, 113, and 115) showed that conversion of monomer-to-polymer was essentially complete at the end of 1 hour, and that longer reaction times may introduce undesirable high molecular weight species. The conversion of monomer-to-polymer at the reflux temperature of methylene chloride was not complete in 1 hour (run 120), but was complete in 3 hours (run 123).

Polymerization in Higher Boiling Solvents. Because the reaction at the reflux temperature of methylene chloride yielded a BAMO polymer with a narrower molecular weight distribution than that obtained at room temperature, two solvents with higher boiling points were examined: chloroform (boiling point 61 to 62 C) and 1,2-dichloroethane (boiling point 83 to 84 C). GPC analyses of the polymer obtained in chloroform (run 117) showed a very broad dispersity and several low molecular weight peaks. Refluxing chloroform was therefore judged to be an undesirable polymerization medium. The molecular weight distribution of the polymer obtained in 1,2-dichloroethane (run 118) was very narrow, but the molecular weight was low.

Effect of Scaleup on Polymer Molecular Weight. The BAMO polymerizations were run at three different monomer levels: 1-gram (0.006 mole), 5-gram (0.03 mole), 33-gram (0.2 mole). The trend observed was pronounced; with all other conditions held constant, a 30+ fold scaleup produced a polymer of lower average molecular weight. Thus it would appear that scaleup requires less catalyst to produce a polymer in the desired molecular weight range.

Optimization of the Glycerol System

Run 132 was made to investigate the use of a reduced amount of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at the reflux temperature of methylene chloride, in order to increase the molecular weight (compared to polymer obtained from run 123) while maintaining good molecular weight distribution. The experiment was successful in this respect. However, when 33 grams of BAMO were polymerized using the conditions of run 132, the reaction yielded a BAMO/glycerol polymer with a weight-average molecular weight of 1790, a dispersity, Q , of 1.3, a calculated functionality of 2.6 (run 139), and a melting point of 75 to 78 C.

Trimethylpropane (TMP) as the Initiating Species

Room-Temperature Polymerization. The early polymerization experiments with TMP as the chain initiator were not successful. The conversion of monomer-to-polymer was poor, and the average molecular weight of the polymer obtained

(runs 111 and 114, Table 3) was very low ($<1000 M_w$). TMP is a solid, unlike glycerol which is a liquid and normally contains a small amount of water. Water was therefore added to the polymerization medium in run 124, but no polymer was obtained. The high monomer-to-catalyst ratio (20:1) used was probably the reason for these results.

Aqueous fluoboric acid (48%) was next investigated as a catalyst. No polymer could be isolated by use of this material (runs 125 through 127). A catalyst combination (fluoboric acid plus $BF_3 \cdot Et_2O$) gave a high yield of polymer (run 128). The next run (130) used one-half the quantity of TMP. The polymer yield and the nature of the polymer (molecular weight, molecular weight distribution) were virtually identical in these two runs, indicating that the water in the aqueous fluoboric acid is more important than TMP for polymer molecular weight control.

To determine if fluoboric acid was a necessary co-catalyst with $BF_3 \cdot Et_2O$, a polymerization (run 129) was attempted without fluoboric acid but with an amount of water equivalent to that present in the fluoboric acid used in run 128. This experiment (run 129) demonstrated that, indeed, fluoboric acid was not required to obtain complete conversion of monomer to polymer. In run 131, only one-tenth the amount of water was added (10:1 mole ratio of $BF_3 \cdot Et_2O$ to H_2O vs. 1:1 mole ratio in run 129). The amount of water was decreased further in run 136. Polymer yield was high in all these experiments.

The functionality of the polymer from run 129 was very good (2.9), while those for the polymers obtained from runs 131 and 136 were low ($<.5$). Therefore, a rather large quantity of water is needed in the BAMO/TMP system to allow the TMP to function as a chain initiator and obtain a functionality above 2.0.

TABLE 4. POLYMERIZATION OF 3,3-bis (AZIDOMETHYL) OXETANE IN THE PRESENCE OF TRIMETHYLOXETANE (TMP)

RUN NO.	OXETANE, MOLE	B ^F ₃ ·Et ₂ O MOLE	HF ₄ , (48% Aq)	WATER, MOLE	TMP, MOLE	CH ₂ Cl ₂ , ml	TEMPERATURE, C	REACTION TIME, HOURS	M _w	M _n	f
111	0.006	0.006	-	-	0.0045	5	24	3	SMALL AMOUNT OF POLYMER.		
114	0.006	0.006	-	-	0.0045	5	RT	3	SMALL AMOUNT OF POLYMER.		
122	0.015	0.03	-	-	0.04	25	RT	3	NO POLYMERIZATION		
124	0.03	0.0015	-	0.006	0.0015	10	RT	5	NO POLYMERIZATION		
125	0.03	-	0.12g	*	0.0006	10	RT	5	NO POLYMERIZATION		
126	0.03	-	0.25g	*	0.0006	25	RT	3	NO POLYMERIZATION		
127	0.03	-	0.5g	*	0.0006	10	RT	7	NO POLYMERIZATION		
128	0.03	0.015	0.5g	*	0.0015	10	RT	4.5	NO POLYMERIZATION		
129	0.03	0.015	-	0.015	0.0015	10	RT	3	1640	1360	2.9
130	0.03	0.015	0.5g	*	0.0008	10	RT	3	1850	1510	2.9
131	0.03	0.015	-	0.0015	0.0015	10	RT	3	1720	1410	1.7
136	0.03	0.015	-	0.00015	0.0015	10	RT	3	2350	1840	1.3
138	0.03	0.015	-	0.00015	0.0015	25	40	3	2310	1770	1.6
140	0.03	0.015	-	0.015	0.0015	10	40	3	1975	1615	1.6
									1728	1454	

*-WATER PRESENT IN Aq HBF₄

Higher-Temperature Polymerization Studies. Two experiments with the BAMO/TMP system were carried out at the reflux temperature of the solvent methylene chloride. The polymer isolated from run 138 had a large amount of low molecular weight material ($\sim 1400 M_w$). The reaction conditions for run 140 were the same as those employed in run 129 except for the reaction temperature. The polymer molecular weight was somewhat lower ($\sim 1700 M_w$).

Ethylene Glycol as the Initiating Species

With ethylene glycol dried over molecular sieves prior to use, no polymerization occurred (run 133, Table 5). When a small amount of water was added to the reaction mixture (run 135), the BAMO polymer was obtained in good yield ($\sim 90\%$). Reagent grade ethylene glycol, as received, also produced a polymer of the desired molecular weight and dispersity (run 137). Therefore, it is not necessary to dry the ethylene glycol before use. (Because ethylene glycol is very hygroscopic compared with glycerol and water, a factor in molecular weight control, it was necessary to determine this experimentally). The functionality of the polymer from run 137 was 2.0, which is equal to the theoretical value for an ethylene-glycol-initiated BAMO polymer.

A substantial exotherm was observed in the ethylene glycol experiments. When the polymerization was initiated at the reflux temperature of methylene chloride (run 141), essentially the same product was obtained. The polymer obtained from run 141 was the best produced by use of ethylene glycol.

TABLE 5. POLYMERIZATION OF 3,3-bis (AZIDOMETHYL) OXETANE IN THE PRESENCE OF ETHYLENE GLYCOL (EG)

RUN NO.	OXETANE, MOLE	BF ₃ -ETHERATE, MOLE	H ₂ O, MOLE	EG, MOLE	CH ₂ Cl ₂ , ml	TEMPERATURE, C	REACTION TIME, HOURS	M _w	M _n	f
133	0.03	0.015	-	0.023*	25	RT	5	NO POLYMERIZATION.		
135	0.03	0.015	0.00017	0.003*	10	RT	3	2210	1680	
137	0.03	0.015	-	0.003	10	RT	3	2464	1959	2.0
141	0.03	0.015	-	0.003	.0	40	4	2231	1734	

*-DRIED OVER MOLECULAR SIEVES.

High Molecular Weight BAMO Polymer

The feasibility of obtaining a high molecular weight BAMO polymer ($\sim 10,000 M_w$ or higher), regardless of the functionality of the polymer, was investigated. The polymerization was carried out in methylene chloride at 5 C using a 10:1 molar ratio of BAMO to $BF_3 \cdot Et_2O$ catalyst in the absence of water or chain initiator. This experiment was highly successful. A polymer was obtained in essentially 100% yield. During the polymerization, the polymer formed remained soluble in the solvent (methylene chloride). Upon evaporation of the solvent, a white film-like material was obtained which had a peak molecular weight of 19,000.

CONCLUSIONS

Three different hydroxy-terminated BAMO prepolymers were obtained with glycerol, trimethylolpropane, or ethylene glycol as the initiator. The molecular weights ranged from 1800 to 3000, with functionalities of two or greater. However, all of the homopolymers were solids, with a melting point of 75 to 78 C. Furthermore, the melting point was not affected by changing the molecular weight. As the objective of the program was to produce a liquid polyol at room temperature, it was concluded that this could not be met by the homopolymerization of BAMO. Consequently, emphasis was shifted to the preparation of the BAMO/THF copolymer.

A safe and reproducible process was developed for the production of the 50/50 mol % BAMO/THF copolymer at the 15- to 26-pound level in a 5-gallon Pfaudler reactor, and yields of 84 to 88% were obtained. The properties of the copolymers were quite comparable in terms of M_w (3833-4022), M_n (2541 to 2578), f (2.07 to 2.13), and Eq. Wt. (1210 to 1323).

The method of addition of the monomers to the initiating solution (catalyst + BDO) was found to be important. Addition of the mixed monomers (BAMO and THF) to the initiating solution was the preferred technique, since it gave a more random distribution of the monomers in the polymer chain. This minimized the homopolymerization of BAMO., thereby yielding a less crystalline (lower viscosity) copolymer.

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1. Energetic Azido Compounds, Report No. RI/RD80-124, Rocketdyne Division of Rockwell International, Canoga Park, CA 91304, 28 March 1980.
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3. Research in Energetic Compounds, Report No. ONR2-2, Fluorochem Inc., Azusa, CA 91702, March 1980.
4. Dee, L. A., et al, Use of N-Methylimidazole as a Catalyst for Acetylation of Hydroxyl Terminated Polymers, AFRPL Chemical Branch, LKLR, Edwards, CA 93523.

APPENDIX A

BAMO PRODUCTION

EQUIPMENT

A 5-gallon, jacketed, glass-lined Pfaudler reactor, which is fitted for heating and cooling via a pumped lexsol system.

PROCEDURE

Twelve liters of dry dimethylformamide are charged into the reactor and 12.20 pounds (85.2 moles) of solid sodium azide are added with vigorous agitation. This mixture is heated to 85-90 C (185-193 F) and 13.23 pounds (38.7 moles) of fractionally distilled (99+% purity) 3,3-bis(chloromethyl) oxetane (BCMO) are added from the addition reservoir at such a rate, initially 55 to 60 cm³/min, that the temperature is maintained by the heat of reaction. Heating by the lexsol system is terminated at this point. The BCMO addition rate is adjusted to maintain the reaction temperature, and the total time required for its addition is approximately 90 minutes. After the BCMO is added, the reservoir and addition system is washed with 200 ml of dimethylformamide. The reaction mixture is stirred until its temperature starts to fall (~ 15 minutes), after which time heating is restarted and the temperature is maintained between 85 and 90 C for 75 additional minutes (total reaction time: 3 hours). At this point, a sample is withdrawn and analyzed by GC to verify the absence of BCMO. The reaction mixture is then cooled to 50 C (120 F) and filtered through a sintered glass funnel to remove solid sodium chloride and the unreacted sodium azide from the product solution. The solid is then washed with methylene chloride to recover any entrained product. The washings and the product solution are combined (~ 16 l) and washed six times with equal volumes of deionized water to remove dimethylformamide (verified via GC). The product solution is dried and purified by diluting it to ~ 20% BAMO and passing this solution through a 2-inch-diameter column containing 36 inches of fine basic alumina below 60 inches of coarse basic

alumina. The column is subsequently washed with 3 liters of fresh methylene chloride and the washings are combined with the product solution. The methylene chloride is stripped from the product in vacuo at 40 C/1 mm to give 11.8 pounds (82% yield) of 99+% pure BAMO by GC analyses.

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A-2

APPENDIX B

BAMO/THF COPOLYMER PRODUCTION

EQUIPMENT

A 5-gallon, jacketed, glass-lined Pfaudler reactor fitted for cooling via a pumped lexsol system which provides lexsol at -29 C (-20 F).

PROCEDURE

Preparation of the Initiator

Spectrographic grade tetrahydrofuran (634.0 g, 8.79 moles) and reagent grade 1,4-butanediol (339.4 g, 3.77 moles) are weighed into a 3-liter, 3-necked, round-bottom flask which is equipped with a mechanical stirrer, thermometer, GN_2 purge system, and immersed in a cooling bath. The tetrahydrofuran/butanediol solution is cooled to -5 C (23 F) and 1071.8 g (7.55 moles) of freshly distilled boron trifluoride diethyl etherate is added over a 1-hour period. The initiator mixture is stirred for 1 hour at -5 C after the addition is complete. The mixture is then transferred to the Pfaudler reactor which has been precooled to -5 C.

Copolymer Preparation

Agitation of the initiator mixture is initiated, and addition of a solution of BAMO (6349.7 g, 37.79 moles) and THF (2088.6 g, 28.97 moles) is started. The temperature of the reaction mixture is maintained at -5 C, and addition requires approximately 4 hours. The reaction mixture is stirred for 1 hour following addition of the BAMO/THF solution. Agitation is then stopped for the remainder of the reaction time (68 hours). After this time, a sample of the reaction mixture is taken and analyzed by GC to verify the absence of monomeric BAMO.

When the GC analyses indicated a BAMO content < 0.5 area %, the following procedure was followed for workup of the polymer. Methylene chloride (6.4 liters) was added and the mixture stirred. After stirring for 15 minutes, 10 liters of a 10 w/o sodium chloride solution are added to deactivate the catalyst. This mixture is stirred vigorously for 5 minutes, the agitation is stopped, and the aqueous and organic phases are allowed to separate. The organic phase is then washed three times with 20 liters of a 70/30 methanol/10 w/o NaCl solution by volume. Following the third wash, the methylene chloride/polymer solution is diluted with additional solvent to give a 20 w/o polymer concentration.

Purification

The 20% solution of polymer is passed through a 2-inch-diameter column containing 60 inches of coarse basic alumina over 36 inches of fine basic chromatographic alumina for final drying and purification. A small sample of the solution is then stripped to determine the final polymer concentration. From these data, the yield was 18.0 pounds (86.7%).

APPENDIX C



Rocketdyne Division
6633 Canoga Avenue
Canoga Park, California 91304

**Rockwell
International**

Telex. 698478

11 November 1981

In reply refer to 81RC11918

Commander
Naval Sea Systems Command
Washington, D.C. 20362

Attention: SEA-04H, Ed Klinghoffer

Dear Mr. Klinghoffer:

As you know, we are developing a new energetic polymer for the Navy under Contract N0014-79-C-0043. The program requires that quantities of this material be shipped to various laboratories for evaluation. In order to do so, a shipping classification is needed. Pursuant to our telecon, we have run the standard explosive classification tests and are submitting the data with our recommendations for classification.

Explosive classification tests were conducted on the copolymer of BAMO/THF and a 30% solution of BAMO/THF in methylene chloride. The standard tests were carried out as described in Technical Bulletin TB700-2. The results are summarized below.

<u>Test</u>	<u>Results</u>
Detonation Test (#8 Cap):	
BAMO/THF	Negative
30% Soln-BAMO/THF in CH ₂ Cl ₂	Negative
Open Burning Test:	
BAMO/THF	Burned smoothly for approximately 2 minutes with a white flame.
30% BAMO/THF in CH ₂ Cl ₂	Burned poorly with a pale yellow flame. Sample took about 3 minutes to boil off CH ₂ Cl ₂ so it could ignite. Burned for approximately five minutes.

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C-1

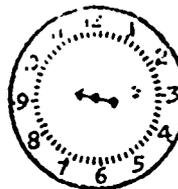


DEPARTMENT OF THE NAVY
NAVAL SEA SYSTEMS COMMAND
WASHINGTON, D C. 20382

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ROCKETDYNE
CORRESPONDENCE

M. B. Frankel
Manager, Chemical Processing
Advanced Programs
Rockwell International
Rocketdyne Division
6633 Canoga Avenue
Canoga Park, California 91304

Dear Mr. Frankel:

Based on the descriptive and test data provided in your letter of 11 November 1981, a shipping classification of "Flammable Liquid, N.O.S." is assigned to BAMO/THF copolymer in a 30% methylene chloride solution. This material has been classed and approved for shipment in accordance with paragraph 173.86 of CFR 49. Shipment of the copolymer solution must comply with the packaging, marking and labelling requirements of CFR 49.

Sincerely,

Milton R. Van Slyke
Milton R. Van Slyke

11-258

Copy to:
ONR (Code 473)

13496 AC

APPENDIX D

BAMO/THF SHIPMENTS*

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Thiokol Corp, Elkton Div. Receiving Dept. 55 Thiokol Road Elkton, MD 21921 Attn: Dr. C. W. Vriesen	1	-	-
Thiokol Corp, Huntsville Div. Receiving Dept. Redstone Arsenal Huntsville, AL 35809 Attn: Dr. D. A. Flanigan	1	-	-
Thiokol Corp., Wasatch Div. Receiving Dept. Brigham City, UT 84302 Attn: Dr. J. C. Hinshaw	3.8	-	-
Professor Sue Kim Science Bldg., Dept. of Chemistry California State University Sacramento, CA 95819	0.2	0.2	0.2

*All shipments in pounds

Recipients	Polymer Lot		
	5-1	5-2	5-3
United Technology Chemical Systems Division Receiving Department 1050 East Arques Sunnyvale, CA 94086	-	-	5
Aerojet Strategic Propulsion Co. Highway 50 and Hazel Ave. Receiving Dock, Gate 1 Building 4911 Nimbus, CA Attn: Dr. Richard L. Lou	-	-	5
Atlantic Research Corp. Pine Ridge Plant 7511 Wellington Road Gainesville, VA 22065 Attn: Dr. W. E. Stephens	-	-	5
Hercules, Inc. Allegheny Ballistics Laboratory Cumberland MD 21502 Attn: Dr. Kenneth Hartman	-	2	-
Professor Edward Price Georgia Institute of Technology School of Aerospace Engineering Atlanta, GA 30332	-	2	-
Professor Alen Gent Institute of Polymer Science Auburn Science Center Room 201 University of Akron Akron, Ohio 44325	-	5	-
Dr. Yogi Gupta S.W. 845 Mies Street Pullman, WA 99163	-	5	-

Recipients	Polymer Lot		
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Naval Surface Weapons Center Building 600 Indian Head, Md 20640 Attn: Mr. Robert Gill	-	3	-
Trans Technology Space Ordnance Systems Receiving Dept. 25977 Sand Canyon Road Canyon Country, CA 91351 Attn: Mr. Edward van Ribbink	-	1	-
Commander U.S. Army Missile Command Redstone Arsenal, AL 35898 Attn: DRSMI-RKL Dr. E. Allan	-	0.5	-

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D-3/D-4

APPENDIX E

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