E96-66
August 26, 1966

FIRST QUARTERLY REPORT

CONTRACT NAS7-478

Thiokol

FACILITY FORM 602

N66 37945	
(ACCESSION NUMBER)	(THRU)
26	1
(PAGES)	(CODE)
CR-78450	06
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

GPO PRICE $

CFSTI PRICE(S) $

Hard copy (HC) $2.00

Microfiche (MF) .50

ff 653 July 65

E96-66

THIOKOL CHEMICAL CORPORATION
ELKTON DIVISION
ELKTON, MARYLAND

FIRST QUARTERLY REPORT

CONTRACT NAS7-478

PREPARED FOR:

NASA RESIDENT OFFICE
JET PROPULSION LABORATORY
PASADENA, CALIFORNIA

August 26, 1966

HG Jones

H. G. Jones
General Manager

FOREWORD

This first quarterly report of progress under Contract NAS7-478 covers the technical program at the Elkton Division of Thiokol Chemical Corporation during the period May 10 through August 10, 1966.

The program is being conducted under the sponsorship of the National Aeronautics and Space Administration. Technical direction is provided by the Jet Propulsion Laboratory, Pasadena, California; Mr. Floyd Anderson, JPL, is Technical Manager.

Dr. C. W. Vriesen is Thiokol's Principal Investigator for this program. Dr. Vriesen prepared this report with the assistance of Mr. C. R. Brenn. The Program Manager is Mr. F. X. Cunningham.

ABSTRACT

The best functionality of the carboxyl-terminated butadiene isoprene (BD/IP) copolymer was obtained when the removal of residual naphthalene was improved and when carbonation was accomplished by means of a jet tube.

The use of a different source for butadiene and isoprene monomers has not resulted in increased functionality.

A 1, 3-butadiene-1, 3-pentadiene copolymer has been hydrogenated to an iodine value of zero; the product will be subjected to compatibility and stability tests with SPO.

Additional samples of the CT-BD/IP copolymer have been hydrogenated in the presence of palladium on barium sulfate catalyst and will be used in curing agent and physical property studies.

The aliphatic initiator, DiLi-1 (Lithium Corp. of America) is being evaluated. Its use would eliminate the possible source of incompatibility introduced by the use of the aromatic hydrocarbon naphthalene.

Initial experiments have been carried out on the copolymerization of 1, 3-butadiene with 1, 3-hexadiene and 2-(4-methylpentenyl-3) butadiene-1, 3. These experiments are designed to provide improved fluidity.

The synthesis of 1, 3-dilithio-2 ethyl-2 butyl propane from the corresponding dibromo compound is being investigated in order to provide an aliphatic initiator which should be more soluble in aliphatic hydrocarbons because of the side chains.

TABLE OF CONTENTS

I. INTRODUCTION

The objective of this program (Contract NAS7-478) is to synthesize and develop a hydrocarbon-type of polymer which possesses the characteristics required for use as a binder for uncoated SPO. The program is a segment of a continuing NASA/JPL/Thiokol effort to exploit the potential of SPO as a propellant ingredient.

Work conducted under previous programs has shown that the concept of using uncoated SPO is valid, as demonstrated by the fact that propellant samples compounded with a polyester binder have been stable at 72°F for periods in excess of one year. However, the polyester binder contains 23% oxygen and thus offers lower theoretical specific impulse than does a hydrocarbon polymer. Therefore, the present program effort is concentrated on hydrocarbon polymer work, particularly a carboxyl terminated butadiene/isoprene copolymer (BD/IP) polymerized by anionic techniques and subsequently hydrogenated to minimum residual unsaturation. Propellant made from BD/IP polymer and SPO has been stable for 150 days at 72°F and is still under test.

The principal tasks being undertaken in this program are:

A. BD/IP POLYMER IMPROVEMENT AND PROCESS MODIFICATIONS

This task is primarily one of improving functionality and saturation.

1. Improved Functionality

Improved functionality is important in order to develop desirable cured physical properties in propellant based on the BD/IP polymer. The objective here is to develop synthetic techniques which will result in difunctional polymer; i. e., provide two cure sites per polymer chain and, thus, sufficient crosslinking that interchain slippage under applied load is minimized.

2. Hydrogenation Studies

Unsaturated sites on the polymer chain are subject to attack by uncoated SPO and result in poor propellant stability and compatibility. Hydrogenation studies are aimed at the removal of all residual unsaturation in the BD/IP polymer. Progress in this area is followed by determining the iodine number of the product; zero iodine number implies that the polymer is completely saturated.

B. COMPATIBILITY AND FLUIDITY IMPROVEMENT

In this task, experiments are designed to improve compatibility and fluidity of the candidate polymer by modifying the polymerization initiator and solvent, as well as by substituting other monomers for isoprene. Maximum fluidity (minimum viscosity) of the uncured polymer, consistent with optimum cured physical properties, is important to permit optimum oxidizer loading in processible propellant.

C. COMPATIBILITY AND STABILITY TESTS

D. PROPELLANT PROCESSING TECHNIQUE STUDIES

E. LONG TERM PROPELLANT STABILITY TESTS

Progress under these tasks is discussed in detail below.

II. BD/IP POLYMER IMPROVEMENT AND PROCESS MODIFICATIONS

A. IMPROVEMENT OF FUNCTIONALITY

Improvement of functionality has been demonstrated in several procedures.*

1) Careful purification of the solvent, tetrahydrofuran, and of the 1, 3-butadiene monomer.
2) Removal of residual naphthalene.
3) Carbonation in a T-tube.

As a result of these experiments, the butadiene was passed through the ethylene glycol-sodium ethylene glycollate and calcium sulfate towers at a slower rate to ensure adequate removal of water. The tetrahydrofuran is normally distilled from lithium aluminum hydride; in the more rigorous purification it is distilled from lithium aluminum hydride and then from a solution containing butadienyl or isoprenyl sodium prepared, in turn, from sodium naphthalene. The second procedure is avoided, if possible, because it is time consuming and more costly.

The removal of residual naphthalene is important in the determination of functionality since a small amount of this impurity significantly decreases the observed value of molecular weight. Naphthalene is removed when the polymer is heated in water for the removal of tetrahydrofuran solvent and during the subsequent vacuum treatment on the Buchler Evaporator.

Carbonation in a T-tube has resulted in increases in functionality, but is difficult to control. If the pressures on the carbon dioxide and the polymer solution are not adjusted properly, carbon dioxide enters the polymer supply tube, causing gelation and stoppage.

Investigations designed to improve functionality are listed in Table I. The special purification procedure for tetrahydrofuran was applied to a double batch in Experiment 147-4, and the functionality was not satisfactory. In Experiments 149-3 and-5, Phillips isoprene and butadiene were evaluated (Matheson butadiene and Eastman isoprene are normally used) but no improvement was noted.

In Experiment 151-12, tetrahydrofuran was saturated with carbon dioxide at a temperature of -78°C and the solution was added to the living polymer solution at

---

*E58-66 (Title Classified), Final Report, Contract NAS 7-399. Thiokol Chemical Corporation, Elkton Division, May,1966.

TABLE I

POLYMER SYNTHESIS AND FUNCTIONALITY STUDIES

Sample	Formulation[1]	Procedure	Acid Number	Molecular Weight	Functionality	Yield, Percent
147-4	3A	THF distilled from Na naphthalene	51.8	1260	1.2	68
149-3	2A	Phillips isoprene	37.3	1800	1.2	78
149-5	A	Phillips butadiene and isoprene	29.8	1445	0.8	74
151-12	A	Addition of THF solution of CO_2	21.5			
153-3	2A	Reaction flask not flamed, T-tube	20.1			
153-4	2A	Reaction flask not flamed	29.1	1240	0.7	
157-1	2A	Reaction flask not flamed, jet	26.7	1385	0.7	84
157-3	A	Carbonation at room temperature				
157-4	A	Improved jet	55.8	1680	1.7	
157-5	A	THF distilled from Na naphthalene	54.8	1240	1.2	
158-2	A	Jet	57.4	1470	1.5	
159-1	A	Solid CO_2	48.1	1260	1.1	66
159-2	A	Argon through $CaSO_4$ tower	46.5	1310	1.1	72
159-3	2A	Jet	43.9	1160	0.9	83
159-4	A	Killed with ethyl chlorocarbonate	0			
159-5	2A	Excess THF and 700 ml n hexane added before carbonation	39.6	1030	0.7	79
160-3	A	900ml hexane added before carbonation	56.4	1220	1.2	
		Additional boiling to remove naphthalene	57.8	1850	1.9	
160-5	B	Integral isoprene still, reduced initiator	93 8	1200	2.0	28
162-1	B	Same as 160-5	66.8	1240	1.5	42
162-2	B	Same as 160-5	58.5	1760	1.8	45
162-4	2B	Double batch, 1/2 carbonated	49.4	1160	0.9	

---

1. A Formulation: 0.67 g (0.097 moles) lithium, 12.6 g (0.098 moles) naphthalene, 77.5 g (1.41 moles) 1,3-butadiene, 34 g (0.5 moles) isoprene, 450 ml tetrahydrofuran. The prefix 2 indicates a double batch.

   B Formulation: 0.52 (0.075 moles) lithium, 10.4 g (0.078 moles) naphthalene, 77.5 g (1.41 moles) 1,3-butadiene, 34 g (0.5 moles) isoprene, 450 ml tetrahydrofuran.

-78°C. The mixture was left to stand at reduced temperatures for two days, and was then worked up. The acid number obtained, 21.5, was not satisfactory.

Sample 153-3 was prepared in a double-walled reaction flask with a bottom outlet (Lab Glass LG 8025). Alcohol cooled with dry ice was circulated through the external chamber to cool the reaction mixture. Such a flask was necessary since it was not feasible to cool a conventional flask with a bottom outlet in the alcohol-dry ice bath. A portion of the sample was passed through a chromatographic spray (Kontes K42250) into an atmosphere of carbon dioxide, but stoppage of the spray occurred. Another portion was passed through a T-tube but control was again difficult, and the color of the living polymer was not completely removed. This resulted in an acid number of 20.1.

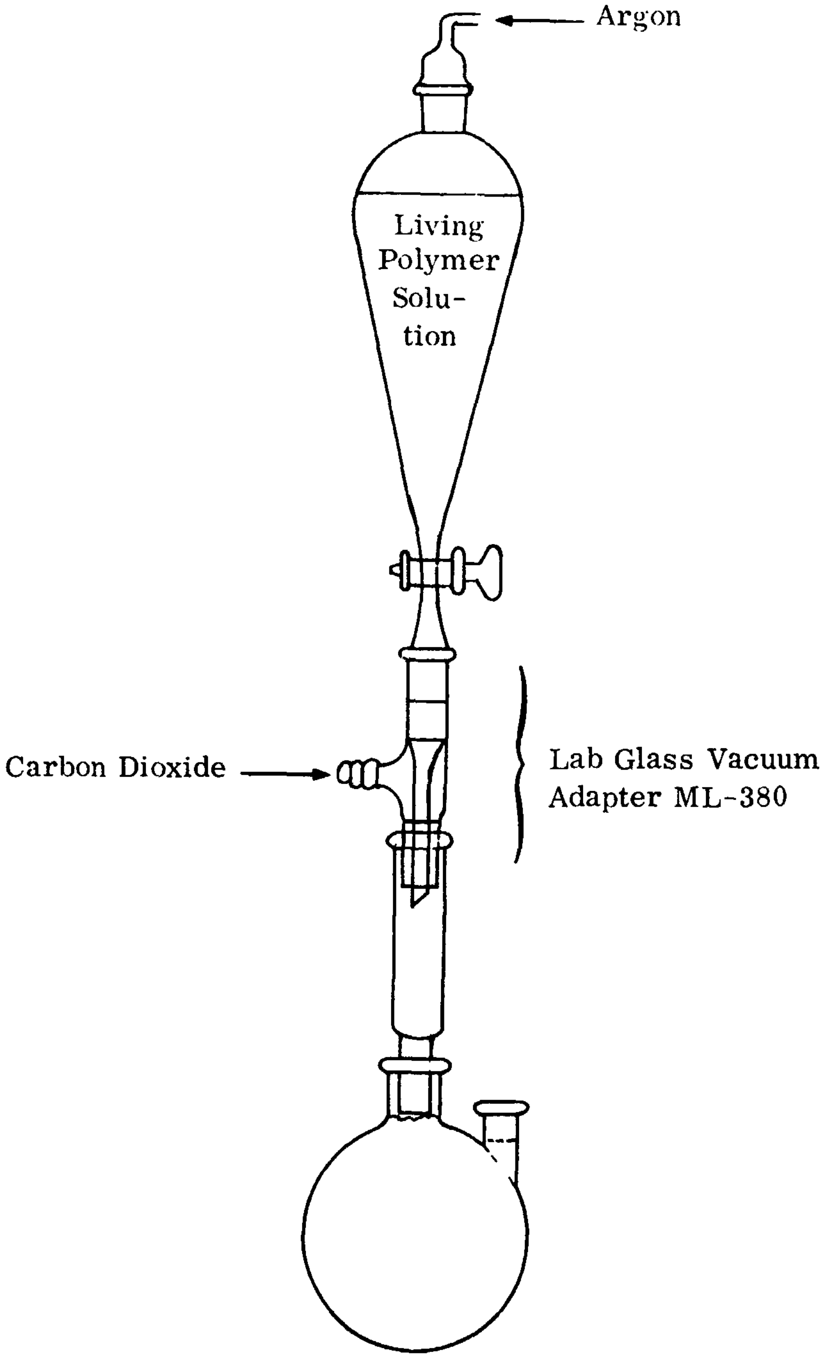
A portion of Sample 153-4 was led into an A. F. Smith Rota-Film Molecular Still and carbon dioxide was simultaneously introduced. It was anticipated that the reaction of carbon dioxide with a thin film of the polymer would provide the excess of the gas which would be desirable for complete carbonation. However, the wiper blades of this equipment were not able to remove the gelled tetrahydrofuran solution of the lithium carboxylate of the polymer from the walls of the still. Another portion of the sample was manually stirred in a 3-liter flask with a glass tube which was connected to a carbon dioxide source. The acid number, 29.1, was not satisfactory.

In Experiment 157-1, the polymer was led from the bottom outlet of the flask into a jet (see figure) which is a Mini-Lab vacuum adapter. Carbon dioxide was introduced through the side arm. The acid number, 26.7, was also low. It was concluded that the use of the double-walled reaction flask with a bottom outlet was causing low functionality since it is not possible to flame this type of flask.

The conventional reaction flask was used in Experiments 157-4 and 158-2, and the living polymer solution was transferred by vacuum from the flask to a separatory funnel which had been flamed. The solution was then passed through the jet (see figure) and decolorization of the polymer solution was efficient. The functionalities (1.7, 1.5) obtained indicate that this method is promising. This arrangement of equipment can be controlled much more efficiently than when the solution is passed through a T-tube. A disadvantage, however is the large quantity of carbon dioxide necessary.

In Experiment 157-3, the reaction mixture was warmed to room temperature before carbonation began. The gelled mass became too stiff, however, for efficient carbonation.

E96-66-01



LABORATORY JET FOR CARBONATION OF POLYMERS

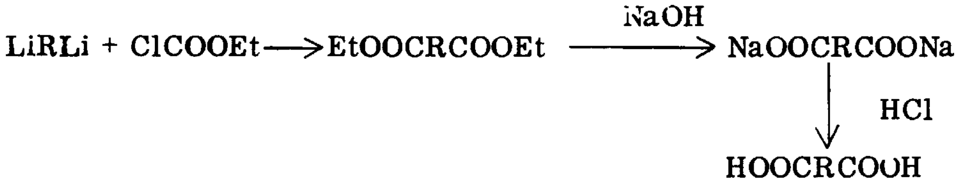
In Experiment 157-5, the tetrahydrofuran was subjected to additional purification by distilling it from sodium naphthalene, but the carbonation was carried out by bubbling carbon dioxide into the polymer solution. The functionality obtained, 1.2, again indicates the necessity for efficient carbonation.

In Experiment 159-1, carbon dioxide gas from dry ice was passed through sulfuric acid and calcium sulfate towers and resolidified in a reaction flask by means of liquid nitrogen. The polymer solution was placed on this bed of "dried" dry ice. Manual stirring was necessary to achieve adequate contact. The functionality obtained, 1.1, was not adequate.

Argon gas used in Experiment 159-2 was passed through a calcium sulfate tower, but the functionality obtained indicated that possible moisture from this source was not causing difficulty.

In Experiment 159-3, a portion of a double batch was passed through the jet and inadequate functionality resulted.

Another type of carbonation was attempted in Experiment 159-4:



$$\begin{tikzcd} \text{LiRLi} + \text{ClCOOEt} \arrow[r] & \text{EtOOCRCOOEt} \arrow[r, "\text{NaOH}"] & \text{NaOOCRCOONa} \arrow[d, "\text{HCl}"] \\ & & \text{HOOCRCOOH} \end{tikzcd}$$

The initial product, a diester, would most likely not form a gel in tetrahydrofuran as does the lithium dicarboxylate of the polymer. The zero acid number, however, indicated the failure of this approach.

In Experiments 159-5 and 160-3, n-hexane was distilled into the reaction mixture in an effort to solubilize the lithium dicarboxylate of the polymer as it formed during carbonation, but functionality was not improved.

Two variants were introduced in Experiments 160-5, 162-1, -2. The isoprene still (containing $LiAlH_4$) was made an integral part of the polymerization train to prevent accumulation of impurities during transfer. The amount of lithium initiator was reduced, because this has been shown* to result in reduced yields and increased functionality. Improved functionality was obtained in these three experiments.

---

*E58-66 (Title Classified), Final Report, Contract NAS 7-399, Thiokol Chemical Corporation, Elkton Division, May, 1966.

In Experiment 162-4, a double batch was prepared and half of the living polymer solution was removed. The fact that a poor functionality was obtained is an indication that the size of the batch may be a factor.

Sample 160-3 was subjected to additional boiling with water (steam distillation) to remove excess naphthalene. A significant increase in molecular weight and functionality was obtained. It is planned to treat a double batch of polymer in the same manner.

In summary, it is seen that the use of the jet results in the most efficient carbonation, but the removal of residual naphthalene from larger batches must be explored further.

B. HYDROGENATION STUDIES

Hydrogenations are listed in Table II. The viscosity of Sample 149-2H, a 1, 3-butadiene-1, 3-pentadiene copolymer is favorable, but the molecular weight is low. The procedure used in the preparation of this polymer will be used in the preparation of a 1, 3-butadiene-1, 3-hexadiene copolymer, and it is expected that increased fluidity will be obtained. It is significant that the iodine value of Sample 138-2H could be reduced to a value of 0.56. This polymer contains 31.1 percent isoprene; previous investigators were unable to completely hydrogenate polyisoprene glycols*. Sample (151-8, 157-4) H was hydrogenated in the presence of palladium-on-barium sulfate catalyst and is being used in stability studies.

---

*Hayaschi and Marvel, J. Polymer Sc. 2A, 2571 (1964).

TABLE II

HYDROGENATION STUDIES

Sample	Composition	Iodine Value	Molecular Weight[1]	Viscosity (poises at 25°C)
149-2H[2]	CT-1, 3-Butadiene-1, 3-pentadiene Copolymer*	0	980	328
138-2H[2]	CT-1, 3-Butadiene-isoprene Copolymer*	0.56	1290	476
(151-8, 157-4) H	CT-1, 3-Butadiene-isoprene Copolymer	0.39	ca. 1400	

---

[1] Molecular weight of unhydrogenated precursor.

[2] A small amount of glacial acetic acid was added to the hydrogenation adduct.

---

*E58-66 (Title Classified), Final Report, Contract NAS 7-399, Thiokol Chemical Corporation, Elkton Division, May, 1966.

III. IMPROVEMENT OF COMPATIBILITY AND FLUIDITY THROUGH SYNTHESIS

This phase is concerned with modifications of the synthesis of the candidate polymer to improve compatibility and fluidity. Approaches involve initiator, monomer and 1,2/1,4 adduct ratio variation.

A. INITIATOR VARIATION

It would be desirable to use an aliphatic initiator. When lithium naphthalene is used, there is a possibility that aromaticity may enter the chain. Also, naphthalene could be carried through the hydrogenation. If naphthalene is hydrogenated to tetralin, aromaticity would remain. If naphthalene is completely hydrogenated to decalin, this product could be sensitive to the oxidizer because of the tertiary hydrogen.

Experiments conducted during this period are listed in Table III. Another attempt was made to utilize 1,10-dilithiodecane (153-2) by using a mixture of petroleum ether and diethyl ether (50/50) as solvent. Formation of the dilithio compound was apparent, but when removal of the lithium bromide was attempted, precipitation occurred in the filtrate and it was not possible to redissolve this precipitate in additional solvent.

The Lithium Corporation of America prepares an initiator, DiLi-1, which is a 1.1 molar solution of dilithio polyisoprene in benzene and dimethyl ether. An initial experiment using this initiator (153-5) with 1,3-butadiene was carried out in a pressure reaction flask (Ace Glass 6501). This living polymer was killed with water to result in a product with a viscosity of 8.7 poises (25°C) and with a vinyl content of 53.4 percent. The 1,4-adduct content was expected to be in the medium range because of the presence of the dimethyl ether. A solvent composed entirely of hydrocarbon solvent would give a preponderance of the 1,4-adduct. In Experiment 158-3, the amount of initiator was reduced and tetrahydrofuran and n-hexane were added as solvent. The initiator was insoluble in the solvent and a high molecular weight polymer was obtained with an acid number of 15.0. In an experiment in Mini-Lab equipment, the copolymerization of butadiene and isoprene was attempted in n-hexane (150-3). The product possessed a high molecular weight and an acid number of 17.9. When the same experiment was repeated in benzene (150-4), a molecular weight of 2180 and an acid number of 8.7 were obtained. When DiLi-1 alone was carbonated and worked up, a molecular weight of 640 was obtained, which would represent a good portion of a polymer with a molecular weight of 1500. The evaluation of a limited number of variations is planned to determine the effect of the initiator structure on the polymer viscosity.

An attempt has been made to prepare 1,3-dilithio-2-ethyl-2-butyl propane from 1,3-dibromo-2-ethyl-2-butyl propane which was synthesized during the last program *

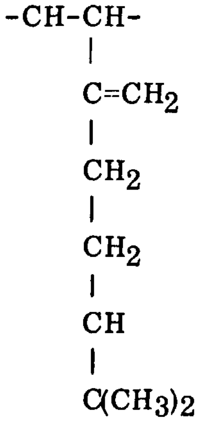
---

*E58-66 (Title Classified), Final Report, Contract NAS7-399, Thiokol Chemical Corporation, Elkton Division, May, 1966.

No lithium bromide formation was apparent after four hours stirring in tetrahydrofuran at ambient temperature but a brightening of the lithium particles indicated the initiation of a reaction. It is planned to study variations of reaction conditions. The selection of this initiator was made because the aliphatic side chains should improve solubility in aliphatic hydrocarbon solvents. The use of such an initiator would permit omission of aromaticity and provide a means for controlling the 1,2/1,4 adduct ratio.

B. MONOMER VARIATION

Initial experiments were carried out in an effort to increase fluidity. 2-(4-Methyl pentyl-3) butadiene-1,3 was copolymerized with butadiene (162-3). It would be expected that the side chain introduced:



$$\begin{array}{l} -CH-CH- \\ | \\ C=CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH \\ | \\ C(CH_3)_2 \end{array}$$

would improve fluidity. However, the polymerization, which was quite exothermic, resulted in a two-phase product which may be a mixture of two homopolymers.

One experiment was carried out in an effort to prepare the copolymer of 1,3-butadiene and 1,3-pentadiene. The acid number was 66.8, the molecular weight was 1640, and the yield was 29%. Additional experiments are planned in which conditions are similar to those used in the preparation of the copolymer of 1,3-butadiene and 1,3-pentadiene.*

---

*E58-66 (Title Classified), Final Report, Contract NAS7-399, Thiokol Chemical Corporation, Elkton Division, May, 1966.

IV. COMPATIBILITY AND STABILITY TESTS

Stability tests have been initiated with a polymer (151-8, 157-4) H of improved functionality which has been hydrogenated in the presence of palladium on barium sulfate catalyst.

V. PROCESSING TECHNIQUES FOR THE PREPARATION OF STABILITY SAMPLES

Samples initiated during this period were prepared in the Remote Control Laboratory without transferring ingredients from a separate dry box. It is planned to evaluate the flaming of all equipment used in the preparation of such samples. A recent experiment in the polymerization step indicated that flaming of the reaction flask was necessary despite the fact that dry nitrogen had been passed through the flask during the preceding night.

VI. LONG TERM STABILITY

Certain of the polyester propellant samples prepared and stored at 72°F during the last program have not gassed to date. These are listed in Table IV.

TABLE IV

STABILITY STUDIES

Sample	Particle Size of SPO	Imine/Carboxyl	Days Stable to Date
131G	-20+30	1.3/1	385
132F	-20+30	1.7/1	372
132N	-20+30	1.8/1	370
133M	-20+30	1.4/1	359
135N	-40+60	2.4/1	333
136F	-40+60	1.1/1	313
136G	-40+60	1.2/1	313
136H	-40+60	1.4/1	313
136I	-20+40	1.4/1	313
136O	-40+60	0.9/1	298
136Q	-40+60	2.3/1	298
136R	-40+60	1.6/1	301
136S	-40+60	1.2/1	305
136T	-40+60	1.2/1	305
136U	-40+60	2.1/1	298

VII. CONCLUSIONS

1) Of the devices and procedures evaluated for the carbonation of the living polymer solution, the most effective was a laboratory jet.

2) There is no improvement in functionality when Phillips butadiene and isoprene are substituted for Matheson butadiene and Eastman isoprene.

3) The use of a tetrahydrofuran solution of carbon dioxide or a bed of "dried" dry ice does not improve functionality.

4) Treatment of the living polymer solution with ethyl chloroformate did not result in the introduction of carboxyl groups under the experimental conditions used.

5) The incorporation of the isoprene still into the polymerization train may reduce the amount of impurities.

6) The efficient removal of residual naphthalene from larger batches must be investigated.

7) It is possible to effect essentially complete hydrogenation of BD/IP copolymer containing 31.3 percent isoprene.

8) The molecular weight of DiLi-1, 640, may preclude the use of this initiator since its structure may contribute too greatly to a polymer with a molecular weight of 1500.

9) The copolymerization of 1,3-butadiene and 2-(4-methylpentenyl-3) butadiene-1,3 may result in a mixture of homopolymers.

VIII. FUTURE WORK

- Define the effect on functionality of removing residual naphthalene content and the use of the jet tube in carbonation of larger polymer batches.
- Prepare additional quantities of higher functionality CT BD/IP copolymer and hydrogenate with palladium on barium sulfate for further studies.
- Perform limited experiments with DiLi-1 initiator and evaluate DiLi-3 when it becomes available.
- Modify experimental conditions in the copolymerization of 2-(4-Methylpentenyl-3) butadiene 1,3 and 1,3-butadiene.
- Modify experimental conditions in the copolymerization of 1,3-hexadiene and 1,3-butadiene.
- Continue the examination of 1,3-dilithio-2-ethyl-2-butyl-propane as an initiator.
- Evaluate the effect of varying the procedure in the preparation of stability samples.

TABLE III

EVALUATION OF ALTERNATIVE INITIATORS AND MONOMERS

Sample	Moles Initiator	Initiator	Grams Monomer	Monomer	Solvent	Acid Number	Molecular Weight
150-3	0.015	DiLi-1	18.0 7.8	Butadiene Isoprene	n-Hexane	17.9	High
150-4	0.015	DiLi-1	18.0 3.4	Butadiene Isoprene	Benzene	8.7	2180
153-2		$Li(CH_2)_{10}Li$			Petroleum ether Diethyl ether		
153-5	0.088	DiLi-1	77.5	Butadiene			960
158-3	0.044	DiLi-1	77.5	Butadiene	n-Hexane Tetrahydrofuran	15.0	
160-2				DiLi-1			640
162-3	0.015	LiNaphthalene	17.0 15.0	Butadiene 2-(4-methylpentenyl-3) butadiene-1,3	Tetrahydrofuran Tetrahydrofuran		
163-1	0.015	LiNaphthalene	13.6 7.2	Butadiene 1,3-Hexadiene	Tetrahydrofuran	63.8	1640
163-2	0.015	1,3-Dilithio-2-ethyl-2-butyl propane			Tetrahydrofuran		