

N 70 39749

CR113589

POLY (VINYL ETHERS) SYNTHESIS
FUNDAMENTAL STUDY OF VISCOELASTIC STATE

FINAL REPORT
on
Contract No. NAS7-735

April 1970

by
H. A. Anderson
B. J. Burreson
W. P. Fitzgerald Jr.

CASE FILE
COPY

Submitted to
Jet Propulsion Laboratory
National Aeronautics and Space Administration
Oak Grove Drive
Pasadena, California

by
WHITTAKER CORPORATION
Research and Development Division
3540 Aero Court
San Diego, California 92123

POLY(VINYL ETHERS) SYNTHESIS FOR
FUNDAMENTAL STUDY OF VISCOELASTIC STATE

FINAL REPORT
on
Contract No. NAS7-735

April 1970

by
H. A. Anderson
B. J. Burreson
W. P. Fitzgerald Jr.

Submitted to
Jet Propulsion Laboratory
National Aeronautics and Space Administration
Oak Grove Drive
Pasadena, California

by
WHITTAKER CORPORATION
Research and Development Division
3540 Aero Court
San Diego, California 92123

TABLE OF CONTENTS

	<u>Page</u>
OBJECTIVE AND INTRODUCTION	1
DISCUSSION	2
EXPERIMENTAL	14
CONCLUDING REMARKS	16
RECOMMENDATIONS FOR FUTURE RESEARCH.	16
APPENDIX - DISTRIBUTION LIST	17

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	X-Ray Diffractogram of Unresolved Polyisobutyl Vinyl Ether	11
2	X-Ray Diffractogram of Polycetyl Vinyl Ether BJB-2157-32	12
3	Possible Correlation of Halo Position to Side Chain Length in Polyvinyl Ethers.	13

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Typical Properties of the Alkyl Vinyl Ether Monomers	4
II	Poly(Vinyl Ether) Synthesis.	5
III	Molecular Weights of Poly(Alkyl Vinyl Ethers)	8
IV	X-Ray Diffraction Analysis of Polyvinyl Ethers	10

OBJECTIVE AND INTRODUCTION

The objective of this program is to synthesize and deliver 10 kg quantities each of nine amorphous and well-characterized poly(alkyl vinyl ether) elastomers from the following commercially-available vinyl ether monomers: methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether, n-hexyl vinyl ether, phenyl vinyl ether, n-decyl vinyl ether, and n-hexadecyl vinyl ether. The polymers were to be prepared in an amorphous a state as possible by the utilization of relatively high reaction temperatures (35°-120°) and the specific catalyst system, aluminum hexahydrosulfate heptahydrate. Such polymers are desired for a fundamental study of the visco-elastic state. The criterion for an amorphous polymer is room-temperature solubility in methyl ethyl ketone (MEK). It is recognized with the long-chain alkyl members of the series (n-decyl and over) tend to form with side-chain crystallization, although the backbone may be amorphous. The desired molecular weight range for each member is characterized by inherent viscosity and by light-scattering molecular weight, as well as by spectral methods.

*

DISCUSSION

CATALYST SYSTEM

The catalyst system specified for this program is the aluminum hydro-sulfate/Nujol system, $\text{Al}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$, coded AHS. This catalyst has been prepared several times according to the procedure of Lal, et al.* A ca. 5-micron dispersion of the catalyst in mineral oil was obtained by ball-milling the as-prepared product. The catalyst has displayed unlimited shelf stability, and enhanced efficiency due to the smaller particle size. No other catalysts were considered, since most are more efficient in producing the undesirable crystalline polymer forms.

MONOMERS

Methyl vinyl ether was obtained (50-lb cylinder) from the Matheson Company. Other available monomers, namely ethyl-, n-propyl, n-butyl-, isobutyl-, n-decyl-, and cetyl-vinyl ethers, have been obtained in 50-lb lots from General Aniline & Film Company. These monomers have been obtained in varying states of purity, as assayed by vapor phase chromatography. Samples of these monomers, which were initially received from GAF, were analyzed for purity, using vapor phase chromatography (VPC). They were found to be of low purity. For example, the n-butyl monomer was found to have a purity of 88% with two impurities, and the n-decyl monomer contained seven impurities that amounted to 70% of the sample. These results were discussed with the GAF Commercial Development Department, and we were assured that high purity monomers (>96%) could be delivered. This proved to be the case, and all of the samples taken from the second 50-pound quantities of monomers were found to contain less than 3% impurities. Purification, when necessary for higher molecular weight polymer, has been accomplished by fractional distillation. It was necessary to distill n-decyl vinyl ether before any polymerization at all could be initiated.

Two vinyl ether monomers, n-hexyl vinyl ether and phenyl vinyl ether, formerly available in developmental/experimental quantities from General Aniline & Film Company have been discontinued. When asked by WRD to supply these needed monomers on a custom-synthesis basis, GAF quoted prices so prohibitively high as to render the consideration of these monomers for large-scale polymerization impossible. Upon subsequent recommendation of the project officer, these poly(hexyl vinyl ether) and poly(phenyl vinyl ether) monomers were dropped from the program.

* J. Lal, J. E. McGrath and G. S. Trich, J. Polymer Sci., A-5, 795 (1967) and refs. loc. cit.

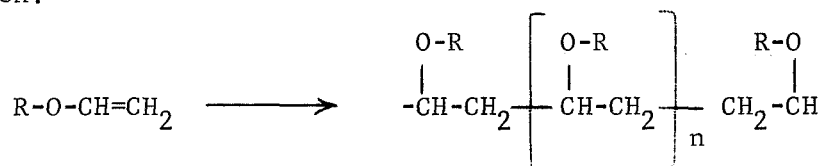
A small feasibility preparation of hexyl vinyl ether was performed by the mercuric acetate-catalyzed exchange reaction between hexyl alcohol and iso-octyl vinyl ether. A yield of ca. 50% was obtained. The yield and purity of the product were seriously effected by the tendency of hexyl alcohol to co-distill with the hexyl vinyl ether. This reaction is probably only acceptable for the preparation of small amounts (~ 500 g) of hexyl vinyl ether, and was not, therefore, applicable to a large-scale, single-batch preparation of this unavailable monomer.

Typical properties for the alkyl vinyl ethers used on this program are listed in Table I.

POLYMERIZATIONS

Homopolymerization of the alkyl vinyl ethers was readily effected by the addition of 1%, by volume, of the ionic catalyst, AHS, to the monomer at the desired temperature with stirring under nitrogen. Small-scale polymerizations were run initially to determine whether bulk polymerization or solution homopolymerization produced the more desirable products. It was found that only cetyl vinyl ether monomer could be efficiently homopolymerized in bulk. The other monomers were polymerized in hexane solutions, except methyl vinyl ether, which was most effectively run in heptane.

The homopolymerization reaction may be represented by the following equation:



where R - for this program included: (1) methyl, (2) ethyl, (3) n-propyl, (4) isobutyl, (5) n-butyl, (6) n-decyl and (7) cetyl (hexadecyl).

Each of the polymerizations is discussed in detail below. The polymer properties are listed in Table II.

TABLE I
TYPICAL PROPERTIES OF THE ALKYL VINYL ETHER MONOMERS

Vinyl Ether	Melting Point °C	Boiling Point Temp °C at mm Hg Pressure		Refractive Index	Specific Gravity
Methyl	-122	5-6	760	$1.3947 \frac{25}{D}$	$0.7694 \frac{5.7}{4}$
Ethyl	-115.8	35-6	760	$1.3767 \frac{20}{D}$	$0.7589 \frac{20}{4}$
<u>n</u> -Propyl	--	63-4	760	$1.3902 \frac{20}{D}$	$0.7680 \frac{20}{4}$
<u>n</u> -Butyl	-92	93-94	760	$1.3997 \frac{25}{D}$	$0.744 \frac{25}{4}$
Isobutyl	-112	25 83	77 760	$1.3965 \frac{20}{D}$	$0.768 \frac{20}{4}$
Decyl	-41	60-98	5	$1.4278 \frac{25}{D}$	$0.812 \frac{20}{4}$
Cetyl	16	142 173	1 5	$1.4444 \frac{25}{D}$	$0.822 \frac{27}{15}$

TABLE II

POLY(VINYL ETHER) SYNTHESIS

<u>Vinyl Polymer</u>	<u>Notebook Number</u>	<u>Polymer η_{inh} (Toluene)</u>	<u>Polymerization Method</u>	<u>Comments</u>
Methyl	HA-225-21	0.20 ^b	26% Solids in hexane	Exothermic polymerization, red-brown solid
Ethyl	BJB-2157-27	0.86 ^a	39% Solids in hexane	Light yellow, amorphous elastomer
<u>n</u> -Propyl	HA-225-23	0.78 ^b	22% Solids in hexane	Off-white, tacky solid
<u>n</u> -Butyl	BJB-2157-21	3.0 ^a 0.57 ^b	22% Solids in hexane	Dark tacky mass
	BJB-2157-31	2.84 ^a 1.01 ^b	37% Solids in hexane	Light yellow amorphous elastomer
Isobutyl	BJB-2157-26	0.57 ^b	55% Solids in hexane	White amorphous solid
<u>n</u> -Decyl	BJB-2157-28	0.16 ^b	Neat	Viscous, amber liquid
	HA-225-13A	0.62 ^a	55% Solids in hexane	Viscous amber liquid, insoluble in MEK
<u>n</u> -Cetyl	BJB-2157-32	0.02 ^b	Neat	Amber solid
	HA-225-12	0.79 ^a	Neat	Yellow wax, insoluble in MEK

^a Dried polymer before MEK resolution

^b Dried amorphous polymer after MEK resolution

(1) Methyl Vinyl Ether

Methyl vinyl ether is a gas at room temperature (b.p. 2°C) and thus posed unique problems in polymerization, especially on a large scale. These problems were compounded by the discovery that the AHS catalyst failed to initiate polymerization at 25°. Polymerization was found to take place at 35° in heptane or xylene which requires dilution of 25-40% solids. The polymers were obtained as amorphous solids with inherent viscosities of 0.2-0.7. A second method more amenable to scale-up was by merely bubbling the gas into boiling hexane containing the catalyst. The polymer, which precipitated as it formed, had an inherent viscosity of 0.26, and the same physical appearance as the other preparations. This second method, although more satisfactory for larger scale preparations, produced a polymer which was less soluble in MEK than polymer produced by the first method at the 25-40% solids level.

(2) n-Butyl Vinyl Ether

Two large-scale polymerizations of this monomer were performed on this program. The first preparation was run at 22% solids with an initial reaction temperature of 20° with an exotherm to 65°. The dried polymer had an inherent viscosity of 3.0. In drying the polymer, after dissolution in MEK, overheating produced polymer which was rather dark amber and very tacky. The inherent viscosity was reduced to 0.57. This was undoubtedly due to depolymerization during drying. A second polymerization of n-butyl vinyl ether was performed in hexane using 36% solids to facilitate solvent removal. Careful drying of the amorphous polymer gave a light yellow amorphous mass with inherent viscosity of 1.0.

(3) Ethyl Vinyl Ether

The ethyl vinyl ether was polymerized essentially in the same manner as the butyl homologue except that the reaction temperature was maintained at 65°. From a polymerization at 39% solids, a polymer with η_{inh} 0.86 in toluene was obtained.

(4) Isobutyl Vinyl Ether

The as-received monomer would not polymerize successfully and required distillation from calcium hydride. When thus purified, polymerization was easily performed as in the previous cases; at the 55% solids level. The product was an amorphous white solid, η_{inh} 0.57 in toluene.

(5) Cetyl Vinyl Ether

Two polymerizations were performed with this monomer with results very similar to that of the decyl vinyl ether. Both reactions were performed without solvent at 100°. In the initial reaction excess catalyst was used as the reaction was very slow. The product was a semi-solid largely MEK-soluble, with low inherent viscosity (0.02) indicating low

molecular weight. The second preparation was performed using freshly prepared catalyst and gave a yellow wax with an inherent viscosity of 0.79. This polymer was insoluble in MEK as was the high viscosity decyl vinyl ether (cf. below) again indicating side chain-crystallization.

(6) n-Decyl Vinyl Ether

This monomer was also unsatisfactory for polymerization as-received and was vacuum distilled from calcium hydride. The initial large polymerization was performed without solvent at 110° to yield MEK-soluble polymer with the low inherent viscosity of 0.16. A second polymerization was performed in hexane at 75-80° and the product had an inherent viscosity of 0.62. Only about 5% of this polymer was MEK soluble. The soluble product was obtained as a mobile liquid with an inherent viscosity of 0.02. The insoluble portion had an inherent viscosity of 0.69. This insolubility is indicate of crystallinity which was expected to occur in the side chain of the long chain homologous with increasing molecular weight. This phenomenon was also observed in the case of cetyl (hexadecyl) vinyl ether.

(7) n-Propyl Vinyl Ether

This monomer was successfully polymerized as-received. The reaction was run at 22% solids with initial reaction temperature of 30°C, followed by exotherm to 65°C. The dried polymer had an inherent viscosity of 0.78 for the MEK-soluble portion which amounted to 85% of the total polymer. With a previous reaction on a smaller scale run, the resulting polymer was an amorphous solid with an inherent viscosity of 2.74.

REACTION PARAMETERS

The effects of time, temperature, catalyst concentration and solids-percentage on molecular weight, as measured by inherent viscosity, have been evaluated. As expected, the hexane solvent system has proven amenable to successful scale-up. A definite catalyst concentration effect has been found at the 500-gram scale-up level. Conducting the polymerization at 20-22% solids has given the most satisfactory results. In most cases the polymerizations were carried out most readily in the 40°-65°C temperature range. The products were generally obtained as viscous solutions in hexane. Workup was accomplished by solvent-evaporation or by methanol-precipitation and redissolution of amorphous polymer in methyl ethyl ketone.

POLYMER CHARACTERIZATION

1. Molecular Weight Analysis

Light scattering molecular weight analyses were performed by Dr. William G. Stevens of WRD using a Bryce-Phoenix light scattering photometer. The polarizabilities of the polymer solution were determined using a Bryce-Phoenix differential refractometer. All measurements were corrected for depolarization. The results are tabulated in Table III.

TABLE III

MOLECULAR WEIGHTS OF POLY(ALKYL VINYL ETHERS)

<u>Alkyl Group</u>	<u>Solvent</u>	<u>MW</u>	<u>DP</u>	<u>Comments</u>
Methyl (HA-225-21)	Toluene	6,840,000	142,000	Possibly fluorescent
Ethyl (BJB-2157-27)	Toluene	860,000	12,000	Possibly fluorescent
<u>n</u> -Propyl (HA-225-23)	Toluene	60,500	700	Fluorescent
<u>n</u> -Butyl (BJB-2157-31)	Hexane	218,000	2,200	--
<u>Isobutyl</u> (BJB-2157-26)	Toluene	807,000	8,000	--
<u>n</u> -Decyl (HA-225-13A)	Toluene	5,150,000	28,000	Fluorescent
(BJB-2157-28)	Toluene	469 (VPO)		
<u>n</u> -Hexadecyl(cetyl)				
(HA-225-12)	Hexane	6,000,000	20,000	--
(BJB-2157-32)	Toluene	359 (VPO)		

The molecular weights cited for the propyl and ethyl vinyl ether polymers are an upper limit values, as solution of these polymers were fluorescent in ultraviolet light. These polymers should not be fluorescent and this phenomenon is unexplained, and may be due to the presence of small amounts of sulfuric acid from residual catalyst. This acid is known to fluorescence strongly to the radiation wavelengths used.

Two lower viscosity products were prepared in separate large-scale batches to the above preparations; one from decyl vinyl ether and one from cetyl vinyl ether. These products were of too low a molecular weight to be determined by light scattering. These were done by vapor phase osmometry (VPO). These results are also indicated in Table II.

2. X-Ray Analysis of Poly(alkyl vinyl ethers)

X-ray studies were also performed by Dr. W. G. Stevens of WRD using a Norelco vertical goniometer and scintillation counter. The sample polymers were analyzed using the K_{α} line of copper with the data readout using a Norelco Model 12206/7 electronic circuit panel.

The results of these analyses indicated that only one poly(cetyl vinyl ether) sample contained crystalline material. All of the other polyvinyl ethers were ordered, but not crystalline. These results are summarized in the following Table IV. Typical X-ray diffraction patterns observed for the polyvinyl ethers are shown in Figures 1 and 2. The X-ray diffractogram shown in Figure 1 is typical of all the polyvinyl ethers except the cetyl case. The halo occurring at 4.76 Å was observed for all samples and was roughly at the same position for each (see Table IV and underlined d spacings for halos). The position of the halo shown in Figure 1 at 10.28 Å was observed to vary with the length of the side chain as is shown in Figure 3. In two samples, cetyl and n-butyl, a third halo was observed, however, but no conclusions have been drawn concerning its origin.

The X-ray diffractogram (Figure 2) of polycetyl vinyl ether (BJB-2159-32) was the only crystalline diffractogram observed in this investigation. Compared with the results shown in Figure 1, the sharp peaks shown in Figure 2 obviously correspond to crystalline material in this sample and the broad halo, area C, results from scattering of X-rays by noncrystalline material. Theoretically, the total radiation scattered from a mass of materials is independent of the physical state of the material, thus the percent crystallinity of this material was calculated by determining the areas under the curve A + B + C + D and then taking the following calculation:

$$2 \text{ crystallinity} = \frac{(A+B+D) \times 100}{A+B+C+D}$$

The main conclusion from this investigation is that none of the polyvinyl ethers prepared on this program are very crystalline, on the basis of X-ray diffraction analysis.

TABLE IV
X-RAY DIFFRACTION ANALYSIS
OF POLYVINYL ETHERS

<u>Polyvinyl Ether</u>	<u>Halos</u>	<u>d Spacings A° Peaks</u>	<u>% X tallinity</u>
Cetyl (BJB-2157-32)	<u>4.53</u>	40.2, 14.7, 4.11	9.5
Cetyl	8.85, 4.14, 2.26		<1
Decyl	21.4, <u>4.68</u>	--	<1
<u>n</u> -Butyl	29.4, 10.5, <u>4.48</u>	--	<1
<u>n</u> -Butyl (unresolved)	11.02, <u>4.66</u>	--	<1
Isobutyl (insoluble)	10.28, <u>4.76</u>	--	<1
Isobutyl (unresolved)	10.05, <u>4.87</u>	--	<1
Ethyl	7.77, <u>4.27</u>	--	<1
Methyl (soluble in MEK)	6.58, 4.35	--	<1
Methyl (insoluble HA-225-14)	6.32, <u>4.23</u>	--	<1
Polyethylene*	4.53	4.15, 3.74	38.6

* Included for reference purposes only.

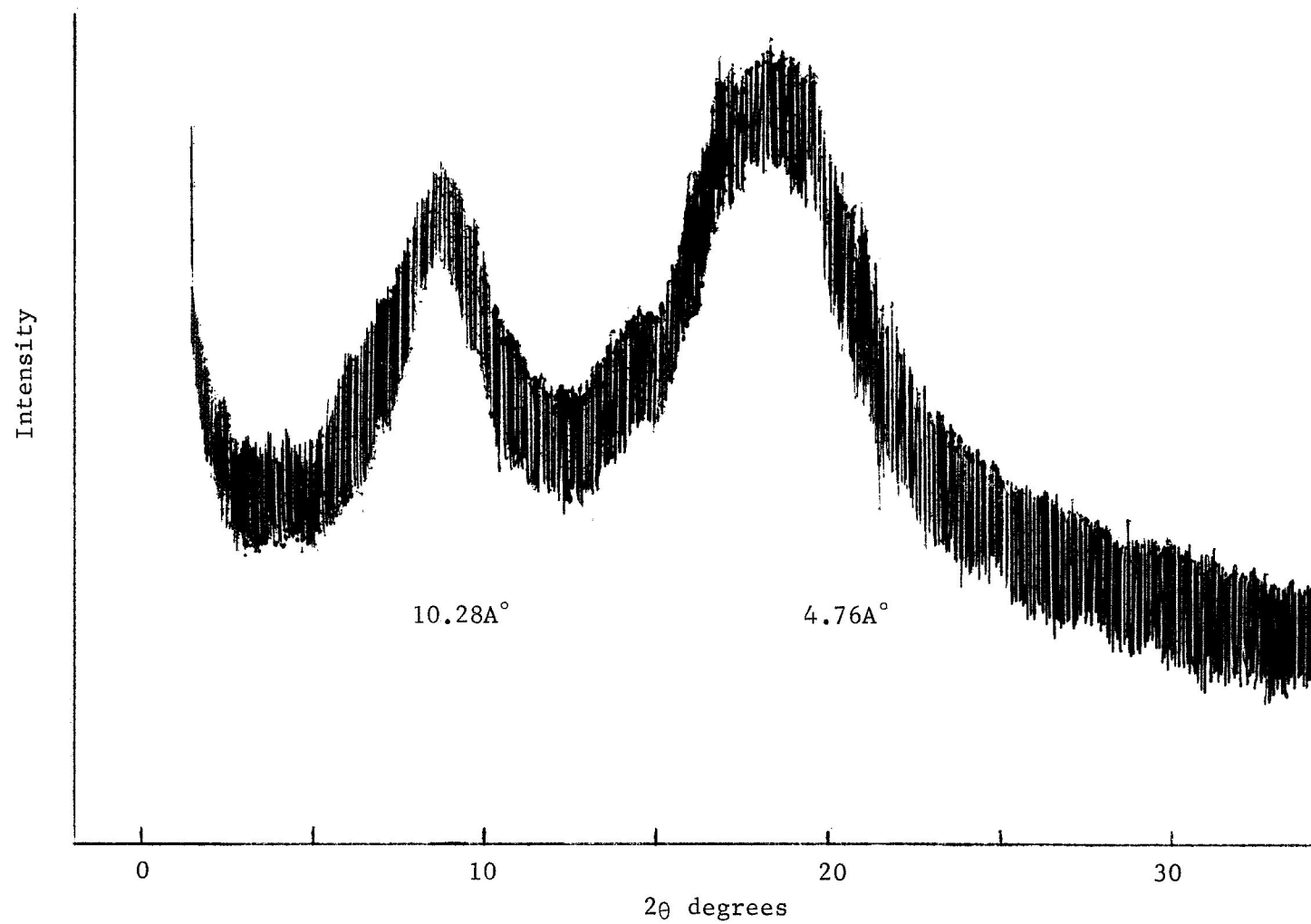


Figure 1. X-Ray Diffractogram of Unresolved Polyisobutyl Vinyl Ether

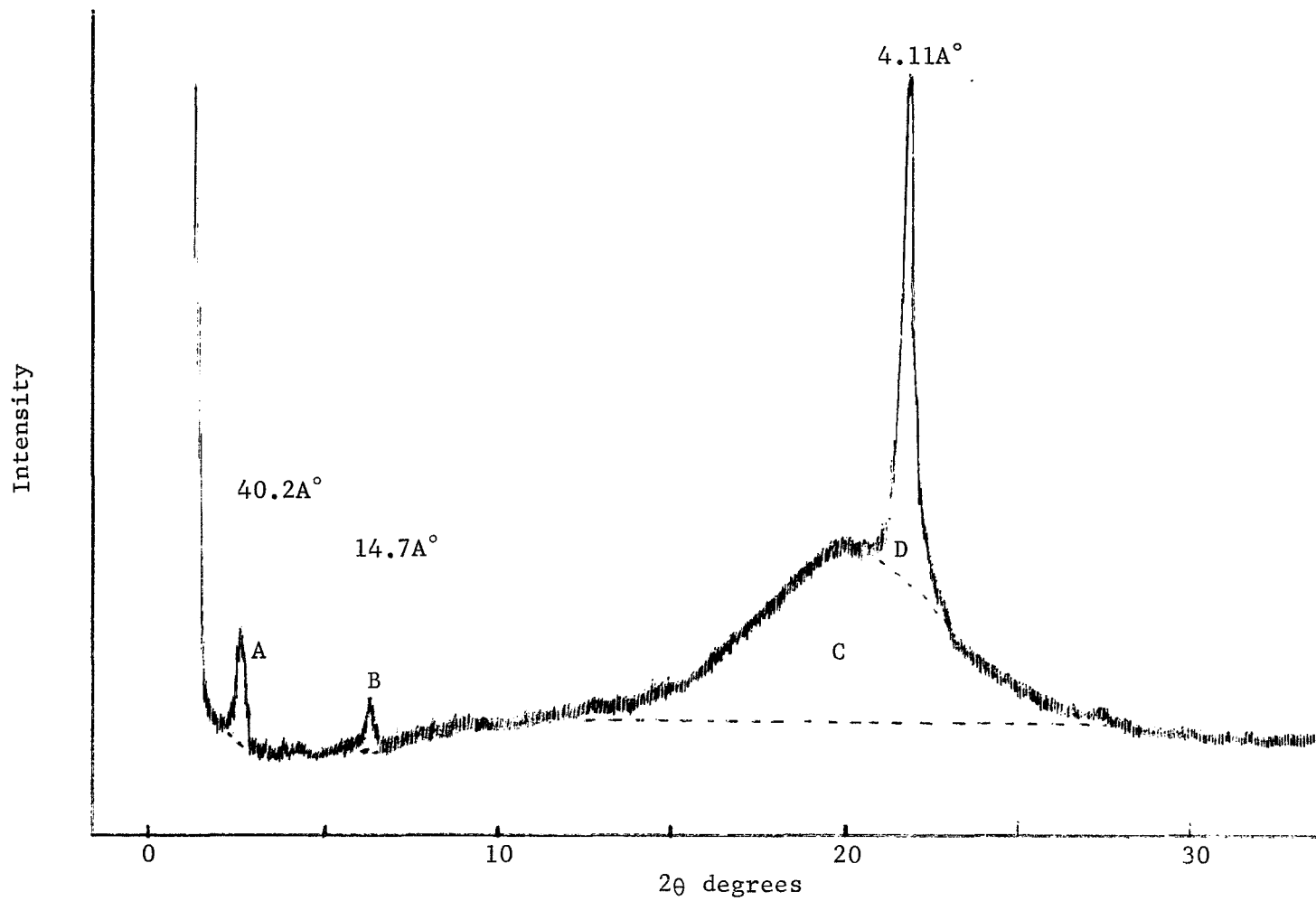


Figure 2. X-Ray Diffractogram of Polycetyl Vinyl Ether
BJB-2157-32

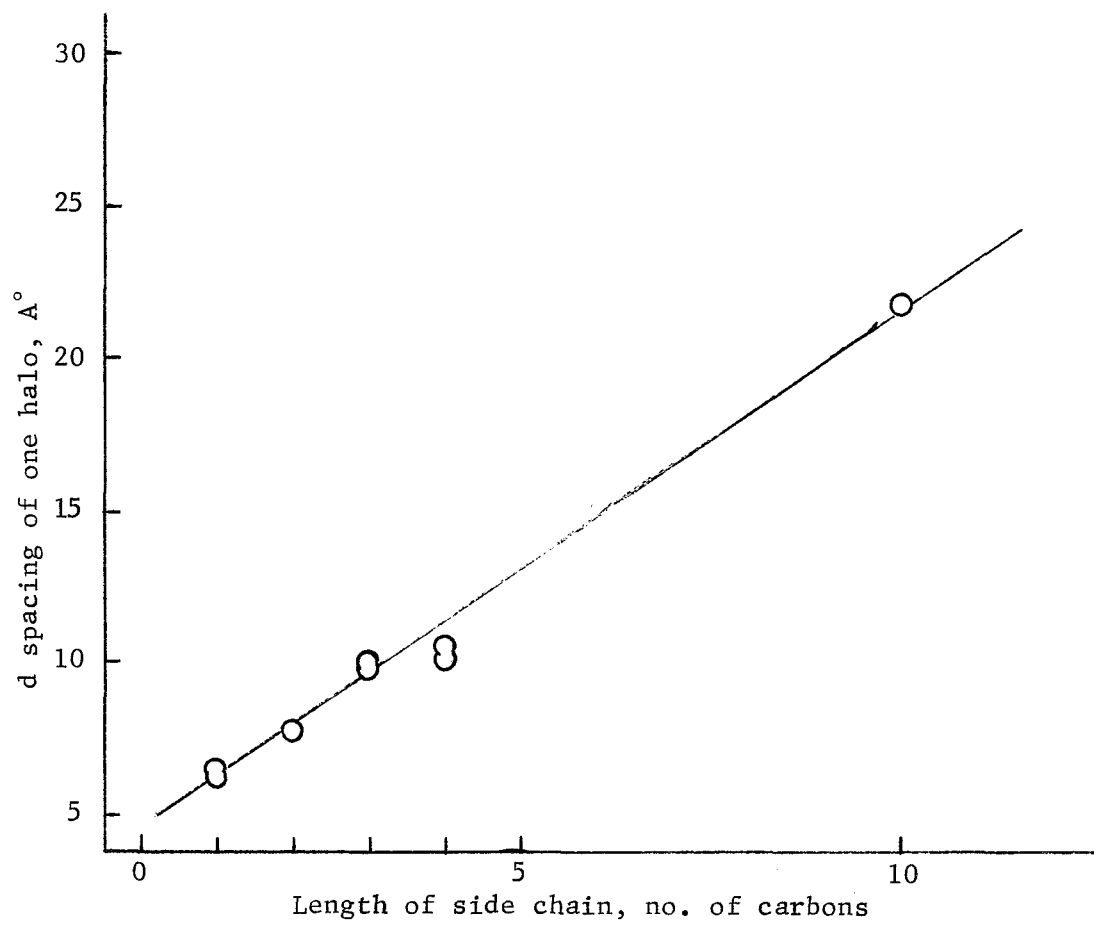


Figure 3. Possible Correlation of Halo Position to Side Chain Length in Polyvinyl Ethers

EXPERIMENTAL

Methyl Vinyl Ether

A charge of 17.3 kg of the monomer was condensed into 45 kg of dry heptane solvent. The heptane was dried overnight over CaCl_2 . The solution was heated initially to 30°C and 0.17 kg AHS catalyst added to initiate polymerization. The solution was stirred rapidly to ensure maximum homogeneity in polymerization, with an efficient dry ice cooling system employed to handle the exothermic reaction. During the polymerization, the temperature rose to 89°C . Stirring was continued until the temperature returned to about 40°C . (Note: It was found that without stirring the newly-formed polymer would char if allowed to settle at 89°C in the reaction vessel.)

The second method for methyl vinyl ether polymerization required less of a cooling system. The same amounts of heptane (45 kg) and catalyst AHS (0.17 kg) were initially added together and heated to 60°C . The monomer was bubbled into the heated solution with polymerization maintaining the temperature at 60°C - 65°C without external heating. The polymer prepared by this second method was largely insoluble in MEK.

Ethyl Vinyl Ether

A charge of 13.2 kg of the monomer was dissolved in 50.8 kg of dry hexane solvent. With the solution constantly stirred, 0.15 kg AHS catalyst was added at room temperature. The temperature slowly rose to 30°C , at which point the polymerization proceeded rapidly, with exothermicity to 65°C , with large amounts of solvent evaporating off in the process.

n-Propyl Vinyl Ether

An available total of 6.2 kg of the monomer was dissolved in 19.5 kg of dry hexane. The solution was stirred vigorously at room temperature and 0.08 kg AHS catalyst was added to initiate polymerization. The temperature increased slowly to 65°C , the solvent was removed from the viscous solution, and the product was recovered after redissolution in MEK. The yield was 5.1 kg which was delivered.

n-Butyl Vinyl Ether

14 kg of the monomer was dissolved in 24.4 kg of dry hexane. Then 0.17 kg AHS catalyst was added to the solution at room temperature. The temperature rose very slowly to 65°C with polymerization occurring along with reflux of solvent. The product was isolated as above, by dissolution in MEK after solvent removal.

Iso-Butyl Vinyl Ether

24 kg of the monomer was dissolved in 24 kg of dry hexane. Then 0.39 kg of the catalyst AHS was added to the solution at room temperature with constant stirring. The temperature reached maximum of 65°C vigorously with nearly complete removal of hexane solvent by distillation during polymerization.

Decyl Vinyl Ether

23 kg of the distilled monomer was dissolved in 19.5 kg of dry hexane. The solution was then heated to reflux and 0.28 kg AHS catalyst was added to initiate polymerization. A slight exotherm to 85°C was observed. After 2 days of stirring at reflux, the polymerization appeared complete by infrared spectroscopy. The product was isolated as above.

Hexadecyl(cetyl) Vinyl Ether

13.0 kg of the bulk monomer was placed under an atmosphere of nitrogen with efficient stirring. The monomer was heated to 60°C with 0.15 kg AHS catalyst added for polymerization. The heat source was removed when the exothermic polymerization reached 120°C. This reaction required only 3 hours to complete polymerization.

AHS Preparation

A charge of 30 g of aluminum sulfate octadecylhydrate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, was added to 150 ml of concentrated sulfuric acid with stirring. The temperature spontaneously increases to 36°C. The solution was heated slowly to 90°C and stirred at that temperature for 1 hour. The solution was then cooled to 10°C and 1 liter of anhydrous ether was added very carefully. (Caution: Exothermic reaction at this point caused ether to be expelled rapidly if the addition rate was too fast.) The white precipitate was allowed to settle, the ether layer was siphoned off, with the ether wash repeated 10 times or more. The final ethereal slurry was filtered and the powdery white precipitate was collected and dried. The catalyst suspension was then prepared using 10.9 g of this solid in 534 g of Nujol, with ball-milling in a jar mill for 24 hours. The suspension was stored in a sealed vessel and withdrawn with a hypodermic syringe as needed under nitrogen, after shaking the container.

CONCLUDING REMARKS

The large-scale synthesis of amorphous poly(vinyl ethers) using the aluminum hydrosulfate catalyst system in hydrocarbon solvent has been demonstrated. The lower members of the homologous polymer series were amorphous, elastomeric masses, soluble in methyl ethyl ketone, whereas the higher members tended to be insoluble. Based on several types of evidence, this solubility has been attributed to increasing hydrocarbon-like character to the polymer. These high molecular-weight, long side-chain-systems show negligible crystallinity, and retain solubility in hydrocarbon solvent.

The poly(cetyl vinyl ether) was obtained as a resilient solid material, which would appear to have potential as a molding material. This modification was obtained by facile bulk polymerization.

RECOMMENDATIONS FOR FUTURE RESEARCH

It would be most informative to prepare other more interesting structurally-modified polyvinyl ethers, for comparison of effect on viscoelastic properties. Among the more interesting candidates for the amorphous polymerization would be cyclopropylvinyl ether, cyclohexylvinyl ether and adamantylvinyl ether. The batch size would be much smaller owing to the necessity to synthesize the needed monomers.

Another interesting area for desired research in this area would be a study of simple efficient curing procedure for the various vinyl ether homopolymers. Correlations could then be made of the effect on viscoelastic properties between the linear systems and their cross-linked analogues.

Both these areas would be of fundamental interest to proposed follow-on research in this area.

APPENDIX

DISTRIBUTION LIST FOR FINAL TECHNICAL REPORT

<u>Copies</u>	<u>Receiptent</u>	<u>Designee</u>
1	NASA Headquarters Washington, D.C. 20546 Contracting Officer	X
1	NASA Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Office of Technical Information	X
1	NASA Manned Spacecraft Center Houston, Texas 77001 Office of Technical Information	X
2	NASA Marshall Space Flight Center Huntsville, Alabama 35812 Office of Technical Information, MS-1P	X
1	Technical Library	X
1	Dale Burrows S&E - ASTN - PJ	X
2	Jet Propulsion Laboratory 4800 Oak Grove Drive Pasadena, California 91103 Louis Toth	X
3	Chief, Liquid Propulsion Technology RPL Office of Advanced Research and Technology NASA Headquarters Washington, D.C. 20546	X
1	Director, Technology Utilization Division Office of Technology Utilization NASA Headquarters Washington, D.C. 20546	X
20	NASA Scientific and Technical Information Facility P.O. Box 33 College Park, Maryland 20740	X
1	Director, Launch Vehicles and Propulsion, SV Office of Space Science and Applications NASA Headquarters Washington, D.C. 20546	X
1	Director, Advanced Manned Missions, MT Office of Manned Space Flight NASA Headquarters Washington, D.C. 20546	X

<u>Copies</u>	<u>Recipient</u>	<u>Designee</u>
1	NASA Pasadena Office 4800 Oak Grove Drive Pasadena, California 91103 Patents and Contracts Management	X
1	Western Support Office 150 Pico Boulevard Santa Monica, California 90406 Office of Technical Information	X
1	Jet Propulsion Laboratory 4800 Oak Grove Drive Pasadena, California 91103 D. D. Lawson, Technical Monitor	X
<u>NASA Field Centers</u>		
1	Ames Research Center Moffett Field, California 94035	Hans M. Mark
1	Goddard Space Flight Center Greenbelt, Maryland 20771	Merland L. Moseson Code 620
2	Jet Propulsion Laboratory California Institute of Technology 4800 Oak Grove Drive Pasadena, California 91103	Henry Burlage, Jr. Propulsion Div. 38
1	Langley Research Center Langley Station Hampton, Virginia 23365	Ed Cortwright Director
1	Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135	Director
1	Marshall Space Flight Center Huntsville, Alabama 35812	Hans G. Paul Code R-P & VED
1	Manned Spacecraft Center Houston, Texas 77001	J. G. Thibodaux, Jr. Chief, Prop. & Power Div.
1	John F. Kennedy Space Center, NASA Cocoa Beach, Florida 32931	Dr. Kurt H. Debus
2	Western Operations Office 150 Pico Boulevard Santa Monica, California 90406	Robert W. Kamm, Director

<u>Copies</u>	<u>Recipient</u> <u>Government Installations</u>	<u>Designee</u>
1	Air Force Missile Test Center Patrick Air Force Base, Florida	L. J. Ullian
1	Space and Missile Systems Organization Air Force Unit Post Office Los Angeles, California 90045	Colonel Clark Technical Data Center
1	Arnold Engineering Development Center Arnold Air Force Station Tullahoma, Tennessee 37388	Dr. H. K. Doetach
1	Bureau of Naval Weapons Department of the Navy Washington, D.C. 20546	J. Kay, RTMS-41
1	Defense Documentation Center Headquarters Cameron Station, Building 5 5010 Duke Street Alexandria, Virginia 22314	TISIA
1	Headquarters, U. S. Air Force Washington, D.C. 20546	Colonel C. K. Stambaugh AFRST
1	Picatinny Arsenal Dover, New Jersey 07801	T. Forsten, Chief Liquid Propulsion Laboratory
1	Air Force Rocket Propulsion Laboratory Research and Technology Division Air Force Systems Command Edwards, California 93523	RPRPD/Mr. H. Main
1	U.S. Army Missile Command Redstone Arsenal Alabama 35809	Mr. Walter Wharton
1	U.S. Naval Ordnance Test Station China Lake, California 93557	Code 4562 Chief, Missile Propulsion Div.
1	Aeronautical Systems Division Air Force Systems Command Wright-Patterson Air Force Base, Ohio 45433	D. L. Schmidt Code ASRCNC-2
1	Air Force Missile Development Center Holloman Air Force Base, New Mexico 88330	Major R. E. Bracken

<u>Copies</u>	<u>Receiptient</u>	<u>Designee</u>
	<u>CPIA</u>	
1	Chemical Propulsion Information Agency Applied Physics Laboratory 8621 Georgia Avenue Silver Spring, Maryland 20910	Tom Reedy
	<u>Industry Contractors</u>	
1	Aerojet-General Corporation P.O. Box 296 Azusa, California 91703	W. L. Rogers
1	Aerojet-General Corporation P.O. Box 1947 Technical Library, Bldg. 2015, Dept. 2410 Sacramento, California 95809	R. Stiff
1	Space Division Aerojet-General Corporation 9200 East Flair Drive El Monte, California	S. Machlawski
1	Aerospace Corporation 2400 East El Segundo Boulevard P.O. Box 95085 Los Angeles, California 90045	John G. Wilder MS-2293
1	Atlantic Research Company Edsall Road and Shirley Highway Alexandria, Virginia 22314	Dr. Ray Friedman
1	Avco Systems Division Wilmington, Massachusetts	Howard B. Winkler
1	Beech Aircraft Corporation Boulder Division Box 631 Boulder, Colorado	J. H. Rodgers
1	Bell Aerosystems Company P.O. Box 1 Buffalo, New York 14240	W. M. Smith
1	Bellcomm 955 L'Enfant Plaza, S.W. Washington, D.C.	H. S. London

<u>Copies</u>	<u>Recipient</u>	<u>Designee</u>
1	Bendix Systems Division Bendix Corporation 3300 Plymouth Road Ann Arbor, Michigan 48105	John M. Brueger
1	Boeing Company P.O. Box 3707 Seattle, Washington 98124	J. D. Alexander W. W. Kann
1	Boeing Company 1625 K Street, N.W. Washington, D.C. 20006	Library
1	Missile Division Chrysler Corporation P.O. Box 2628 Detroit, Michigan 48231	John Gates
1	Wright Aeronautical Division Curtis-Wright Corporation Woodridge, New Jersey 07075	G. Kelley
2	Research Center Fairchild Hiller Corporation Germantown, Maryland	Ralph Hall
1	Republic Aviation Corporation Fairchild Hiller Corporation Farmingdale, Long Island, New York	Library
1	General Dynamics, Convair Division Library & Information Services (128-00) P.O. Box 1128 San Diego, California 92112	Frank Dore
1	Missile and Space Systems Center General Electric Company Valley Forge Space Technology Center P.O. Box 8555 Philadelphia, Pennsylvania	F. Mezger F. E. Schultz
1	Grumman Aircraft Engineering Corporation Bethpage, Long Island, New York 11714	Joseph Gavin
1	Honeywell, Inc. Aerospace Division 2600 Ridgway Road Minneapolis, Minnesota	Gordon Harms

<u>Copies</u>	<u>Recipient</u>	<u>Designee</u>
1	Hughes Aircraft Company Aerospace Group Centinela and Teale Streets Culver City, California 90230	F. H. Meter V.P. and Div. Mgr. Research & Development Div.
1	Walter Kidde and Company, Inc. Aerospace Operations 567 Main Street Belleville, New Jersey	R. J. Hanville Dir. of Research Engineering
1	Ling-Temco-Vought Corporation P.O. Box 5907 Dallas, Texas 75222	Warren G. Trent
1	Arthur D. Little, Inc. 20 Acorn Park Cambridge, Massachusetts 02140	Library
1	Lockheed Missiles and Space Company ATTN: Technical Information Center P.O. Box 504 Sunnyvale, California 94088	J. Guill
1	Lockheed Propulsion Company P.O. Box 111 Redlands, California 92374	Library
1	The Marquardt Corporation 16555 Saticoy Street Van Nuys, California 91409	Library
1	Baltimore Division Martin Marietta Corporation Baltimore, Maryland 21203	John Calathes (3214)
1	Denver Division Martin Marietta Corporation P.O. Box 179 Denver, Colorado 80201	Dr. Morganthaler A. J. Kullas
1	Astropower Laboratory McDonnell Douglas Astronautics Company 2121 Campus Drive Newport Beach, California 92663	Dr. George Moe Director, Research
1	Astrosystems International, Inc. 1275 Bloomfield Avenue Fairfield, New Jersey 07007	A. Mendenhall

<u>Copies</u>	<u>Recipient</u>	<u>Designee</u>
1	Missile and Space Systems Division McDonnell Douglas Astronautics Company 3000 Ocean Park Boulevard Santa Monica, California 90406	Mr. R. W. Hallet Chief Engineer Adv. Space. Tech.
1	Space & Information Systems Division North American Rockwell 12214 Lakewood Boulevard Downey, California 90241	Library
1	Rocketdyne (Library 586-306) 6633 Canoga Avenue Canoga Park, California 91304	Dr. R. J. Thompson S. F. Iacobellis
1	Northrop Space Laboratories 3401 West Broadway Hawthorne, California 90250	Dr. William Howard
1	Aeronutronic Division Philco Corporation Ford Road Newport Beach, California 92663	D. A. Garrison
1	Astro-Electronics Division Radio Corporation of America Princeton, New Jersey 08540	Y. Brill
1	Rocket Research Corporation 520 South Portland Street Seattle, Washington 98108	Foy McCullough, Jr.
1	Sunstrand Aviation 2421 11th Street Rockford, Illinois 61101	R. W. Reynolds
1	Stanford Research Institute 333 Ravenswood Avenue Menlo Park, California 94025	Dr. Gerald Marksmen
1	TRW Systems Group TRW Incorporated One Space Park Redondo Beach, California 90278	G. W. Elverum
1	Thiokol Chemical Corporation Aerospace Services Elkton Division Bristol, Pennsylvania	Library

<u>Copies</u>	<u>Recipient</u>	<u>Designee</u>
1	Research Laboratories United Aircraft Corporation 400 Main Street East Hartford, Connecticut 06108	Erle Martin
1	Hamilton Standard Division United Aircraft Corporation Windsor Locks, Connecticut 06096	R. Hatch
1	United Technology Center 587 Methilda Avenue P.O. Box 358 Sunnyvale, California 94088	Dr. David Altman
1	Republic Aviation Corporation Farmingdale, Long Island, New York	Dr. William O'Donnell
1	Space General Corporation 9200 East Flair Avenue El Monte, California 91734	C. E. Roth
1	Thiokol Chemical Corporation Huntsville Division Huntsville, Alabama	John Goodloe
1	Calmec Manufacturing Corporation 5825 District Boulevard Los Angeles, California 90022	Library
1	Carleton Controls Corporation East Aurora, New York 14052	Library
1	J. C. Carter Company 671 W. Seventeenth Street Costa Mesa, California 92626	Library
1	Holex Incorporated 2751 San Juan Road Hollister, California 95023	Library
1	Parker Aircraft 5827 W. Century Boulevard Los Angeles, California 90009	Library
1	Pelmec Division Quantic Industries, Inc. 1011 Commercial Street San Carlos, California	Library

<u>Copies</u>	<u>Recipient</u>	<u>Designee</u>
1	Pyronetics, Inc. 10025 Shoemaker Avenue Santa Fe Springs, California 90670	Library
1	Stratos Western Division of Fairchild-Hiller Corporation 1800 Rosecrans Boulevard Manhattan Beach, California	Library
1	Solar Division of International Harvester Company 2200 Pacific Avenue San Diego, California	Library
1	Vacco Valve Company 10350 Vacco Street South El Monte, California	Library
1	Valcor Engineering Corporation 365 Carnegie Avenue Kenilworth, New Jersey 07033	Library
1	Vickers, Inc. Division of Sperry Rand Corporation 2160 E. Imperial Highway El Segundo, California	Library
1	Whittaker Corporation 9601 Canoga Avenue Chatsworth, California 91311	Library
1	Wintec Corporation 343 Glasgow Inglewood, California	Library