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.

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

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>OBJECTIVE AND INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>DISCUSSION</td>
<td>2</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>14</td>
</tr>
<tr>
<td>CONCLUDING REMARKS</td>
<td>16</td>
</tr>
<tr>
<td>RECOMMENDATIONS FOR FUTURE RESEARCH</td>
<td>16</td>
</tr>
<tr>
<td>APPENDIX - DISTRIBUTION LIST</td>
<td>17</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure		Page
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

Table		Page
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 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 chroma-
tography. 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% im-
purities. 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.

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:

\[
R\text{-O-CH=CH}_2 \xrightarrow{\text{O-R}} \left[ \text{-CH-CH}_2 \left[ \text{-CH-CH}_2 \right]_n \text{CH}_2-\text{CH} \right] \xrightarrow{\text{R-O}}
\]

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**

<table>
<thead>
<tr>
<th>Vinyl Ether</th>
<th>Melting Point °C</th>
<th>Boiling Point Temp °C at mm Hg Pressure</th>
<th>Refractive Index</th>
<th>Specific Gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>-122</td>
<td>5-6</td>
<td>1.3947 (\frac{25}{D})</td>
<td>0.7694 (\frac{5.7}{4})</td>
</tr>
<tr>
<td>Ethyl</td>
<td>-115.8</td>
<td>35-6</td>
<td>1.3767 (\frac{20}{D})</td>
<td>0.7589 (\frac{20}{4})</td>
</tr>
<tr>
<td>(n)-Propyl</td>
<td>--</td>
<td>63-4</td>
<td>1.3902 (\frac{20}{D})</td>
<td>0.7680 (\frac{20}{4})</td>
</tr>
<tr>
<td>(n)-Butyl</td>
<td>-92</td>
<td>93-94</td>
<td>1.3997 (\frac{25}{D})</td>
<td>0.744 (\frac{25}{4})</td>
</tr>
<tr>
<td>Isobutyl</td>
<td>-112</td>
<td>25</td>
<td>1.3965 (\frac{20}{D})</td>
<td>0.768 (\frac{20}{4})</td>
</tr>
<tr>
<td>Decyl</td>
<td>-41</td>
<td>60-98</td>
<td>1.4278 (\frac{25}{D})</td>
<td>0.812 (\frac{20}{4})</td>
</tr>
<tr>
<td>Cetyl</td>
<td>16</td>
<td>142</td>
<td>1.4444 (\frac{25}{D})</td>
<td>0.822 (\frac{27}{15})</td>
</tr>
<tr>
<td>Vinyl Polymer</td>
<td>Notebook Number</td>
<td>Polymerization Method</td>
<td>Comments</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>----------------</td>
<td>----------------------</td>
<td>----------</td>
<td></td>
</tr>
<tr>
<td>Methyl</td>
<td>HA-225-21</td>
<td>0.20(^a)</td>
<td>26% Solids in hexane</td>
<td>Exothermic polymerization, red-brown solid</td>
</tr>
<tr>
<td>Ethyl</td>
<td>BJB-2157-27</td>
<td>0.86(^a)</td>
<td>39% Solids in hexane</td>
<td>Light yellow, amorphous elastomer</td>
</tr>
<tr>
<td>n-Propyl</td>
<td>HA-225-23</td>
<td>0.78(^b)</td>
<td>22% Solids in hexane</td>
<td>Off-white, tacky solid</td>
</tr>
<tr>
<td>n-Butyl</td>
<td>BJB-2157-21</td>
<td>3.0(^a) 0.57(^b)</td>
<td>22% Solids in hexane</td>
<td>Dark tacky mass</td>
</tr>
<tr>
<td></td>
<td>BJB-2157-31</td>
<td>2.84(^a) 1.01(^b)</td>
<td>37% Solids in hexane</td>
<td>Light yellow amorphous elastomer</td>
</tr>
<tr>
<td>Isobutyl</td>
<td>BJB-2157-26</td>
<td>0.57(^b)</td>
<td>55% Solids in hexane</td>
<td>White amorphous solid</td>
</tr>
<tr>
<td>n-Decyl</td>
<td>BJB-2157-28</td>
<td>0.16(^b)</td>
<td>Neat</td>
<td>Viscous, amber liquid</td>
</tr>
<tr>
<td></td>
<td>HA-225-13A</td>
<td>0.62(^a)</td>
<td>55% Solids in hexane</td>
<td>Viscous amber liquid, insoluble in MEK</td>
</tr>
<tr>
<td>n-Cetyl</td>
<td>BJB-2157-32</td>
<td>0.02(^b)</td>
<td>Neat</td>
<td>Amber solid</td>
</tr>
<tr>
<td></td>
<td>HA-225-12</td>
<td>0.79(^a)</td>
<td>Neat</td>
<td>Yellow wax, insoluble in MEK</td>
</tr>
</tbody>
</table>

\(^{a}\) Dried polymer before MEK resolution
\(^{b}\) Dried amorphous polymer after MEK resolution
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.

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.

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 ηinh 0.86 in toluene was obtained.

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, ηinh 0.57 in toluene.

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 indicative 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)

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

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 fluoresce 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 Kα 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

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

* 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 CaCl₂. 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°-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, Al2(SO4)3-18H2O, 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

<table>
<thead>
<tr>
<th>Copies</th>
<th>Recipient</th>
<th>Designee</th>
</tr>
</thead>
</table>
| 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  
<pre><code>    | Washington, D.C. 20546 | X |
</code></pre>
<table>
<thead>
<tr>
<th>Copies</th>
<th>Recipient</th>
<th>Designee</th>
</tr>
</thead>
</table>
| 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 |

**NASA Field Centers**

| 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 |
<table>
<thead>
<tr>
<th>Copies</th>
<th>Recipient</th>
<th>Designee</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Government Installations</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Air Force Missile Test Center</td>
<td>L. J. Ullian</td>
</tr>
<tr>
<td></td>
<td>Patrick Air Force Base, Florida</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Space and Missile Systems Organization</td>
<td>Colonel Clark</td>
</tr>
<tr>
<td></td>
<td>Air Force Unit Post Office</td>
<td>Technical Data Center</td>
</tr>
<tr>
<td></td>
<td>Los Angeles, California 90045</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Arnold Engineering Development Center</td>
<td>Dr. H. K. Doetach</td>
</tr>
<tr>
<td></td>
<td>Arnold Air Force Station</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tullahoma, Tennessee 37388</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Bureau of Naval Weapons</td>
<td>J. Kay, RTMS-41</td>
</tr>
<tr>
<td></td>
<td>Department of the Navy</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Washington, D.C. 20546</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Defense Documentation Center Headquarters</td>
<td>TISIA</td>
</tr>
<tr>
<td></td>
<td>Cameron Station, Building 5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5010 Duke Street</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alexandria, Virginia 22314</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Headquarters, U.S. Air Force</td>
<td>Colonel C. K. Stambaugh</td>
</tr>
<tr>
<td></td>
<td>Washington, D.C. 20546</td>
<td>AFRST</td>
</tr>
<tr>
<td>1</td>
<td>Picatinny Arsenal</td>
<td>T. Forsten, Chief</td>
</tr>
<tr>
<td></td>
<td>Dover, New Jersey 07801</td>
<td>Liquid Propulsion Laboratory</td>
</tr>
<tr>
<td>1</td>
<td>Air Force Rocket Propulsion Laboratory</td>
<td>RPRPD/Mr. H. Main</td>
</tr>
<tr>
<td></td>
<td>Research and Technology Division</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Air Force Systems Command</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Edwards, California 93523</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>U.S. Army Missile Command</td>
<td>Mr. Walter Wharton</td>
</tr>
<tr>
<td></td>
<td>Redstone Arsenal</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alabama 35809</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>U.S. Naval Ordnance Test Station</td>
<td>Code 4562</td>
</tr>
<tr>
<td></td>
<td>China Lake, California 93557</td>
<td>Chief, Missile Propulsion Div.</td>
</tr>
<tr>
<td>1</td>
<td>Aeronautical Systems Division</td>
<td>D. L. Schmidt</td>
</tr>
<tr>
<td></td>
<td>Air Force Systems Command</td>
<td>Code ASRCNC-2</td>
</tr>
<tr>
<td></td>
<td>Wright-Patterson Air Force Base, Ohio 45433</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Air Force Missile Development Center</td>
<td>Major R. E. Bracken</td>
</tr>
<tr>
<td></td>
<td>Holloman Air Force Base, New Mexico 88330</td>
<td></td>
</tr>
<tr>
<td>Copies</td>
<td>Recipient</td>
<td>Designee</td>
</tr>
<tr>
<td>--------</td>
<td>-----------</td>
<td>----------</td>
</tr>
<tr>
<td>1</td>
<td>CPIA</td>
<td>Tom Reedy</td>
</tr>
<tr>
<td></td>
<td>Chemical Propulsion Information Agency</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Applied Physics Laboratory</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8621 Georgia Avenue</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Silver Spring, Maryland 20910</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Industry Contractors</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Aerojet-General Corporation</td>
<td>W. L. Rogers</td>
</tr>
<tr>
<td></td>
<td>P.O. Box 296</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Azusa, California 91703</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Aerojet-General Corporation</td>
<td>R. Stiff</td>
</tr>
<tr>
<td></td>
<td>P.O. Box 1947</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Technical Library, Bldg. 215, Dept. 2410</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sacramento, California 95809</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Space Division</td>
<td>S. Machlawski</td>
</tr>
<tr>
<td></td>
<td>Aerojet-General Corporation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9200 East Flair Drive</td>
<td></td>
</tr>
<tr>
<td></td>
<td>El Monte, California</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Aerospace Corporation</td>
<td>John G. Wilder</td>
</tr>
<tr>
<td></td>
<td>2400 East El Segundo Boulevard</td>
<td>MS-2293</td>
</tr>
<tr>
<td></td>
<td>P.O. Box 95085</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Los Angeles, California 90045</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Atlantic Research Company</td>
<td>Dr. Ray Friedman</td>
</tr>
<tr>
<td></td>
<td>Edsall Road and Shirley Highway</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alexandria, Virginia 22314</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Avco Systems Division</td>
<td>Howard B. Winkler</td>
</tr>
<tr>
<td></td>
<td>Wilmington, Massachusetts</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Beech Aircraft Corporation</td>
<td>J. H. Rodgers</td>
</tr>
<tr>
<td></td>
<td>Boulder Division</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Box 631</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Boulder, Colorado</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Bell Aerosystems Company</td>
<td>W. M. Smith</td>
</tr>
<tr>
<td></td>
<td>P.O. Box 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Buffalo, New York 14240</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Bellcomm</td>
<td>H. S. London</td>
</tr>
<tr>
<td></td>
<td>955 L'Enfant Plaza, S.W.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Washington, D.C.</td>
<td></td>
</tr>
<tr>
<td>Copies</td>
<td>Recipient</td>
<td>Designee</td>
</tr>
<tr>
<td>--------</td>
<td>-----------</td>
<td>----------</td>
</tr>
</tbody>
</table>
| 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 |
<table>
<thead>
<tr>
<th>Copies</th>
<th>Recipient</th>
<th>Designee</th>
</tr>
</thead>
</table>
| 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 |
<table>
<thead>
<tr>
<th>Copies</th>
<th>Recipient</th>
<th>Designee</th>
</tr>
</thead>
</table>
| 1      | Missile and Space Systems Division  
         McDonnell Douglas Astronautics Company  
         3000 Ocean Park Boulevard  
         Santa Monica, California 90406 | Mr. R. W. Hallet  
         Chief Engineer  
| 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 Marksman |
| 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 |
<table>
<thead>
<tr>
<th>Copies</th>
<th>Recipient</th>
<th>Designee</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Research Laboratories, United Aircraft Corporation, 400 Main Street, East Hartford, Connecticut 06108</td>
<td>Erle Martin</td>
</tr>
<tr>
<td>1</td>
<td>Hamilton Standard Division, United Aircraft Corporation, Windsor Locks, Connecticut 06096</td>
<td>R. Hatch</td>
</tr>
<tr>
<td>1</td>
<td>United Technology Center, 587 Methilda Avenue, P.O. Box 358, Sunnyvale, California 94088</td>
<td>Dr. David Altman</td>
</tr>
<tr>
<td>1</td>
<td>Republic Aviation Corporation, Farmingdale, Long Island, New York</td>
<td>Dr. William O'Donnell</td>
</tr>
<tr>
<td>1</td>
<td>Space General Corporation, 9200 East Flair Avenue, El Monte, California 91734</td>
<td>C. E. Roth</td>
</tr>
<tr>
<td>1</td>
<td>Thiokol Chemical Corporation, Huntsville Division, Huntsville, Alabama</td>
<td>John Goodloe</td>
</tr>
<tr>
<td>1</td>
<td>Calmec Manufacturing Corporation, 5825 District Boulevard, Los Angeles, California 90022</td>
<td>Library</td>
</tr>
<tr>
<td>1</td>
<td>Carleton Controls Corporation, East Aurora, New York 14052</td>
<td>Library</td>
</tr>
<tr>
<td>1</td>
<td>J. C. Carter Company, 671 W. Seventeenth Street, Costa Mesa, California 92626</td>
<td>Library</td>
</tr>
<tr>
<td>1</td>
<td>Holex Incorporated, 2751 San Juan Road, Hollister, California 95023</td>
<td>Library</td>
</tr>
<tr>
<td>1</td>
<td>Parker Aircraft, 5827 W. Century Boulevard, Los Angeles, California 90009</td>
<td>Library</td>
</tr>
<tr>
<td>1</td>
<td>Pelmec Division, Quantic Industries, Inc., 1011 Commercial Street, San Carlos, California</td>
<td>Library</td>
</tr>
<tr>
<td>Copies</td>
<td>Recipient</td>
<td>Designee</td>
</tr>
<tr>
<td>--------</td>
<td>-----------</td>
<td>----------</td>
</tr>
</tbody>
</table>
| 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 |