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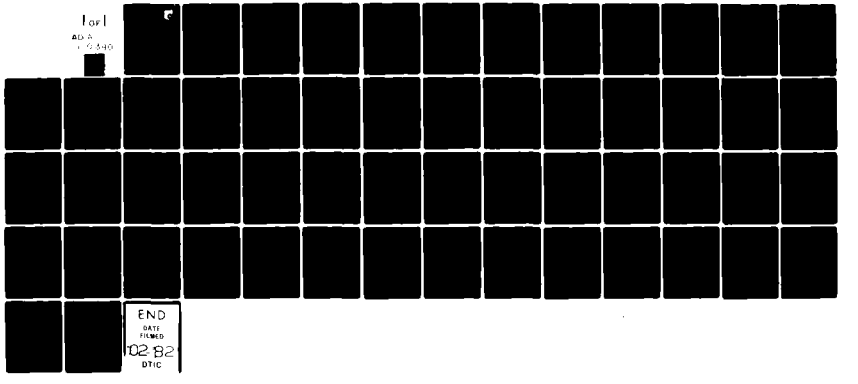

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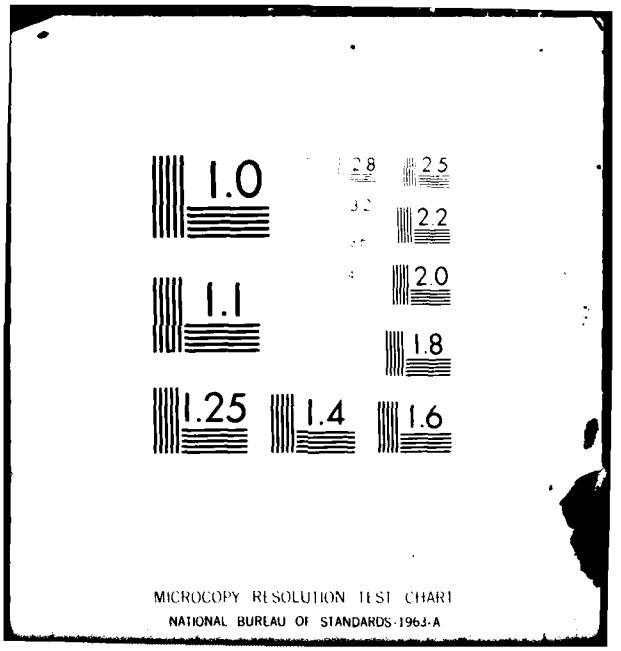
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SYNTHESES OF SYNTHETIC HYDROCARBONS VIA ALPHA OLEFINS

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This technical report has been reviewed and is approved for publication.

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FOR THE COMMANDER

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Nonmetallic Materials Division

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This work involved (1) review of literature data, (2) acquisition of experimental data, and (3) development of a correlation diagram for relating the structure of paraffinic hydrocarbons with physical properties such as viscosity, pour point, and thermal stability. Further work involved (4) evaluation of several catalysts, (5) comparison of high and low conversion runs in the BF_3-catalyzed oligomerization of 1-decene, and (6) screening synthetic procedures for preparing tetra-substituted methanes having three equal groups and a methyl group.

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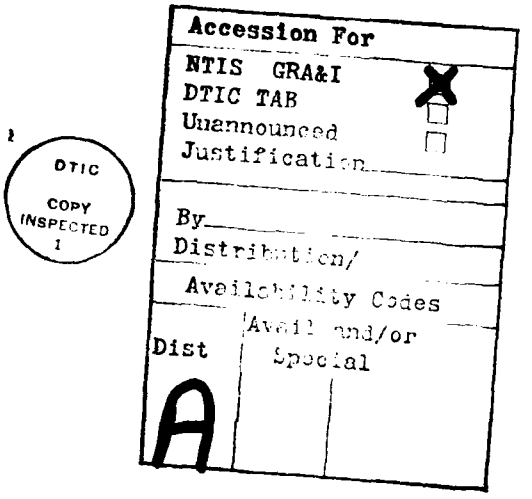
FOREWORD

This report was prepared by Gulf Research & Development Company, Chemicals and Minerals Division. The work was initiated under contract No. F33615-80-C-5086, "Synthesis of Synthetic Hydrocarbons Via Alpha Olefins." It was administered under the direction of the Air Force Wright Aeronautical Laboratories, Materials Laboratory, Air Force Systems Command, Wright-Patterson AFB, Ohio. Co-authors were Dr. B. L. Cupples, Mr. A. N. Kresge, Dr. A. Onopchenko, and Dr. J. P. Pellegrini, Jr.

This report covers research conducted from July 28, 1980 to June 30, 1981.



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I. INTRODUCTION

This report summarizes our work conducted from July 28, 1980 to June 30, 1981, on USAF Contract No. F33615-80-C-5086. This work involved (1) review of literature data, (2) acquisition of experimental data, and (3) development of a correlation diagram for relating the structure of paraffinic hydrocarbons with physical properties such as viscosity, pour point, and in some cases thermal stability. Further work included (4) evaluation of several cationic types and one free radical system for oligomerizing olefins, (5) comparison of high and low conversion runs in the BF_3 system, and (6) screening synthetic procedures for the preparation of tetrasubstituted methanes having three approximately equal alkyl branches, and a methyl branch.

II. DISCUSSION

A. Background

Before the synthesis of novel fluids with improved physical and thermal properties can be attempted for use in engine oils, hydraulic oils, lubricants, and functional fluids in general, some understanding of the structure-property relationship is required. The literature shows that various cationic, anionic, free radical, and thermal processes have been used to prepared oligomeric materials.[1] But unfortunately, most researchers were concerned with the evaluation of novel catalysts and promoters, and little attention was made to relate the performance of fluids with the structure of hydrocarbons. Very often only minimal information is given about the product such as viscosity index (VI), viscosity at some odd temperature on the total product, and even less information on the structure of products.

Historically, viscosity index (VI) has often been used for comparison of fluids. However, VI by itself is not sufficient data with which to discern the differences between fluids. For example, a 95 VI hydraulic fluid clearly does not have the same viscosity characteristics as a 95 VI heavy neutral fluid. Furthermore, because the VI is determined by only the 100 and 210°F viscosities, it offers no information about the low temperature properties. Because synthetic hydrocarbons must meet specific pour points and -40 and -60°F viscosity requirements, it is necessary that these properties not be estimated from VI index, but be measured experimentally to ensure accurate fluid properties. Brennan,[2] for example, states that measured low temperature viscosities of oligomers are actually less than predicted from their high temperature viscosities.

The use of ASTM D-341 viscosity-temperature charts does not provide a satisfactory solution to this problem either. About the only information that the chart can provide is that the viscosities are "different." Even if significant differences between fluids are observed, nothing in the chart suggests reasons for the difference in fluid behavior.

Correlations have been developed in this laboratory which avoid many of the limitations and which have been found to be considerably more useful in predicting the behavior of hydrogenated polyolefins over a wide temperature range. Furthermore, such correlations proved to be useful for relating and correlating a vast amount of literature data on viscosity, catalysts, promoters, etc.

B. Correlation of Viscosity Data of Oligomers

Our interest in synthetic lubricants has been primarily in the area of cationic oligomerization of olefins, particularly those processes using boron trifluoride complexes as catalysts. These catalysts afford oligomers with a degree of oligomerization of around 2 to 5, and the products, after hydrogenation, are useful as wide temperature fluids. Therefore, most of our correlations have been derived from the BF_3 catalyzed oligomerization reactions, but are believed to have general applicability to all catalytic systems.

It was discovered in our laboratories that when hydrogenated oligomers are distilled, and when the viscosity of each fraction at some convenient temperature is plotted on a log-log chart against the molecular weight of the fraction, carbon number distribution, the degree of oligomerization, or some reference viscosity, a family of nearly straight-line relationships is generated which are characteristic of each monomer olefin. In practice it has been most convenient to measure the viscosities at -40°, 0°, 100°, and 210°F (-40°, -17.8°, 37.8°, and 98.9°C), although measurements can be made at any temperature of choice. When the viscosities of fluids at -40°, 0°, and 100°F were plotted against the ln of 210°F viscosity, the reference viscosity, a series of fan-shaped families of lines were developed according to the carbon number of the olefin and the type of the olefin. Such a relationship is graphically demonstrated for the hydrogenated oligomers from alpha olefins (Figures 1 and 2), internal olefins (Figure 3), vinylidene olefins (Figure 4), and highly branched olefins (Figure 5).

Looking at Figure 1, for example, a hydrogenated 1-decene-derived fluid whose 210°F viscosity is 4 cSt, has -40°, 0°, and 100°F viscosities of 2600, 360, and 19.8 cSt, respectively, indicating the manner in which this fluid moves along the 1-decene viscosity-temperature curve. A 4 cSt propylene-derived fluid, on the other hand, has -40°, 0°, and 100°F viscosities of 85,000, 2310, and 26.0 cSt, respectively, showing how at equal 210°F viscosity the low temperature viscosity changes as the carbon number of the monomer feed decreased from C_{10} to C_3. Note that for 1-decene fluid with a 210°F viscosity of 4.53 cSt (ln 4.53 = 1.51), the -40°F viscosity of 3700 cSt is the same as the 0°F viscosity for the corresponding propylene fluid, and that the -40°F viscosity for the propylene fluid is off the chart at about 160,000 cSt. The viscosities for 1-dodecene oligomers and oligomers from still higher alpha-olefins can be determined only at higher temperatures as their high pour points will preclude the determination of their low temperature viscosities. In the course of present work, the viscosities for the hydrogenated alpha olefin-derived oligomers were determined for propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, and 1-dodecene. The viscosities for the hydrogenated ethylene-derived oligomers were not measured as these would represent a special case (unsubstituted olefin), and the products would be highly dependent on the catalyst used for the oligomerization reaction. If polyethylene produced is considerably linear, the products after hydrogenation will behave like the higher molecular weight n-alkanes, which are solid at room temperature.

Several generalizations can be made based on data represented in Figures 1 and 2:

1. Very nearly straight lines result from plotting the logarithm of the viscosity of a hydrogenated oligomer system at some temperature against the logarithm of the viscosity at a reference temperature such as 98.9°C (210°F).

2. Not only do the individual carbon number oligomers from an alpha olefin system fall on the corresponding curves, but mixtures of the oligomers also fall on the same curve.

3. At any temperature, a family of fan-shaped curves exist with the alpha olefin feed carbon number as the parameter.

4. As the carbon number of the feed decreases, the low temperature viscosities increase for fluids having the same 98.9°C (210°F) viscosity.

Because low viscosities are desirable at the lower temperatures, the hydrogenated 1-decene-derived oligomer system is the best of those reported; and the viscosity-temperature relationship worsens as the alpha olefin carbon number decreases.

The viscosity data for the hydrogenated internal olefin oligomers are graphically shown in Figure 3 using 2-butene, 5-decene, and 7-tetradecene as the starting monomers. These data show that 2-butene-derived oligomers behave like the expected "ethylene" oligomers, the 5-decene oligomers are comparable to the 1-pentene products, and the 7-tetradecene oligomers are similar to the 1-heptene products.

The data for the hydrogenated vinylidene olefin oligomers are graphically shown in Figure 4. In this work, 2-methyl-1-pentene, 2-butyl-1-octene, and 2-hexyl-1-decene were used as representative olefins. The behavior of vinylidene olefins was similar to those of the internal olefins. This, of course, is not surprising as both olefins have two alkyl branches per molecule, although the substitution in the first case is of 1,1-type and in the second case of 1,2-type. The hydrogenated isobutylene oligomers also behaved like the expected "ethylene" products, 2-methyl-1-pentene oligomers were similar to propylene products, 2-butyl-1-octene oligomers were comparable to 1-hexene-derived products, and 2-hexyl-1-decene oligomers behaved like the 1-octene products.

Comparison of data in Figures 3 and 4 with that of Figures 1 and 2 simply indicates that as more branching is introduced into the molecule, the viscosity of oligomers worsens.

In the case of trisubstituted and tetrasubstituted olefins, no work has been carried out on model compounds as the properties of the oligomers were expected to be quite inferior. Furthermore, many of the desired model olefins were not commercially available. Two olefinic streams nevertheless which have considerable branching were oligomerized. These include Dimersol's octenes (butene dimers) and Exxon's nonenes (propylene trimers). It turns out that the resulting oligomers from both feedstocks after hydrogenation are similar and, within the experimental error, their viscosities fall on the same polypropylene line (Figure 5).

C. Correlation of Viscosity Data of Model Paraffins at 32°F (0°C)

To show that correlations developed for the hydrogenated olefin-based oligomers are valid, a correlation of the 32°F viscosity for several pure paraffins was made against the 210°F viscosity (Figure 6). These data show that n-paraffins have the best viscosities of all alkanes, but unfortunately the viscosities for n-alkanes above C_{13} could not be measured because of their high melting points. The projected straight line nevertheless can be used as the "hypothetical" line to indicate the theoretical viscosities for the higher molecular weight paraffins, assuming that such measurements would have been possible. Introduction of a short chain (methyl) in the 2- position of n-alkane practically had no effect on the viscosity, but lowered the melting point so that viscosity of a C_{16} alkane such as 2-methylpentadecane could be measured. Moving the methyl group toward the center of an alkane backbown showed some deviation of the viscosity from the n-paraffin curve. In this case the viscosity for a C_{21} alkane (10-methyleicosane, m.p. -3.8°C) could be measured.

The top line (Figure 6) is for the correlation of trisubstituted methanes having three approximately equal alkyl branches. In the latter case, the viscosity of a C_{32} hydrocarbon, 11-decyldoeicosane, m.p. 0-1°C, could be measured. These data suggest that if compounds of this type are to be used as low temperature lubricants, the isomeric mixtures of alkanes should be used to depress the pour point of the product. The open triangles on the top line are

for the hydrogenated 1-decene oligomers which are included for comparison purposes. Interestingly, the point for the decene derived dimer is right on the trisubstituted methane line, while the corresponding trimer and tetramer points are slightly off, perhaps indicative of more extensive branching in the higher oligomers.

D. Correlation of Viscosity Data of Paraffins at 100°F (37.8°C)

Viscosities at 37.8 and 98.9°C (100 and 210°F) of normal paraffins having carbon numbers from 14 to 20 were obtained and are reported in Table 4. Also included are viscosities for methyl-branched paraffins of carbon number 14 to 28 where the methyl group is located near the midpoint of the skeletal chain. The 37.8°C (100°F) viscosity could not be determined for materials of higher molecular weight in either series due to the materials being solids.

A comparison of the viscosities of the n-paraffins and the methyl-branched paraffins described in Table 4 with the viscosity-temperature relationship of the oligomers of 1-decene, also shown in Table 4, is made in Figure 7. This is a log-log plot of the viscosities at the two temperatures which, as we have observed previously for the various olefin-oligomer systems, yields a straight line for the fluids (oligomers) belonging to a particular system. In Figure 7 three straight lines are shown representing the viscosities of the three paraffinic hydrocarbon systems for which data are contained in Table IV. Due to freezing of the higher molecular weight n-paraffins, the line for those materials had to be extrapolated beyond about 5.5 mm^2/s at 37.8°C (100°F). From Figure 7 it is apparent that the viscosity-temperature relationships of the normal and methyl-branched paraffins are significantly better than that of the 1-decene oligomers. Furthermore, the viscosity-temperature behavior of the n-paraffins is slightly better than that of the methyl-branched paraffins.

E. Correlation of the Structure of Paraffins with Melting Points (or Pour Points)

When considering the low temperature performance of fluids including both viscosity and pour point, it should be noted that the structural requirements for good low temperature viscosity and low pour point are conflicting. The low degree of branching of the n-α-olefin oligomers which imparts their superior viscosity properties is precisely what will cause the n-α-olefin oligomers to be the first to fail a given pour point. Hence, a certain amount of branching is necessary in order to meet a given pour point, but any branching is detrimental to the oligomer low temperature viscosity. At temperatures above the pour point the n-α-olefin oligomers will give the best viscosity performance when monomers are compared on the basis of equal carbon number.

Table 5 lists the melting (or pour) points for various normal and branched paraffins as well as for several hydrogenated oligomers of n-α-olefins. These data are plotted against carbon number of the paraffin in Figure 8. It is evident that for those materials of interest as functional fluids (C_{20} and above) the melting points are too high for the fluids to be useful over a wide temperature range.

On the other hand, polydecene synthetic hydrocarbons (hydrogenated) are known to have excellent low temperature characteristics. In Figure 8 the pour points of a few dimers and trimers of three alpha olefins are shown. Although the polydecenes possess pour points below -79°C (<-110°F), the pour point of the various olefin oligomers tends to increase with increasing chain length of the monomer unit. For any particular carbon number of the hydrocarbon, however, the pour points of the polyalphaolefins are substantially lower than those of the more linear paraffins.

The effect of branching on melting point is also demonstrated by the other methyl- and butyl-branched paraffins reported in Table V and shown in Figure 8. The introduction of a single methyl branch into the linear chain lowers the melting point significantly, but the effect is most pronounced when the branch is near the center of the chain. Lengthening the branch to C_4 or

longer reduces the melting point still further. The pour points of the dimers and trimers of the polyalphaolefins reflect their more highly branched structures.

Thus, we are faced with the situation where a high degree of branching in the molecule is desirable to provide low melting (or pour) points, but as observed earlier, the more nearly linear paraffinic molecules exhibit the best viscosity-temperature behavior. From a rheological viewpoint then, the preferred structure would appear to be a molecule having linear characteristics but with just sufficient branching to provide the needed pour point.

F. Thermal Stability

For some applications, particularly in the areas where heat generation can be a problem, besides viscosity and pour points, thermal stability becomes an area of concern.

The thermal stabilities of several fluids were determined through the use of a test procedure similar to that described in MIL-H-27601A. The fluid degradation, as measured by the loss in 37.8°C (100°F) viscosity after exposure to 371°C (700°F) for 6 hours, is reported in Table 6. Three fluids are included for which data were available from test measurements previously made by the Materials Laboratory of AFWAL. In all cases the results obtained by the procedure used in this study were slightly greater than those reported by AFWAL.

Of the fluids tested, the best stability (4%) was exhibited by n-eicosane and the second best (11%) by two methyl-branched hydrocarbons, one a C_{20} and the other a C_{28}. The hydrogenated alpha olefin oligomers showed much greater viscosity losses, which seemed to increase with an increase in the degree of oligomerization.

Oligomer (1-Hexene)	Viscosity Loss In Thermal Stability Test, %
Dimer	30-45
Trimer	59-70
Tetramer	64
Pentamer	77

By comparison, a highly refined mineral oil hydraulic fluid base stock, MLO 78-59, showed a viscosity loss of 31%. These results suggest that thermal stability is favored by less branched, more nearly linear structures, but this point needs to be further resolved. The actual viscosity data before and after thermal stability tests for various feeds are shown in Table VI and graphically represented in Figure 9.

To determine the effect of structure of alkanes on the thermal stability, several model hydrocarbons were tested (Table 7). The alkanes chosen included C_{19} and C_{20} paraffins having 0, 1, 2, and 4 tertiary hydrogens, a C_{28} paraffin with one tertiary hydrogen, and a C_{30} paraffin with 6 tertiary hydrogens. The data clearly shows that as the number of tertiary hydrogens increases, the viscosity loss increases. This result, of course, is consistent with the data of Benson, who reported that the tertiary-carbon-hydrogen bonds have the lowest bond dissociation energies, and are therefore considered the weak points with regard to thermal stability.[3]

Bond	Bond Dissociation Energy (BDE), kcal/mol
CH_3CH_2–H	98
$(CH_3)_2CH$–H	94.5
$(CH_3)_3C$–H	91

The thermal stability, however, is not linear. For example, a C_{19} alkane with four tertiary hydrogens was expected to have a viscosity loss of about 44.4% (4 x 11.1), compared to actual value of 22%. Similarly, a C_{30} alkane with six tertiary hydrogens showed a viscosity loss of 41.8%, compared to expected value of 67% (11.1 x 6).

It has been mentioned that the thermal stability is favored by nearly linear structures and that branching favors instability. Generally, it has been observed that as the number of branches in a hydrocarbon increases, so does the number of tertiary hydrogens, which are believed to be responsible for thermal instability. We are of the opinion, that branching as such, does not necessarily lead to thermal instability. This point, however, still needs to be verified, by investigating the stability of tetrasubstituted methanes, which we believe will have thermal stabilities comparable to the n-paraffins.

The thermal stability data for model alkanes are plotted as a function of the carbon number in Figure 10.

G. Evaluation of Catalyst Systems

All of the data on the hydrogenated olefin oligomer systems reported thus far have been obtained on products made by the boron trifluoride catalyzed olefin oligomerization. To determine what effect catalyst type has on the oligomer properties, fluids were prepared from 1-decene using several different catalysts. The catalysts selected represent free radical and anionic types in addition to further examples of cationic catalysts.

Table 8 summarizes the pour points and viscosities of decene oligomers, after hydrogenation, prepared using various catalysts. Figures 11 and 12 compare the viscosities of these materials with those of the 1-decene oligomer system obtained with BF_3 under "standard" conditions (1% 1-butanol, 50°C, 50 psig BF_3, 90% conversion).

The oligomers made with BF_3 and reported in Table 8 differ from polydecene prepared under "standard" conditions in that the decene conversion during the reaction was kept low (30%). The oligomer viscosities from this run were identical to those of the decene oligomer system at more typical conversion levels (>80%). The pour points of the dimer and the trimer were also comparable to the high conversion runs.

Other catalysts found to yield products very similar to those obtained with BF_3 under standard conditions were tungsten hexafluoride (WF_6/H_2O) and a sodium hydride moderated titanium tetrachloride-aluminum chloride mixture ($TiCl_4$-NaH-$AlCl_3$).

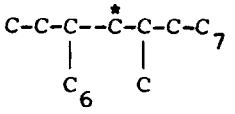
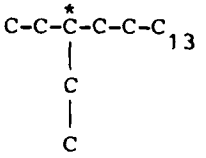
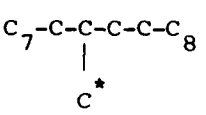
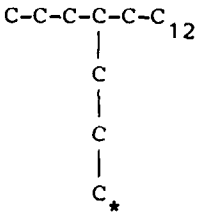
Use of di-t-butylperoxide as a catalyst resulted in oligomers having a better viscosity-temperature response but much higher pour points. The dimer from this product was partially solid at room temperature.

Aluminum chloride ($AlCl_3$) catalyst yielded a broad range of oligomers of decene. The dimer-trimer fraction, after hydrogenation, exhibited a somewhat poorer viscosity-temperature response whereas the more viscous fraction showed a better relationship than usually found. This behavior is believed to be due to the presence of higher molecular weight oligomers present in the heavy fraction which are acting as a VI improver.

Another catalyst tried was silicotungstic acid which is a known isomerization catalyst, but which also has some oligomerization activity. Both the dimer and trimer of this product, after hydrogenation, had viscosity-temperature responses which were poorer than observed for decene oligomers under standard conditions.

The hydrogenated dimer fraction from a tert-butyl peroxide-initiated oligomerization of 1-decene possessed very good thermal stability (12% viscosity loss). Analysis by GLC (Figure 13) showed only three major components (~76% of total), which corresponded to the simplest composition encountered to date. This fraction was, therefore, further examined by ^{13}C and ^{1}H NMR spectroscopy. Based on the intensities of signals at 41.67, 39.36, 19.95, and

15.72 ppm peaks in the ^{13}C NMR spectrum, the following structural features are believed to be present in the C_{20} isomers:

		*	Composition, %
(1)		41.67 ppm	14%
(2)		39.34	57%
(3)		19.95	17%
(4)		15.72	12%

This analysis is based in essence on the method used to determine the nature of 1-butene polymers.[4] It should be kept in mind, however, that the methyl group in isomer 3 is not fixed, and can therefore move up and down the chain, without influencing the shift of the methyl group. The ^{1}H NMR spectrum showed on an average 3.7 methyl groups/molecule. This indicates that C_{13} alkyl group in isomer 2, or a C_{12} alkyl group in isomer 4, could have additional branching, without altering the shift of peaks on the left end of the molecule.

In any event, since the dimer in question is partially solid at room temperature, it obviously lacks sufficient branching to impart the desired fluidity.

The data in Figure 16 show the viscosity correlations at several temperatures for 1-decene, 5-decene, and a mixture of 1- and 5-decenes oligomers using either the conventional BF_3 or silicotungstic acid system. It is evident that correlations developed in the course of our work can be used not only to evaluate various catalytic systems, but are useful for correlations of olefinic mixtures as well.

H. Synthesis of Tetraalkylmethanes

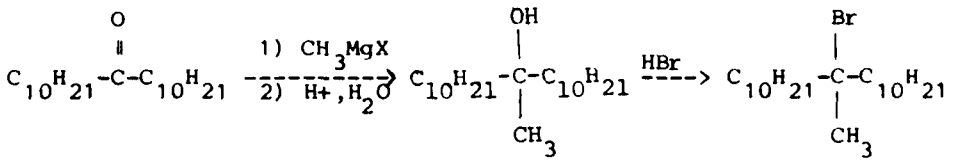
This section concerns attempted synthesis of model tetraalkylmethanes, particularly the 11-methyl-11-octatheneicosane. Compounds of this type are needed to determine the effect of structures on viscosity and thermal stability. Basically, there are two approaches to the synthesis of tetrasubstituted methanes:

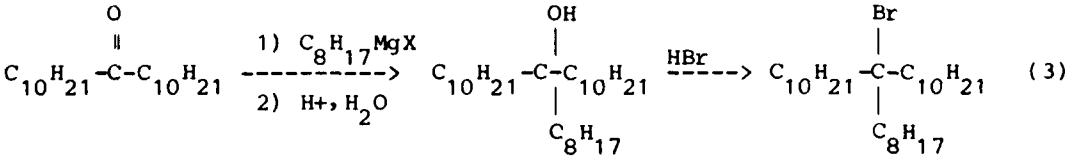
$$R_3CX \xrightarrow{RM} R_4C + MX \qquad (1)$$

$$R_3CM \xrightarrow{RX} R_4C + MX \qquad (2)$$

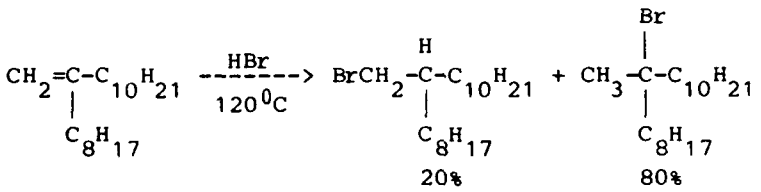
In the first approach, the tertiary alkyl halide is treated with some organometallic reagent, while in the second approach, the tertiary carbanion that is a part of organometallic reagent is treated with an alkyl halide. The literature shows that the second procedure should be preferred,[5] although in practice it is difficult to generate the tertiary carbanions. Several references, however, report that tert-alkyl halides have been reacted with alkyl sodium, magnesium, or zinc compounds and with cuprates (first procedure), although the yields have generally been below 50%.[6] The same authors[7] report on the use of dimethyl titanium compounds to afford high yields of tetrasubstituted methanes starting with tert-alkyl halides.

In our work, the tertiary-alkyl halides needed for the above reactions were synthesized either by the addition of a Grignard reagent to a high molecular weight ketone, followed by treatment with hydrogen bromide, or by hydrogen bromide addition to a C_{20} vinylidene olefin:



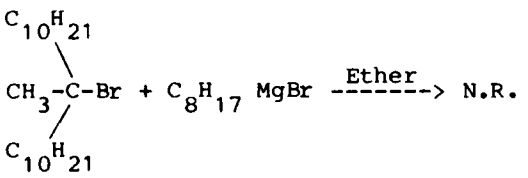


(3)

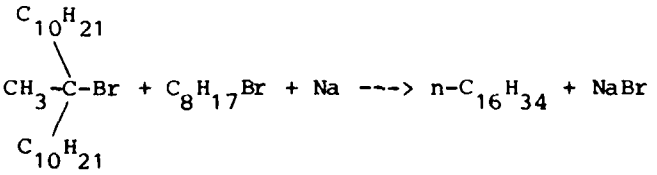


(4)

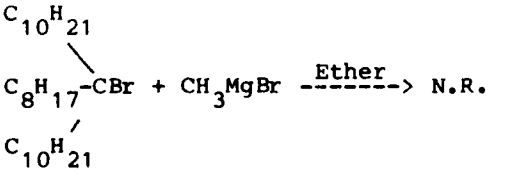
The reactions tried included the following:



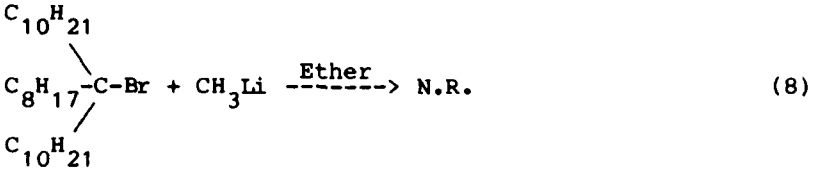
(5)



(6)



(7)



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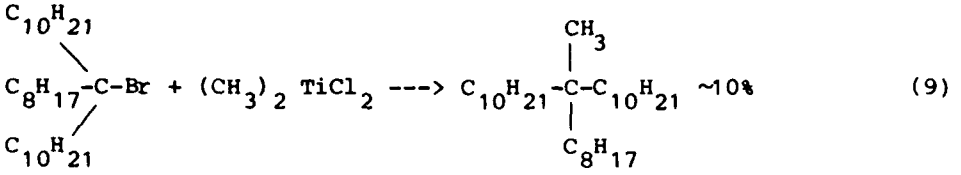
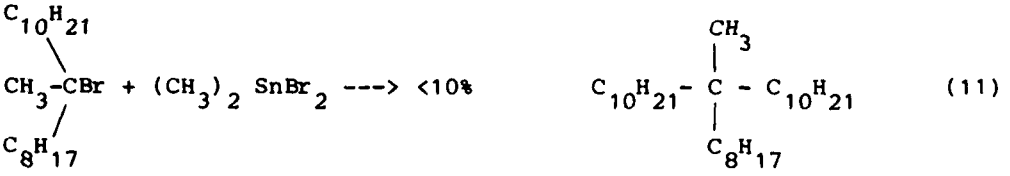


(9)

(10)



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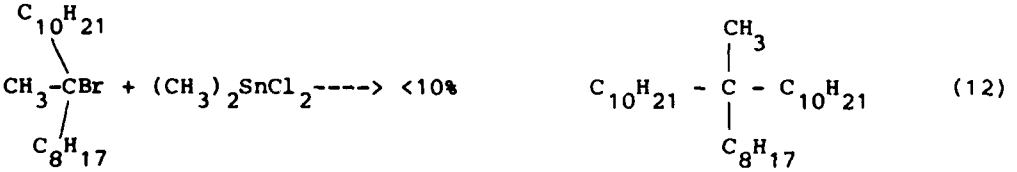

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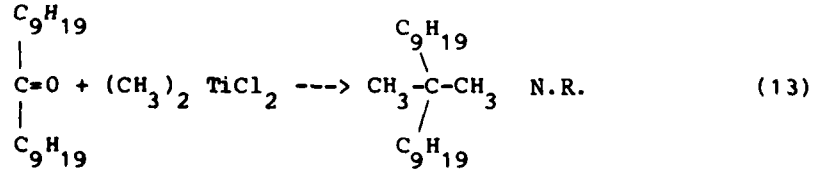
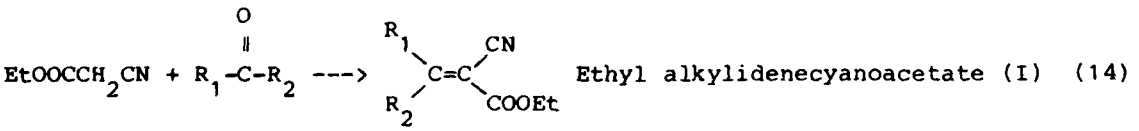
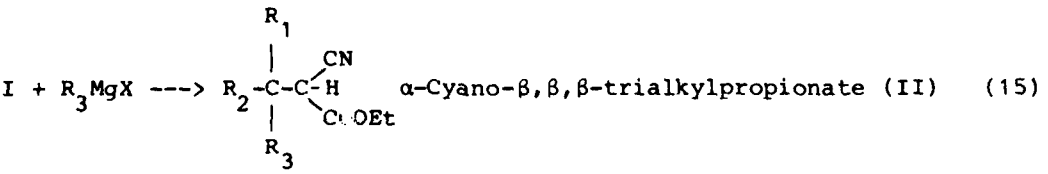


(13)

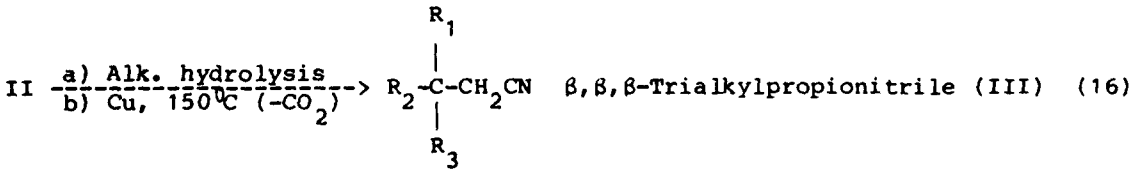
Since we could not get reasonable yields of the sought-after tetraalkyl substituted methane by the most direct route, an indirect procedure was started. This procedure represents a general method for the synthesis of tetraalkylmethanes in high yields.[8] While this route may not necessarily be economical, it will afford the desired compound for evaluation purposes. The procedure involves (1) condensation of ethyl cyanoacetate with ketone to afford ethyl alkylidenecyanoacetate, followed by (2) the 1,4-addition of a Grignard reagent to give α-cyano-β,β,β-trialkylpropionate, followed by (3) alkaline hydrolysis and decarboxylation to give β,β,β-trialkylpropionitrile, followed by (4) the addition of another Grignard reagent to afford a ketone, and finally the reduction of the ketone to the alcohol, dehydration, and hydrogenation of the olefin produced. The last three steps could probably be carried out as one, greatly simplifying the synthetic procedure. The first step of the synthesis involving condensation of ethyl cyanoacetate with 2-decanone was carried out in 90+% yield. Unfortunately, it was later discovered that commercial 2-decanone was only 50% pure by *GLC* (50% was 2-octanone). Hence, the product was a mixture of isomers (I), where R, = nC_8H_{17} and nC_6H_{13}.



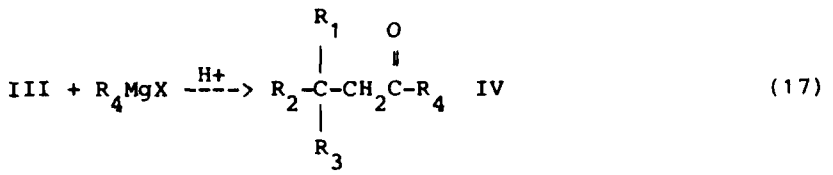
Ethyl alkylidenecyanoacetate (I) (14)



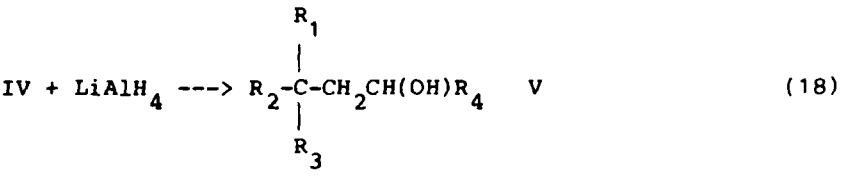
α-Cyano-β,β,β-trialkylpropionate (II) (15)



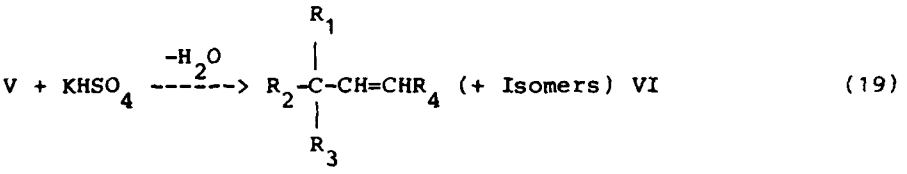
β,β,β-Trialkylpropionitrile (III) (16)



(17)



(18)



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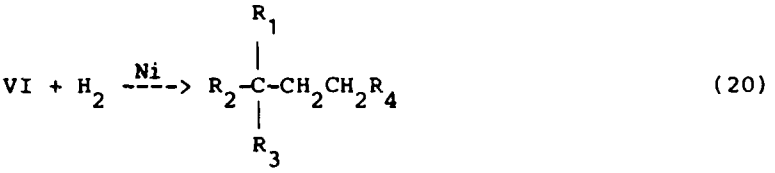

(20)

III. EXPERIMENTAL SECTION

A. Apparatus and Materials

Oligomerization of olefins was carried out in a 1-ℓ, 316 stainless steel, magnetically-stirred autoclave (The Autoclave Engineers, Inc., Erie, PA), typically at 25-50°C and 50 psig of pressure. The autoclave was equipped with a cooling coil and heaters, and was connected to a boron trifluoride cylinder, temperature and pressure controllers, and recording instruments. Hydrogenations were carried out in a 700 ml autoclave using Ni-0104P catalyst (200°C, 700-800 psig H_2). The reaction products were analyzed by GLC on a Hewlett-Packard 5710A Gas Chromatograph using a 1/8 in. x 2.5 ft, 5% Dexsil 300 on Chrom column, programmed from 80 to 390°C at 32°/min (T.C. detector temperature, 350°C; injection port, 400°C; attenuation, 1) to determine the distribution of oligomers. Occasionally, polyphenyl ether capillary column was used to determine the composition of isomers in a particular oligomer fraction. All olefins were obtained from commercial sources and were used as received. The purity by glc in most cases was 99% or better.

B. Oligomerization with BF_3

In a typical experiment, 450 g of 1-decene and 4.5 g of n-butanol were placed into the autoclave at 25°C and pressurized with BF_3 to 50 psig. After the temperature had stabilized at 50°C, the reaction was continued for 60 min, maintaining a pressure of 50 psig by periodic repressuring with BF_3. The autoclave was cooled to ~20°C, depressured, and its contents were added to 1200 ml of aqueous 25% sodium hydroxide solution. The organic layer that formed was washed three times with 600 ml portions of water, dried ($MgSO_4$, anh.), and filtered. After hydrogenation over 15 g of nickel catalyst, under above reaction conditions, the product was filtered and distilled. Distillation was carried out under reduced pressure (0.5 mm of Hg) using a glass-packed, 5-theoretical plate, Oldershaw column to give the respective dimer, trimer, and higher boiling oligomers, whose viscosities were then determined. These data, along with the data for other alpha olefins are shown in Tables 1 and 2.

A typical distribution of oligomers from a conventional BF_3 catalyzed oligomerization of 1-decene, after hydrogenation, is shown in Figure 17.

C. Thermal Stability Measurements

Thermal stability measurements were made on fluid samples using a test procedure similar to that described in MIL-H-27601A with the following modifications:

The thermal stability test vessel was altered in size from 17.8 cm (7 in.) length and 19.0 mm (0.75 in.) OD to 22.9 cm (9 in.) and 12.7 mm (0.5 in.), respectively, and the fluid sample size was reduced from 20 ml to 8.5 ml. Due to the reduction in the size of the test vessel and because of the screening nature of this test, no metal catalysts were included in the test vessel. The vessel containing the fluid to be tested was exposed to 371°C (700°F) for 6 hr in a forced-air circulation, electrically heated, thermostatically controlled oven (Blue M Electric Company). Prior to testing fluid samples, the repeatability of the test procedure was demonstrated with a 4 mm^2/s fluid comprised of a mixture of trimer and tetramer of 1-decene. Although some fluid test samples were chromatographed, no quantitative results are available due to a baseline drift which prevented accurate area measurements on the chromatogram.

D. Evaluation of Catalysts

The evaluation of catalysts was carried out under reported reaction conditions.

Catalyst	Conditions
$AlCl_3$	2%, 50°C[10]
$AlCl_3$-NaH-$TiCl_4$	Follow Ex. 6 of Table IV, 2% of equimolar amount of 3 reactants, 120°C[11]
di-t-butyl peroxide	Follow Ex. 1 of Patent. Add 15% t-butylperoxide incrementally, 140°C[12]
SiO_2•12 WO_3	Stir at 140°C, 2% Catalyst, 20 hr, under N_2

E. Preparation of Vinylidene Olefins

A typical procedure for the preparation of vinylidene olefins is described for the C_{24} product. A mixture of 1-dodecene (5411 g) and triisobutylaluminum (275 g) in a 12-ℓ flask was heated, while stirring, at 170-180°C for 4 hr. The reaction mixture was cooled to 50°C, and the hydrocarbon mixture was slowly added to dilute caustic to hydrolyze the product. The product was then distilled using a five-tray Oldershaw column to give a 99.5% purity C_{24} vinylidene olefin (1214 g). On hydrogenation under standard reaction conditions (Ni 0104p catalyst, 200°C, 700-1000 psig H_2), a quantitative yield of 11-methyltricosane was obtained, m.p. 21 °C.

In a similar manner, a C_{28} vinylidene olefin was prepared from 1-tetradecene and triisobutylaluminum. On hydrogenation, 13-methylheptacosane was obtained, m.p. 29°C, in essentially 100% yield.

Numerous other vinylidene olefins were available in our laboratory from previous studies. These were simply hydrogenated to provide a series of methyl-branched paraffins. The viscosities of these paraffins are listed in Tables 3 and 4, and their pour (melting) points in Table 5.

F. Attempted Syntheses of Model Hydrocarbons

1. Preparation of tertiary alcohols via Grignard reaction. In a typical procedure, magnesium turnings (2.4 g) were addded to diethyl ether

(200 mls), maintained at 15°C. Methyl iodide (14.2 g) in diethyl ether (20 ml) was then gradually added over 1/2 hr, maintaining a temperature during addition below 20°C. When addition of halide was completed, the reaction mixture was stirred for 1/2 hr. A total of 31 g of 11-heneicosanone dissolved in benzene (150 ml; ketone was insoluble in ether) was gradually added to the above reaction mixture and allowed to react for 2 hr at 35°C. The reaction mixture was poured over ice and hydrolyzed with dilute hydrochloric acid. On workup, 30 g of product were obtained. Analysis showed the product to contain 84.5% of di-n-decylmethylcarbinol, and 15.5% of the starting ketone.

2. Bromination of tertiary alcohols. The alcohol prepared above was heated to 100-120°C, and anhydrous hydrogen bromide was passed through the alcohol until no further gas uptake was evident. The resulting product was taken up in hot benzene, dried, and evaporated on a rotary evaporator to give 28.7 g of 11-bromo-11-methylheneicosane.

3. Bromination of C_{20} vinylidene olefin. A total of 200 g of C_{20} vinylidene olefin (2-n-octyl-dodecene-1) in a dark container was treated by passing anhydrous hydrogen bromide until 75 g of gas were consumed, maintaining a temperature during addition below 60°C. The product was taken up in n-heptane, washed with water, dried, and treated with charcoal (5 g) to give 242 g of the corresponding halides. Analysis by glc and nmr showed that two isomers were formed, 2-bromo-2-methylnonadecane and 9-bromomethylnonadecane, in a ratio of 80 and 20%, respectively.

4. Preparation of Tetrasubstituted methanes. In a typical procedure,[6] 19 g of titanium tetrachloride in 10 ml of n-heptane were slowly added to diethyl ether (50 mls), resulting in a yellow precipitate. While stirring, and maintaining a temperature below 70°C, 118 ml of methyllithium (1.7M in diethyl ether) was added over a 1 hr period. After reacting for 1 hr at 60°C, the 80:20 mixture of alkylbromides prepared above (36 g) was added over 20 min, and the resulting mixture allowed to come to room temperature over 1.5 hr. After hydrolysis and neutralization with dilute sodium hydroxide, 30 g of organic product was obtained. Analysis by ^{13}C nmr showed that at best only 10% of the tetrasubstituted methane was formed, too little to be of

synthetic importance. Other reagents screened for the quaternization of tertiaryalkyl bromide, under similar conditions, included n-octylmagnesium bromide, n-octyl bromide and sodium metal, methyllithium in ether, tetramethyl titanium, dimethyltitanium dichloride, dimethyltindibromide, and dimethyltindichloride, but with little succcess.

5. Condensation of 2-Decanone with Ethyl Cyanoacetate. A mixture consisting of 2-decanone (141 g), ethyl cyanoacetate (102 g), ammonium acetate (14 g), and acetic acid (43 g) in benzene (180 ml) were heated under reflux (98°C) until 18 g of water had been collected in a Dean-Stark trap. On workup under reported conditions,[13] 213 g of product were obtained. Unfortunately, later it was found that 2-decanone was contaminated with 50% of another ketone, probably 2-octanone. Hence, the product formed was a mixture of two different compounds.

REFERENCES

1. The literature dealing with the general subject of olefin oligomerization or polymerization runs into hundreds of references. For this reason, we limit references to those directly related to our work rather than providing a comprehensive review.

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6. M. T. Reetz, J. Westerman, and R. Steinbach, Angew. Chem. Int. Ed., 19, 900, (1980).

7. M. T. Reetz, J. Westerman, and R. Steinbach, 1 Bid., 19, 901, (1980).

8. N. Rabjohnn, L. V. Phillips, and R. J. DeFoo, J. Org. Chem., 24, 1964 (1959).

9. Properties of Hydrocarbons of High Molecular Weight, API Research Project 42, 1940-1966, Pennsylvania State University

10. C. W. Montgomery, et. al., U.S. Patent 2,559,984.

11. H. Isa, et. al., U.S. Patent 3,947,507.

12. L. Hamilton, et. al., U.S. Patent 3,149,178.

13. A. C. Cope, et. al., J. Am. Chem. Soc., 63, 3452 (1941).

VISCOSITY DATA FOR HYDROGENATED α-OLEFIN OLIGOMERS (Even carbon numbers)

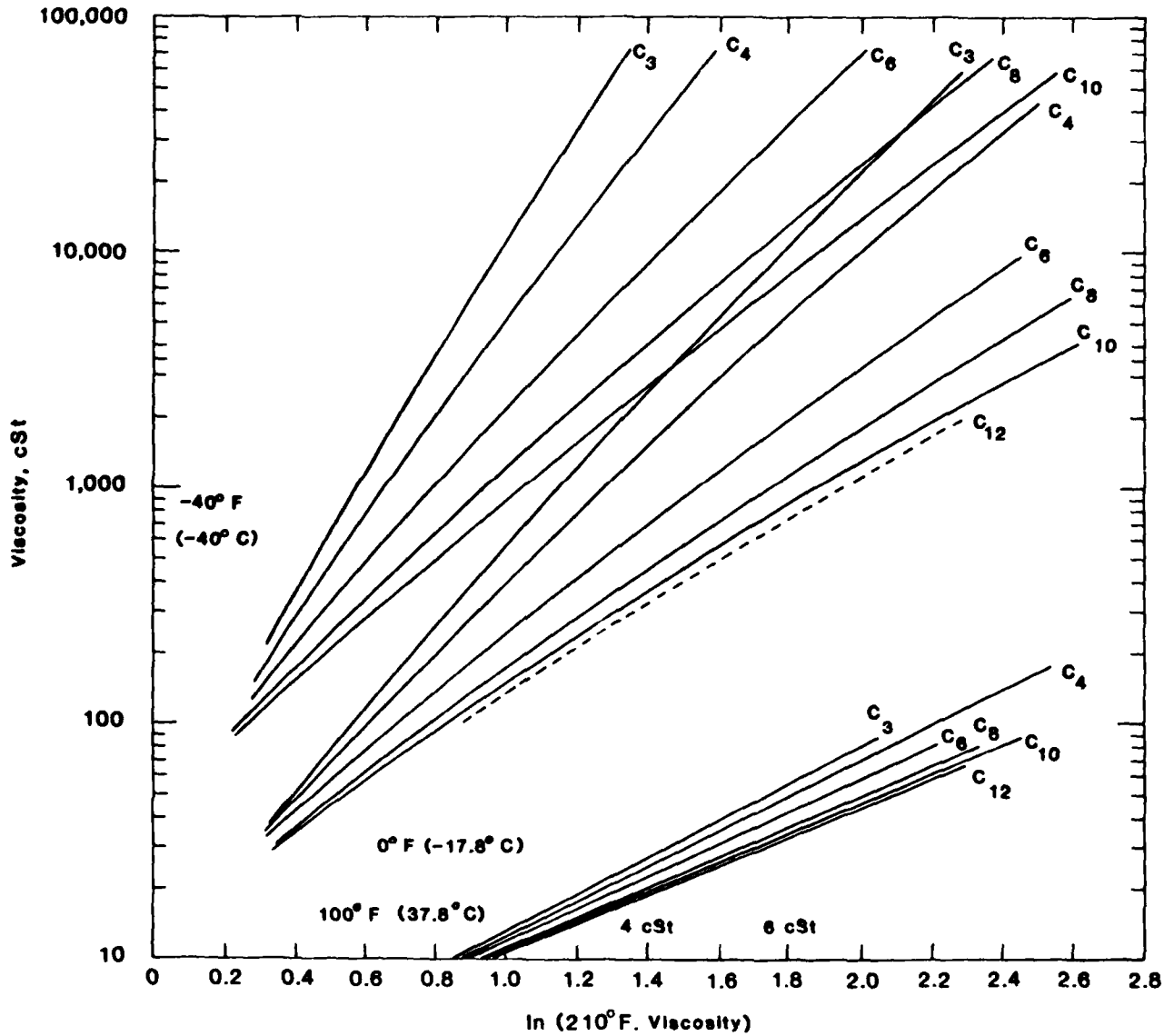


Figure 1

VISCOSITY DATA FOR HYDROGENATED α-OLEFIN OLIGOMERS (Odd carbon numbers)

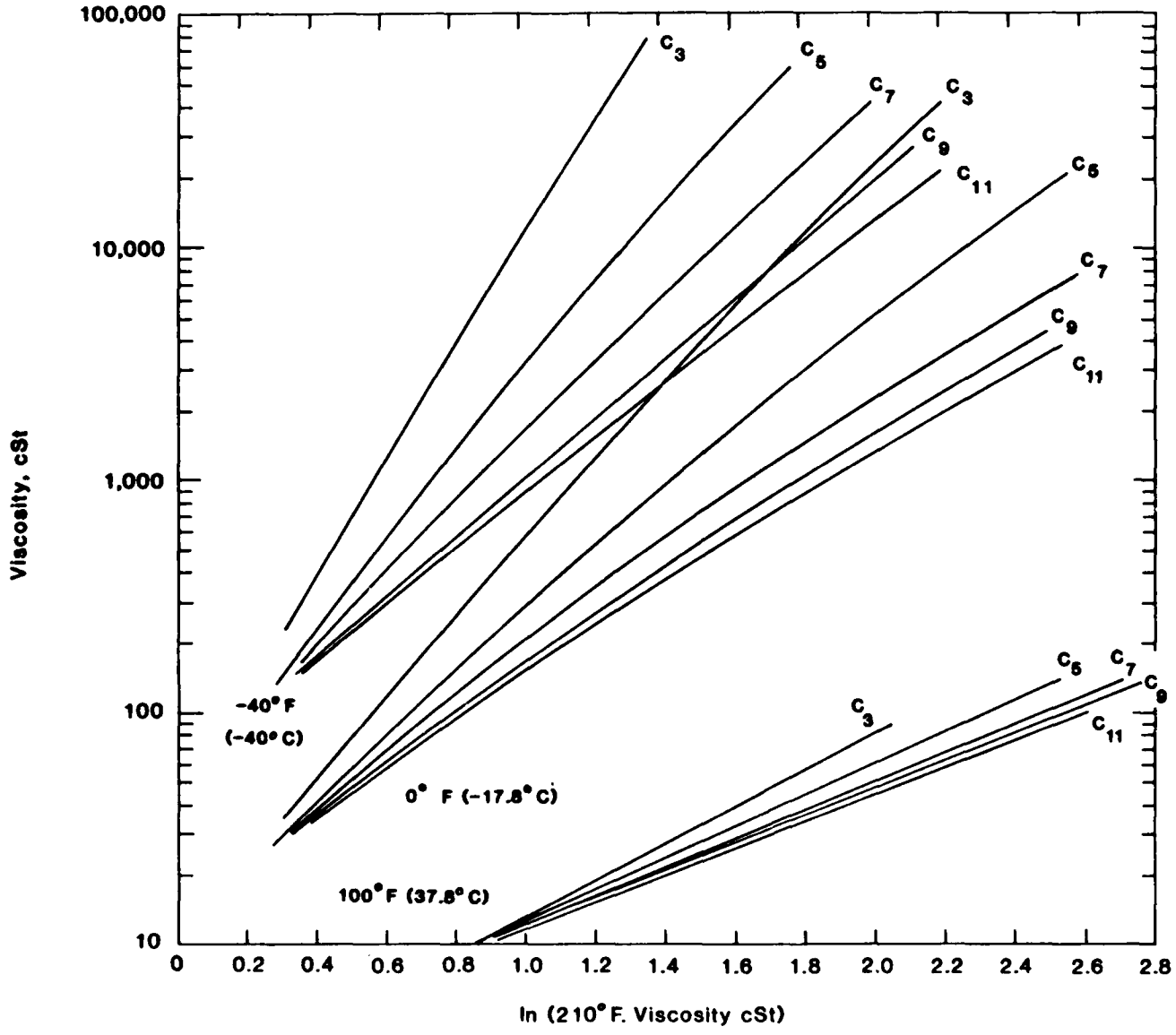


Figure 2

VISCOSITY DATA FOR INTERNAL OLEFIN OLIGOMERS (Hydrogenated)

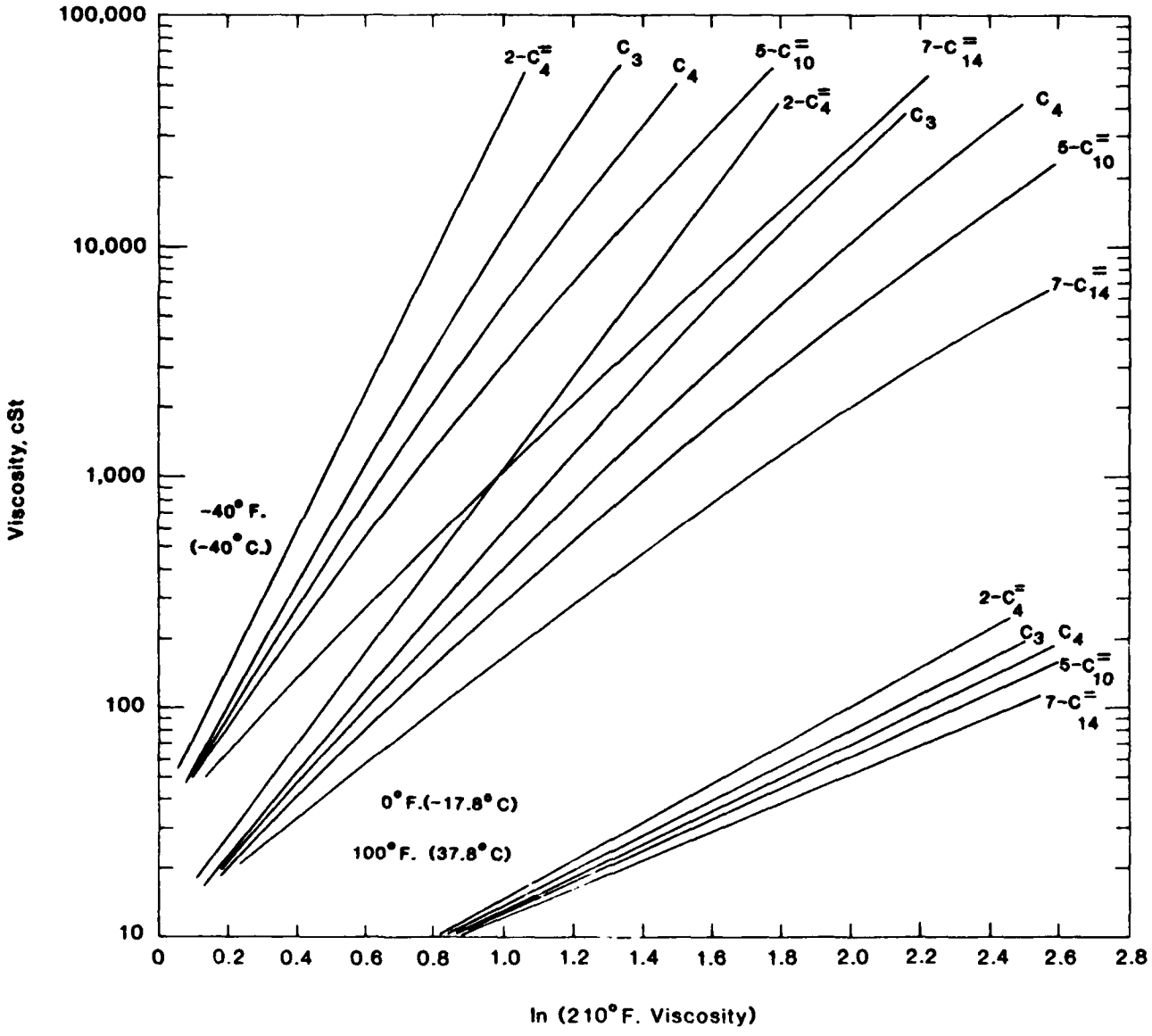


Figure 3

VISCOSITY DATA FOR HYDROGENATED VINYLIDENE OLEFIN OLIGOMERS

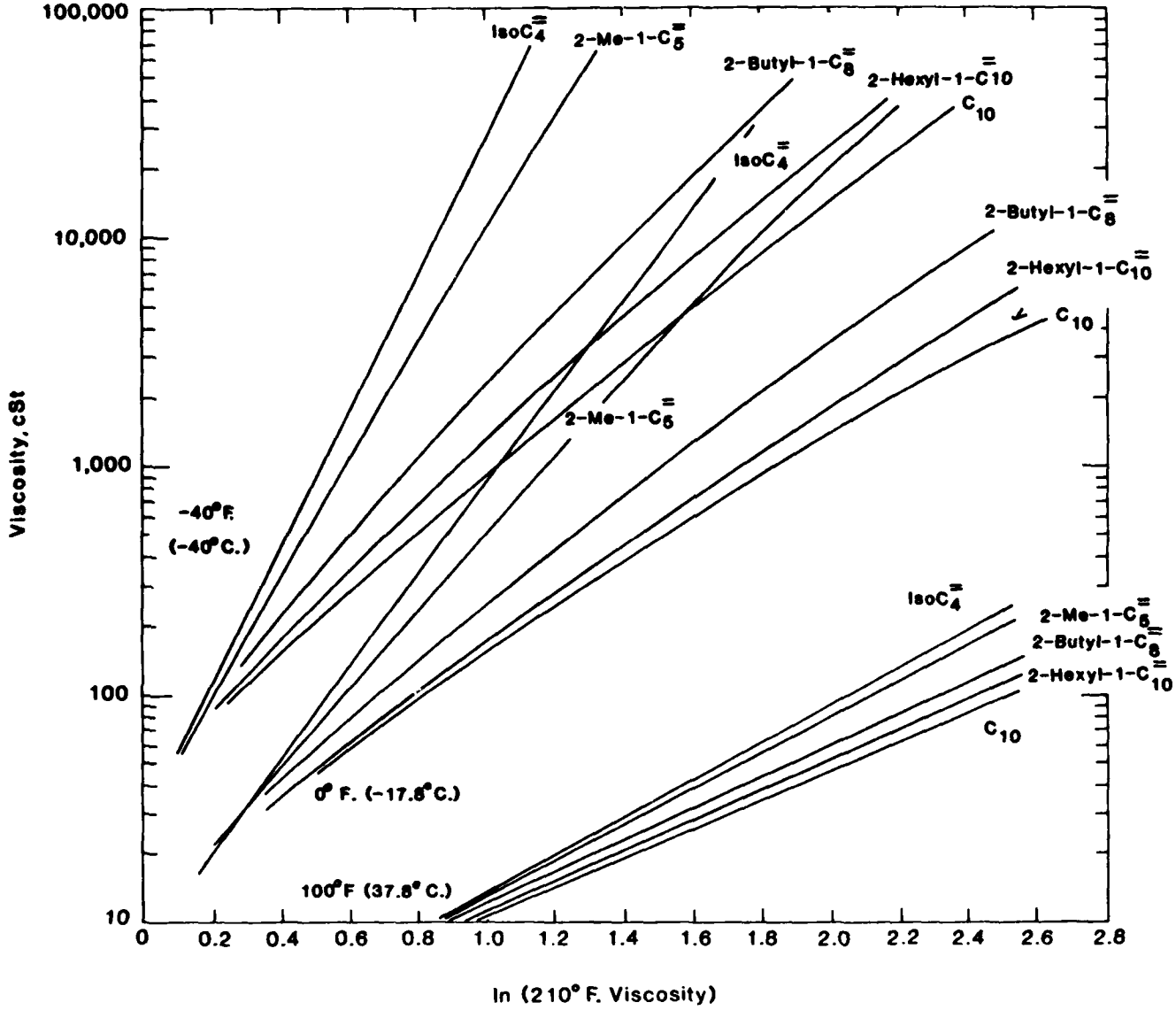


Figure 4

VISCOSITY DATA FOR HYDROGENATED BRANCHED INTERNAL OLEFIN OLIGOMERS

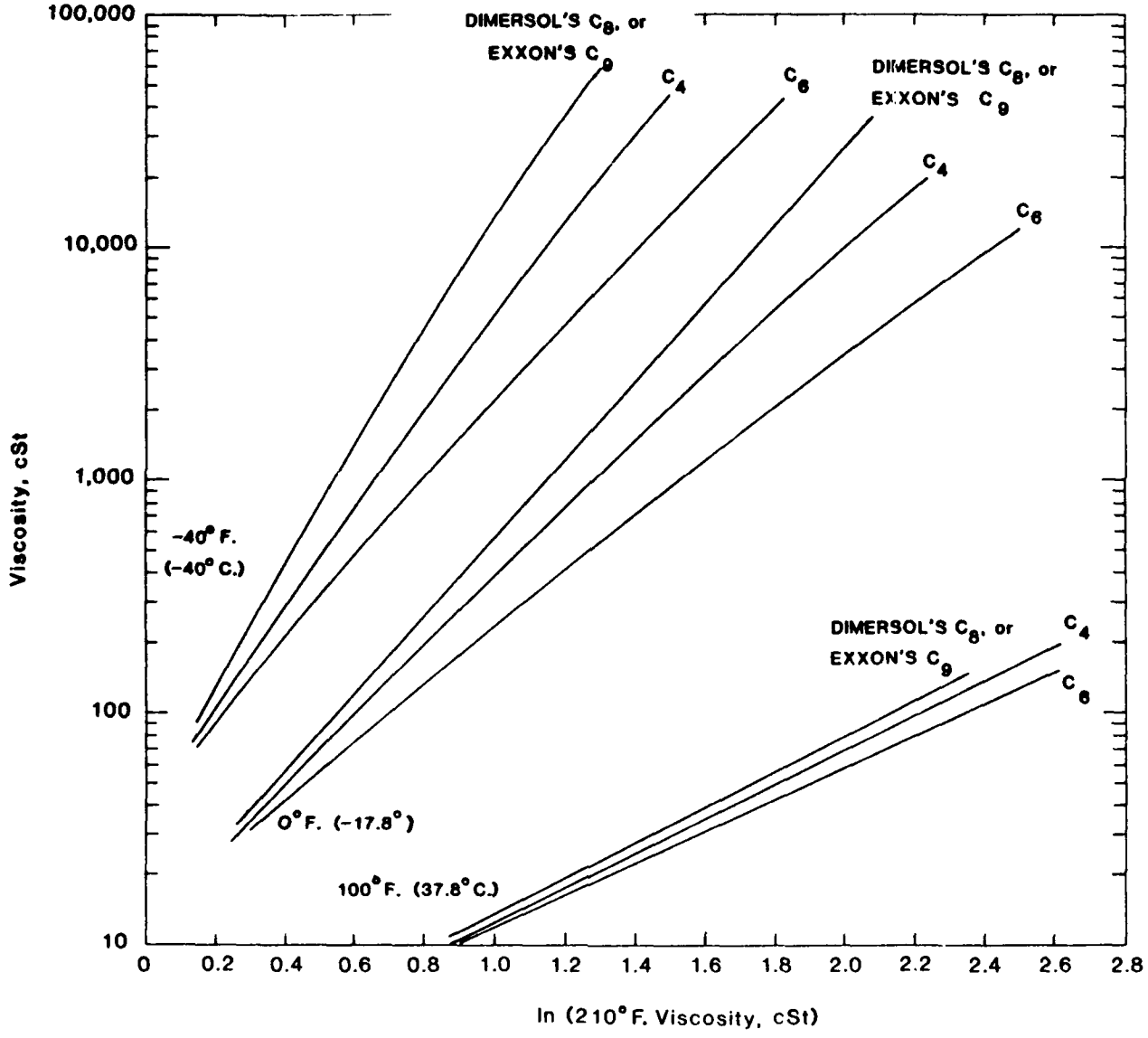


Figure 5

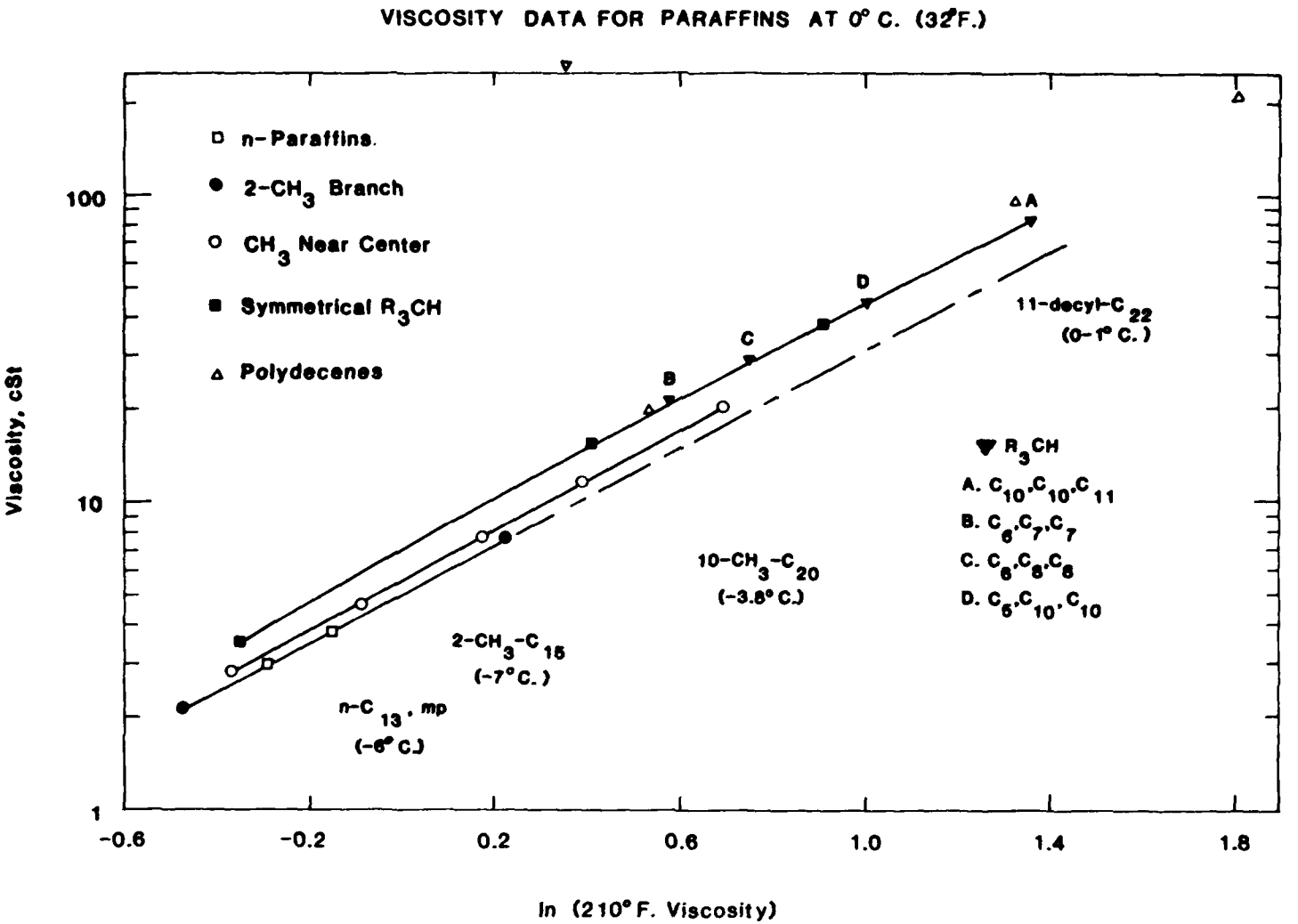

VISCOSITY DATA FOR PARAFFINS AT 0° C. (32°F.)
n-Paraffins
2-CH3 Branch
CH3 Near Center
Symmetrical R3CH
Polydecenes
100
10
1
Viscosity, cSt
-0.6
-0.2
0.2
0.6
1.0
1.4
1.8
ln (210° F. Viscosity)
A
B
C
D
11-decyl-C22
(0-1° C.)
R3CH
A. C10,C10,C11
B. C8,C7,C7
C. C8,C8,C8
D. C5,C10,C10
10-CH3-C20
(-3.8° C.)
2-CH3-C15
(-7° C.)
n-C13, mp
(-6° C.)

Figure 6

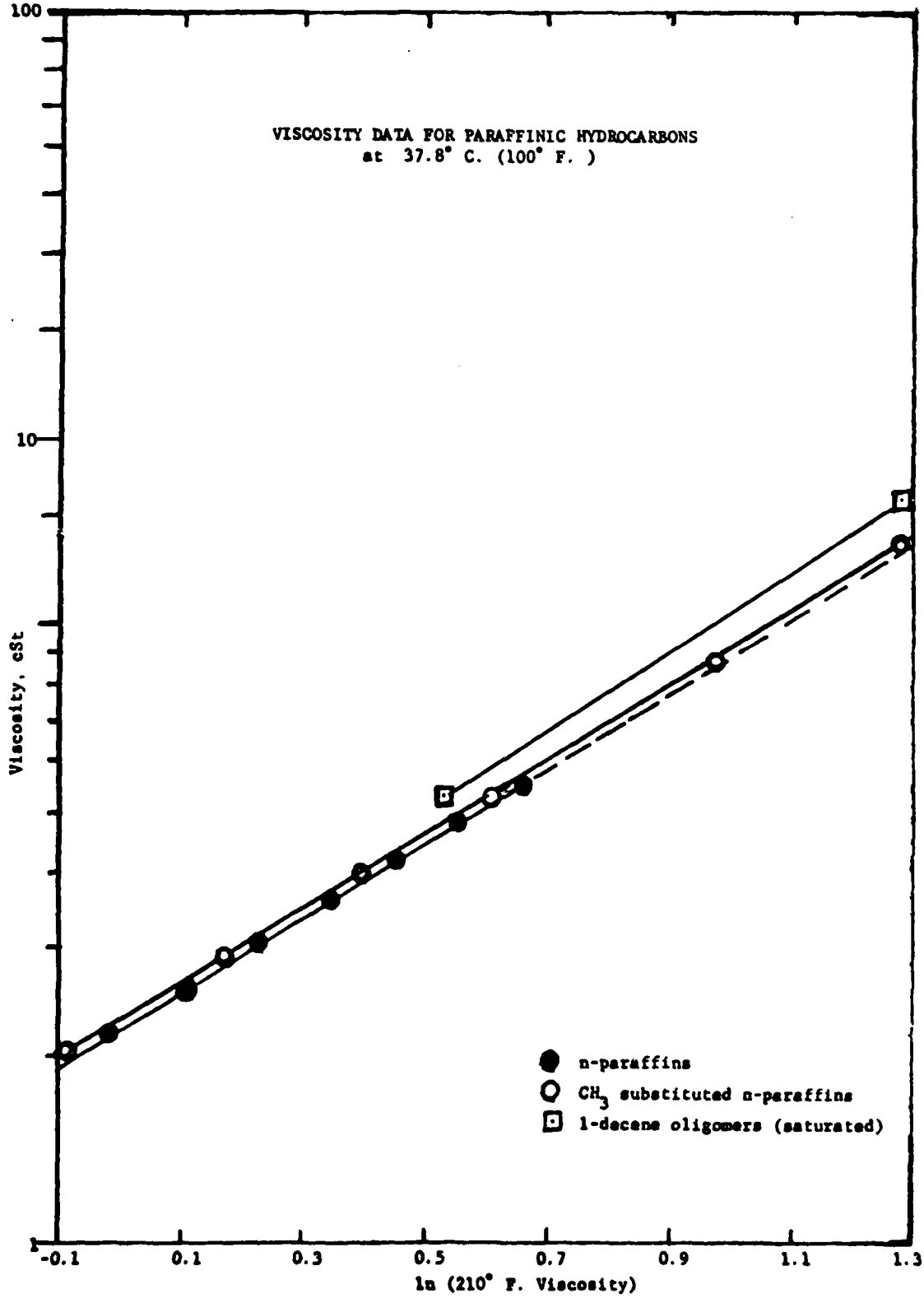

VISCOSITY DATA FOR PARAFFINIC HYDROCARBONS
at 37.8° C. (100° F.)
100
10
1
Viscosity, cSt
-0.1
0.1
0.3
0.5
0.7
0.9
1.1
1.3
ln (210° F. Viscosity)
n-paraffins
CH3 substituted n-paraffins
1-decene oligomers (saturated)

Figure 7

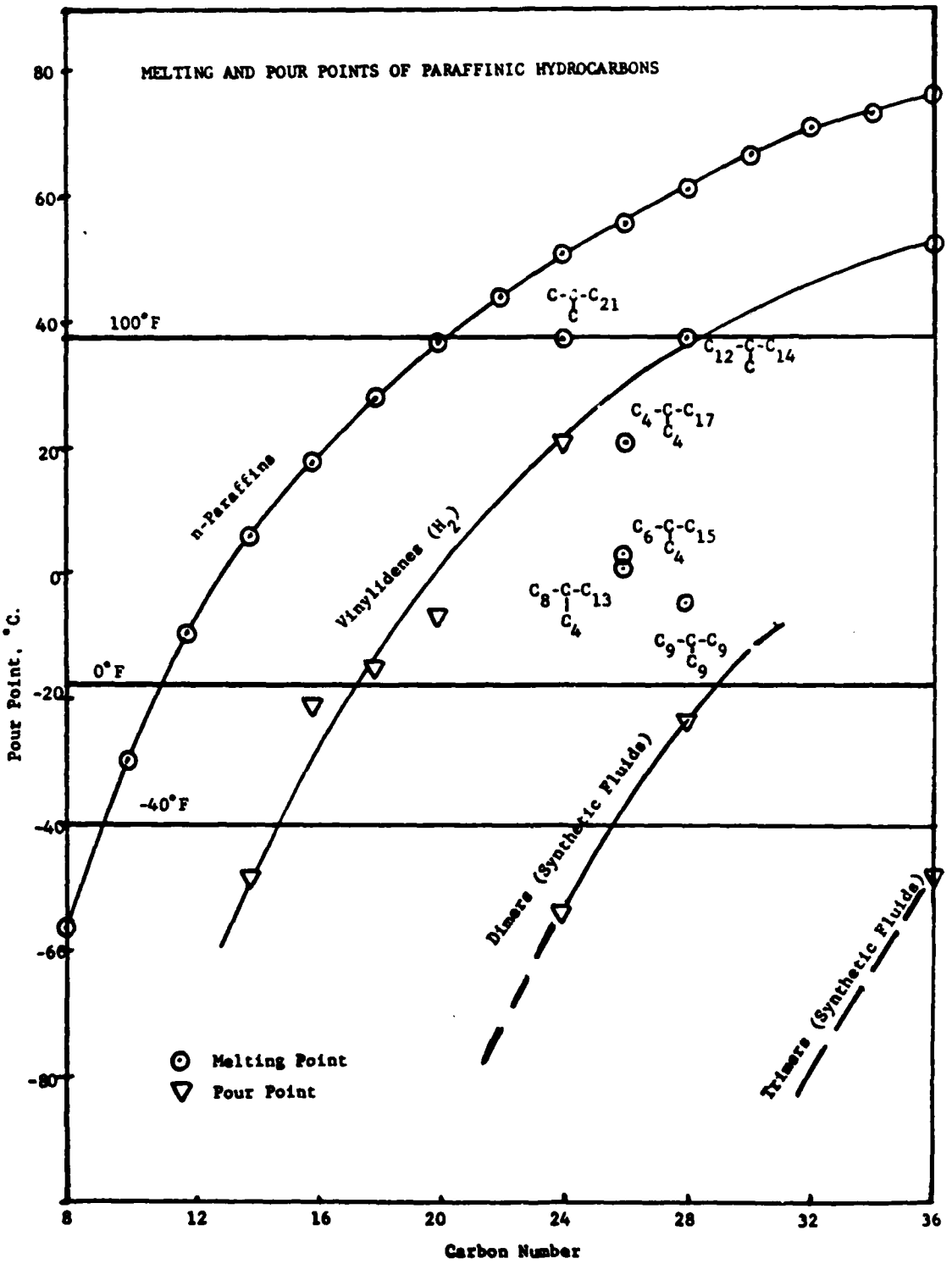

MELTING AND POUR POINTS OF PARAFFINIC HYDROCARBONS
Pour Point, °C.
80
60
40
20
0
-20
-40
-60
-80
100°F
0°F
-40°F
n-Paraffins
Vinylidenes (H_2)
Dimers (Synthetic Fluids)
Trimers (Synthetic Fluids)
$C-\overset{C}{\underset{C}{|}}-C_{21}$
$C_{12}-\overset{C}{\underset{C}{|}}-C_{14}$
$C_4-\overset{C_4}{\underset{C}{|}}-C_{17}$
$C_6-\overset{C_4}{\underset{C}{|}}-C_{15}$
$C_8-\overset{C_4}{\underset{C}{|}}-C_{13}$
$C_9-\overset{C_9}{\underset{C}{|}}-C_9$
Melting Point
Pour Point
8
12
16
20
24
28
32
36
Carbon Number

Figure 8

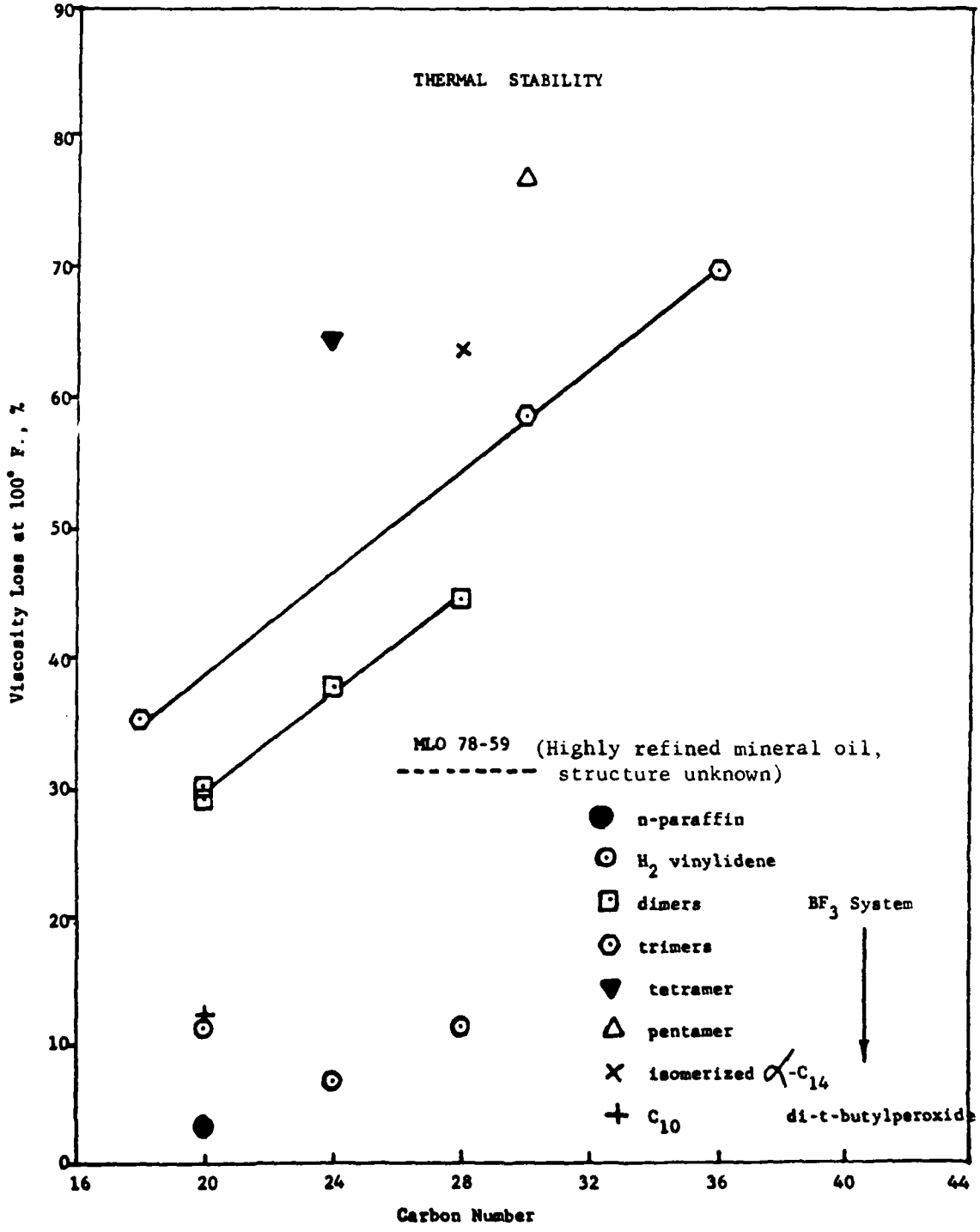

THERMAL STABILITY
Viscosity Loss at 100° F., %
Carbon Number
MLO 78-59 (Highly refined mineral oil, structure unknown)
n-paraffin
H2 vinylidene
dimers
trimers
tetramer
pentamer
isomerized α-C14
C10
BF3 System
di-t-butylperoxide
0
10
20
30
40
50
60
70
80
90
16
20
24
28
32
36
40
44

Figure 9

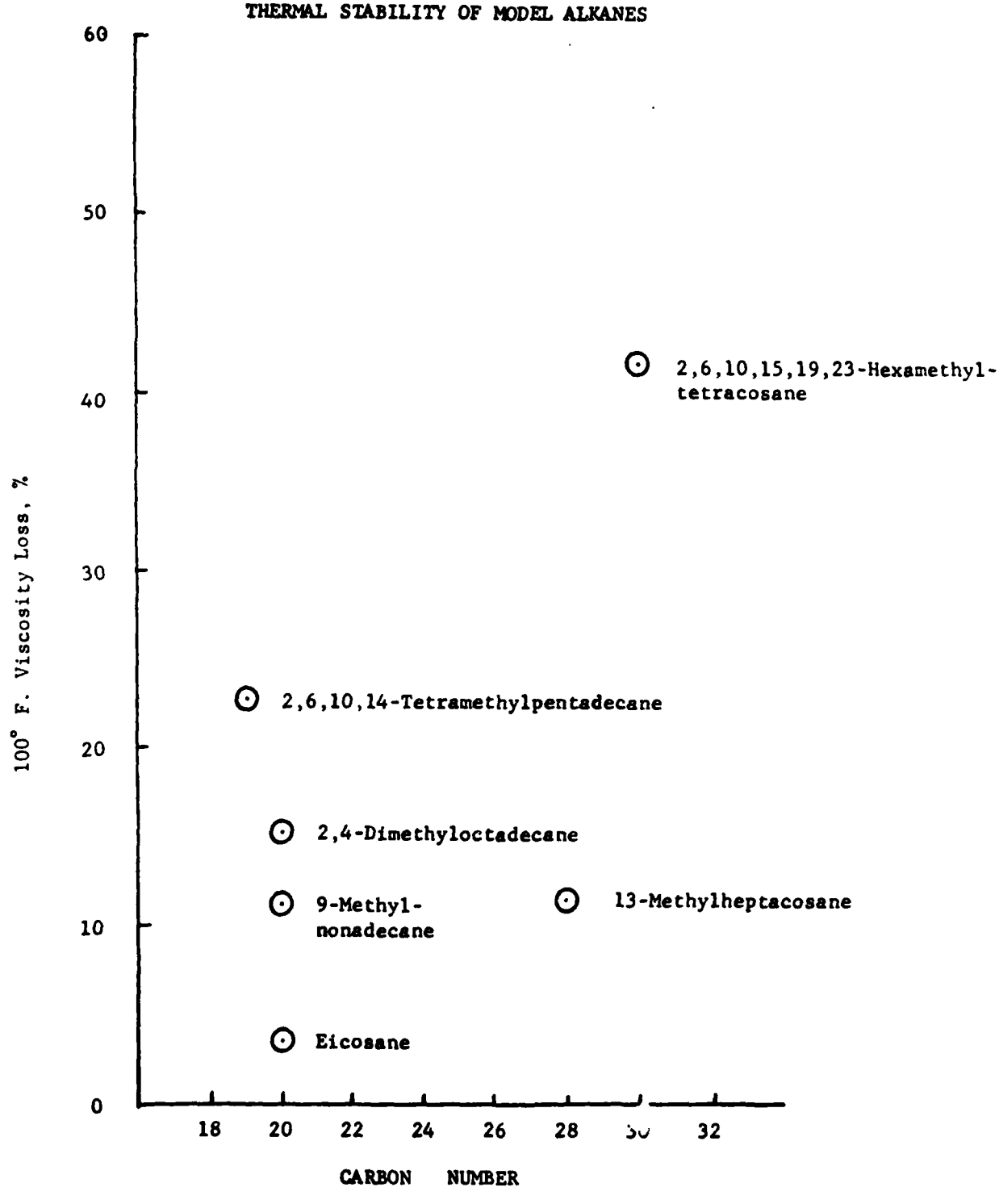

THERMAL STABILITY OF MODEL ALKANES
100° F. Viscosity Loss, %
60
50
40
30
20
10
0
18
20
22
24
26
28
30
32
CARBON NUMBER
2,6,10,15,19,23-Hexamethyl-tetracosane
2,6,10,14-Tetramethylpentadecane
2,4-Dimethyloctadecane
9-Methyl-nonadecane
13-Methylheptacosane
Eicosane

Figure 10

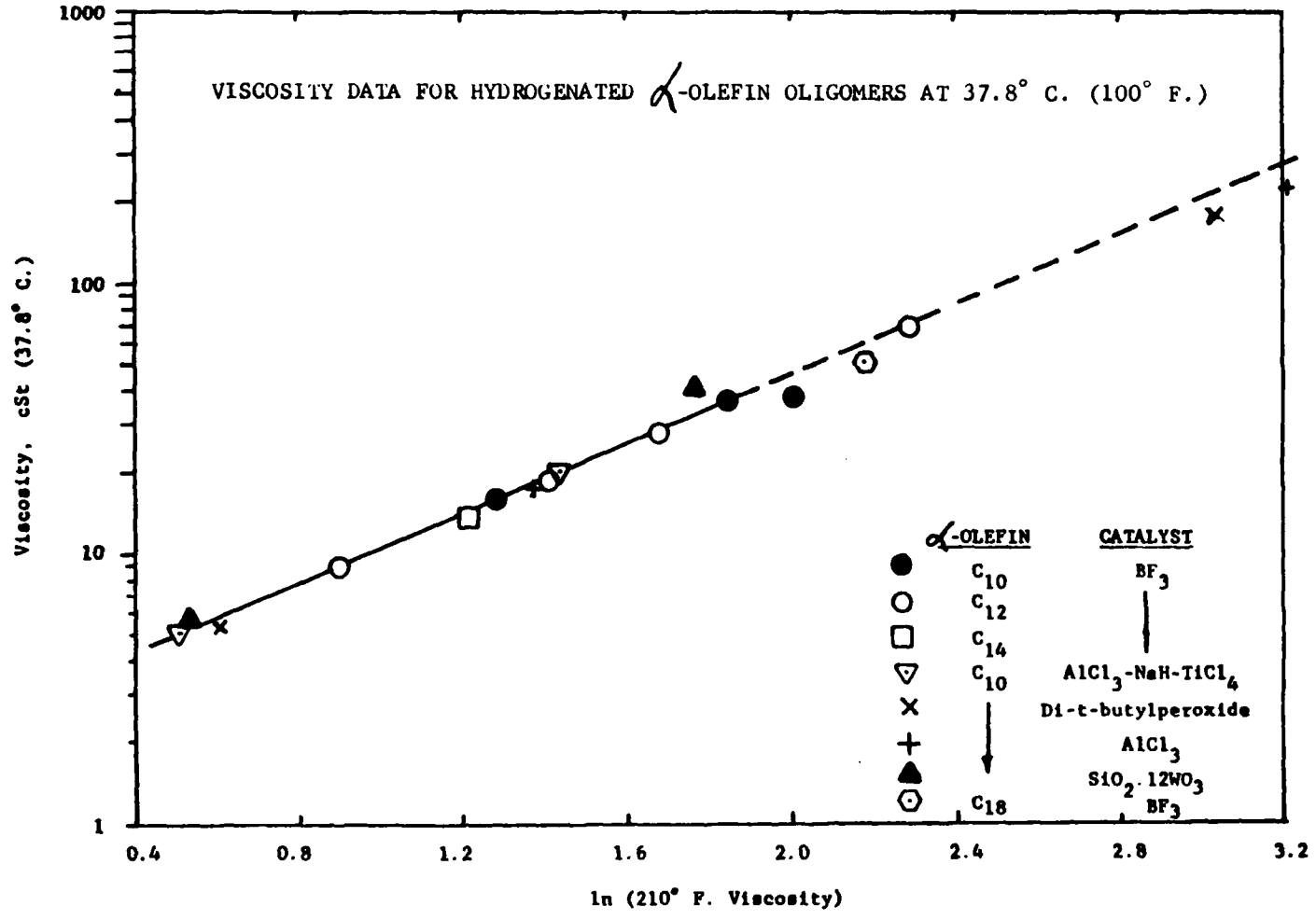

VISCOSITY DATA FOR HYDROGENATED α-OLEFIN OLIGOMERS AT 37.8° C. (100° F.)
Viscosity, cSt (37.8° C.)
1000
100
10
1
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
ln (210° F. Viscosity)
α-OLEFIN
CATALYST
C10
C12
C14
C10
C18
BF3
AlCl3-NaH-TiCl4
Di-t-butylperoxide
AlCl3
SiO2·12WO3
BF3

Figure 11

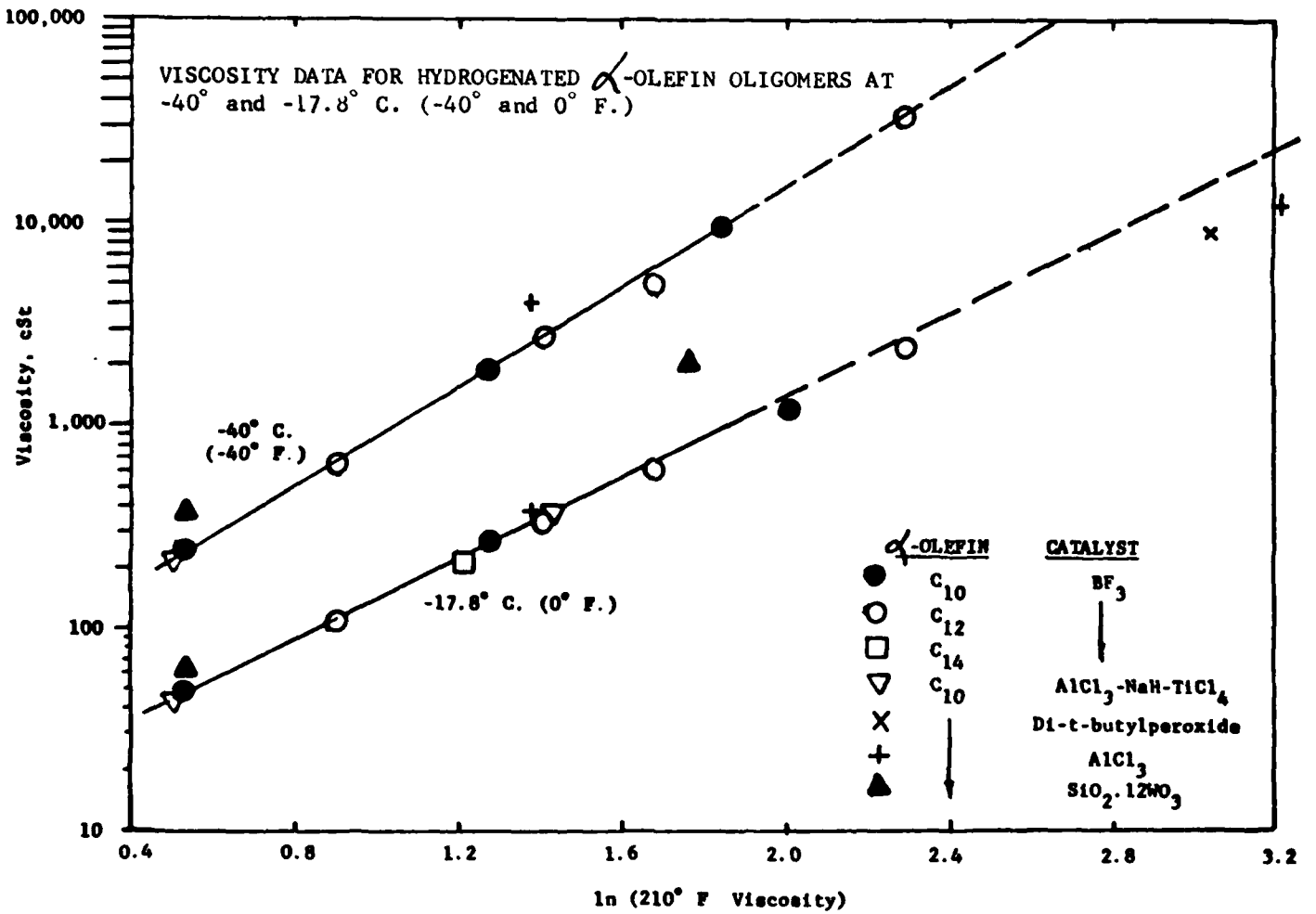
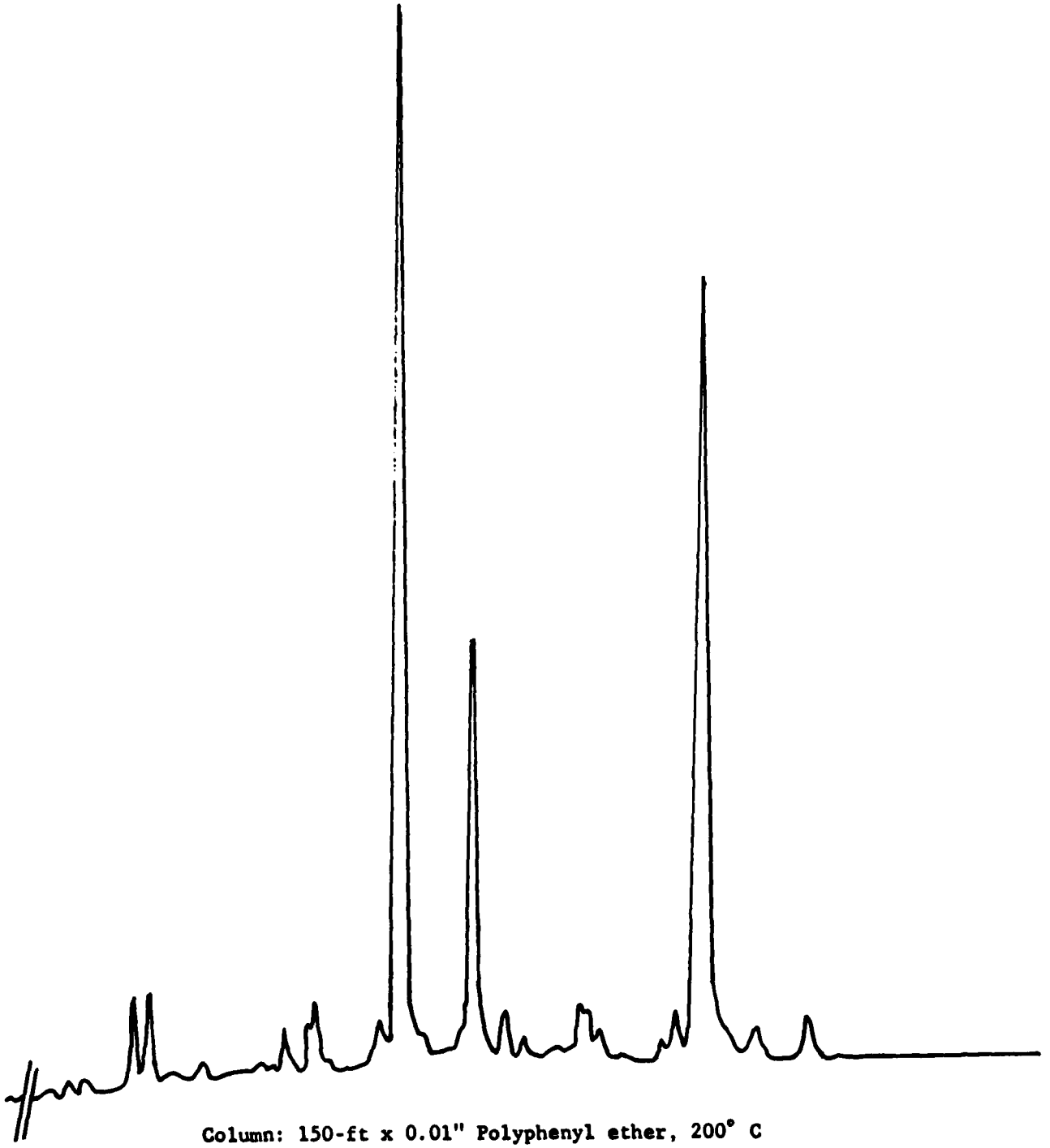

VISCOSITY DATA FOR HYDROGENATED α-OLEFIN OLIGOMERS AT
-40° and -17.8° C. (-40° and 0° F.)
100,000
10,000
1,000
100
10
Viscosity, cSt
-40° C.
(-40° F.)
-17.8° C. (0° F.)
α-OLEFIN
CATALYST
C10
C12
C14
C10
BF3
AlCl3-NaH-TiCl4
Di-t-butylperoxide
AlCl3
SiO2.12WO3
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
ln (210° F Viscosity)

Figure 12

GLC CHROMATOGRAM OF $C_{20}H_{42}$ (Hydrogenated 1-decene dimer, di-t-butylperoxide)



Column: 150-ft x 0.01" Polyphenyl ether, 200° C

Figure 13

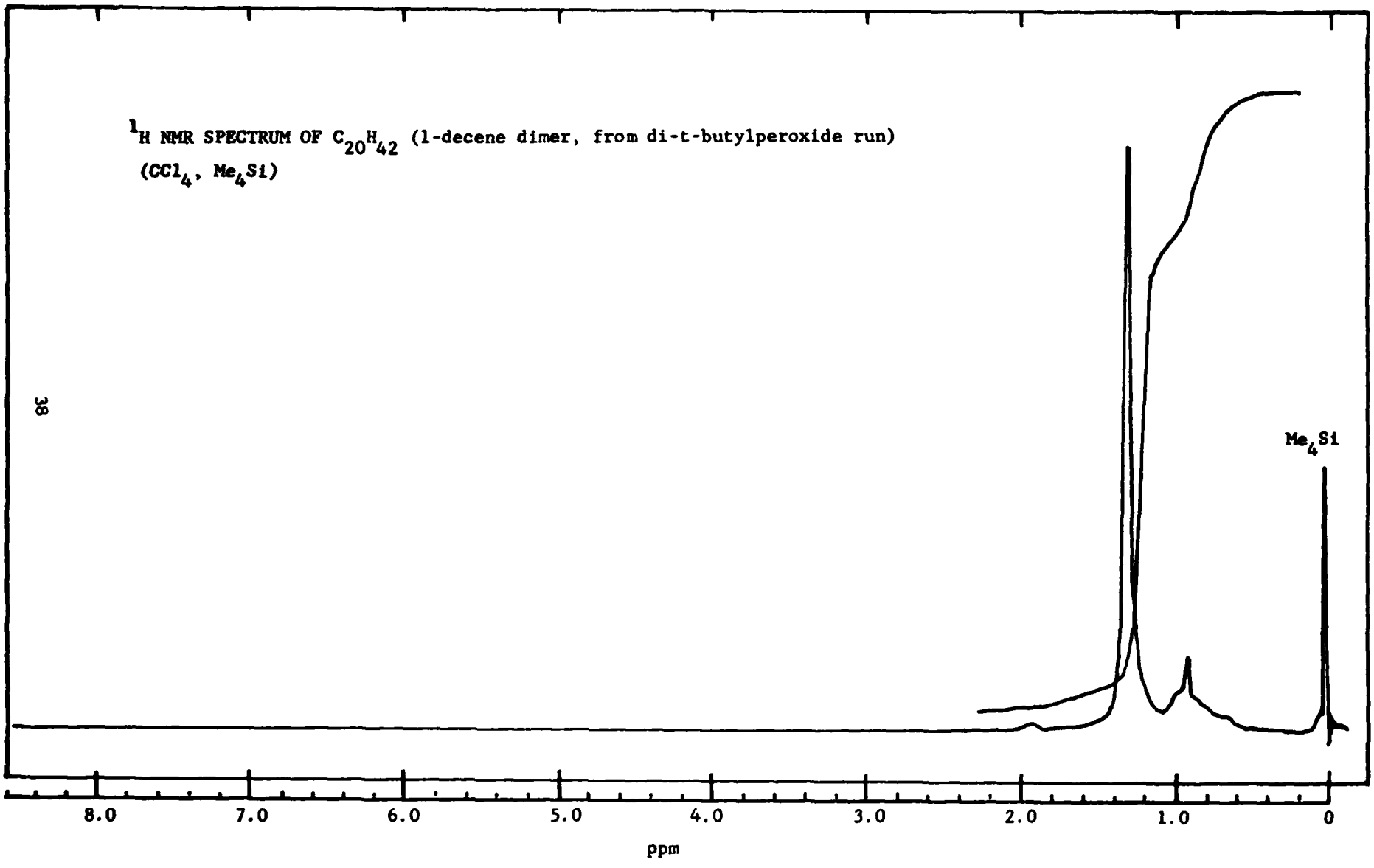
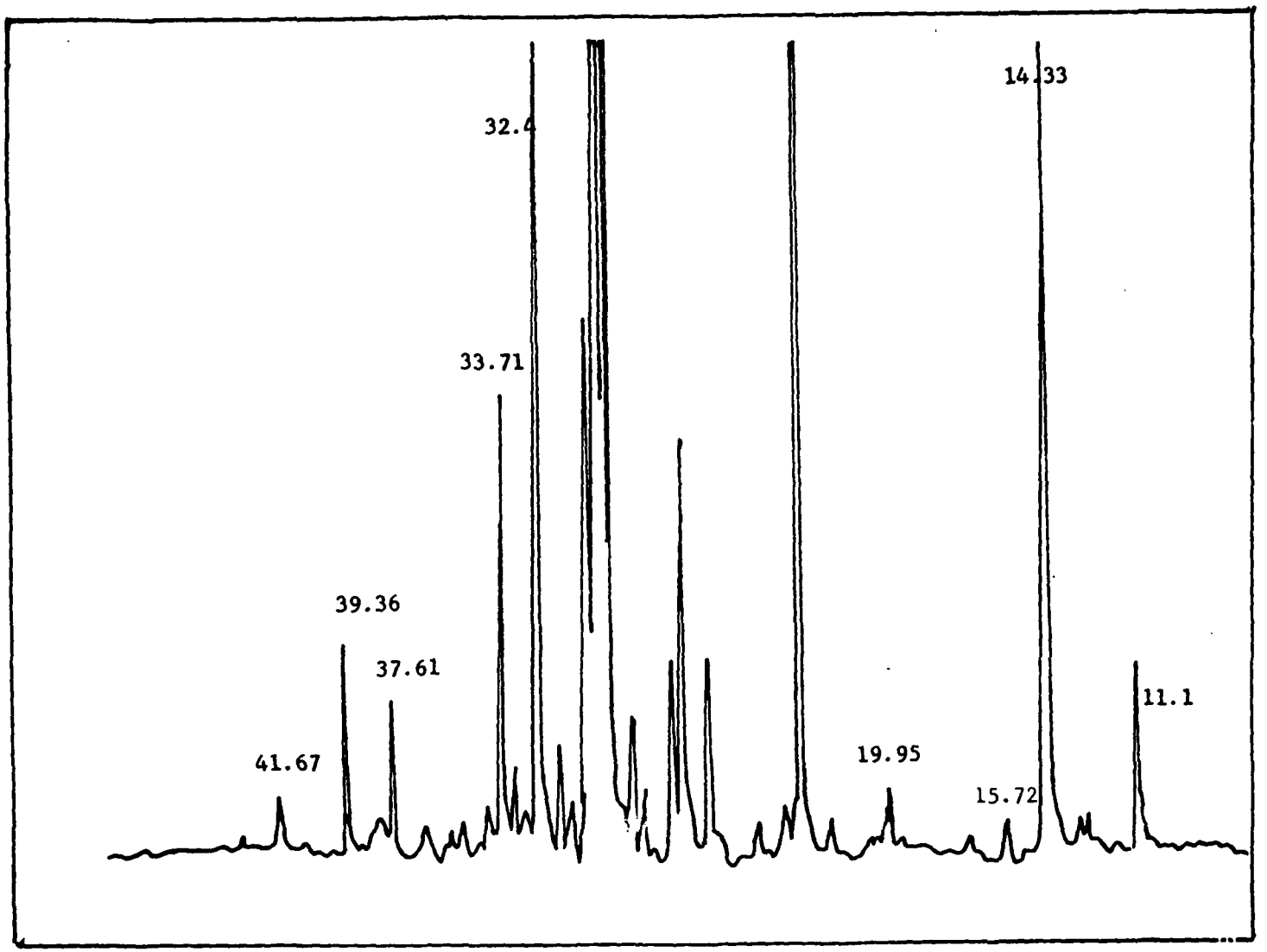

^{1}H NMR SPECTRUM OF $C_{20}H_{42}$ (1-decene dimer, from di-t-butylperoxide run)
(CCl_4, Me_4Si)
38
Me_4Si
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
ppm

Figure 14



^{13}C NMR SPECTRUM OF $C_{20}H_{42}$ (Hydrogenated 1-decene dimer, di-t-butylperoxide)

Figure 15

VISCOSITY DATA FOR HYDROGENATED OLIGOMERS FROM 1-DECENE, 5-DECENE, and MIXTURES

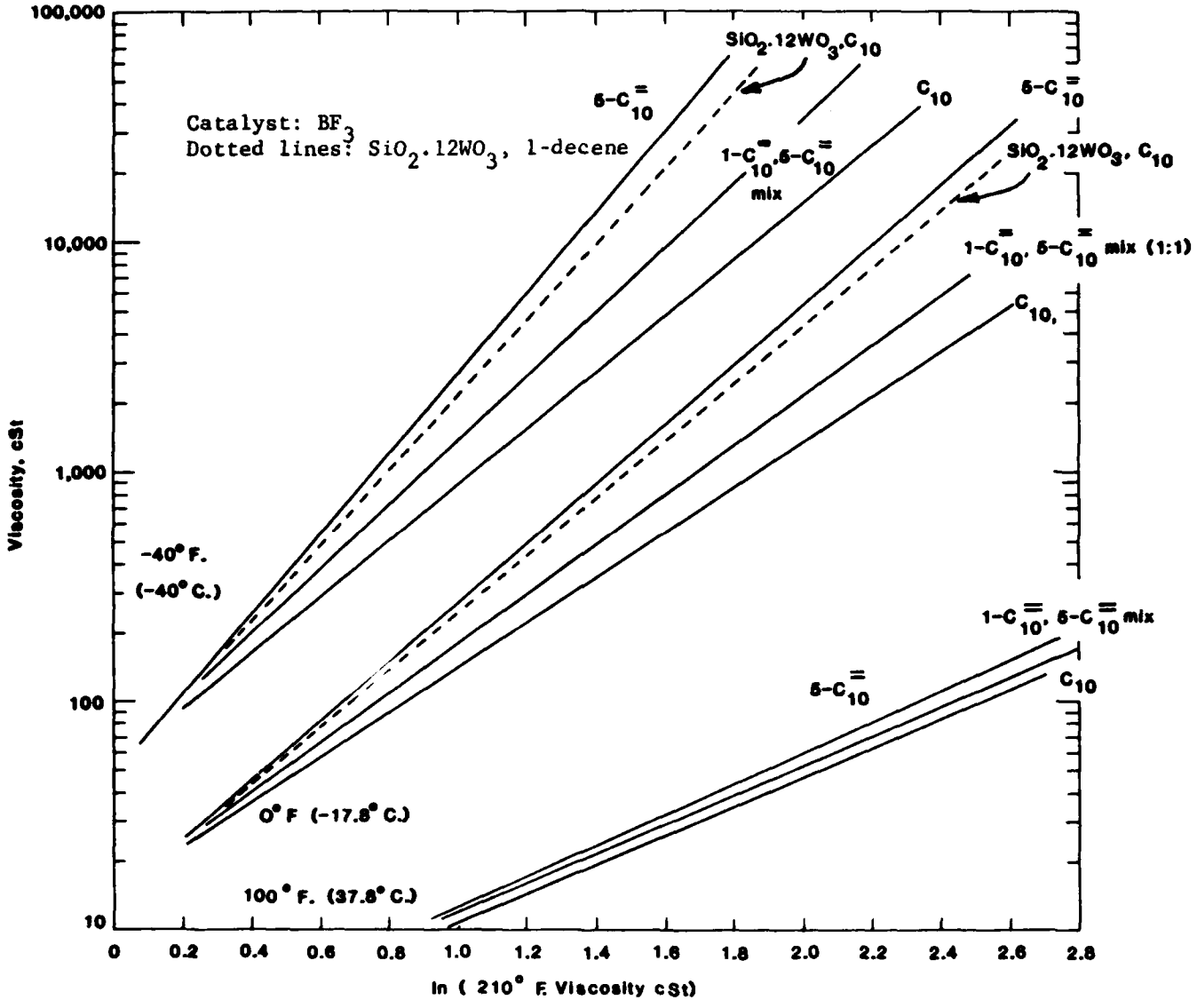


Figure 16

Typical GLC chromatogram of 1-Decene Oligomers.
(Column: 1.8-in x 2.5 ft, 5% Dexsil 300 on Chrom W, 80 to 390° C. at 32°/min)

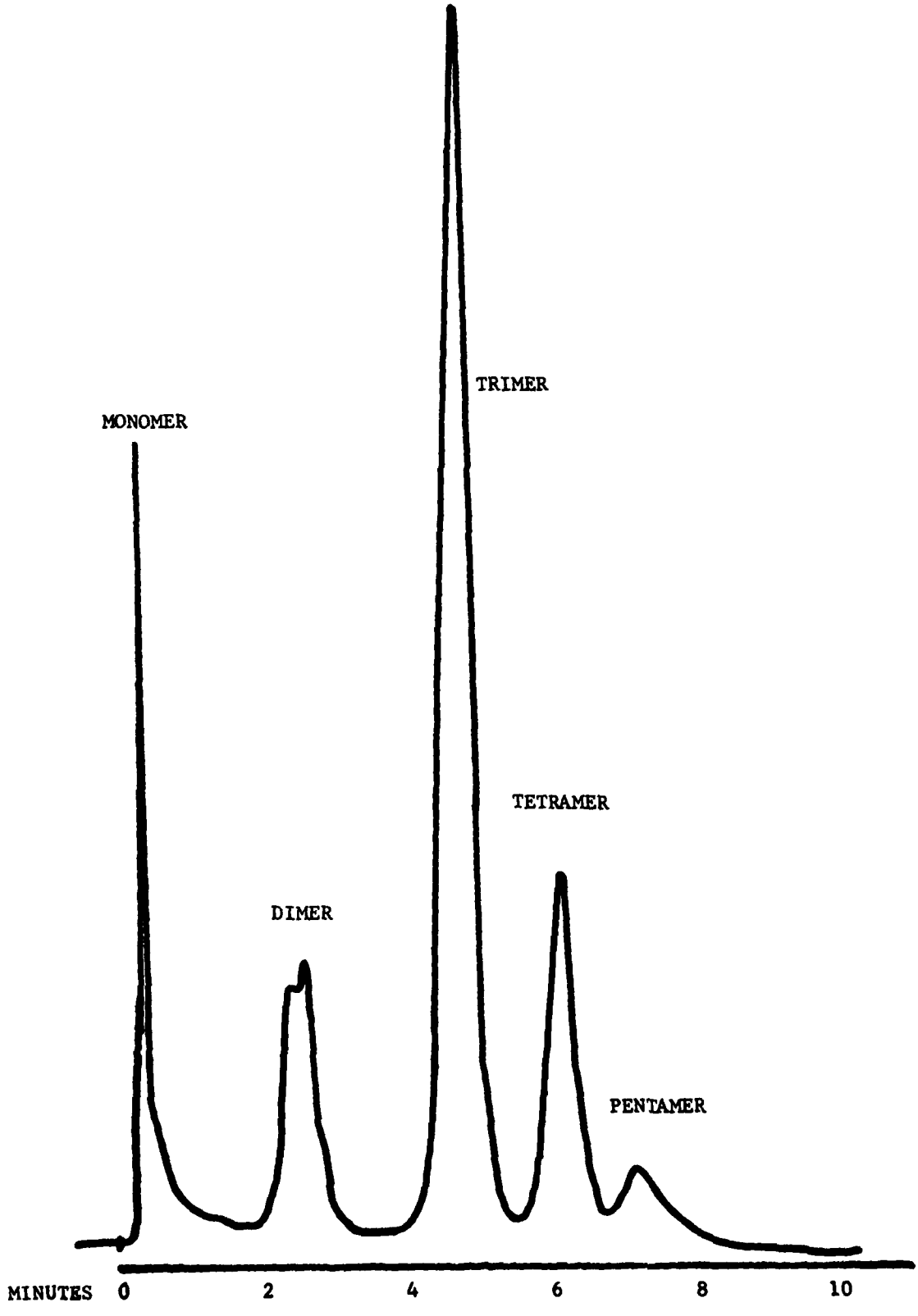


Figure 17

Table 1

VISCOSITIES OF OLIGOMERS OF EVEN CARBON NUMBER ALPHA OLEFINS

Carbon Number	Viscosity, mm^2/s (cSt) -40°C (-40°F)	-17.8°C (0°F)	37.8°C (100°F)	98.9°C (210°F)	ln (210°F Visc.)
		C_4 Oligomers			
C_{16}-C_{20}	115.6	23.26	3.27	1.23	0.207
C_{20}	1061	113.3	6.94	1.93	0.658
C_{24}	5635	382	12.72	2.75	1.012
C_{28}	42100	1710	27.33	4.29	1.456
C_{32}	BSOM[a]	7522	61.78	6.82	1.920
		C_6 Oligomers			
C_{18}	171	34.2	4.03	1.38	0.322
C_{24}	1650	196	10.6	2.51	0.920
C_{30}	9870	765	23.6	4.17	1.428
C_{36}	39100	2145	43.6	6.22	1.828
C_{42}	135000	5200	74.0	8.60	2.152
		C_8 Oligomers			
C_{16}	68.1	17.1	2.81	1.11	0.104
C_{24}	749	122	9.02	2.38	0.867
C_{32}	4310	488	21.4	4.18	1.430
C_{40}+	27500	2010	52.8	7.73	2.045
		C_{10} Oligomers			
C_{20}	243	48.7	5.28	1.70	0.531
C_{30}	1880	271	15.9	3.59	1.278
C_{40}	9500	977	36.4	6.29	1.839
C_{30}-C_{40}[b]	2330	324	17.80	3.87	1.353
C_{20}-C_{50}[c]	7938	861	34.00	6.01	1.793
C_{30}-C_{50}+[d]	17940	1616	50.86	7.94	2.072
		C_{12} Oligomers			
C_{24}	645	110	8.94	2.46	
C_{24}-$_{36}$[e]	2750	336	18.75	4.09	
C_{36}	4990	610	27.96	5.36	
C_{48}+[f]	33700	2460	68.86	9.88	
		C_{14} Oligomers			
C_{28}	--	212	13.84	3.38	
		C_{18} Oligomers			
C_{36}+	--	--	51.17	8.87	

a Beyond Scope of Method.
b 82% C_{30}, 18% C_{40}
c 1% C_{20}, 29% C_{30}, 48% C_{40}, 22% C_{50}
d 7% C_{30}, 56% C_{40}, 37% C_{50}+
e 92.9% C_{36}, 6.3% C_{48}
f 18% C_{36}, 82% C_{48}

Table 2

VISCOSITIES OF OLIGOMERS OF ODD CARBON NUMBER ALPHA OLEFINS

Carbon Number	Pour Point °C(°F)	Viscosity, mm^2/s (cSt) -40°C (-40°F)	-17.8°C (0°F)	37.8°C (100°F)	98.9°C (210°F)	ln (210°F Visc.)
			C_3 Oligomers			
C_{12}-C_{21}		280	40.63	4.23	1.44	0.365
C_{21}-C_{27}		15560	650	14.31	2.89	1.061
C_{27}-C_{30}		1352000	3421	31.02	4.39	1.479
C_{30}-C_{36}^+		BSOM**	21030	81.17	7.50	2.015
			C_5 Oligomers			
C_{20}		1548	147.1	7.68	2.02	0.703
C_{25}		14908	803	17.91	3.31	1.197
C_{30}		61442	2329	33.3	4.69	1.545
C_{35}		215785	6639	59.25	6.73	1.906
			C_7 Oligomers			
C_{21}	<-70.6 (<-95)	423	72.85	6.32	1.86	0.621
C_{21}-C_{28}	--	1080	154.3	10.22	2.53	0.928
C_{28}^+	-65 (-85)	10156	869	28.27	4.85	1.579
			C_9 Oligomers			
C_{18}	<-70.6 (<-95)	149.1	30.66	3.95	1.41	0.344
C_{27}	<-70.6 (<-95)	1423	206	12.90	3.07	1.122
C_{36}^+	-62 (-80)	15800*	1381	43.08	6.81	1.918
			C_{11} Oligomers			
C_{33}	-48.3 (-55)	3729	468	23.47	4.76	1.560
C_{33}-C_{44}	-56.7 (-70)	8665	913	36.55	6.45	1.864
C_{33}^+	-51.1 (-60)	38370*	2509	70.39	10.17	2.319

* Result could not be closely reproduced; usually indicative of a high value.

** Beyond Scope of Method.

Table 3

VISCOSITIES (32°F AND 210°F) OF MODEL COMPOUNDS AND POLYDECENES

	Viscosity, mm^2/s (cSt)		
	32°F	210°F	ln (210°F)
n-Paraffins			
n-Dodecane	2.966	0.7465	-0.2924
n-Tridecane	3.827	0.8581	-0.1530
2-Methyl Substituted Paraffins			
2-Methyldecane	2.180	0.6220	-0.47482
2-Methylpentadecane	7.787	1.250	0.2227
Methyl Substitution Near Center			
5-Methylundecane	2.85	0.6905	-0.3703
7-Methyltridecane	4.66	0.9152	-0.0886
7-Methylpentadecane	7.74	1.1961	0.1791
7-Methylheptadecane	11.78	1.4841	0.3948
10-Methyleicosane	20.46	2.002	0.6940
Trialkylmethanes (Symmetrical)			
5-Butylnonane	3.571	0.7037	-0.3514
7-Hexyltridecane	15.56	1.510	0.4118
9-Octylheptadecane	37.79	2.478	0.9073
Trialkylmethanes (Nonsymmetrical)			
8-Hexylpentadecane	21.74	1.786	0.5801
9-Hexylheptadecane	29.17	2.125	0.7537
11-Pentylheneicosane	44.89	2.723	1.0018
11-Decyldocosane	82.25	3.906	1.3624
Polydecenes (Hydrogenated)			
Dimer ($C_{20}H_{42}$), 2 cSt	19.40	1.73	0.54812
Trimer ($C_{30}H_{62}$), 4 cSt	94.82	3.77	1.32708
Tetramer, 6 cSt (C_{30}, 30%; C_{40}, 63%; C_{50}, 7%)	229.0	6.04	1.79840
Pentamer, 8 cSt (C_{30}, 4%; C_{40}, 50%, C_{50}, 33%; C_{60}, 13%)	397.0	8.03	2.08318

Table 4

VISCOSITIES OF PARAFFINIC HYDROCARBONS

Carbon Number	Viscosity, mm^2/s (cSt) 37.8°C (100°F)	38.9°C (210°F)	ln(38.9°C Viscosity)
		n-Paraffins[9]	
C_{14}	2.168	0.9815	-0.01867
C_{15}	2.583	1.116	0.10975
C_{16}	3.062	1.259	0.23032
C_{17}	3.581	1.414	0.34642
C_{18}	4.16	1.577	0.45552
C_{19}	4.793	1.748	0.55847
C_{20}	5.522	1.935	0.66011
		Methyl-Branched Paraffins (CH_3 Near Center)	
C_{14}	2.02	0.92	-0.08338
C_{16}	2.91	1.19	0.17395
C_{18}	3.98	1.49	0.39878
C_{20}	5.30	1.83	0.60432
C_{24}	8.79	2.65	0.97456
C_{28}	13.54	3.59	1.27815
		1-Decene Oligomers	
C_{20} (Dimer)	5.28	1.70	0.53063
C_{30} (Trimer)	15.9	3.59	1.27815

Table 5

MELTING AND POUR POINTS OF PARAFFINIC HYDROCARBONS

Carbon Number	Melting Point[a] °C	(°F)	Carbon Number	Melting Point[a] °C	(°F)
C_8	-56.5	(-69.7)	24	55	(124)
C_{10}	-29.7	(-21.5)	26	56	(133)
C_{12}	-9.6	(15)	28	61.5	(143)
C_{14}	6	(43)	30	66.6[b]	(152)
C_{16}	18	(64)	32	71.3[b]	(160)
C_{18}	28	(82)	34	73.3[b]	(164)
C_{20}	36.8	(98.2)	36	76.6[b]	(170)
C_{22}	44	(111)			

Branched Paraffins

Carbon Number	Name	Melting Point[b] °C	(°F)	Pour Point[c] °C	(°F)
C_{14}	(d)			-48	(-55)
C_{16}	7-methylpentadecane			-21	(-5)
C_{18}	(e)			-15	(+5)
C_{20}	9-methylnonadecane			-7	(+20)
C_{24}	11-methyltricosane			21	(+70)
C_{24}	2-methyltricosane	37.6	(99.7)		
C_{26}	5-butyldocosane	20.8	(69.4)		
C_{26}	7-butyldocosane	3.1	(37.6)		
C_{26}	9-butyldocosane	1.3	(34.3)		
C_{28}	13-methylheptacosane	37.8[c]	(100)		
C_{28}	10-nonylnonadecane	-5.0	(23)		
C_{36}	17-methylpentatriacontane	52.2[c]	(126)		

n-α-Olefins Oligomers

Carbon Number	Oligomer	Pour Point[c] °C	(°F)
C_{20}	α-C_{10} Dimer	<-79	(<-110)
C_{24}	α-C_{12} Dimer	-54	(-65)
C_{28}	α-C_{14} Dimer	-23	(-10)
C_{30}	α-C_{10} Trimer	<-79	(<-110)
C_{36}	α-C_{12} Trimer	-48	(-55)

---

a Handbook of Chemistry and Physics, 45th Edition, The Chemical Rubber Co., Cleveland, Oh

b The Chemistry and Technology of Waxes, Albin H. Warth, Reinhold Publishing Corp., 1960.

c Gulf Science and Technology Company data.

d 50-50 Molar mixture of 5-methyltridecane and 7-methyltridecane.

e 50-50 Molar mixture of 7-methylheptadecane and 9-methylheptadecane.

Table 6

HYDROCARBON THERMAL STABILITY TEST RESULTS[a]

Fluid	Carbon Number	37.8°C (100°F) Viscosity, mm^2/s Before	After[a]	Loss	Viscosity Loss %
Trimer of 1-Hexene	18	4.03	2.61	1.42	35.2
Dimer of 1-Decene[b]	20	5.43	4.76	0.67	12.3
Dimer of 1-Decene (SF-0203-4)	20	5.20	3.69	1.51	29.0[c]
11-Methyltricosane	24	8.79	8.16	0.63	7.2
Dimer of 1-Dodecene	24	8.94	5.56	3.38	37.8
MLO 78-59[g]	-	14.90	10.26	4.64	31.1[d]
n-Eicosane	20	5.53	5.33	0.20	3.6
9-Methylnonadecane	20	5.30	4.71	0.59	11.1
Dimer of 1-Decene (SF-0203-4)	20	5.20	3.64	1.56	30.0
Tetramer of 1-Hexene	24	10.51	3.74	6.77	64.4[e]
13-Methylheptacosane	28	13.54	11.99	1.55	11.5
Dimer of 1-Tetradecene	28	13.84	7.70	6.14	44.4
Dimer of Isomerized 1-Tetradecene	28	14.70	5.34	9.36	63.7
Trimer of 1-Decene (SF-0409-1)	30	16.49	6.82	9.67	58.6[f]
Pentamer of 1-Hexane	30	23.56	5.44	18.12	76.9
Trimer of 1-Dodecene	36	27.96	8.48	19.48	69.7

---

a Test conditions: 371°C (700°F), 6 hr, 8.5 ml fluid in 22.9 cm x 12.7 mm OD (9 in. x 0.5 in. OD) type 304SS tube with 316SS Swagelok end caps, N_2 purged.

b Using di-t-butylperoxide as oligomerization catalyst.

c Repeated test. Previously obtained result was 30.0%.

d A 25.4% loss was earlier obtained. Private communication from C. E. Snyder, Jr., WPAFB, Ohio, to B. L. Cupples, Gulf Research & Development Co., July 27, 1978.

e 57.4% loss reported by Snyder, ibid.

f 54.1% loss reported by Snyder on a similar sample containing 83.3% trimer and 26.7% tetramer, ibid.

g Highly refined mineral oil; structure unknown.

Table 7

THERMAL STABILITY OF MODEL ALKANES

Fluid	Carbon Number	100°F Viscosity Before	After	Loss	Viscosity Loss, %	Number Tertiary H'S	% Tertiary H'S
n-Eicosane	20	5.53	5.33	0.20	3.6	0	0
9-Methylnonadecane	20	5.30	4.71	0.59	11.1	1	2.4
2,4-Dimethyloctadecane	20	5.17	4.39	0.78	15.1	2	4.8
2,6,10,14-Tetramethyl-pentadecane	19	4.94	3.84	1.10	22.3	4	10.0
13-Methylheptacosane	28	13.54	11.99	1.55	11.5	1	1.7
2,6,10,15,19,23-Hexa-methyltetracosane	30	19.78	11.51	8.27	41.8	6	9.7

Table 8

EFFECTS OF OLIGOMERIZATION CATALYST ON 1-DECENE OLIGOMER VISCOSITIES AND POUR POINTS

Catalyst	Fraction Carbon Number	Pour Point °C (°F)	Viscosity, mm^2/s -40°C (-40°F)	-17.8°C (0°F)	37.8°C (100°F)	98.9°C (210°F)
BF_3•n-Butanol[a]	20	<53 (<-65)	377	48.34	5.25	1.7
	30	<-54 (<-65)	1907	272	16.11	3.62
WF_6•H_2O	20	--	--	41.06	4.81	1.58
	30	--	--	243	15.35	3.57
SiO_2•$12WO_3$	20	<-54 (<-65)	376	63.73	5.75	1.71
	30+	<-54 (<-65)	--	2036	41.42	5.83
Di-t-butylperoxide	20	>25 (>77)	--	--	5.43	1.83
	30+	-43 (-45)	--	9094	178.7	20.89
$AlCl_3$-NaH-$TiCl_4$	20	<-71 (<-95)	216	44.19	5.05	1.66
	30+	<-71 (<-95)	2864	383	19.97	4.18
$AlCl_3$	20-30	--	4104	385	18.36	3.96
	30+	-46 (-50)	277500	12340	222	24.77

[a] Decene conversion was limited to 30%.


DATE
ILME