

Post-Oligomerization of α -Olefin Oligomers: A Route to Single-Component and Multicomponent Synthetic Lubricating Oils

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ABSTRACT: This article describes a synthetic route to single-component and multicomponent base stocks for synthetic lubricated oils. The synthesis was carried out in two stages. First, oligomers of α -olefins (1-hexene, 4-methyl-1-pentene, and 1-decene) were prepared via reactions catalyzed by metallocene catalysts. The distribution of the oligomers with respect to their oligomerization number could be controlled by the reaction temperature. The oligomer mixtures were then fractionated, and the lightest components, dimers and trimers, were separated. Finally, the latter materials, branched α -olefins containing vinylidene double bonds, were further oligomerized with cationic cata-

lysts. One such material prepared in the two-stage process, the dimer of the 1-decene dimer (C_{40} product), has a kinematic viscosity of 6.4 cs at 100°C and a viscosity index of 147. It represents the first example of a single-component base stock for synthetic lubricating oils. The post-oligomerization procedure was performed on unfractionated oligomer mixtures as well, leading to an improved distribution of the final materials with respect to the carbon atom number. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 273–280, 2009

Key words: cationic polymerization; chromatography; metallocene catalysts; oligomers

INTRODUCTION

Synthetic lubricating oils contain, as their base stocks, specially synthesized oligomers of α -olefins.¹ The base stocks constitute 60 to 80% of the oils, the other components being viscosity index (VI) improvers, detergents, dispersants, corrosion inhibitors, antiwear additives, and so forth. Synthetic base stocks possess good mechanical properties in a broad range of temperatures. The oligomers of α -olefins are highly branched and amorphous, and they retain sufficiently high viscosity at high temperatures and good flow properties at low temperatures. An arbitrary indicator of oil quality, VI was established by the Society of Automotive Engineers and is universally used in the industry as a measure of the change in the kinematic viscosity with temperature. The VI value is calculated from tabulated data based on oil viscosity at 40 and 100°C: the higher the VI number is, the smaller the variation is of the oil viscosity with temperature. Typically, the best mineral lubricating oils have VI values of ~ 100 , whereas the VI values of synthetic oils are signifi-

cantly higher, usually in the 130–140 range, and this is a great advantage.

The base stocks for high-quality synthetic lubricating oils are typically synthesized by oligomerization of 1-decene, either at low temperatures with a cationic initiator (usually BF_3)^{1,2} or with chromium oxide catalysts.³ In both processes, the resulting materials are mixtures of oligomers of different molecular weights [different values of the oligomerization number (m)] and different degrees of branching. In some cases, vacuum distillation of the oligomer mixtures is used to remove from the products the lightest, low-viscosity oligomers, dimers and trimers, which have a relatively low commercial value.³

This article describes a synthetic route to single-component and multicomponent base stocks for synthetic lubricated oils. The synthesis was carried out in two stages. First, mixtures of α -olefin oligomers were prepared via reactions catalyzed by metallocene catalysts. The distribution of the oligomers with respect to their m values could be controlled by the reaction temperature. The oligomer mixtures were then fractionated, and the lightest components, dimers and trimers, were separated. Finally, these lightest materials (which are not useful lubrication oils because of their very low viscosity), branched α -olefins containing vinylidene double bonds, were further oligomerized with cationic catalysts. This

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post-oligomerization procedure was performed on unfractionated oligomer mixtures as well, leading to an improved distribution of the final materials with respect to the carbon atom number.

EXPERIMENTAL

Catalytic oligomerization reactions of three α -olefins, 1-hexene, 4-methyl-1-pentene, and 1-decene, were performed. The experiments were carried out in two types of stainless-steel autoclaves, 3.8-L and 0.5-L, equipped with magnet-driven propeller stirrers, manometers, and external heating jackets. The reactors were dried in a nitrogen flow at 90°C for 60 min and then cooled to \sim 50°C. Neat α -olefins or 1 : 1 mixtures of liquid monomers and *n*-heptane were added to the reactors in the required quantities under a nitrogen blanket, and they were followed by 10 mmol of Al*i*-Bu₃ (an impurity scavenger mostly used to remove moisture from the monomers and solvents) and 20–30 mmol of methylalumoxane (MAO) as a 25 wt % solution in toluene. The reactors were then heated to a desired temperature, and a solution of a metallocene complex, Cp₂ZrCl₂ or (*n*-Bu-Cp)₂ZrCl₂ (0.05–0.15 mmol) in toluene, corresponding to [Al]/[Zr] ratios ranging from 200 to 500, was added. The oligomerization reactions were carried out for 1–4 h, and they produced liquid oligomers with yields ranging from \sim 30 to >90%.

The reaction products were quenched with ethanol, unreacted monomers were removed from them, and the oligomers were separated into fractions by distillation *in vacuo*. The boiling ranges of the 1-hexene and 4-methyl-1-pentene oligomers were \sim 45–50°C at 0.5–0.9 mmHg for the dimers and \sim 90–110°C at 0.4–0.7 mmHg for the trimers; the boiling point of the 1-decene dimer was \sim 140°C at 0.8 mmHg.

Post-oligomerization reactions of individual olefin oligomers and their mixtures were carried out with EtAlCl₂, AlCl₃, and a supported EtAlCl₂/SiO₂ catalyst. The latter was prepared by the slurring of 1.0 g of silica (955, Davison, W. R. Grace-Davidson, Columbia, MD; precalcined at 600°C) in 4 cc of *n*-heptane and by the addition to the slurry of 2 cc of a 25 wt % solution of EtAlCl₂ in hexane followed by drying at 60°C for 3 h. Mixtures containing 20 cc of the oligomers and \sim 0.50 g of the supported catalyst were reacted at 50–60°C for several hours.

The distribution of α -olefin oligomers produced in metallocene-catalyzed reactions and the conversion of the oligomers in post-oligomerization reactions were measured by the gas chromatography (GC) method. The GC analysis was carried out with a Hewlett-Packard 5890 gas chromatograph equipped with a Restek (Restek Corp., Bellefonte, PA) MXT-1 60-m stainless-steel column and a flame ionization detector. Nitrogen was used as a carrier gas at a rate

of 1.1 cc/min and with a split ratio of 60 : 1. The injection temperature was 300°C, and the column temperature was increased from 40 to 300°C at a rate of 5°C/min.

¹³C-NMR analysis of the oligomers was carried out at 100.4 MHz on a JEOL Eclipse 400 NMR spectrometer at 130°C with typical experimental parameters for acquiring quantitative spectra of polyolefins. The pulse angle was 90°, and the pulse delay was 15 s. Continuous ¹H decoupling was applied throughout. The samples were prepared as solutions in a 3 : 1 mixture of 1,3,5-trichlorobenzene and *o*-dichlorobenzene-*d*₄. IR spectra were recorded with a PerkinElmer 1600 Fourier transform infrared spectrophotometer.

The kinematic viscosity of the oligomers at 40 and 100°C was measured in centistokes with a calibrated glass capillary viscometer according to the ASTM D 445-06 (May 2006) method. VI values were calculated according to the ASTM D 2270-04 method, procedure 2.

RESULTS AND DISCUSSION

Oligomerization of 1-hexene

Oligomerization reactions of α -olefins with standard metallocene catalysts easily proceeded at temperatures ranging from 70 to 90°C. The molecular weights of the lightest oligomers were relatively low, and the oligomer mixtures were easily analyzed by GC. As an example, Table I gives the results of 1-hexene oligomerization reactions with the (*n*-Bu-Cp)₂ZrCl₂-MAO system at different temperatures. The data show that two opposing effects, an increase in the reaction rate with temperature and a decrease in catalyst stability, resulted in a plateau of the highest productivity from 60 to 80°C, whereas the activity of the catalyst fell dramatically at temperatures over 90°C.

These reactions produced mostly 1-hexene oligomers with the regular structure with the vinylidene

TABLE I
Oligomerization Reactions of 1-Hexene with the
(*n*-Bu-Cp)₂ZrCl₂-MAO System

Temperature (°C)	Conversion (%)	Productivity (g/mmol [Zr])
40	52.5	2.95×10^5
60	75.6	4.24×10^5
80	68.9	3.87×10^5
80	72.9	4.09×10^5
90	31.2	2.50×10^5
100	13.9	0.78×10^5

The reaction conditions were as follows: 1-hexene/*n*-heptane mixture ratio = 1 : 1, [1-hexene] = 4.1 M, [(*n*-Bu-Cp)₂ZrCl₂] = 6.0×10^{-4} mmol, [Al]/[Zr] = 200, impurity scavenger = Al*i*-Bu₃, and reaction time = 4 h.

TABLE II
Compositions of the Oligomerization Products of
1-Hexene Produced with the (*n*-Bu-Cp)₂ZrCl₂-MAO
Catalyst System (GC Data)

Oligomer	Content (wt %)		Content of olefin with vinylidene C=C bonds (%)
	Reaction at 70°C	Reaction at 90°C	
Dimer	61.6	71.5	93.2
Trimer	21.1	15.5	95.5
Tetramer	11.1	7.6	87.3
Pentamer	4.5	2.7	— ^a
Hexamer	1.8	2.0	— ^a

^a Oligomers with high m values are mixtures of numerous stereomers, and a GC analysis of their structures is difficult.

double bond at the end: $\text{CH}_2=\text{C}(\text{n-C}_4\text{H}_9)-[\text{CH}_2-\text{CH}(\text{n-C}_4\text{H}_9)]_{m-2}-\text{CH}_2-\text{CH}_2-\text{n-C}_4\text{H}_9$. m varied from 2 for dimers to 7–10. IR spectra confirmed that the vinylidene bond was the main chain end in the oligomer molecules; its out-of-plane C—H bending band was at 888 cm^{-1} .

Table II gives the distribution of the 1-hexene oligomers prepared at 70 and 90°C with respect to m . The dimers consisted of a single α -olefin (89–93%), 2-butyl-1-octene, and olefins with the same skeletal structure and isomerized double bonds (3–6%). A small fraction of the dimer mixture, $\sim 4\%$, was the saturated compound with the same skeleton, 5-methylundecane. The most probable cause of its formation was a chain transfer reaction to molecular hydrogen.⁴ The literature data show that polymerization and copolymerization reactions of 1-alkenes with metallocene catalysts are accompanied by the generation of small amounts of H_2 .^{5,6} The dimers with the isomerized skeleton (linear dodecenes with internal CH=CH bonds), which were produced via the secondary insertion of the 1-hexene molecule into the Zr—C bond in the Zr—CH₂—CH₂—C₄H₉ species, were formed with a combined yield of merely 0.2–0.7%.

Regularly built trimers and tetramers with the vinylidene double bond also constituted the majority of the respective oligomers, as shown in Figure 1. In both cases, the contents of the expected regular products were $\sim 90\%$. The structural uniformity of these oligomers represents a sharp contrast to 1-hexene oligomers produced with cationic initiators. For example, GC analysis of products formed in a cationic oligomerization reaction of 1-hexene with AlMeCl_2 under ambient conditions showed the presence of over 14 dimers (C_{12} products) in comparable yields as well as 18 trimers (C_{18} products) and numerous higher oligomers.

The molar yields of the 1-hexene oligomers prepared with the metallocene catalysts were distributed with respect to m according to a power law:⁴

$$\text{Molar yield}(m) = A \times \gamma^m \quad (1)$$

where A is a normalization parameter. γ is the probability of the chain growth: $\gamma = R_p / (R_p + \Sigma R_t^i)$, where R_p and ΣR_t^i are the rate of chain propagation ($R_p \sim k_p \times C_{\text{monomer}}$) and the sum of all chain transfer reactions (k_p is the rate constant of the chain propagation reaction and C_{monomer} is the α -olefin concentration). Kinetic studies of polymerization reactions with metallocene catalysts⁴ have shown that the chain transfer reaction to a monomer (at rate $R_t^M \sim k_t^M \times C_{\text{monomer}}$, where k_t^M is the rate constant of the chain transfer reaction to the monomer) dominates at high temperatures, that is, $\Sigma R_t^i \approx R_t^M$. In such a case, the expression for γ can be approximated as $\gamma \approx R_p / (R_p + R_t^M) = k_p / (k_p + k_t^M)$. The areas under GC peaks of particular oligomers are proportional to their weight contents: GC peak area \sim Weight yield(m) = $m \times$ Molar yield(m). Therefore, GC data on the oligomer distributions could be linearized in the coordinates with a slope of $\log \gamma$:

$$\begin{aligned} \log [\text{Weight yield}(m)/m] &\equiv \log(\text{peak area}/m) \\ &= \log A + m \times \log \gamma \quad (2) \end{aligned}$$

Figure 2 shows one example of the distribution of oligomers produced in a 1-hexene oligomerization reaction with the (*n*-Bu-Cp)₂ZrCl₂-MAO catalyst

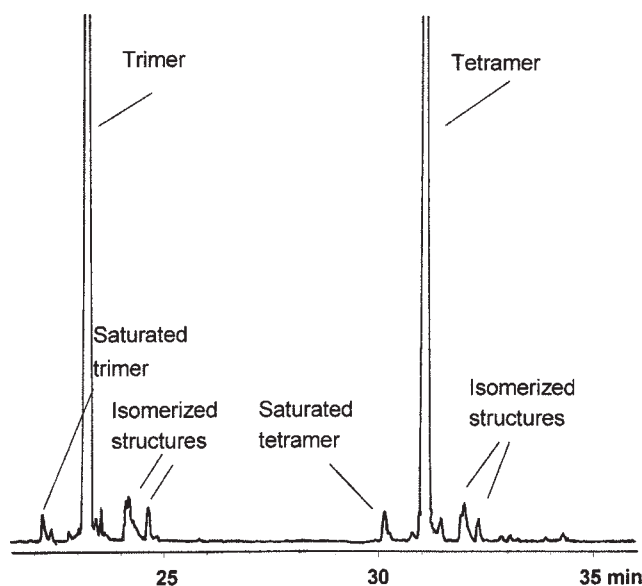


Figure 1 Gas chromatogram of the 1-hexene oligomers produced with (*n*-Bu-Cp)₂ZrCl₂-MAO as the catalyst at 70°C (C_{18} and C_{24} ranges).

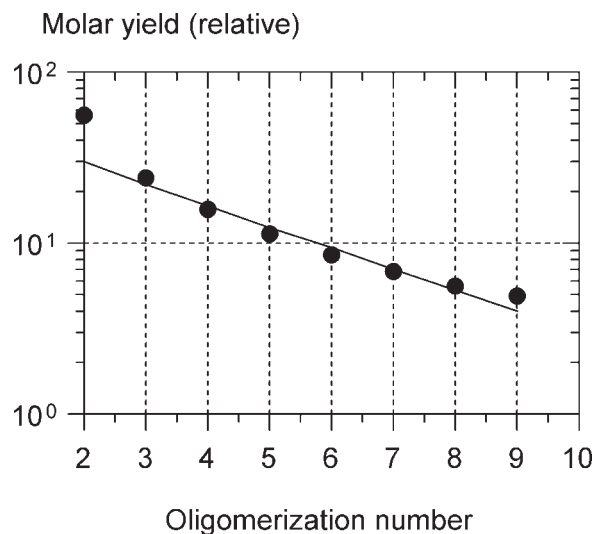


Figure 2 Distribution of the 1-hexene oligomers produced with $(n\text{-Bu-Cp})_2\text{ZrCl}_2\text{-MAO}$ as the catalyst at 70°C.

system at 70°C. As the reaction temperature increased, the γ value for the oligomerization reactions decreased from ~ 0.45 to ~ 0.30 ; that is, the probabilities of chain propagation and termination in these reactions were similar, and their ratio, k_p/k_t^M , decreased with temperature.

These structural data emphasize both the advantages and disadvantages of using metallocene catalysts for α -olefin oligomerization as a means of producing raw materials for synthetic lubricating oils. The advantages include a relatively fast, easily sustainable reaction under mild conditions and the virtual absence of high-molecular-weight byproducts (polymers). Another advantage is the structural uniformity of the oligomers. The principal disadvantage is a relatively low-molecular-weight product mix, which is not, as such, suitable as a base stock for synthetic lubricating oils. This problem can be remedied in two ways. The first one is the removal by distillation of the lightest products, dimers and trimers. The remaining mixture has a sufficiently high average molecular weight to be useful as a base stock, and the distilled light oligomers can be converted to products of a higher molecular weight, as described later. The second approach to the utilization of these relatively light oligomer mixtures is focusing their distribution in post-oligomerization reactions, as also described later.

Co-oligomerization of 1-hexene and ethylene

Ionic metallocene catalysts containing alkylated metallocene complexes and cation-forming cocatalysts such as $\text{B}(\text{C}_6\text{F}_5)_3$ are the second important group of catalysts potentially useful for the synthesis of lubricating oils. However, these catalysts are relatively

poorly suited for homo-oligomerization reactions of α -olefins.⁴ For example, when a combination of $\text{Ind}_2\text{ZrMe}_2$ and $\text{B}(\text{C}_6\text{F}_5)_3$ was used to oligomerize 1-hexene at 70°C under conditions similar to those in Table I, the conversion in the reaction (the first line in Table III) was much lower in comparison with the results produced with standard metallocene catalysts using MAO as a cocatalyst (Table I). The viscous properties of this 1-hexene oligomer ($\text{VI} = 127$) were essentially the same as those of the 1-hexene oligomers produced with the $(n\text{-Bu-Cp})_2\text{ZrCl}_2\text{-MAO}$ catalyst. However, when small amounts of ethylene were added to the reaction, the conversion increased, and a small increase in the VI value was also observed. The VI increase effect was more significant when the oligomerization reactions were carried out at 90°C. Potentially, the use of ethylene in such oligomerization reactions has a commercial advantage because of a large difference in the costs of ethylene and higher α -olefins.

Oligomerization of 1-decene

Oligomerization reactions of 1-decene were carried out with the $(n\text{-Bu-Cp})_2\text{ZrCl}_2\text{-MAO}$ catalyst system under the same conditions used for the oligomerization reactions of 1-hexene (Table I). The structure of the oligomers was similar to that of the 1-hexene oligomers, $\text{CH}_2=\text{CR}-(\text{CH}_2-\text{CHR})_{m-2}-\text{CH}_2-\text{CH}_2\text{R}$ with $\text{R} = n\text{-C}_8\text{H}_{17}$, and the vinylidene double bond was again the main chain end in the oligomer molecules (the IR band at 888 cm^{-1}). The catalyst productivity in the 4-h reactions depended on the temperature: it was $3.80 \times 10^5\text{ g/mmol [Zr]}$ at 70°C, $4.67 \times 10^5\text{ g/mmol [Zr]}$ at 80°C, and $2.7\text{--}2.9 \times 10^5\text{ g/mmol [Zr]}$ at 90°C. The conversion of 1-decene in the 4-h experiment at 90°C was 92%. As with the 1-hexene oligomerization reactions, the productivity of the catalyst tended to decrease at high temperatures. The oligomer mixtures prepared at temperatures above 80°C contained over 50 wt % dimers and 15–20% trimers.

TABLE III
1-Hexene/Ethylene Co-Oligomerization Reactions with the $\text{Ind}_2\text{ZrMe}_2\text{-B}(\text{C}_6\text{F}_5)_3$ Catalyst

Temperature (°C)	P_E (kPa)	Conversion (%)	Viscosity at 100°C (cs)	VI
70	0	10	22.3	127
70	7	35	27.8	135
70	69	70	21.7	133
90	69	63	7.8	147
90	138	54	14.1	152

For the experimental conditions, see Table I. An ethylene pressure (P_E) of 70 kPa corresponds to an [ethylene]/[1-hexene] weight ratio of ~ 0.015 .

TABLE IV
Post-Oligomerization of the 1-Hexene Dimer with the Cationic Catalysts

Catalyst	Amount	Temperature (°C)	Conversion (%) ^a	C ₂₄ products (%)	C ₃₆ products (%)
EtAlCl ₂	0.7 mmol/g	55	69	62	~ 7
AlCl ₃	0.06 g/g	25	70	68	~ 2
EtAlCl ₂ /SiO ₂	0.06 g/g	60	89	87	~ 2

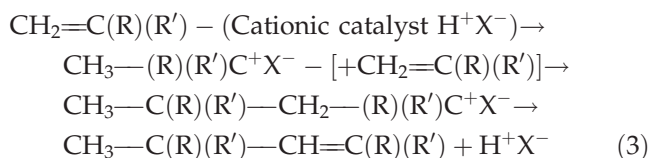
The reactions were performed in oligomer (25 vol %)/*n*-heptane mixtures (5 h).

^a C₁₂ products contained unreacted 1-hexene dimer, products of C=C bond isomerization, and hydrogenated dimer.

Oligomer mixtures produced from 1-decene, as prepared, can be used as base stocks for lubricating oils. Viscosity measurements of the raw mixture prepared with the (*n*-Bu-Cp)₂ZrCl₂-MAO catalyst system at 90°C gave the following results: the kinematic viscosity of the oligomer mixture (containing 30% of the dimer) at 100°C was 7.4 cs, and VI was 170.

Post-dimerization of α -olefin oligomers

The utility of α -olefin oligomers as base stocks of synthetic lubricating oils can be significantly increased by their post-oligomerization. Our ¹³C-NMR and IR data showed that most of the original oligomer molecules were α -olefins containing the vinylidene double bond, CH₂=CR-. Such olefins can be readily oligomerized with a variety of cationic initiators in reactions similar to polymerization reactions of isobutene. When such cationic post-oligomerization reactions are carried out at sufficiently high temperatures, they predominantly produce dimers:



The high stability of tertiary carbocations in cationic oligomerization reactions of vinylidene olefins explains the high degree of chemical regularity of the final products, in contrast to cationic oligomerization reactions of α -olefins with vinyl double bonds, which lead to strongly isomerized products.¹ The post-oligomerization reaction can be applied both to individual oligomers separated by distillation (e.g., to

dimers and trimers of 1-hexene and dimers of 1-decene) and to unfractionated oligomer mixtures.

Cationic post-oligomerization of 1-hexene oligomers

The oligomer mixture of 1-hexene was produced by the reaction of 1-hexene (1 L) with the catalyst system consisting of (*n*-Bu-Cp)₂ZrCl₂ (0.14 mmol Zr) and MAO (28 mmol of Al) at 87°C for 4 h. The yield of 1-hexene oligomers in the experiment was 91%. The reaction products were quenched with ethanol and distilled *in vacuo*.

Three different cationic catalysts were used to oligomerize the separated 1-hexene dimer (mostly 2-butyl-1-octene), EtAlCl₂, AlCl₃, and supported cationic EtAlCl₂/SiO₂ catalyst. The results are shown in Table IV. These data demonstrate that the 1-hexene dimer, an olefin with the vinylidene double bond, was easily converted by the cationic catalysts into heavier products. A detailed GC analysis of the reaction products showed that the dimer's dimer of 1-hexene in all three examples was a mixture of three products with very close boiling points. The yields of the products were in a 0.58 : 0.34 : 0.08 ratio. Their possible structures were CH₃-C(*n*-C₄H₉)(*n*-C₆H₁₃)-CH=C(*n*-C₄H₉)(*n*-C₆H₁₃) (the main product expected in reaction 3) and the products of double-bond isomerization in it.

A mixture of the 1-hexene dimer and the trimer (25% solution in heptane) was also post-oligomerized with two cationic catalysts. The results are shown in Table V. These examples demonstrate the concept of the two-stage process for the preparation of base stocks for synthetic lubricating oils from α -olefins. The first step of the process is oligomerization of the

TABLE V
Post-Oligomerization of a Mixture of the 1-Hexene Dimer and Trimer with Cationic Catalysts

Catalyst	Amount	Temperature (°C)	Total conversion (%)	C ₁₂ → C ₂₄ (%)	C ₁₂ + C ₁₈ → C ₃₀ (%)	C ₁₂ , C ₁₈ → C ₃₆ (%)
EtAlCl ₂ ^a	0.7 mmol/g	55	38	42.5	18.5	8
AlCl ₃ ^b	0.06 g/g	25	77	84	55	45

^a The reaction was performed in oligomer (25 vol %)/*n*-heptane mixtures (7 h).

^b The reaction was performed in oligomer (40 vol %)/*n*-heptane mixtures (6 h).

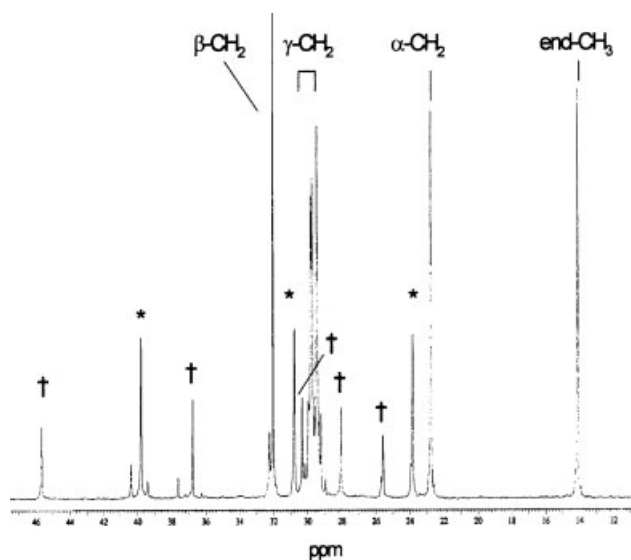


Figure 3 ^{13}C -NMR spectrum of the post-dimerization product of the 1-decene dimer. The signal assignment is discussed in the text.

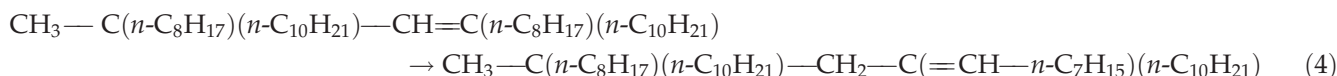
olefins with a metallocene catalyst followed by separation of the lightest products, dimers and trimers, from the heavier oligomer mixtures. The second step is cationic post-oligomerization of the dimers and trimers (or their co-oligomerization) with cationic catalysts. These products can be either combined with

the original heavier olefin oligomers or used separately.

Cationic post-oligomerization of the 1-decene dimer

A neat 1-decene dimer (separated by vacuum distillation from the 1-decene oligomer mixture) was oligomerized with the supported cationic $\text{EtAlCl}_2/\text{SiO}_2$ catalyst (0.025 g/cc) at 60°C for 7 h. The conversion of the C_{20} feed to the C_{40} product was $>75\%$.

The ^{13}C -NMR spectrum of the C_{40} product (isolated by distillation *in vacuo*) is shown in Figure 3. The main signals in the spectrum belong to linear alkyl chains in the product of the formula $\text{CH}_3-\text{C}(n-\text{C}_8\text{H}_{17})(n-\text{C}_{10}\text{H}_{21})-\text{CH}=\text{C}(n-\text{C}_8\text{H}_{17})(n-\text{C}_{10}\text{H}_{21})$. The signal positions are as follows: the end- CH_3 group at 14.1 ppm, the $\alpha\text{-CH}_2$ group $[(\text{CH}_3)\text{CH}_2]$ at 22.8 ppm, the $\beta\text{-CH}_2$ group $[(\text{CH}_3)\text{CH}_2]$ at 32.0 ppm, and the $\gamma\text{-CH}_2$ group $[(\text{C}_2\text{H}_5)\text{CH}_2]$ multiplet at 29.4–29.8 ppm. The signals of the carbon atoms at the double bond (outside of the range of Fig. 3) are at 129.1 (the quaternary C atom) and 137.6 ppm ($=\text{CH}-$). The signals marked with an asterisk in Figure 3 belong to the CH_3 group attached to the quaternary C atom (25.6 ppm) and to $\alpha\text{-CH}_2$ and $\beta\text{-CH}_2$ groups with respect to the $\text{CH}_3\text{-CRR}'\text{-CH}=\text{CRR}'$ moiety. The intrachain isomerization of the double bond, most likely



produces the signal at 128.4 ppm. On the basis of its area, the double-bond isomerization in reaction 4 does not exceed 15%, and the main chain in the dimer's dimer remains intact. The signals marked † in the spectrum are assigned to the hydrogenized analog of the dimer's dimer, $\text{CH}_3-\text{C}(n-\text{C}_8\text{H}_{17})(n-\text{C}_{10}\text{H}_{21})-\text{CH}_2-\text{CH}(n-\text{C}_8\text{H}_{17})(n-\text{C}_{10}\text{H}_{21})$. In particular, the signal of its CH_3- group is at 30.3 ppm, the signals of $\alpha\text{-CH}_2$ and $\beta\text{-CH}_2$ groups attached to its quaternary C atom are at 45.7 and 25.6 ppm, respectively, and the signals of $\alpha\text{-CH}_2$ and $\beta\text{-CH}_2$ groups attached to its CH group are at 36.8 and 28.3 ppm, respectively. IR analysis of the 1-decene dimer's dimer is in agreement with this structure. The dominant band in the spectrum of the original 1-decene dimer, the band of the vinylidene bond at 888 cm^{-1} , disappears from the spectrum and is replaced with a weak broad band at $\sim 860\text{ cm}^{-1}$.

This purified C_{40} product has a kinematic viscosity of 6.4 cs at 100°C and VI of 147. It represents the first example of a single-component base stock for synthetic lubricating oils.

Base stock based on 4-methyl-1-pentene

4-Methyl-1-pentene is an important commercially available α -olefin. 4-Methyl-1-pentene was easily oligomerized with metallocene catalysts under the same conditions used for 1-hexene. As an example, the oligomerization reaction of the neat monomer (100 cc) with $(n\text{-Bu-Cp})_2\text{ZrCl}_2$ (0.75 mmol of Zr) and MAO (9 mmol of Al) at 80°C resulted in $\sim 94\%$ conversion after 4 h. The products contained mostly light oligomers: 70.1 wt % dimer, 15.0 wt % trimer, 7.2 wt % tetramer, 3.8 wt % pentamer, and 1.9 wt % hexamer. On the basis of GC and IR data, the main components of each oligomer were α -olefins with vinylidene double bonds. The oligomer mixture was quenched with ethanol and distilled *in vacuo*; the boiling point of the dimer was 44°C at 0.5 mm, and that of the trimer was 87°C at 0.4 mmHg.

Post-oligomerization of the 4-methyl-1-pentene dimer (2-isobutyl-1,6-methyl-1-heptene) over the cationic $\text{EtAlCl}_2/\text{SiO}_2$ catalyst (0.05 g/cc, 60°C , 8 h) also proceeded easily. The conversion was over 67%, and

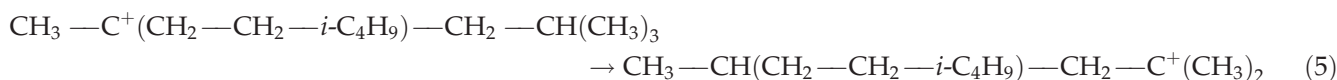
TABLE VI
Relative Reactivities of the Oligomers of 1-Hexene in Post-Oligomerization Reactions with the Cationic Catalysts

	Cationic catalyst			
	AlEtCl ₂ (60°C, 7 h)		AlCl ₃ (25°C, 2 h)	
	Conversion (%)	Reactivity	Conversion (%)	Reactivity
Dimer	80	1 ^a	92	1*
Trimer	61	0.50	79	0.63
Tetramer	52	0.34	73	0.52
Pentamer			63	0.40

^a The reactivity of the dimer was used as a standard.

the products contained 30% of the C₂₄ product (the dimer of the 4-methyl-1-pentene dimer), ~24% of the C₃₆ product, and 13% of the C₄₈ product. However, GC analysis of these products showed that the nature of the cationic oligomers produced from the dimer of 4-methyl-1-pentene was significantly different from that of those derived from the dimer of 1-hexene. The 1-hexene dimer's dimers were structurally uniform and mostly consisted of three olefin molecules with the same skeleton and isomerized double bonds (discussed previously). In contrast, the dimer's dimer derived from 4-methyl-1-pentene and prepared with

the same cationic catalyst was in reality a mixture of 14 products with different boiling points, which were formed with broadly comparable yields. Apparently, the reason for such a broad structural distribution is the presence of tertiary C—H bonds in the molecule of the 4-methyl-1-pentene dimer. Carbocationic growing centers have a tendency to migrate along polymer chains through an intramolecular hydride shift into more thermodynamically stable centers. For example, reaction 5 shows a charge migration in the carbocation of the 4-methyl-1-pentene dimer to the nearest isobutyl group:



Cationic oligomerization of the mixture of the 4-methyl-1-pentene dimer and trimer over the EtAlCl₂/SiO₂ catalyst (60°C, 8 h) also produced numerous products in each of the C₂₄ and C₃₆ ranges.

Focusing the molecular weight distribution of the α -olefin oligomers

As described previously, oligomerization products of α -olefins prepared with metallocene catalysts contain high quantities of light oligomers (dimers, trimers, etc.), which complicate their immediate use as base stocks for synthetic lubricating oils. As described previously, these lightest oligomers can be separated by distillation and post-oligomerized with cationic catalysts into compounds of higher molecular weights. The same approach can be used to focus the molecular weight distributions of the raw oligomer mixtures. Most of these oligomers have the general formula CH₂=CR—(CH₂—CHR)_{*m*-2}—CH₂—CH₂R, where R is the alkyl substituent in the α -olefin used for their synthesis. When such oligomer

mixtures are post-reacted with cationic polymerization catalysts, one may expect the reactivity of the vinylidene double bond in the oligomers to depend on the size and bulkiness of the second alkyl group attached to the double bond (apart from the R group); that is, it may depend on *m*. To verify this assumption, raw mixtures of 1-hexene oligomers with a known molecular weight distribution (similar to that shown in Fig. 2) were post-oligomerized with several cationic catalysts. An internal standard, *n*-nonane, was added to the mixtures before the reactions to measure the consumption of different oligomers. This approach is similar to that used for the estimation of reactivities of different linear α -olefins in their copolymerization reactions with ethylene catalyzed by heterogeneous Ziegler-Natta catalysts.⁷ A relative decrease in the content of each oligomer (with respect to the internal standard) after the second reaction stage was measured by GC and was compared to the conversion of the dimer into the dimer's dimer.

Table VI lists the relative reactivities of oligomers of 1-hexene in the cationic post-oligomerization

reactions. The results show that, as expected, the oligomers of lower molecular weights have higher reactivities in these reactions in comparison with the heavier oligomers. This difference in reactivity provides a means for the selective redistribution of the product composition, in which the lightest oligomers, the original dimers and trimers (components of the least value), can be nearly completely consumed. Their derivatives, C_{24} , C_{36} , and C_{48} products in these examples, mixed with the heavier original oligomers and the products of their post-dimerization, represent suitable base stocks for synthetic lubricating oils.

^{13}C -NMR spectra were recorded by D. D. Haney (Edison Research Laboratory, Mobil Chemical Co.).

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