PATENT SPECIFICATION

NO DRAWINGS

1,023,299

1,023,299

Date of Application and filing Complete Specification May 22, 1964.
No. 21274/64.
Application made in United States of America (No. 283672) on May 28, 1963.
Application made in United States of America (No. 357294) on April 3, 1964.
Complete Specification Published March 23, 1966.

Index at acceptance:—C3 P12; C5 F1

Int. Cl.:—C 08 f//C 10 m

COMPLETE SPECIFICATION

Polymeric Viscosity Index Improvers for Lubricating Oils

We, PRINCETON CHEMICAL RESEARCH INC., a Corporation organised under the laws of the State of New Jersey, United States of America, of P.O. Box 652, Princeton, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to certain hydrocarbon block copolymers which are useful as viscosity index improvers for lubricating oils; to lubricating oils of improved viscosity index containing these polymers, and to a process for improving viscosity characteristics of oils with the polymers.

Ordinary lubricating oils, and particularly petroleum oils which are conventionally used in internal combustion engines generally show a decrease in viscosity with increasing temperatures. If the internal combustion engine or the machinery containing the oil is to be initially started and operated at a low temperature for example in the colder climates or in the winter, it is necessary to use a thinner, lighter weight oil if the oil is to have initial fluidity at the low temperature for starting and initial lubrication. Such oils are commonly available, for example, as winter-grade oil, such as SAE 10 weight or lower. As the engine operates and heats up the oil, these oils become thinner, and at higher operating temperatures the thinner, lighter weight oil may not have sufficient viscosity for optimum lubrication. Furthermore, in warmer weather, such as in summer, the lighter weight oil is not suitable, and it is necessary to change to a heavier weight oil, for example to a 20 or 30 weight oil. This characteristic of oil changing its viscosity with temperature is measured by a value referred to as the "viscosity index".

In order to improve the viscosity index of conventional petroleum lubricating oils and thus obtain an oil, such as the present commercially available multi-grade, for example the 10—30 weight oils, it has been proposed to add to the oil certain oil soluble polymers which act as viscosity index improvers. The efficiency (referred to as "E") of the viscosity index improver is measured as the ratio of the specific viscosity of the oil containing the improver at 210° F to its specific viscosity at 100° F. An "E" value higher than 1 is generally desirable because an oil which has a reduced tendency to thin with increase in temperature is necessary to meet the engine lubrication needs at higher operating temperatures. The viscosity improving efficiency, "E" of commercial products generally ranges from 1.0 to 1.6.

The methacrylate polymers, such as polymethacrylate esters are most commonly commerically used as viscosity index improvers for lubricating oils. Polyisobutylene and polyfumarate esters are also used.

While these viscosity index improvers effectively improve the viscosity index of the lubricating oil and thus overcome the abovementioned problem and allow the marketing of a multi-grade oil which is suitable for all-season use, having an initial viscosity low enough for starting in cold weather and yet sufficient viscosity at higher temperatures, they also have a number of disadvantages, such as high initial cost and tendency to undergo thermal depolymerisation with a resultant limited life.

The invention provides a viscosity index improver for lubricating oil comprising a block copolymer having stereo-regular hydrocarbon polymer blocks insoluble in oil at below 0° C, and amorphous hydrocarbon polymer blocks, the molecular weight of the amorphous blocks preferably being at least

50% of the molecular weight of the stereo-regular blocks, soluble in oil at above −20° C, the copolymer being progressively solvatable in lubricating oil with increasing temperature and completely solvatable below 150° C.

The molecular weights and oil solubility characteristics of the stereo-regular and amorphous blocks specified herein are those that the blocks per se would have as independent unattached polymers.

The viscosity index improvers of the invention have high efficiency, excellent compatability with lubricating oil and its additives, and high thermal stability. They may be produced at a relatively low cost.

The stereo-regular polymer blocks in the copolymers used in the invention are composed of linear polymer chains consisting substantially solely of methylene units and branched chains of methylene units or hydrocarbon rings which are arranged in an orderly spatial distribution to give the polymer its stereo-specific characteristics. Such stereo-regular hydrocarbon polymers as a class are well known as are methods for their preparation by polymerisation.

The stereo-regular polymer blocks in accordance with the invention generally have a collective molecular weight between 1,000 and 1,000,000, preferably between about 50,000 and 1,000,000, as measured by intrinsic viscosity. They are preferably insoluble in lubricating oil at below 20° C. These blocks are preferably completely solvatable below 110° C.

Oil insolubility indicates a solubility of less than 0.1% by weight in an SAE 5w paraffinic stock, and oil solubility indicates a solubility of at least 10% by weight in an SAE 5w paraffinic stock.

Preferably the stereo-regular polymer blocks are isotactic polypropylene and/or polybutene-1 blocks. Other suitable stereo-regular polymer blocks include stereo-specifically polymerised polymers or 4-methylpentene-1, 3-methyl-butene-1, and styrene; copolymers of propylene and butene-1 containing, for example, from 5—30 mol % of butene-1, and preferably from 5—20 mol % of butene-1; stereo-specifically polymerised copolymers of propylene and styrene containing for example 10—40 mol % of styrene and preferably from 15—30 mol % of styrene; stereo-specifically polymerised copolymers of propylene and ethylene containing from 5—25% of ethylene and preferably from 10 to 20 mol % of ethylene; stereo-specifically polymerised copolymers of ethylene and butene-1 containing, for example, 5—30 mol percent of butene-1 and preferably 15—25 mol % butene-1; and isotactic polypentene-1.

The amorphous blocks are simply amorphous hydrocarbon chains collectively having a molecular weight of 1,000 to 1,000,000 and preferably from 50,000 to 1,000,000 which if in the form of a polymer per se would be soluble in lubricating oil at a temperature of −20° C and above, and preferably at a temperature of −30° C and above.

Examples of the amorphous hydrocarbon polymer blocks include copolymers of propylene and butene-1 containing from 30—70 mol % of butene-1, atactic polybutene-1, copolymers of ethylene and butene-1 containing from 40—70 mol % of butene-1, copolymers of propylene and C_5—C_{20} alpha olefins containing from 30—90 mol % of the higher alpha olefins, copolymers of propylene and ethylene containing from 25—70 mol % ethylene and preferably from 30—60 mol % of ethylene, interpolymers of C_5—C_{20} alpha olefins, terpolymers of C_2—C_{20} alpha olefins, copolymers of ethylene and C_5—C_{20} alpha olefins containing from 30—90 mol % of higher olefins, and C_5—C_{20} alpha-olefin homopolymers.

The amorphous hydrocarbon polymer blocks are preferably formed by the co- or interpolymerisation of the monomer or monomers used to form the stereo-regular block with one or more differing alpha-olefins having for example a carbon content between C_2—C_{20}. Alternatively, the amorphous hydrocarbon polymer block may be formed from the same monomer used to form the stereo-regular block under polymerisation conditions which will not produce a stereo-regular polymer, but which will produce the required amorphous oil soluble block.

The block copolymers used in the invention may be produced by known polymerisation techniques. Thus, for example, the stereo-regular block may first be formed by polymerising the monomer, such as butene-1 under conditions which will produce a stereo-regular polymer. After stereo-regular polymer blocks of the desired molecular size have been built, polymerisation is continued under conditions which will allow the polymer chain to continue to grow by polymerisation with the formation of a structure which is amorphous by the addition of further monomer components, under polymerisation conditions which will not form a stereo-regular chain. The initial stereo-specific polymerisation and the continuation thereof with the formation of the amorphous block may be effected in the same reaction zone using the batch method or may be continuously effected in a two-reaction zone with the stereo-regular chain polymer passing into the second reaction zone for the continuation of the polymerisation with the formation of the amorphous block. Preferably, however, the block copolymers are formed from monomer mixtures which will form both the stereo-regular and amorphous blocks. The block copolymers in accordance with the invention may be formed directly from a mixture of monomers by utilising the difference in their respective reactivities. Thus, for example, it is possible to start with a mixture of propylene and butene-1. Isotactic polypropylene will initially form due to its greater reactivity, and thereafter polymerisation of amorphous blocks will occur, with the amounts of the amorphous material progressively increasing without any requirement for temperature adjustment, etc.

Generally, the polymerisation is initially effected to form the stereo-regular block using highly dispersed stereo-specific catalysts, for example the well-known Ziegler catalysts formed from organo metallic compounds, such as aluminium trialkyls or alkyl aluminium halides, and transition metal salts, for example halides or alcoholates. Examples of such catalyst systems include aluminium triethyl, with titanium, or vanadium tetra- or tri-chloride, diethyl-aluminium chloride with titanium or vanadium tetra- or tri-chloride, lithium aluminium tetraethyl with titanium or vanadium tetra- or tri-chloride, and butyl lithium with titanium tetra- or tri-chloride or vanadium tetra- or tri-chloride. The polymerisation is effected in an inert hydrocarbon solvent, for example normal heptane or pentane under inert atmosphere, for example nitrogen at moderate temperatures for example between 30° and 150° C and preferably 80° and 120° C at normal or slightly elevated pressures. The initial monomer, for example, the butene-1 alone or in mixture with the ethylene or propylene, the propylene and styrene, or the propylene and ethylene, is fed into the reactor, for example an autoclave containing the above-described polymer system and the polymerisation allowed to proceed, for example, for a period of ½ to 1 hour and then the polymerisation may be continued under non stereo-specific conditions. When effected in two stages, the second stage may be initiated by adding one or more further alpha olefins and on increasing the temperature, as for example to between 60° and 130° C. Thus, in the second stage, the temperature in the autoclave may be raised to between 105° and 115° C and the butene-1 addition continued in admixture with a further alpha-olefin, as for example ethylene, propylene, a C_5—C_{20} alpha-olefin or mixtures thereof. After the polymerisation reaction is completed with the formation of the amorphous block of the desired molecular size, the reaction is discontinued by cooling and venting the autoclave and the formed polymer recovered and isolated in the conventional manner, as for example by washing with ethylene glycol and water to remove the catalyst residue and precipitating the polymer with methanol or distilling off the solvent leaving the polymer residue.

For continuous operation, the polymerisation may be basically effected in the same manner and under the same conditions with the catalyst solution being continuously pumped in series through two reactor stages with the necessary residence time in each stage, and with each stage being effected under the conditions and with the reactants specified above for the stereo-specific and amorphous polymerisations respectively.

The block copolymers obtained in accordance with the invention are admixed with the conventional lubricating oils in the conventional manner as viscosity index improvers. Thus, the block copolymers may be added to the lubricating oils in amounts of 0.1 to 30% and preferably 0.3 to 10% and most preferably 0.5 to 5% by weight of the lubricating oil. The oils may be of any of the known or conventional lubricating oils for example petroleum lubricating oils of the conventional weights used in internal combustion engines, such as automotive engines. The oil, for example, may have a viscosity so that after the addition of the block copolymer in accordance with the invention, the oil will have an SAE rating of 10w—30. The oil may, of course, contain any of the known and conventional additives, such as the conventional detergents, dispersing aids, pour point depressants, anti-oxidants and known viscosity improvers.

In addition, to use with the conventional petroleum lubricating oils, which, for example, consist of conventional base stocks or base stock blends with or without conventional additives, the block copolymers, in accordance with the invention, may be added to any other liquid hydrocarbons for viscosity index improvement, as for example synthetic lubricating oils, such as Fischer-Tropsch produced oils.

Viscosity index improvers are often marketed as concentrated solutions in the base oil, as for example in concentrations between 10 and 30 and preferably 20 and 30% by weight of the base oil, which is blended with the lubricating oil. The base oil of the concentrate may, for example, be a 100 S.U.S. (Saybolt Universal Second) paraffinic oil. In connection with block copolymers in accordance with the invention containing amorphous hydrocarbon polymer blocks formed from lower alpha olefins, that is alpha-olefins containing up to 4 carbon atoms, the same may tend to unduly thicken the base oil rendering handling of the concentrate difficult.

In accordance with a preferred embodiment of the invention, it has been found that this undue tendency to thicken the base oil of the concentrate may be avoided if the amorphous hydrocarbon polymer blocks are C_2—C_{20} alpha olefin polymer blocks and the block copolymer is formed as a terpolymer additionally containing a component formed from 0.5 to 25 mol % and preferably from 1 to 20 mol % based on the total monomer charged of a higher alpha olefin containing 5—25 and preferably 7—15 carbon atoms. The higher alpha olefin should be present in the polymerisation mixture between complete formation of the block copolymer and should be preferably present during the formation of the isotactic blocks. Examples of higher alpha olefins which may be used include pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, dodecene-1, octadecene-1, and mixtures of alpha-olefins available as fractions, as for example C_5—C_7 fractions, C_7—C_9 fractions, C_9—C_{11} fractions and C_{11}—C_{16} fractions. Branched alpha olefins, such as 3-methyl-butene-1, 4-methyl-pentene-1, *iso*-butylethylene, neopentylethylene, and *iso*-amylethylene may also be used.

It is believed that the alpha olefin in the formation of the terpolymer randomly distributes in or adjacent to the isotactic polymer blocks or in or adjacent to both the isotactic and amorphous polymer blocks. The terpolymer, having the higher alpha olefin component, however, enables the preparation of pourable concentrated oil solutions of the polymer without adversely affecting the efficiency of the polymer as a viscosity index improver.

Preferably the stereoregular blocks have progressively increasing oil solubility with increasing temperature at a rate of between 10 and 60% per 10° C. in between 20° and 100° C. and complete oil solubility at a temperature below 100° C.

It is believed that the block copolymers in accordance with the invention perform their viscosity index improving function by the initial dissolution of the amorphous block in the oil at a lower temperature which holds the entire polymer in solution while actually the stereo-regular block remains substantially unsolvated but progressively is solvated in the oil with a temperature increase causing the desired compensation for the natural decrease in viscosity with increasing temperatures. It is thus believed that the unique oil-solubility characteristics of polypropylene as for example compared to linear polyethylene makes it preferable as the stereo-regular polymer block in accordance with the invention. Other usable stereo-regular polymer blocks, are for example, isotactic polybutene-1 or isotactic polypentene-1, which latter disolves in oil at about 20° C and is completely soluble at 30° C so that the same is not as desirable as isotactic polybutene-1 for normal lubricating oil use, but is a highly desirable component of a block copolymer useful as a viscosity index improver for low temperature applications.

In view of the fact that the block copolymers in accordance with the invention are substantially pure hydrocarbon products, they are completely compatible with the oils and any additive which, in turn, is compatible with the oil itself. Furthermore, the products may be considered ashless as they by conventional catalyst removal techniques, such as alcohol washing, may be reduced to an ash content below 0.1% which is preferable for the use herein. As compared with the conventional viscosity index improvers, as for example, the methacrylate polymers, the polymers in accordance with the invention are highly stable in use, do not undergo thermal depolymerisation and have high shear stability. Furthermore, they may be easily and inexpensivly produced by known polymerisation techniques.

While the block copolymers in accordance with the invention preferably have a number of alternating stereo-regular and oil-soluble segments, it is however also possible to prepare the block copolymers having single, stereo-regular and amorphous blocks and the term "blocks" as used in the claims is intended to include the limiting case a single block of a component.

For the highest viscosity index (V.I.) improving efficiency, the relative length of the oil-soluble block should be the minimum required to hold the polymer in solution at a low temperature, as for example at 0° F. This is dependent, to a degree, on the type of the oil stock in connection with which the improver is being used. In general, the molecular weight of the amorphous hydrocarbon polymer block should be at least 50% of the molecular weight of the stereo-regular block with stereo-regular and amorphous segments of approximate equal length being satisfactory for most purposes.

The following Examples are given by way of illustration and not of limitation:

EXAMPLE 1.

To a one litre autoclave under a dry nitrogen atmosphere was added a solution of 1.9 ml. (15 m. mols) of diethyl aluminium chloride in 350 ml. of *n*-heptane. A titanium trichloride catalyst (1.5 g) containing 1/3 mol of aluminium trichloride per mol of titanium trichloride was then added to the autoclave, and the temperature was adjusted to 50° C. 50 grams of butene-1 was charged to the autoclave, and polymerisation was allowed to continue at that temperature for 45 minutes. 100 grams of a mixture containing 53 mol % propylene and 47 mol % butene-1 was then charged, the reactor was heated to 110° C over a 30 minute period, and was held at that temperature for an additional 30 minutes. The autoclave was then cooled and vented. The viscous solution in the autoclave was removed, washed with ethylene glycol and water to remove catalyst residue and the polymer was isolated by precipitation with methanol. After drying in a vacuum oven, 98 g. of polymer were obtained. The polymer was completely soluble in warm heptane and showed a melt index (190° C, 2160 g load) of 4.0. The specific viscosity of a 0.5% solution of the polymer dissolved in an SAE 20 weight Mid-Continent stock was

1.4 at 100° F and 1.75 at 210° F. Calculation of the ratio gives a V.I. improving efficiency of 1.25. In shear stability tests conducted on 1.0% solutions of the polymer in a naphthenic base stock, the polymer was greatly superior to commercial methacrylate V.I. improvers.

EXAMPLE 2.

The catalyst was the same as that used in Example 1. A mixture containing 18 g. of styrene and 40 g of propylene was added to the autoclave at 60° C. Polymerisation was allowed to proceed for one hour. A small sample of polymer was removed at this point. Infra-red analysis indicated that the polymer contained 16 mol % styrene. 100 grams of an equimolar mixture of propylene and butene-1 was then charged and the temperature was raised to 100° C over a 30 minute period, and was kept at that temperature for an additional 30 minutes. The polymer was worked up as in Example 1. 84 grams of polymer, having a melt index of 11.9, was obtained. A 1% solution of this polymer in a solvent refined SAE 30 weight Mid-Continent stock showed a V.I. improving efficiency of 1.2.

EXAMPLE 3.

To a 1 litre autoclave under a dry nitrogen atmosphere was added a solution of 2.2 ml. (20 m. mols) of titanium tetrachloride in 250 ml. of a straight mineral oil (Texaco (Registerd Trade Mark) Regal Oil B) previously treated with molecular sieves. A solution of 1 ml. (7.5 m. mols) of triethyl aluminium in 100 ml. *n*-heptane was added and the mixture was warmed to 180° C over an hour. The autoclave was then cooled to 50° C and 7.0 ml. (52.5 m. mols) of triethyl aluminium in 50 ml. of mineral oil was added. Butene-1 (50 g.) was charged and polymerisation was allowed to proceed 30 minutes, at which time the pressure dropped from 50 lbs. gauge to atmosphereic pressure. A mixture (100 g.) containing equal molar amounts of propylene and butene-1 was charged, and polymerisation was allowed to continue as the temperature was increased to 100° C over 45 minutes. The autoclave was then cooled and vented. The viscous solution was washed with ethylene glycol and water. The heptane was stripped in vacuo. A viscous residue weighing 368 g. and containing 128 g. of polymer was obtained. Dilution of a sample to 1% concentration in a typical Mid-Continent SAE 10 weight stock gave a solution which showed a viscosity improving efficiency of 1.22.

EXAMPLE 4.

The catalyst was the same as that used in Example 1. 100 g. of butene-1 was charged to the autoclave at 55° C. After 1 hour polymerisation time, the autoclave was vented to remove any unpolymerised butene-1 and 60 g of octene-1 were charged. The temperature was raised to 90° C over 20 minutes, and polymerisation was allowed to continue at that temperature for an additional 40 minutes. The polymer was worked up as in Example 1, and 132 grams of material were obtained. A 1% solution of this polymer in an SAE 10 weight East Texas Neutral stock showed a V.I. improving efficiency of 1.18.

EXAMPLE 5.

Example 1 is repeated, the temperature of the polymerisation being raised to 110° C and the propylene-butene-1 being charged after the initial butene-1 had polymerised to isotactic butene-1 with a molecular weight of about 100,000. The polymerisation at the higher temperature was discontinued when the amorphous copolymer block of propylene and butene-1 had reached a molecular weight between 200,000 and 300,000. A 1% solution of the block copolymer formed acted as a viscosity index improver when used as a 1% solution in a conventional lubricating oil (Texaco (Registered Trade Mark) Regal Oil B).

EXAMPLE 6.

Polymerisation is effected in the manner described in Example 1 using the catalyst system described therein, with however, a mixture of propylene and butene-1 as the monomer containing amounts of propylene ranging between 25—75 mol % propylene. In each case an excellent viscosity index improver for lubricating oil is formed.

EXAMPLE 7.

Example 5 is repeated except that in place of the mixture of propylene and butene-1, a mixture of propylene and ethylene containing about 30—50 mol % of ethylene is introduced in the second polymerisation stage where the polymerisation is effected at the higher temperature.

EXAMPLE 8.

Example 7 is repeated, except in the second stage instead of the propylene-ethylene mixture, an alpha-olefin having an average carbon content between C_6 and C_{20} is used.

EXAMPLE 9.

Example 4 is repeated but in place of the octene-1, a mixture of ethylene and butene-1 containing 40—70 mol % of butene-1 is introduced. The polymerisation is continued until the amorphous ethylene-butene-1 copolymer is built up to a molecular weight of 200,000.

EXAMPLE 10.

Example 9 is repeated except that the polymerisation is continued at the higher temperature of 90° C and with a mixture of propylene and C_5—C_{20} alpha olefins contining about 30—90 mol % of the C_5—C_{20} alpha olefins. The polymerisation of the propylene-higher alpha olefin amorphous block was continued to a molecular weight of 200,000—300,000.

EXAMPLE 11.

Example 1 is repeated but the butene-1 initially charged is mixed with 80—85 mol % of propylene and the polymerisation of the stereo-specific copolymer is continued to a molecular weight of about 100,000. The mixture containing the larger amount of butene-1, that is 47 mol % was then introduced and the polymerisation continued at the higher temperature until the amorphous polymer block reached a molecular weight of 300,000.

EXAMPLE 12.

Example 2 is repeated with the initial stereo-specific polymerisation being effected to a molecular weight of 90,000. Thereafter the polymerisation is continued at the increased temperature of 100° C utilizing propylene and an alpha olefin of an average carbon content of C_5—C_{20} in substantially equal parts. The polymerisation of the amorphous copolymer is discontinued after a molecular weight of 150,000 is achieved.

EXAMPLE 13.

A mixture of propylene and ethylene containing about 10—20 mol percent of ethylene was stereo-specifically polymerised with the catalyst system of Example 1 at a temperature of about 40° C to a molecular weight of about 20,000. Thereafter, the quantity of ethylene in the gas mixture was raised to about 50% and the polymerisation temperature to about 90° C and the polymerisation continued to a total molecular weight of the block copolymer formed of about 250,000, the block copolymer being purified by removal of the solvent and washing in methyl alcohol. It is a good viscosity index improver for lubricating oil.

EXAMPLE 14.

Example 11 is repeated except that ethylene is used in place of the propylene.

EXAMPLE 15.

Example 1 is repeated initially using, however, pentene-1 in place of the butene-1 to form an isotactic polypentene-1 block in place of the isotactic polybutene-1 block. Additionally, in place of the amorphous propylene-butene-1 copolymer block an atactic polybutene-1 block may be formed.

EXAMPLE 16.

To a one gallon autoclave, under a dry nitrogen atmosphere is added a solution of 3.7 ml. (30 m.mols.) of diethyl aluminium chloride in one-litre of heptane. A titanium trichloride catalyst (3.0 g) containing 1/3 mol of aluminium trichloride per mol of titanium trichloride is added and the temperature is raised to 65° C. Sixteen grams of hexene-1 is added followed immediately by 56 g. of butene-1. Polymerisation is allowed to continue for 30 minutes at 65° C. The reactor is then vented and 60 g of a mixture of butene-1 and propylene containing 52 mol % propylene is charged. Polymerisation is allowed to proceed for an additional 60 minutes at 65° C. The autoclave is then emptied and polymer is precipitated from the viscous heptane solution with isopropanol. After drying, 85 grams of polymer are obtained. This polymer, as a 1% solution in a 100 S.U.S. paraffinic oil, exhibits a viscosity index improving efficiency of 1.23, and a 10% solution of the polymer in the same base oil is readily pourable. The hexene-1 constitutes 7.9 mol % of the monomer charge.

EXAMPLE 17.

To a one gallon autoclave was charged a solution of 5.1 ml (40 m. mols) of diethyl aluminium chloride in 2-l. of *n*-heptane. Titanium trichloride (4.0 g) containing 1/3 mol of $AlCl_3$ per mol of $TiCl_3$ was added and the temperature was raised to 75° C. A C_7—C_9 alpha-olefin fraction (50 g) was added followed immediately by 200 g of a butene-1-propylene mixture containing 52 mol % propylene. Polymerisation was allowed to continue two hours, whereupon the pressure in the reactor had dropped to less than 5 psi. The polymer was isolated by conventional techniques. After drying, 163 grams of polymer was obtained. A 1% solution of this polymer in a 100 S.U.S. paraffinic oil showing a viscosity index improving efficiency of 1.28, and a 10% solution of the polymer in the same base stock was readily pourable. The molecular weight of the polymer was estimated to be 800,000 from dilute solution viscosity measurements. The C_7—C_9 alpha-olefin fraction constituted 10 mol % of the monomer charge.

EXAMPLE 18.

To a one gallon autoclave, under a nitrogen atmosphere, was added 2 litres of heptane containing 3.0 g of $TiCl_3$ containing 1/3 mol of $AlCl_3$ per mol of $TiCl_3$ and 3.75 ml. of diethyl aluminium chloride. The reactor was closed and the temperature was raised to 60° C. 4-methyl-pentene-1 was then pumped into the reactor at a rate of 5 g/minute, and butene-1 was pumped into the reactor at a rate of 2 g/minute. After 20 minutes, the addition of 4-methyl pentene-1 was terminated. The addition of butene-1 was allowed to continue for a total of 50 minutes. After an additional hour of polymerisation, the reaction was terminated by the addition of methanol. After isolating and drying in the conventional manner, 71 g. of a block copolymer (4-Methyl-Pentene-1-Butene-1 Copolymer) having a molecular weight of 900,000 was obtained.

A 1% solution of this polymer in a 100 S.U.S. neutral paraffinc oil after standing three days showed a viscosity index improving efficiency of 1.99.

EXAMPLE 19.

Example 18 was repeated, using styrene in place of 4-methyl-pentene-1. The reaction was carried out at 80° C. After 2 hours, 45 g. of a block copolymer (Styrene-Butene-1 Copolymer) was obtained which showed a viscosity index improving efficiency of 1.4 when measured at the conventional temperatures of 100° F and 210° F. When the viscosity index improving efficiency was calculated from measurements made at 100° F and 250° F, the efficiency was 1.8, indicating that this copolymer is suitable for use at temperatures higher than those normally encountered in automobile engines.

WHAT WE CLAIM IS:—

1. A viscosity index improver for lubricating oil comprising a block copolymer having stereo-regular hydrocarbon polymer blocks, insoluble in oil at below 0° C, and amorphous hydrocarobn polymer blocks soluble in oil at above −20° C, the copolymer being progressively solvatable in lubricating oil with increasing temperature and completely solvatable below 150° C.

2. A viscosity index improver according to claim 1, in which the molecular weight of the amorphous blocks is at least 50% of that of the stereo-regular blocks.

3. A viscosity index improver according to claim 1 or claim 2, in which said stereo-regular hydrocarbon polymer blocks have a collective molecular weight between 50,000 and 1,000,000, are insoluble in lubricating oil at below 20° C, and completely solvatable in lubricating oil at below 110° C.

4. A viscosity index improver according to claim 1, claim 2 or claim 3 in which the amorphous hydrocarbon polymer blocks have a collective molecular weight between 50,000 and 1,000,000 and are soluble in lubricating oil at above −30° C.

5. A viscosity index improver according to any one of the preceding claims in which the amorphous hydrocarbon polymer blocks are C_3—C_{20} alpha-olefin polymer blocks and in which the block copolymer is a terpolymer additionally containing a component formed from 0.5 to 25 mol %, based on the total monomer charged, of an alpha olefin having 5 to 25 carbon atoms.

6. A viscosity index improver according to any one of the preceding claims in which the stereo-regular hydrocarbon polymer blocks consist of isotactic polybutene-1, isotactic polypropylene, isotactic poly - 4 - methyl-pentene-1, isotactic poly-3-methyl-butene-1, isotactic polystyrene, propylene-butene-1 copolymers, propylene-styrene copolymers propylene-ethylene copolymers, ethylene butene-1 copolymers or isotactic polypentene-1, and in which the amorphous hydrocarbon polymer blocks consist of a polymer of at least one alpha olefin having from 2 to 20 carbon atoms.

7. A viscosity index improver according to any one of the preceding claims in which the amorphous hydrocarbon polymer blocks are C_2—C_{20} alpha olefin polymer blocks and in which the block copolymer is a terpolymer additionally containing a component formed from 1 to 20 mol %, based on the total monomer charged, of an alpha olefin having 7 to 15 carbon atoms.

8. A viscosity index improver according to any one of the preceding claims in which said stereo-regular hydrocarbon polymer blocks have progressively increasing oil solubility with increasing temperature at a rate of between 10 and 60% per 10 degrees C. in between 20 and 100° C and complete oil solubility at a temperature below 100° C.

9. A viscosity index improver prepared substantially as hereinbefore described in any of the Examples.

10. A lubricating oil containing from 0.1 to 30% by weight based on the oil of a viscosity index improver according to any one of the preceding claims.

11. A method for improving the viscosity index of lubricating oil which comprises admixing with the lubricating oil 0.1 to 30% by weight, based on the oil of a viscosity index improver according to any of claims 1 to 9.

12. A method for improving the viscosity index of lubricating oil substantially as hereinbefore described in any one of the Examples.

13. Lubricating oil modified by the method of claim 11 or claim 12.

ERIC POTTER AND CLARKSON
Chartered Patent Agents
317 High Holborn,
London, W.C.1.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1966.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.