P/00/008b 12/11/91
Section 29 (1)
Regulation 3.1 (2)

AUSTRALIA

Patents Act 1990

NOTICE OF ENTITLEMENT

(To be filed before acceptance)

We, **EXXON CHEMICAL PATENTS INC.**, of 1900 East Linden Avenue, Linden, New Jersey 07036, United States of America, being the applicant in respect of Application No. 15864/92 state the following:-

The Person nominated for the grant of the patent has entitlement from the actual inventors by assignment.

The person nominated for the grant of the patent has entitlement from the applicant of the application listed in the declaration under Article 8 of the PCT by assignment.

The basic application listed on the request form is the first application made in a Convention country in respect of the invention.

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

.... DATED 27 September 1994

Darryl B. Mischlewski
Registered Patent Attorney

AU9215864

(12) PATENT ABRIDGMENT (11) Document No. AU-B-15864/92
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 657319

(54) Title
IMPROVED VISCOSITY MODIFIER POLYBUTADIENE POLYMERS

International Patent Classification(s)
(51)[5] C08F 008/04 C10M 143/12

(21) Application No. : 15864/92 (22) Application Date : 06.03.92

(87) PCT Publication Number : WO92/16568

(30) Priority Data

(31) Number (32) Date (33) Country
670114 15.03.91 US UNITED STATES OF AMERICA

(43) Publication Date : 21.10.92

(44) Publication Date of Accepted Application : 09.03.95

(71) Applicant(s)
EXXON CHEMICAL PATENTS INC.

(72) Inventor(s)
MARK JOSEPH STRUGLINSKI; GARY WILLIAM VERSTRATE; LEWIS JOHN FETTERS

(74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122

(56) Prior Art Documents
AU 16834/92 C08F 8/04
US 5002676
EP 318848

(57) Claim

1. A polybutadiene block copolymer comprising polymerization products derived from monomeric units of 1,4-butadiene and 1,2-butadiene, the copolymer being hydrogenated and comprising at least 10 percent by weight of at least one crystallizable segment comprised of methylene units and having an average methylene content corresponding to a 1,4-polybutadiene content of at least about 20 mole percent, and more than one low crystallinity segment comprised of methylene units and substituted methylene units and having an average 1,4-polybutadiene content up to about 20 mole percent.

OPI DATE 21/10/92 APPLN. ID 15864 / 92

AOJP DATE 26/11/92 PCT NUMBER PCT/US92/01937

RATION TREATY (PCT)

(51) International Patent Classification 5 : C08F 8/04, C10M 143/12

A1

(11) International Publication Number: WO 92/16568

(43) International Publication Date: 1 October 1992 (01.10.92)

(21) International Application Number: PCT/US92/01937

(22) International Filing Date: 6 March 1992 (06.03.92)

(30) Priority data:
670,114 15 March 1991 (15.03.91) US

(71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US).

(72) Inventors: STRUGLINSKI, Mark, Joseph ; 379 Rolling Knolls Way, Bridgewater, NJ 08807 (US). VERSTRATE, Gary, William ; 28 Bayside Drive, Atlantic Higlands, NJ 07716 (US). FETTERS, Lewis, John ; 8 Bedford Court, Annandale, NJ 08801 (US).

(74) Agent: MAGGIO, Robert, A.; Exxon Chemical Company, P.O. Box 710, Linden, NJ 07036 (US).

(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent).

Published

With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

657319

(54) Title: IMPROVED VISCOSITY MODIFIER POLYBUTADIENE POLYMERS

(57) Abstract

The present invention relates to hydrogenated polybutadiene comprising monomeric units of 1,4-butadiene and 1,2-butadiene addition products. The copolymer is hydrogenated and comprises at least 10 % by weight of at least one crystallizable segment and at least one low crystallinity segment.

IMPROVED VISCOSITY MODIFIER POLYBUTADIENE POLYMERS

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to hydrogenated polybutadiene comprising monomeric units of 1,4-butadiene and 1,2-butadiene addition products. More particularly, it relates to polybutadiene comprising hydrogenated blocks or segments of monomeric units of 1,2-butadiene and 1,4-butadiene addition products containing at least one crystallizable segment or block comprising an average of at least about 10 weight percent of the total hydrogenated copolymer chain, and at least one low crystallinity segment or block. The instant invention also relates to oleaginous compositions containing said copolymers as viscosity index improver additives, a process for making these copolymers and a method to control the viscosity of oleaginous compositions.

DESCRIPTION OF RELATED ART

Various copolymers of butadiene with other olefins are known to be used as oil additives. These include hydrogenated copolymers of butadiene with another conjugated diene such as isoprene. The copolymers are disclosed to be random or block copolymers. The following review of the related art illustrates attempts which have been made to develop hydrogenated butadiene base copolymers for use as an oil additive including a viscosity modifier.

U. S. Patent No. 4,804,794 discloses segmented copolymers of ethylene and at least one other α-olefin monomer. Each copolymer is intramolecularly heterogeneous and intramolecularly homogeneous. At least one segment of the copolymer constituting at least 10% of the copolymer chain, is a crystallizable segment. The remaining segments of the copolymer chain are termed low crystallinity segments, and are characterized by an ethylene content of not greater than about 53 weight percent.

The α-olefin can include those containing 3 to 18 carbon atoms. α-olefins having 3 to 6 carbon atoms are indicated to be preferred. With the most preferred copolymers being copolymers of ethylene with propylene or ethylene with propylene and diene. The copolymers are disclosed to improve the properties in oleaginous fluids, in particular lubricating oil.

U. S. Patent No. 3,419,365 discloses hydrogenated copolymers of butadiene and styrene as pour point depressants for distillate fuel oil; U. S. Patent No. 3,393,057 discloses polymers of butadiene C10 to C24 normal alpha-monoolefins and styrene or indene as pour point depressants for fuel and lubricating oils; and U. S. Patent No. 3,635,685 discloses pour point depressants comprising hydrogenated butadiene-styrene copolymers which contain a hydroxy, carboxy, or pyridyl terminal group.

U. S. Patent No. 3,312,621 discloses polymers of conjugated diolefins which are predominantly in the 1,4-addition configuration, as viscosity index (V.I.) improvers. Butadiene, isoprene, 1,3-pentadiene, and copolymers of such diolefins are specifically disclosed as suitable.

U. S. Patent No. 3,600,311 discloses viscosity index improvers of hydrogenated homopolymers of butadiene in which about 45 to 95 % of the butadiene monomers are in the 1,4-configuration.

U. S. Patent No. 3,795,615 discloses viscosity index improvers of hydrogenated copolymers of butadiene with a different conjugated diene, e.g., isoprene in which the monomer units in the polymer are predominantly in the 1,4-configuration. This patent discloses that hydrogenated 1,4-polybutadiene is not useful as a viscosity index improver, since the final product is an oil-insoluble polyethylene. Hydrogenated polybutadienes with an appropriate amount of 1,2-structure would give the necessary solubility and would have viscosity index improving properties. However, this references teaches that it is necessary to very precisely control the amount of 1,2-structure formed. If an inadequate amount of 1,2-structure is formed, the polymer is not sufficiently soluble; if too much 1,2-structure is formed, the polymer is not as effective in increasing the viscosity index. The patent further discloses that when polybutadiene is anionically polymerized to the high degree of polymerization needed for viscosity index improvers , it is very difficult to obtain precise control of the amount of 1,2-addition product by variations in reaction conditions.

U. S. Patent No. 3,965,019 discloses hydrogenated random, tapered or block copolymers of butadiene and isoprene to be useful as viscosity modifiers.

U. S. Patent No. 4,032,459 discloses a viscosity index improver comprising a copolymer of butadiene and isoprene having between 20-55% 1,4-configuration, this polymer then having been hydrogenated to remove substantially all of the olefinic unsaturation.

U. S. Patent No. 4,073,737 discloses viscosity index improver comprised of a hydrogenated copolymer produced by copolymerization of from about 1 to about 10 mole percent butadiene, at least one other C5 to C12 conjugated diene, and up to 45 mole percent of a vinyl aromatic monomer.

A useful class of viscosity index improvers for lube oil compositions are star-shaped polymers comprising a nucleus such as divinylbenzene with polymeric arms linked to it. Such polymers are disclosed in patents, such as U. S. Patent No. 4,358,565 and 4,620,048. Generally star-shaped polymers are disclosed to be formed by polymerizing one or more conjugated dienes and optionally, one or more monoalkenylarene compound in solution in the presence of an ionic initiator to form a living polymer. For the purpose of the present invention the term "living polymer" is used consistent with Billmeyer, Textbook of Polymer Science, 2d Ed., page 348, Wiley-Interscience, John Wiley and Sons, page 318 (1971). Specific conjugated dienes include conjugated dienes having 4 to 12 carbon atoms and optionally, one or more monoalkenylarene compounds. Typical and useful conjugated dienes include butadiene (1,3-butadiene) and isoprene. The living polymers thereby produced are then reacted with a polyalkenyl coupling agent to form star-shaped polymers. The coupling agents have at least two non-conjugated alkenyl groups. The groups are usually attached to the same or different electron drawing groups, e.g., an aromatic nucleus. Such compounds have the property that at least two of the alkenyl groups are capable of independent reaction with different living polymers, and in this respect, are different from conventional dienes polymerizable monomers, such as butadiene and isoprene. The coupling agents may be aliphatic, aromatic or heterocyclic. Examples of aliphatic compounds include polyvinyl and polyallyl acetylenes, diacetylenes, phosphates, and phosphites, as well as the dimethacrylates, e.g., ethyl dimethacrylate. Examples of suitable heterocyclic compounds include divinyl pyridine and divinyl thiophene. Coupling agents disclosed to be preferred in the U. S. Patent No. 4,358,565 patent are polyalkenyl aromatic compounds with the most preferred being indicated to be polyvinyl aromatic compounds. Examples of such compounds include those aromatic compounds, e.g., benzene, toluene, xylene, anthracene, naphthalene, and durene which are substituted by at least two alkenyl groups, preferably directly attached thereto. Specific examples include polyvinyl benzenes, e.g., divinyl, trivinyl, and tetravinyl benzenes; divinyl, trivinyl and tetravinyl, ortho ~~autho~~, meta and para-xylenes, divinyl naphthalene, divinyl ethyl benzene, divinyl biphenyl, diisobutenyl benzene, diisopropanol benzene, and diisopropanol biphenyl. The polyalkenyl coupling agent should be added to the living polymer after the polymerization of the monomers is substantially complete, i.e., the agent should only be added after substantially all of the monomer has been converted to living polymer.

The amount of polyalkenyl coupling agent added may vary, but preferably, at least 0.5 moles is used per mole of unsaturated living polymer. Amounts from 1 to 15 moles, and preferably 1.5 to 5 moles are preferred.

There exists a need for viscosity index improvers which, when added to oleaginous compositions, such as lube oil compositions, yield compositions exhibiting better or improved low temperature viscometric characteristics than are obtainable by the use of conventional viscosity index improver additives. The copolymers of the instant invention provide oleaginous compositions exhibiting such improved low temperature viscometric characteristics, and additionally, improved shear stability.

For convenience, certain terms that are repeated throughout the present specification and claims are defined below.

a. Viscosity Index (V.I.) is the ability of a lubricating oil to accommodate increase in temperature with a minimum decrease in viscosity. The greater this ability, the higher the V.I.

b. A block copolymer is a copolymer having at least one sequence (also referred to as block or segment) of the same monomer units. Each sequence has at least two monomer units. Block copolymers typically have a plurality of each type of monomer making up the copolymer. The terms relating to block copolymer are consistent with those given in Billmeyer, Jr., <u>Textbook of Polymer Science, Second Edition</u>, Wiley-Interscience (1971). For the purpose of the present invention the term block or segmented copolymer includes a copolymer comprising monomeric units of 1,2-butadiene and 1,4-butadiene.

c. Average methylene content of a segment of the hydrogenated copolymer is the average number of methylene moieties or units present in the segment. The methylene units are those present in the particular segment as a result of the polymerization and hydrogenation of butadiene and at least one other conjugated diene, such as isoprene. Thus, for example, the hydrogenation product of the 1,4-addition product of two 1,4-butadiene molecules contains one methylene segment comprised of eight methylene units and has a methylene content of 100%, i.e., $-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2$. The hydrogenation product of the 1,2-addition product of 1,2-butadiene contains one methylene units alternating with an ethylene substituted methylene unit, i.e.,

$$-CH_2-\underset{}{\overset{C_2H_5}{\overset{|}{CH}}}-CH_2-\overset{C_2H_5}{\overset{|}{CH}}-CH_2-\overset{C_2H_5}{\overset{|}{CH}}-$$

The following defines how percent methylene units are calculated from the percentages of hydrogenated 1,2 and 1,4 polybutadiene in the polymer. Each enchained 1,4-butadiene ($B_{1,4}$) unit contributes four methylenes. Each 1,2-butadiene contributes one methylene and one substituted methylene. Where B represents the mole fraction 1,4-butadiene then (1-B) is the fraction 1,2-butadiene. The mole fraction methylenes present, X_{CH_2} is then

$$X_{CH_2} = \frac{3\ B_{1,4} + 1}{2\ B_{1,4} + 2} \qquad (1)$$

where $B_{1,4}$ is the fraction of 1,4-addition of butadiene. For $B_{1,4} = 1$, $X_{CH_2} = 1$. For all 1,2-addition $X_{CH_2} = 0.5$, but there can be no long methylene sequences.

To obtain crystallizable sequences there must be sequences of 1,4 enchained units. For random addition of 1,2-butadiene and 1,4-butadiene units $B_{1,4}$ is approximately 0.3 or 30 percent to obtain crystallinity. From formula (1) X_{CH_2} = .73 at $B_{1,4}$ = .3. In principle, if the statistical distribution of 1,2 and 1,4-butadiene additions is of a block type, rather than random crystallinity could occur at $B_{1,4}$ below .3.

In all cases where sequences of methylenes are long enough to crystallize at least two adjacent hydrogenated 1,4-butadiene units are present, and generally 3 or more are present. In such cases, methylenes from 1,2-butadiene becomes less important for crystallization since they add only one or two units to an 8 to 12 unit sequence. For purposes of the present invention the composition of crystallizable segments is in terms of 1,4-butadiene content, i.e, only those methylene segments contributed by 1,4-butadiene units are counted

d. By "crystallize" it is meant that the methylene sequences in the polymer associate into ordered state consistent with the classical definition of polymer crystallinity as set forth, for example, by Flory, Principles of Polymer Chemistry, Cornell University Press (1953).

e. Crystallizable units are defined as methylene groups in sequence which exhibit a heat of fusion when measured by differential scanning calorimetry (DSC) upon cooling from the melt. In a procedure useful for the present invention a sample can be formed into an approximately 0.030 inch thick sheet for 30 minutes at 150°C and then annealed at 20°C for 48 hours prior to measurement, loaded into the calorimeter at that temperature, rapidly cooled to -100°C and scanned to 150°C at 20°C/minute. Only sequences melting between 20°C and 140°C are included.

f. The weight percent crystallizable units is:

$$\frac{\underline{\text{Heat of fusion measured cal/gm}}}{69\ \text{cal/gm}} \cdot 100\%$$

On this basis pure melt crystallized polymethylene of high Mw (i.e., where the end groups effects are not significant; typically greater equal or about 20,000) has about 60% crystallizable units. Kinetic restrictions prevent them from all crystallizing. Percent crystallinity can be measured by a techniques, as defined in G. Ver Strate, Z. W. Wilchinsky, J. Pol. Sci. Physics, A2, 9, 127 (1971), which is incorporated herein by reference. The degree of crystallinity measured is a function of the sample's annealing history. Some low amount is desirable in this product when the sample is annealed at 20°C. for more than 48 hours after preparation of a void-free, strain-free specimen by heating to 150°C. for 30 minutes in a suitable mold. Crystallizability also depends on other factors: temperature, diluent, and the composition of the copolymer.

g. The association temperature (T_a), is the temperature at which crystallization of the copolymer of the present invention can be determined by studying the temperature dependance of the relative viscosity (ηrel). Deviation from an established ($d\eta$rel/dT) trend occurs when significant association at polymer segments due to crystallinity starts. (ASTM method D-445 for kinematic viscosity can be run at a series of temperatures. The polymer concentration in these measurements should be the same as that in the formulated oil, for example, 1%).

h. The cloud point temperature is the temperature (T_c) at which crystalline clouds (turbidity) are first observable upon cooling of oil when tested according to ASTM D-2500. The cloud point temperature can be correlated with the association temperature.

i. A crystallizable segment of the hydrogenated copolymer chain is rich in methylene units, with an average methylene content of at least about 75 mole percent. The methylene content depends on the monomers used to prepare the polymer and the nature of their inclusion in the polymer. The methylene units will crystallize at a given temperature and concentration in solution only if they are in long enough sequences, with only a limited number of interruptions due to substituted methylene units. More interruptions are acceptable with methyl substitutions than with larger groups since methyl groups can enter the polymethylene crystal lattice. Methylene units can be identified by C_{13} NMR, T. Hayashi, Y. Iroue, R. Chujo, Macromolecules, 21, 3139, 1988, and references therein. Sequences of 5 or more cannot be distinguished. However units are actually crystallizable only if they are present in sequences of about 13 methylenes or longer.

j. A low crystallinity segment has an average methylene content less than about 75 mole percent, and is characterized in the unoriented bulk state after at least 24 hours annealing by a degree of crystallinity of less than about 0.2% at 23°C.

k. Molecular weights of the hydrogenated copolymer were measured by a combination of gel permeation chromatography and on line laser light scattering and described in G. Ver Strate, C. Cozewith, S. Ju, Macromolecules, 21, 3360, 1989. The specific refractive index increment in trichlorobenzene at 135°C. was assumed to be -0.104 M^3/kg (-0.104 cc/g) for all hydrocarbon structures.

SUMMARY OF THE INVENTION

The present invention is directed to a hydrogenated block copolymer, a process to make the copolymer, compositions containing the copolymer and methods to use the copolymer.

The block copolymer of the present invention comprises a hydrogenated polybutadiene block copolymer comprising polymerization products derived from monomeric units of 1,4-butadiene and 1,2-butadiene. The copolymer is hydrogenated and comprises at least 10 weight percent by weight of at least one crystallizable segment comprised of methylene units. Correspondingly, the crystallizable segment has an average 1,4-polybutadiene content of at least about 20 mole percent and preferably at least 30 mole percent. The block copolymer has more than one low crystallinity segment comprised of methylene units and substituted methylene units and has an average 1,4-polybutadiene content of up to 20 mole percent and preferably less than 10 mole percent. Preferably, 1,4-butadiene and 1,2-butadiene units are present in amounts effective to provide at least one crystallizable segment and at least one low crystallinity segment. A preferred block copolymer is where the copolymer is in star copolymer form having from 4 to 25 and preferably 5 to 15 arms.

Preferably, the crystallizable segments have a number average molecular weight of at least 500. The average 1,4-polybutadiene content is at least 20 mole percent and preferably at least 50 percent of the methylene units are connected in series of at least 13 adjacent methylene units in length. The remaining segments of the copolymer chain are the low crystallinity segments preferably having an average 1,4-polybutadiene content of ~~less than~~ up to about 20 mole percent.

The present invention includes compositions comprising oleaginous compounds and the above recited hydrogenated block copolymer. Preferably the oleaginous component is an oil composition comprising oil, such as lubricating oil. Typically, the oleaginous composition comprises from 0.1 to 50, preferably from 0.05 to 25 percent by weight of the hydrogenated copolymer of the present invention. Preferred compositions of the present invention comprise copolymer as recited above having an ~~crystallization~~ association temperature (T_a) and oil having a cloud point temperature (T_c), where (T_a) is greater than (T_c). The lubricating oil compositions can contain additional additives, such as other viscosity modifiers, ashless dispersants, antioxidants, corrosion inhibitors, detergents, pour point depressants, anti-wear agents, and the like.

The copolymers have been found to impart excellent low temperature viscometric properties to oleaginous fluids, particularly lubricating oils. The compositions have satisfactory viscosities at room temperatures and at higher temperatures. The compositions of the present invention are useful for typical lubricating oil compositions such as automatic transmission fluids, heavy duty oil suitable for use in crankcases of gasoline and diesel engines, and any machinery containing gears and power transmitting ur

The present invention additionally comprises a process to make the hydrogenated block copolymer recited above. The process comprises the steps of polymerizing a precursor block copolymer comprising at least one segment comprising at least 20 percent by mole of monomeric units of 1,4-butadiene, and at least one comonomer segment comprising comonomer units of 1,2-butadiene. The process further comprises substantially hydrogenating the precursor copolymer to form the above recited hydrogenated block copolymer. The process is preferably an anionic polymerization. In forming the precursor block copolymer the polymerization process preferably takes either of two approaches. The first is to first control the polymerization to form 1,4-butadiene segments, and then control the polymerization to form comonomer segments comprising at least 70, and preferably at least 75, and more preferably at least 80 mole percent of 1,2-butadiene monomeric units. Alternatively, the comonomer can first be polymerized to form comonomer segments comprising at least 70, preferably at least 75, and more preferably at least 80 mole percent of 1,2-butadiene monomeric units. The polymerization is then controlled to form 1,4-butadiene segments. Upon completion of the polymerization of the 1,4-butadiene additional comonomer can be added and the polymerization then controlled to form comonomer segments comprising at least 75 mole percent of 1,2-butadiene monomeric units.

The present invention also relates to the process of modifying the viscosity of an oleaginous composition, having a cloud point temperature (T_c) when tested according to ASTM D-2500, comprising the step of :

adding to the oleaginous composition, a sufficient amount of at least one polybutadiene block copolymer comprising monomeric units derived from 1,4-butadiene and 1,2-butadiene polymerization products, the copolymer being hydrogenated and comprising at least 10 percent by weight of at least one crystallizable segment comprised of methylene units and having an average methylene content corresponding to a 1,4-polybutadiene content of at least about 20 mole percent, and more than one low crystallinity segment comprised of methylene units and substituted methylene units and having an average methylene content corresponding to a 1,4-polybutadiene content up to about 20 mole percent, wherein the hydrogenated block copolymer has an associated temperature (T_a) which is greater than T_c.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to hydrogenated block copolymers based on butadiene comprising monomeric units derived from 1,4-butadiene and 1,2-butadiene addition products. The copolymer contains at least one crystallizable segment or block and more than ~~at least~~ one low crystallinity segment or block. The hydrogenated copolymers are made by the controlled polymerization of butadiene, preferably by addition polymerization. The polymerization results in a precursor block copolymer comprising at least one 1,4-butadiene segment and at least one comonomer segment comprising comonomer units derived 1,2-butadiene, the copolymer comprising at least 10 percent by weight of the 1,4-butadiene segments. The precursor copolymer is then hydrogenated to substantially saturate the olefinic bonds and to form a hydrogenated copolymer containing at least one crystallizable segment and at least one low crystallinity segment. The crystallizable segment comprises at least an average of about 10 weight percent of the hydrogenated copolymer chain and contains an average 1,4-polybutadiene content of at least about 20 mole percent, preferably at least about 30 mole percent. An adequate amount of the methylene units are joined in sequences preferably containing at least about 13 methylene units to permit crystallization.

The low crystallinity segment has an average 1,4-polybutadiene content of less than 30 mole percent, preferably less than about 20 mole percent, and rich in substituted methylene units. The low-crystallinity segment correspondingly preferably contains an average of at least about 22 mole percent, more preferably at least about 24 mole percent substituted methylene units. The substituted methylene units from the 1,2-butadiene are represented by the formula

$$\begin{array}{c} R \\ | \\ -\ CH\ - \end{array}$$

wherein R is an ethyl group.

The low crystallinity segment can contain, in addition to the hydrogenated 1,2-addition butadiene comonomer, hydrogenated 1,4-addition butadiene and minor amounts, i.e., from 0 to 5 mole percent, of other conjugated diene polymerization products. Such other conjugated dienes include those having from 5 to 24 carbon atoms. Thus, for example, the low crystallinity segment may contain the hydrogenated polymerization products of 1,2-butadiene, i.e., poly-1,2-butadiene, 1,4-butadiene, i.e., hydrogenated poly-1,4-butadiene, and isoprene, i.e., hydrogenated polyisoprene.

The copolymer may also optimally contain up to 5 mole percent of the hydrogenated polymerization product of other monomers such as, for example, monovinyl arenes such as styrene or substituted styrene methacrylates, vinyl pyridines or other anionically polymerizable monomers.

The size of the crystallizable segment which is present in the hydrogenated copolymer is in general dependent upon the relative amounts of 1,4-butadiene present in the precursor polymer. The crystallizable segment comprises at least about 10 weight percent, preferably from about 10 to about 90 weight percent, more preferably from about 20 to about 85 weight percent, and most preferably from about 40 to 65 weight percent of the total hydrogenated copolymer chain. Correspondingly, the precursor copolymer contains at least about 10 weight percent, preferably at least about 20 weight percent (e.g., from about 25 to about 60), and more preferably at least about 35 weight percent of 1,2-butadiene. Generally, the greater the amount of 1,4-butadiene present in the precursor copolymer, the larger the crystallizable segment in the hydrogenated copolymer.

In order to attain the preferred hydrogenated copolymer comprising copolymer chains containing at least one crystallizable segment comprised of methylene units and at least one low crystallinity segment comprised of methylene units and methylene units substituted with ethyl groups, the polymerization of the butadiene is controlled to control the amount of 1,2-butadiene which forms.

Not all of the 1,4-butadiene present in the precursor copolymer forms (upon hydrogenation) the crystallizable segment. Some of the hydrogenated 1,4-butadiene may be present in the low crystallinity segment. Thus, for example, the low crystallinity segment may comprise the hydrogenation products of 1,4-addition butadiene, and 1,2-addition butadiene.

The crystallizable segment can also contain some of the hydrogenation product of 1,2-butadiene, provided the amounts of those other hydrogenated moieties are insufficient to lower the average 1,4-polybutadiene content of the crystallizable segment below about 20 mole percent.

The copolymers are preferably produced by anionic polymerization followed by hydrogenation. ~~The hydro-~~

~~genated reaction products of 1,4-butadiene and 1,2-~~ of butadiene, ~~The~~ wherein the 1,4-configuration species predominate. The 1,2-addition of butadiene will yield a recurring structure represented by the formula

$$-\!\!\left(CH_2 - \underset{\substack{| \\ CH \\ \| \\ CH_2}}{CH}\right)\!\!-.$$

Hydrogenation of this structure results in a structure represented by the formula

$$-\!\!\left(CH_2 - \underset{\substack{| \\ CH_2 \\ | \\ CH_3}}{CH}\right)\!\!-.$$

Therefore, a hydrogenated copolymer of butadiene contains the following species:

$$-\!\!\left(CH_2 - CH_2 - CH_2 - CH_2\right)\!\!-$$

obtained from the hydrogenation of 1,4-butadiene; and

$$-\!\!\left(CH_2 - \underset{\substack{| \\ CH_2 \\ | \\ CH_3}}{CH}\right)\!\!-$$

obtained from the hydrogenation of 1,2-addition butadiene.

The recurring structural units other than those obtained by the hydrogenation of the 1,4-addition and 1,2-addition of butadiene may be present in both the crystallizable and low crystallinity segment. If they are present in the crystallizable segment, however, they are present in amounts which are insufficient to affect the crystallizable characteristics of said segment.

The crystallizable segments or blocks present in the hydrogenated copolymer are comprised predominantly of methylene units which are, inter alia, provided by the hydrogenation of the 1,4-butadiene present in the precursor copolymer. Thus, polymerizing butadiene monomer, i.e., $CH_2 = CH - CH = CH_2$, by 1,4-addition yields a precursor polymer segment containing recurring structural unit of the formula

$$-(CH_2 - CH = CH - CH_2)-$$

Hydrogenating this precursor polymer chain yields a polymer segment containing the following recurring structural unit

$$-(CH_2 - CH_2 - CH_2 - CH_2)-$$

i.e., containing only methylene units. This recurring structural unit, provided it is sufficiently long, e.g., contains at least about 13 methylene units, forms the crystallizable segment of the polymer chain.

Thus, there are two requirements that must be fulfilled in order for a segment to be crystallizable. The first requirement is that the segment have an average 1,4-polybutadiene content of at least about 20 mole percent, preferably at least about 30 weight percent (e.g., from about 20 to about 80 weight percent). The second is that the methylene units be in sequences sufficiently long to impart crystallinity to said segment. Generally, these sequences are preferably at least 13 methylenes or longer, more preferably at least 17 methylenes or longer, and ~~more~~ most preferably at least about 21 methylenes or longer.

Where there are relatively large amounts of these substituted methylene moieties in a polymer segment, generally greater or equal to about 30 mole percent, the resulting hydrogenated polymer segment is a low crystallinity segment. The segment containing at least about 20 mole percent 1,4-polybutadiene units, and if these methylene segments are of sufficient length, is a crystallizable segment.

A segment containing the recurring unit

$$-\!\left(\mathrm{CH_2 - \underset{\underset{\displaystyle CH_2CH_3}{|}}{CH} - CH_2 - \underset{\underset{\displaystyle CH_2CH_3}{|}}{CH} - CH_2 - CH_2 - CH_2 - CH_2}\right)\!-$$

derived from the hydrogenation of the 1,2-addition product of two moles of butadiene for every mole of 1,4-butadiene, will generally not be a crystallizable segment because it is relatively rich in substituted methylene units, and the methylene sequences are not sufficiently long. A segment containing the recurring structural unit

$$-\!\left(\mathrm{CH_2 - \underset{\underset{\displaystyle CH_2CH_3}{|}}{CH_2} - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2}\right)\!-$$

derived from the hydrogenation of the 1,4-addition of three moles of butadiene for every mole of 1,2-butadiene, will be a crystallizable segment since it contains at least 30 mole percent 1,4-polybutadiene units, and since it contains uninterrupted methylene sequences containing at least about 13 methylene units.

The copolymers of this invention preferably contain at least one crystallizable segment rich in methylene units (hereinafter called an "M" segment) and at least one low crystallinity segment relatively rich in substituted methylene units (hereinafter called a "T" segment). The copolymers may be therefore illustrated by copolymers selected from the group consisting of copolymer chain structures having the following segment sequences:

$$T - M \qquad \text{(III)}$$

$$T_1-(M_1-T_2)_x-M_2-T_3, \text{ and} \qquad \text{(IV)}$$

wherein M and T are defined above, M_1 and M_2 can be the same or different and are each M segments, T_1, T_2 and T_3 can be the same or different and are each T segments, and x is an integer of from 0 to 3.

When x=0, the copolymer's M, i.e., M_2 segment is positioned between two T segments, and the M segment can be positioned substantially in the center of the polymer chain (that is, the T_1 and T_3 segments can be substantially the same molecular weight and the sum of the molecular weight of the T_1 and T_3 segments can be substantially equal to the molecular weight of the M2 segment), although this is not essential to the practice of this invention. Preferably, the copolymer will contain only one M segment per chain. Therefore, structures III and IV (x=0) are preferred, with structure IV being more preferred.

The preferred copolymer chain structures, from the standpoint of providing oleaginous compositions such as lube oil compositions have excellent low temperature viscometric properties.

Preferably, the M segments and T segments of the copolymer are located along the copolymer chain so that only a limited number of the copolymer chains can associate before the steric problems associated with packing the low crystallinity T segments prevents further agglomeration. Therefore, in a preferred embodiment, the M segment is located near the center of the copolymer chain and only one M segment is in the chain. In the case where x is one or larger it is important that the T_1 and T_3 segments be sufficiently large to prevent association of the M segments from different polymer chains.

Generally, copolymers of the structure

$$M_1 - (T-M_2)_z \qquad (V)$$

wherein M_1, M_2 and T are as defined above, and wherein z is an integer of at least 1, are undesirable as viscosity modifier polymers. Solutions of structure V copolymers in oil tend to gel even when the M and T portions have exactly the same composition and molecular weight as structure IV copolymers (with x=z=1). It is believed this poor viscosity modifier performance is due to the inability of a center T segment to sterically stabilize against association.

The M segments of the copolymers of this invention comprise the 1,4-addition product of butadiene which has been hydrogenated, but can also comprise at least one other hydrogenated diolefin monomer, provided the 1,4-polybutadiene content of said M segment is at least about 30 mole percent and a majority of the methylene sequences are sufficiently long, e.g., contain at least about 13 methylene units. The T segments comprise a mixture of hydrogenated butadiene in the 1,2-configuration and the 1,4-configuration and have a 1,4-polybutadiene content not greater than about 20 mole percent. The T and T_2 segments can contain amounts of hydrogenated 1,4-configuration butadiene monomers, i.e., 1,4-polybutadiene units, provided the total methylene content of said segments does not exceed about 70 mole percent.

A preferred embodiment, a hydrogenated block or segmented copolymer of 1,4-butadiene and 1,2-butadiene contains at least one crystallizable block or segment and at least one non-crystallizable block or segment. Such block or segment copolymers may be represented by formula IV described hereinbefore, i.e., $T_1-(M_1-T_2)_x-M_2-T_3$ wherein M_1, M_2, T_1, T_2, T_3 and x are as defined hereinbefore. Preferably, M_1 and M_2 are comprised predominantly or solely of methylene units derived from the polymerized 1,4-butadiene which has subsequently been hydrogenated. T_1 T_2 and T_3 contain adequate substituted methylenes to render the segments of low crystallinity and may generally be derived, from 1,2-polymerized butadiene which has been hydrogenated. In forming a block copolymer of the structure $T_1 - M_2 - T_3$, butadiene is first polymerized to form 1,2-butadiene monomer units, to form a precursor copolymer T_1' segment containing a recurring structure represented by the formula

$$-\!\!\left(CH_2 - \underset{\displaystyle CH = CH_2}{\overset{}{CH}}\right)_{\!a}$$

wherein a is a number of at least 1. Upon hydrogenation this structure becomes

$$-\!\!\left(CH_2 - \underset{\displaystyle CH_2-CH_3}{\overset{}{CH}}\right)_{\!a} .$$

Upon complete or substantially complete polymerization by 1,2-addition, butadiene monomer is reacted with the "living" 1,2-butadiene segment. The butadiene is polymerized via 1,4-addition (generally there may be some fraction of 1,2-butadiene addition, although this may be kept to a minimum by appropriate reaction conditions), to form a precursor copolymer segment M' containing a recurring structure represented by the formula $-(CH_2 - CH = CH - CH_2)_{a'}$

wherein a' is a number of at least 1. Upon hydrogenation this structure becomes $(CH_2 - CH_2 - CH_2 - CH_2)_a$.

Upon completion or substantial completion of polymerization to by 1,4-addition, the 1,2-addition reaction is resumed with the precursor block copolymer $T_1' - M_2'$ -, with M_2' being the "living" butadiene block. The 1,2-addition polymerization is continued to form precursor copolymer segment T_3' containing the same recurring structure as precursor copolymer segment T_1'. The precursor copolymer containing segments $T_1' - M_2' - T_3'$ is then hydrogenated to form hydrogenated copolymer of structure $T_1 - M_2 - T_3$.

The present invention relates to novel segmented hydrogenated copolymers of butadiene wherein the copolymer's chain contains at least one crystallizable segment rich in methylene units and ~~at least~~ more than one low crystallinity segment relatively rich in substituted methylene units, wherein the low crystallinity copolymer segment is characterized in the unoriented bulk state after at least about 48 hours annealing at 23°C by a degree of crystallinity of less than about 0.2% at 23°C, and wherein the copolymer's chain is intramolecularly heterogeneous. The crystallizable segments preferably comprise an average of from about 20 to 90 weight percent, more preferably from about 25 to 85 weight percent, and ~~more~~ most preferably from about 30 to about 80 weight percent of the total copolymer chain, and contain an average 1,4-polybutadiene content which is at least about 20 mole percent, preferably at least about 30 weight percent. The low crystallinity copolymer segments comprise an average of from about 80 to 10 weight percent, preferably from about 75 to 15 weight percent, and more preferably from about 70 to 20 weight percent of the total copolymer chain, and have a 1,4-polybutadiene content not greater than about 20 mole percent. The copolymers in accordance with the present invention comprise intramolecularly heterogeneous chains, with substantially each chain containing both crystallizable and low crystallinity segments.

The hydrogenated copolymers of the instant invention have weight-average molecular weights ($\overline{Mw}$) as low as about 2,000. The preferred minimum is about 10,000. The more preferred minimum is about 20,000. The maximum weight-average molecular weight can be as high as 2,000,000. The preferred maximum is about 500,000. The more preferred maximum is about 250,000. The M segments have a $\overline{Mw}$ of from about 1,000 to about 1,000,000, preferably from about 10,000 to about 2,000,000, and more preferably about 20,000 to about 100,000. The T segments have a $\overline{Mw}$ of from about 1,000 to about 1,000,000, preferably about 5,000 to about 200,000, and more preferably from about 10,000 to about 100,000. The weight average molecular weights are determined by gel permeation chromatography (GPC) using tetrahydrofuran (THF) and light scattering as discussed above.

The copolymers of the instant invention have a molecular weight distribution ($\overline{Mw}/\overline{Mn}$) of about 2.0 or less, preferably about 1.9 or less, and more preferably about 1.8 or less, as determined by ~~SEC~~ GPC as discussed in G. Ver Strate, C. Cozewith, S. Ju, in Macromolecules, 21, 3360, 1988.

It is believed the novel copolymer's improved function as viscosity modifiers can be at least partially attributed to the ability of a controlled portion of the copolymer's molecules to crystallize in oleaginous compositions such as lubricating oils at temperatures above the cloud point of the lubricating oil. This occurs both inter- and intra-molecularly.

Typical lubricating oil contains paraffinic and isoparaffinic waxy components which are capable of crystallizing. As the lubricating oil is cooled from high temperatures (above T_c), these waxy components begin to crystallize. When the crystals become large they scatter light and make the oil turbid (the cloud point, T_c). Below the cloud point, waxes in the oil can co-crystallize with the crystallizable viscosity modifier crystallizable segments, effectively crosslinking the viscosity modifier polymer molecules, resulting in high "effective" polymer molecular weights, or causing "gelation" of the oil. This is observed by the appearance of a yield stress upon shearing. Such effectively high molecular weights are undesirable, as they increase the oil viscosity at low temperatures making it difficult for the oil to be pumped or poured.

The associated copolymer molecules of this invention are believed to have a smaller effective hydrodynamic volume per molecule than in their unassociated state, which lowers the relative viscosity of the lubricating oil solution thereof and provides low formulated oil viscosities at low temperatures. It is believed the copolymer's characteristics of exhibiting a higher polymer association temperature than the oil's cloud point minimizes interaction with the wax in the oil and accordingly decreases the tendency of oils to undergo gelation. Also, only a portion of these copolymer molecules is crystallizable under the use conditions. The non-crystallizable portion is believed to act as a steric barrier to help prevent excessive intermolecular association. The controlled segmented nature of the polymers is essential to their performance.

If the polymer has already associated above the cloud point temperature, the polymer and wax have little opportunity to interact. Furthermore, if the polymer contains segments which are low enough in methylene to completely avoid crystallization and are properly located along the contour, these will act as steric blocks to wax or excessive polymer/polymer interaction. Thus, two polymer characteristics are needed: crystallization above the wax appearance temperature and a segmented structure to stabilize agglomeration before gels form.

The copolymers of the present invention are preferably prepared by anionic polymerization. This method of polymerization offers certain unique advantages which makes it extremely useful in the synthesis of the polymers of the present invention. In particular, by the use of anionic polymerization, it is possible to obtain polymers having a narrow molecular weight distribution, to obtain tapered or block polymers, and to control the structure of the polymers derived from conjugated dienes.

Unlike free-radical polymerization reactions, anionic polymerizations can be performed where there is no facile chemical termination step. Of course, termination reactions do occur, but under carefully selected conditions with the monomers of the present invention, using inert solvents and highly pure reactants, the end groups have indefinite lifetimes. The non-terminated chains derived from anionic homopolymerization can be used for the synthesis of block polymers by sequential addition of different monomers as described hereinbefore. Thus anionic polymerization offers flexibility in allowing either block or tapered polymers to be readily produced. As mentioned hereinbefore polymers with narrow molecular weight distribution having better shear stability than those with broader distributions can be produced. Shear stability is a desirable property in polymers used as viscosity index improvers.

Anionic polymerization generally offers a wider latitude of techniques for producing varied structures of conjugated diolefin polymers. With butadiene monomer, 1,4- and 1,2-addition can be regulated by the appropriate combination of reaction conditions, including catalyst, solvent type, and temperature. Hydrogenated precursor copolymers containing butadiene units predominantly in the 1,4-configuration are much more effective in increasing the V.I. than hydrogenated precursor copolymers containing butadiene units predominantly in the 1,2-configuration.

The polymers of the present invention can be prepared with known metallic and organometallic catalysts such as lithium metal or sodium metal and organo-lithium or organosodium catalysts. Preferred lithium compounds are compounds containing two lithium atoms per compound molecule and include LiR^LLi wherein R^L is an organic compound, preferably a hydrocarbon having at least one carbon atom and preferably from 3 to 6 carbon atoms. Useful dilithium (DiLi) compounds are disclosed in A. F. Halasa et al. Organolithium Catalysis of Olefin and Diene Polymerization, Advances in Organometallic Chemistry, Vol. 18, pages 55-97, Academic Press, Inc. (1980). Suitable organo-lithium catalysts may be represented by the formula R^2Li wherein R^2 is a C_3 to C_{30}, and preferably C_3 to C_{10} alkyl, aralkyl, or cycloalkyl group. Specific examples of suitable catalysts include n-propyllithium, isopropyllithium, n-butyllithium, tertiarybutyllithium, n-decyllithium, benzyllithium, 4-phenyl-n-butyllithium, etc. Particularly preferred are the butyllithiums, i.e., normal-, sec-, iso-, and tertiary-butyllithiums.

An inert diluent, in which the catalyst is soluble, may be employed. By "inert" it is meant that the diluent does not react, although the nature of the solvent may affect the relative amount of 1,2- and 1,4-configuration that is obtained. The inert diluent will generally be a hydrocarbon free of olefinic unsaturation containing from 3 to 16 carbon atoms. Suitable inert diluents include aliphatics, such as n-pentane, n-hexane, isooctane, n-nonane, etc.; alicyclics, such as cyclopentane, cyclohexane, cycloheptane, etc., aromatics such as benzene, toluene, xylene, chlorobenzene, etc. The amount of diluent employed in the preparation is not critical, except that sufficient amounts should be used to solubilize the amount of organolithium catalyst used. Generally, 0.5 to 200, preferably 1 to 50 liters of the diluent per gram mole of organo-lithium catalyst are employed during the preparation of the polymer.

The amount of catalyst employed primarily depends upon the degree of polymerization desired. The term "degree of polymerization," as employed herein, means the total number of monomeric units present in the polymer. Ordinarily, each mole of organo-lithium catalyst will generate a mole of polymer. Thus, "degree of polymerization" may be conveniently defined by the generalization:

$$\text{Degree of polymerization} = \frac{\text{total moles of monomer}}{\text{moles of organo-lithium catalyst}}$$

Since to obtain the desired molecular weights, the average number of monomeric units in the polymer will generally be from about 500 to about 10,000. About 0.0001 to 0.002 mole of organolithium catalyst per mole of monomer will ordinarily be utilized.

The polymerization reaction generally takes place at about -50° to about 150°C, and preferably at 20° to 60°C. Reaction times as short as 1 minute or as long as 75 hours may be employed. Preferably, the polymerization reaction is carried out for from 4 minutes to 24 hours. Reaction pressure is not critical; pressures may range from atmospheric to super-atmospheric. Preferably for economy and ease of handling, atmospheric pressure is utilized.

In one embodiment the monomers are added sequentially whereby block or segment copolymers may be obtained. For example in the preparation of a copolymer of structure III, i.e., T - M, one of the monomers, e.g., butadiene, is polymerized in the presence of the catalyst via 1,4-addition for a period of time, e.g., 2 hours, to form a unhydrogenated precursor copolymer segment M' containing at least about 65 weight percent butadiene in the 1,4-configuration. Then the conditions of polymerization are changed for polymerization to take place through 1,2-addition. The comonomer forms 1,2-butadiene units resulting in unhydrogenated precursor segment T'. The segmented copolymer is then hydrogenated to form methylene rich segment M, corresponding to a 1,4-polybutadiene content of at least about 20 weight percent, and substituted methylene rich segment T having a methylene content corresponding to 1,4-polybutadiene of less than about 20 mole percent.

A hydrogenated copolymer having structure IV, i.e., T_1-M_2-T_3, can be prepared by first polymerizing butadiene by 1,2-addition, to form unhydrogenated precursor segment T_1' containing predominantly 1,2-butadiene units; the reaction conditions are changed and the butadiene monomer is polymerized (in the presence of T_1') via 1,4-addition mechanism to form unhydrogenated precursor segment M_2' containing at least about 20 mole percent of 1,4-configuration butadiene; and then the reaction conditions changed to polymerize the butadiene via 1,2-addition to form unhydrogenated precursor segment T_3' containing predominantly 1,2-butadiene. The segmented copolymer T_1'-M_2'-T_3' is then hydrogenated to form the T_1-M_2-T_3 structure.

In the foregoing discussion concerning the preparation of copolymers of structures M - T and T_1 - M_2 - T_3 it is to be understood that the M segment need not contain, and usually does not contain, only methylene units derived from the hydrogenation of 1,4-addition butadiene. It may also contain some substituted methylene units derived from the hydrogenation of the 1,2-addition butadiene so long as those substituted methylene units do not exceed about 80 mole percent of the total units. Likewise, segments T, T_1 and T_3 may contain, and usually do contain, methylene units derived from the hydrogenation of 1,4-addition butadiene, so long as the total methylene units present in T, T_1 and T_3 do not correspond to a 1,4-polybutadiene content exceeding 20 mole percent.

An alternate and preferred embodiment of the present invention is one wherein the copolymer is in a star polymer form, i.e., a star block copolymer. A living block copolymer having monomeric units derived from 1,4-butadiene and 1,2-butadiene addition products of the polymerization of butadiene is formed as recited above. The copolymer has the above structures of T-M and T_1-M_2-T_3. When the copolymer reaches a desired molecular weight a polyalkenyl coupling agent is introduced. The polyalkenyl coupling agent acts as a nucleus of the star. The living polymers react at one end with the ~~polyalakenyl~~ polyalkenyl coupling agent. The living polymer is then deactivated or killed in a known manner. Each arm of the star is thereby attached at one end to the nucleus with the opposite end preferably being a "T" segment. That is, the free ends of the arms of the star are preferably rich in substituted methylene units making them amorphous.

Each arm of the star preferably has the character of the straight chain copolymer from which it forms. For the purposes of the present invention the term block copolymer will therefore include star copolymers containing arms which have blocks consistent with the straight chain block copolymers recited above. Preferred molecular weights for star polymers are higher than their linear counterparts.

Apart from the specific and improved character of the block copolymer structure of the arms, the star polymers of the present invention are made in accordance with procedures disclosed in patents such as U. S. Patent No. 4,358,565 and U. S. Patent No. 4,620,048. The improvement of the star copolymer of the present invention being that it is a copolymer having arms wherein there are sharp blocks characterized by their amorphous and crystalline properties. The configurations having methylene rich groups at the arms of the stars near the star center are useful in lubricating oils which contain paraffin and isoparaffinic waxy components capable of crystallizing to prevent crystalline gelling.

More particularly, the star polymers of the present invention are made by forming block copolymers as recited above. The block copolymers have a structure as presented in formulas III, and IV with the structure of IV being most preferred. The living block copolymer is first prepared by copolymerizing blocks of butadiene and isoprene as recited above.

In a preferred method the living block copolymers produced are reacted with a polyalkenyl coupling agent such as a polyvinyl compound, or halosilane compounds such as $SiCl_4$. Such polyalkenyl coupling agents capable of forming star-shaped polymer are known and indicated to be disclosed in polymers such as in U. S. Patent No. 3,985,830.

The polyalkenyl coupling agent should be added to the living polymer after the polymerization of the monomers is substantially complete, i.e., the agent should only be added after substantially all of the monomers (formulas I and II) have been converted to the living block copolymer.

The amount of polyalkenyl coupling agent added is preferably at least 0.5 moles per mole of unsaturated living polymer. Amounts of from 1 to 15 moles, preferably 1.5 to 5 moles are preferred. The amount which may be added in two or more stages is usually such so as to convert at least 80-85 weight percent of the living polymers into star-shaped polymers.

The reaction between the living polymer and the polyalkenyl coupling agent or nucleator can be carried out in the same solvent as the reaction to form the living polymer. The reaction temperature can also be varied from 0° to 150°C, and preferably 20° to 120°C. The reaction may also take place in an inert atmosphere such as nitrogen under pressure of from 0.5 to 10 bars.

The star-shaped polymers prepared are characterized by having a dense center nucleus of crosslinked polyalkenyl coupling agent and a number of arms of substantially linear unsaturated polymers extending outwardly therefrom. The number of arms may vary considerably, but is typically from 4 and 25, preferably from 5 to about 15, and most preferably from 5 to 10 arms. It is reported that the greater number of arms employed improves both thickening ~~of the~~ efficiency and shear stability of the polymer since it is possible to prepare a viscosity index improving molecule having a high molecular weight (resulting in increased thickening efficiency) without the necessity of excessively long arms.

The star-shaped polymers, which are still living, may be deactivated or killed in a known manner by the addition of a second compound which reacts with the carbon-ionic end group. Examples of suitable de-activators include compounds with one or more active hydrogen such as water, alcohol, such as methanol, ethanol, isopropanol, 2-ethylhexanol, or carboxylic acids such as acetic acid, compounds with one active halogen atom, such as chlorine atoms (benzyl chloride or fluoromethane), compounds with one ester group and carbon dioxide. If not deactivated in this way, the living star-shaped polymers will be killed by the hydrogenation step. Before being killed, the living star-shaped polymers may be reacted with further amounts of monomers, such as the same or different dienes, or functional monomers.

The molecular weights of the star-shaped polymer to be hydrogenated may vary between relatively wide limits. However, they are typically between molecular weights from about 25,000 to 1,500,000, and preferably from 100,000 to 500,000. The molecular weights are weight average molecular weights determined by gel permeation chromatography.

The hydrogenation of the polymers of the present invention is carried out using conventional hydrogenation procedures. The polymer is diluted with an inert solvent, such as those previously mentioned, or in the original polymerization medium, and the polymer solution and hydrogenation catalyst are added to a high pressure autoclave. The autoclave is pressured with hydrogen to about 100 to 3,000 p.s.i.g., and then heated to 50° to 220°C, (preferably 75° to 150°C), for about 0.1 to 24, preferably 1 to 24 hours (preferably 2 to 10 hours), while mixing. The reactor is then depressurized, the catalyst removed by filtering, and the hydrogenated polymer recovered from the solvent by conventional stripping procedures.

The hydrogenation catalyst will generally be used in an amount of 0.1 to 20 weight percent based upon the weight of the polymer to be hydrogenated. The specific amount of catalyst employed depends somewhat upon the specific catalyst used. Any material functioning as an olefin hydrogenation catalyst can be used; suitable catalysts include Raney nickel, platinum oxide, platinum on alumina, palladium or charcoal, copper chromate, nickel supported on kieselguhr, molybdenum sulfide, and the like. The best hydrogenation results were obtained with Raney nickel, in large excess, at high temperatures and pressure. Co or Ni carboxylates reduced with aluminum alkyls can also be used.

Hydrogenation is carried out to remove the olefinic unsaturation present in the precursor copolymer. Hydrogenation may be complete or substantially complete. By complete hydrogenation is meant that all of the olefinic bonds are saturated. By substantially complete hydrogenation is meant that substantially all of the olefinic unsaturation is saturated. By substantially all olefinic unsaturation is meant at least about 80%, preferably at least about 90% of the olefinic unsaturation and most preferably greater than 98%.

Another embodiment of the present invention is a tapered block or segmented copolymer of the hydrogenated 1,2- and 1,4-butadiene. A tapered block or segmented copolymer according to this invention is a copolymer obtained by anionically copolymerizing in hydrocarbon solution in, for example, a batch reactor a mixture containing butadiene monomer to form a precursor copolymer having at least 75 weight percent 1,4-configuration of the 1,4-butadiene and then hydrogenating said precursor copolymer.

The anionic polymerization and subsequent hydrogenation conditions used in the preparation of the tapered segmented or block copolymer are substantially the same as those described hereinbefore. The weight-average molecular weights of these tapered segmented or block hydrogenated copolymers are generally the same as those described above.

The weight percent of the butadiene present in the reaction mixture is that which is effective to form a tapered segmented or block copolymer having at least one crystallizable segment and at least one low crystallinity segment. Generally this amount of butadiene is from about 20 to about 90 weight percent. Additionally, the amount of the 1,4-configuration butadiene present in the precursor copolymer must be an amount which is effective to form a crystallizable segment upon hydrogenation of the precursor copolymer. Generally, this amount is at least about 20 mole percent.

The polymers can be recovered by procedures well known in the art. For example, polar materials, such as water or C_1 to C_5 alkanols can be added to inactivate the catalyst. Preferably, the reaction is terminated by dropping the reaction system into 2 to 10 volumes of methanol containing about 0.1 weight percent antioxidant. After termination of the reaction, the hydrocarbon solution is washed with water or dilute mineral acid. Alternatively, the active polymer solution can be treated with hydrated clays, such as natural Attapulgus clay, which functions to both inactivate the catalyst and to chemically absorb the lithium component. The polymer may be recovered by filtering the resultant polymer solution, drying if necessary, and stripping of remaining inert diluent at elevated temperatures (e.g., 70° to 120°C) and reduced pressures (e.g., 0.1 to 100 mm. Hg). For the isolation of higher molecular weight polymers steam stripping or precipitation with anti-solvents is preferred.

By controlling the ratio of 1,4- to 1,2-butadiene in the anionic polymerization it is possible to obtain an effective wide range of methylene to substituted methylene ratio in the hydrogenated product.

When the polymerization of the dienes has been completed, the copolymer thus obtained can be hydrogenated either immediately or after recovery to obtain the desired hydrogenated copolymers according to the invention.

The present invention includes compositions comprising an oleaginous material such as lubricating oil and at least one hydrogenated block copolymer as described. There can be a minor amount, e.g. 0.01 up to 50 weight percent, preferably 0.05 to 25 weight percent, based on the weight of the total composition, of the hydrogenated copolymer produced in accordance with this invention can be incorporated into a major amount of an oleaginous material, such as a lubricating oil or hydrocarbon fuel, depending upon whether one is forming finished products or additive concentrates. When used in lubricating oil compositions, e.g. automotive or diesel crankcase lubricating oil, copolymer concentrations are usually within the range of about 0.01 to 10 weight percent, of the total composition. The copolymers of the invention may be utilized in a concentrate form, e.g., from about 5 weight percent up to about 50 weight percent, preferably 7 to 25 weight percent oil, e.g., mineral lubricating oil, for ease of handling, and may be prepared in this form by carrying out the reaction of the invention in oil as previously discussed. The lubricating oils to which the products of this invention can be added include not only hydrocarbon oil derived from petroleum, but also include synthetic lubricating oils such as esters of dibasic acids; complex esters made by esterifications of monobasic acids, polyglycols, dibasic acids and alcohols; polyolefin oils, etc. The hydrogenated copolymers of the present invention are particularly useful as fuel and lubricating oil additives, particularly as Viscosity Index improver lubricating oil additives.

The hydrogenated copolymers of the instant invention are oil-soluble, dissolvable in oil with the aid of a suitable solvent, or are stably dispersible therein. The terms oil-soluble, dissolvable in oil, or stably dispersible in oil as that terminology is used herein does not necessarily indicate that the materials are soluble, dissolvable, miscible, or capable of being suspended in oil in all proportions. It does mean, however, that the additives for instance, are soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular copolymer hereof, if desired.

The copolymers are particularly useful in lubricating oil compositions, which employ a base oil in which these copolymers are dissolved or dispersed.

Base oils suitable for use in preparing the lubricating compositions of the present invention include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like. Advantageous results are also achieved by employing the additives of the present invention in base oils conventionally employed in and/or adapted for use as power transmitting fluids such as automatic transmission fluids, tractor fluids, universal tractor fluids and hydraulic fluids, heavy duty hydraulic fluids, power steering fluids and the like. Gear lubricants, industrial oils, pump oils and other lubricating oil compositions can also benefit from the incorporation therein of the additives of the present invention.

The above oil compositions may optionally contain other conventional additives, pour point depressants, antiwear agents, antioxidants, other viscosity-index improvers, dispersants, corrosion inhibitors, anti-foaming agents, detergents, rust inhibitors, friction modifiers, and the like.

Corrosion inhibitors, also known as anti-corrosive agents, reduce the degradation of the metallic parts contacted by the lubricating oil composition. Illustrative of corrosion inhibitors are phosphosulfurized hydrocarbons and the products obtained by reaction of a phosphosulfurized hydrocarbon with an alkaline earth metal oxide or hydroxide, preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of carbon dioxide. Phosphosulfurized hydrocarbons are prepared by reacting a suitable hydrocarbon such as a terpene, a heavy petroleum fraction of a C_2 to C_6 olefin polymer such as polyisobutylene, with from 5 to 30 weight percent of a sulfide of phosphorus for 1/2 to 15 hours, at a temperature in the range of about 66 to about 316°C. Neutralization of the phosphosulfurized hydrocarbon may be effected in the manner taught in U. S. Patent No. 1,969,324.

Oxidation inhibitors, or antioxidants, reduce the tendency of mineral oils to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces, and by viscosity growth. Such oxidation inhibitors include alkaline earth metal salts of alkylphenolthioesters having preferably C_5 to C_{12} alkyl side chains, e.g., calcium nonylphenol sulfide, barium toctylphenyl sulfide, dioctylphenylamine, phenylalphanaphthylamine, phosphosulfurized or sulfurized hydrocarbons, etc.

Other oxidation inhibitors or antioxidants useful in this invention comprise oil-soluble copper compounds. The copper may be blended into the oil as any suitable oil-soluble copper compound. By oil soluble it is meant that the compound is oil soluble under normal blending conditions in the oil or additive package. The copper compound may be in the cuprous or cupric form. The copper may be in the form of the copper dihydrocarbyl thio- or dithio-phosphates. Alternatively, the copper may be added as the copper salt of a synthetic or natural carboxylic acid. Examples of same thus include C_{10} to C_{18} fatty acids, such as stearic or palmitic acid, but unsaturated acids such as oleic or branched carboxylic acids such as napthenic acids of molecular weights of from about 200 to 500, or synthetic carboxy'ic acids, are preferred, because of the improved handling and solubility properties of the resulting copper carboxylates. Also useful are oil-soluble copper dithiocarbamates of the general formula $(RR,NCSS)_nCu$ (where n is 1 or 2 and R and R, are the same or different hydrocarbyl radicals containing from 1 to 18, and preferably 2 to 12, carbon atoms, and including radicals such as alkyl, alkenyl, aryl, aralkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R, groups are alkyl groups of from 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-heptyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethyl hexyl, phenyl, butylphenyl, cyclohexyl, methyl-cyclopentyl, propenyl, butenyl, etc. In order to obtain oil solubility, the total number of carbon atoms (i.e., R and R,) will generally be about 5 or greater. Copper sulphonates, phenates, and acetylacetonates may also be used.

Exemplary of useful copper compounds are copper CuI and/or CuII salts of alkenyl succinic acids or anhydrides. The salts themselves may be basic, neutral or acidic. They may be formed by reacting (a) poly-alkylene succinimides (having polymer groups of Mn of 700 to 5,000) derived from polyalkylene-polyamines, which have at least one free carboxylic acid group, with (b) a reactive metal compound. Suitable reactive metal compounds include those such as cupric or cuprous hydroxides, oxides, acetates, borates, and carbonates or basic copper carbonate.

Examples of these metal salts are Cu salts of polyisobutenyl succinic anhydride, and Cu salts of polyisobutenyl succinic acid. Preferably, the selected metal employed is its divalent form, e.g., Cu^{+2}. The preferred substrates are polyalkenyl succinic acids in which the alkenyl group has a molecular weight greater than about 700. The alkenyl group desirably has a $\overline{Mn}$ from about 900 to 1,400, and up to 2,500, with a $\overline{Mn}$ of about 950 being most preferred. Especially preferred is polyisobutylene succinic anhydride or acid. These materials may desirably be dissolved in a solvent, such as a mineral oil, and heated in the presence of a water solution (or slurry) of the metal bearing material. Heating may take place between 70 and about 200°C. Temperatures of 110°C to 140°C are entirely adequate. It may be necessary, depending upon the salt produced, not to allow the reaction to remain at a temperature above about 140°C for an extended period of time, e.g., longer than 5 hours, or decomposition of the salt may occur.

The copper antioxidants (e.g., Cu-polyisobutenyl succinic anhydride, Cu-oleate, or mixtures thereof) will be generally employed in an amount of from about 50 to 500 ppm by weight of the metal, in the final lubricating or fuel composition.

Friction modifiers serve to impart the proper friction characteristics to lubricating oil compositions such as automatic transmission fluids.

Representative examples of suitable friction modifiers are found in U. S. Patent No. 3,933,659 which discloses fatty acid esters and amides; U. S. Patent No. 4,176,074 which describes molybdenum complexes of polyisobutenyl succinic anhydride-amino alkanols; U. S. Patent No. 4,105,571 which discloses glycerol esters of dimerized fatty acids; U. S. Patent No. 3,779,928 which discloses alkane phosphonic acid salts; U. S. Patent No. 3,778,375 which discloses reaction products of a phosphonate with an oleamide; U. S. Patent No. 3,852,205 which discloses S-carboxyalkylene hydrocarbyl succinimide, S-carboxyalkylene hydrocarbyl succinamic acid and mixtures thereof; U. S. Patent No. 3,879,306 which discloses N(hydroxyalkyl)alkenyl-succinamic acids or succinimides; U. S. Patent No. 3,932,290 which discloses reaction products of di- (lower alkyl) phosphites and epoxides; and U. S. Patent No. 4,028,258 which discloses the alkylene oxide adduct of phosphosulfurized N-(hydroxyalkyl) alkenyl succinimides. The disclosures of the above references are herein incorporated by reference. The most preferred friction modifiers are succinate esters, or metal salts thereof, of hydrocarbyl substituted succinic acids or anhydrides and thiobis-alkanols such as described in U. S. Patent No. 4,344,853.

Dispersants maintain oil insolubles, resulting from oxidation during use, in suspension in the fluid thus preventing sludge flocculation and precipitation or deposition on metal parts. Suitable dispersants include high molecular weight polyalkenyl succinimides, the reaction product of oil-soluble polyisobutylene succinic anhydride with ethylene amines such as tetraethylene pentamine and borated salts thereof.

Pour point depressants, otherwise known as lube oil flow improvers, lower the temperature at which the fluid will flow or can be poured. Such additives are well known. Typically of those additives which usefully optimize the low temperature fluidity of the fluid are C_8-C_{18} dialkylfumarate vinyl acetate copolymers, polymethacrylates, and wax naphthalene. Foam control can be provided by an antifoamant of the polysiloxane type, e.g., silicone oil and polydimethyl siloxane.

Anti-wear agents, as their name implies, reduce wear of metal parts. Representatives of conventional antiwear agents are zinc dialkyldithio- phosphate and zinc diaryldithiosphate.

Detergents and metal rust inhibitors include the metal salts of sulphonic acids, alkyl phenols, sulfurized alkyl phenols, alkyl salicylates, naphthenates and other oil soluble mono- and dicarboxylic acids. Highly basic (viz, overbased) metal sales, such as highly basic alkaline earth metal sulfonates (especially Ca and Mg salts) are frequently used as detergents. Representative examples of such materials, and their methods of preparation, are found in co-pending Serial No. 754,001, filed July 11, 1985, the disclosure of which is hereby incorporated by reference.

Some of these numerous additives can provide a multiplicity of effects, e.g., a dispersant-oxidation inhibitor. This approach is well known and need not be further elaborated herein.

Compositions when containing these conventional additives are typically blended into the base oil in amounts which are effective to provide their normal attendant function. Representative effective amounts of such additives are illustrated as follows:

Additive	Wt. %. (Broad)	Wt. % (Preferred)
Viscosity Modifier	.01-12	.01-4
Corrosion Inhibitor	0.01-5	.01-1.5
Oxidation Inhibitor	0.01-5	.01-1.5
Dispersant	0.1-20	0.1-8
Pour Point Depressant	0.01-5	.01-1.5
Anti-Foaming Agents	0.001-3	.001-0.15
Anti-Wear Agents	0.001-5	.001-1.5
Friction Modifiers	0.01-5	.01-1.5
Detergents/Rust Inhibitors	0.01-10	.01-3
Mineral Oil Base	Balance	Balance

When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the viscosity index modifying copolymers (in concentrate amounts hereinabove described), together with one or more of said other additives (said concentrate when constituting an additive mixture being referred to here in as an additive package) whereby several additives can be added simultaneously to the base oil to form the lubricating oil composition. Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The concentrate or additive-package will typically be formulated to contain the viscosity index improving copolymer additive and optional additional additives in proper amounts to provide the desired concentration in the final formulation when the additive-package is combined with a predetermined amount of base lubricant. Thus, the products of the present invention can be added to small amounts of base oil or other compatible solvents along with other desirable additives to form additive-packages containing active ingredients in collective amounts of typically from about 2.5 to about 90%, and preferably from about 5 to about 75%, and most preferably from about 8 to about 50% by weight additives in the appropriate proportions with the remainder being base oil.

The additives of the present invention may be suitably incorporated into synthetic base oils such as alkyl esters of dicarboxylic acids, polyglycols and alcohols; polyalpha-olefins, polybutenes, alkyl benzenes, organic esters of phosphoric acids, poly-silicone oils, etc.

The final formulations may employ typically about 10 weight percent of the additive-package with the remainder being base oil.

Accordingly, while any effective amount, i.e., viscosity index improving effective amount, of the additives of the present invention can be incorporated into the fully formulated lubricating oil composition, it is contemplated that such effective amount be sufficient to provide said lube oil composition with an amount of the additive of typically from about 0.01 to about 10, preferably 0.1 to 6.0, and more preferably from 0.25 to 3.0 weight percent, based on the weight of said composition.

Low temperature properties of the lubricating oils of the present invention are evaluated by a number of significant tests:

MRV (Mini Rotary Viscometer), using a technique described in ASTM-D3829, measures viscosity in centipoise and yield stress in Pascals. MRV is determined at -25°C.

CCS (Cold Cranking Simulator), using a technique in ASTM-D2502, a high shear viscosity measurement in centipoises. This test is related to a lubricating oil's resistance to cold engine starting.

TP1 cycle MRV--Determined by ASTM D4684. This is essentially the same as the ASTM MRV noted above, except a slow cooling cycle is used. The cycle is defined in SAE Paper No. 850443, K. O. Henderson et al.

The copolymer of the present invention, when used to formulate lubricating oils, will lower the viscosity measured using the Cold Cranking Simulator Test. At the same time, low TP-1 cycle MRV is maintained or lowered. The thickening efficiency (TE) is improved and the lube oil has high viscosity at high temperatures and low viscosity at low temperatures.

The following Example further illustrates the present invention. Unless otherwise stated, all of said weight percents expressed herein are based on active ingredient (a.i.) content of the additive, and/or upon the total weight of any additive-package, or formulation which will be the sum of the a.i. weight of each additive plus the weight of total oil or diluent.

EXAMPLE

Thickening efficiency (T.E.) is defined as the ratio of the weight percent of a polyisobutylene (sold as an oil solution by Exxon Chemical Company as Paratone® N), having a Staudinger molecular weight of 20,000, required to thicken a solvent-extracted neutral mineral lubricating oil, having a viscosity of 150 SUS at 37.8°C, a viscosity index of 105 and an ASTM pour point of O.F. (Solvent 150 Neutral) to a viscosity of 12.4 centistokes at 98.9°C to the weight percent of a test copolymer required to thicken the same oil to the same viscosity at the same temperature. For linear polymers of a given methylene content, the thickening efficiency is approximately proportional to the 0.75 power of the weight-average molecular weight.

In this Example a polymer having crystallizable and non-crystallizable segments is prepared from butadiene by controlling the relative proportions of 1,2 butadiene and 1,4 butadiene, using a high vacuum polymerization techniques. The experimental procedure is of the type described in M. Morton, L. J. Fetters, Rubber Chem. Tech., 48, 359 (1975).

500 grams of cyclohexane is charged to a 2 liter reaction flask. To this is added 0.5 millimeters of dilithium isoprene oligomer initiator (DILI) sold by Lithcoa and 54 grams of butadiene. The mixture is allowed to react to form a predominantly (1,4 poly butadiene) at 24°C for about 24 hours.

Dipiperidylethane (DPE) from Reilly Tire and Chemical Co. or Aldrich is then added as a modifier at 2:1 mole ratio based on Li, as discussed in A. Halasa, D. Schulz, D. Tate, V. Mochel, Adv. Organometallic Chem., 18, 55, (1980). An additional 54 grams of butadiene is added and the polymerization proceeds at about 0°C for 48 hours to form a block of predominantly 1,2 poly butadiene and at each end of the (1,4 polybutadiene) center block. The reaction is then terminated by adding degassed methanol.

The polymer is hydrogenated by heterogeneous catalysis. The butadiene portion polymerized prior to the addition of the modifier is substantially in the 1,4 configuration and is hydrogenated to a crystallizable polyethylene-like segment. The butadiene added in the presence of the modifier is substantially in the 1,2-form, and becomes a poly(ethylene-butene)-like after hydrogenation and is non-crystallizable.

Due to the use of the di-initiator the crystallizable segments are formed in the center M block with amorphous T end blocks of 1,2-butadiene.

While exemplary embodiments of the invention have been described, the true scope of the invention is to be determined from the following claims.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A polybutadiene block copolymer comprising polymerization products derived from monomeric units of 1,4-butadiene and 1,2-butadiene, the copolymer being hydrogenated and comprising at least 10 percent by weight of at least one crystallizable segment comprised of methylene units and having an average methylene content corresponding to a 1,4-polybutadiene content of at least about 20 mole percent, and more than one low crystallinity segment comprised of methylene units and substituted methylene units and having an average 1,4-polybutadiene content up to about 20 mole percent.

2. The hydrogenated copolymer as recited in claim 1 containing a chain segment sequence represented by the structure :

$$T_1 - (M_1 - T_2)_x - M_2 - T_3$$

wherein x is a number of from 0 to 3, M_1 and M_2 are the same or different and each comprises said crystallizable segment, and T_1, T_2 and T_3 are the same or different and each comprises said low crystallinity segment.

3. The hydrogenated copolymer as recited in claim 2 wherein x is zero.

4. The hydrogenated copolymer as recited in claim 3 wherein said T_1 and T_3 segments are the same weight average molecular weight.

5. The hydrogenated copolymer as recited in claim 1 wherein the 1,4-butadiene and 1,2-butadiene are present in amounts effective to provide said at least one crystallizable segment and said more than one low crystallinity segment.

6. The hydrogenated copolymer as recited in claim 5 wherein said amount of 1,4-butadiene is at least about 30 mole percent.

7. The hydrogenated copolymer as recited in claim 1 wherein said

copolymer has a molecular weight distribution characterized by a ratio of $\overline{Mw} / \overline{Mn}$ of less than 2.

8. The hydrogenated copolymer as recited in claim 1 wherein the crystallizable segment comprises sequences of at least 13 adjacent methylene units in series.

9. The hydrogenated copolymer as recited in claim 8 wherein the low crystallinity segment comprises sequences of less than 13 adjacent methylene units in series.

10. The hydrogenated copolymer as recited in claim 9 wherein the low crystallinity segment comprises sequences of less than 7 adjacent methylene units in series.

11. The hydrogenated copolymer as recited in claim 1 wherein the low crystallinity segment has an average methylene content of less than about 70 mole percent.

12. The hydrogenated copolymer as recited in claim 1 wherein the crystallizable segment has a number average molecular weight of at least 500.

13. The hydrogenated copolymer as recited in claim 1 wherein the copolymer is a star block copolymer.

14. The hydrogenated copolymer as recited in claim 13 wherein the star block copolymer has from 4 to 25 arms.

15. The hydrogenated copolymer as recited in claim 14 wherein the star block copolymer has from 5 to 15 arms.

16. The hydrogenated copolymer as recited in claim 13 wherein the star block copolymer has a weight average molecular weight of from 100,000 to 500,000.

17. A process comprising the steps of :

polymerizing a precursor polybutadiene block copolymer comprising at least one crystallizable segment comprising 1,4-butadiene and more than one comonomer low crystallinity segment comprising comonomer units of 1,2-butadiene, the copolymer comprising at least 10 percent by weight of the crystallizable segments,

substantially hydrogenating the precursor block copolymer to form a hydrogenated polybutadiene block copolymer comprising at least 10 percent by weight of at least one crystallizable segment comprised of methylene units and having an average methylene content corresponding to a 1,4-polybutadiene content of at least about 20 mole percent, and more than one low crystallinity segment comprised of methylene units and substituted methylene units and having an average methylene content corresponding to a 1,4-polybutadiene content of up to about 20 mole percent.

18. The process as recited in claim 17 where the butadiene comprises at least 30 mole percent 1,4-butadiene.

19. The process as recited in claim 17 wherein the polymerization is anionic polymerization.

20. The process as recited in claim 19 for polymerizing a precursor block copolymer further comprising

first controlling the polymerization to form crystallizable segments, and

then controlling the polymerization to form low comonomer crystallinity segments comprising at least 70 mole percent of 1,2-butadiene monomeric units.

21. The process as recited in claim 19 for polymerizing a precursor block copolymer further comprising

first controlling the polymerization to form a comonomer segment comprising at least 70 mole percent of 1,2-butadiene monomeric units;

then controlling the polymerization to form 1,4-butadiene segments; and

then controlling the polymerization to form comonomer segments comprising at least 70 mole percent of 1,2-butadiene monomeric units.

22. The process as recited in claim 21 further comprising the step of introducing a coupling agent after forming the precursor block copolymer to form a star block copolymer.

23. The process as recited in claim 22 wherein the star block copolymer has from 4 to 25 arms.

24. The process as recited in claim 23 wherein the star block copolymer has from 5 to 15 arms.

25. The process as recited in claim 22 wherein the star block copolymer has a weight average molecular weight of from 100,000 to 500,000.

26. A composition comprising (a) oil; and (b) at least one polybutadiene block copolymer comprising polymerization products derived from monomeric units of 1,4-butadiene and 1,2-butadiene, the copolymer being hydrogenated and comprising at least 10 percent by weight of at least one crystallizable segment comprised of methylene units and having an average methylene content corresponding to a 1,4-polybutadiene content of at least about 20 mole percent, and more than one low crystallinity segment comprised of methylene units and substituted methylene units and having an average methylene content up to about 75 mole percent.

27. The composition as recited in claim 26 wherein said hydrogenated copolymer is comprised of a chain segment sequence represented by the structure :

$$T_1 - (M_1 - T_2)_x - M_2 - T_3$$

wherein x is a number of from 0 to 3, M_1 and M_2 are the same or different and each comprises said crystallizable segment, and T_1, T_2 and T_3 are the same or different and each comprises said low crystallinity segment.

28. The composition as recited in claim 27 wherein x is zero.

29. The composition as recited in claim 28 wherein said T_1 and T_3 segments are the same weight average molecular weight.

30. The composition as recited in claim 26 wherein the 1,4-butadiene is present in at least about 20 mole percent in said at least one crystallizable segment and is present in not greater than 20 mole percent in said more than one low crystallinity segment.

31. The composition as recited in claim 30 wherein said amount of 1,4-polybutadiene is at least about 30 mole percent.

32. The composition as recited in claim 26 wherein said hydrogenated copolymer has a molecular weight distribution characterized by a ratio of $\overline{Mw} / \overline{Mn}$ of less than 2.

33. The composition as recited in claim 26 which contains a viscosity index improving effective amount of said hydrogenated copolymer.

34. The composition as recited in claim 28 wherein said oil is lubricating oil.

35. The composition as recited in claim 28 which is a lubricating oil concentrate.

36. The composition as recited in claim 28 which is a fully formulated lubricating oil composition.

37. The composition as recited in claim 26 wherein the crystallizable segment comprises at least 13 adjacent methylene units in series.

38. The composition as recited in claim 26 wherein the low crystallinity segment comprises less than 7 adjacent methylene units in series.

39. The composition as recited in claim 26 wherein the crystallizable segment has a number average molecular weight of at least 500.

40. The composition as recited in claim 26 wherein the copolymer is a star block copolymer.

41. The composition as recited in claim 40 wherein the star block copolymer has from 4 to 25 arms.

42. The composition as recited in claim 41 wherein the star block copolymer has from 5 to 15 arms.

43. The composition as recited in claim 40 wherein the star block copolymer has a weight average molecular weight of from 100,000 to 500,000.

44. A process of modifying the viscosity of an oleaginous composition, having a cloud point temperature (T_c) when tested according to ASTM D-2500, comprising the step of :

adding to the oleaginous composition, a sufficient amount of at least one polybutadiene block copolymer comprising monomeric units derived from 1,4-butadiene and 1,2-butadiene polymerization products, the copolymer being hydrogenated and comprising at least 10 percent by weight of at least one crystallizable segment comprised of methylene units and having an average methylene content corresponding to a 1,4-polybutadiene content of at least about 20 mole percent, and more than one low crystallinity segment comprised of methylene units and substituted methylene units and having an average methylene content corresponding to a 1,4-polybutadiene content up to about 20 mole percent, wherein the hydrogenated block copolymer has an associated temperature (T_a) which is greater than T_c.

45. The process as recited in claim 44 wherein said hydrogenated copolymer is comprised of a chain segment sequence represented by the structure :

$$T_1 - (M_1 - T_2)_x - M_2 - T_3$$

wherein x is a number of from 0 to 3, M_1 and M_2 are the same or different and each comprises said crystallizable segment, and T_1, T_2 and T_3 are the same or different and each comprises said low crystallinity segment.

46. The process as recited in claim 45 wherein x is zero.

47. The process as recited in claim 46 wherein said T_1 and T_3 segments are the same weight average molecular weight.

48. The process as recited in claim 44 wherein the 1,4-butadiene and 1,2-butadiene are present in amounts effective to provide said at least one crystallizable segment and said more than one low crystallinity segment.

49. The process as recited in claim 48 wherein said amount of 1,4-butadiene is at least about 20 mole percent.

50. The process as recited in claim 44 wherein said hydrogenated copolymer has a molecular weight distribution characterized by a ratio of $\overline{Mw} / \overline{Mn}$ of less than 2.

51. The process as recited in claim 44 wherein said oleaginous composition

is a lubricating oil.

52. The process as recited in claim 51 wherein said oleaginous composition is a lubricating oil concentrate.

53. The process as recited in claim 51 wherein said oleaginous composition is a fully formulated lubricating oil composition.

54. The process as recited in claim 44 wherein the crystallizable segment comprises at least 11 adjacent methylene units in series.

55. The process as recited in claim 54 wherein the low crystallinity segment comprises less than 11 adjacent methylene units in series.

56. The process as recited in claim 55 wherein the low crystallinity segment comprises less than 7 adjacent methylene units in series.

57. The process as recited in claim 44 wherein the crystallizable segment has a number average molecular weight of at least 500.

58. The process as recited in claim 44 wherein the copolymer is a star block copolymer.

59. The process as recited in claim 58 wherein the star block copolymer has from 4 to 25 arms.

60. The process as recited in claim 59 wherein the star block copolymer has from 5 to 15 arms.

61. The process as recited in claim 58 wherein the star block copolymer has a weight average molecular weight of from 100,000 to 500,000.

DATED THIS 27TH DAY OF SEPTEMBER, 1994

EXXON CHEMICALS PATENTS INC.

WATERMARK PATENT & TRADEMARK ATTORNEYS
290 BURWOOD ROAD
HAWTHORN VICTORIA 3122
AUSTRALIA

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/01937

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08F8/04; C10M143/12

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08F ; C10M ; C08C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[o]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	EP,A,0 318 848 (BASF AKTIENGESELLSCHAFT) 7 June 1989 see the whole document ---	1-14, 19-23, 28-44, 49-65
A	EP,A,0 024 314 (THE FIRESTONE TIRE & RUBBER COMPANY) 4 March 1981 see claims 1-5 ---	1
A	EP,A,0 344 836 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 6 December 1989 see claims 1-10 ---	17-22
A	EP,A,0 029 622 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 3 June 1981 see claims 1-20 ---	17-22

-/--

[o] Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
1 23 JULY 1992	17. 08. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	PERMENTIER W.A.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	CHEMICAL ABSTRACTS, vol. 97, no. 18, November 1982, Columbus, Ohio, US; abstract no. 146011D, M. MORTON: 'ELASTOMERIC POLYDIENE ABA TRIBLOCK COPOLYMERS WITH CRYSTALLINE END BLOCKS' page 60 ;column 1 ; see abstract ---	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9201937
SA 58254

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 23/07/92

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0318848	07-06-89	DE-A-	3741097	15-06-89
EP-A-0024314	04-03-81	US-A-	4237245	02-12-80
		AU-B-	534923	23-02-84
		AU-A-	6105380	26-02-81
		CA-A-	1139490	11-01-83
		JP-C-	1441786	30-05-88
		JP-A-	56030404	27-03-81
		JP-B-	62045883	29-09-87
EP-A-0344836	06-12-89	US-A-	4877836	31-10-89
		DE-U-	6890037	05-12-91
		JP-A-	2051552	21-02-90
EP-A-0029622	03-06-81	JP-C-	1468752	30-11-88
		JP-A-	56084704	10-07-81
		JP-B-	63018605	19-04-88
		US-A-	4358565	09-11-82

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82