

**STAR POLYMER VISCOSITY INDEX IMPROVER  
FOR LUBRICATING OIL COMPOSITIONS**

The present invention relates to star polymers, a process for their preparation, and to lubricating oil compositions and lubricating oil concentrates containing them.

The viscosity of lubricating oil compositions varies with temperature. In general, lubricating oil compositions are identified by a viscosity index which is a function of the lubricating oil composition viscosity at a given lower temperature and a given higher temperature. The given lower temperature and the given higher temperature have varied over the years but are fixed at any given time in an ASTM test procedure (ASTM D2270). Currently, the lower temperature specified in the test is 40°C and the higher temperature is 100°C. For two engine lubricating oil compositions with the same kinematic viscosity at 100°C, the one having the lower kinematic viscosity at 40°C will have the higher viscosity index. The lubricating oil composition with the higher viscosity index undergoes less kinematic viscosity change between the temperatures of 40°C and 100°C. In general, viscosity index improvers that are added to engine lubricating oil compositions increase the viscosity index as well as the kinematic viscosities.

Viscosity index improvers that are hydrogenated star polymers containing hydrogenated polymeric arms of copolymers of conjugated dienes, including polybutadiene made by the high 1,4-addition of butadiene, are known from United States Patent 4,116,917. In said document the anionic polymerisation of butadiene and isoprene is described to prepare star

polymers with hydrogenated poly(butadiene/isoprene) tapered arms wherein the star arms contained hydrogenated polybutadiene blocks that were external to the coupled nucleus, before coupling with divinylbenzene to prepare the unhydrogenated star polymer. Since butadiene initially reacts faster than isoprene when the anionic polymerisation is initiated with secondary butyllithium, a polybutadiene block is first formed. As the butadiene concentration is lowered through polymerisation, isoprene begins to add to the living polymer so that when the polymerisation reaction is complete, the chain is made up of a polybutadiene block, a tapered segment containing both butadiene and isoprene addition product, and a polyisoprene block, to give a living tapered polymer that, when coupled with divinylbenzene, produces a star polymer with the polybutadiene content becoming dominant away from the divinylbenzene-coupled nucleus. Since polymerisation conditions favoured high-1,4 addition of butadiene, rather than 1,2-addition, vinylic pendant group attachment to the carbon-carbon backbone of the linear chain is minimized, so that, after hydrogenation, the external positions of the arms, remote from the nucleus, resemble polyethylene-like blocks. Then, if there is 90 percent 1,4-addition and 10 percent 1,2-addition of butadiene, after coupling and hydrogenation the polyethylene-like segments will contain 18 ethylene  $-(CH_2CH_2)-$  segments for every  $-(CH_2-CHR)-$ , where R represents a pendant side-chain ethyl pendant group. Thus, the polymerisation method used results in the placement of polyethylene-like segments at the external positions of the hydrogenated arms of the star polymer, remote from the coupled nucleus.

The present invention relates to star polymers useful as viscosity index improvers in lubricating oil

compositions formulated for high performance engines. The star polymers have specific triblock copolymer arms of poly(isoprene-butadiene-isoprene) which significantly improves low temperature performance of the polymers as viscosity index improvers when a) the star polymers comprise less than 15% by weight of the polybutadiene blocks which have at least 85% 1,4-polymerisation of the butadiene and when b) the ratio of the number average molecular weight of the outer polyisoprene blocks to the inner polyisoprene blocks is from 0.75:1 to 7.5:1. The star polymers in accordance with the invention provide reduced viscosity at low temperatures in comparison to star polymers having block ratios lower than 0.75:1 or higher than 7.5:1 (which includes diblock arms) as measured by a smaller contribution to pumping viscosity and no yield stress in the TP1-MRV. The star polymers of this invention offer reduced viscosity at low temperatures when in company with lower pour point concentrations than poly(isoprene-butadiene) stars, that is (EP-EB)<sub>n</sub> stars, of comparable and higher butadiene contents.

Accordingly, the present invention provides a star polymer, useful as a viscosity index (VI) improver, which comprises polyisoprene blocks and polybutadiene blocks combined in molecules having the structure (EP-EB-EP')<sub>n</sub>-X, wherein EP is an outer block of polyisoprene having a number average molecular weight (MW<sub>1</sub>) between 6,500 and 85,000, EB is a block of polybutadiene having at least 85% 1,4-polymerisation of the butadiene and having a number average molecular weight (MW<sub>2</sub>) between 1,500 and 15,000, EP' is an inner block of polyisoprene having a number average molecular weight (MW<sub>3</sub>) of between 1,500 and 55,000, wherein the star polymer comprises less than 15% by weight of the polybutadiene, the ratio of EP/EP' is from 0.75:1 to 7.5:1, X is a nucleus of a polyalkenyl coupling agent,

and n is the average number of (EP-EB-EP') arms per star molecule formed by the reaction of 2 or more moles of the polyalkenyl coupling agent per mole of arms.

Prior to coupling, the arms have the structure polyisoprene-polybutadiene-polyisoprene'-Li (I-B-I'-Li). The living polymer molecules are coupled with a polyalkenyl coupling agent such as divinylbenzene wherein the ratio of moles of divinylbenzene to living polymer molecules is at least 2:1, and preferably at least 3:1. The star polymer can then selectively at least partially be hydrogenated to saturate isoprene and butadiene units. Suitably, at least 98% by weight of the isoprene and butadiene unit is hydrogenated. Preferably, at least 95% by weight. The star polymers can be prepared by the type of processes as described in Canadian Patent No. 716,645 and United States Patent No. Re 27,145 which are hereby incorporated by reference.

The star polymers of the present invention have molecular weights which are not taught by the references and are selected to obtain surprisingly improved low temperature performance in multigrade oils that contain surprisingly low pour point depressant concentrations. The star polymers of the present invention do not provide gelled oil concentrates at room temperature, and do not provide multigrade oils with time-dependent 40°C kinematic viscosities and with time-dependent viscosity indexes. Preferably, the star polymer comprises from 3% to 15% by weight of the butadiene, more preferably less than 10% by weight.

In the solid state, differential scanning calorimetry (DSC) results indicate that polymers of this invention are semicrystalline polymers whose melting point and crystalline character is derived from the inclusion of the EB hydrogenated blocks. These blocks are somewhat similar to polyethylene blocks that

contain a small amount of copolymerised butylene since the addition of butadiene is not entirely via 1,4-addition. Thus, in anionic polymerisation if there is 90 percent 1,4-addition and 10 percent 1,2-addition of butadiene, after coupling and hydrogenation the polyethylene-like segments will contain 18  $-(CH_2-CH_2)-$  segments for every  $-(CH_2-CHR)-$ , where R represents a pendant ethyl group. It is the polyethylene-like block that can potentially interact negatively with the paraffinic and isoparaffinic wax formers that are present in basestocks.

Star polymers that contain hydrogenated polyisoprene arms do not suffer this interaction with wax precursors because of the abundance of pendant alkyl side-chain groups that are present when 1,4-addition, 3,4-addition, or 1,2-addition occurs with isoprene. The star polymers of the present invention are designed to be non-interactive to wax, like the hydrogenated all-polyisoprene-arm star polymers, but have better performance than the all-polyisoprene-arm stars because they undergo coil volume collapse at low temperature due to crystallization.

The star polymers of the present invention can be dissolved in oil above room temperature. When the oil is heated, the EB portion of the star molecule melts and is solubilised in the oil. This increases the oil's viscosity when it is needed for higher temperature protection of the engine. When the temperature is lowered, the polymers undergo intramolecular crystallization of the EB blocks occur. The EP blocks are required to retain polymer solubility in oil, and to minimize or prevent intermolecular crystallization. In oil, crystallization occurs somewhat below the melting point of the solid polymers. For the star polymers of the present invention, crystallization in oil occurs below 40°C. Likewise, the

viscosity index determination does not increase or decrease due to very slow crystallization of the star polymer in oil.

The performance advantages of the present star polymers relative to the prior art can readily be observed by a reduced contribution to low-shear-rate viscosity and the absence of a yield stress, which results in an automatic failure, at lower temperatures in the TP1-MRV test. The TP1-MRV improvements for the present star polymers occur with reduced pour point depressant concentrations compared to those required for (EP-EB)<sub>n</sub> stars.

Common practice dictates that engine lubricating oil compositions have viscosity indexes that are not variable; however, for the engine lubricating oil composition comparison examples which follow which contain (EP-EB)<sub>n</sub> star polymers and butadiene contents of more than 10 percent weight, the viscosity index changes with time because the crystallization of the polymer in oil is slow, and occurs above 40°C. For such polymers in a lubricating oil composition, the 40°C kinematic viscosity is time dependent, thus the viscosity index is also time dependent. The viscosity indexes reported herein in Tables 3 and 4 are those obtained when there is no further change in kinematic viscosity at 40°C. For such polymers it take up to several days before a constant kinematic viscosity is arrived at after blending the formulated oil is completed.

The kinematic viscosity at 40°C, and thus the viscosity index, can either increase or decrease after a freshly-prepared oil blend is stored several days at room temperature. If only intra-molecular crystallization occurs, the coil volume decreases, kinematic viscosity at 40°C decreases, and this causes viscosity index to go up. If there is inter-molecular

crystallization of EB blocks from different star polymer molecules, however, 40°C viscosity increases, and the determined viscosity index decreases to a constant value with time. It is believed that the extent of inter-molecular crystallization relative to intra-molecular crystallization can be altered by the selection of pour point depressants; thus, a given polymer may provide a 40°C viscosity increase in some formulations and a decrease in others. However, inter-molecular crystallization is favoured for (EP-EB)<sub>n</sub> star polymers if the crystallization sites are made from high 1,4-addition of butadiene, EB has relatively high number average molecular weight, and the EP block has a relatively low number average molecular weight, so that when star-star entanglements occur there are some EB blocks from neighbouring molecules that are in close proximity.

In examples which follow for (EP-EB)<sub>n</sub> star polymers in formulated oils, examples where kinematic viscosity increases and viscosity index decreases occur when EB molecular weight is greater than 10,000 and EP block size is relative low.

The star polymers in accordance with the present invention, (EP-EB-EP')<sub>n</sub> star polymers, provide multigrade oils with 40°C kinematic viscosities and viscosity indexes that are not time dependent; in this case it is believed that crystallization of EB blocks occurs in oil below 40°C. Because crystallization rate is a function of temperature, crystallization is rapid below 40°C and this is reflected in the low contribution of the polymers to viscosity in the TP1-MRV test.

Thus, it is believed that the polymers of the present invention offer improved function as viscosity index improvers because of a) specific location of the hydrogenated polybutadiene (polyethylene-like) block and b) the limitation placed on butadiene content.

Limitations on block location and percent butadiene minimizes or eliminates the interaction and co-crystallization of wax precursors with the polyethylene-like blocks, minimizes or eliminates the inter-molecular crystallization of the polyethylene-like blocks with each other, which can lead to cross-linking of different star polymer molecules, and maximizes the coil volume size reduction that should result at low temperatures when intra-molecular crystallization of the arms attached to the nucleus occurs.

It is also believed that by minimization of polybutadiene, and its appropriate placement within the star polymer, so as to be less or non-interactive with the paraffinic and isoparaffinic wax-forming components that are contained in conventional basestocks, a viscosity index improver is produced which can be used with less pour point depressant, which is less sensitive to the composition of the pour point depressant, and which also does not require the use of speciality pour point depressants to minimize the interaction of the viscosity index improver with the wax precursors. Pour point depressants, such as fumarate-vinyl acetate flow improvers, which are effective with viscosity index improvers having polyethylene-like segments have been described in European Patent Application Number 296,714.

Interactions of the viscosity index improver with waxy components of basestock is to be avoided, for the imposition of low-temperature cooling in the MRV tests can result in polymer-wax lattice formation that results in high MRV pumping viscosity or gelation of the oil which is evidenced by yield stress failure.

The attachment of many arms to the star nucleus by coupling with divinylbenzene, results in a star polymer with a relatively high density of arms which are in

close proximity to each other, particularly at the centre of the star. It appears that placement of a high density of polyethylene-like blocks adjacent to the star centre, such as would be the case of hydrogenated poly(isoprene-butadiene) block copolymers, that is  $(EP-EB)_n$  stars, provides a strong affinity for a paraffinic and isoparaffinic wax molecules, which have  $\angle(CH_2-CH_2)-$  segments, to interact with more than one of the hydrogenated polybutadiene blocks coupled to the nucleus of the star and either interfere with the crystallization process, thus preventing complete coil volume shrinkage as the oil is cooled, or associate with the polybutadiene block surfaces, as crystallization takes place. This interaction process may account for failing low-temperature results in fully-formulated oils unless a) relatively high pour point depressants are co-blended into the formulations, or b) special pour point depressants are used that are predisposed to interact with the polyethylene-like segments. The use of such speciality pour point depressants does not necessarily preclude the need of an additional pour point depressant, of a different composition, to properly interact with the wax precursors of the basestocks that are included in the formulated oil.

To counteract the high polyethylene-like density near the centre of the star, the hydrogenated butadiene blocks may be placed further from the nucleus. It is not known with certainty why such positioning should be favoured, however it is believed that when hydrogenated star polymers are used as viscosity index improvers which have hydrogenated poly(isoprene-butadiene-isoprene) arms, that is,  $(EP-EB-EP')_n$  star polymers, the hydrogenated polyethylene-like segment of one arm is further away from adjacent neighbours in solution and the interaction of a wax precursor with multiple

hydrogenated polybutadiene blocks of the same polymer molecule is less favoured.

On the other hand, polyethylene-like hydrogenated polybutadiene blocks cannot be placed too close to the outer edge or periphery of the star polymer molecule. While wax-polyethylene interaction is to be minimized, the placement of the hydrogenated polybutadiene blocks too close to the outside of the star molecule will result in the inter-molecular crystallization of these arms in solution. The result of intermolecular crystallization is the same as for (EP-EB)<sub>n</sub> star polymers; an increase in viscosity and possibly gelling occurs, which is brought about by the three dimensional crystallization of many star polymer molecules to form a lattice structure.

The crystallization temperature of hydrogenated poly(isoprene-butadiene) star polymers may be lowered by reducing the block molecular weight of hydrogenated polybutadiene together with placement of the hydrogenated polybutadiene between hydrogenated polyisoprene segments, and this reduction results in improved low-temperature TP1-MRV test results. It also results in the additional benefit of butadiene-containing star polymers that are not sensitive to pour point depressant type or concentration, and which do not provide oils which have time-dependent viscosity indexes. The invention thus describes semicrystalline star polymer viscosity index improvers that provide superior low-temperature performance and which do so without the use of relatively high concentrations of pour point depressant or the need for supplemental pour point depressants.

The star polymers of the present invention which are useful as VI improvers are preferably prepared by anionically polymerising isoprene in the presence of sec-butyllithium, adding butadiene to the living

polyisopropyl lithium, adding isoprene to the polymerised living block copolymer, and then coupling the living block copolymer molecules with a polyalkenyl coupling agent to form a star polymer. The star polymer so attained can then be hydrogenated. Suitably, butadiene, is added to the living polyisopropyl lithium after the polymerisation of the outer block is substantially complete. It is important to maintain high 1,4-addition throughout the polymerisation of the butadiene block of the block copolymer so that polyethylene-like blocks of sufficient molecular weight are also obtained. However, it is not important that the inner polyisoprene block be made by high 1,4-addition of isoprene. Thus, it should be feasible to add a randomizer such as diethyl ether to the living block copolymer after the attainment of a sufficient molecular weight of high 1,4-addition butadiene had been obtained.

The randomizer can be added at the conclusion of the butadiene polymerisation, and before introduction of more isoprene to give the second polyisoprene block. Alternatively, the randomizer could be added before substantial completion of the butadiene block polymerisation, and concurrent with the introduction of isoprene; in this case, after coupling and hydrogenation, the star polymer would be represented by  $(EP-EB-EB/EP-EP')_nX$ , wherein EB/EP is a small hydrogenated tapered butadiene/isoprene polymer block. The hydrogenated polyisoprene blocks and hydrogenated polybutadiene blocks have the previously described molecular weights and the tapered block would generally be smaller than the butadiene block.

The star polymers of the present invention may be characterized prior to the hydrogenation as having a dense centre or nucleus of crosslinked poly(polyalkenyl

coupling agent) and a number of block copolymer arms extending outwardly therefrom. The number of arms, as determined by conventional gel permeation chromatography (GPC), may vary considerably but typically range from about 6 to 13. The number average molecular weights of the blocks are also suitably determined by means of gel permeation chromatograph.

In general, the star polymers may be hydrogenated using any of the techniques known in the prior art to be suitable for hydrogenation of olefinic unsaturation. Suitably, however, the hydrogenation conditions are chosen so as to hydrogenate at least 95%, preferably at least 98%, of the original olefinic unsaturation, and conditions must be employed so that the partially-hydrogenated or fully-hydrogenated polybutadiene blocks do not crystallize and separate from solvent before hydrogenation, or catalyst wash-out is complete. Depending on the percentage of butadiene used in preparation of the star polymer, during and subsequent to hydrogenation in cyclohexane, there is sometimes a marked increase in the viscosity of the solution. To avoid crystallization of the polybutadiene blocks, the solvent temperature should be maintained above the temperature where crystallization would occur.

In general, hydrogenation involves the use of a suitable catalyst as for instance described in U.S. Patent No. Re 27,145 which is hereby incorporated by reference. A mixture of nickel ethylhexanoate and triethylaluminum having from 1.8 to 3 moles of aluminum per mole of nickel is preferred.

The hydrogenated star polymers of the present invention may be added to a variety of lubricating oil compositions to improved viscosity index characteristics.

Suitable lubricating oils are natural, mineral or synthetic lubricating oils.

Natural lubricating oils include animal and vegetable oils, such as castor oil. Mineral oils comprise the lubricating oil fractions derived from crude oils, coal or shale, which fractions may have been subjected to certain treatments such as clay-acid, solvent or hydrogenation treatments. Synthetic lubricating oils include synthetic polymers of hydrocarbons, modified alkylene oxide polymers, and ester lubricants, which are known in the art. These lubricating oils are preferably crankcase lubricating oils for spark-ignition and compression-ignition engines, but include also hydraulic lubricants, metal-working fluids and automatic transmission fluids.

Preferably the lubricating base oil component of the compositions according to the present invention is a mineral lubricating oil or a mixture of mineral lubricating oils, such as those sold by member companies of the Royal Dutch/Shell Group under the designations "HVI", or "XHVI" (Trade Mark).

The viscosity of the lubricating base oils present in the compositions according to the present invention may vary within wide ranges, and is generally from 3 to 35 mm<sup>2</sup>/s at 100°C.

Accordingly, the present invention also provides a lubricating oil composition comprising a major amount (more than 50%w) of a lubricating oil and a minor amount (less than 50%w), preferably from 0.05 to 10%w, more preferably from 0.2 to 8%w, of a star polymer according to the present invention, all percentages by weight based on total composition.

The present invention still further provides a lubricating oil concentrate comprising at least 85% by weight of a base oil and from 5 to 15% by weight of a star polymer according to the invention, based on total concentrate. Such a concentrate generally comprises an

inert carrier fluid, e.g. a lubricating oil, and one or more additives in a concentrated form.

Lubricating oil compositions prepared with the present hydrogenated star polymers may also contain other additives such as anti-corrosive additives, antioxidants, detergents, pour point depressants, one or more additional VI improvers and the like. Typical additives which are useful in the lubricating oil compositions according to the present invention are described in U.S. Patent Nos. 3,772,196 and 3,835,083, which are hereby incorporated by reference.

Preferred star polymers of the present invention combine polyisoprene blocks and polybutadiene blocks in molecules having the structure  $(EP-EB-EP')_n-X$ , wherein EP is an outer block of polyisoprene having a number average molecular weight ( $MW_1$ ) between 15,000 and 65,000, EB is a block of polybutadiene having at least 89% 1,4-polymerisation of the butadiene and having a number average molecular weight ( $MW_2$ ) between 2,000 and 6,000, EP' is an inner block of polyisoprene having a number average molecular weight ( $MW_3$ ) of between 5,000 and 40,000, wherein the star polymer comprises less than 10% by weight of the polybutadiene, the ratio of EP/EP' is from 0.9:1 to 5:1, X is a nucleus of a polyalkenyl coupling agent, and n is the average number of (EP-EB-EP') arms per star molecule.

The coupled polymers can then selectively be hydrogenated for instance with a solution of nickel ethylhexanoate and triethylaluminium having a Al/Ni ratio of 1.8:1 to 2.5:1 to saturate at least 98% of the isoprene and butadiene units.

The present invention will now be illustrated by means of the following Examples.

Example 1      mpa  
                  mpa a    e example    a    a    p l me  
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                  mp

hydrogenated butadiene was prepared. In the first step of the preparation, living molecules of polyisoprene were prepared by anionically polymerising isoprene in cyclohexane. The polymerisation of the isoprene was initiated by adding sec-butyllithium. The polymerisation of the isoprene was completed to produce living polyisoprene molecules having a number average molecular weight of 45,000. Polybutadiene blocks were formed by adding butadiene to the solution of living polyisoprene molecules. The polymerisation of butadiene was completed to produce polybutadiene blocks having a number average molecular weight of 4,800 as determined by gel permeation chromatography. Proton NMR analysis indicated that in the absence of a microstructure modifier, the isoprene block contained 6.1 percent vinylic substituents while the butadiene block contained 11.7 percent vinyl substituents as a result of 1,2-addition. Thus, 89.3 percent of the butadiene was polymerised by 1,4-addition. From proton NMR it was also determined that 10.5 percent of the polymer was comprised of polybutadiene.

The living diblock copolymer arms were then coupled with divinylbenzene using 3 moles of divinylbenzene per mole of the living block copolymer molecules. The coupling reaction was allowed to proceed to completion after which the lithium sites remaining in the star polymer were deactivated by adding an alcohol. Subsequent proton NMR analysis of the coupled polymer indicated that the butadiene block contained 12.1 percent vinyl substituents, or that 87.9 percent of the butadiene polymerised by 1,4-addition.

The star polymer was next hydrogenated at 75°C to saturate more than 98% of the olefinic unsaturation originally contained in the isoprene and butadiene blocks using a catalyst prepared by combining nickel ethylhexanoate and triethylaluminium (2.3 moles of

aluminium per mole of nickel). The hydrogenation catalyst was then extracted by an aqueous acidic water-wash at room temperature, using a high dilution ratio. Steam/hot water devolatilization was used to coagulate the polymer. Differential scanning calorimetry was used to determine the melting point of the PE-like blocks. The melting point occurred at 89°C as determined by differential scanning calorimetry. The data and results are summarized in Table 1.

Example 2 (Comparison)

In this comparative example, a star polymer comprising hydrogenated poly(isoprene-butadiene) diblock copolymer arms was prepared using the procedure as summarized in Example 1 except that the number average molecular weight of the polyisoprene blocks as determined by gel permeation chromatography was 41,600 and the number average molecular weight of the polybutadiene blocks was 12,700. Nmr analysis indicated that 90.5 percent of the butadiene had been incorporated by 1,4-addition, and the butadiene represented 20.5 percent of the total polydiene content of the arms. After coupling with divinylbenzene, NMR analysis indicated that the 1,4-addition of butadiene was 90.5 percent, and that butadiene represented 20.4 percent of the diene content. The star polymer was next hydrogenated at 75°C to saturate more than 98% of the olefinic unsaturation originally contained in the isoprene and butadiene blocks. The solution was washed at 100°C before polymer separation from solvent. The data and results are summarized in Table 1.

Example 3 (Comparison)

In this comparative example, a star polymer comprising hydrogenated poly(isoprene-butadiene) diblock copolymer arms was prepared using the procedure as summarized in Example 1 except that the number average molecular weight of the polyisoprene blocks as

determined by gel permeation chromatography was 31,700 and the number average molecular weight of the polybutadiene blocks was 15,500. Nmr analysis indicated that 90.8 percent of the butadiene had been incorporated by 1,4-addition, and the total butadiene represented 29.9 percent of the total polydiene content of the arms. After coupling with divinylbenzene, analysis of the coupled, unhydrogenated star polymer indicated that the 1,4-addition of butadiene was 90.9 percent, and that the butadiene contained therein was 29.9 percent. The star polymer was next hydrogenated to remove more than 99% of the olefinic unsaturation originally contained in the isoprene and butadiene blocks. The polymer solution became extremely viscous upon hydrogenation; it was diluted further with cyclohexane before acid-wash and polymer separation. The melting point of the PE-like blocks was determined to be 98.5°C by differential scanning calorimetry. The data and results are summarized in Table 1.

Example 4 (Comparison)

In this comparative example, a star polymer comprising hydrogenated poly(isoprene-butadiene) diblock copolymer arms was prepared using the procedure as summarized in Example 1 except that the number average molecular weight of the polyisoprene blocks as determined by gel permeation chromatography was 58,000 and the number average molecular weight of the polybutadiene blocks was 11,200. Nmr analysis indicated that 90.6 percent of the butadiene had been incorporated by 1,4-addition, and the butadiene represented 14.7 percent of the total polydiene content of the arms. After coupling with divinylbenzene, analysis of the coupled, unhydrogenated star polymer indicated that the 1,4-addition of butadiene was 90.2 percent, and that butadiene represented 14.5 percent of the polydiene content. The star polymer was next

hydrogenated so as to saturate more than 98% of the olefinic unsaturation originally contained in the isoprene and butadiene blocks. The melting point of the PE-like blocks was determined to be 95.0°C by differential scanning calorimetry. The data and results are summarized in Table 1.

Example 5 (Comparison)

In this comparative example, a star polymer comprising hydrogenated poly(isoprene-butadiene) diblock copolymer arms was prepared using the procedure as summarized in Example 1 except that a ratio of 4 moles of divinylbenzene per mole of living polymer was used for coupling purposes and the number average molecular weight of the polyisoprene blocks as determined by gel permeation chromatography was 30,100 and the number average molecular weight of the polybutadiene blocks was 5,250. The polybutadiene content appeared to be 14.8 percent. The star polymer was next hydrogenated to saturate more than 98% of the olefinic unsaturation originally contained in the isoprene and butadiene blocks, and the resultant solution was acid washed and the polymer separated. Finished product NMR analysis indicated that 99.1 percent of the olefinic unsaturation had been removed. The results are summarized in Table 1.

Example 6 (Comparison)

In this comparative example, a star polymer comprising hydrogenated poly(isoprene-butadiene) diblock copolymer arms was prepared using the procedure as summarized in Example 1 except that a ratio of 4 moles of divinylbenzene per mole of living polymer was used for coupling purposes and the number average molecular weight of the polyisoprene blocks as determined by gel permeation chromatography was 38,800 and the number average molecular weight of the polybutadiene blocks was 10,400. It appeared that the

butadiene represented 21.2 percent of the total polydiene content of the arms. The star polymer was hydrogenated and the resultant solution was aqueous acid and water washed at 90°C. Nmr analysis of the final product showed that 99.2 percent of the olefinic unsaturation had been removed by hydrogenation. The melting point of the PE-like blocks was determined to be 94.9°C by differential scanning calorimetry. The data and results are summarized in Table 1.

Example 7 (Comparison)

In this comparative example, a star polymer comprising hydrogenated poly(isoprene-butadiene) diblock copolymer arms was prepared using the procedure as summarized in Example 1 except that a ratio of 4 moles of divinylbenzene per mole of living polymer was used for coupling purposes. The number average molecular weight of the polyisoprene blocks (I) as determined by gel permeation chromatography was 56,250, and the number average molecular weight of the polybutadiene blocks (B) was 12,000. The butadiene content appeared to be 17.6 percent. Analysis of the diblock polymer indicated that 10.5 percent of butadiene was incorporated into the block copolymer. After coupling with divinylbenzene, the star polymer was hydrogenated and the resultant reaction mixture was aqueous acid and water washed at 100°C. It was subsequently determined that 99.3 percent of the olefinic unsaturation originally contained in the isoprene and butadiene blocks had been removed by hydrogenation. The melting point of the polyethylene-like blocks are determined to be 92.0°C by differential scanning calorimetry. The data and results are summarized in Table 1.

Example 8

In this example in accordance with the invention, a star polymer comprising hydrogenated poly(isoprene-

butadiene-isoprene) triblock copolymer arms was prepared using the procedure as summarized in Example 1 except that after the poly(isoprene-butadiene) blocks were incorporated, isoprene monomer was again added to the living polymer. The number average molecular weight of the outer polyisoprene blocks as determined by gel permeation chromatography was 34,200, the number average molecular weight of the polybutadiene blocks was 5,300 and the number average molecular weight of the inner polyisoprene blocks was 11,100. NMR analysis of the triblock polymer arms indicated that 10.5 percent of butadiene was incorporated into the block copolymer and that 90.0 percent of the butadiene polymerised by 1,4-addition. After coupling with divinylbenzene, the star polymer cement was reduced from 20 percent to 10 percent solids content, hydrogenated at 65°C and the resultant reaction mixture aqueous acid and water washed at 50°C. It was subsequently determined that 99.3 percent of the olefinic unsaturation originally contained in the isoprene and butadiene blocks had been removed by hydrogenation. The melting point of the PE-like blocks was determined to be 84.8°C by differential scanning calorimetry. The data and results are summarized in Table 1.

#### Example 9

In this example in accordance with the invention, a star polymer comprising hydrogenated poly(isoprene-butadiene-isoprene) triblock copolymer arms was prepared using the procedure summarized in Examples 1 and 8. The number average molecular weight of the outer polyisoprene blocks as determined by GPC was 26,000, the number average molecular weight of the polybutadiene blocks was 5,200, and the number average molecular weight of the inner polyisoprene blocks was 22,300. NMR analysis of the triblock polymer indicated

that 10.5 percent of butadiene was incorporated and that 90.0 percent of the butadiene had been added by 1,4-addition. After coupling with divinylbenzene, the star polymer cement was hydrogenated and the resultant reaction mixture was aqueous acid and water washed. It was subsequently determined that 99.3 percent of the olefinic unsaturation originally contained in the isoprene and butadiene blocks had been removed by hydrogenation. The data and results are summarized in Table 1.

Example 10 (Comparison)

In this comparative example, a selectively hydrogenated star polymer comprising arms of a single block of polystyrene and a single block of hydrogenated polyisoprene was prepared. In the first step of the preparation, living molecules of polystyrene were prepared by anionically polymerising styrene in cyclohexane. The polymerisation of the styrene was initiated by adding sec-butyllithium. The polymerisation of the styrene was completed to produce living polystyrene molecules having a number average molecular weight of 3,200. Polyisoprene blocks were then formed by adding isoprene to the solution of living polystyrene molecules. The polymerisation of isoprene was then completed to produce polyisoprene blocks having a number average molecular weight of 51,000.

The living polymer molecules were then coupled with divinylbenzene using 3 moles of divinylbenzene per mole of the polymer molecules. The coupling reaction was allowed to proceed to completion after which the lithium sites remaining in the star polymer were deactivated by adding methanol.

The star polymer was next hydrogenated so as to saturate more than 98% of the olefinic unsaturation originally contained in the polyisoprene and less than

15% of the aromatic unsaturation using the catalyst of Example 1 (2.3:1 Al/Ni).

Example 11 (Comparison)

In this comparative example, a star polymer comprising homopolymer arms of hydrogenated polyisoprene was prepared using the procedure as summarized in Example 1 except that butadiene was omitted and the number average molecular weight of the polyisoprene blocks was 35,000. The data and results are summarized in Table 1.

Example 12 (Comparison)

In this comparative example, a star polymer comprising homopolymer arms of hydrogenated polyisoprene was prepared using the procedure as summarized in Example 1 except that butadiene was omitted and the number average molecular weight of the polyisoprene blocks was 46,000. The data and results are summarized in Table 1.

Example 13 (Comparison)

In this comparative example, a linear hydrogenated poly(isoprene-butadiene-isoprene) block copolymer was prepared. In the first step of the preparation, living molecules of polyisoprene were prepared by anionically polymerising isoprene in cyclohexane. The polymerisation of the isoprene was initiated by adding sec-butyllithium. The polymerisation of the isoprene was completed to produce living polyisoprene molecules having a number average molecular weight of 91,400. Polybutadiene blocks were formed by adding butadiene to the solution of living polyisoprene anion. The polybutadiene blocks had a number average molecular weight of 16,500. The living polymer anion was then reacted with additional isoprene. The second block of polyisoprene had a number average molecular weight of 116,000. Proton NMR indicated that 89.5 percent of butadiene polymerised by 1,4-addition. From proton NMR

it was also determined that 7.9% of the polymer was comprised of polybutadiene. The polymer was then hydrogenated using a catalyst prepared by combining nickel ethylhexanoate and triethylaluminum (2.3 moles of aluminum per mole of nickel). Proton NMR indicated that the polymer was 98.81% hydrogenated. The results are summarized in Table 1.

#### Examples 14-26

In these examples, 5% oil concentrates were prepared from the polymers indicated in Table 1. The polymers were dissolved with stirring and at 115°C in HVI 100 neutral (Exxon low pour basestock). The concentrates were allowed to cool to room temperature overnight. Table 2 identifies the polymer concentrates that were fluid or gelled at room temperature.

#### Examples 27-40

A SAE 10W-30 multigrade was made using the polymer made in example 1, and SAE 10W-40 multigrade engine oils were prepared using the polymers as prepared in examples 2-13. For the SAE 10W-40 oils the amount of each VI improver used was controlled so as to provide lubricating oil compositions having kinematic viscosities in the range of 13.5-15.0 centistokes ( $\text{mm}^2/\text{s}$ ) at 100°C. Lubricating oil compositions for both the SAE 10W-30 and the SAE 10W-40's contained, in addition to the polymer, 11.60 percent weight of "DI" (dispersant-inhibitor) package ECA 12850 (available from Exxon Chemical), 0.1 wt% "Acryloid 155" polymethacrylate pour point depressant (available from Rohm and Haas), 8.5 percent weight "HVI 250 N" (Shell Deer Park), and "HVI 100N" (Shell Deer Park). Example 40 was carried out without a polymer composition, for reasons of comparison.

Table 1

| Example | Isoprene,<br>I (Mw <sub>1</sub> ) | Butadiene,<br>B (Mw <sub>2</sub> ) | Isoprene,<br>I' (Mw <sub>3</sub> ) | I/I' | Melting<br>Point, °C | %B   |
|---------|-----------------------------------|------------------------------------|------------------------------------|------|----------------------|------|
| 1       | 45,000                            | 4,800                              | na*                                | -    | 89                   | 10.5 |
| 2       | 41,600                            | 12,700                             | na*                                | -    | -                    | 20.5 |
| 3       | 31,700                            | 15,500                             | na*                                | -    | 98.5                 | 29.9 |
| 4       | 58,000                            | 11,200                             | na*                                | -    | 95.0                 | 14.5 |
| 5       | 30,100                            | 5,250                              | na*                                | -    | 89.9                 | 14.8 |
| 6       | 38,800                            | 10,400                             | na*                                | -    | 94.9                 | 21.2 |
| 7       | 56,250                            | 12,000                             | na*                                | -    | 92.0                 | 17.6 |
| 8       | 34,200                            | 5,300                              | 11,100                             | 3.1  | 84.8                 | 10.5 |
| 9       | 26,000                            | 5,200                              | 22,300                             | 1.2  | -                    | 10.5 |
| 11      | 35,000                            | na*                                | na*                                | -    | -                    | na*  |
| 12      | 46,000                            | na*                                | na*                                | -    | -                    | na*  |
| 13      | 91,400                            | 16,500                             | 116,000                            | 0.79 | -                    | 7.9  |

\*na - not applicable

Table 2

| Example | Polymer | Concentrate Fluidity  |
|---------|---------|-----------------------|
| 14      | 1       | flows readily-no gel  |
| 15      | 2       | flows very slowly-gel |
| 16      | 3       | would not flow-gel    |
| 17      | 4       | would not flow-gel    |
| 18      | 5       | flows readily-no gel  |
| 19      | 6       | would not flow-gel    |
| 20      | 7       | would not flow-gel    |
| 21      | 8       | flows readily-no gel  |
| 22      | 9       | flows readily-no gel  |
| 23      | 10      | flows readily-no gel  |
| 24      | 11      | flows readily-no gel  |
| 25      | 12      | flows readily-no gel  |
| 26      | 13      | would not flow-gel    |

The viscosity index (VI), the cold cranking simulator (CCS) viscosity at -20°C (in centipoise), the engine oil pumping viscosity (in poise) at -25°C using the mini-rotary viscometer TP1-MRV method (ASM D3684), were determined for each lubricating oil composition. TP1-MRV results are failing if viscosity is above 300 poise or if there is a yield stress exhibited in the test. The data and results are summarized in Table 3.

Example 41-54

A series of SAE 10W-40 multigrades were prepared using the same materials as in Examples 27-40, except that the pour point depressant was changed to 0.5 percent weight "Acryloid 160", a polymethacrylate available from Rohm and Haas Company. The properties of the multigrades are given in Table 4.

Table 3

| Example | Polymer | Polymer<br>W% | KV 100°C<br>mm <sup>2</sup> /s | VI    | CCS -20°C,<br>cP (x10 <sup>-3</sup> Pa s) | TPI MRVa)<br>-25°C, cP (x10 <sup>-3</sup> Pa s) |
|---------|---------|---------------|--------------------------------|-------|-------------------------------------------|-------------------------------------------------|
| 27      | 1       | 1.04          | 11.20                          | 175** | 2,710                                     | fail-y.s.                                       |
| 28      | 2       | 1.10          | 15.03                          | 185** | 3,180                                     | fail-y.s.                                       |
| 29      | 3       | 1.07          | 13.65                          | 33*** | 2,860                                     | fail-y.s.;<br>pass, 205 P;<br>Pass-224 P b)     |
| 30      | 4       | 0.84          | 13.54                          | 217** | 2,760                                     | fail-y.s.                                       |
| 31      | 5       | 1.18          | 13.61                          | 205** | 2,850                                     | fail-y.s.                                       |
| 32      | 6       | 0.98          | 13.82                          | 193** | 3,090                                     | fail-y.s.                                       |
| 33      | 7       | 0.75          | 13.65                          | 214** | 2,780                                     | fail-y.s.                                       |
| 34      | 8       | 0.98          | 13.77                          | 157   | 2,820                                     | pass-160 P                                      |
| 35      | 9       | 1.01          | 13.64                          | 159   | 2,860                                     | pass-111 P                                      |
| 36      | 10      | .97           | 13.75                          | 158   | 3,040                                     | pass-150 P                                      |
| 37      | 11      | 1.27          | 14.17                          | 160   | 3,190                                     | pass-172 P                                      |
| 38      | 12      | 1.02          | 13.5                           | 158   | 3,010                                     | pass-147 P                                      |
| 39      | 13      | 0.74          | 13.90                          | 159   | 3,140                                     | fail-y.s.                                       |
| 40      | none    | 0.0           | 6.36                           | 119   | 2,510                                     | pass-66 P                                       |

a) Y.s = yield stress

b) in three tests: two passes, one fail

\*\* time dependent increase

\*\*\* time dependent decrease

Table 4

| Example | Polymer | Polymer<br>%w | Kin Vis<br>100°C | CCS -20°C,<br>cP (x10 <sup>-3</sup> Pa s) | TPI MRV | VI     |
|---------|---------|---------------|------------------|-------------------------------------------|---------|--------|
| 41      | 1       | 1.04          | 13.82            | 2,970                                     | 143     | 186**  |
| 42      | 2       | 1.10          | 13.88            | 2,880                                     | 113     | 176**  |
| 43      | 3       | 1.07          | 13.96            | 3,000                                     | fail*   | -      |
| 44      | 4       | 0.84          | 14.09            | 2,800                                     | 128     | 211**  |
| 45      | 5       | 1.18          | 13.81            | 2,980                                     | 128     | 211**  |
| 46      | 6       | 0.98          | 14.1             | 2,990                                     | 112     | 134*** |
| 47      | 7       | 0.75          | 13.91            | 2,890                                     | 133     | 211*   |
| 48      | 8       | 0.98          | 14.06            | 2,910                                     | 120     | 158    |
| 49      | 9       | 1.01          | 13.94            | 2,980                                     | 129     | 158    |
| 50      | 10      | 0.97          | 14.13            | 3,200                                     | 173     | 159    |
| 51      | 11      | 1.27          | 14.41            | 3,430                                     | 176     | 161    |
| 52      | 12      | 1.02          | 13.83            | 3,250                                     | 174     | 159    |
| 53      | 13      | 0.74          | 14.12            | 3,330                                     | 177     | 159    |
| 54      | none    | 0.0           | 6.47             | 2,360                                     | 72      | 124    |

\* fail by yield stress

\*\* VI increases

\*\*\* VI decreases

C L A I M S

1. A star polymer, useful as a viscosity index (VI) improver, which comprises polyisoprene blocks and polybutadiene blocks combined in molecules having the structure  $(EP-EB-EP')_n-X$ , wherein

EP is an outer block of polyisoprene having a number average molecular weight ( $MW_1$ ) between 6,500 and 85,000,

EB is a block of polybutadiene having a number average molecular weight ( $MW_2$ ) between 1,500 and 15,000 and having at least 85% 1,4-polymerisation; and

EP' is an inner block of polyisoprene having a number average molecular weight ( $MW_3$ ) between 1,500 and 55,000,

wherein the star polymer comprises less than 15% by weight of the butadiene, the ratio of  $MW_1/MW_3$  is from 0.75:1 to 7.5:1, X is a nucleus of a polyalkenyl coupling agent, and n is the number of block copolymer arms in the star polymer when coupled with 2 or more moles of the polyalkenyl coupling agent per mole of living block copolymer molecules.

2. The star polymer according to claim 1, wherein the polyalkenyl coupling agent is divinylbenzene.

3. The star polymer according to claim 1 or 2, wherein the number average molecular weight of the outer polyisoprene blocks ( $MW_1$ ) is between 15,000 and 65,000.

4. The star polymer according to any one of claims 1-3, wherein the number average weight of the polybutadiene block ( $MW_2$ ) is between 2,000 and 6,000.

5. The star polymer according to any one of claims 1-4, wherein the number average molecular weight of the inner polyisoprene blocks ( $MW_3$ ) is between 5,000 and 40,000.



6. The star polymer according to any one of claims 1-5, comprising less than 10% by weight of the butadiene.
7. The star polymer according to any one of claims 1-6, wherein the ratio of  $MW_1/MW_3$  is from 0.9:1 to 5:1.
8. The star polymer according to any one of claims 1-7, wherein the 1,4-polymerisation of the polybutadiene block is at least 89%.
9. The star polymer according to any one of claims 1-8, wherein n is the number of arms when coupled with at least 3 moles of divinylbenzene per mole of living block copolymer molecules.
10. The star polymer according to any one of claims 1-8 wherein the polyisoprene blocks and the polybutadiene blocks are at least partially hydrogenated.
11. The star polymer according to claim 10, wherein the polyisoprene blocks and the polybutadiene blocks are at least 98% hydrogenated.
12. Process for preparing a star polymer as claimed in any one of claim 1-11, which comprises anionically polymerising isoprene in the presence of sec-butyllithium, adding butadiene to the living polyisopropyl lithium, adding isoprene to the polymerised living block copolymer, and then coupling the living block copolymer molecules with a polyalkyl coupling agent to form the star polymer.
13. A lubricating oil composition comprising a base oil and a viscosity improving amount of a star polymer as claimed in any one of claims 1-11.
14. A lubricating oil concentrate comprising at least 85% by weight of a base oil and from 5% to 15% by weight of a star polymer as claimed in any one of claims 1-11.



A B S T R A C T

STAR POLYMER VISCOSITY INDEX IMPROVER  
FOR LUBRICATING OIL COMPOSITIONS

The present invention provides star polymers which are useful as viscosity index improvers in oil compositions formulated for high performance engines. the star polymers have triblock copolymer arms of hydrogenated polyisoprene-polybutadiene-polyisoprene, which provide excellent low temperature performance in lubricating oils, and can be used in the present of low pour point depressant concentrations.