

STAR POLYMER VISCOSITY INDEX IMPROVER
FOR OIL LUBRICATING COMPOSITIONS

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

5 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
10 kinematic 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
15 temperature specified in the test is 40°C and the higher temperature specified in the test 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
20 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
25 viscosities.

Numerous methods have been proposed for improving the rheological properties of lubricating compositions. Generally, these methods involve the use of a polymeric additive which cannot be handled as a solid.

30 Recently it has been discovered that certain asymmetric star polymers are both solid polymers and effective VI improvers for lubricating oil compositions

as disclosed in United States Patent No. 4,849,481. The patent describes asymmetric star polymers of conjugated diolefin blocks, such as polyisoprene, and monoalkenyl aromatic blocks, such as polystyrene. The asymmetric star polymers have sufficient amounts of the monoalkenyl aromatic blocks to be cyclone finishable as a polymer crumb. The star polymers contain a substantial amount of external monoalkenyl aromatic blocks and produce lubricating oil compositions having reduced high temperature, high shear rate (HTHSR) viscosities. However, along with 100°C kinematic viscosity, minimum HTHSR viscosity limits are also now used to grade oils by the SAE J300 standard of the SAE Engine Oil Viscosity Classification System.

Although reduced HTHSR viscosities likely indicate good fuel efficiency, increased HTHSR viscosities are needed for high performance engines which operate at higher temperatures and rpms, or for engines having marginally designed journal bearings. The Star polymers disclosed in U. S. Patent 4,849,481 are crumb, cyclone-finishable polymers which generally can provide sufficient 100°C kinematic viscosities but provide insufficient HTHSR viscosity to meet the SAE J300 requirements. To improve their HTHSR viscosity contribution, a sufficiently low amount of monoalkenyl aromatic blocks may be used, but this reduces cyclone finishability. On the other hand, if more, or larger monoalkenyl blocks are used, then the polymer becomes gelated in oil at low temperatures, and this results in a failing yield stress when the oil is evaluated in the TP1-MRV test, ASTM D4684.

In United States patent 4,116,917 viscosity improvers for lubricating oil compositions have been described which comprise a star polymer having arms linked to a nucleus. The arms may for instance comprise a poly(isoprene/styrene/isoprene) three block

copolymer in which the styrene blocks are located close to the outer edge of the star polymer (see Example 16). It appears that the viscosity characteristics of such a star polymer comprising three block copolymer arms and of conventional star polymers having all-polyisoprene arms do not differ particularly.

In accordance with the present invention, however, it has now surprisingly been found that star polymers having poly(isoprene/styrene/isoprene) three block copolymer arms display an improved performance when the styrene blocks are located close to the nucleus of the star polymer.

Accordingly, the present invention provides a star polymer, useful as a viscosity index (VI) improver, which comprises polystyrene blocks and hydrogenated polyisoprene blocks combined in molecules having the structure $(EP'-S-EP'')_n-X$, wherein EP' is a first hydrogenated block of polyisoprene (I') having a number average molecular weight (M_n) between 10,000 and 100,000 before hydrogenation, S is a block of polystyrene having a number average molecular weight (M_n) between 6,000 and 50,000, and EP'' is a second hydrogenated blocks of polyisoprene (I'') having a number average molecular weight (M_n) between 2,500 and 50,000 before hydrogenation, the molecular weight ratio of (M_w) I'/I'' is at least 1.4, X is a nucleus of a polyalkenyl coupling agent, and n is the average number of $(EP'-S-EP'')$ arms per star molecule formed by reaction of 2 or more moles of the polyalkenyl coupling agent per mole of the arms.

The star polymers in accordance with the present invention show enhanced cyclone-finishability and lower pumping viscosity in fully formulated multigrade engine lubricants, and do not gel engine oils.

It is also surprising that while good melt viscosity and good thickening efficiency in multigrade

oils is retained with appropriate internal location of polystyrene blocks relative to an external location, the viscosity of heavily-doped oil concentrates can sometimes be reduced. Thus, VI improver oil concentrates may contain more polymer and less oil if the polystyrene block is appropriately positioned internally along the arm of the star polymer. This is particularly favored if the polystyrene block number average molecular weight is kept on the low side of the range, preferably between about 6,000 to 9,000. Some of the star polymers of this invention also have improved oil concentrate fluidity, relative to other hydrogenated star polymers. With either improvement, the polystyrene block is internal, yet the star polymers have good melt viscosities at 121°C. Prior to coupling, the arms have the structure polyisoprene-polystyrene-polyisoprene (I'-S-I"-Li). The star polymer is selectively hydrogenated to saturate at least 95% by weight of the isoprene units and less than 15% by weight of the styrene units.

The star polymers of the present invention 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.

Although the reason for the improvement at low temperatures is not fully understood, it is believed that modification of the star arms by placement of a polystyrene block between two polyisoprene blocks as described above causes a smaller effective chain length at lower temperatures as a result of intramolecular association of the styrene blocks. When the temperature increases the styrene blocks can disassociate giving longer effective chain lengths and a greater contribution to kinematic viscosity, which is not desired at the lower temperatures. Both the size

and placement of the styrene blocks are critical for improved performance. The star polymes according to the present invention contribute less to viscosity as measured in the TP1-MRV and Scanning Brookfield tests.

5 Some of the star polymers in accordance with this invention also provide multigrade oils with higher viscsosity indexes than hydrogenated, all-polyisoprene star polymers or other hydrogenated poly(styrene/isoprene) block copolymer star polymers.

10 The appropriately sized and placed polystyrene in accordance with the invention lower lubricating oil concentrate viscosities at 100°C relative to all-polyisoprene-armed stars, yet this placement does not decrease the polymer's contribution to 100°C kinematic
15 viscosity in fully-formulated multigrade oils.

The present star polymers which are useful as VI improvers are suitably prepared by anionically polymerising isoprene in the presence of an initiator such as sec-butyllithium, adding styrene, and then more
20 isoprene to the living polystyrene molecules to make the living block copolymer molecules, coupling the living block copolymer molecules with a polyalkenyl coupling agent to form a star polymer, and selectively hydrogenating the polyisoprene blocks.

25 The star polymers of the present invention may be characterized prior to hydrogenation as having a central core or nucleus of crosslinked poly(polyalkenyl coupling agent) and a number of block copolymer arms extending outwardly therefrom. The number of arms, as
30 determined by conventional gel permeation chromatography (GPC), may vary considerably but typically range from 6 to 13.

In general, the star polymers may be selectively hydrogenated to saturate the polyisoprene blocks using
35 any of the techniques known in the prior art to be

suitable for selective hydrogenation of olefinic unsaturation over aromatic unsaturation.

5 The hydrogenation conditions must be sufficient to hydrogenate at least 95% of the original olefinic unsaturation. Hydrogenation of aromatic unsaturation must be less than 15% to avoid reduction of the amount of polystyrene needed to finish the star polymers.

10 In general, hydrogenation involves the use of a suitable catalyst as described in U.S. Patent No. Re 27,145 which is herein incorporated by reference. A mixture of nickel ethylhexanoate and triethylaluminium having 2.3 moles of aluminium per mole of nickel is preferred.

15 The hydrogenated star polymers in accordance with the present invention may be added to a variety of lubricating oil compositions to improve viscosity index characteristics.

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

20 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
25 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
30 oils for spark-ignition and compression-ignition engines, but include also hydraulic lubricants, metal-working fluids and automatic transmission fluids.

35 Preferably the lubricating base oil component of the compositions according to the present invention is a mineral lubricating oil or a mixture of a mineral lubricating oils, such as those sold by member

companies of the Royal Dutch/Shell Group under the designations "HVI", or "XHVI" (Trade Mark).

5 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 mm²/s at 100°C.

Accordingly, the present invention also provides a lubricating oil composition comprising a major amount (more than 50%w) and a minor amount (less than 50%w),
10 preferably from 0.05 to 10%w, more preferably from 0.2 to 5%w, and especially from 0.5 to 2.5%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
15 lubricating oil concentrate comprising from 10 to 80%w, based on the total concentrate, of a star polymer according to the present invention. Such a concentrate generally comprises an inert carrier fluid, e.g. a lubricating oil, and one or more additives in a
20 concentrated form.

Lubricating oil compositions prepared with the present selectively hydrogenated star polymers may also contain other additives such as anti-corrosive additives, antioxidants, detergents, pour point
25 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 can be found in U.S. Patent Nos. 3,772,196 and 3,835,083, which are hereby incorporated by
30 reference.

In a preferred embodiment of the present invention, the polystyrene blocks and the hydrogenated isoprene blocks are combined in molecules having the structure (EP'-S-EP")_n-X, wherein the first hydrogenated block of
35 polyisoprene (I') has a number average molecular weight (M_n) from 20,000 to 60,000 before hydrogenation, the

polystyrene block (S) has a number average molecular weight (M_n) from 10,000 to 35,000, the second hydrogenated block of polyisoprene (I'') has a number average molecular weight (M_n) from 5,500 to 33,000
5 before hydrogenation, the molecular weight ratio (M_w) of I'/I'' is from 1.8 to 10.9, X is a nucleus of a polyalkenyl coupling agent, and n is the average number of ($EP'-S-EP''$) arms per star molecule formed by
10 reaction of 2 or more moles of the polyalkenyl coupling agent per mole of the arms.

The star polymer is suitably prepared by anionically polymerising isoprene, then styrene, and then isoprene to prepare living polyisoprene-polystyrene-polyisoprene-Li molecules. The living
15 block copolymer molecules are preferably coupled with divinylbenzene using 3 moles of divinylbenzene per mole of copolymer molecules. The coupled polymers can suitably be selectively hydrogenated with a solution of nickel ethylhexanoate and triethylaluminium having a
20 preferred Al/Ni molar ratio of 2.3:1 to saturate at least 98% of the isoprene units and less than 10% of the styrene units.

Such star polymers are cyclone finishable as a polymer crumb and produce lubricating oil compositions
25 having excellent high and low temperature viscosities suitable for high performance engines.

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

Example 1

30 In this example, a star polymer comprising triblock arms of hydrogenated isoprene and styrene was prepared. In the first step of the preparation, living polyisoprene blocks (I') were prepared by anionically polymerising isoprene in cyclohexene. The
35 polymerisation of the isoprene was initiated by adding sec-butyllithium. The polymerisation of the isoprene

was completed to prepare living polyisoprene blocks (I') having a number average molecular weight (M_n) of 58,000. Polystyrene blocks were then formed by adding styrene to the solution of living polyisoprene blocks.

5 The polymerisation of styrene was completed to prepare polystyrene blocks having a number average molecular weight (M_n) of 36,000. Polyisoprene blocks were then formed by adding isoprene to the solution of living polyisoprene-polystyrene blocks. The second

10 polymerisation of isoprene was completed to prepare second polyisoprene blocks (I'') having a number average molecular weight (M_n) of 7,000. The I'/I'' molecular weight ratio (M_w) was 8.3.

The living tri-block copolymer arms were then

15 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

20 adding an alcohol.

The star polymer was next hydrogenated so as to saturate more than 98% of the olefinic unsaturation originally contained in the isoprene blocks and less than 15% of the aromatic unsaturation using a catalyst

25 prepared by combining nickel ethylhexanoate and triethylaluminium (2.3 moles of aluminium per mole of nickel). The melt viscosity of the star polymer was sufficiently high to permit finishing as a solid polymer crumb. The melt viscosity of the star polymer

30 was 37 megapoise ($\times 10^5$ Pa s) at 121°C. The data and results are summarized in Table 1.

Example 2

In this example, a star polymer comprising isoprene/styrene/isoprene triblock copolymer arms was

35 prepared using the procedure described in Example 1 except that the number average molecular weight (M_n) of

the first polyisoprene block (I'') was 56,400, the number average molecular weight (M_n) of the polystyrene block (S) was 30,000, and the number average molecular weight (M_n) of the second polyisoprene block (I'') was 2,500. The I'/I'' molecular weight ratio (M_w) was 22.6. The melt viscosity of the star polymer was 28 megapoise ($\times 10^5$ Pa s) at 121°C. The data and results are summarized in Table 1.

Example 3 (Comparison)

In this comparative example, a star polymer comprising isoprene/styrene/isoprene triblock copolymer arms was prepared using the procedure described in Example 1 except that the number average molecular weight (M_n) of the first polyisoprene block (I') was 2,800, the number average molecular weight (M_n) of the polystyrene block (S) was 34,100, and the number average molecular weight (M_n) of the second polyisoprene block (I'') was 59,000. The I'/I'' molecular weight ratio (M_w) was 0.05. The melt viscosity of the star polymer was 122 megapoise ($\times 10^5$ Pa s) at 121°C. The data and results are summarized in Table 1.

Example 4

In this example, a star polymer comprising isoprene/styrene/isoprene triblock copolymer arms was prepared using the procedure described in Example 1 except that the number average molecular weight (M_n) of the first polyisoprene block (I') was 38,400, the number average molecular weight (M_n) of the polystyrene block was 11,200 (S), and the number average molecular weight (M_n) of the second polyisoprene block (I'') was 11,200. The molecular weight ratio (M_w) of I'/I'' was 3.4. The melt viscosity of the star polymer was 17.6 megapoise ($\times 10^5$ Pa s) at 121°C. The data and results are summarized in Table 1.

Example 5 (Comparison)

In this comparative example, a star polymer comprising isoprene/styrene/isoprene triblock copolymer arms was prepared using the procedure described in Example 1 except that the number average molecular weight (M_n) of the first polyisoprene block (I') was 24,700, the number average molecular weight (M_n) of the polystyrene block (S) was 7,100, and the number average molecular weight (M_n) of the second polyisoprene blocks (I'') was 46,800. The molecular weight ratio (M_w) of I'/I'' was 0.5. The melt viscosity of the star polymer was 64 megapoise ($\times 10^5$ Pa s) at 121°C. Compositional data and melt viscosity results are summarized in Table 1.

Example 6 (Comparison)

In this comparative example, a star polymer comprising isoprene/styrene/isoprene triblock copolymer arms was prepared using the procedure described in Example 1 except that the number average molecular weight (M_n) of the first polyisoprene block (I') was 10,000, the number average molecular weight (M_n) of the polystyrene block (S) was 8,600, and the number average molecular weight (M_n) of the second polyisoprene block (I'') was 44,900. The molecular weight ratio (M_w) of I'/I'' was 0.2. The melt viscosity of the star polymer was 64 megapoise ($\times 10^5$ Pa s) at 121°C. Compositional data and melt viscosity results are summarized in Table 1.

Example 7

In this example, a star polymer comprising isoprene/styrene/isoprene triblock copolymer arms was prepared using the procedure described in Example 1 except that the number average molecular weight (M_n) of the first polyisoprene block (I') was 39,700, the number average molecular weight (M_n) of the polystyrene block (S) was 6,200, and the number average molecular weight (M_n) of the second polyisoprene block (I'') was

15,700. The molecular weight ratio (M_w) of I'/I" was 2.5. The melt viscosity of the star polymer was 19.5 megapoise ($\times 10^5$ Pa s) at 121°C. Compositional data and melt viscosity results are summarized in Table 1.

5 Example 8

In this example, a star polymer comprising isoprene/styrene/isoprene triblock copolymer arms was prepared using the procedure described in Example 1 except that the number average molecular weight (M_n) of the first polyisoprene block (I') was 35,200, the
10 the number average molecular weight (M_n) of the polystyrene block (S) was 15,700, and the number average molecular weight (M_n) of the second polyisoprene block (I") was 17,300. The molecular weight ratio (M_w) of I'/I" was
15 2.0. The melt viscosity of the star polymer was 52 megapoise ($\times 10^5$ Pa s) at 121°C. Compositional data and melt viscosity results are summarized in Table 1.

Example 9

In this example, a star polymer comprising isoprene/styrene/isoprene triblock copolymer arms was prepared using the procedure described in Example 1 except that the number average molecular weight (M_n) of the first polyisoprene block (I') was 35,000, the
20 the number average molecular weight (M_n) of the polystyrene block (S) was 24,900, and the number average molecular weight (M_n) of the second polyisoprene block (I") was 18,700. The molecular weight ratio (M_w) of I'/I" was 1.9. The melt viscosity of the star polymer was 61
25 megapoise ($\times 10^5$ Pa s) at 121°C. Compositional data and melt viscosity results are summarized in Table 1.
30

Example 10 (Comparison)

In this comparative example, a star polymer comprising isoprene/styrene/isoprene triblock copolymer arms was prepared using the procedure
35 described in Example 1 except that the number average molecular weight (M_n) of the first polyisoprene block

(I') was 29,800, the number average molecular weight (M_n) of the polystyrene block (S) was 15,600, and the number average molecular weight (M_n) of the second polyisoprene block (I'') was 23,000. The molecular weight ratio (M_w) of I'/I'' was 1.3. The melt viscosity of the star polymer was 55 megapoise ($\times 10^5$ Pa s) at 121°C. Compositional data and melt viscosity results are summarized in Table 1.

Example 11 (Comparison)

10 In this comparative example, a star polymer comprising arms of a block copolymer containing a single block of polystyrene and a single block of hydrogenated polyisoprene was prepared. In the first step of the preparation, living molecules of
15 polystyrene were prepared by anionically polymerising styrene in cyclohexene. The polymerisation of styrene was initiated by adding sec-butyllithium. The polymerisation of the styrene was completed to produce living polystyrene molecules having a number average
20 molecular weight (M_n) of 3,300. Polyisoprene blocks were then formed by adding isoprene to the solution of living polystyrene molecules. The polymerisation of isoprene was completed to produce polyisoprene blocks having a number average molecular weight (M_n) of
25 51,200.

The living block 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
30 after which the lithium sites remaining in the star polymer were deactivated by adding an alcohol.

The star polymer was next hydrogenated so as to saturate more than 98% of the olefinic unsaturation originally contained in the isoprene blocks and less
35 than 15% of the aromatic unsaturation using a catalyst prepared by combining nickel ethylhexanoate and

triethylaluminium (2.3 moles of aluminium per mole of nickel). The melt viscosity of the star polymer was sufficiently high to permit finishing as a solid polymer crumb. The melt viscosity of the star polymer was 25.1 megapoise ($\times 10^5$ Pa s) at 121°C. The data and results are summarized in Table 1. The composition of this polymer is similar to "SHELLVIS 260" (Trade Mark) VI improver available from Shell Chemical Company.

Example 12 (Comparison)

In this comparative example, an all-polyisoprene star polymer, having a polyisoprene molecular weight of 35,000 was prepared and hydrogenated, in accordance with known procedures to be representative of "SHELLVIS 200" (Trade Mark), a commercial VI improver. The melt viscosity of this star polymer is much less than 1 megapoise ($\times 10^5$ Pa s) at 121°C; it cannot be cyclone finished, and exhibits cold-flow properties at room temperature.

Example 13 (Comparison)

In this comparative example, an all-polyisoprene star polymer, having a polyisoprene arm molecular weight of 46,000 was prepared and hydrogenated, in accordance with known procedures to be representative of "SHELLVIS 250" (Trade Mark), a commercial VI improver. The melt viscosity of this star polymer is much less than 1 megapoise ($\times 10^5$ Pa s) at 121°C. The data and results are summarized in Table 1.

Examples 14 and 15 (Comparison)

In these comparative examples the star polymers produced in Examples 11 and 13 were used as VI improvers in a SAE 10W-40 multi-grade lubricating oil composition. The basestock used in the preparation of the multigrade lubricating oil composition was a blend of an "HVI 100N" oil (trade designation, available ex Shell Oil Company, USA) (a bright and clear high viscosity index base oil having viscosity at 40°C of

20.0 to 21.0 mm²/s (ASTM D445), viscosity index of 88 to 93 (ASTM D2270) and minimum flash point of 190.6 to 196°C (ASTM D92)) and an "HVI 250N" oil (trade designation, available ex Shell Oil Company, USA) (a
5 bright and clear high viscosity index base oil having viscosity at 40°C of 50.7 to 54.0 mm²/s (ASTM D445), viscosity index of 89 to 96 (ASTM D2270) and minimum flash point of 221°C (ASTM 92)).

The amount of each VI improver was varied so as to
10 provide a lubricating oil composition having a kinematic viscosity of 14 centistokes (mm²/s) at 100°C. The multigrade lubricating oil compositions prepared in these examples contained 31.0%w of "HVI 250N" oil, 7.75%w of a commercially available API AG quality
15 additive package ("Lubrizol 7573A" (Trade Mark)) and 0.3 %w "Acryloid 160" (Trade Mark) low point depressant. the viscosity index (VI), the cold cranking simulator 9CCS) viscosity at -20°C, the engine oil pumpability (TP1) at -25°C using the mini-rotary viscometer (ASTM
20 D4684), and the high temperature, high shear rate (HTHSR) viscosity at 150C at 1×10^6 seconds⁻¹ in the tapered bearing simulator (TBS) (ASTM D4683) were determined for each lubricating oil composition.

All of these examples produced lubricating oil
25 compositions from cyclone finished polymer crumb. The lubricating oil compositions have good HTHSR viscosities and excellent low temperature viscosities. The data and results are summarized in Table 2. It is seen from examples 14 and 15 that polymer 11 appears to
30 contribute more to TP1-MRV viscosity than polymer 13. However, example 26 contains 25% of the more viscous "HVI 250" base stock.

TABLE 1

Example	Isoprene (I') M _n	Styrene M _n	Isoprene (I'') M _n	I'/I''	Finish as Crumb	Melt Viscosity 121°C M Poise (x10 ⁵ Pa s)
1	58,000	36,000	7,000	8.3	Yes	37
2	56,400	30,000	2,500	22.6	Yes	28
3	2,800	34,600	59,000	0.05	No	12
4	38,400	11,200	11,200	3.4	Yes	18
5	24,700	7,100	46,800	0.5	Yes	64
6	10,000	8,600	44,900	0.2	Yes	64
7	39,700	6,200	15,700	2.5	Yes	19.5
8	35,200	15,700	17,300	2.0	Yes	52
9	35,000	24,900	18,700	1.9	Yes	61
10	29,800	15,600	23,000	1.3	Yes	55
11	0	3,300	51,200	--	Yes	25.1
12	0	0	35,000	--	No	<1
13	0	0	46,500	--	No	<1

TABLE 2

Ex.	Polymer Ex.	Polymer (%w)*.	CCS -20°, cP (x10 ⁻³ Pa s)	TP1 MRV, cP (x10 ⁻³ Pa s)	VI	TBS, cP (x10 ⁻³ Pa s)
14	11	0.97	3,490	220	153	3.49
15*	13	1.12	3,020	177	158	3.61

* %w based on the total composition

Examples 16 and 17 (Comparison)

In these comparative examples the star polymers produced in Examples 11 and 13, were used as VI improvers in a SAE 5W-30 multigrade lubricating oil composition. The base stock used in the preparation of the multigrade contained only Atlas "HVI 100N" oil. The amount of each VI improver was varied so as to provide a lubricating oil composition having a kinematic viscosity of 10.5 centistokes (mm²/s) at 100° C. The multigrade lubricating oil compositions prepared in these examples contained 9.1 %w of a "DI" (dispersant-inhibition) additive package (from Ethyl Corporation) and 0.3 %w Hitec 623 pour point depressant. The viscosity index (VI), the cold cranking simulator (CCS) viscosity at -25°C, the engine oil pumpability (TP1) at -30°C using the mini-rotary viscometer (ASTM D4684), and the high temperature, high shear rate (HTHSR) viscosity at 150°C at 1x10⁶ seconds⁻¹ in the tapered bearing simulator (TBS) (ASTM D4683) were determined for each lubricating oil composition. Results are in Table 3, which show that each polymer in examples 16 and 17 provide comparable TP1-MRV viscosities.

Table 3

Ex.	Polymer Ex.	Polymer (%w)*.	CCS -20°, cP (x10 ⁻³ Pa s)	TP1 MRV, cP (x10 ⁻³ Pa s)	VI	TBS, cP (x10 ⁻³ Pa s)
16	11	0.83	3,020	201	160	2.91
17	13	0.98	3,330	213	160	2.98

* %w based on the total composition

Examples 18-29

In these examples the star polymers of examples 1-11, and 13 were used as VI improvers in a SAE 10W-40 multigrade lubricating oil composition. The basestock used in the preparation of the multigrade lubricating oil composition was a blend of an "HVI 100N" oil and an "HVI 250N" oil. The amount of each VI improver was varied so as to provide a lubricating oil composition having a kinematic viscosity of 14 centistokes (mm²/s) at 100°C. The multigrade lubricating oil compositions prepared in these examples contained 11.6 %w of a commercially available DI package (ECA 12850, available from Exxon Chemical), and 0.3 %w pour point depressant "Acryloid 160" (available from Rohm and Haas). The viscosity index (VI), the cold cranking simulator (CCS) viscosity at -20°C, the engine oil pumpability (TP1) at -25°C using the mini-rotary viscometer (ASTM D4684), and the high temperature, high shear rate (HTHSR) viscosity at 150°C at 1 x 10⁶ seconds⁻¹ in the tapered bearing simulator (TBS) (ASTM D4683) were determined for each lubricating oil composition and are reported in Table 4.

Examples 30-40

In these examples the star polymers produced in polymer examples 1 through 13 were used as VI improvers in a SAE 5W-30 multigrade lubricating oil

composition. The basestock used in the preparation of the multigrade lubricating oil was Exxon "HVI 100N" low-pour basestock. The amount of each VI improver was varied so as to provide a lubricating oil composition having a kinematic viscosity of 10.5 centistokes (mm²/s) at 100°C. The multigrade lubricating oil compositions prepared in these examples contained 11.60 %w of a commercially available DI additive package, ECA 12850 (from Exxon Chemical-Paramins), 0.5 %w "Acryloid 160" pour point depressant, and Exxon "HVI 100 N" low-pour point basestock. The Control sample contains these same ingredients, at the same percent weights, but there is no polymer in the blend. The viscosity index (VI), the cold cranking simulator (CCS) viscosity at -25°C, the engine oil pumpability (TP1) at -30°C using the mini-rotary viscometer (ASTM D4684), and the high temperature, high shear rate (HTHSR) viscosity at 150°C at 1×10^6 seconds⁻¹ in the tapered bearing simulator (TBS) (ASTM D4683) were determined for each lubricating oil composition. Results are in Table 5. Scanning Brookfield tests (ASTM D5133) were also run; results are reported at the temperature where viscosity was 5,000, 10,000, 20,000, 30,000, and 40,000 cP ($\times 10^{-3}$ Pa s). Scanning Brookfield results are in Table 6.

Table 4

Ex.	Polymer Ex.	Polymer (%w) *.	CCS -20°, cP (x10 ⁻³ Pa s)	TP1 MRV, cP (x10 ⁻³ Pa s)	VI	TBS, cP (x10 ⁻³ Pa s)
18	1	1.20	3,050	146	162	3.62
19	2	1.33	3,060	148	161	3.64
20 ¹	3	-----	-----	---	---	-----
21	4	1.07	3,110	131	173	3.62
22	5	0.80	3,160	266	160	3.46
23	6	0.96	3,150	y.s. ²	161	3.51
24	7	0.97	2,940	140	162	3.62
25	8	1.10	2,600	98	189	3.65
26	9	1.28	2,600	97	185	3.71
27 ³	10	1.07	2,610	127	Var.	3.62
28	11	0.97	3,200	173	159	3.60
29	13	1.02	3,250	174	159	3.66

1) Oil sample a gel at room temperature

2) yield stress failure

3) Variable kinematic viscosity at 40°C, variable VI, on storage; some evidence of gelation at room temperature, not suitable for use as engine oil.

Table 5

Ex.	Polymer Ex.	Polymer (%w) *.	CCS -20°, cP (x10 ⁻³ Pa s)	TP1 MRV, cP (x10 ⁻³ Pa s)	VI	TBS, cP (x10 ⁻³ Pa s)
30	1	0.93	3,110	136	162	-
31	2	0.97	3,090	125	162	-
32	4	0.80	3,290	147	172	3.09
33	5	0.60	3,100	178	161	-
34	7	0.73	3,100	131	163	3.03
35	8	0.81	3,050	116	190	3.07
36	9	0.93	3,110	116	185	3.10
37*	10	0.76	3,100	125	Var	3.01
38	11	0.72	3,380	168	159	3.08
39	12	0.89	3,180	140	161	---
40	13	0.78	3,390	145	161	3.12
Control	None	----	2,810	82	129	2.13

* Variable 40°C kinematic viscosity and viscosity index on storage, some gelation tendency at room temperature but no evidence in TP1-MRV At -30°C.

Table 6

		Scanning Brookfield, Temperature where viscosity is:				
5	Ex. Polymer Ex.	5,000	10,000	20,000	30,000	40,000
		cP	cP	cP	cP	cP
		(x10 ⁻³ Pa s)	(x10 ⁻³ Pa s)	(x10 ⁻³ Pa s)	(x10 ⁻³ Pa s)	(x10 ⁻³ Pa s)
	30 1	-22.9	27.1	-29.7	-31.9	-33.5
	31 2	-23.5	27.4	-29.9	-32.1	-33.7
10	32 4	-23.6	-27.1	-30.4	-32.7	-34.1
	33 5	-21.9	-25.3	-28.1	-29.6	-31.0
	34 7	-23.5	-27.6	-30.6	-33.0	-34.6
	35 8	-25.0	-28.4	-31.2	-33.5	-35.0
	36 9	-24.0	-28.4	-31.2	-33.5	-35.0
15	37 10	-23.2	-27.5	-30.1	-32.3	-34.0
	38 11	-22.4	-26.6	-29.7	-32.0	-33.5
	39 12	-23.3	-27.4	-30.3	-32.6	-34.2
	40 13	-22.3	-26.6	-29.9	-32.2	-33.7

20 It can clearly be seen from Tables 1-5 that the star polymers according to the present invention are both cyclone finishable and possess good viscosity characteristics.

25 In comparison, the star polymers of the comparative examples a) possess acceptable viscosity characteristics, but they are not cyclone finishable, b) are cyclone finishable, but do not possess acceptable viscosity characteristics (note, in particular, the poor performance in the engine oil pumpability (TP1) test), or c) are not cyclone
30 finishable and do not possess acceptable viscosity characteristics.

CLAIMS

1. A star polymer useful as a viscosity index (VI) improver, which comprises polystyrene blocks and hydrogenated polyisoprene blocks combined in molecules having the structure $(EP'-S-EP'')_n-X$,
5 wherein EP' is a first hydrogenated block of polyisoprene (I') having a number average molecular weight (M_n) between 10,000 and 100,000 before hydrogenation, S is a block of polystyrene having a number average molecular weight (M_n) between 6,000 and
10 50,000, EP'' is a second hydrogenated block of polyisoprene (I'') having a number average molecular weight (M_n) between 2,500 and 50,000 before hydrogenation, the molecular weight ratio (M_w) of I'/I'' is at least 1.4, X is a nucleus of a polyalkenyl
15 coupling agent, and n is the average number of (EP'-S-EP'') arms per star molecule formed by reaction of 2 or more moles of the polyalkenyl coupling agent per mole of the arms.
2. A star polymer according to claim 1, wherein the
20 polyalkenyl coupling agent is divinylbenzene.
3. A star polymer according to claim 1 or 2, wherein the number average molecular weight (M_n) of the first polyisoprene block (I') is between 20,000 and 60,000, the number average molecular weight (M_n) of the second
25 polyisoprene block (I'') is between 5,500 and 33,000, and the ratio of the molecular weight (M_w) ratio of I'/I'' is between 1.8 and 10.9.
4. A star polymer according to any one of claims 1-3, wherein the number average molecular weight (M_n) of the
30 polystyrene block is from 10,000 to 35,000.
5. A star polymer according to any one of claims 1-4, wherein n is the average number of arms per molecule



when coupled with 3 moles of divinylbenzene per mole of the arms.

6. A star polymer according to any one of claims 1-5, wherein the polyisoprene block is at least 98%
5 hydrogenated.

7. A star polymer according to any one of claims 1-6, wherein less than 10% of the aromatic unsaturation is hydrogenated.

8. Process for preparing a star polymer as claimed in
10 any one of claims 1-7, which comprises anionically polymerising isoprene in the presence of sec-butyllithium, adding styrene, and then more isoprene to the living polystyrene molecules to make the living block copolymer molecules, coupling the living block
15 copolymer molecules with polyalkenyl coupling agent to form a star polymer, and selectively hydrogenating the polyisoprene blocks.

9. A lubricating oil composition comprising a base oil and
20 a viscosity improving amount of a star polymer, as claimed by anyone of claims 1-7.

10. A lubricating oil concentrate comprising 10 to 80 %w, based on a total concentrate, of a star polymer as claimed in any one of claims 1-7.

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