

ASYMMETRIC TRIBLOCK COPOLYMER VISCOSITY
INDEX IMPROVER FOR OIL COMPOSITIONS

The present invention relates to copolymers useful as viscosity index improvers, 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 kinematic viscosity at a given lower temperature and a
10 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 temperature of 40°C and 100°C. In general, viscosity index improvers that are added to engine lubricating oil composition increase the viscosity index as well as the kinematic
25 viscosities.

 The limitation on the amount of polymer than can be used in a VI improver concentrate is dependent on the concentrate's viscosity at storage and handling temperatures. Sufficient fluidity must be maintained
30 so that the concentrate can be readily pumped from the storage vessel into the oil blending vessel. The

amount of polymer that can be added to a concentrate to ensure handleability can be determined by measuring the low-shear rate viscosity of the oil concentrate.

5 Engine power losses are generally reduced when viscous friction is reduced through a reduction in an engine lubricant's HTHSR viscosity. This manifests itself in improved fuel efficiency. However, to ensure adequate engine journal bearing protection, minimum HTHSR viscosity limits are now included in SAE Standard
10 J300, which defines the viscosity grading system for SAE grade designations. (The present version of the Standard is SAE J300, revision MAR93.)

One approach to the obtainment of improved fuel efficiency within a particular SAE grade is to
15 formulate with a VI improver that contributes enough HTHSR viscosity so that the resultant engine oil is above the HTHSR viscosity minimum defined by SAE J300, but close to the minimum. Using such an approach, VI improvers such as those disclosed in US 3,775,329 which
20 offer a relatively high contribution to kinematic viscosity at 100°C (kinematic viscosity limits are also included in SAE J300), and a relatively low contribution to HTHSR viscosity are preferred. Two polymers representative of this prior art are given in
25 examples 6c and 12c of this document. US 3,772,196, which is hereby incorporated by reference discloses linear block copolymers of styrene (S) and hydrogenated polyisoprene (EP), having the structure S-EP.

In comparison to the S-EP polymers, a different
30 balance between thickening efficiency, and HTHSR viscosity has been achieved with linear triblock copolymers of styrene (S) and hydrogenated isoprene (EP) having the block structure EP-S-EP as described in US 4,788,361, which is hereby also incorporated by
35 reference. However, the EP-S-EP copolymers provide substantially higher HTHSR viscosities than the S-EP

copolymers described in US 3,775,329. For fuel economy savings, however, the S-EP polymers are preferred, provided that their HTHSR viscosity contributions are sufficient to meet SAE J300 requirements. The EP-S-EP
5 polymers described in US 4,788,361 are illustrated by symmetric polymers although said document places no limitations on the relative sizes of the first and second EP blocks.

The present invention relates to asymmetric
10 triblock copolymers useful as viscosity index improvers in lubricating oil compositions. The triblock copolymers have the block structure hydrogenated polyisoprene-polystyrene-hydrogenated polyisoprene (EP-S-EP) wherein the first EP block has a number
15 average molecular weight at least 4 times greater than the number average molecular weight of the second EP block. The difference in EP block sizes significantly reduces the HTHSR viscosity of lubricating oil compositions in comparison to EP-S-EP block copolymers
20 having similarly sized EP number average molecular weights. The contribution of the asymmetric triblock EP-S-EP polymers to HTHSR viscosity is comparable to that of prior art S-EP polymers, and sufficient for the making of SAE multigrade engine lubricants. The
25 differences in EP block sizes does not adversely impact other properties needed for good performance, but facilitates dissolution of the polymer into lubricating oil to make lubricating oil concentrates which contain more polymer and are more fluid than those containing
30 S-EP copolymers.

Accordingly, the present invention provides an asymmetric triblock copolymer, useful as a viscosity index (VI) improver, comprising polystyrene blocks and hydrogenated polyisoprene blocks combined in molecules
35 having the structure EP'-S-EP", wherein EP' is a first block of hydrogenated polyisoprene having a number

average molecular weight (M_n) between 40,000 and 150,000 before hydrogenation, S is a block of polystyrene having a number average molecular weight (M_n) between 25,000 and 60,000, EP" is a second block
5 of hydrogenated polyisoprene having a number average molecular weight (M_n) between 2,500 and 30,000 before hydrogenation and wherein the molecular weight ratio of EP'/EP" is at least 4.

The triblock copolymer is suitably selectively
10 hydrogenated to saturate at least 95% by weight of the polymerised isoprene units and less than 15% by weight of the polymerised styrene units.

The polymers of the present invention are readily produced as described in US No. 4,788,361. However,
15 the polymers of the present invention have molecular weights which are not taught by said reference and are selected to obtain surprisingly improved performance as a viscosity index improver, especially in terms of their ease of blending and handleability as viscosity
20 index lubricating oil concentrates.

The polymers of this invention which are useful as VI improvers are preferably prepared by anionically polymerising isoprene in the presence of sec-butyllithium, adding styrene, and then more isoprene to
25 the living polystyrene molecules to make the living block copolymer molecules, and selectively hydrogenating the polyisoprene blocks. The present invention further provides an asymmetric triblock copolymer comprising polystyrene blocks (S) and
30 unhydrogenated polyisoprene blocks (EP) combined in molecules having the structure EP'-S-EP",

wherein EP' is a first block of unhydrogenated polyisoprene having a number average molecular weight between 40,000 and 150,000,

35 S is a block of polystyrene having a number average molecular weight between 25,000 and 60,000,



EP" is second block of unhydrogenated polyisoprene having a number average molecular weight between 2,500 and 30,000, and wherein the molecular weight ratio of EP'/EP" is at least 4.

5 In general, the polymers of the invention may be selectively hydrogenated to saturate the unhydrogenated polyisoprene blocks using any of the techniques known in the art to be suitable for selective hydrogenation of olefinic unsaturation over aromatic unsaturation.
10 The hydrogenation conditions are suitably selected to hydrogenate at least 95% of the original olefinic unsaturation. Hydrogenation of aromatic unsaturation is suitably less than 15% to avoid reduction of the amount of polystyrene needed to give desired thickening
15 efficiency.

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

The hydrogenated polymers of this invention may be added to a variety of lubricating oil compositions to improve viscosity index characteristics.

25 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
30 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
35 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.

5 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).

10 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.

15 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 5%w, and especially from 0.5 to 2.5%w, of a triblock copolymer according to the present invention, all percentages by weight based on
20 total composition.

The present invention still further provides a lubricating oil concentrate comprising from 10 to 80%w, based on total concentrate, of a triblock copolymer
25 according to the invention. 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 selectively hydrogenated polymers may also
30 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
35 lubricating oil compositions according to the present

invention are described in US 3,772,196 and US 3,835,083, which are hereby incorporated by reference.

In a preferred embodiment of the present invention, the polystyrene blocks and the hydrogenated isoprene
5 blocks are combined in molecules having the structure EP'-S-EP", wherein the first hydrogenated block of polyisoprene has a number average molecular weight between 50,000 and 110,000 before hydrogenation, the polystyrene block has a number average molecular weight
10 between 35,000 and 50,000, the second hydrogenated block of polyisoprene having a number average molecular weight between, 3,000 and 18,000 before hydrogenation, and wherein the molecular weight ratio of EP'/EP" is between 6.0 and 25.

15 The polymers can selectively be hydrogenated with a solution of nickel ethylhexanoate and triethylaluminium having a preferred Al/Ni molar ratio of 2.3:1 to saturate at least 90% of the isoprene units and less than 10% of the styrene units.

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

Example 1

In this example, a triblock copolymer of hydrogenated isoprene and styrene was prepared. In the
25 first step of the preparation, living polyisoprene blocks 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
30 living polyisoprene blocks having a number average molecular weight of 60,900. Polystyrene blocks were then formed by adding styrene to the solution of living polyisoprene blocks. The polymerisation of styrene was completed to produce polystyrene blocks having a number
35 average molecular weight of 42,100. Polyisoprene blocks were then formed by adding isoprene to the

solution of living polyisoprene-polystyrene blocks. The second polymerisation of isoprene was completed to produce second polyisoprene blocks having a number average molecular weight of 9,100. The lithium sites remaining in the polymer were deactivated by adding an alcohol.

The 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 prepared by combining nickel ethylhexanoate and triethylaluminium (2.3 moles of aluminium per mole of nickel). The melt viscosity of the polymer was 4.9 megapoise ($\times 10^5$ Pa s) at 121°C. The data and result are summarised in Table 1.

Example 2

In this example, a triblock copolymer was prepared using the procedure described in Example 1 except that the number average molecular weight of the second polyisoprene block was 14,300. The melt viscosity of the polymer was 3.4 megapoise ($\times 10^5$ Pa s) at 121°C. The data and results are summarised in Table 1.

Example 3

In this example, a triblock copolymer was prepared using the procedure described in Example 1 except that the number average molecular weight of the second polyisoprene block was 3,700. The data and results are summarised in Table 1.

Example 4 (Comparison)

In this comparative example, a diblock copolymer was prepared using the procedure described in Example 1 except that the second addition of isoprene was omitted. The melt viscosity of the polymer was 4.3 megapoise ($\times 10^5$ Pa s) at 121°C. The data and results are summarised in Table 1.

Example 5

In this example, a triblock copolymer was prepared using the procedure described in Example 1 except that the number average molecular weight of the first polyisoprene block was 60,800, the number average
5 molecular weight of the polystyrene block was 38,000, and the number average molecular weight of the second polyisoprene block was 6,400. The melt viscosity of the polymer was 2.5 megapoise ($\times 10^5$ Pa s) at 121°C. The data and results are summarised in Table 1.

10 Example 6 (Comparison)

In this comparative example, a diblock copolymer was prepared using the procedure described in Example 1 except that the number average molecular weight of the first polyisoprene block was 62,000, the number average
15 molecular weight of the polystyrene block was 36,000, and the number average molecular weight of the second addition of isoprene was omitted. The melt viscosity was 1.7 megapoise ($\times 10^5$ Pa s) at 121°C. Compositional data are summarised in Table 1.

20 Example 7 (Comparison)

In this comparative example, a triblock copolymer was prepared using the procedure described in Example 1 except that the number average molecular weight of the first polyisoprene block was 66,100, the number average
25 molecular weight of the polystyrene block was 33,100, and the number average molecular weight of the second polyisoprene block was 68,600. The melt viscosity of the polymer was 2.4 megapoise ($\times 10^5$ Pa s) at 121°C. Compositional data and melt viscosity results are
30 summarised in Table 1.

Example 8

In this example, a triblock copolymer was prepared using the procedure described in Example 1 except that the number average molecular weight of the first
35 polyisoprene block was 106,700, the number average molecular weight of the polystyrene block was 49,100,

and the number average molecular weight of the second polyisoprene block was 14,100. The melt viscosity of the polymer was 5 megapoise ($\times 10^5$ Pa s) at 121°C.

Compositional data and melt viscosity results are summarised in Table 1.

Example 9

In this example, a triblock copolymer was prepared using the procedure described in Example 8 except that the number average molecular weight of the second polyisoprene block was 19,000. The melt viscosity of the polymer was 4.4 megapoise ($\times 10^5$ Pa s) at 121°C. Compositional data and melt viscosity results are summarised in Table 1.

Example 10

In this example, a triblock copolymer was prepared using the procedure described in Example 8 except that the number average molecular weight of the second polyisoprene block was 5,900. Compositional data are summarised in Table 1.

Example 11 (Comparison)

In this comparative example, a diblock copolymer was prepared using the procedure described in Example 8 except that the second addition of isoprene was omitted. The melt viscosity was 5.2 megapoise ($\times 10^5$ Pa s) at 121°C. Compositional data are summarised in Table 1.

Example 12 (Comparison)

In this comparative example, a diblock copolymer was prepared using the procedure described in Example 1 except that the number average molecular weight of the first polyisoprene block was 106,000, the number average molecular weight of the polystyrene block was 44,000, and the second addition of isoprene was omitted. The melt viscosity was 2.6 megapoise ($\times 10^5$ Pa s) at 121°C. Compositional data are summarised in Table 1.

Example 13 (Comparison)

In this comparative example, a triblock copolymer was prepared using the procedure described in Example 1 except that the number average molecular weight of the first polyisoprene block was 57,900, the number average molecular weight of the polystyrene block was 47,000, and the number average molecular weight of the second polyisoprene block was 55,000. Compositional data are summarised in Table 1.

Examples 14-26

In these examples the polymers produced in Example 1-13 were used as VI improvers in a SAE 10W-40 multigrade lubricating oil composition. The base stock 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 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 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 8.5 %w of "HVI 250N", 11.5 %w of a commercially available API AG quality additive package (ECA 12850), 0.5% w "Acryloid 160" (Trade Mark) the identified polymer, and "HVI 100N". 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 1×10^6 seconds⁻¹ in the tapered bearing simulator (TBS) (ASTM D4683) were determined for each oil composition.

5 All of these examples produced lubricating oil compositions from a concentrate of 6% w of the polymer in "HVI 100N".

10 The asymmetric polymers of the invention dissolved much quicker than the comparative samples and a separate evaluation established that the asymmetric polymers readily dissolve at significantly lower temperatures than the comparative polymers. For example, the asymmetric linear polymer of example 5 could be completely dissolved in oil at 78°C, whereas 15 the S-EP polymers of example 4, 6, 11 and 12 required a blending temperature of 115°C for complete dissolution over a longer period of time. Also, at 7 percent or greater polymer-in-oil concentrates, the S-EP block copolymers of examples 6 and 12 show evidence of 20 gellation at room temperature. At 9.3 %w in oil, the concentrate of the asymmetric EP-S-EP polymer of example 5 is fluid with no evidence of gelation at room temperature.

25 The data and results for the SAE 10W-40 formulations are summarised in Table 2.

Examples 27-32

30 The fluidity of concentrates is determined by the measurement of viscosity at a low-shear-rate. When comparing polymer-in-oil concentrate viscosities, it is important to keep in mind the relative amount of the polymer that is required to achieve a specified kinematic viscosity in finished oil. For example, a 6 %w lubricating oil concentrate containing a higher molecular weight polymer such as of example 12, which 35 requires less polymer for SAE 10W-40 multigrade in example 25, will have a higher concentrate viscosity

than a 6 %w lubricating oil concentrate containing a lower molecular weight polymer such as of example 6, which requires more polymer for SAE 10W-40 multigrade in example 19.

5 Multigrade oils of example 14, 15, 17 and 19 in Table 2, which contain polymers of examples 1, 2, 4 and 6, require similar amounts of polymer. Their lubricating oil concentrate viscosities as measured in a Haake rotational viscometer at 82°C and 10 reciprocal
10 seconds rate-of-shear are given in respect of examples 27-32 in Table 3.

Examples 33-39

Multigrade oils of examples 21, 22, 23 and 25 as shown in Table 2, which contain polymers of examples 8,
15 9, 10 and 12, require similar amounts of polymer. The lubricating oil concentrate viscosities of these polymers as measured in a Haake rotational viscometer at 82°C and 10 reciprocal seconds rate-of-shear are given in respect of examples 33-30 in Table 4.

20

TABLE 1

	Ex.	Isoprene M_n'	Styrene M_n	Isoprene M_n''	Melt Viscosity 121°C M Poise (x 10 ⁵ Pa s)
25	1	60,900	42,100	9,100	4.9
	2	60,900	42,100	14,300	3.4
	3	60,900	42,100	3,700	--
	4	60,900	42,100	0	4.3
	5	60,800	38,600	6,400	2.5
30	6	62,000	36,000	0	1.7
	7	66,100	33,100	68,600	2.4
	8	106,700	49,100	14,100	5
	9	106,700	49,100	19,000	4.4
	10	106,700	49,100	5,900	--
35	11	106,700	49,100	0	5.2
	12	106,000	44,000	0	2.6
	13	57,900	47,000	55,000	--

TABLE 2

5	Ex.	Polymer Ex.	Polymer % W	CCS	TP1	VI	TBS
				-20°C, cP (x 10 ⁻³ Pa s)	MRV, cP (x 10 ⁻³ Pa s)		cP (x 10 ⁻³ Pa s)
10	14	1	1.19	2,880	12.7	164	3.46
	15	2	1.19	2,860	12.7	163	3.51
	16	3	1.18	2,810	13.3	164	3.44
	17	4	1.24	2,800	13.1	164	3.46
	18	5	1.20	2,960	14.8	163	3.40
	19	6	1.18	2,920	14.1	163	3.40
	20	7	0.98	2,870	13.2	167	3.62
	21	8	0.80	2,960	12.5	162	3.27
	22	9	0.81	2,760	12.5	162	3.32
15	23	10	0.80	2,930	12.6	163	3.23
	24	11	0.86	2,920	12.5	165	3.23
	25	12	0.78	2,840	13.5	159	3.26
	26	13	1.13	2,820	13.9	165	3.67

TABLE 3

20	Example	Polymer Example	Polymer %wt.	Haake vis., Poise
25	27	1	6.0	5.4
	28	1	8.0	12.6
	29	2	6.0	4.8
	30	2	8.0	16.5
	31	4	6.0	20.3
	32	6	6.0	19.4

TABLE 4

	Example	Polymer Example	Polymer %wt.	Haake vis., Poise
5	33	8	6	20.7
	34	8	8	36.3
	35	9	6	15.2
	36	9	8	29.0
	37	10	6	17.8
10	38	10	8	36.1
	39	12	6	31.6

C L A I M S

1. An asymmetric triblock copolymer, useful as a viscosity index (VI) improver, comprising polystyrene blocks (S) and hydrogenated polyisoprene blocks (EP) combined in molecules having the structure EP'-S-EP",

5 wherein EP' is a first block of hydrogenated polyisoprene having a number average molecular weight between 40,000 and 150,000 before hydrogenation,

 S is a block of polystyrene having a number average molecular weight between 25,000 and 60,000,

10 EP" is second block of hydrogenated polyisoprene having a number average molecular weight between 2,500 and 30,000 before hydrogenation, and wherein the molecular weight ratio of EP'/EP" is at least 4.

2. The copolymer according to claim 1, wherein the
15 number average molecular weight of EP' is between 50,000 and 110,000, the number average molecular weight of EP" is between 3,000 and 18,000, and the molecular weight ratio of EP'/EP" is between 6.0 and 25.

3. The copolymer according to claim 1 or 2, wherein
20 the number average molecular weight of the polystyrene block is between 35,000 to 50,000.

4. The copolymer according to any one of claims 1-3, wherein the EP' and EP" blocks are at least 98% hydrogenated.

25 5. The copolymer according to claim 4, wherein less than 10% of the aromatic unsaturation is hydrogenated.

6. Process for preparing an asymmetric triblock
30 copolymer as claimed in any one of claims 1-5, 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, and selectively hydrogenating the polyisoprene blocks.

7. A lubricating oil composition comprising

5 a base oil and a viscosity improving amount of an asymmetric triblock copolymer as claimed in any one of claims 1-5.

8. A lubricating oil concentrate comprising 10 to 80%w, based on total concentrate, of an asymmetric triblock copolymer as claimed in any one of claims 1-5.

10 9. An asymmetric triblock copolymer comprising polystyrene blocks (S) and unhydrogenated polyisoprene blocks (EP) combined in molecules having the structure EP'-S-EP",

wherein EP' is a first block of unhydrogenated polyisoprene having a number average molecular weight
15 between 40,000 and 150,000,

S is a block of polystyrene having a number average molecular weight between 25,000 and 60,000,

20 EP" is second block of unhydrogenated polyisoprene having a number average molecular weight between 2,500 and 30,000, and wherein the molecular weight ratio of EP'/EP" is at least 4.

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* C L M S *

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ASYMMETRIC TRIBLOCK COPOLYMER VISCOSITY
INDEX IMPROVER FOR OIL COMPOSITIONS

5 The present invention provides asymmetric triblock copolymers which are useful as viscosity index improvers in oil compositions formulated for high performance engines. The triblock copolymers have the block structure hydrogenated polyisoprene-polystyrene-hydrogenated polyisoprene wherein the ratio of the number average molecular weights of the first and second hydrogenated polyisoprene blocks is at least 4.

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average molecular weight (M_n) between 40,000 and 150,000 before hydrogenation, S is a block of polystyrene having a number average molecular weight (M_n) between 25,000 and 60,000, EP" is a second block
5 of hydrogenated polyisoprene having a number average molecular weight (M_n) between 2,500 and 30,000 before hydrogenation and wherein the molecular weight ratio of EP'/EP" is at least 4.

The triblock copolymer is suitably selectively
10 hydrogenated to saturate at least 95% by weight of the polymerised isoprene units and less than 15% by weight of the polymerised styrene units.

The polymers of the present invention are readily produced as described in US No. 4,788,361. However,
15 the polymers of the present invention have molecular weights which are not taught by said reference and are selected to obtain surprisingly improved performance as a viscosity index improver, especially in terms of their ease of blending and handleability as viscosity
20 index lubricating oil concentrates.

The polymers of this invention which are useful as VI improvers are preferably prepared by anionically polymerising isoprene in the presence of sec-butyllithium, adding styrene, and then more isoprene to
25 the living polystyrene molecules to make the living block copolymer molecules, and selectively hydrogenating the polyisoprene blocks. The present invention further provides an asymmetric triblock copolymer comprising polystyrene blocks (S) and
30 unhydrogenated polyisoprene blocks (EP) combined in molecules having the structure EP'-S-EP",

wherein EP' is a first block of unhydrogenated polyisoprene having a number average molecular weight between 40,000 and 150,000,

35 S is a block of polystyrene having a number average molecular weight between 25,000 and 60,000,

C L A I M S

1. An asymmetric triblock copolymer, useful as a viscosity index (VI) improver, comprising polystyrene blocks (S) and hydrogenated polyisoprene blocks (EP) combined in molecules having the structure EP'-S-EP",
5 wherein EP' is a first block of hydrogenated polyisoprene having a number average molecular weight between 40,000 and 150,000 before hydrogenation,
 S is a block of polystyrene having a number average molecular weight between 25,000 and 60,000,
10 EP" is second block of hydrogenated polyisoprene having a number average molecular weight between 2,500 and 30,000 before hydrogenation, and wherein the molecular weight ratio of EP'/EP" is at least 4. ✓
2. The copolymer according to claim 1, wherein the
15 number average molecular weight of EP' is between 50,000 and 110,000, the number average molecular weight of EP" is between 3,000 and 18,000, and the molecular weight ratio of EP'/EP" is between 6.0 and 25.
3. The copolymer according to claim 1 or 2, wherein
20 the number average molecular weight of the polystyrene block is between 35,000 to 50,000.
4. The copolymer according to any one of claims 1-3, wherein the EP' and EP" blocks are at least 98% hydrogenated.
- 25 5. The copolymer according to claim 4, wherein less than 15% of the aromatic unsaturation is hydrogenated.
6. Process for preparing an asymmetric triblock copolymer as claimed in any one of claims 1-5, which
30 comprises anionically polymerising isoprene in the presence of sec-butyllithium, adding styrene, and then more isoprene to the living polystyrene molecules to



Date: 10-1-98

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make the living block copolymer molecules, and
selectively hydrogenating the polyisoprene blocks.

7. A lubricating oil composition comprising
a base oil and a viscosity improving amount of an
5 asymmetric triblock copolymer as claimed in any one of
claims 1-5.
8. A lubricating oil concentrate comprising 10 to
80%w, based on total concentrate, of an asymmetric
triblock copolymer as claimed in any one of claims 1-5.
- 10 9. An asymmetric triblock copolymer comprising
polystyrene blocks (S) and unhydrogenated polyisoprene
blocks (EP) combined in molecules having the structure
EP'-S-EP",
wherein EP' is a first block of unhydrogenated
15 polyisoprene having a number average molecular weight
between 40,000 and 150,000,
S is a block of polystyrene having a number average
molecular weight between 25,000 and 60,000,
EP" is second block of unhydrogenated polyisoprene
20 having a number average molecular weight between 2,500
and 30,000, and wherein the molecular weight ratio of
EP'/EP" is at least 4.

