



Office de la Propriété

Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2321006 C 2008/01/22

(11)(21) **2 321 006**

(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 1999/02/16
(87) Date publication PCT/PCT Publication Date: 1999/08/26
(45) Date de délivrance/Issue Date: 2008/01/22
(85) Entrée phase nationale/National Entry: 2000/08/17
(86) N° demande PCT/PCT Application No.: EP 1999/001003
(87) N° publication PCT/PCT Publication No.: 1999/042542
(30) Priorité/Priority: 1998/02/19 (US60/075,230)

(51) Cl.Int./Int.Cl. *C10M 143/12*(2006.01),
C08F 297/04(2006.01), *C08L 53/02*(2006.01),
C10M 143/10(2006.01)

(72) Inventeur/Inventor:
RHODES, ROBERT BARNETT, US

(73) Propriétaire/Owner:
SHELL INTERNATIONALE RESEARCH
MAATSCHAPPIJ B.V., NL

(74) Agent: OGILVY RENAULT LLP/S.E.N.C.R.L.,S.R.L.

(54) Titre : POLYMERES ETOILES AUGMENTANT L'INDICE DE VISCOSITE D'HUILES

(54) Title: STAR POLYMER VISCOSITY INDEX IMPROVER FOR OIL COMPOSITIONS

(57) Abrégé/Abstract:

Star polymers which can be used as viscosity index improvers in oil compositions formulated for high performance engines. The star polymers have tetrablock copolymer arms of hydrogenated polyisoprene-polybutadiene-polyisoprene with a block of polystyrene and which provide excellent low temperature performance in lubricating oils, exhibit good thickening efficiency, and are finishable as polymer crumb.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C10M 143/12, C08F 297/04 // (C10M 143/12, 143:10), C10N 20:02, 30:04, 40:25, 60:02		A1	(11) International Publication Number: WO 99/42542
			(43) International Publication Date: 26 August 1999 (26.08.99)
(21) International Application Number: PCT/EP99/01003	(22) International Filing Date: 16 February 1999 (16.02.99)		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
(30) Priority Data: 60/075,230 19 February 1998 (19.02.98) US	(71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).		
(72) Inventor: RHODES, Robert, Barnett; 11735 Normont Drive, Houston, TX 77070 (US).			Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: **STAR POLYMER VISCOSITY INDEX IMPROVER FOR OIL COMPOSITIONS**

(57) Abstract

Star polymers which can be used as viscosity index improvers in oil compositions formulated for high performance engines. The star polymers have tetrablock copolymer arms of hydrogenated polyisoprene-polybutadiene-polyisoprene with a block of polystyrene and which provide excellent low temperature performance in lubricating oils, exhibit good thickening efficiency, and are finishable as polymer crumb.

STAR POLYMER VISCOSITY INDEX
IMPROVER FOR OIL COMPOSITIONS

Field of the Invention

This invention relates to star polymers of hydrogenated isoprene and butadiene, and to oil compositions containing the star polymers. More 5 particularly, this invention relates to such oil compositions with excellent low temperature properties and thickening efficiency and star polymers with excellent finishing characteristics.

Background of the Invention

10 The viscosity of lubricating oils varies with temperature. In general, oils are identified by a viscosity index which is a function of the oil viscosity at a given lower temperature and a given higher temperature. The given lower temperature and the given 15 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 lubricants with the same kinematic 20 viscosity at 100°C, the one having the lower kinematic viscosity at 40°C will have the higher viscosity index. The oil with the higher viscosity index undergoes less kinematic viscosity change between the temperatures of 40°C and 100°C. In general, viscosity index improvers 25 that are added to engine oils increase the viscosity index as well as the kinematic viscosities.

The SAE Standard J300 viscosity classification system does not specify the use of viscosity index to

- 2 -

classify multigrade oils. At one time, however, the Standard did require that certain grades meet low-temperature viscosities that were extrapolated from kinematic viscosity measurements taken at higher 5 temperatures, for it was recognized that oils that were exceedingly viscous at low-temperatures caused engine starting difficulties in cold weather. For this reason, multigrade oils which possessed high viscosity index values were favoured. These oils gave the lowest low- 10 temperature extrapolated viscosities. Since then, ASTM has developed the cold cranking simulator (CCS), ASTM D5293 (formerly ASTM D2602), a moderately high-shear-rate viscometer which correlates with engine cranking speed and starting at low temperatures. Today cranking 15 viscosity limits, determined by the CCS, are defined in the SAE J300 Standard and viscosity index is not used. For this reason, polymers that improve the viscosity characteristics of lubricating oils are sometimes referred to as viscosity modifiers instead of viscosity 20 index improvers.

Today, it is also recognized that cranking viscosity is not sufficient to fully estimate a lubricant's low-temperature performance in engines. SAE J300 also requires that pumping viscosity be determined 25 in a low-shear-rate viscometer called the mini-rotary viscometer (MRV). This instrument can be used to measure viscosity and gel formation, the latter by the measurement of yield stress. In this test, an oil is slowly cooled over a two-day period to a specified 30 temperature before viscosity and yield stress are determined. A yield stress observation constitutes an automatic failure in this test, while pumping viscosity must be below a specified limit to ensure that the oil

- 3 -

will not cause an engine to experience a pumping failure during cold weather conditions. The test is sometimes referred to as the TPI-MRV test, ASTM D4684.

Numerous materials are used in the formulation of 5 fully-formulated multigraded engine oils. Besides the basestocks, which may include paraffinic, naphthenic, and even synthetically-derived fluids, the polymeric VI improver, and the pour point depressants, there are numerous lubricant additives added which act as antiwear 10 agents, antirust agents, detergents, dispersants, and pour point depressant. These lubricant additives are usually combined in diluent oil and are generally referred to as a dispersant-inhibitor package, or as a "DI" package.

Common practice in the formulation of a multigrade oil is to blend to a target kinematic viscosity and cranking viscosity, which is determined by the specified SAE grade requirements in SAE J300. The DI package and pour point depressant are combined with a VI improver 20 oil concentrate and with one basestock, or two or more basestocks having different viscosity characteristics. For example, for an SAE 10W-30 multigrade, the concentration of the DI package and the pour point depressant might be held constant, but the amounts of 25 HVI 100 neutral and HVI 250 neutral or HVI 300 neutral basestock might be adjusted along with the VI improver until the target viscosities are arrived at.

The pour point depressant's selection normally depends on the type of wax precursors in the lubricant 30 basestocks. However, if the viscosity index improver itself is prone to interact with wax precursors, it may be necessary to add an additional pour point depressant of a different type, or an additional quantity of the

- 4 -

pour point depressant used for the basestocks to compensate for that interaction. Otherwise, low-temperature rheology will deteriorate, and TPI-MRV failures will result. The use of additional pour point depressant generally increases the cost of formulating an engine lubricant.

Once a formulation has been arrived at that has the targeted kinematic viscosities and cranking viscosities, the TPI-MRV viscosity is determined. A relatively low pumping viscosity and the absence of yield stress is desirable. The use of a VI improver which contributes little to low-temperature pumping viscosity or yield stress is very desirable in the formulation of multigrade oils. It minimizes the risk of formulating an oil that may cause an engine pumping failure and it provides the oil manufacturer with additional flexibility in the use of other components which contribute to pumping viscosity.

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, were previously described in US-A-4116917. US-A-5460739 describes star polymers with (EP-EB-EP') arms as VI improvers. Such polymers produce good thickening characteristics but are difficult to finish. US-A-5458791 describes star polymers with (EP-S-EP') arms as VI improvers. Said EP and EP' are hydrogenated blocks of polyisoprene, said EB is a hydrogenated block of polybutadiene and S is a block of polystyrene. Such polymers have excellent finishability characteristics and produce oils with good low temperature performance but the thickening characteristics are diminished. It

- 5 -

would be advantageous to be able to produce a polymer with good thickening characteristics and excellent finishing characteristics. The present invention provides such a polymer.

5 Summary of the Invention

In accordance with the present invention there is provided a star polymer having the structure selected from the group consisting of

(I) $(S-EP-EB-EP')_n-X$

10 (II) $(EP-S-EB-EP')_n-X$

(III) $(EP-EB-S-EP')_n-X$

wherein

EP is an outer hydrogenated block of polyisoprene having a number average molecular weight (MW_1) between 15 6,500 and 85,000 before hydrogenation;

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

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

S is a block of polystyrene having a number average molecular weight (MW_s) of 1,000 to 4,000 when the S block 25 is external (I) and 2,000 to 15,000 when the S block is internal (II or III);

wherein the star polymer structure comprises from 3% to 15% by weight of the polybutadiene, the ratio of 30 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.

Said star polymers are useful as viscosity index improvers in oil compositions formulated for high performance engines. The tetrablocks significantly improve low temperature performance of the polymers as viscosity index improvers. They 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.

5

These polymers can therefore be used with a base oil to make a viscosity improved oil composition.

10

Concentrates can also be made, which will contain at least 75% by weight of the base oil and 5 to 25% by weight of the star polymer.

Detailed Description of the Invention

15

The star polymers of the present invention are readily produced by the processes described in CA-A-716645 and US-RE-27145. However, the star polymers of the present invention have molecular weights and compositions which are not taught by the references and are selected to obtain surprisingly improved low temperature performance as a viscosity index improver.

20

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.

25

The star polymer is then selectively hydrogenated to saturate at least 95% by weight, preferably at least 98% by weight, of the isoprene and butadiene units.

30

Both the size and placement of the styrene blocks are critical for improved performance. The polymers described by this invention contribute less to viscosity, as measured in the TPI-MRV test, than

- 7 -

polymers that do not have the additional polystyrene block. Some of the polymers described by this invention also provide multigrade oils with higher viscosity indexes than hydrogenated, all-polyisoprene star 5 polymers or other hydrogenated poly(styrene/isoprene) block copolymer star polymers.

The present invention has an advantage of a previous discovery that cyclone finishable star polymers which provide high high-temperature, high-shear rate 10 (HTHSR) viscosities in engine oils are prepared by addition of small polystyrene blocks to the star polymers. The previous discovery showed that polystyrene blocks enhanced cyclone-finishing without gelling the oil when the polystyrene block has a 3,000 15 to 4,000 number average molecular weight and were at the external position, farthest away from the core. In this invention, it has been discovered that the same advantage is achieved when the polystyrene blocks are internal in a tetrablock copolymer and, in the internal 20 case, the polystyrene block molecular weight does not need to be limited to 4,000 maximum.

Star polymers that contain hydrogenated polyisoprene arms do not suffer interaction with wax precursors because of the abundance of pendant alkyl 25 side-chain groups that are present when 1,4-addition, 3,4-addition, or 1,2-addition occurs with isoprene. The star polymers of this invention are designed to be minimally interactive to wax, like the hydrogenated all-polyisoprene-arm star polymers, but have better 30 performance than the all-polyisoprene-arm stars.

To counteract the high polyethylene-like density near the centre of the star, the hydrogenated butadiene blocks are placed further from the nucleus by insertion

- 8 -

of an internal EP' block. 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 5 have hydrogenated arms containing polybutadiene and polyisoprene blocks, 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 10 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 molecule. While wax-polyethylene interaction is to be minimized, the 15 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. An increase in viscosity and possibly gelling occurs, which is brought about by the three dimensional 20 crystallization of many star molecules to form a lattice structure. S-EP outer blocks (see I), EP-S outer blocks (II), or the EP outer blocks (as in III) are needed so that intramolecular association predominates. To 25 achieve the dual goals of minimizing intermolecular crystallization and interaction with wax, the ratio of EP/EP' molecular weights (MW_1/MW_3) should be from 0.75:1 to 7.5:1.

The crystallization temperature of these 30 hydrogenated star polymers in oil may be lowered by reducing the block molecular weight of hydrogenated polybutadiene together with placement of the hydrogenated polybutadiene between hydrogenated polyisoprene segments and by substitution of S blocks

- 9 -

for EB blocks. This reduction in EB results in improved low-temperature TPI-MRV test results. It also results in the additional benefit of butadiene-containing star polymers that are less sensitive to pour point
5 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
10 without the use of relatively high concentrations of pour point depressant or the need for supplemental pour point depressants.

The star polymers of this invention which are useful as VI improvers are preferably prepared by
15 anionically polymerizing isoprene in the presence of sec-butyllithium, adding butadiene to the living polyisopropyl lithium after the polymerization of the outer block is complete, adding isoprene to the polymerized living block copolymer, adding styrene at
20 the desired point depending upon the desired location of the polystyrene block, and then coupling the living block copolymer molecules with a polyalkenyl coupling agent to form a star polymer, followed by hydrogenation.
25 It is important to maintain high 1,4-addition throughout the polymerization 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
30 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.

- 10 -

The randomizer could be added at the conclusion of the butadiene polymerization, and before introduction of more isoprene to give the second polyisoprene block. Alternatively, the randomizer could be added before 5 completion of the butadiene block polymerization, and concurrent with the introduction of isoprene.

The star polymers of the present invention may be characterized prior to hydrogenation as having a dense 10 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 laser light angle scattering studies may vary considerably but typically ranges from about 13 to about 22.

15 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. However, the hydrogenation conditions must be sufficient to hydrogenate at least 95% of the original olefinic 20 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 25 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 30 above the temperature where crystallization would occur.

In general, hydrogenation involves the use of a suitable catalyst as described in US-E-27145. A mixture of nickel ethylhexanoate and triethylaluminium having

- 11 -

from 1.8 to 3 moles of aluminium per mole of nickel is preferred.

The hydrogenated star polymers of this invention may be added to a variety of lubricating oils to improve 5 viscosity index characteristics. For example, the selectively hydrogenated star polymers may be added to fuel oils such as middle distillate fuels, synthetic and natural lubricating oils, crude oils and industrial oils. In addition to engine oils, they may be used in 10 the formulation of automatic transmission fluids, gear lubricants, and hydraulic fluids. In general, any amount of the selectively hydrogenated star polymers may be blended into the oils, with amounts from about 0.05 to about 10 wt% being most common. For engine oils, 15 amounts within the range from about 0.2 to about 2 wt% are preferred.

Lubricating oil compositions prepared with the hydrogenated star polymers of this invention may also contain other additives such as anti-corrosive 20 additives, antioxidants, detergents, pour point depressants, and one or more additional VI improvers. Typical additives which are useful in the lubricating oil composition of this invention and their description will be found in US-A-3772196 and US-A-3835083.

25 Preferred Embodiment of the Invention

In preferred star polymers of the present invention, the number average molecular weight (MW_1) of the outer polyisoprene block is between 15,000 and 30 65,000 before hydrogenation, the number average molecular weight (MW_2) of the polybutadiene block is between 2,000 and 6,000 before hydrogenation, the number average molecular weight (MW_3) of the inner polyisoprene block is between 5,000 and 40,000, the number average

- 12 -

molecular weight (MW_s) of the polystyrene block is between 2,000 and 4,000 when the S block is external and between 4,000 and 12,000 when the S block is internal, the star polymer comprises less than 10% by weight of 5 the polybutadiene, and the ratio of MW_1/MW_3 is from 0.9:1 to 5:1. The 1,4-polymerization of the polybutadiene block is preferably at least 89%. The star polymers of the present invention are preferably of the structure, $(S-EP-EB-EP')_n-X$.

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

15 Having thus broadly described the present invention and the preferred embodiment, the invention is further described by the following examples which should not be construed as the limits of the invention.

EXAMPLES

20 Polymers 1 to 3 were made according to the present invention. Polymers 1 and 2 have internal polystyrene blocks and Polymer 3 has an external polystyrene block on each star arm. These polymers were compared to two polymers made according to US-A-5460739, Polymers 4 and 25 5, two commercial polymers, Polymers 6 and 7, and a polymer made according to US-A-5458791, Polymer 8. The polymer compositions and melt viscosities of these polymers are shown in Table 1.

Table 1
Polymer Composition and Melt Viscosity

Polymer	Step 1 block	Step 2 block	Step 3 block	Step 4 block	Step 1 MW (true)	Step 2 MW (true)	Step 3 MW (true)	Step 4 MW (true)	Polystyrene Content, % calc. basis arm MW	Melt Vis, 120°C, MPa-s	I ₁ /I ₂
1	I ₁	S	B	I ₂	32,500	10,200	3,300	19,500	15.6	2.8	1.67
2	I ₁	S	B	I ₂	36,000	5,800	7,300	14,000	9.2	2.2	2.57
3	S	I ₁	B	I ₂	3,100	26,100	6,000	14,200	6.3	1.6	1.84
4	I ₁	B	I ₂	--	31,500	4,400	21,400	--	0	1.3	1.47
5	I ₁	B	I ₂	--	37,600	3,600	13,600	--	0	1.1	2.76
6 ^a	I	S	na	na	65,000	35,000	na	na	35	1.7	--
7	S	I	--	--	3,500	51,000	--	--	6.4	1.7	--
8	I ₁	S	I ₂	--	34,200	9,100	14,300	--	16.5	1.8	2.39

na = not applicable or available.

^a = a linear polymer.

Table 2
Performance in SAE 10W-40 Multigrade Oils

Polymer	Polymer % wt	Kin Vis, 100°C, CST	VI	TBS, ^b 150°C, cP	DIN Vis Loss, %	DIN P, MPa	CCS ^c -20°C cP	TPI ^d -30°C, cP
1	1.02	13.92	163-200 ^a	3.67	10.4	14.2	2,740	22,900
2	0.96	14.02	161	3.67	10.9	14.2	2,980	32,800
3	1.08	13.92	161	3.69	4.0	14.2	2,890	24,400
4	0.93	13.97	163	3.51	11.0	14.7	2,800	24,100
5	0.94	13.87	161	3.59	8.8	13.4	2,850	23,300
6	1.21	13.47	164	3.37	2.0	13.4	2,750	37,200
7	0.95	14.00	162	3.58	11.8	17.0	2,970	36,600
8	1.06	13.93	169	3.58	8.2	14.5	2,980	30,200

na = not applicable or available.

- a) VI increased with time
- b) HTHSR viscosity limit is 2.9 cP min (SAE Standard J300)
- c) Cranking viscosity limit is 3500 cP max (SAE Standard J300)
- d) Pumping viscosity limit is 60,000 cP max (SAE Standard J300)

- 15 -

Polymers 1 and 2 clearly have superior melt viscosities to the commercial polymers and the polymers of US-A-5460739 and US-A-5458791. Polymer 3 has a superior melt viscosity to those of US-A-5460739. The 5 melt viscosity of Polymer 3 is slightly lower than the commercial star Polymer 7, although the polymers have approximately the same polystyrene contents. However, the total arm molecular weight, which is the sum of the Step 1 to Step 4 molecular weights, is lower for Polymer 3 10 than the total arm molecular weight of Polymer 7, which is the sum of the Step 1 and Step 2 molecular weights. If Polymer 3 were modified by increasing the Step 2, Step 3, or Step 4 molecular weight so that the total arm 15 molecular weight approximated that of Polymer 7, it is expected that the melt viscosity values would match or exceed that of Polymer 7. Generally, polymers with higher melt viscosities are easier to cyclone finish.

Polymer concentrates were prepared using Exxon (trade-mark) HVI 100N LP basestock. The concentrates were 20 used to prepare fully formulated SAE 10W-40 multigrade oils. In addition to VI improver concentrate, these oils contained a pour point depressant, dispersant inhibitor package, and Shell HVI100N and HVI250N base oil. Diesel injector rig (DIN) testing for lubricant viscosity loss 25 according to test procedure CEC L-14-A-93 shows that Polymers 1 to 3 are representative of VI improvers having high to intermediate mechanical shear stability. These results are shown in Table 2. The high shear rate viscosity, as measured in the Tapered Bearing Simulator 30 (TBS) at 150°C was typical of conventional star polymers having this level of permanent stability. This is significant because the results easily exceed the

- 16 -

minimum requirement of SAE Standard J300. Polymers 1 and 3 matched the outstanding TPI-MRV performance of Polymers 4 and 5.

The SAE 10W-40 multigrade oil which contained 5 Polymer 1 also exhibited a viscosity index time dependence. Over a three week period of room temperature storage, the viscosity index increased from 163 to 200. The kinematic viscosity at 100°C did not change but the 40°C viscosity dropped from 88 to 72 10 centistokes. Polymers 2 and 3 did not show a time dependence.

The Exxon HVI100N polymer concentrates were also used to prepare fully-formulated SAE 5W-30 multigrade oils. These results are given in Table 3. In addition 15 to the VI improvers, these oils contained pour point depressant, a dispersant inhibitor package, and additional Exxon HVI100N LP base oil. Given the reproducibility of the TPI-MRV test at -35°C, there was no significant difference in performance between 20 Polymers 1, 2 and 3, versus 4 and 5, but all were significantly better than Polymer 8, as well as the commercial Polymers 6 and 7.

- 17 -

Table 3
Performance in SAE 5W-30 Multigrade Oils

Polymer	Polymer %wt	Kin Vis, 100°C, cSt	VI	TBS, 150°C, cP	CCS, -25°C, cP	TPI, -35°C, cP
1	0.72	10.40	161 ^a	3.05	3,290	29,000
2	0.67	10.40	159	3.07	3,490	31,200
3	0.76	10.38	159	3.07	3,510	31,000
4	0.66	10.66	162	3.05	3,230	27,600
5	0.68	10.65	161	3.02	3,220	28,700
6	0.89	10.35	162	2.88	3,280	46,800
7	0.68	10.62	166	3.01	3,330	47,000
8	0.75	10.54	165	3.02	3,290	41,400

a) the time-dependent behaviour was not verified in
5 this case by monitoring kinematic viscosity with time.

VI is the viscosity index and it is determined by
10 ASTM D2270. High-temperature high-shear rate viscosity
(HTHSR) at 150°C is determined in the tapered bearing
simulator (TBS) by ASTM 4683. DIN VIS loss is the
viscosity loss at 100°C and is determined by CEC L-14-A-
93. CCS is the cold cranking simulator viscosity and is
determined by ASTM D5293. TPI represents the TPI-MRV
viscosity as determined in the mini-rotary viscometer
test method, ASTM D4684.

- 18 -

CLAIMS:

1. A star polymer having the structure selected from the group consisting of

(I) $(S-EP-EB-EP')_n-X$

(II) $(EP-S-EB-EP')_n-X$

5 (III) $(EP-EB-S-EP')_n-X$

wherein

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

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

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

20 S is a block of polystyrene having a number average molecular weight (MW_S) of 1,000 to 4,000 when the S block is external (I) and 2,000 to 15,000 when the S block is internal (II or III);

25 wherein the star polymer structure comprises from 3% to 15% by weight of the polybutadiene, the ratio of MW_1/MW_3 is from 0.75:1 to 7.5:1, X is a nucleus of crosslinked poly(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.

- 19 -

2. A star polymer of claim 1, wherein the polyalkylene coupling agent is divinylbenzene.
3. A star polymer of claim 2, wherein n is the number of arms when coupled with at least 3 moles of divinylbenzene per mole of living block copolymer molecules.
4. A star polymer of claim 1, 2 or 3, wherein the number average molecular weight (MW_1) of the outer polyisoprene block is between 15,000 and 65,000 before hydrogenation, the number average molecular weight (MW_2) of the polybutadiene block is between 2,000 and 6,000 before hydrogenation, the number average molecular weight (MW_3) of the inner polyisoprene block is between 5,000 and 40,000 before hydrogenation, the number average molecular weight (MW_s) of the polystyrene block is between 2,000 and 4,000 when the S block is external (I) and between 4,000 and 12,000 when the S block is internal, the star polymer comprises less than 10% by weight of the polybutadiene, and the ratio of MW_1/MW_3 is from 0.9:1 to 5:1.
5. A star polymer of any one of claims 1 to 4, wherein the 1,4-polymerization of the polybutadiene block is at least 89%.
6. A star polymer of any one of claims 1 to 4, wherein the polyisoprene blocks and the polybutadiene blocks are at least 95% hydrogenated.
7. An oil composition comprising:
a base oil; and

- 20 -

a viscosity index improving amount of the star polymer of any one of claims 1 to 6.

8. A polymeric concentrate for oil compositions comprising:

at least 75% by weight of a base oil; and
from 5% to 25% by weight of the star polymer of any one of claims 1 to 6.