

STAR-SHAPED POLYMERS

The present invention relates to star-shaped polymers having useful properties as additives for lubricating oil compositions, to their preparation and to lubricating oil compositions containing them.

5 Star-shaped polymers are macromolecules consisting of linear polymer arms that radiate outward from a central core, which are of substantial commercial interest due to their markedly different dilute solution behaviour compared to linear, random-coil
10 counterparts. In addition, they have important commercial applications, most notably as viscosifiers in lubricating oil compositions, due to their superior resistance to shear-induced thermal degradation. With the exception of classical condensation polymerisation
15 systems and closely related ring-opening polymerisations, star-shaped polymers have been produced by three different methods using, in most cases, living anionic polymerisation. The most popular method, termed the "linking" method, involves the
20 initiation of monomers such as styrene, butadiene, or isoprene with an organolithium initiator to produce living polymeric monoanions that are subsequently reacted, in exact stoichiometric proportions or in slight excess, with a multifunctional linking agent to
25 form star-shaped polymers. The advantage of this method is that the number of arms per molecule within a given sample is invariant and precisely controlled by the functionality of the linking agent.

Star-shaped polymers have also been synthesised by
30 sequential addition of a di- or polyfunctional vinyl compound such as divinylbenzene to living, monofunctional polymeric anions. This second general method which may be described as an "arm-first, core-

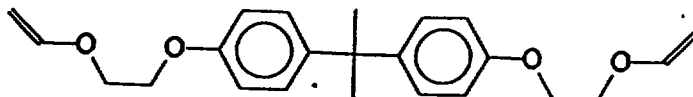
last" method, is particularly suited to the preparation of star-shaped polymers with many arms. The first step of the synthesis involves the generation of living polystyryllithium. A small amount of difunctional vinyl compound such as divinylbenzene is charged to the reaction, and this initially forms a short block segment of divinylbenzene with pendent vinyl groups. The last step of the mechanism involves inter- and intramolecular reactions (microgel formation) of these vinyl groups with living anions to give a star-shaped polymer in which the arms are radially attached to a microgel core.

The third general method for producing star-shaped polymers, termed the "core-first, arm-last" method, involves the use of a multifunctional initiator that is either prepared externally to the polymerisation reaction or in-situ, just prior to polymerisation of the arm-forming monomer. Externally prepared multifunctional anionic initiators have been generally less successful due to poor solubility of low-molecular weight polyanions, and the few reported examples require polar-solvent conditions.

A successful variation of this method, which is also closely related in principle to the arm-first, core-last method, involves the in-situ formation of a plurifunctional anionic initiator by reaction of an excess of difunctional vinyl compound such as divinylbenzene with butyllithium in dilute solution. This reaction produces a population of soluble gel particles, each of which is coated with a number of carbanions which are capable of initiating a subsequent charge of monomer to produce a star-shaped polymer molecule.

Recent developments in the field of living carbocationic polymerisation have enabled the synthesis of various vinyl ether star-shaped polymers by the arm-first, core-last method. An HI/ZnI_2 initiating system

has been used at -40°C in toluene to produce living poly(isobutyl vinyl ether) cations to which a small amount of divinyl ether such as that shown below,



was added to produce star-shaped polymers. Polymers ranging in arm number from 3 to 60 were produced by this method. The Hi/ZnI_2 initiating system provides living character to the isobutyl vinyl polymerisation through the intimate interaction between growing chain ends and the binary $\text{I}^-\dots\text{I}_2$ counterionic moieties which render the chain ends reactive toward propagation but unreactive toward higher energy chain transfer and termination reactions. This method of living carbocationic polymerisation has been termed "stabilisation by a suitably nucleophilic counterion," and has been successfully used to produce living carbocationic polymerisations of monomers such as vinyl ethers, p-methoxystyrene, and N-vinyl carbazole, which form highly stabilised carbocations.

A more recent development, involving the addition of Lewis bases such as ethyl acetate, dimethyl sulfoxide, and dimethyl acetamide to the reaction medium of a carbocationic polymerisation, has been found to provide living characteristics to the cationic polymerisation of monomers which form relatively unstable carbocations, such as isobutylene (IB) and styrene, in addition to those monomers which form relatively stable carbocations. This method of living carbocationic polymerisation has been termed "electron donor mediated cationic polymerisation," since the Lewis base or a Lewis base:Lewis acid (coinitiator) complex is believed to provide stabilisation to growing polymer chains. The most obvious manifestation of this

stabilisation is a dramatic decrease in the overall rate of polymerisation, which is often attributed to the formation of an equilibrium between a large number of dormant (reversibly terminated) chain ends and a
5 small number of active chains.

An improved Lewis base mediated polymerisation system for the living carbocationic polymerisation of isobutylene (IB) consists of a di- or trifunctional cumyl chloride-type initiator in conjunction with TiCl_4
10 as coinitiator and pyridine as an externally added Lewis base (electron donor) in a 60/40 hexane/methyl chloride solvent system at -80°C . The improved system has been utilized to produce telechelic ionomers possessing a narrow MWD between ionic groups,
15 poly(styrene-b-isobutylene-b-styrene) (S-IB-S) block copolymers, and S-IB-S- block copolymer ionomers.

The present invention, however, provides the synthesis of star-shaped polymers containing polyisobutylene (PIB) via the arm-first, core-last
20 method. These star-shaped polymers are superior in properties to known hydrogenated polyisoprene star-shaped polymers for use as viscosifiers for lubricating oil compositions due to their inherent lack of unsaturation and their relatively flat
25 temperature/viscosity profiles.

Accordingly, the present invention relates to a star-shaped polymer comprising a core of polymerized diisopropenylbenzene and at least three polymeric arms connected to the core, wherein the polymeric arms
30 comprise polyisobutylene.

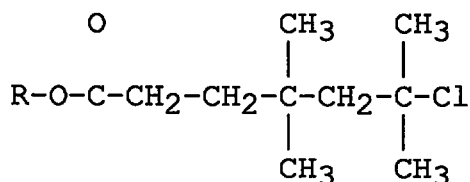
Preferably, the polymeric arms comprise polyisobutylene having a peak molecular weight from 500 to 1,000,000.

The present invention further provides a process
35 for preparing the above star-shaped polymers which comprises (a) polymerising isobutylene with an

initiator to form living polymers, and (b) coupling the living polymers with diisopropenylbenzene.

The synthesis of star-shaped polymers comprising polyisobutylenes suitably involves first the living carbocationic polymerisation of isobutylene homopolymers, random copolymers, or block copolymers using a monofunctional initiator and preferably in addition a TiCl_4 /pyridine cocatalyst as described in U.S. Patent No. 5,219,948, which is hereby incorporated by reference. The monofunctional initiator is a monochloro hydrocarbon which initiates living carbocationic polymerisation. Preferably, the living initiator is 2-chlor-2,4,4-trimethylpentane, which must be distilled just prior to use to obtain lower polydispersity, 1-(2-chloro-2-propyl)-3,5-di-tert-butylbenzene, which is most preferred for its stability and resulting low polydispersity, 2-chloro-2-propylbenzene (cumylchloride), which can be used alone or as a 1:1 adduct with isobutylene, or 2-chloro-2,4-dimethyl-4-phenylpentene.

The initiator could contain non-polymerising ester groups such as the following known initiator:



wherein R is an alkyl group having from 1 to 8 carbon atoms. Other useful initiators include the peroxide derived initiators as described in European Patent No. 355,957.

The chloro initiators can be substituted by closely related compounds in which the chloride function has been replaced by -OMe, -OAc, -OH, -OOH, -OOR, -OCOOR, and -OCOAc.

The initiator system readily polymerises olefins, conjugated dienes, monoalkenyl aromatic compounds, and combinations thereof to form living polymers as described in U.S. Patent No. 5,219,948. Then, to the living polymer chains, a small amount of 1,3-diisopropenylbenzene is added to form the crosslinked core of the star-shaped polymers. Although the mechanism is not fully understood, the 1,3-diisopropenylbenzene is surprisingly superior to divinylbenzene for coupling of the described living polymers to make star-shaped polymers.

The rate of polymerisation of the living polymer chains must be known so that the optimum time of addition of 1,3-diisopropenylbenzene can be determined. As described in U.S. Patent No. 5,219,948, addition of a second monomer to living polyisobutylene chains must be done within a relatively narrow window of isobutylene conversion to achieve satisfactory results. Generally, the isobutylene conversion should be at least 70, but not higher than 95%, and most preferably between 80% and 93%.

The star-shaped polymers of the present invention are excellent viscosity index improvers for lubricating oil compositions when the peak molecular weight of the arms ranges from 500 to 1,000,000, when the number of arms exceeds 3 per molecule. Thus the present invention also provides a lubricating oil composition comprising a lubricating oil and a viscosity modifying amount of a star-shaped polymer as defined above.

Suitably, the lubricating oil composition comprises a major proportion (more than 50%w) of a lubricating oil and a minor proportion, preferably from 0.1 to 10%w, based on the total composition, of the star-shaped polymer.

The invention is further illustrated by means of the following Examples which are not intended to limit the invention to specific embodiments.

Preparation of the Chemical Compounds as applied in the Examples

Hexane and 1,3-diisopropenylbenzene were distilled from calcium hydride just prior to use. Isobutylene and methyl chloride (Linde Div., Union Carbide Corp.) were dried by passing the gaseous material through a column packed with BaO and CaCl₂. 2,4,4-Trimethyl-1-pentene, 1,3,5-tri-tert-butylbenzene, titanium tetrachloride, pyridine, and anhydrous methanol were used as received from Aldrich Chemical Co., Sulfuric acid, methylene chloride, calcium chloride, and sodium chloride were used as received from Fisher Chemical Co.

The initiators, 2-chloro-2,4,4,-trimethylpentane (TMPCl), 2-chloro-2-propylbenzene (cumyl chloride), 1-(2-chloro-2-propyl)-3,5-di-tert-butylbenzene, and 2-chloro-2,4-dimethyl-4-phenyl-pentane, are prepared as follows:

Preparation of 2-chloro-2,4,4-trimethylpentane (TMPCl)

Into a three-necked, round-bottomed flask equipped with gas inlet and outlet tubes, magnetic stirrer, and external ice/water cooling bath were charged 21 g 2,4,4-trimethyl-1-pentene (TM1P) and 200 mL MeCl₂. HCl gas was produced in a separate reactor by addition of sulfuric acid to solid NaCl. The gas was passed through a column packed with anhydrous CaCl₂ and then bubbled continuously into the TM1P solution with stirring for 6 hours at ice bath temperature. Excess HCl and MeCl₂ were vacuum stripped leaving a near-quantitative yield of very pale green liquid. ¹H NMR (ppm): 1.05 (9H), 1.67 (6H), 1.87 (2H).

Preparation of 2-chloro-2-propylbenzene (Cumyl chloride)

Into a three-necked, round-bottomed flask equipped with gas inlet and outlet tubes, magnetic stirrer, and external ice/water cooling bath were charged 20 g isopropenylbenzene (α -methylstyrene) and 200 mL MeCl₂. HCl gas was produced in a separate reactor by addition

of sulfuric acid to solid NaCl. The gas was passed through a column packed with anhydrous CaCl_2 and then bubbled continuously into the isopropenylbenzene solution with stirring for 6 hours at ice bath temperature. Excess HCl and MeCl_2 were vacuum stripped leaving a clear liquid product.

Preparation of 1-(2-chloro-2-propyl)-3,5-di-tert-butylbenzene

Preparation of methyl 3,5-di-tert-butylbenzoate.
10 Into a 250 mL three-necked, round-bottomed flask equipped with a magnetic stirrer and reflux condenser are charged 23.4 g (0.1 mole) 3,5-tert-butylbenzoic acid (Aldrich), 100 mL methanol, and 1 mL sulfuric acid. The reaction mixture is allowed to reflux
15 overnight, cooled to room temperature, and then refrigerated overnight, during which time the product precipitates from the solution. The crude product is collected by filtration, washed with distilled water several times to remove sulfuric acid, dried at 50°C ,
20 and recrystallised from methanol.

Preparation of 1-(2-hydroxy-2-propyl)-3,5-di-tert-butylbenzene. Into a 500 mL round-bottomed flask, equipped with a mechanical stirrer, dry nitrogen inlet and outlet tubes, dripping funnel with a pressure
25 equalising side-arm, and external ice water cooling bath, are charged 19.8 g (0.08 mole) methyl 3,5-di-tert-butylbenzoate and 100 mL anhydrous THF. A solution of methyl magnesium bromide in THF (65 mL of a 3 M solution) is added dropwise to the solution at 0°C
30 over a period of 30 minutes. The reaction is allowed to stand at room temperature overnight and the charge is slowly added to a mixture of 11 g of NH_4Cl and 160 g ice. The product is extracted from the mixture using several aliquots (100 mL) of diethyl ether. The
35 extract is dried over magnesium sulfate, the diethyl ether is removed by vacuum-stripping, and the product is recrystallised from ethyl acetate.

Preparation of 1-(2-chloro-2-propyl)-3,5-di-tert-butylbenzene. To a 1000 mL three necked, round-bottom flask equipped with gas inlet and outlet tubes, mechanical stirrer, and external ice water cooling bath, are charge 9.92 (0.04 mole) 1-(2-hydroxy-2-propyl)-3,5-di-tert-butylbenzene, 10 g anhydrous CaCl_2 , and 100 mL methylene chloride. HCl gas is generated in a separate reactor by addition of concentrated sulfuric acid to solid NaCl. The gas is passed through a column packed with anhydrous CaCl_2 and then bubbled continuously into the solution with stirring for 10 hours. The alcohol is not soluble in methylene chloride but is observed to slowly go into solution as it reacts. Excess HCl and MeCl_2 are vacuum stripped, and the product is twice recrystallised from hexanes.

Preparation of 2-chloro-2,4-dimethyl-4-phenylpentane

The following procedure is conducted in a dry box under dry N_2 atmosphere at -40°C . Into a 500 mL three-necked, round-bottomed flask equipped with mechanical stirrer are added 30 g (0.19 mole) cumyl chloride, 200 mL hexane, 200 mL methyl chloride, and 11.4 g (0.20 mole) isobutylene. With vigorous stirring, 50 g (0.43 mole) BCl_3 is added rapidly to the mixture. After 10 minutes, 45 mL pre-chilled MeOH is added to terminate the reaction, and the reactor is removed from the dry-box. The MeCl_2 is caused to evaporate as the contents of the reactor are allowed to warm to room temperature with stirring. The remaining mixture is washed twice with 200 mL of 0.5 N aqueous HCl and twice with 200 mL distilled water and then dried over MgSO_4 . The product is isolated by evaporation of the hexane.

Example 1

Polymerisation was conducted in a glove box, equipped with an integral cold bath, under a dry nitrogen atmosphere at -80°C . In one experiment, a chilled 2000 ml three-necked, round-bottomed flask was charged with 400 ml methyl chloride, 600 ml methyl

chloride, 600 ml hexane, 87 ml (1.1 mole) isobutylene, 0.2 g (1.3×10^{-3} mole) 2-chloro-2,4,4-trimethylpentane, and 0.1 ml (1.3×10^{-3} mole) pyridine. After stirring the solution for approximately 15 min, 1.5 ml (1.3×10^{-2} mole) TiCl_4 was added quickly to the vigorously stirred reaction mixture to initiate the polymerisation. At a reaction time of 40 min, an aliquot of approximately 100 ml was taken from the reaction mixture and immediately quenched with methanol. Just after removal of the aliquot, 0.2 ml (1.17×10^{-3} mole) 1,3-diisopropenylbenzene was added to the reaction mixture. The polymerisation was allowed to continue for an additional 210 min before quenching with 30 ml of pre-chilled methanol.

The aliquot and the remaining terminate reaction mixture was allowed to warm to room temperature with stirring to remove methyl chloride. A volume of hexane was added to each sample, approximately equal to the volume lost by methyl chloride evaporation. The hexane solutions were then washed twice with 5.0% aqueous HCl and then twice with DI water. Finally, the solutions were dried with magnesium sulfate and freed of hexane by vacuum-stripping.

25 Example 2

In a second experiment, a chilled 3000 ml three-necked, round-bottomed flask was charged with 920 ml methyl chloride, 1380 ml hexane, 200 ml (2.5 mole) isobutylene, 0.46 g (3.1×10^{-3} mole) 2-chloro-2,4,4-trimethylpentane, and 0.25 ml (3.1×10^{-3} mole) pyridine. After stirring the solution for approximately 15 min, 3.5 ml (3.1×10^{-2} mole) TiCl_4 was added quickly to the vigorously stirred reaction mixture to initiate the polymerisation. At reaction times of 20, 40, 64, and 88 min, additional charges of IB (75 ml, 0.95 mole) were added to the reaction mixture. At a reaction time of 217 min, 1400 ml of the

reaction mixture was transferred to a chilled 2000 ml three-necked, round-bottomed flask via a chilled graduated cylinder, and to this portion was immediately added 0.27 ml (1.6×10^{-3} mole) 1,3-diisopropenyl-
5 benzene. Just after the addition of 1,3-diisopropenylbenzene, approximately 800 ml of the original reaction mixture (no 1,3-diisopropenylbenzene added) was poured into a chilled 2000 ml round, bottomed flask and immediately quenched with 30 ml
10 methanol. The remaining original reaction mixture, and the reaction mixture to which 1,3-diisopropenylbenzene was added, were each quenched with methanol at a reaction time of 500 min.

Gel permeation chromatography (GPC) was performed
15 using a Waters Associates GPC system equipped with a Rheodyne injector, a Waters model 510 HPLC solvent delivery pump, three Ultrastyrigel columns of nominal pore sizes 500, 10^3 , and 10^4 Å, and a Waters model 410 differential refractometer detector operating at 33°C.
20 Tetrahydrofuran (THF), freshly distilled from calcium hydride, served as the mobile phase, and was delivered at a flow rate of 1.0 ml/min. Sample concentrations were approximately 0.5% (w/w) in THF, with an injection volume of 50 ml. Molecular weights were calculated
25 relative to PIB standards of narrow molecular weight distribution.

The compound, 2-chloro-2,4,4-trimethylpentane (TMPCl), has been used frequently as a monofunctional initiator for the carbocationic polymerisation of
30 isobutylene and as a result was chosen for use as initiator in PIB star-shaped polymer synthesis. Two commercially available core-forming comonomers were considered as candidates for PIB star-shaped polymer synthesis those being divinylbenzene and 1,3-
35 diisopropenylbenzene (DiPB). It was thought that divinylbenzene would provide the best results, since styrene has been shown to react readily with PIB

carbocationic chain carriers derived from the dicumyl chloride/TiCl₄/pyridine initiating system, while α -methylstyrene has not. Commercially available divinylbenzene (Aldrich Chemical Co.) comes as a mixture of isomers with purity of only 55.0%, with the major contaminants being 3- and 4-ethylvinylbenzene. DiPB, which is 97.0% pure, was chosen from the investigation to avoid the possibility of side reactions.

In Example 1, living PIB cations with number average molecular weight (M_n) of 14,400 g/mole by (GPC) were produced using the TMPCl/TiCl₄/pyridine initiating system and subsequently reacted with an amount of DiPB calculated to provide a 1:1 molar ratio between living arms and DiPB, assuming 100% initiation efficiency of TMPCl. The molecular weight of the living arm was considerably lower than theoretical indicating a rather low (~30%) conversion of IB at the time of DiPB addition. The molecular weight of the polymers produced in the presence of DiPB (star) were much higher than those removed prior to the addition of DiPB (arm) as evidenced by the shift to lower elution time upon the addition of DiPB. This result shows that DiPB did indeed react with polyisobutylene carbocations and effectively linked PIB chains. The GPC trace of the arm simply displays a lower elution time (high molecular weight) should which may be due to initiation by impurities.

Due to the fact that in the above experiment DiPB was added at a time when substantial amounts of IB remained in the reaction mixture, it remained to be shown that the increase in molecular weight after the addition of DiPB was due to core formation and star-shaping and not just simply further conversion of isobutylene. Thus, the polymerisation of Example 2 was conducted in which a fraction of the living polyisobutylene chains was not subjected to the DiPB

addition but rather was allowed to propagate for the same period of time as the polymers receiving DiPB. In addition, an incremental monomer addition (IMA) technique was utilised during arm formation in an attempt to obtain higher molecular weight arms ($M_n = 40,500$ g/mole) while maintaining a relatively high rate of polymerisation.

As can be seen from GPC traces, the molecular weight of the star sample was higher than that of the control sample, yielding further support to the conclusion that DiPB reacted with, and subsequently linked, polyisobutylene arms to produce star-shaped polymers.

Although the previously discussed GPC results for Examples 1 and 2 demonstrate that DiPB can be used to link living PIB chains, they do not allow for a determination of the average number of PIB chains (arms) linked per molecular, due to the well known fact that star-shaped polymers possess lower hydrodynamic volumes in solution than linear counterparts of equivalent molecular weight. The number of arms in the star-shaped polymer can only be calculated by comparing the molecular weight of the arm sample to that of the star sample, the latter determined using some method of absolute molecular weight determination, such as membrane osmometry or light scattering.

It has been shown by GPC that the production of the living carbocationic polymerisation of IB using a $\text{TMPCl/TiCl}_4/\text{pyridine}$ initiating system in conjunction with a subsequent addition of DiPB to the reaction medium is a viable method for the synthesis of PIB star-shaped polymers. Relationships between the effect of relative DiPB concentration to TMPCl concentration, as well as the effect of reaction time, both before and after the addition of DiPB, on the average number of arms per molecule are readily determined by persons skilled in the art.

Example 3

To a chilled 3000 mL three-necked, round-bottomed flask equipped with mechanical stirrer were charged 1200 mL hexane, 800 mL methyl chloride, 171 mL (2.17 mole) isobutylene, 0.33 mL (4.1×10^{-3} mole) pyridine, and 0.60 g (4.1×10^{-3} mole) 2-chloro-2,4,4-trimethylpentane. The solution was allowed to stir for approximately 20 minutes, at which time the mixture was divided evenly (four 500 mL portions) into four 1 L three-necked, round-bottomed reaction flasks. Polymerisation was initiated in reactors 1 and 2 by the addition, with vigorous stirring, of 0.97 mL (9.3×10^{-4} mole) TiCl_4 to each flask; reaction mixtures 3 and 4 were set aside for use in Example 4 below.

After a reaction time of 6 h (70% conversion) a 100 mL aliquot was removed from reactor 1 and quenched with prechilled methanol, and immediately 0.12 mL (7.0×10^{-4} mole) 1,3 diisopropenylbenzene (DIPB) was added to the remaining volume of reactor 1. Reaction mixtures 1 and 2 were allowed to continue to react for 3 hours, at which time they were terminated with 30 mL pre-chilled methanol. The reaction mixtures were then allowed to warm to room temperature with the accompanying evolution of methyl chloride. To each sample was added 300 mL hexane and the resulting solutions were washed 3 times with 5% aqueous HCl and 2X with distilled water. The solutions were dried over MgSO_4 and filtered, and then the hexane was removed using a rotary evaporator and by subsequent storage of the samples in a vacuum oven for 4 days.

Example 4

Reaction mixtures 3 and 4 from above were initiated by addition of 0.97 mL (9.3×10^{-4} mole) TiCl_4 to each reactor. After a reaction time of 7.5 h (85% conversion), a 100 mL aliquot was removed from reactor 3 and quenched with prechilled methanol, and immediately 0.12 mL (7.0×10^{-4} mole) 1,3

diisopropenylbenzene (DIPB) was added to the remaining volume of reactor 3. Reaction mixtures 3 and 4 were allowed to continue to react for 3 hours, at which time they were terminated with 30 mL pre-chilled methanol. The reaction mixtures were then subjected to the same work-up as described above.

In Example 3, the DIPB was added at too low an isobutylene conversion GPC traces of the 100 mL aliquot (arm) and fully reacted star-shaped polymer (star) were obtained from reactor 1. Examination of the GPC trace for the star peak revealed that it is trimodal, consisting of two high weight average molecular weight (M_w) fractions that are presumably star-shaped, and a low M_w fraction that appears to consist of arms that have increased in M_w due to further polymerisation, but that have not become incorporated into star-shaped polymers. Apparently, DIPB and leftover IB compete for the living chains, and the star formation process is slow and incomplete. It is believed that the existence of two higher M_w fractions is related to the presence of a high M_w tail that is visible in the GPC trace of the arm. In contrast, GPC traces of the precursor arm and star-shaped product formed by addition of DIPB at 85% IB conversion (Example 4) shows that the star peak is now only slightly bimodal, and there appears to no longer be any unreacted arm. It is believed that if the precursor arm peak had not had the pronounced high M_w tail, that the star would have been monomodal. The experiments demonstrate the importance of proper timing of DIPB addition. In addition, to obtain well-defined products and easily interpretable results, the precursor arm must possess a narrow, monomodal molecular weight distribution.



C L A I M S

1. A star-shaped polymer comprising a core of polymerised diisopropenylbenzene and at least three polymeric arms connected to the core, wherein the polymeric arms comprise polyisobutylene.
- 5 2. The star-shaped polymer according to claim 1, wherein the polymeric arms comprise polyisobutylene having a peak molecular weight from 500 to 1,000,000.
3. A process for preparing star-shaped polymer according to claim 1 or 2, comprising (a) polymerising
10 isobutylene with an initiator to form living polymers, and (b) coupling the living polymers with diisopropenylbenzene.
4. A process according to claim 3, wherein the living polymers are homopolymers of isobutylene, random
15 copolymers of isobutylene and another monomer, or block copolymers of isobutylene and another monomer.
5. A process according to claim 3 or 4, wherein the initiator is 2-chloro-2,4,4-trimethylpentane or 1-(2-chloro-2-propyl)-3,5-di-tert-butylbenzene.
- 20 6. A process according to any one of claims 3-5, wherein the polymerisation of the isobutylene occurs in the presence of $TiCl_4$ and pyridine.
7. A process according to claim 6, wherein the initiator is 1-(2-chloro-2-propyl)-3,5-di-tert-
25 butylbenzene.
8. A process according to any one of claims 3-7, wherein the isobutylene is polymerised to at least 70% completion before coupling with the diisopropenylbenzene.
- 30 9. A lubricating oil composition comprising a lubricating oil and a viscosity modifying amount of a star-shaped polymer according to claim 1 or 2.

A B S T R A C T

STAR-SHAPED POLYMERS

The present invention provides star-shaped polymers comprising cores of polymerised diisopropenylbenzene and at least three polymeric arms connected to each core, the polymeric arms comprising polyisobutylene; a process for their preparation; and lubricating oil compositions containing them.