

Preparation and Characterization of a Star-Shaped Polystyrene-*b*-Poly(ethylene-*co*-propylene) Block Copolymer as a Viscosity Index Improver of Lubricant

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Received 27 December 1999; accepted 31 March 2000

ABSTRACT: A saturated star-shaped polystyrene-*b*-poly(ethylene-*co*-propylene) block copolymer, (SEP)_{star}, was synthesized for use as a viscosity index improver in lubricants. Polystyrene-*b*-polyisoprene arms were first made anionically, followed by a linking reaction at the optimum temperature of 60°C with divinylbenzene. The resulting star-shaped (SI)_{star} was hydrogenated to eliminate the double bonds on the polyisoprene segment, thus forming the star-shaped (SEP)_{star}. The number of arms on each molecule increased with an increase in the mol ratio of divinylbenzene to *n*-butyllithium. Increasing the arm length adversely affected the linking efficiency but caused a slight increase in the degree of branching. The T_g of the poly(ethylene-*co*-propylene) block was 13°C higher than that of the original polyisoprene block. Compared with (SI)_{star}, (SEP)_{star} has a thermal decomposition temperature 50°C higher but independent of the arm length or the degree of branching. Viscosity measurements for (SEP)_{star} revealed that intrinsic viscosity depends only on the arm length, but not on the degree of branching. Adding 1 wt % of (SEP)_{star} markedly increased the viscosity index of a HN base oil. With a fixed arm length, a (SEP)_{star} having a higher degree of branching increased the viscosity index more than that having a lower degree of branching. On the other hand, the viscosity index increased with an increase in the arm length when the degree of branching was fixed. The addition of 1wt % of (SEP)_{star} increased the viscosity index up to a number between 111 and 166, with the exact number depending upon its arm length and degree of branching. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1838–1846, 2001

Key words: viscosity index improver; block copolymer; hydrogenation; lubricant

INTRODUCTION

The viscosity index (VI) has traditionally been the parameter for expressing the temperature-vis-

cosity relationship of an oil or lubricant. For an oil or lubricant to have better low-temperature viscosity and high-temperature volatility characteristics, the addition of a viscosity index improver (VII) is necessary.^{1,2} The molecular weight and structure of a VII molecule significantly affect its ability to thicken the oil or lubricant and a VII molecule with a narrow molecular weight distribution was found to provide maximal thickening.³ Extensive studies have been done on hydrogenated polybutadiene, polyisobutylene, and poly-

Correspondence to: C.-C.Tsiang.
Contract grant sponsor: National Science Council of the Republic of China; contract grant number: NSC87-CPC-E-194-004.

Journal of Applied Polymer Science, Vol. 79, 1838–1846 (2001)
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(alkylmethacrylate)s regarding their efficiencies as a VII. Copolymerization with a stabilizing comonomer, such as the copolymerizations of 2-decylmethacrylate and α -tetradecene, isobutylene, and dicyclopentadiene, or decylmethacrylate and dicyclopentadiene, was also examined to reduce the solidification point and to enhance the thermal and shear stability.^{4,5} By far, the commonly used VIIs are diblock copolymers of a polyA-*b*-polyB type with A being a monoalkenyl arene compound and B being a conjugated diene. Because block copolymers of styrene and butadiene (SB) and a block copolymer of styrene and isoprene (SI) have been known to have good solubility in paraffinic and naphthenic oils, they are particularly suitable for functioning as a VII. The SI-based VII has been commercially formulated with various oils to make multigrade lubricants.

Owing to the request of more gas-efficient, lighter, and smaller engines for modern automobiles, a lubricant has to meet more stringent VI requirements under concomitant high-temperature and high-shear (HTHS) conditions. Although increasing the molecular weight of a VII molecule improves its thickening ability, a linear VII molecule of high molecular weight suffers from poor shear stability due to the drastic molecular weight drop caused by chain breakage under HTHS conditions.⁶ However, since a star-shaped molecule having multiple arms can dilute the impact of chain breakage,⁷ a star-shaped VII molecule having an equal molecular weight to its linear counterpart should be able to avoid the drastic decrease of molecular weight and better maintain the viscosity of the lubricant. Typically, star-shaped polymers can be produced via a "arms-first, core-last" method by reacting monofunctional polymeric arms with crosslinkable, core-forming comonomers such as 1,3-diisopropenylbenzene and divinylbenzene (DVB).⁸⁻¹² Furthermore, novel star-shaped polyisobutylenes comprising more than 20 arms have been synthesized using a core-core coupling of methylcyclosiloxanes.⁹ A GPC instrument equipped with an on-line refractive index and laser light-scattering detector was often used for the determination of molecular weights, the molecular weight distribution, and the number of arms of the star-shaped polymers. The number of arms and the total molecular weight increase with the weight percent of the core materials. The solution viscosity behavior is dependent upon the number of arms per star molecule and the intrinsic viscosities of star

polymers are much lower than are those of linear polymers of the same molecular weight.

Because DVB enabled the star polymers to be formed more rapidly and the resulting polymers contained a much lower amount of residual uncoupled arms,¹¹ it was used in this work as the core-forming comonomer. The aim of this work was to study the synthesis of a star-shaped polystyrene-*b*-poly(ethylene-*co*-propylene) block copolymer and its use as a VII for making a lubricant.

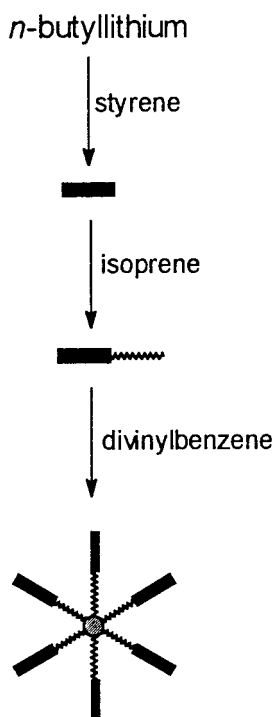
EXPERIMENTAL

Materials

The styrene and isoprene used in this work were purchased from the Tokyo Chemical Industry (Tokyo, Japan) and pretreated under nitrogen with activated alumina (from Alcoa Co., Pittsburgh, PA, USA) prior to their use. Cyclohexane was obtained from the Taiwan Synthetic Rubber Corp. (TSRC, Kaohsiung, Taiwan) and was distilled and treated with activated alumina. Tetrahydrofuran (THF) was purchased from BDH (Darmstadt, Germany) and pretreated with activated alumina. *n*-Butyllithium was purchased from Merck (Darmstadt, Germany) as a 15 wt % solution in hexane. DVB was purchased from the Tokyo Chemical Industry at a 55% purity. HN base oil was provided by the Chinese Petroleum Corp. (Kaohsiung, Taiwan).

Synthesis of the Star-shaped Polystyrene-*b*-Polyisoprene molecules, (SI)_{star} (Scheme 1)

The synthesis of star-shaped polystyrene-*b*-polyisoprene molecule, (SI)_{star}, was accomplished in a cyclohexane solvent via anionic polymerization. Generally, a star-shaped block copolymer can be synthesized via two routes, either a core-first method—by reacting monoinitiators with a dialkenyl arene to construct a multifunctional reactive core followed by the growth of arms consisting of various polymeric blocks—or an arm-first method—by synthesizing the polymeric arms followed by a reaction with dialkenyl arene to form a multiple-armed star molecule. In this work, the latter synthesis route was chosen. A small amount of polar species, THF, was added to accelerate the formation of the polystyrene block so as to ensure the overall formation of well-defined polymeric arms. An appropriate amount of cyclohexane and



Scheme 1 Synthesis of multiple-armed copolymer ($(SI)_{star}$: (—■—) polystyrene; (~~~~) polyisoprene.

200 ppm THF at room temperature were first put into a 1-L pressure vessel under a slight nitrogen overpressure. The vessel was then heated to 40°C prior to the addition of an *n*-butyllithium solution. Afterward, 30 g of the styrene monomer was charged and the color turned dark red, indicating the formation of a living polystyryl-lithium anion. Thirty minutes later, 70 g isoprene was charged into the vessel to continue the polymerization. The yellowish color of the solution indicated the formation of poly(styryli-soprenyl)lithium ends. After 1 h, DVB of a specified amount was added to the living polymeric chains, forming the desired $(SI)_{star}$ copolymer.

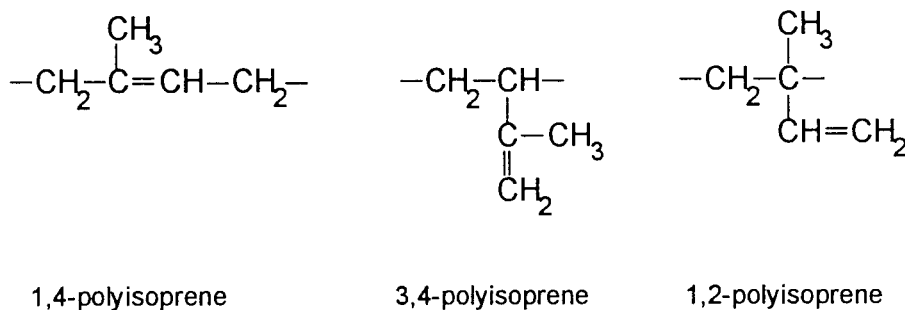
This reaction step was allowed for 30 min before quenching with methanol and precipitating the final polymer in isopropanol. The precipitated sample was then oven-dried.

Hydrogenation of the $(SI)_{star}$

The hydrogenation reaction was conducted following well-established procedures^{13–15} using nickel octoate and triethylaluminum as the catalysts with a loading of 7000 ppm Ni and an Al/Ni molal ratio of 2.3. The hydrogenation reaction was carried out in a 2-L mechanically stirred autoclave (made by PPI, rated to 6000 psi) at 80°C for 7 h. A $(SI)_{star}$ copolymer solution, 330 g, previously prepared at a concentration of 7.3 wt % in the cyclohexane solvent, was first charged into the autoclave, followed by the catalyst solution. The hydrogen pressure was then kept constant at 3000 psi, with the reaction mixture saturated with the hydrogen. Samples of the reaction mixture were taken at fixed time intervals and were repeatedly washed with dilute sulfuric acid to remove the residual catalyst. After adding Ir-ganox 1076 as a stabilizer, the hydrogenated copolymer was then precipitated in isopropanol and dried at 40°C in a vacuum oven. This hydrogenated copolymer, $(SEP)_{star}$, exhibited in its soft block a structure comprising 95% of ethylene and propylene elements and 5% of the methyl butene element, arising from the hydrogenated forms of various isomeric polyisoprene elements in the unhydrogenated $(SI)_{star}$ ¹⁶ (Scheme 2).

Analysis of Synthesized Polymer

The molecular weight and molecular weight distribution of synthesized $(SEP)_{star}$ were determined by Waters gel permeation chromatography (GPC) equipped with a Waters M-486 adsorbance (UV) and a Waters 410 differential refractive in-



Scheme 2 Isomeric structures of polyisoprene.

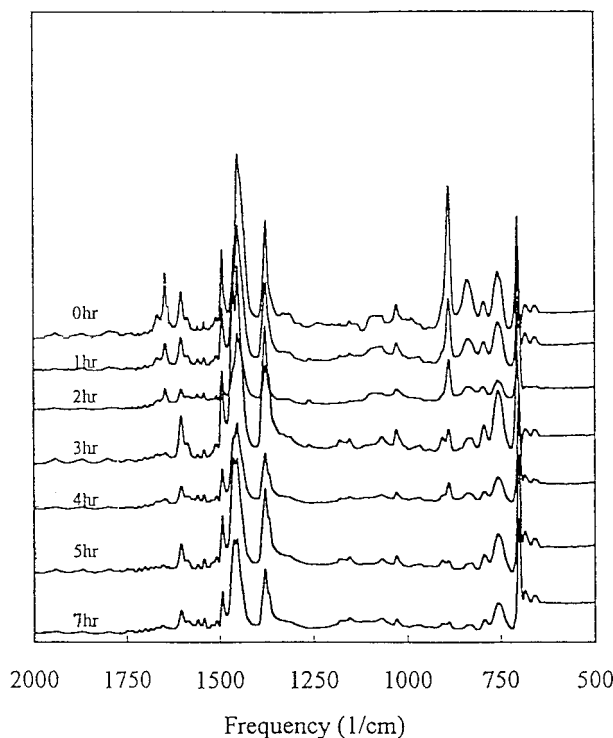


Figure 1 FTIR spectrum of star-shaped copolymer at various hydrogenation times.

dex (RI) detectors. The GPC was typically operated using three Waters Styragel columns (HR 3, HR 4, and HR 5) at a nominal flow rate of 1 mL/min with a sample concentration of 0.1% in the THF solvent. Since the GPC was calibrated using polystyrene standards (from Polymer Laboratories, UK), the determined molecular weight was actually a "polystyrene-equivalent" molecular weight. Therefore, a multiple-angle laser light-scattering (MALLS) detector was also used. This detector (miniDAWN Model, Wyatt Technology Corp.) was equipped with a 20-mW semiconductor laser and enabled us to determine the "true" molecular weight. The dn/dc (specific refractive index increment) of the synthesized polymer, at the same wavelength of light as that of the MALLS, needed for the molecular weight calculation was measured by a Wyatt/Optilab DSP interferometric refractometer. The hydrogenation efficiency was monitored by the disappearance of the double-bond signals of the *trans*-1,4, *cis*-1,4, vinyl-1,2, and 3,4 units in the FTIR spectrum (at 1663, 1644, 888, and 836 cm^{-1} , respectively) as shown in Figure 1. A Shimadzu FTIR-8101M instrument with a liquid N_2 -cooled MCT detector was used. The spectral resolution was 2 cm^{-1} and

the samples were prepared as cast films on KBr plates for IR scans.

RESULTS AND DISCUSSION

Effect of Temperature on the Linking Efficiency of Polymeric Arms

In accordance with a typical GPC chromatogram of the (SEP)_{star} molecule shown in Figure 2, the linking efficiency of arms by DVB is defined as

Linking efficiency

$$= \frac{\text{area of peak A}}{\text{total area of peak A and peak B}}$$

where peak A corresponds to (SEP)_{star}, and peak B, to the arm. Under a constant DVB/arm molar ratio of 6, arms having identical molecular weights have been linked by DVB at various linking temperatures. The results shown in Figure 3 suggest, having in mind that these data were subject to experimental and analytical error, that the temperature exerts an effect on the linking efficiency and an optimal linking temperature may occur at about 60°C. The decrease in linking efficiency at temperatures higher than 60°C may be attributed to the thermal deactivation of the arms prior to the linking. The maximal efficiency ever achieved was 85%, primarily resulting from the low chemical purity (55%) of DVB due to the presence of ethyl vinylbenzene. Furthermore, the coexistence of DVB isomers also caused a drop in linking efficiency because *p*-DVB links less efficiently than does *m*-DVB.¹⁷

Effect of Arm Length on Linking Efficiency

Polymeric arms having two different arm lengths of 15,600 \pm 4% (group A) and 57,400 \pm 10% (group B) were used to construct the star-shaped molecules. The linking reaction was conducted at various DVB/arm molar ratios, namely, 4, 6, 8, 10, 12, and 20. As a result, a total of 12 (SEP)_{star} was synthesized in this study. The molecular structures characterized using both GPC and MALLS are tabulated in Table I. Polymeric arms of lower molecular weights (group A) afford a 81.6 \pm 1% linking efficiency, which is higher than the 73.6 \pm 5% for arms of higher molecular weights (group B). It is conceivable that a shorter arm length

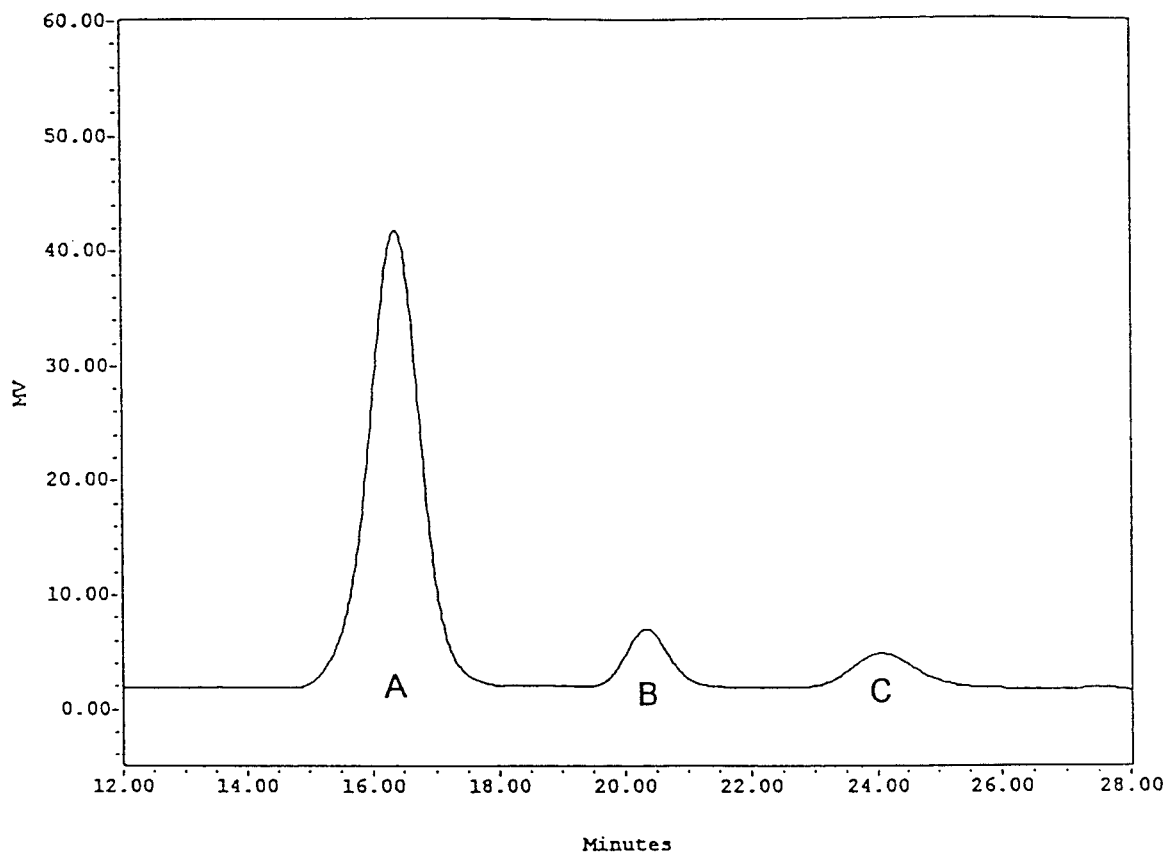


Figure 2 GPC chromatogram for a typical star-shaped $(SEP)_{star}$: (A) star molecule; (B) linear diblock arm; (C) polystyrene.

produces less steric hindrance and thus tends to react with DVB easier.

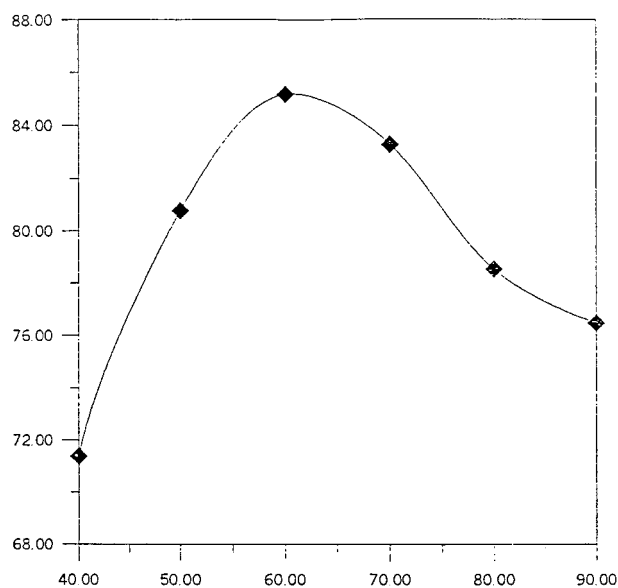


Figure 3 Effect of temperature on linking efficiency.

Effect of Arm Length on Degree of Branching

Among the 12 $(SEP)_{star}$ samples, the degree of branching (the average number of arms in each star-shaped molecule) determined from GPC measurements was consistent with that determined from MALLS measurements. At a DVB/arm ratio of up to 12, the degree of branching was slightly higher for $(SEP)_{star}$ composed of longer arms. The steric hindrance of the longer arms obstructed the linking reaction between the DVB and the arm and, consequently, enhanced the relative amount of homopolymerization of DVB, thus providing more branching sites.

Effect of Molecule Structure on dn/dc

The molecular weight determination using MALLS necessitates the measuring of the refractive index increment, dn/dc . Whereas for most

Table I Molecular Weight Measurements for Star-shaped (SEP)_x

Sample No.	<i>R</i>	MALLS Measurements			GPC Measurements			Linking Efficiency	
		(MW) _{arm} by MALLS	(MW) _{star} by MALLS	<i>F</i> _{MALLS}	(MW) _{arm} by GPC	(MW) _{star} by GPC	<i>F</i> _{GPC}		
A	A4	4	1.55 × 10 ⁴	11.50 × 10 ⁴	7.4	3.13 × 10 ⁴	21.42 × 10 ⁴	6.8	82.3
	A6	6	1.61 × 10 ⁴	15.10 × 10 ⁴	9.3	3.33 × 10 ⁴	28.86 × 10 ⁴	8.6	81.6
	A8	8	1.60 × 10 ⁴	19.50 × 10 ⁴	12.2	3.25 × 10 ⁴	36.08 × 10 ⁴	11.1	81.2
	A10	10	1.55 × 10 ⁴	23.98 × 10 ⁴	15.4	3.10 × 10 ⁴	45.73 × 10 ⁴	14.6	82.2
	A12	12	1.49 × 10 ⁴	26.18 × 10 ⁴	17.2	3.00 × 10 ⁴	56.57 × 10 ⁴	16.8	81.4
	A20	20	1.54 × 10 ⁴	33.88 × 10 ⁴	22.0	3.08 × 10 ⁴	67.57 × 10 ⁴	21.9	80.7
B	B4	4	5.60 × 10 ⁴	43.7 × 10 ⁴	7.8	12.4 × 10 ⁴	94.3 × 10 ⁴	7.6	72.3
	B6	6	6.35 × 10 ⁴	61.6 × 10 ⁴	9.7	10.5 × 10 ⁴	93.0 × 10 ⁴	8.9	77.3
	B8	8	6.14 × 10 ⁴	80.4 × 10 ⁴	13.1	12.1 × 10 ⁴	152.5 × 10 ⁴	12.6	73.1
	B10	10	5.68 × 10 ⁴	95.4 × 10 ⁴	16.8	12.4 × 10 ⁴	194.7 × 10 ⁴	15.7	72.6
	B12	12	5.50 × 10 ⁴	105.6 × 10 ⁴	19.2	11.5 × 10 ⁴	210.5 × 10 ⁴	18.3	73.8
	B20	20	5.17 × 10 ⁴	131.0 × 10 ⁴	25.3	12.1 × 10 ⁴	256.5 × 10 ⁴	21.2	72.7

R: molar ratio of DVB to arm; *F*_{MALLS}: degree of branching based on MALLS (= [(MW)_{star} by MALLS]/[(MW)_{arm} by MALLS]); *F*_{GPC}: degree of branching based on GPC (= [(MW)_{star} by GPC]/[(MW)_{arm} by GPC]).

polymers (except electrolytes) the *dn/dc* is a constant,¹⁸ it is worthwhile to study whether the value of a (SEP)_{star} molecule would vary with the arm length or degree of branching. Our results indicate that the difference is insignificant (less than 1%). The *dn/dc* data determined for all (SEP)_{star} samples synthesized in this work are tabulated in Table II.

DSC, DMA, and TGA Analyses

Owing to the phase separation, our (SEP)_x block copolymer exhibits separate *T_g*'s for the hard and

soft blocks individually. A typical DSC graph (shown in Fig. 4) indicates that prior to hydrogenation the *T_g* of the polyisoprene phase is −57°C, and for polystyrene, it is 66°C. After the hydrogenation, the *T_g* of the polystyrene phase remains unchanged but the *T_g* of the poly(ethylene-*co*-propylene) phase becomes −44°C, an increase of 13°C. Additional DMA analysis was also conducted for corroboration. As seen in Figure 5, the *T_g*'s identified from the storage modulus *E'* or the loss modulus *E''* curves are in good agreement with those measured by DSC.

TGA results are tabulated in Table III. Under a nitrogen environment, the decomposition temperature *T_D* of (SEP)_x is between 398 and 420°C, which is approximately 50°C higher than that of unhydrogenated (SI)_x. It is also noteworthy that the effects of arm length and degree of branching appear insignificant.

Table II Refractive Index Increments for Star-shaped (SEP)_x

	Sample No.	<i>dn/dc</i>
A	A4	0.1360
	A6	0.1362
	A8	0.1361
	A10	0.1360
	A12	0.1364
	A20	0.1365
B	B4	0.1363
	B6	0.1365
	B8	0.1366
	B10	0.1360
	B12	0.1367
	B20	0.1365

Intrinsic Viscosity

For each (SEP)_{star} sample, the specific viscosity (*η_{sp}*) and the relative viscosity (*η_{rel}*) of the sample solution were measured at several concentrations. The intrinsic viscosity was then determined through the intersection of the extrapolated curves at zero concentration. As depicted in Table IV, group B samples exhibit higher intrinsic viscosity than do group A samples, thus indicating that the intrinsic viscosity increases with in-

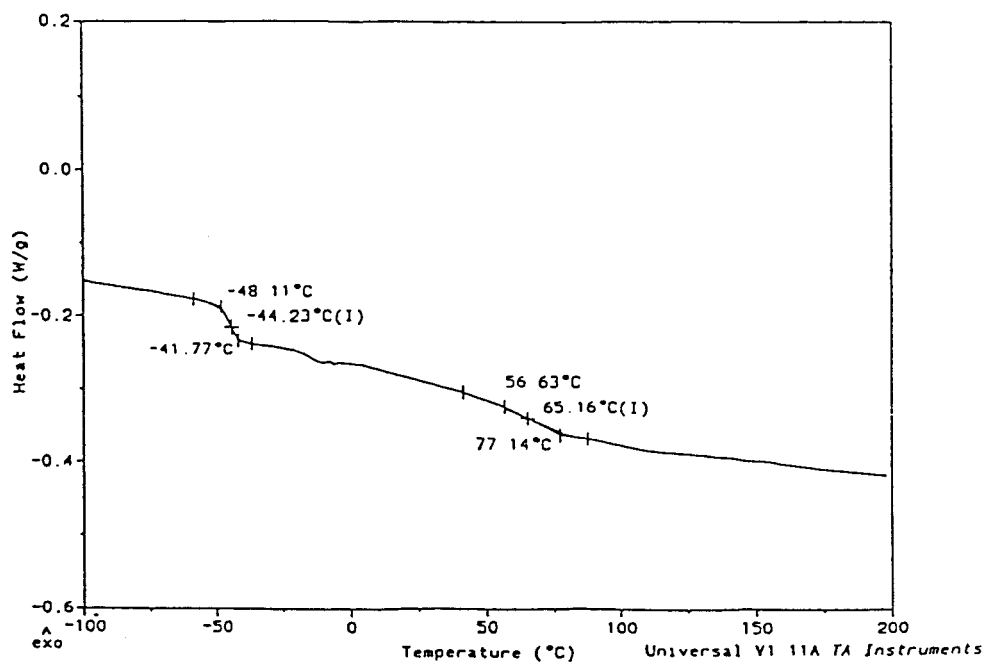
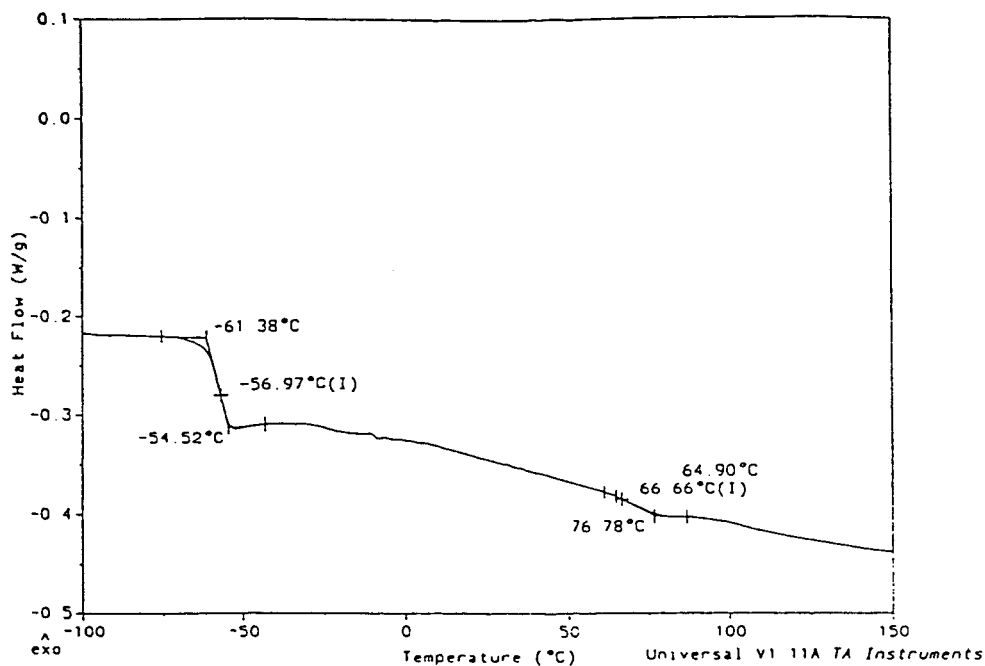


Figure 4 DSC curves of the star molecule before and after hydrogenation: (top) before hydrogenation; (bottom): after hydrogenation.

crease in the arm length. However, at a fixed arm length (i.e., within each group), the degree of branching exerts little effect. Since viscosity arises primarily from intermolecular chain entanglement, it is conceivable that the intramolecular

arm entanglement of our star-shaped $(SEP)_x$ thwarts the intermolecular chain entanglement. As a result, the intrinsic viscosity remains approximately the same regardless of the number of arms of the star molecule.

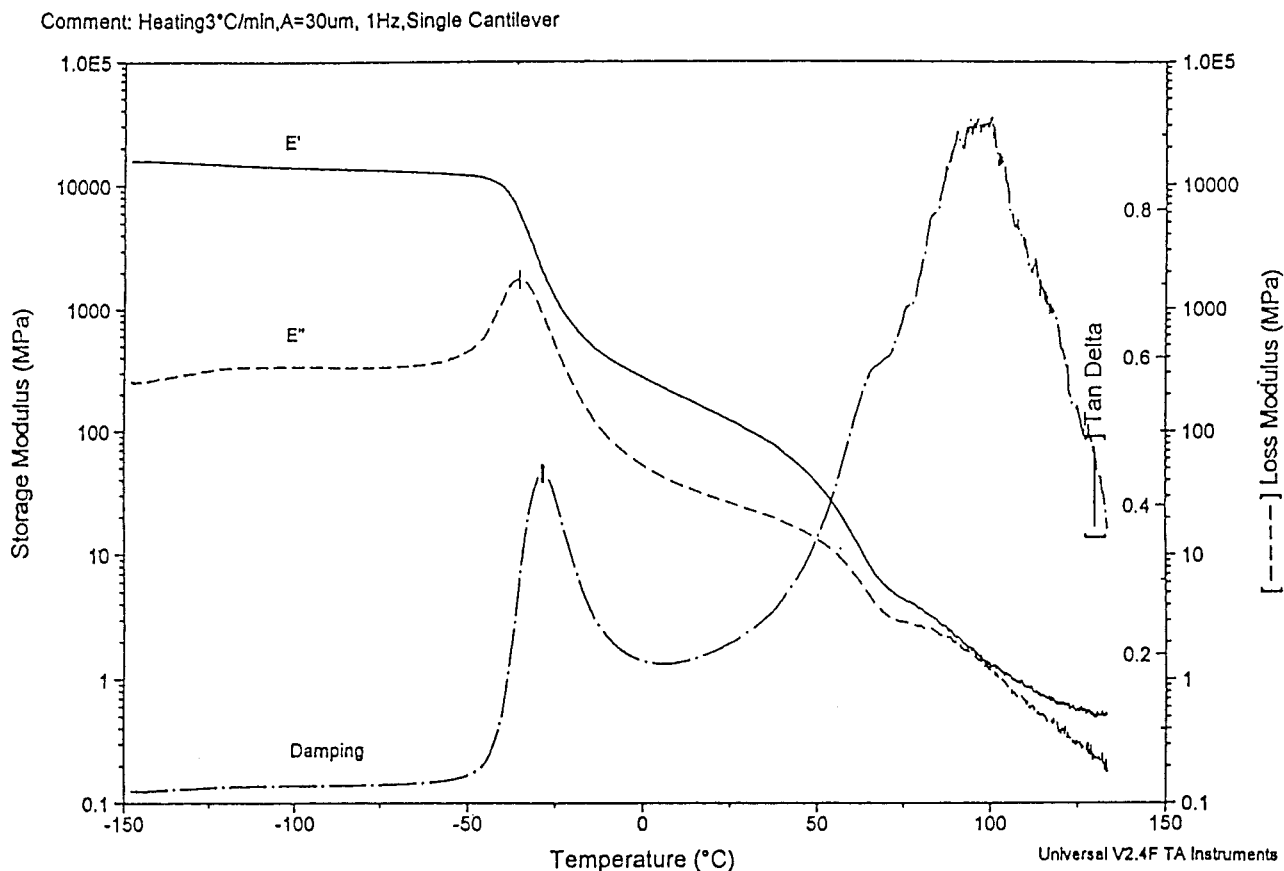


Figure 5 DMA curve of the (SEP)_{star}.

VI

The VI of a HN base oil containing 1 wt % of (SEP)_{star} was measured according to ASTM D445 and D2270 methods using a #300 Cannon Fenske

routine viscometer. First, the kinematic viscosities at 100 and 40°C were measured. The measured kinematic viscosity at 100°C (Y) was then used to find the L and H values directly from an ASTM reference table. Finally, the VI of the HN

Table III Thermal Decomposition Temperatures of All Samples Under N₂

Sample No.	<i>T_D</i> (°C) Before Hydrogenation	<i>T_D</i> (°C) After Hydrogenation
A A4	367.4	414.9
A A6	363.2	413.6
A A8	363.8	415.9
A A10	364.0	398.3
A A12	364.4	400.5
A A20	372.1	419.3
B B4	354.9	410.1
B B6	362.5	417.1
B B8	359.7	399.5
B B10	353.9	398.2
B B12	364.2	412.8
B B20	363.1	417.9

Table IV Intrinsic Viscosity of All Samples

Sample No.	$\eta_{intrinsic}$ (dL/g)
A A4	0.3994
A A6	0.4016
A A8	0.3947
A A10	0.4018
A A12	0.3882
A A20	0.3981
B B4	0.8756
B B6	0.9181
B B8	0.8875
B B10	0.8767
B B12	0.8669
B B20	0.8084

Table V Viscosity Index of HN Base Oil Plus 1 Wt % of (SEP)_x

Sample No.		Viscosity Index
A	A4	111
	A6	111
	A8	112
	A10	115
	A12	127
	A20	128
B	B4	139
	B6	141
	B8	152
	B10	161
	B12	162
	B20	166

base oil containing (SEP)_{star} was measured based on the L and H values and the kinematic viscosity at 40°C (U) using one of the following equations:

$$VI = [(L - U)/(L - H)] \times 100 \quad \text{if } VI \leq 100$$

$$VI = \{[\log^{-1}[(\log H - \log U)/\log Y] - 1]/0.0075\} + 100 \quad \text{if } VI > 100$$

The results are summarized in Table V. When compared at a fixed arm length (i.e., within each group), a (SEP)_{star} having a higher degree of branching increases the VI of the base oil more than that having a lower degree of branching. In addition, the VI can be further increased by an increase in the arm length when the degree of branching is fixed. Compared against a standard HN oil (VI was measured as 96), the addition of 1 wt % of (SEP)_{star} increased the VI up to a value between 111 and 166, with the exact value depending upon its arm length and degree of branching.

CONCLUSIONS

A saturated star-shaped polystyrene-*b*-poly(ethylene-*co*-propylene) block copolymer, (SEP)_{star}, was synthesized for use as a VII in lubricants. This molecule was made by linking polystyrene-*b*-polyisoprene arms at the optimum temperature of 60°C with DVB followed by a hydrogenation reaction to eliminate the unsaturates on the polyisoprene block, thus forming the star-shaped (SEP)_{star}. The number of arms on each molecule

increases with increase in the mol ratio of DVB to *n*-butyllithium. Increasing the arm length adversely affects the linking efficiency but causes a slight increase in the degree of branching. The T_g of the poly(ethylene-*co*-propylene) block is 13°C higher than that of the original polyisoprene block. The thermal decomposition temperature of (SEP)_{star} is 50°C higher than that of its unhydrogenated counterpart but independent of the arm length or degree of branching. Intrinsic viscosity for (SEP)_{star} depends only on the arm length but not on the degree of branching. Adding 1 wt % of (SEP)_{star} markedly increases the VI of a HN base oil. The addition of this VII increased the VI of the HN base oil up to a value between 111 and 166, with the exact value dependent upon its arm length and degree of branching.

Financial support provided by the National Science Council of the Republic of China under the program NSC87-CPC-E-194-004 is greatly appreciated by the authors.

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