Synthesis of a Star-Shaped Poly(Ethylene-*co*-Propylene) Copolymer as a Viscosity Index Improver for Lubricants

I-CHUN LIOU,[1] RAYMOND CHIEN-CHAO TSIANG,[1] JAMES WU,[2] JIN-SHANG LIOU,[2] HUN-CHANG SHEU[2]

[1] Department of Chemical Engineering, National Chung Cheng University, Chiayi, Taiwan 621, Republic of China

[2] Refining & Manufacturing Research Center, Chinese Petroleum Corp., Chiayi, Taiwan 60036, Republic of China

ABSTRACT: A saturated star-shaped poly(ethylene-*co*-propylene) copolymer, $(EP)_{star}$, has been synthesized for use as a viscosity index improver in lubricants. Polyisoprene arms were first anionically synthesized using *n*-butyllithium as the initiator, followed by a linking reaction with divinylbenzene at the optimum temperature of 60°C. The resulting star-shaped polyisoprene, $(I)_{star}$, was then hydrogenated to eliminate the double bonds of the polyisoprene forming the poly(ethylene-*co*-propylene) structure. The degree of branching (number of arms on each molecule) increases with increase in the mole ratio of divinylbenzene to *n*-butyllithium. Increasing the arm length adversely affects the linking efficiency and a minimum amount of tetrahydrofuran (THF) at a THF:*n*-butyllithium molar ratio of 1.12 was needed in order to achieve a maximum linking efficiency of approximately 85%. The T_g of poly(ethylene-*co*-propylene) is about 10°C higher than that of the original polyisoprene. Compared with $(I)_{star}$, $(EP)_{star}$ has a thermal decomposition temperature that is 50°C higher but is independent of the arm length or the degree of branching. Viscosity measurement results for $(EP)_{star}$ reveal that intrinsic viscosity depends only on the arm length but not the degree of branching. Adding 1 wt % of $(EP)_{star}$ markedly increases the viscosity index of a LN base oil. The addition of 1 wt % of $(EP)_{star}$ increases the viscosity index (95 for base oil) up to a number between 111 and 145, with the exact number depending upon its arm length and degree of branching. With a fixed arm length, an $(EP)_{star}$ having a higher degree of branching increases the viscosity index more than one having a lower degree of branching. On the other hand, the viscosity index increases with increase in the arm length when the degree of branching is fixed. Adding 1 wt % of $(EP)_{star}$ also causes a change in the pour point of the lubricant with the pour point decreasing with increase in the degree of branching. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1911–1918, 2002

Key words: viscosity index improver; copolymer; hydrogenation; lubricant; pour point

INTRODUCTION

The temperature–viscosity relationship of an oil or lubricant has traditionally been characterized by the viscosity index (VI). In order for an oil or lubricant to have a better low-temperature viscosity and high-temperature volatility properties, the addition of a viscosity index improver (VII) is necessary.[1,2] Various polymers, such as hydrogenated polybutadiene or polyisoprene, polyisobutylene, poly(alkylmethacrylates), copolymers of 2-decylmethacrylate and α-tetradecene, isobutylene or dicyclopentadiene, copolymers of decyl-

methacrylate and dicyclopentadiene, have been studied with regard to their use as VIIs.[3–5] By far, the commonly used VIIs are conjugated-diene based polymers—namely, hydrogenated poly-butadiene and polyisoprene. These polymers are particularly suitable for functioning as VII by virtue of their good solubility in paraffinic and naphthenic oils. The isoprene-based VII has been commercially formulated with various oils to make multigrade lubricants.

The use of more gas-efficient, lighter, and smaller engines for modern automobiles has resulted in a need for lubricants that must meet more stringent VI requirements under high temperature and high shear (HTHS) conditions. Although increasing the molecular weight of a VII molecule improves the VI of the lubricant, a linear VII molecule of high molecular weight suffers from a poor shear stability due to the drastic molecular weight drop caused by the chain breakage under HTHS conditions.[6] However, since a star-shaped molecule can dilute the impact of chain breakage,[7,8] a star-shaped VII molecule having an equal molecular weight to its linear counterpart should be able to avoid the drastic drop of molecular weight and better maintain the viscosity of the lubricant. Typically, star-shaped polymers can be produced via an "arms-first, core-last" method by reacting monofunctional polymeric arms with crosslinkable, core-forming comonomers such as 1,3-diisopropenylbenzene and divinylbenzene,[9–12] or a core-core coupling of methylcyclosiloxanes.[13] The number of arms and the total molecular weight increases with the weight percent of 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 those of linear polymers of the same molecular weight.

In this work, divinylbenzene was used as the core-forming comonomer owing to its ability to rapidly form the star polymers with a low amount of residual uncoupled arms.[11] The aim of this work was to study the synthesis of a star-shaped hydrogenated polyisoprene, i.e., poly(ethylene-*co*-propylene), and to study its use as a VII to better formulate lubricants.

EXPERIMENTAL

Materials

Isoprene was purchased from Tokyo Chemical Industry and pretreated under nitrogen with acti-
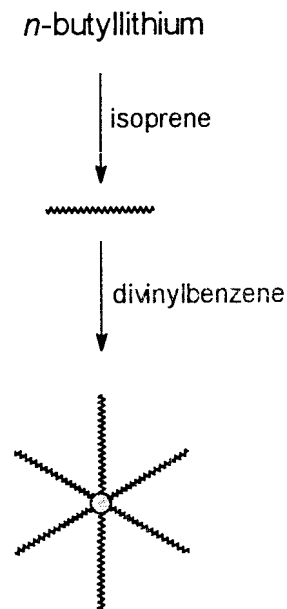
Scheme 1 Synthesis of (I)$_{\text{star}}$.

vated alumina (from Alcoa Co.) prior to its use. Cyclohexane was obtained from Taiwan Synthetic Rubber Corporation (TSRC), and was distilled and treated with activated alumina. Tetrahydrofuran (THF) was purchased from BDH and pretreated with activated alumina. *n*-Butyllithium (*n*-BuLi) was purchased from Merck as a 15 wt % solution in hexane. Divinylbenzene (DVB) was purchased from Tokyo Chemical Industry at 55% purity. LN base oil was provided by Chinese Petroleum Corp.

Synthesis of Star-Shaped Polyisoprene, (I)$_{\text{star}}$

The synthesis of (I)$_{\text{star}}$ was accomplished via anionic polymerization in cyclohexane. (See Scheme 1.) To a 1 L pressure vessel under a slight nitrogen overpressure were added 550 mL of cyclohexane and 0.1 mL of tetrahydrofuran (THF) (200 ppm, to accelerate the polymerization). The vessel was then heated to 40°C followed by the addition of *n*-BuLi solution. Subsequently, 100 g isoprene monomer was charged to the reactor. The color turned to light yellow, indicating the presence of living polyisoprenyllithium anions. Thirty minutes later 2 mL of THF was charged to the vessel to facilitate the successive linking reaction. DVB at a desired [DVB]/[*n*-BuLi] ratio was then added to the living polymeric chains to form the desired (I)$_{\text{star}}$. The linking reaction was allowed to take place for 45 min before quenching with methanol
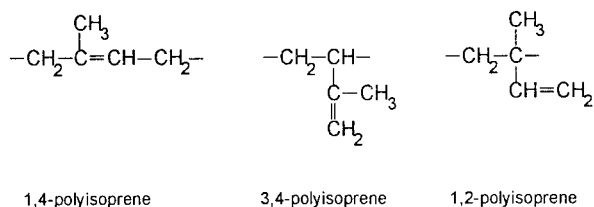
Scheme 2 Isomeric polyisoprene units.

and precipitating the final polymer in isopropanol. The precipitated sample was then oven dried.

Hydrogenation of $(I)_{star}$

The hydrogenation reaction was conducted following well-established procedures[14–16] using nickel octoate and triethylaluminum as the catalysts. The hydrogenation reaction was carried out in a 2 L mechanically stirred autoclave (made by PPI, rated to 6000 psi) at 80°C for 8 h. $(I)_{star}$, 330 g of a 7.3 wt % solution in cyclohexane was charged to the autoclave, followed by the premixed catalyst solution with a loading of 7000 ppm Ni at an Al/Ni molal ratio of 2.3. 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 Irganox 1076 as a stabilizer, the hydrogenated copolymer was then precipitated in isopropanol and dried at 50°C in a
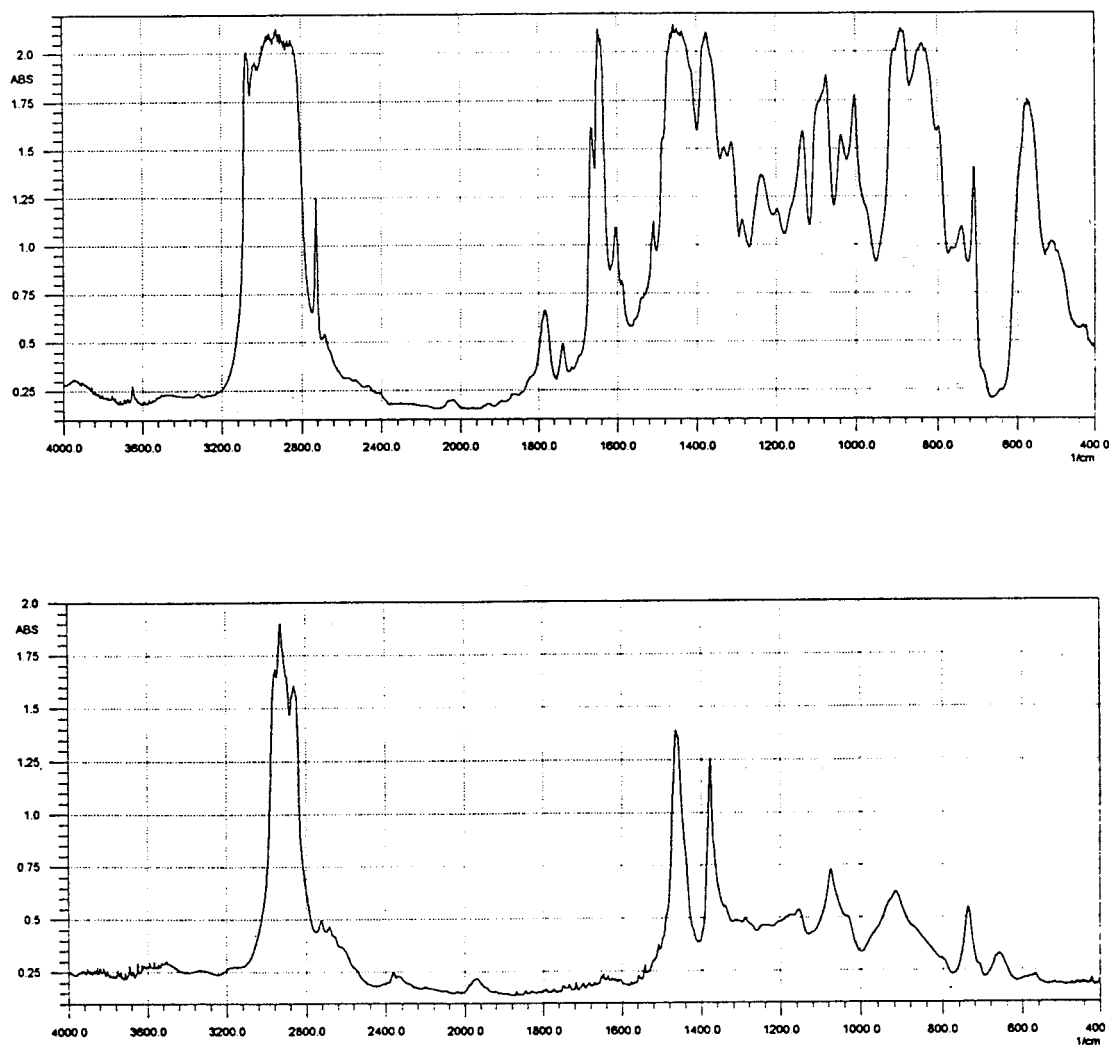

Figure 1 FTIR spectra of the star molecule (sample B2) before and after hydrogenation (top: before hydrogenation; bottom: after hydrogenation).
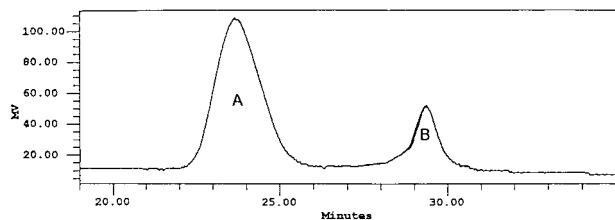
Figure 2   GPC chromatogram for star-shaped $(EP)_{star}$ (sample A2) (A: star molecule; B: linear arm).

vacuum oven. This hydrogenated copolymer, $(EP)_{star}$, exhibited a structure consisting of 95% ethylene and propylene units and 5% methyl butene unit, arising from the hydrogenated forms of various isomeric polyisoprene elements in the unhydrogenated $(I)_{star}$.[17] (See Scheme 2.)

Analysis of $(EP)_{star}$

The molecular weight and molecular weight distribution of synthesized $(EP)_{star}$ were determined by Waters gel permeation chromatography (GPC) equipped with a Waters 410 differential refractive index (RI) detector and a multiple angle laser light scattering (MALLS, miniDAWN model, Wyatt Technology Corporation) detector. The GPC was typically operated using three Waters Styragel columns (HR 3, HR 4, and HR 5) at a norminal flow rate of 1 mL/min with a sample concentration of 0.1% in THF solvent. The MALLS detector was equipped with a 20 mW semiconductor laser. The molecular weight determination using MALLS necessitates the measuring of refractive index increment, dn/dc (specific refractive index increment). The dn/dc of the synthesized polymer, at the same wavelength of light as the MALLS, was measured by the Wyatt/Optilab DSP interferometric refractometer. Our results indicate that the dn/dc of an $(EP)_{star}$ molecule does not vary with the arm length or the degree of branching. The dn/dc value determined for all $(EP)_{star}$ samples synthesized in this work is $0.1027 \pm 1\%$. The hydrogenation reaction was confirmed by the disappearance of the double bond peaks of the *trans*-1,4, *cis*-1,4, vinyl-1,2, and 3,4 units in the Fourier transform infrared (FTIR) spectrum (at 1663, 1644, 888, 836 cm^{-1}, respectively) as shown in Figure 1. A Shimadzu FTIR-8101M instrument with a liquid N_2 cooled MCT detector was used with a spectral resolution of 2 cm^{-1}. The samples were prepared as cast films on KBr plates. T_gs were measured using a modulated differential scanning calorimeter (TA In-

strument, MDSC 2910) and T_Ds were measured using a thermogravimetric analyzer (TA Instrument, TGA 2050).

Characterization of Lubricants Containing VII

The pour point was measured using a Phase Technology PPA-70 instrument. The intrinsic viscosity of the sample solution was measured in THF using a Ubbelohde viscometer. The kinematic viscosity and the VI were measured and determined directly by a Cannon CAV3 automatic viscometer.

RESULTS AND DISCUSSION

The linking efficiency of arms by DVB (i.e., the fraction of arms that have been linked into star molecules) can be determined according to the GPC chromatogram of the $(EP)_{star}$ molecule (Fig. 2) based on a method described in a previous report.[3] Under a constant DVB/n-BuLi molar ratio, polymeric arms have been linked by DVB at various temperatures. The results indicate an optimal linking temperature of 60°C, as seen in Figure 3, which was observed to be independent
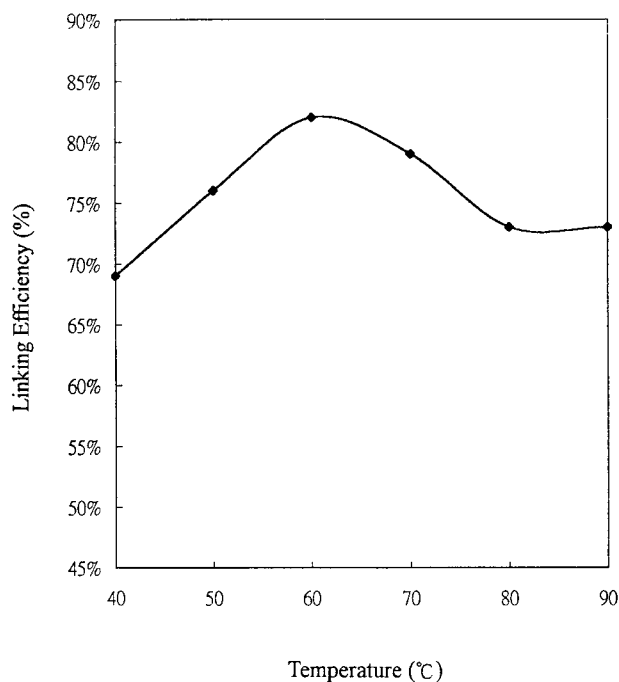

Figure 3   Effect of temperature on linking efficiency under typical linking conditions: [DVB]/[n-BuLi] = 3 and 0.35 wt % of THF.

Table I Effect of THF on Linking Efficiency

			[THF]/[n-BuLi]			
	0	0.56	1.12	1.68	2.2	2.8
Linking efficiency (%)	13	66	84	82	85	83

$T = 60°C$, [DVB]/[n-BuLi] = 3.

of the molecular weight of arms. The decrease in linking efficiency at temperatures higher than 60°C may stem from the thermal deactivation of the arms prior to the linking. A minimum amount of THF at a [THF]/[n-BuLi] =1.12 was needed (shown in Table I) in order to reduce the association of polyisoprenyllithium chains and achieve the maximum linking efficiency. The maximum linking efficiency was approximately 85%, and was primarily limited by the low chemical purity (55%) of DVB. Furthermore, the coexistence of DVB isomers also caused a drop in linking efficiency; *p*-DVB links less efficiently than *m*-DVB.[18]

At the optimum linking temperature of 60°C and [THF]/[n-BuLi]=1.12, polymeric arms having three different arm lengths of 26400 ± 6% (group A), 57200 ± 4% (group B), and 120000±3% (group C) were used to synthesize the targeted star-shaped molecules. The linking reaction was conducted at various DVB/n-BuLi molar ratios, namely 3, 6, and 9. As a result, a total of nine (EP)$_{star}$ samples were synthesized. The molecular structures determined by GPC are reported in

Table II. The degree of branching increases with an increase in the mole ratio of DVB to n-BuLi. Polymeric arms of lower molecular weight (group A) afforded a 83% linking efficiency which was higher than that of group B (64%) and group C (51%) for arms of medium and high molecular weights, respectively. Molecules with shorter arm lengths produce less steric hindrance and tend to react with DVB more easily. Conversely, within each group (i.e., at fixed arm length) the number of arms of each molecule has little effect on the linking efficiency.

DSC thermograms (Fig. 4) of (EP)$_{star}$ polymers exhibit a T_g at −57°C prior to hydrogenation and at −48°C after hydrogenation, an increase of approximately 10°C. TGA results are reported in Table III. Under a nitrogen environment, T_D of (EP)$_{star}$ is between 395 and 415°C, which is approximately 50°C higher than that of the unhydrogenated (I)$_{star}$. It is also noteworthy that the effects of arm length and degree of branching appear insignificant.

For each (EP)$_{star}$ solution the specific viscosity (η_{sp}) and the relative viscosity (η_{rel}) were measured at several concentrations. As depicted in Table IV, group C samples exhibit the highest intrinsic viscosities and group A samples the lowest, thus indicating that intrinsic viscosity increases with an increase in the arm length. The longer arm length affords more intermolecular chain entanglement causing an increase in viscosity. However, at a fixed arm length (i.e., within each group), the degree of branching shows little effect. It is conceivable that the intramolecular

Table II Molecular Weight Measurements for Star-Shaped (EP)$_{star}$

Sample No.	R^a	(MW)$_{arm}$ by GPC	(MW)$_{star}$ by GPC	F_{GPC}^b	Polydispersity	Linking Eff.
A						
A1	3	2.81×10^4	29.63×10^4	10.5	1.25	82.3
A2	6	2.51×10^4	48.16×10^4	19.2	1.25	83.6
A3	9	2.61×10^4	60.52×10^4	23.2	1.19	82.2
B						
B1	3	5.62×10^4	29.37×10^4	5.2	1.32	65.3
B2	6	5.61×10^4	74.80×10^4	13.3	1.27	62.1
B3	9	5.92×10^4	88.48×10^4	14.9	1.20	63.3
C						
C1	3	12.29×10^4	92.35×10^4	7.5	1.23	50.1
C2	6	11.39×10^4	139.7×10^4	12.3	1.43	52.3
C3	9	12.31×10^4	178.3×10^4	14.5	1.35	50.2

^a R: molar ratio of DVB to n-butyllithium.
^b F_{GPC}: degree of branching based on GPC (= (MW)$_{star}$ by GPC/(MW)$_{arm}$ by GPC).
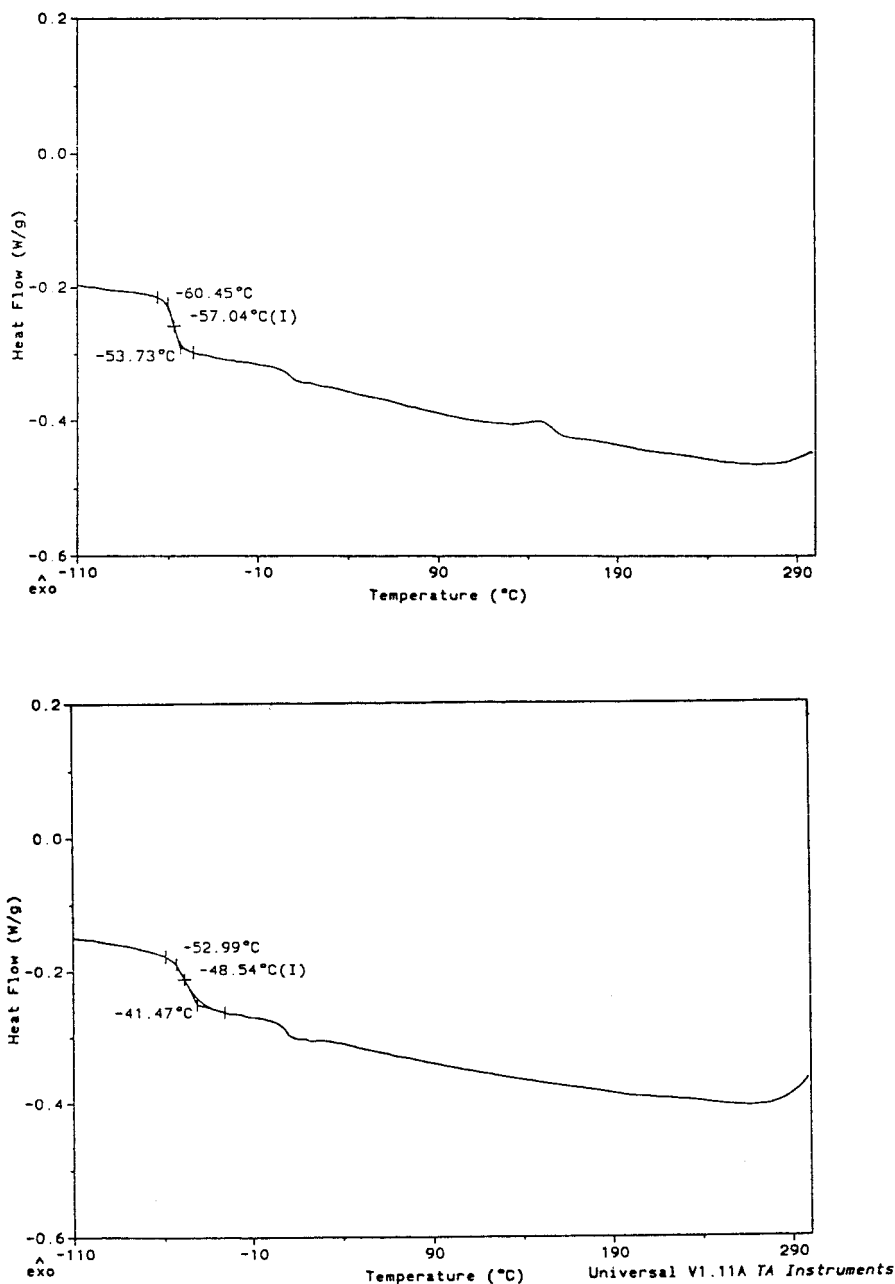
Figure 4 DSC thermograms of the star molecule (sample B2) before and after hydrogenation (top: before hydrogenation; bottom: after hydrogenation).

arm entanglement of the star-shaped $(EP)_{star}$ molecules thwarts the intermolecular chain entanglement. To further explore the effect of the number of arms on viscosity, the radii of gyration (R_g) of samples A1, A2, and A3 having equal arm length but different number of arms were measured using the light scattering technique. The measured R_gs were $14.1 \pm 0.3\%$ nm. These almost identical R_g values thus fortify our conclusion

that as long as the arm length is constant the intrinsic viscosity remains approximately the same regardless of the number of arms.

The viscosity indexes for LN base oil containing 1 wt % of $(EP)_{star}$ were measured according to ASTM D445 and D2270 methods using a Cannon CAV3 automatic Viscometer. The kinematic viscosities at 100 and 40°C were measured. The kinematic viscosity at 100°C (Y) was then used

Table III Thermal Decomposition Temperatures of All Samples Under N$_2$

Sample No.	T_D (°C) before Hydrogenation	T_D (°C) after Hydrogenation
A		
A1	360.6	395.2
A2	360.2	398.3
A3	358.7	412.5
B		
B1	358.2	407.3
B2	357.6	412.8
B3	363.5	414.5
C		
C1	353.3	399.2
C2	368.4	413.4
C3	367.3	402.5

to find the *L* and *H* values directly from an ASTM reference table. Finally, the VI of the LN base oil containing (EP)$_{star}$ was measured based on the *L* and *H* values and the kinematic viscosity at 40°C (*U*) using one of the following equations:

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

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

Results are summarized in Table V. When compared at a fixed arm length (i.e., within each group), an (EP)$_{star}$ having a higher degree of branching increases the VI of base oil more than one having a lower degree of branching. In addi-

Table IV Intrinsic Viscosities of All Samples

Sample No.	$\eta_{intrinsic}$ (dL/g)
A	
A1	0.3708
A2	0.3571
A3	0.3978
B	
B1	0.6825
B2	0.6829
B3	0.7125
C	
C1	0.8766
C2	0.8691
C3	0.8815

Table V Characteristics of LN Base Oil Containing 1 wt % of (EP)$_{star}$

Sample No.	Kinematic Viscosity at 40°C (cSt)	Kinematic Viscosity at 100°C (cSt)	VI	Pour Point[a] (°C)
A				
A1	29.37	5.33	115	−33
A2	29.92	5.47	119	−33
A3	29.16	5.54	122	−36
B				
B1	30.22	5.52	121	−27
B2	30.24	5.62	124	−30
B3	31.85	5.88	130	−33
C				
C1	31.23	5.67	127	−33
C2	31.64	6.19	134	−33
C3	32.64	6.27	145	−36

[a] Flow point was measured in the presence of 0.3 wt % pour point depressant.

tion, the VI can be further increased by increasing the arm length when the degree of branching is fixed. Compared with a standard LN base oil (VI = 95), the addition of 1 wt % (EP)$_{star}$ increases the VI to a value between 115 and 145, with the exact value depending upon the arm length and degree of branching.

The pour point, defined as the minimum temperature for a lubricant to flow, of the LN base oil containing 1 wt % various (EP)$_{star}$ samples was measured in the presence of 0.3 wt % of a pour point depressant. As exhibited in Table V, whereas no effect of the arm length is observed, the pour point decreases with an increase in the number of arms. The independence of arm length has been corroborated by comparing the pour points of lubricants each containing linear EP molecules of varied molecular weight (from 15,900 to 357,300). The results indicate a minimal, if not zero, effect.

CONCLUSIONS

A saturated star-shaped poly(ethylene-*co*-propylene) copolymer, (EP)$_{star}$, has been synthesized for use as a viscosity index improver in lubricants. The degree of branching increases with an increase in the mole ratio of DVB to *n*-BuLi. Increasing the arm length adversely affects the linking efficiency and a minimum THF/*n*-BuLi

molar ratio of 1.12 was needed to achieve a maximum linking efficiency of approximately 85%. The T_g of poly(ethylene-*co*-propylene) is about 10°C higher than that of the original polyisoprene. The thermal decomposition temperature of $(EP)_{star}$ is 50°C higher than that of $(I)_{star}$ but independent of the arm length or degree of branching. Intrinsic viscosity for $(EP)_{star}$ depends only on the arm length—not the degree of branching. Adding 1 wt % of $(EP)_{star}$ markedly increases the viscosity index of the LN base oil; the VI of the oil increases from 95 to a value between 115 and 145, with the exact value dependent upon the arm length and degree of branching. The pour point of the lubricant decreases with an increase in the degree of branching of $(EP)_{star}$.

REFERENCES

1. Litt, F. A. Lubrication Eng 1986, 42(5), 287.
2. van der Waal, G.; J Synth Lubrication 1987, 4(4), 267.
3. Wang, T. Y.; Tsiang, R. C. J Appl Polym Sci 2001, 79, 1838.
4. Akhmedov, A. I.; Isakov, E. U. Chem Technol Fuels Oils 1989, 25(3-4), 156.
5. Ver Strate, G.; Struglinski, M. J. Proc ACS Div Polym Mat Sci Eng 1989, 61, 252.
6. Eckert, R. J. A. U.S. Patent No. 4 156 673, May 29, 1979.
7. Eckert, R. J. A. U.S. Patent No. 4 116 917, Sept. 26, 1978.
8. Kiovsky, T. E. U.S. Patent No. 4 077 893, May 7, 1978.
9. Storey, R. F.; Shoemake, K. A.; Mays, J. W.; Harville, S. J Polym Sci Part A Polym Chem 1997, 35, 3767.
10. Frater, D. J.; Mays, J. W.; Jackson, C. J Polym Sci Part B Polym Phys 1997, 35, 141.
11. Storey, R. F.; Shoemake, K. A.; Chisholm, B. J. J Polym Sci Part A Polym Chem 1996, 34, 2003.
12. Tsitsilianis, C.; Graff, S.; Rempp, P. Eur Polym J 1991, 27, 243.
13. Omura, N.; Kennedy, J. P. Macromolecules 1997, 30, 3204.
14. Hoxmeier, R. J. U.S. Patent 4,879,349, 1989.
15. Breslow, D. S.; Matlack, A. S. U.S. Patent 3,113,986, 1963.
16. Wald, M. W.; Quam, M. G. U.S. Patent 3,595,942, 1971.
17. Hou, H.; Tsiang, R. C.; Hsieh, H. C. J Polym Sci Part A Polym Chem 1997, 35, 2969.
18. Young, R. N.; Fetters, L. J. Macromolecules 1978, 11, 5, 899.