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Synthesis of Poly(1,3-cyclohexadiene) Containing Star-Shaped Elastomers

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Summary: The synthesis of high molecular weight star-shaped polymers comprising poly(1,3-cyclohexadiene-*block*-isoprene) diblock arms coupled to a divinyl benzene (DVB) core is reported. The number average molecular weights of the diblock arms were varied from 30000 to 50000 and the ratio of DVB to n-butyllithium (nBuLi) was systematically varied from 3:1 to 12:1. Size exclusion chromatography coupled with light scattering detection was utilized to detect the formation of star-shaped polymers and the presence of star-star coupling. The molecular weight distribution ($<M_w>/<M_n>$) of the star polymers ranged from 1.25 to 1.50. The effect of poly(1,3-cyclohexadiene) content on the mechanical properties of these novel elastomers is reported. The elastic modulus, elongation at break, and tensile strength of these elastomers were all found to be a function of the percentage of poly(1,3-cyclohexadiene). The glass transition temperatures were determined using both differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Atomic force microscopy was performed in the tapping mode (TMAFM) to verify the presence of microphase separation.

Keywords: anionic polymerization; atomic force microscopy; 1,3-cyclohexadiene; star-shaped polymer; thermoplastic elastomer

Introduction

Poly(styrene-*block*-butadiene-*block*-styrene) (SBS) and poly(styrene-*block*-isoprene-*block*-styrene) (SIS) triblock copolymers are well known to exhibit an excellent combination of elasticity and thermoplasticity. These triblock copolymers are multiphase materials, wherein the polystyrene blocks microphase separate from the polydiene blocks. The microphase-separated domains are responsible for the remarkable elastomeric properties of these macromolecules. This elastomeric behavior persists over a wide temperature range with the lower temperature limit dictated by the T_g of the poly(1,3-butadiene) (-90 °C) or polyisoprene (-60 °C) domains and the upper temperature limit dictated by the T_g of the polystyrene (100 °C) domains. The polystyrene domains lose physical integrity and thus these elastomers are unable to maintain their elastomeric properties, when the temperature approaches 100 °C.[1]

Numerous studies were performed to increase the upper use temperature of thermoplastic

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elastomers in order to compete with vulcanized rubber.[2] Jerome and coworkers recently synthesized triblock copolymers of poly(isobornyl methacrylate)-*block*-poly(1,3-butadiene)-*block*-poly(isobornyl methacrylate).[2] These elastomers exhibited improved tensile strength (30 MPa), high percent elongation (1000 %), and a high upper use temperature of 160 °C. Earlier efforts involved the preparation of thermoplastic elastomers containing poly(α-methylstyrene)[3], poly(ethylene sulfide),[4] and poly(*p*-methylstyrene).[5] While these polymer blocks exhibited a higher glass transition temperature, the resulting elastomers exhibited either a low ceiling temperature or poor ultimate mechanical properties.

In contrast to other polydienes, poly(1,3-cyclohexadiene) PCHD exhibits a remarkably high T_g (150 °C), 50 °C higher than the T_g of polystyrene.[1] Unfortunately, the polymerization of 1,3-cyclohexadiene is plagued by a number of molecular weight limiting side reactions. While a wide variety of polymerization techniques were studied in the mid-1960's and early 1970's to identify a viable polymerization methodology for 1,3-cyclohexadiene, the resulting polymers exhibited unpredictable molecular weights and broad molecular weight distributions. [6-10]

In 1997, Natori reported the first living anionic polymerization of 1,3-cyclohexadiene in the presence of the ligating agent N,N,N'N'-tetramethylethylenediamine (TMEDA). As an indication of the living nature of the reaction, the polymerization exhibited a linear relationship between number average molecular weight and percent conversion. A series of studies was reported, in which the synthesis and characterization of poly(1,3-cyclohexadiene)-*block*-poly(1,3-butadiene)-*block*-poly(1,3-cyclohexadiene) triblock copolymers were examined. [11-14] These triblock copolymers exhibited relatively narrow molecular weight distributions with varying percentages of 1,3-cyclohexadiene. Increased incorporation of 1,3-cyclohexadiene broadened the molecular weight distributions. The presence of TMEDA during the polymerization increased the T_g of the poly(1,3-butadiene) block.

In later studies, Natori et al. altered the synthetic strategy and utilized both a difunctional initiator and sequential addition.[14] A difunctional initiator was utilized, in the presence TMEDA, to initiate the polymerization of the poly(1,3-butadiene) block. Following the synthesis of the poly(1,3-butadiene) blocks, 1,3-cyclohexadiene was added to synthesize the PCHD blocks. In a difunctional system such as this, the outer blocks of the copolymer were the same molecular weight. However, in a sequential addition, the last block of a triblock copolymer does not typically exhibit the same molecular weight as the first block.[1] It is therefore a concern that the asymmetric triblock structure will affect the elastomeric properties and corresponding morphologies.[15] An alternative approach to PCHD containing thermoplastic elastomers involves coupling strategies which permit the synthesis of highly branched polymeric structures, such as star-shaped polymers.[16] Star-shaped polymers exhibit useful rheological properties and are used as additives to improve polymer viscosity. [17,18] The synthesis of PCHD star-shaped polymers was recently reported. [19,20]

Star-shaped polymers, wherein the arms of the star are nearly identical in chain length, are readily prepared using living anionic polymerization methodologies.[1,16] Typically, two methods are utilized for the synthesis of star-shaped macromolecules. These approaches are the "core-first" and the "arm-first" methods.[16,21-25] The “core-first” and “arm-first” methods may also be combined in a single synthesis to generate stars with two different types of polymer arms via the “in-out” method. In the "arm-first" method, a living monofunctional arm of known length is reacted with a plurifunctional compound. "Arm-first" methods can be employed with various linking agents such as silicon tetrachloride and *p*- and *m*-divinylbenzene.[16] When chlorosilane based linking agents are used, the functionality of the chlorosilane dictates the number of arms in the star polymer. When using divinyl linking agents, the divinyl compounds undergo homopolymerization and form star polymers with a DVB core.[1] These star-shaped polymers exhibit a greater number of arms than the functionality of a single divinyl compound.[26] An advantage of the “arm-first” method is the facile synthesis of star-shaped polymers with narrow molecular weight distributions. In contrast to the "arm-first" method, "core-first" methods generate a reactive core prior to the addition of arm forming monomers.[16] The arm forming monomers then polymerize in a radial fashion from the core in a living manner. This enables the outer chain ends of the star-shaped macromolecule to be functionalized using various termination agents.[16] The outer chain ends of a star can be functionalized when the “arm-first” route is used, however, this approach requires the use of protected functionalized initiators.[1] The functionalized periphery can subsequently be utilized for the preparation of networks or star-shaped polymers containing copolymeric branches.[16] The disadvantage of the “core-first” method is the generation of polymers with relatively large molecular weight distributions.[16]

Herein, the synthesis of poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled, star-shaped elastomers via the arm-first method is reported. The molecular weight characteristics of these novel elastomers were examined using size exclusion chromatography in combination with multiple angle laser light scattering (MALLS). The effect of poly(1,3-cyclohexadiene) content on the elastomeric properties was examined and the presence of microphase separation was verified using atomic force microscopy.

Experimental Section

Materials. 1,3-cyclohexadiene (Aldrich, 98%) and isoprene (Aldrich, 99%) were degassed several times and distilled at reduced pressure (0.10 mmHg, 10 °C) from dibutylmagnesium (DBM, 0.84 M). Divinylbenzene (DVB) (Aldrich, 80% divinylbenzene comprising a mixture of the meta and para isomers and 20 wt% ethylvinylbenzene) was distilled under reduced pressure (0.10 mm, 25 °C) from calcium hydride (Aldrich, 95%) and dibutylmagnesium immediately prior to use. The ethylvinylbenzene was not removed and all further references to DVB assume the presence of the ethylvinylbenzene (20 mol%). n-Butyllithium (FMC Corporation, Lithium Division, 1.35 M in n-hexane) was used without further purification. TMEDA (Aldrich, 99%) was distilled at reduced pressure (0.13-0.16 mmHg, 10 °C) from calcium hydride and stored under nitrogen at –25 °C until ready for use. Cyclohexane (Burdick-Jackson, HPLC grade) was stirred over sulfuric acid (10:1 cyclohexane:sulfuric acid) for 7-10 days, decanted, and distilled from a sodium dispersion under nitrogen. The cyclohexane was then vacuum distilled from poly(styryllithium) immediately prior to use. All reagents were transferred using syringe and cannula techniques under ultrapure (99.999%) nitrogen.

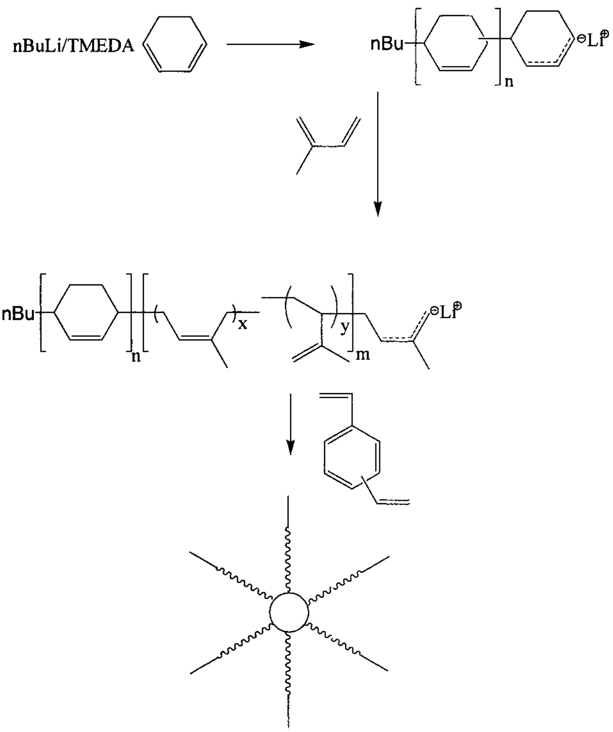
Synthesis of a Pre-formed TMEDA/nBuLi Adduct. A 25-mL round-bottomed flask was charged with nBuLi (5 mL, 8 mmol) and cooled to -20 °C. The tertiary diamine TMEDA (0.59 mL, 4 mmol) was added drop-wise. Upon addition of the tertiary diamine, the white TMEDA/nBuLi adduct formed rapidly. The adduct was re-dissolved by heating to 67 °C and used to initiate the polymerization.

Synthesis of Poly(1,3-cyclohexadiene)-*block*-Poly(isoprene)-*block*-DVB. A 500-mL round-bottomed flask containing anhydrous cyclohexane (60 mL, 0.54 mol) and 1,3-cyclohexadiene (6.70 mL, 62.5 mmol) was maintained at 25 °C. The preformed TMEDA/nBuLi adduct (0.56 mmol) was added using a syringe and the polymerization was maintained at 25 °C for 120 minutes. Following the polymerization of 1,3-cyclohexadiene, isoprene (17 mL, 78 mmol) and cyclohexane (300 mL, 1.71 mol) were added to the reaction. Upon addition of isoprene, the polymerization immediately changed to a light green color, indicative of the poly(isoprenyllithium) species in the presence of TMEDA. The isoprene was polymerized for 2 h prior to the addition of DVB (0.72 mL, 3.51 mmol). Upon addition of DVB, the polymerization immediately changed to a deep red color, indicative of the divinylbenzyllithium species. The DVB coupling reaction was allowed to proceed for 12 h at 40 °C. The polymerization was terminated using degassed methanol (Burdick-Jackson, HPLC grade). The resulting polymer was precipitated into isopropanol (2.5 L), filtered, and dried at 50 °C in vacuo for 12-18 h. An antioxidant such as Irganox 1010 (0.10 weight % compared to the polymer) was added to the precipitation solvent to retard oxidative degradation during subsequent storage.

Polymer Characterization. ^{1}H NMR spectra were determined in $CDCl_3$ at 400 MHz with a Varian Spectrometer. Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 DSC at a heating rate of 10 °C/min under nitrogen. Glass transition temperatures are reported as the midpoint of the change in heat capacity during the second heat. Molecular weights were determined using size exclusion chromatography with a Waters 2410 refractive index detector (SEC-DRI) in combination with a Wyatt Technology Minidawn MALLS detector (SEC-MALLS) for absolute molecular weight measurements. The dn/dc values were determined on-line using the calibration constant for the RI detector and the mass of the polymer sample. For all samples, it was assumed that 100% of the polymer eluted from the column during the measurement. SEC measurements were performed at 40 °C in chloroform at a flow rate of 1.0 mL/min.

Film Preparation. Film samples for viscoelastic measurements were prepared by dissolving the block copolymers in chloroform (10 wt%) in the presence of an antioxidant (Irganox 1010, Ciba-Geigy Group). The polymer solution was poured into a Petri dish and the solvent was allowed to slowly evaporate over 5-7 days at 25 °C. The films were then dried under vacuum at 40 °C for 4 h and finally dried at 80 °C under vacuum for 24 h to a constant weight. These films were clear, colorless and elastomeric. The average film thickness (0.25 mm, n = 5) was measured using a metric micrometer.

Dynamic Mechanical Analysis. Dynamic mechanical analysis (DMA) was performed using a TA-instruments 2988 dynamic mechanical analyzer. The storage modulus (G') and loss modulus (G'') were measured at a fixed frequency and strain (110%). Samples were cut (1 x 8 mm) from the 0.25 mm solution cast films and deformed at a constant rate (1Hz) while heating at a rate of 5 °C/min. The glass transition temperature for the polyisoprene block was determined by measuring the peak in the loss modulus. The glass transition temperature of the poly(1,3-cyclohexadiene) block was estimated by measuring the temperature where the elastomer mechanically failed. It was assumed that at this elevated temperature the onset of the poly(1,3-cyclohexadiene) glass transition resulted in the failure of the poly(1,3-cyclohexadiene) domains and subsequent mechanical failure of the elastomer.



Scheme 1. Synthesis of poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled star-shaped elastomers.

Tensile Measurements. The tensile properties of the polymers were determined using a Texture Analyzer, (Texture Analysis Inc). Films samples were solution cast as described above, cut into microdumbells (10 x 2.70 x 0.25 mm), and characterized as outlined in ASTM D 882-01. Data are reported as the average of 3 or more measurements.

Atomic Force Microscopy. Tapping mode atomic force microscopy (TMAFM) was performed on a Nanoscope III microscope from Digital Instruments Inc. at room temperature in air using microfabricated cantilevers provided by the manufacturer (spring constant of 30 N m^{-1}).[27] Digital Instruments image processing software was used for image analysis. The set point and tapping amplitude were 1.80 and 2.80 V, respectively. Silicon wafers were prepared by sonication in methanol and subsequently dried under nitrogen. Polymer samples were prepared for AFM analysis by dissolving the polymer in toluene (4 wt%) and spin coating the solution onto prepared silicon wafers at 2000 rpm. The samples were annealed at 120 °C for 12 h.

Results and Discussion

Star-shaped polymers with poly(1,3-cyclohexadiene-*block*-isoprene) arms were prepared using the "arm-first" method with divinylbenzene as the coupling agent (Scheme 1). The poly(1,3-cyclohexadiene-*block*-isoprene) arms were prepared via sequential addition of the monomers and the viscosity of the reaction solution remained low during the synthesis of the arms. The poly(1,3-cyclohexadiene) block remained soluble during the polymerization and the crossover to the isoprene was efficient, as indicated by the rapid color change (yellow to green). It was previously demonstrated that monomer concentration effects the degree of livingness of 1,3-cyclohexadiene polymerizations.[28] As such, the synthesis of the poly(1,3-cyclohexadiene) block was performed at a monomer concentration of 10 wt%. To minimize the reaction viscosity during the synthesis of the diblocks, the reaction was diluted to a total polymer concentration of 8 wt% when the isoprene charge was added. Upon addition of DVB to the poly(1,3-cyclohexadiene)-*block*-poly(isoprenyllithium) solution, the reaction color immediately changed from green to a deep red color indicative of the formation of a highly delocalized benzylic anion resulting from the rapid crossover from the poly(1,3-cyclohexadiene)-*block*-poly(isoprenyllithium) anion to the DVB monomer. The SEC molecular weight characterization of a star-shaped polymer with poly(1,3-cyclohexadiene-*block*-isoprene) arms is shown in Figure 1. The degree of coupling was estimated from the SEC-DRI measurements, although in some cases the peak from the residual uncoupled diblock could not be deconvoluted from the star polymer peak and no attempts to isolate the star-shaped elastomers by fractionation were made. For all samples synthesized in this study, the degree of coupling of the poly(1,3-cyclohexadiene-*block*-isoprene) arms to the DVB core was approximately 90-95%.

To study the effect of the DVB/nBuLi ratio on the coupling efficiency and number of arms per star, a series of star- shaped polymers was synthesized using a constant diblock arm length of 40000 g/mol (10000 PCDH-30000 PI) with varying molar ratios of DVB to nBuLi (Table 1). The resulting polymers exhibited high number average molecular weights (80000 to 192000) and narrow molecular weight distributions (1.25 to 1.31). As expected, an important factor for the control of the star polymer number average molecular weight ($<M_n>$) was the DVB/nBuLi ratio. Star-shaped polymers comprising arms with a number average molecular weight of 40,000 g/mol were prepared at a linking efficiency of approximately 90-95%. The resulting polymers all exhibited relatively narrow molecular weight distributions and a high percent of conversion of the living anionic arms to the DVB core (Table 1).

Table 1. Molecular weights, molecular weight distribution, coupling efficiency of poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled star-shaped polymers synthesized with varying ratios of DVB/nBuLi.

Polymer	Block size PCHD-b-PI	DVB/nBuLi	$<M_n>$**	$<M_w/M_n>$**	Coupling Efficiency (%)*	Number of Arms (f)
30TPE31	10K-30K	3:1	80000	1.27	98	2.7
30TPE61	10K-30K	6:1	120000	1.27	98	4.0
30TPE81	10K-30K	8:1	192000	1.25	95	6.4
30TPE121	10K-30K	12:1	140000	1.31	96	4.7

SEC Conditions: 40 °C, Chloroform, *SEC-DRI, **SEC-MALLS

At a low DVB/nBuLi ratio of 3:1 (sample # 30TPE31), the average number of arms per star (f) was 2.7, which indicated that approximately 30% of the coupled diblocks were dimers. The remaining 70% was comprised of three arm stars. As the DVB/nBuLi ratio was increased in the range of 3:1 to 8:1, the core size increased and a greater number of arms attached to the core. When the DVB/nBuLi ratio was further increased from 8:1 (sample # 30TPE81) to 12:1 (sample # 30TPE121), the average number of arms decreased from 6.4 to 4.7. Previous studies have demonstrated that increased ratios of DVB/nBuLi do not necessarily result in more highly branched star-shaped polydienes, rather that at higher DVB/nBuLi ratios, star formation is more quantitative, i.e., more arm polymers are coupled, but does not always increase the branch functionality.[26] It was also shown that at higher DVB/nBuLi ratios, there was a higher propensity for star-star coupling, increasing the higher molecular weight fraction of the polymer sample

(sample # 30TPE121). Characterization of the star-shaped polymers using SEC-MALLS enabled the identification of these higher molecular weight species. As shown in Figure 1, the relative amount of higher molecular weight species increased at higher molar ratios of DVB/nBuLi. This was attributed to star-star coupling, which was shown to occur in polyisoprene based star-shaped polymers using DVB as the coupling agent.[26] The chromatograms in Figure 1 are depicted in the descending order that reflects a qualitative improvement in the uniformity of the molecular weight distribution, and the 8:1 DVB:nBuLi molar ratio was preferred based on this qualitative analysis.

In spite of the introduction of these higher molecular weight species, the molecular weight distribution of these star-shaped, elastomeric polymers did not increase significantly when the DVB/nBuLi ratio was increased. A ratio of DVB/nBuLi of 8:1 (sample # 30TPE81) resulted in elastomeric, star-shaped materials with the highest molecular weight (192000) and narrowest molecular weight distribution (1.25). As such, a ratio of DVB/nBuLi of 8:1 was used to synthesize a series of polymers containing varying compositions of 1,3-cyclohexadiene.

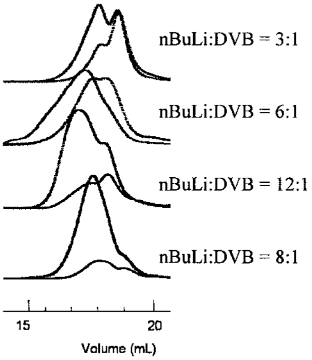


Figure 1. Molecular weight characterization of the series of star-shaped polymers with varying ratios of DVB/nBuLi. The light scattering data (top curve) is superimposed on the refractive index data (bottom trace).

The relative volume fraction of the component blocks in a block copolymer was previously shown to determine the morphology of the block copolymers in both the solid state and in solution.[29] The morphology in the solid state impacts the thermal and mechanical properties of the elastomeric material. A series of poly(1,3-cyclohexadiene) star-shaped elastomers were synthesized with varying volume fractions of poly(1,3-cyclohexadiene) repeat units (15% to 50%) and a constant 8:1 ratio of DVB/nBuLi to investigate the effect of polymer composition on morphology and mechanical properties (Table 2). The composition of the resulting polymers was determined using ^{1}H NMR spectroscopy and agreed well with the relative monomer amounts charged to the reactions. With the exception of sample # 15TPE81, the resulting polymers exhibited high molecular weights and narrow molecular weight distributions. The broad molecular weight distribution and reduced coupling efficiency for sample 15TPE81 was attributed to an increase in viscosity and loss of stirring efficiency upon DVB addition

Table 2. Molecular weight characterization of poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled star-shaped polymers synthesized with varying percentages of poly(1,3-cyclohexadiene).

Polymer	Block Size PCHD-b-PI	DVB/nBuLi	$<M_n>$**	$<M_w/M_n>$**	Coupling Efficiency (%)*
15TPE81	10K-40K	8:1	350000	1.50	75
30TPE81	10K-30K	8:1	192000	1.25	95
50TPE81	10K-10K	8:1	120000	1.28	85

SEC Conditions: 40 °C, Chloroform, *SEC-DRI, **SEC-MALLS

The glass transition temperatures of the polymers were characterized using both differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) (Table 3). The glass transition temperature (T_g) of the polyisoprene block ranged from -15 °C to -13 °C. These elevated glass transition temperatures relative to polyisoprene containing a high percentage of 1,4-addition (T_g = -65 °C) were attributed to the high percentage of 3,4-addition that resulted from the presence of TMEDA in the polymerization solution. The average percentage of 3,4-addition was estimated as 53% using ^{1}H NMR spectroscopy. As expected, the volume fraction of the poly(1,3-cyclohexadiene) block was too low to accurately measure a T_g using DSC analysis. A poly(1,3-cyclohexadiene) homopolymer control was synthesized ($<M_n>$ = 10000, $<M_w>/<M_n>$ = 1.05) and the glass transition temperature of the control was measured. The T_g for this polymer was 138 °C, in good agreement with our earlier studies.[30]

DMA was used to effectively measure the T_g of both the poly(1,3-cyclohexadiene) and

Table 3. Thermal analysis of poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled star-shaped polymers synthesized with varying ratios of DVB/nBuLi.

Polymer	T_g polyisoprene*	T_g polyisoprene**	T_g PCHD*	T_g PCHD**
PCHD(10K)			138 °C	Not Determined
30TPE31	-15 °C	-5 °C	Not Detected	146 °C
30TPE61	-14 °C	-2 °C	Not Detected	148 °C
30TPE81	-13 °C	-3 °C	Not Detected	145 °C
30TPE121	-14 °C	-1 °C	Not Detected	151 °C

*DSC Conditions: 20 °C/min, second heat, N_2
**DMA Conditions: 5 °C/min, second heat, N_2, 1Hz

polyisoprene blocks. The glass transition temperature for the polyisoprene block (-5 to -1 °C) was measured as the peak in the loss modulus and was within the error of the measurement. These T_gs varied from -5 to -1 °C, which was within the error of the measurement. The glass transition temperature for the poly(1,3-cyclohexadiene) block was measured using the DMA as approximately 148 °C and agreed well with the T_g measured by DSC analysis for the poly(1,3-cyclohexadiene) homopolymer control ($<M_n> = 10000$, $T_g = 138$ °C). The presence of two different glass transition temperatures indicated that the polyisoprene blocks phase separated from the poly(1,3-cyclohexadiene) blocks.

Elastomeric properties were expected to arise from the phase separation between the high T_g poly(1,3-cyclohexadiene) domains and the low T_g polyisoprene domains. Tensile tests were performed to determine the effect of the DVB/nBuLi ratio on the elastomeric properties of the polymers. The tensile properties of samples that were synthesized with a DVB/nBuLi ratio of 3:1, 6:1, 8:1, and 12:1 were compared. All four polymers exhibited an average elongation at break of 633% and an average tensile strength of 17.0 MPa. As expected, the ratio of DVB/nBuLi did not affect the elastic modulus, elongation at break, or the tensile strength of the polymers.

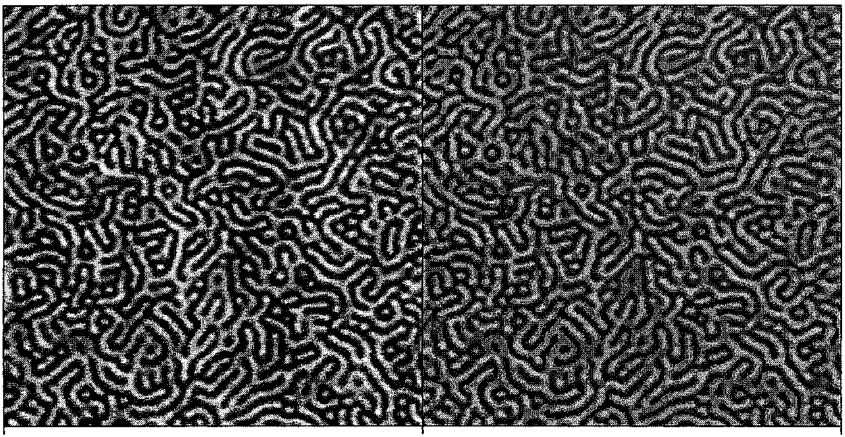
A number of previous studies have shown the impact of composition on the tensile properties of the polymer.[29] Increasing the percentage of the high T_g component was shown to alter the polymer morphology and impact the tensile properties of the polymer. Tensile tests were performed on polymers with varying volume fractions of poly(1,3-cyclohexadiene) (15%, 30%, 50%, and 100%) to examine the effect of polymer composition on the elastomeric properties of the polymers (Table 4). As the percentage of poly(1,3-cyclohexadiene) increased, the elongation at break decreased and the tensile strength increased. The elastic modulus also increased as the percentage of 1,3-cyclohexadiene increased. Previous studies by Natori et al. reported the synthesis of poly(1,3-cyclohexadiene-*block*-butadiene-*block*-1,3-cyclohexadiene) that were prepared via sequential addition with approximately 30% poly(1,3-cyclohexadiene) content.[14] These polymers typically exhibited a tensile strength of 20-25 MPa and a percent elongation of 700%. The star-shaped elastomers prepared in this study exhibit similar mechanical properties to linear polymers with a similar composition.

Table 4. Mechanical analysis of poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled star-shaped polymers synthesized with varying percentages of poly(1,3-cyclohexadiene).

Polymer	Elastic Modulus (MPa)	Elongation at Break (%)	Tensile Strength (MPa)
15TPE81	0.5 ± 0.1	745 ± 81	7.2 ± 0.2
30TPE81	2.2± 0.1	650 ± 24	15.1 ± 0.1
50TPE81	9.1± 0.1	212 ± 39	17.0 ± 0.1
Poly(1,3-CHD)	23.0± 0.1*	1.8 ± 0.1	Not Determined

Tensile testing performed according to ASTM D-882-01
Youngs Modulus

Multiple glass transition temperatures in combination with excellent elastomeric properties strongly indicated that the poly(1,3-cyclohexadiene) domains phase separated from the polyisoprene domains.[31] Tapping mode atomic force microscopy (TMAFM) was used to examine the microphase separation of the poly(1,3-cyclohexadiene) and the polyisoprene blocks (Figure 2). Silicon wafers were spin coated with a 4 wt% solution of the elastomer (30TPE81) in toluene and the samples were annealed at 120 °C for 12 h under vacuum. The presence of microphase separation between the poly(1,3-cyclohexadiene) block and the polyisoprene block was readily apparent (Figure 2A and B). The image on the left is a topographical image of the surface (Figure 2A) and the image on the right is the phase contrast image of the surface (Figure 2B). Previous studies described the utility of the phase contrast image for the detection of microphases based on the differences in the viscoelastic response of the various blocks.[27] The reduced interaction time of the AFM tip with the poly(1,3-cyclohexadiene) domains resulted in near zero phase lag values causing the poly(1,3-cyclohexadiene) domains to appear darker (Figure 2B). The polyisoprene domains remained in contact with the AFM tip forcing a delay in the tip motion and an increase in the phase lag, giving rise to the brighter areas in the image (Figure 2B). The topographical image of the surface was also used to characterize the polymer surface (Figure 2A). Previous studies suggested that the height difference between the different domains arises from the ability of the lower T_g domains to relax by protruding out of the surface of the film. Accordingly, the lighter regions in the image were attributed to the protruding domains of the polyisoprene blocks, which constituted approximately 70% of the TMAFM image. The relative percentages of the two domains in the AFM image (30% poly(1,3-cyclohexadiene) and 70% polyisoprene) agreed well with the composition of the star-shaped elastomer, which was 30% poly(1,3-cyclohexadiene) and 70% polyisoprene. To our knowledge, this is the first report verifying the presence of microphase separation in poly(1,3-cyclohexadiene-*block*-isoprene) block copolymers using atomic force microscopy.



(A) (B)

Figure 2. Microphase separation present in a poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled star-shaped elastomer by TMAFM (Sample # 30TPE81).

Conclusion

A novel series of poly(1,3-cyclohexadiene-*block*-isoprene) star-shaped elastomers was successfully synthesized using a convergent "arm-first" approach with DVB. These star-shaped elastomers exhibited controlled molecular weights and narrow molecular weight distributions indicative of a controlled living anionic polymerization. As expected, increased ratios of

DVB/nBuLi resulted in elevated levels of star-star coupling. The tensile strength, elongation at break, and elastic modulus were dependent on the percentage of poly(1,3-cyclohexadiene) present in the elastomer. Microphase separation of the poly(1,3-cyclohexadiene) and polyisoprene blocks was verified using both DMA and TMAFM analysis. TMAFM was performed and the presence of both poly(1,3-cyclohexadiene) and polyisoprene domains was verified. The domains in the TMAFM image were assigned based on the percent composition of the polymer sample and the relative differences in the viscoelastic response between the poly(1,3-cyclohexadiene) and polyisoprene blocks.

Acknowledgments

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(1) Hsieh, H. L.; Quirk, R. P. Anionic Polymerization: Principles and Practical Applications; Marcel Dekker: New York, 1996.
(2) Ming Yu, J.; Dubois, P.; Jerome, R. *Macromolecules* **1996**, *29*, 7316.
(3) Fetters, L. J.; Morton, M. *Macromolecules* **1969**, *2*, 453.
(4) Morton, M.; Mikesell, S. L. *J. Macromol. Sci., Chem.* **1993**, *A7*, 1391.
(5) Quirk, R. P. *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1985**, *26(2)*, 14.
(6) Sharaby, Z.; Jagur-Grodzinski, J.; Martan, M.; Vofsi, D. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 901.
(7) Lefebvre, G.; Dawans, F. *J. Polym. Sci.* **1964**, *A2*, 3277.
(8) Sharaby, Z.; Martan, M.; Jagur-Grodzinski, J. *Macromolecules* **1982**, *15*, 1167.
(9) Mango, L. A.; Lenz, R. W. *U.S. Nat. Tech. Inform. Serv.* **1972**, *12*, 402.
(10) Mango, L. A.; Lenz, R. W. *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1971**, *12(2)*, 402.
(11) Natori, I.; Inoue, S. *Macromolecules* **1998**, *31*, 982.
(12) Natori, I.; Inoue, S. *Macromolecules* **1998**, *31*, 4687.
(13) Natori, I.; Imaizumi, K.; Yamagish, H.; Kazunori, M. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1657.
(14) Imaizumi, K.; Ono, T.; Natori, I.; Sakuri, S.; Takedo, K. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 13.
(15) Matsen, M. W. *Polymer Science* **2000**, *113*, 5539.
(16) Meneghetti, S. P.; Lutz, P. J.; Rein, D. Star-Shaped Polymers via Anionic Polymerization Methods ; Mishra, M., Kobayashi, S., Eds.; Marcel Dekker: New York, 1999, pp 27.
(17) Fetters, L. J.; Kiss, A. D.; Pearson, D. S. *Macromolecules* **1993**, *25*, 647.
(18) Knischka, R.; Lutz, P. J.; Sunder, A.; Mulhaupt, R.; Frey, H. *Macromolecules* **2000**, *33*, 315.
(19) Hong, K.; Mays, J. W. *Macromolecules* **2001**, *34*, 782.
(20) Williamson, D. T.; Elman, J. F.; Madison, P. H.; Pasquale, A. J.; Long, T. E. *Macromolecules* **2001**, *34*, 2108.
(21) Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1980**, *13*, 193.
(22) Ishizu, K.; Sunahara, K. *Polymer* **1995**, *36*, 4155.
(23) Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem* **1999**, *37*, 857.
(24) Storey, R. F.; Shoemake, K. A. *J. Polym. Sci., Part A: Polym. Chem* **1999**, *37*, 1629.
(25) Ishizu, K.; Kitana, H.; Ono, T.; Uchida, S. *Polymer* **1999**, *40*, 3229.

(26) McGrath, J. E., Ed. *Anionic Polymerization: Kinetics, Mechanisms, and Synthesis*; American Chemical Society: Washington D.C., 1981; Vol. 166.
(27) Leclere, P.; Lazzaroni, R.; Bredas, J. L.; Yu, J. M.; Dubois, P.; Jerome, R. *Langmuir* **1996**, *12*, 4317.
(28) Williamson, D. T.; Long, T. E. *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2001**, *42(2)*, 634.
(29) McGrath, J. E. An Introductory Overview of Block Copolymers; Meier, D. J., Ed.; Harwood Academic Publishers: New York, 1979; Vol. 3.
(30) Williamson, D. T.; Hudelson, C. L.; Long, T. E. *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2002**, *43(1)*, 502.
(31) Stroble, G. The Physics of Polymers; 2nd ed.; Springer-Verlag: Berlin, 1997.
(32) Hashimoto, T.; Mitsuhiro, S.; Fujimura, M.; Kawai, H. Microphase Separation and the Polymer-Polymer Interphase in Block Copolymers; Meier, D. J., Ed.; Hardwood Academic: New York, 1979; Vol. 3.