Synthesis and Characterization of Poly(1,3-cyclohexadiene) Homopolymers and Star-Shaped Polymers

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ABSTRACT: The synthesis of high molecular weight star-shaped polymers comprising poly(1,3-cyclohexadiene) arms coupled to a divinylbenzene (DVB) core is reported. In-situ FTIR spectroscopy was used to verify first-order polymerization kinetics for 1,3-cyclohexadiene at 40 °C in cyclohexane with a 10 wt % monomer concentration using a tetramethylethylenediamine (TMEDA) to *n*-butyllithium (*n*-BuLi) ratio of 5/4. The propagation rate constant was determined to be 0.31 L mol^{-1} s^{-1}. The degree of 1,2-addition (70%) vs 1,4-addition (30%) for 1,3-cyclohexadiene was determined using ^{1}H NMR spectroscopy. The molecular weights of the preformed arms were 10 000 and 5000 g/mol, and the ratio of DVB to *n*-BuLi was systematically varied from 6:1 to 24:1. Gel permeation chromatography coupled with light scattering detection was utilized to detect the formation of star-shaped polymers and the presence of star−star coupling. In-situ spectroscopy and obvious color changes indicated that the addition of DVB to poly(1,3-cyclohexadienyllithium) was rapid. The molecular weight distribution (M_w/M_n) of the star polymers ranged from 1.4 to 1.9. The polymeric materials were thermally stable to 330 °C under a nitrogen environment. The refractive indices of both the homopolymers and star polymers were 1.572 at 600 nm and remained relatively constant from 1600 to 550 nm. The T_g of the high molecular weight star-shaped polymers was 150 °C.

Introduction

Living polymerization strategies permit the synthesis of macromolecules with well-defined architectures.[1−3] These resulting macromolecules exhibit narrow molecular weight distributions and predictable molecular weights.[4] Furthermore, these methods can be utilized to synthesize a myriad of complex polymer architectures including block copolymers, star-shaped polymers, and graft copolymers.[4] In recent years, a number of radical-based polymerization methods have evolved which are capable of producing macromolecules with relatively narrow molecular weight distributions and varied architectures. These methods include stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP), and reversible atom fragment transfer (RAFT). The greatest advantage of these methods is the functional group tolerance exhibited during the polymerization as compared to conventional organolithium-initiated processes. However, compared to living anionic polymerization, slower reaction rates and lower monomer conversions are problematic for the synthesis of block copolymers. In contrast, living anionic polymerizations exhibit rapid reaction times and high monomer conversions. Living anionic polymerization is a commercially viable approach to prepare a vast number of hydrocarbon polymers based on poly(isoprene), poly(butadiene), and poly(styrene) homo and block copolymers.[5] A large number of potential commercial applications exist for hydrocarbon polymers due to their potentially desirable thermal resistance, chemical stability, and superior mechanical strengths.[6]

Various polymerization techniques were utilized in the mid-1960s and early 1970s in an attempt to find a viable polymerization methodology for 1,3-cyclohexadiene.[7−11] Additionally, in the late 1970s a series of patents were issued to Phillips Petroleum that described the process and composition of 1,3-cyclohexadiene-containing polymers.[12−16] The effects of various ligating agents on the resulting composition were also investigated. The ligating agents investigated were TMEDA, dimethoxyethane (DME), and tetrahydrofuran (THF). The compositions were limited to “random” copolymers containing poly(1,3-cyclohexadiene), poly(styrene), poly(isoprene), or poly(butadiene) and prepared using various ligating agents. Despite these early attempts to polymerize 1,3-cyclohexadiene in a controlled fashion, the resulting polymers exhibited unpredictable molecular weights and broad molecular weight distributions. Natori and co-workers recently reported the successful living anionic polymerization of 1,3-cyclohexadiene utilizing *n*-butyllithium (*n*-BuLi) in combination with a single ligation agent (tetramethylethylenediamine (TMEDA)).[17] The resulting homopolymers exhibited relatively narrow molecular weight distributions and modest molecular weights. In addition to the elucidation of the relative reactivities of the monomer pairs, Natori and co-workers also reported the synthesis of di- and triblock copolymers composed of various combinations of styrene, butadiene, and isoprene.[17−19] Mays and co-workers have studied the morphologies of poly(styrene-*b*-1,3-cyclohexadiene) diblock copolymers.[20] In addition, poly(1,3-cyclohexadiene) was utilized as a precursor for the synthesis of poly(phenylene)s via aromatization with the chloranil dehydrogenating agent.[21]

Living anionic polymerizations have been utilized widely in the synthesis of star-shaped polymers. The living nature of the polymerization allows for the linking of preformed arms to a linking agent such as divinylbenzene (DVB). This approach, generally termed the

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"arm-first" method, is commonly used for both living anionic and cationic syntheses of star-shaped polymers.[22−26] "Arm-first" methods can be employed with various linking agents. Two common linking agents are silicon tetrachloride and *p*- and *m*-divinylbenzene. In favorable cases, the functionality of a chlorosilane-based linking agent dictates the number of arms in the star polymer. However, divinyl compounds undergo homopolymerization and form star polymers where the number of arms is greater than the functionality of a single divinyl compound. An advantage of the arm first method is the facile synthesis of narrow molecular weight distribution star-shaped polymers. An alternate method, termed "core-first", involves the generation of a reactive core prior to the addition of arm forming monomers. The advantage of the core-first method is the ability to functionalize the outer chain ends of the star-shaped macromolecule using various termination agents. Although the outer chain ends of a star can be functionalized using the arm-first route, this route requires the use of protected functional initiators. The functionalized periphery can subsequently be utilized for the preparation of networks or star-shaped polymers containing copolymeric branches.[27] The disadvantage of the core-first method is the generation of a relatively large molecular weight distribution.[27] Recently, a number of researchers have combined both the "core-first" and the "arm-first" methods in a single synthesis to generate stars with two different types of polymer arms in what is termed the "in-out" method.[28,29] Star-shaped polymers exhibit useful rheological properties.[30,31] Additionally, star-shaped macromolecules have been used extensively in a number of commerical applications including adhesives, coatings, dispersants, membranes, compatibilizers, thermoplastic elastomers, viscosity-index and melt-strength modifiers, and as vehicles for drug delivery.[32]

These research efforts involve the synthesis via the "arm-first" method of novel star-shaped polymers consisting of poly(1,3-cyclohexadiene) arms coupled to a divinylbenzene core. In addition, in-situ FTIR spectroscopy was utilized to examine the kinetics of the homopolymerization and the rate of crossover upon addition of DVB. The physical performance of the resulting polymers was examined with a special focus on the thermal and optical properties.

Experimental Section

Materials. 1,3-Cyclohexadiene (Aldrich) was degassed several times and vacuum-distilled (0.10 mmHg, 10 °C) from dibutylmagnesium (DBM). Divinylbenzene (DVB) (Aldrich, 80% divinylbenzene comprising a mixture of isomers, 20% ethylvinylbenzene) was distilled under vacuum (0.10 mm, 25 °C) from calcium hydride and dibutylmagnesium immediately prior to use. No attempts to remove the ethylvinylbenzene were made, and all further references to DVB assume the presence of the ethylvinylbenzene. *n*-Butyllithium (FMC Corporation Lithium Division, 1.35 M in *n*-hexane) was used without further purification. TMEDA (Aldrich) was vacuum-distilled from calcium hydride and stored under nitrogen at −25 °C until ready for use. Cyclohexane was stirred over sulfuric acid (10:1 cyclohexane:sulfuric acid) for 7−10 days, decanted, and distilled from a sodium dispersion under nitrogen immediately prior to use.

Polymer Synthesis. The anionic polymerization of 1,3-cyclohexadiene was initiated using *n*-BuLi/TMEDA (4/5) in cyclohexane at 40 °C for 45 min for the 10 000 M_n arms and 25 min for 5000 M_n arms to ensure quantitative conversion of the monomer. In-situ FTIR was utilized to confirm the quantitative disappearance of monomer. Polymerizations were performed under a nitrogen atmosphere at monomer concentrations of approximately 10 wt %. A typical polymerization involved charging a 100 mL round-bottomed flask with anhydrous cyclohexane (60 mL, 0.54 mol) and 1,3-cyclohexadiene (5.95 mL, 62.4 mmol). The solution was allowed to reach 40 °C. TMEDA (0.094 mL, 0.625 mmol) was charged to the vessel. The initiator *n*-BuLi (0.31 mL, 0.5 mmol) was charged to initiate polymerization. The living poly(1,3-cyclohexadienyllithium) anions in cyclohexane were yellow and appeared to be slightly heterogeneous at 40 °C. Upon completion of the 1,3-cyclohexadiene polymerization, the flask was charged with a predetermined amount of DVB. The reaction solution immediately changed from a yellow to a deep red color upon the addition of DVB. DVB was allowed to react for 2 h, as confirmed via in-situ FTIR to ensure complete conversion. The polymerization was terminated with degassed methanol (1.0 mL), and the resulting star polymer was precipitated into 2-propanol (600 mL), filtered, and dried at 50 °C in vacuo overnight. An antioxidant such as Irganox 1010 (0.10 wt % compared to polymer) was added to the precipitation solvent to retard oxidative degradation during subsequent storage.

In-Situ FTIR Spectroscopy. The in-situ FTIR spectroscopic studies were performed using a ReactIR 1000 (ASI Applied Systems) reaction analysis system equipped with a light conduit and DiComp (diamond composite) insertion probe. The specifics of the ReactIR based on attenuated total reflectance (ATR) have been described in detail previously.[33,34]

Polymer Characterization. ^{1}H and ^{13}C 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 inflection point of the change in heat capacity during the second heat. Molecular weights were determined using size exclusion chromatography (SEC) with a Waters Alliance SEC system equipped with a Viscotek 150R viscosity detector. In addition, a Waters 717plus equipped with a Waters 2410 refractive index detector and a Wyatt Technology Minidawn MALLS detector was utilized for absolute molecular weight measurements. The d*n*/d*c* 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 25 °C in chloroform at a flow rate of 1.0 mL/min. TGA measurements were performed on a TA Instruments Hi-Res TGA 2950 thermogravimetric analyzer (TGA) under nitrogen with a heating rate of 10 °C/min.

Thin Film Optical Characterization. The complex refractive index of the material was determined using variable angle spectroscopic ellipsometry (VASE, Tompkins). To determine these optical constants in the deep ultraviolet region, a VUV-VASE (J. A. Woollam Co.) instrument was utilized. The star polymer was dissolved in dichlorobenzene and spun-cast onto silicon substrates. The solvent was removed with mild heating, and X-ray photoelectron spectroscopy (XPS) (PHI 5600) was performed to ensure the removal of the dichlorobenzene. Spectra were acquired from 145 to 1700 nm using three angles of incidence (65°, 70°, 75°). Spectra were then modeled using WVASE32 software. A Herzinger-Johs parametric layer has been used to estimate η and k of the polymer as this imposes a Kramers−Kronig formalism onto the optical constants.[35]

Results and Discusion

Kinetic Study of the Homopolymerization of 1,3-Cyclohexadiene. The synthesis of a 5000 g/mol poly(1,3-cyclohexadiene) homopolymer was monitored using in-situ FTIR spectroscopy. The resulting polymer was characterized using SEC and found to be a single peak with a molecular weight of 5200 g/mol and a molecular weight distribution of 1.01. In-situ near-FTIR spectros-

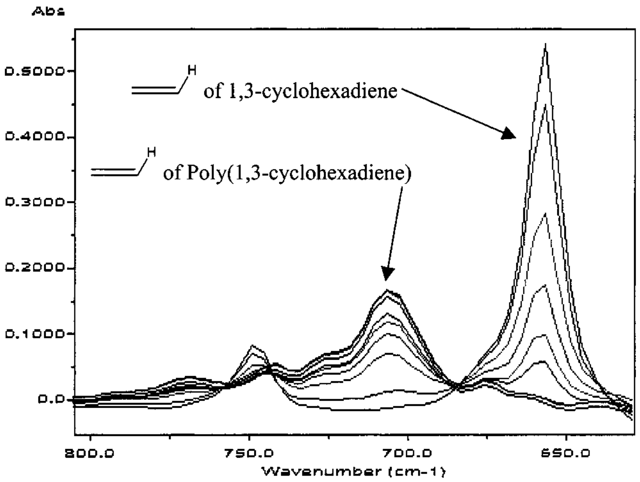

Figure 1. In-situ FTIR spectra illustrating the disappearance of the monomer absorption at 657 cm^{-1} and concomitant polymer absorption increase at 703 cm^{-1}.

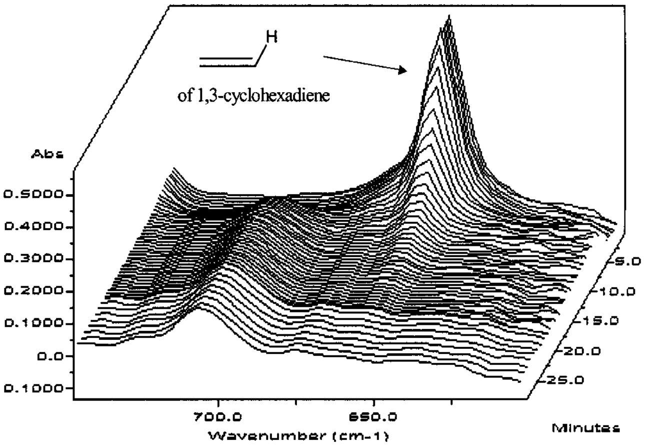

Figure 2. Waterfall plot of the polymerization of 1,3-cyclohexadiene.

copy has been previously employed for determination of the kinetics of the anionic homopolymerization of styrene and isoprene.[36] However, this is the first reported use of in-situ mid-FTIR spectroscopy to study the kinetics of a living anionic polymerization. The monomer and polymer peaks in the spectrum must be clearly resolved as shown in Figure 1 in order to ensure accurate analysis. The decrease in the absorbance of the monomer peak found at 657 cm^{-1} and the increase in the absorbance of the polymer peak at 703 cm^{-1} resulting from the out-of-plane bending vibration of the carbon to hydrogen bond of the alkene are shown in Figure 1. The polymer was synthesized using a 10 wt % monomer/cyclohexane solution at 40 °C using the TMEDA/*n*-BuLi ratio of 5/4. The polymerization was then initiated with *n*-BuLi, and the solution became heterogeneous within 5 min. Despite the heterogeneity of the polymerization solution, molecular weights are predictable and molecular weight distributions are relatively narrow. Figure 2 is a waterfall plot of the polymerization, indicating that complete conversion of the monomer occurred within 13 min. The polymerization kinetics did not change as the polymerization proceeded from a homogeneous solution to a heterogeneous solution as is shown in Figure 2. Because of the excellent resolution of both the monomer and polymer absorbances, the spectral data were utilized in the generation of a pseudo-first-order kinetic plot with monomer concentration plotted against time as shown in Figure 3. The calculated rate constant for propagation was 0.31 L mol^{-1} s^{-1}. Values for the polymerization rate constant of an anionic polymerization are dependent upon the temperature, monomer concentration, and the presence of additives.[4] An understanding of the propagation rate facilitated the minimization of any termination/transfer steps occurring after quantitative polymerization of the arms and prior to the addition of the DVB.

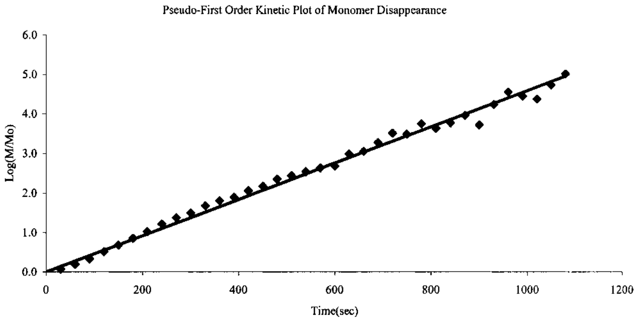

Figure 3. Pseudo-first-order kinetic plot of homopolymerization of 1,3-cyclohexadiene.

Synthesis and Characterization of Star-Shaped Polymers. Scheme 1 illustrates the synthetic methodology used for the preparation of poly(1,3-cyclohexadiene) DVB star-shaped polymers. The convergent linking of poly(1,3-cyclohexadienyllithium) chain ends to the DVB core resulted in the formation of star-shaped polymers. Upon addition of DVB to the poly(1,3-cyclohexadienyllithium) solution, the reaction color immediately changed from yellow 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-cyclohexadienyllithium) anion to the DVB monomer. In-situ spectroscopy of the DVB addition also indicated the crossover reaction occurred in a rapid manner. To study the effect of arm length and DVB/*n*-BuLi ratio on the resulting star polymer formation, a series of star-shaped polymers were synthesized using a constant arm length of 10 000 g/mol with varying ratios of DVB to *n*-BuLi (Table 1). The absolute molecular weights of the resulting macromolecules were approximated using the universal calibration as previously described[37] and using multiple angle laser light scattering (MALLS). The molecular weights were determined using MALLS due to the improved accuracy of MALLS compared to viscometric methods for branched polymer architectures. The resulting polymers exhibited high molecular weights and relatively narrow molecular weight distributions. Table 1 indicates that the maximum number of 10 000 g/mol arms per star occurred using a DVB/*n*-BuLi ratio of 24:1. As expected, an important factor for the control of star polymer molecular weight is the DVB:initiator ratio. It is proposed that the highly rigid nature of the preformed arms may facilitate linking to the core. The average number of arms per star (*f*) were determined using the following formula, where %DVB is the weight percent of the DVB in the star:

$$f = ((M_{n}^{star}) - \%DVB(M_{n}^{star}))/M_{n(th)}^{arms}$$

Star-shaped polymers comprising arms with a number-average molecular weight of 10 000 g/mol were prepared at a linking efficiency ranging from 70% to 80%. Increased linking efficiencies were possible for star-

Scheme 1. Synthetic Methodology for Star-Shaped Polymers

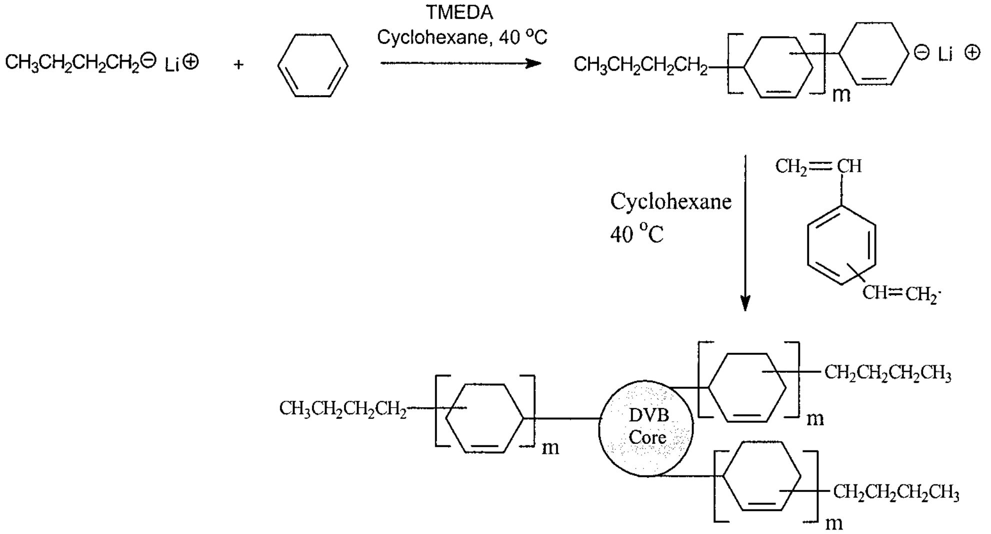

Table 1. Star-Shaped Polymers Synthesized with 10 000 and 5000 g/mol Arms[a]

DVB/ n-BuLi	M_n^{th} (arm), g/mol	M_n[b] (star)	no. of ams[c] (calc)	% conv[d]	M_w/M_n[e]
8:1	10 000	760 000	67	80	1.50
14:1	10 000	1 600 000	135	80	1.85
18:1	10 000	2 200 000	178	70	1.87
24:1	10 000	2 800 000	214	78	1.89
8:1	5 000	490 000	82	90	1.54
14:1	5 000	1 200 000	176	89	2.02

[a] Reaction conditions: cyclohexane at 40 °C with 5/4 ratio of TMEDA/n-BuLi. Number of arms per star (f) were determined by dividing M_n by the M_n^{th} of the arm. [b] The SEC conditions were as follows: $CHCl_3$, 25 °C, DRI/MALLS (absolute molecular weight). [c] The number of arms per star was determined by dividing the M_n by the arm M_n after subtraction of the DVB contribution to the molecular weight of the star-shaped polymer. [d] The percent conversion was determined by dividing the area of the star polymer in the GPC chromatogram by the total area after subtraction of the DVB contribution to the total area. [e] The molecular weight distribution for the star-shaped polymer; this does not include the uncoupled arms.

shaped polymers synthesized using 5000 g/mol arms (Table 1). 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 as shown in Figure 4. As the DVB/n-BuLi ratio was increased, the core size also increased, allowing for a greater number of arms attached to the core. The increase in polydispersity for higher DVB/n-BuLi ratios is likely due to the presence of star–star coupling. Characterization of the star-shaped polymers using MALLS enabled the identification of the larger molecular weight species. Juxtaposition of the light scattering data for star polymers synthesized from the 10 000 g/mol preformed arms (Figure 5) clearly shows the increasing presence of coupled stars as the DVB/n-BuLi ratio is increased. The length of the preformed arms does not appear to impact the degree of star–star coupling. In contrast, the molecular weight of the arms is an important factor that determines the number of arms coupled to the star core. Table 1 clearly indicates for a constant 8:1 DVB/n-BuLi ratio that star polymers with an arm length of 5000 g/mol have more arms (approximately 82 arms) than a star polymer with 10 000 g/mol arms (approximately 67 arms). Table 1 depicts a similar trend based on arm number-average molecular weight for other DVB/n-BuLi ratios. The DVB

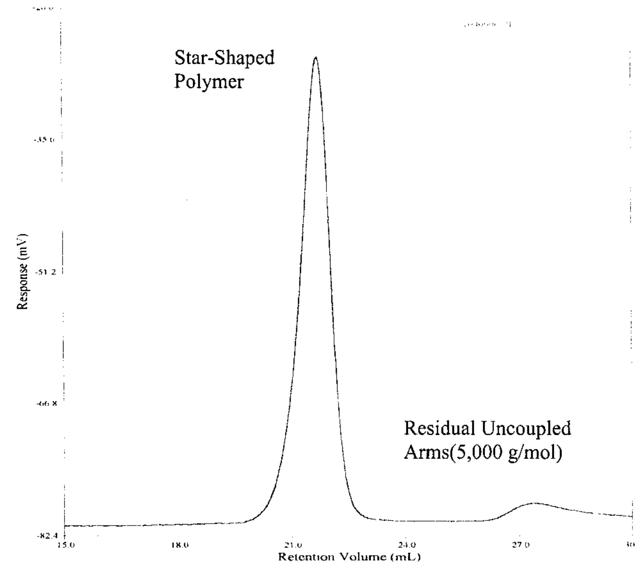

Figure 4. SEC of the star-shaped polymer with a DVB/n-BuLi ratio of 8:1 and an arm length of 5000 g/mol. SEC conditions: $CHCl_3$, 25 °C, DRI detector.

molar charge to the solution of preformed arms is significantly larger than DVB charges reported earlier in the synthesis of star-shaped polymers. To obtain a more comprehensive understanding of the solution properties of the novel star-shaped macromolecules containing poly(1,3-cyclohexadiene), a wide range ofDVB/n-BuLi ratios was studied. This enabled a more thorough study of the effect of architecture on the radius of gyration. In the study of the macromolecules with 10 000 g/mol arms, the radius of gyration (R_z) increased from 17.6 to 27.5 as the ratio of DVB/n-BLi increased from 8:1 to 14.1, as expected for traditional DVB-based star-shaped macromolecules. For the macromolecules synthesized with a ratio of DVB/n-BuLi of 18:1 and 24:1, the radius of gyration was 33.3 and 33.4. This indicates that the radius of gyration reaches a constant value that is independent of the ratio of DVB/n-BuLi. As the ratio exceeds 18:1, the radius of gyration is dependent upon the size of the DVB core. These results suggest that the architecture of the macromolecule changes from a more traditional DVB-based star-shaped polymer to a DVB microgel covered with poly(1,3-cyclohexadiene) arms.

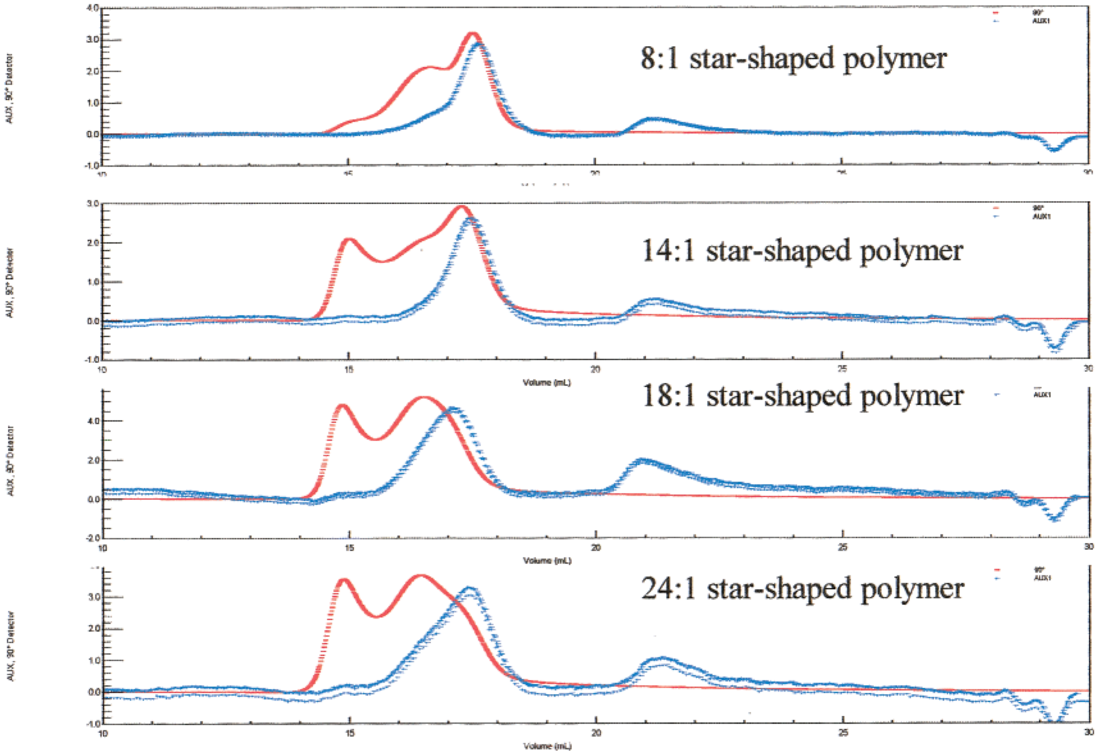

Figure 5. SEC of the 10 000 g/mol series of star-shaped polymers. The light scattering data (red) is superimposed on the refractive index data (blue).

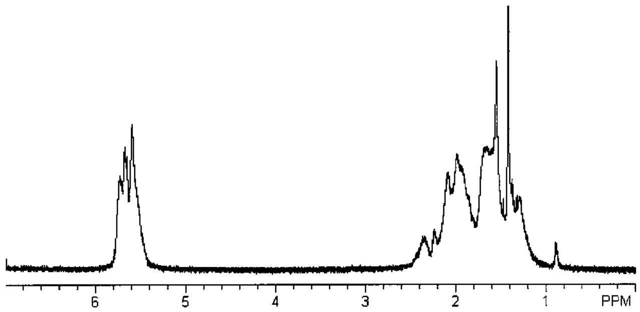

Figure 6. ^{1}H NMR spectra of the poly(1,3-cyclohexadiene) homopolymer.

The resulting polymers were characterized using both ^{13}C and ^{1}H NMR. The degree of 1,2- vs 1,4-addition was determined by comparing the integrations of the olefinic protons to the allylic protons in the spectra (Figure 6) and solving the following set of linear equations:

$$\text{area}_{\text{olefinic}} = 2x + 2y$$

$$x = \text{relative amount of 1,2 addition}$$

$$\text{area}_{\text{allylic}} = 3x + 2y$$

$$y = \text{relative amount of 1,4 addition}$$

The ratio of 1,2 vs 1,4 was found to be 70% 1,2 and 30% 1,4 using this method. Previous researchers have reported that the ratio of 1,2 to 1,4 in poly(1,3-cyclohexadiene) homopolymers is approximately 50% 1,2 and 50% 1,4.[19] However, a different synthetic strategy was employed, and the NMR measurements were performed at 150 °C in deuterated *m*-dichlorobenzene. Our earlier efforts have demonstrated that these NMR conditions may promote oxidation of poly(1,3-cyclohexadiene), altering the ratio of the allylic to olefinic protons.[38] A more comprehensive discussion of the epoxidation, oxidation, and chemical reactivity of poly(1,3-cyclohexadiene) homopolymers, block copolymers, and star-shaped polymers will be presented in a future paper.[39]

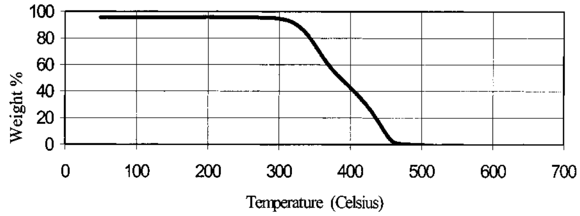

Figure 7. TGA of the star-shaped polymer with a DVB/*n*-BuLi ratio of 8:1 and an arm length of 5000 g/mol.

The thermal stabilities and transition temperatures of the resulting star-shaped polymers were determined using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. Figure 7 illustrates that the onset of weight loss for the star polymers occurs at 330 °C under nitrogen, which is consistent with earlier studies on block copolymers comprising poly(1,3-cyclohexadiene)s.[20] Differential scanning calorimetry indicated the presence of a single glass transition temperature at approximately 150 °C (Figure 8) for all star-shaped polymers. The DVB core size did not influence the glass transition temperature.

Optical Properties. To determine the optical properties of the resulting star polymers, the refractive indices were determined using ellipsometry as described earlier. As shown in Figure 9, both the star and homopolymers exhibited a large constant refractive index of 1.572 over a broad range of wavelengths from 1700 to 550 nm. The large absorbance of the polymer found below 600 nm is attributed to the aromatic core of the star and the olefinic sites in the repeating units. The homopolymer arms in the absence of aromatic inhibitor and the DVB core exhibit less absorbance in

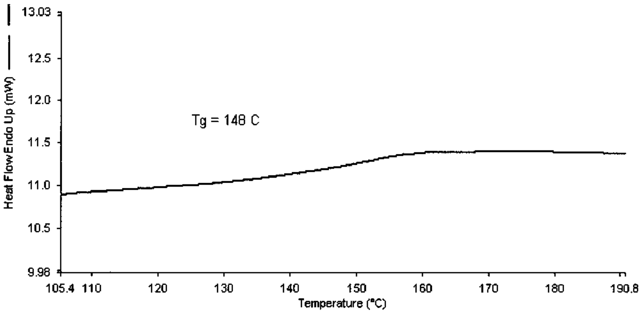

Figure 8. DSC of the star-shaped polymer with a DVB/*n*-BuLi ratio of 18:1 and an arm molecular weight of 10 000 g/mol.

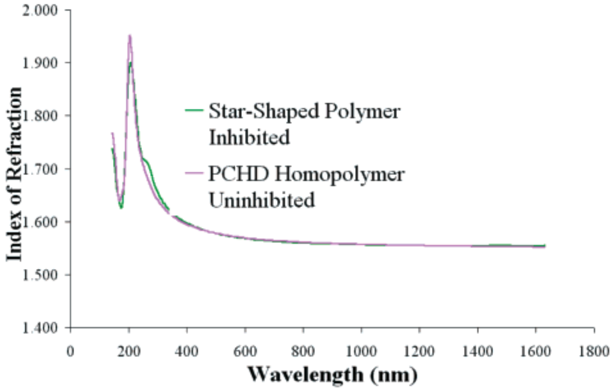

Figure 9. Refractive index of the star-shaped polymer and uninhibited homopolymer as a function of wavelength.

the aromatic region of the spectrum (approximately 250 nm).

Conclusions

These investigations demonstrate the utility of living anionic polymerization for the synthesis of novel poly(1,3-cyclohexadiene) DVB star-shaped polymers with various arm lengths using various DVB/*n*-BuLi ratios. In-situ FTIR spectroscopy was useful for the determination of polymerization kinetics ($k_p = 0.31$ L mol^{-1} s^{-1}), ensuring complete monomer conversion and optimization of DVB coupling. NMR spectroscopic studies indicated that the degree of 1,2-addition vs 1,4-addition was 70% 1,2-addition and 30% 1,4-addition. In-situ spectroscopy and obvious color changes indicated that the addition of DVB to poly(1,3-cyclohexadienyllithium) was rapid. The linking of the arms to the DVB core was improved at lower arm molecular weights of 5000 g/mol. Although increased molecular weights were achieved as the DVB/*n*-BuLi ratio was increased, it is presumed that the architecture changes from a conventional star at low ratios to a poly(1,3-cyclohexadiene)-coated microgel. The resulting star-shaped polymers were thermally stable to 330 °C in a nitrogen environment and exhibited a T_g value of 150 °C and a refractive index of 1.572 at 600 nm. The size of the DVB core did not affect the glass transition temperature. Current efforts are focused on the elucidation of the stereochemistry of poly(1,3-cyclohexadiene) homopolymers, and end-capping strategies will demonstrate the stereochemistry of the adjacent terminal unit. In addition, the preparation of well-defined thermoplastic elastomers comprising poly(1,3-cyclohexadiene) will be reported on the basis of our thorough understanding of the homopolymerization kinetics. Poly(1,3-cyclohexadiene) homopolymers, block copolymers, and star-shaped polymers serve as unique precursors for subsequent chemical modification. The oxidation and controlled epoxidation of a variety of polymer architectures will be reported in a future publication.

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