Synthesis of Block Copolymers Based on the Alternating Anionic Copolymerization of Styrene and 1,3-Cyclohexadiene

D. T. Williamson, T. D. Buchanan, C. L. Elkins, and T. E. Long*

Department of Chemistry and Polymeric Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0212

Received July 20, 2003; Revised Manuscript Received March 25, 2004

ABSTRACT: A series of poly(1,3-cyclohexadiene-*alt*-styrene)-containing block copolymers that exhibited predictable molecular weights and narrow molecular weight distributions were synthesized with various 1,3-cyclohexadiene contents (13−57 mol %). In situ FTIR spectroscopy in combination with the Mayo−Lewis graphical method was employed to determine the reactivity ratios for the anionic copolymerization of styrene and 1,3-cyclohexadiene. The reactivity ratios for 1,3-cyclohexadiene and styrene were 0.022 and 0.024, respectively, which indicated the formation of an alternating copolymer. The alternating copolymers served as suitable precursors for chemical modification and were either quantitatively aromatized or hydrogenated in a controlled fashion. The thermal stabilities of the modified copolymers were determined, and as expected, the hydrogenated copolymers exhibited improved thermal stability compared to that of poly(1,3-cyclohexadiene-*alt*-styrene)-containing block copolymers. However, the aromatized copolymers unexpectedly exhibited reduced thermal stability in both nitrogen and oxygen environments due to the introduction of labile benzylic hydrogens in the repeating unit.

Introduction

The synthesis of polymers containing poly(1,3-cyclohexadiene) (PCHD) has recently received significant interest.[1−9] These polymers exhibited excellent thermal properties due to a high glass transition temperature for both high 1,4-PCHD (80%) and 1,2-PCHD (70%) of approximately 100 and 150 °C, respectively.[4,10,11] The T_g for high 1,2-PCHD is over 200 °C higher than the T_g for high *cis*-1,4-polyisoprene, which demonstrates that poly(1,3-cyclohexadiene) is unique in the polydiene family. This unusually high T_g was attributed to the cyclic structure of the repeat unit of poly(1,3-cyclohexadiene), which obviously increases the degree of polymer rigidity relative to other acyclic dienes.[11] In addition, the cyclic nature of the repeat unit and the presence of a residual double bond renders poly(1,3-cyclohexadiene) as an ideal precursor for the synthesis of a broad range of high-performance functionalized polymers.[2]

Most anionic copolymerizations are "blocky copolymerizations", where one monomer is preferentially polymerized prior to the polymerization of the second monomer.[12] Because of the living nature of these chain growth copolymerizations, compositional heterogeneity is observed within the polymer chain, and a tapered block copolymer is typically formed. The synthesis of tapered block copolymers from the copolymerization of styrene and butadiene is a classical example of this effect.[12] In addition, Long et al. used this straightforward approach to synthesize tapered block copolymers of polystyrene and polyisoprene, while monitoring the copolymerization using in situ near-IR spectroscopy.[13] Although reports of blocky and random copolymerizations are common for anionic copolymerizations, there are no reports that describe alternating, alkyllithium-initiated copolymerizations.

In contrast, the behavior of most free radical copolymerizations lies between an "ideal copolymerization" or an "alternating copolymerization".[14] In an ideal copolymerization, the product of the reactivity ratios (r_1r_2) is 1.0, and the compositional distribution of monomers in the polymer chain at any time during the polymerization is random. In contrast, the product of the reactivity ratios in an alternating copolymerization (r_1r_2) is 0; the polymer composition is 1:1 and independent of the composition of the monomer feed. The polymerization mechanism becomes increasingly alternating as the r_1r_2 product approaches zero. The determination of accurate reactivity ratios is critical to understanding the reaction mechanism and predicting the approximate copolymer composition from the monomer composition.

Traditional approaches for determining accurate polymerization kinetic data include gravimetric and molecular weight analysis or reaction sampling followed by chromatographic or spectroscopic sampling. Reaction sampling techniques are often plagued by the introduction of oxygen or other impurities during sampling, and these impurities are particularly harmful to anionic polymerizations. Previous studies have shown in situ spectroscopy to be a viable alternative, state-of-the-art, real-time, monitoring technique that is well-suited to obtain monomer conversion data for polymerization processes.[15] This robust technique was also used to characterize a number of organolithium processes including the living anionic homopolymerization of 1,3-cyclohexadiene.[1] A number of recent reports have described the application of in situ mid-FTIR spectroscopy for the measurement of monomer conversion and subsequent determination of the reactivity ratios. These studies have included the determination of acrylonitrile/methyl acrylate and norbornene/maleic anhydride reactivity ratios.[16,17]

Facile chemical modification reactions that are directed at the residual double bond in the repeat unit provide for straightforward synthetic routes to PCHD derived polymers. Epoxidation,[18−20] hydrogenation,[18] and maleation[18,21] are a few examples of the modification reactions that were performed on conventional polydienes, such as polyisoprene and poly(1,3-butadiene).[12] Recent studies in our laboratories have examined

* Corresponding author: e-mail telong@vt.edu.

10.1021/ma035040c CCC: $27.50
Published on Web 05/19/2004

the synthesis and characterization of epoxidized poly(1,3-cyclohexadiene).[8] In contrast to other polydienes, poly(1,3-cyclohexadiene) was also previously demonstrated as a well-defined precursor for the synthesis of new families of poly(phenylene)-containing polymers.[22−26] Unfortunately, conventional poly(phenylene) homopolymers are typically intractable and insoluble and generally exhibit poor polymer processability.[21]

A variety of synthetic strategies were investigated to improve the solubility of poly(phenylene)-based polymers. First, the incorporation of pendant aliphatic groups on the polymer backbone was performed in an attempt to improve solubility without disrupting the conjugated backbone.[27] However, this method required the tedious synthesis of novel alkyl-substituted aromatic monomers. A more direct and cost-effective method involved the synthesis of diblock copolymers, wherein the poly(phenylene) block was attached to a more soluble block such as polystyrene.[24−26] This approach has typically employed PCHD blocks and a second solubilizing block, such as polystyrene. The PCHD block was subsequently aromatized at high temperatures (130 °C) in the presence an aromatizing agent, such as chloranil. Francois and co-workers have extensively studied the synthesis and performance of poly(styrene-*block*-phenylene) copolymers.[26,28] The reaction conditions used in these studies resulted in the undesirable oxidation of both the cyclohexene repeat unit and the main-chain benzylic position in the polystyrene repeat units. However, these copolymers exhibited interesting optical and electrical properties that were attributed to extended conjugation in the 1,4-substituted poly(phenylene) repeat unit. A third method that is typically employed to improve the solubility of highly rigid polymers involves the addition of comonomers; however, this approach disrupts the desirable conjugation length at sufficient concentrations of comonomer.[29]

Polyphenylenes exhibit excellent oxidative stability due to the lack of labile hydrogens. On the other hand, polydienes are more sensitive to oxidation due to their ability to form peroxy radicals at the allylic position.[30] For example, polystyrene, poly(1,3-butadiene), and polyisoprene were shown to readily form the peroxy radical, resulting in poor oxidative stability.[30] In contrast, polymers such as polyethylene and polypropylene do not readily form the peroxy radical and are less sensitive to oxidation. A fundamental understanding of thermooxidative stability is not only critical in preventing oxidation but is also important in the design of novel oxygen scavengers.[31,32]

We report herein the use of in situ mid-FTIR spectroscopy to measure the reactivity ratios for 1,3-cyclohexadiene/styrene anionic copolymerization using the Mayo−Lewis graphical approach. The 1,3-cyclohexadiene unit in alternating copolymers was subsequently aromatized using mild conditions (25 °C) in the presence of the quinone derivative, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The use of DDQ facilitated the use of extremely mild conditions and afforded relatively well-defined poly(phenylene-*alt*-styrene)-containing block copolymers.[33] The thermooxidative stability of the alternating copolymers was also investigated. In addition, a series of alternating copolymers that contained hydrogenated poly(1,3-cyclohexadiene) repeat units were synthesized, and the thermal stability in both nitrogen and oxygen environments was determined and compared to that in aromatized analogues.

Experimental Section

Materials. Styrene (Aldrich, 99%) was dried over calcium hydride (Aldrich, 95%) and distilled under reduced pressure (0.10 mmHg, 10 °C). 1,3-Cyclohexadiene (Acros, 99%) was degassed three times and vacuum-distilled (0.10 mmHg, 10 °C) from dibutylmagnesium (DBM, 0.89 M). s*ec*-Butyllithium (s*ec*BuLi) (FMC Corp., Lithium Division, 1.78 M in heptane) was used as received. Cyclohexane (Burdick Jackson, HPLC) 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. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, Acros, 98%) and hydrogen (Holox, 99.99%) were used as received. All reagents were transferred using syringe and cannula techniques under ultrapure (99.999%) nitrogen.

In situ Mid-FTIR. In situ mid-FTIR spectra were collected with a ReactIR 1000 (MCT detector, S/N = 7500, resolution = 4 cm^{-1}) (ASI Applied Systems, Millersville, MD) reaction system equipped with a light conduit and DiComp (diamond composite) insertion probe. Reaction data were analyzed using ASI ReactIR software. The details and capabilities of the ReactIR 1000 reaction analysis system based on total attenuated reflectance (ATR) were described in detail previously.[15,16]

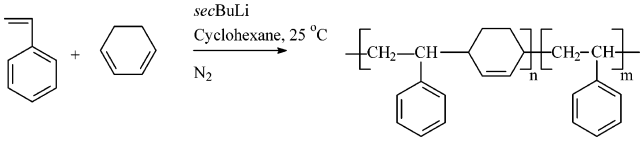
Polymerization. The anionic copolymerization of styrene and 1,3-cyclohexadiene was initiated with *sec*-BuLi in cyclohexane at 25 °C and allowed to proceed for 2 h to ensure quantitative conversion of styrene and 1,3-cyclohexadiene. Polymerizations were performed under a nitrogen atmosphere at 20 wt % monomer concentrations. A typical polymerization involved the addition of anhydrous cyclohexane (60 mL, 0.54 mol), styrene (5.85 g, 0.56 mol), and 1,3-cyclohexadiene (5.85 g, 0.75 mol) to a 100 mL round-bottomed flask. The solution was allowed to reach 25 °C, and *sec*-BuLi (0.65 mL, 1.15 mmol) was added to initiate the polymerization. The polymerization was allowed to proceed for 2 h and was terminated with degassed methanol (Burdick Jackson, HPLC grade, 1.0 mL). The resulting copolymer 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. This antioxidant was present during all subsequent polymer modification reactions.

Aromatization of Poly(1,3-cyclohexadiene-*co*-styrene) Copolymers. A dried, round-bottomed flask was charged with DDQ (18.1 g, 0.80 mol), a poly(1,3-cyclohexadiene-*co*-styrene) copolymer (5.0 g), and 1,2-dichlorobenzene (Aldrich, 99%, 500 mL). The flask was degassed with nitrogen in order to ensure the removal of residual oxygen and maintained at 25 °C for 48 h. The polymer was precipitated into 2-propanol (Burdick Jackson, HPLC grade, 500 mL), filtered, and dried in vacuo at 60 °C for 12 h.

Preparation of the Preformed Nickel Hydrogenation Catalyst. The nickel-based hydrogenation catalyst was prepared as previously described.[34] Cyclohexane (15 mL) and nickel octoate (Shepard Chemical Co., 0.228 g, 0.66 mmol) were added to a sealed round-bottomed flask. Triethyl aluminum (TEA, 1.36 mL, 1.62 mmol) was added dropwise to the homogeneous nickel solution. An opaque, black colloidal suspension formed immediately and was allowed to stir for 15 min at 25 °C under a nitrogen atmosphere.

Hydrogenation of Poly(1,3-cyclohexadiene-*co*-styrene). The copolymer was hydrogenated as previously described.[34] A typical hydrogenation involved the addition of a poly(1,3-cyclohexadiene-*co*-styrene) copolymer (1.0 g, 0.83 mmol), a preformed nickel catalyst (approximately 10 mL, 0.05 mmol), and cyclohexane to a pressure vessel. The pressure vessel was pressurized with hydrogen to 90 psi and vented three times. The vessel was finally pressurized with hydrogen (90 psi) and heated at 50 °C for 24 h. After hydrogenation, the nickel catalyst was extracted from the polymer solution using three citric acid (Aldrich, 98%, 500 mL, 50 mmol) washes. The solution was concentrated to 100 mL and precipitated into

Scheme 1. Alternating Copolymerization of 1,3-Cyclohexadiene and Styrene[a]



[a] Copolymerizations were performed at 25 °C in cyclohexane using *sec*-BuLi.

2-propanol (600 mL), filtered, and dried in vacuo at 60 °C for 24 h.

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 (SEC). 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 online using the calibration constant for the RI detector and the mass of the polymer sample. SEC measurements were performed at 40 °C in chloroform at a flow rate of 1.0 mL/min. For all samples, it was assumed that 100% of the polymer eluted from the column during the measurement. TGA measurements were performed on a TA Instruments Hi-Res TGA 2950 thermogravimetric analyzer (TGA) under nitrogen at a heating rate of 10 °C/min. Mass spectra were collected using a Balzars Quadstar 422 which was attached in series to the TGA instrument.

Results and Discussion

In situ FTIR was used to monitor monomer conversion in real time, and the monomer reactivity ratios for the 1,3-cyclohexadiene/styrene anionic copolymerization (Scheme 1) were determined. The reaction flask including the attached ATR-based infrared probe was purged with nitrogen and maintained at 5−7 psi. The reactor was initially titrated with poly(styryllithium) to remove any deleterious impurities and subsequently rinsed with cyclohexane prior to the addition of the reactants. Strong vinylene carbon−hydrogen (=C−H) absorbances of the monomers were observed and facilitated the kinetic analysis of the copolymerization (Figure 1). The vinylene carbon−hydrogen absorbance for 1,3-cyclohexadiene was observed at 656 cm^{-1}, and the vinylene−carbon hydrogen absorbance for styrene was observed at 776 cm^{-1}.

Anionic reactivity ratios for 1,3-cyclohexadiene and styrene were determined via graphical analysis of the rearranged copolymer composition equation developed by Mayo and Lewis.[14] This method relies on the measurement of copolymer composition at low degrees of conversion (0−10%), which ensures that the monomer feed composition does not change significantly during the polymerization. In situ mid-FTIR spectroscopy was used to determine the monomer concentration at low degrees of conversion (0−10%) in a real-time fashion. The monomer conversion data were subsequently used to calculate the instantaneous copolymer conversion (d[styrene]/d[1,3-cyclohexadiene]) based upon the terminal model. In this study, five initial styrene:1,3-cyclohexadiene molar ratios were analyzed: 40:60, 45:55, 50:50, 55:45, and 60:40. Values of d[styrene]/d[1,3-cyclohexadiene] were calculated from the real-time mid-FTIR data, and the $r_{styrene}$ and $r_{1,3-cyclohexadiene}$ values were determined using the instantaneous copolymer equation. Values ranging from −1 to 2.8 were chosen for $r_{1,3-cyclohexadiene}$, and $r_{styrene}$ values were then calculated for each of the assumed $r_{1,3-cyclohexadiene}$ values. The $r_{styrene}$ and $r_{1,3-cyclohexadiene}$ values were then estimated using the Mayo−Lewis graphical method (Figure 2). The average value of $r_{styrene}$ and $r_{1,3-cyclohexadiene}$ was 0.024 and 0.022 with an error of approximately 10%, respectively. This is the first reported use of in situ mid-FTIR spectroscopy to determine the reactivity ratios for an anionic copolymerization.

Previously, Mays et al. suggested that the copolymerization of styrene and 1,3-cyclohexadiene may be random.[9] In contrast, reports by Francois et al. concluded that the copolymerization of styrene and 1,3-cyclohexadiene had a tendency to polymerize in an alternating fashion.[25] The studies by Francois utilized polymerization rate constants (k_{11} and k_{12}) that were previously reported in the literature or were determined experimentally.[26,27] Francois et al. reported $r_{styrene}$ and $r_{1,3-cyclohexadiene}$ values of 1.86 and 0.11, respectively. Unfortunately, the experimental approach to determine the crossover from poly(1,3-cyclohexadienyllithium) to styrene (k_{21}) and poly(styrylithium) to 1,3-cyclohexadiene (k_{12}) was not described. The differences between our classical Mayo−Lewis approach and the method used by Francois et al. may account for the disparity in the values for $r_{styrene}$ and $r_{1,3-cyclohexadiene}$.

A series of poly(1,3-cyclohexadiene-*alt*-styrene)-containing block copolymers were synthesized according to Scheme 1. These copolymerizations were performed at 25 °C to minimize the occurrence of deleterious side reactions, which are associated with the anionic polymerization of 1,3-cyclohexadiene. These side reactions were attributed earlier to termination and chain transfer of the monomer allylic hydrogens.[22,23] Previous studies have utilized similar strategies to ensure the living nature of the homopolymerization of 1,3-cyclohexadiene.[3,22,23] Upon the addition of the *sec*-BuLi initiator, the copolymerization solution immediately turned yellow. The polymerization remained homogeneous throughout the entire polymerization process. In contrast, previous reports from our laboratories have described the heterogeneous nature of 1,3-cyclohexadiene homopolymerizations at 40 °C in the presence of the additive tetramethylethylenediamine.[1] The improved solubility of the poly(1,3-cyclohexadiene-*alt*-styrene) alternating copolymers relative to poly(1,3-cyclohexadiene) homopolymers was attributed to the presence of the styrene comonomer. A series of copolymers that contained 13−57 wt % cyclohexadiene content were prepared to further examine the effect of polymer composition on the subsequent reactivity and thermal stability.

The unique, alternating nature of the styrene/1,3-cyclohexadiene copolymerization enabled the synthesis of block copolymers comprised of a block of poly(1,3-cyclohexadiene-*alt*-styrene) attached to a block of polystyrene. It was expected that, following the quantitative conversion of 1,3-cyclohexadiene in an alternating fashion, the remaining styrene would form a polystyrene block. The composition, molecular weights, and molecular weight distributions for representative copolymers are summarized in Table 1. The targeted number-average molecular weight for all the block copolymers was 10 000. In general, the molecular weight distributions of the copolymers remained relatively narrow, and the polymer yields were quantitative. The molecular

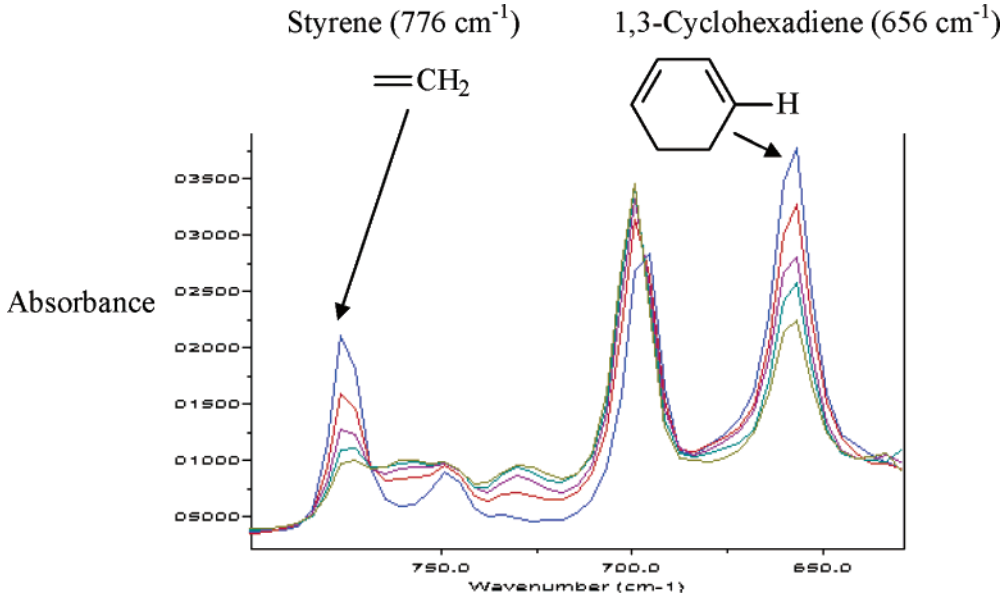


Figure 1. In situ FTIR spectra illustrating both the disappearance of the 1,3-cyclohexadiene absorption at 657 cm^{-1} and the disappearance of the styrene absorption at 776 cm^{-1}. Scan rate = 5 scans/min.

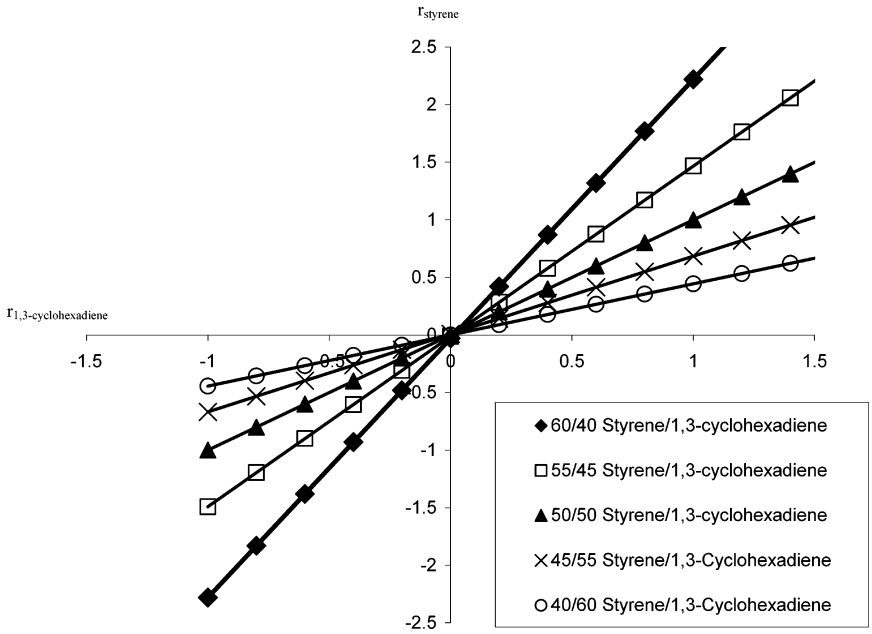


Figure 2. Mayo–Lewis graphical determination of the styrene and 1,3-cyclohexadiene reactivity ratios.

Table 1. Evaluation of Molecular Weights and Composition of the Poly(1,3-cyclohexadiene-*alt*-styrene) Block Copolymers Prepared via Anionic Copolymerization[a]

styrene:CHD (mol: mol):	styrene (mol %)[b]	poly(1,3-CHD-*alt*-styrene) block size[c]	$\langle M_n \rangle^c$ of block copolymer	$\langle M_w \rangle / \langle M_n \rangle^c$
40:60	43	12000	12 000	1.27
70:30	70	7260	12 100	1.09
90:10	87	2240	11 200	1.05

[a] All copolymerizations were performed at 25 °C for 2 h. [b] Determined using ^{1}H NMR spectroscopy. [c] GPC conditions: chloroform, 40 °C, MALLS.

weight distribution of the nearly perfectly alternating copolymer of poly(1,3-cyclohexadiene-*alt*-styrene) increased (1.27) relative to the other copolymers (1.09) that contained a smaller poly(1,3-cyclohexadiene-*alt*-styrene) block. Despite an increase in the molecular weight distribution, which was attributed to competitive termination and chain transfer reactions that occurred at higher 1,3-cyclohexadiene levels (>50%), all polymerizations were quantitative (>95%). Direct determination of the degree of 1,2-addition vs 1,4-addition was not possible using ^{1}H NMR spectroscopy in the copolymers due to the presence of overlapping polystyrene resonances. Therefore, a poly(1,3-cyclohexadiene) homopolymer was synthesized under identical synthetic conditions to estimate the percentage of 1,2- vs 1,4-addition for the poly(1,3-cyclohexadiene) repeat units. Based on previous literature, the homopolymer contained 20% 1,2-addition and 80% 1,4-addition units.[7] All copolymers were assumed to contain approximately 80% 1,4-addition for the cyclohexadiene repeat unit. The residual double bonds in the cyclic 1,3-cyclohexadiene repeat unit were subsequently subjected to aromatization or hydrogenation processes.

A number of previous studies have examined the hydrogenation of poly(1,3-cyclohexadiene) homopoly-

Scheme 2. Synthetic Methodology For the Quantitative Hydrogenation of Poly(1,3-cyclohexadiene-*alt*-styrene)-Containing Block Copolymers

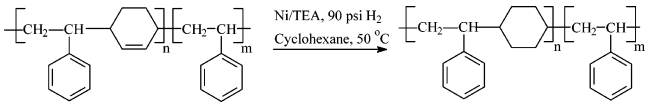


Table 2. DSC and GPC Characterization of Poly(cyclohexane-*alt*-styrene) Block Copolymers Prepared via the Quantitative Hydrogenation of Poly(1,3-cyclohexadiene-*alt*-styrene)-Containing Block Copolymers Using a Preformed Nickel Octoate/ Triethylaluminum Catalyst[a]

precursor mol wt	poly(cyclohexane-*alt*-styrene) block size[c]	% conv[b]	$\langle M_n \rangle^c$	$\langle M_w \rangle / \langle M_n \rangle^c$	T_g (°C)[d]
12 000	13 100	99	13 100	1.27	131
12 100	7 440	99	12 400	1.11	110
11 200	2 280	99	11 400	1.10	104

[a] The percent hydrogenation was determined via ^{1}H NMR spectroscopy. [b] Determined via ^{1}H NMR spectroscopy. [c] GPC conditions: chloroform, 40 °C, MALLS. [d] DSC conditions: 10 °C/min, nitrogen.

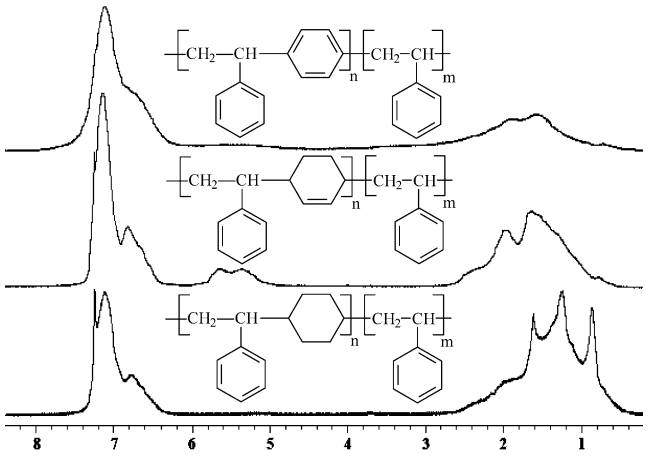


Figure 3. ^{1}H NMR spectra of a poly(phenylene-*alt*-styrene)-*block*-polystyrene (top spectrum), poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene (middle spectrum), and poly(cyclohexane-*alt*-styrene)-*block*-polystyrene.

mers and block copolymers for the synthesis of poly(cyclohexane) copolymers.[4,11] As expected, poly(cyclohexane) containing high levels of 1,2-enchainment typically exhibited an exceptionally high T_g (220 °C) for a cycloaliphatic polymer. Thus, poly(1,3-cyclohexadiene-*alt*-styrene)-containing block polymers were quantitatively hydrogenated (Scheme 2), resulting in a series of poly(cyclohexane-*alt*-styrene)-containing block copolymers (Table 2). Based on the literature, this is the first report of the hydrogenation of poly(1,3-cyclohexadiene) using a nickel octoate and triethylaluminum cocatalyst system. It was expected that these novel copolymers would exhibit a higher glass transition temperature compared to that of polystyrene. An examination of the ^{1}H NMR spectral region from 6.0 to 6.2 ppm revealed that hydrogenation was quantitative (Figure 3). These polymers were further characterized using GPC analysis to ensure that the hydrogenation proceeded in the absence of cross-linking or chain scission. The molecular weights of the hydrogenated copolymers agreed well with the molecular weights of the precursor polymers, and the molecular weight distributions remained narrow. Thus, the quantitative hydrogenation of the copolymers proceeded in the absence of appreciable chain scission or cross-linking. Previous reports using other coordination catalysts have described the partial hydrogenation of polystyrene sequences in block copolymers.[35] To verify the absence of polystyrene hydrogenation, a ^{1}H NMR spectroscopic comparison of the mole percent of the poly(cyclohexane) and polystyrene repeat units was performed to confirm that hydrogenation of the aromatic ring did not occur. ^{1}H NMR spectroscopy confirmed that the mole percent of poly(cyclohexane) repeat units agreed well with the mole percent of poly(1,3-cyclohexadiene) repeat units present in the precursor (Table 1). Hydrogenation of the polystyrene repeat units would have increased the mole percent of cyclohexane containing repeat units. Thus, it was concluded that quantitative hydrogenation of the copolymer was selective for the poly(1,3-cyclohexadiene) repeat unit.

Table 3. GPC Characterization of Poly(phenylene-*alt*-styrene)-Containing Block Copolymers Prepared via the Quantitative Aromatization of Poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene Copolymers[a]

precursor mol wt	poly(phenylene-*alt*-styrene) block size[c]	% conv[b]	$\langle M_n \rangle^c$	$\langle M_w \rangle / \langle M_n \rangle^c$
12 000	*d*	*d*	*d*	*d*
12 100	7200	98	12 000	1.13
11 200	1880	98	9 390	1.08

[a] The percent conversion was greater than 98%. The absence of elimination at the benzylic position was verified using ^{1}H NMR spectrscopy. [b] Determined via ^{1}H NMR. [c] GPC conditions: chloroform, 40 °C, MALLS. [d] The polymers were insoluble in $CHCl_3$.

As previously mentioned, the poly(cyclohexane-*alt*-styrene)-containing block copolymers were expected to exhibit a higher T_g than polystyrene. The T_g of the poly(1,3-cyclohexadiene-*alt*-styrene)-containing block copolymer precursors were approximately 100 °C for all copolymer compositions. Table 2 indicates that the T_g of the copolymers increased with an increase in the poly(cyclohexane) concentration, and the T_g of the poly(cyclohexane-*alt*-styrene) copolymer containing the highest amount of cyclohexane units was 130 °C. The presence of a single glass transition temperature indicated that the poly(cyclohexane-*alt*-styrene) and the polystyrene blocks formed a single phase, likely due to the low molecular weight of the polymer blocks. A linear plot of the T_g vs composition that is expected for random copolymers was observed.[36]

The poly(1,3-cyclohexadiene-*alt*-styrene)-containing block copolymers were aromatized using DDQ in order to investigate the influence of a doubly benzylic carbon on thermal stability. To minimize the possibility of oxidation at the benzylic position in the polystyrene unit, the aromatization reaction was performed at 25 °C in the presence of DDQ. Francois and co-workers demonstrated that the aromatization of poly(styrene-*alt*-1,3-cyclohexadiene) copolymers at elevated temperatures resulted in the introduction of an olefin in the polystyrene repeat unit due to oxidation at the benzylic position.[26] To avoid oxidation at the polystyrene benzylic position, the aromatization reaction was performed at 25 °C with DDQ. The results of the aromatization of these copolymers are summarized in Table 3. Characterization of these copolymers using GPC indicated that the aromatization of the random copolymers was performed in the absence of significant branching or degradation (Figure 4). However, preliminary studies

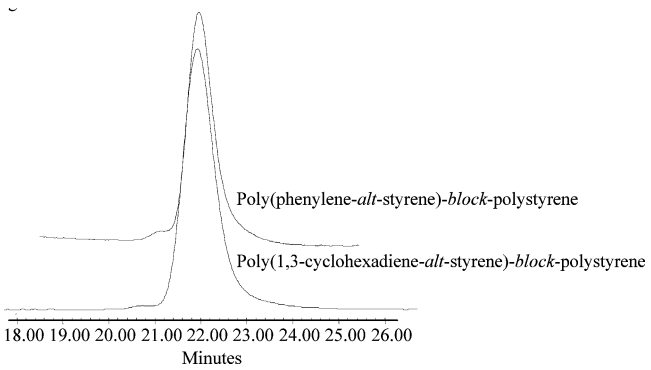


Figure 4. GPC traces of poly(phenylene-*alt*-styrene)-*block*-polystyrene (top curve) and poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene.

indicated that any attempts to perform the aromatization at higher polymer concentrations (>0.02 g/mL) resulted in branching, and GPC analysis indicated an increase in both molecular weight and molecular weight distribution. The copolymers that contained 30 and 13 wt % phenylene repeat units were highly soluble in a variety of organic solvents (chloroform, dichlorobenzene). ^{1}H NMR spectroscopy (Figure 3) was used to determine the degree of aromatization, which was determined to be greater than 95%. The ratio of ortho to para polyphenylene unit repeat units was 1:4 and was calculated on the basis of the ratio of 1,2-addition vs 1,4-addition. The introduction of trace levels of DDQ (<1%) into the polymer during the aromatization reaction was previously described,[37] and no attempts to minimize this minor reaction were performed. Moreover, ^{1}H NMR spectroscopy verified that residual DDQ and any significant related byproducts were removed beyond the NMR detection limit (<1 mol %).

The thermal stabilities of the poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene block copolymers and their hydrogenated and aromatized derivatives were determined via thermogravimetric analysis. As determined using ^{1}H NMR spectroscopy, all the samples contained 30 mol % of the poly(1,3-cyclohexadiene) repeat units. The weight loss profile of these polymers was determined in both nitrogen (Figure 5) and oxygen environments (Figure 6). In a nitrogen environment, the onset of weight loss of poly(1,3-cyclohexadiene-*alt*-styrene)-containing block copolymer was 340 °C. As expected, the hydrogenated analogue, i.e., poly(cyclohexane-*alt*-styrene)-containing block copolymer, was stable to higher temperatures (380 °C). This improved thermal stability was attributed to the removal of the reactive allylic hydrogens upon hydrogenation. Surprisingly, the aromatized analogue, i.e., the poly(phenylene-*alt*-styrene)-containing block copolymer, exhibited reduced thermal stability in nitrogen and proceeded through a stepwise degradation mechanism (Figure 5). Typically, poly(phenylene)-containing polymers exhibit improved thermal stability due to the presence of additional aromatic units. However, the copolymers in this study contained a doubly benzylic linkage that connected a polyphenylene unit to a polystyrene unit (Scheme 3). This doubly benzylic linkage was proposed to account for the initial degradation step in the multistep process. The weight

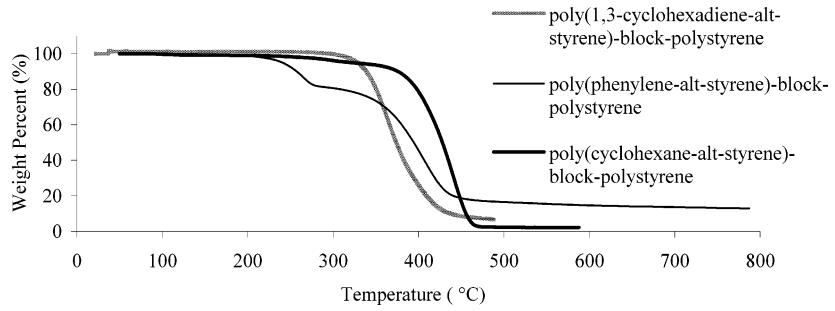


Figure 5. Thermogravimetric analysis of poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene, poly(cyclohexane-*alt*-styrene)-*block*-polystyrene, and poly(phenylene-*alt*-styrene)-*block*-polystyrene in a nitrogen environment. The heating rate was 10 °C/min.

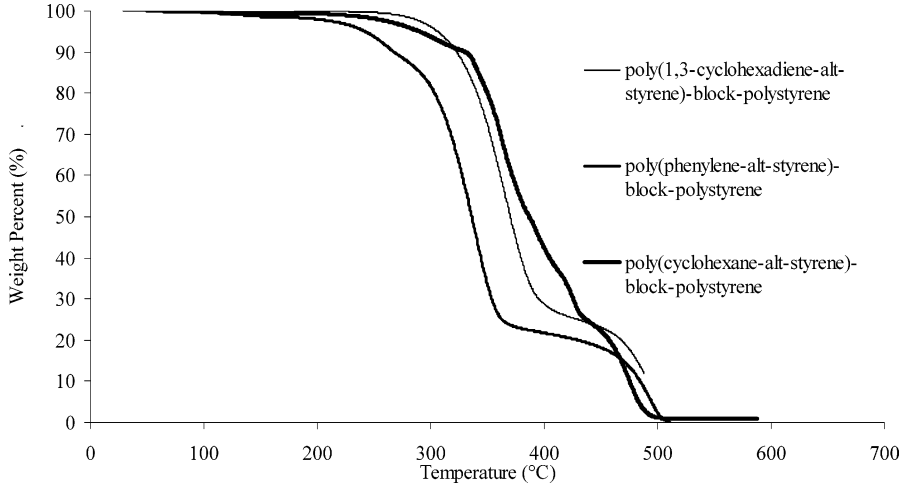
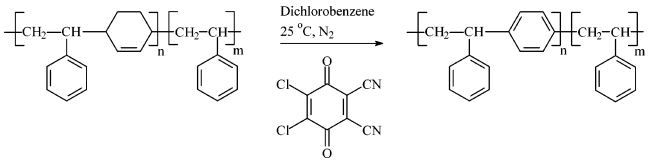


Figure 6. Thermogravimetric analysis of poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene, poly(cyclohexane-*alt*-styrene)-*block*-polystyrene, and poly(phenylene-*alt*-styrene)-*block*-polystyrene in an oxygen environment. The heating rate was 10 °C/min.

Scheme 3. Aromatization of Poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene Copolymers for the Synthesis of Poly(phenylene-*alt*-styrene)-*block*-polystyrene Copolymers



loss in the initial step at 210 °C was approximately 19 wt %, which correlated well with the percentage of polyphenylene present in the polymer (22 wt % as determined by ^{1}H NMR). In addition, the formation of 4,4′-dimethylbiphenyl that resulted from the thermal degradation at the doubly benzylic position was monitored using TGA-MS. 4,4′-Dimethylbiphenyl formation was studied by monitoring molecular ion fragments at 89, 115, 152, 167, and 182 amu.[38] In addition, isothermal analysis performed at 210 °C demonstrated that the production of 4,4′-dimethylbiphenyl was associated with the initial 19 wt % loss. These results supported the role of the doubly benzylic position in the degradation mechanism, which involves chain scission between the benzylic position of the polystyrene repeat unit and the polyphenylene repeat unit. The presence of alternative degradation products, such as xylene or a styrene−cyclohexadiene dimer, was not detected. The thermal stability of the various copolymers differed in the presence of oxygen, and poly(cyclohexane-*alt*-styrene)- and poly(1,3-cyclohexadiene-*co*-styrene)-containing block copolymers both initially lost weight at approximately 300 °C (Figure 6). The poly(phenylene-*alt*-styrene)-containing block copolymers exhibited a weight loss at 250 °C, which was attributed to the presence of the doubly benzylic linkage connecting the polystyrene to the polyphenylene repeat unit.

Conclusion

In situ mid-FTIR was successfully used to determine the reactivity ratios for the anionic copolymerization of 1,3-cyclohexadiene and styrene. The real-time data were readily transformed using the classical Mayo−Lewis approach, and 1,3-cyclohexadiene and styrene exhibited reactivity ratios of 0.022 and 0.024, respectively. Subsequently, the unique, alternating nature of this anionic copolymerization enabled the synthesis of an interesting family of poly(1,3-cyclohexadiene-*alt*-styrene)-containing block copolymers. These copolymers were transformed via both hydrogenation and aromatization to novel poly(cyclohexane-*alt*-styrene)- and poly(phenylene-*alt*-styrene)-containing block copolymers, respectively. These novel copolymers were characterized thermally and were compared to poly(1,3-cyclohexadiene-*alt*-styrene) block copolymer precursors. The poly(cyclohexane-*alt*-styrene)-containing block copolymers were the most thermally stable, while the poly(phenylene-*alt*-styrene) block copolymers were the least thermally stable in both a nitrogen and an oxygen environment. Future studies will utilize the alternating, anionic copolymerization of 1,3-cyclohexadiene and styrene to prepare a series of novel alternating copolymers with unique polar functionality.

Acknowledgment. The authors acknowledge the financial support of Kraton Polymers, the Petroleum Research Fund (ACS−PRF #35190-AC7) as administered by the American Chemical Society, and the NASA−Langley GSRP program. In addition, the FMC Lithium Division is acknowledged for their gracious donation of alkyllithium reagents.

References and Notes

(1) Williamson, D. T.; Elman, J. F.; Madison, P. H.; Pasquale, A. J.; Long, T. E. *Macromolecules* **2001**, *34*, 2108.
(2) Williamson, D. T.; Brazhnik, K.; Pasquale, A. J.; Long, T. E. *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2000**, *41*, 1544.
(3) Hong, K.; Mays, J. W. *Macromolecules* **2001**, *34*, 782.
(4) Imaizumi, K.; Ono, T.; Natori, I.; Sakuri, S.; Takedo, K. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 13.
(5) Natori, I.; Inoue, S. *Macromolecules* **1998**, *31*, 982.
(6) Natori, I.; Inoue, S. *Macromolecules* **1998**, *31*, 4687.
(7) Williamson, D. T.; Glass, T. E.; Long, T. E. *Macromolecules* **2001**, *34*, 6144.
(8) Williamson, D. T.; Mather, B. D.; Long, T. E. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *41*, 84.
(9) Hong, K.; Mays, J. W. *Macromolecules* **2001**, *34*, 3540.
(10) Williamson, D. T.; Long, T. E. *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2002**, *43*, 330.
(11) Natori, I.; Imaizumi, K.; Yamagish, H.; Kazunori, M. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1657.
(12) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel Dekker: New York, 1996.
(13) Long, T. E.; Lui, H. Y.; Schell, D. M.; Teegarden, D. M.; Uerz, D. S. *Macromolecules* **1993**, *26*, 6237.
(14) Painter, P. C.; Coleman, M. M. *Fundamentals of Polymer Science*, 2nd ed.; Technomic: Lancaster, 1997.
(15) Pasquale, A. J.; Long, T. E. *Macromolecules* **1999**, *32*, 7954.
(16) Pasquale, A. J.; Lizotte, J. R.; Williamson, D. T.; Long, T. E. *Polym. News* **2002**, *27*, 272.
(17) Wiles, K. B.; Bhanu, V. A.; Pasquale, A. J.; Long, T. E.; McGrath, J. E. *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2001**, *42*, 608.
(18) Nor, H.; Ebdon, J. R. *Prog. Polym. Sci.* **1998**, *23*, 143.
(19) Sakai, T.; Kihara, N.; Endo, T. *Macromolecules* **1995**, *28*, 4701.
(20) Roland, C. M.; Kallitsis, J. K.; Gravalos, K. G. *Macromolecules* **1993**, *26*, 6474.
(21) Odian, G. *Principles of Polymerization*; John Wiley and Sons: New York, 1991.
(22) Francois, B.; Zhong, X. F. *Makromol. Chem.* **1990**, *191*, 2743.
(23) Zhong, X. F.; Francois, B. *Makromol Chem* **1990**, *191*, 2735.
(24) Mignard, E.; Tachon, C.; Francois, B. *Synth. Met.* **1999**, *102*, 1246.
(25) Francois, B.; Izzillo, S.; Iratcabal, P. *Synth. Met.* **1999**, *102*, 1211.
(26) Francois, B.; Widawski, G.; Rawiso, M.; Cesar, B. *Synth. Met.* **1995**, *69*, 463.
(27) Marsitzky, D.; Brand, T.; Geerts, Y.; Klapper, M.; Mullen, K. *Macromol. Rapid Commun.* **1998**, *19*, 385.
(28) Mignard, E.; Hiorns, R. C.; Francois, B. *Macromolecules* **2002**, *35*, 6132.
(29) Rusanov, A. L.; Keshtov, M. L.; Belomoina, N. M. *High Perform. Polym.* **2001**, *13*, 153.
(30) Grassie, N.; Scott, G. *Polymer Degradation Stabilization*; Cambridge University: Cambridge, 1985.
(31) Karovicova, J.; Simko, P. *J. Chromatogr., A* **2000**, *882*, 271.
(32) Allen, D. W.; Clench, M. R.; Crowson, A.; Leathard, D. A. *J. Chromatogr.* **1993**, *629*, 283.
(33) Hiorns, R. C.; Francois, B. Personal communication.
(34) Hoover, J. M.; Ward, T. C.; McGrath, J. E. *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1985**, *26*, 252.
(35) Falk, J. C. *J. Polym. Sci., Part A: Polym. Chem.* **1971**, *9*, 2617.
(36) Sperling, L. H. *Introduction to Physical Polymer Science*, 3rd ed.; Wiley-Interscience: New York, 2001.
(37) Xhong, X. F.; Francois, B. *Makromol. Chem.* **1991**, *192*.
(38) Stein, S. E. NIST Standard Reference Data Base, 2001; Vol. 2002.

MA035040C