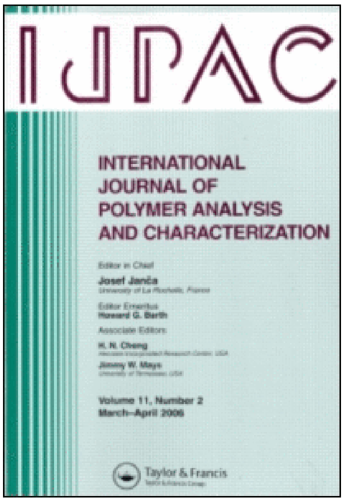

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Synthesis and Molecular and Morphological Characterization of Poly(p-Trimethylsilyl Styrene) and Diblock Copolymers with Poly(1,3-Cyclohexadiene)

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Abstract: We report the synthesis of a silylated monomer, specifically p-trimethylsilyl styrene, its homopolymerization, and its block copolymerization with 1,3-cyclohexadiene. Controlled Grignard reactions were adopted for the preparation of the monomer. Anionic polymerization high-vacuum techniques were employed for all polymerization procedures. The kinetics of poly(p-trimethylsilyl styrene) homopolymers were also studied. Molecular characterization for all intermediate and final products was accomplished via size exclusion chromatography, membrane osmometry, and proton nuclear magnetic resonance spectroscopy. Finally, the self-assembly of the block copolymers was studied with transmission electron microscopy, where well-ordered microstructures were observed (alternating lamellae and hexagonally closed packed cylinders).

Keywords: Block copolymers; Molecular characterization; Morphology; Poly(p-trimethylsilyl styrene); Poly(1,3-cyclohexadiene)

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INTRODUCTION

It is well known that self-assembly is a main characteristic of block copolymers. By carefully selecting the volume fraction and the type of blocks, these copolymers can be utilized for the synthesis of materials with a large range of different symmetries and morphologies leading to nanopatterns with fully controlled number and size of pores. The size and dimensions of these pores can be further manipulated either by achieving mixtures of copolymers with one or more homopolymers or by controlling the molecular weight. The most studied block copolymers are these of the PS-b-PI type (where PS: polystyrene and PI: polyisoprene). Especially in the case where polystyrene is substituted with a silane group, the formation of nanoporous or nanorelief ceramic composites is possible, as already reported in the literature.[1] Actually, it has been reported that the polyisoprene blocks can be exclusively removed utilizing the appropriate oxidation technique (reactive ion etching, ozonolysis, ultraviolet exposure), while the substituted polystyrene block creates a ceramic matrix of silicon oxycarbide when heated up to temperatures as high as 400°C. The uniqueness of the samples synthesized for the aforementioned application was the structure in bulk employed.[2] It was the first time that the double gyroid morphology was observed in a silicon-containing block copolymer consisting of two three-dimensionally continuous, interpenetrating but nonintersecting networks of the minority phase in a matrix of the majority segments.

By using anionic polymerization and controlled chlorosilane chemistry, we were able to synthesize a silylated monomer that has not been extensively studied in the literature.[3–4] In particular, p-trimethylsilyl styrene was synthesized, followed by the synthesis of three low molecular weight homopolymers of poly(p-trimethylsilyl styrene), 3,000 g/mol, 10,000 g/mol, and 25,000 g/mol, in order to verify the kinetics during the stage of propagation and to compare them with those of simple polystyrene.

Another main purpose of this research was the synthesis of linear diblock (A-b-B) copolymers, where A is poly(p-trimethylsilyl styrene) (PTMSS) and B is poly(1,3-cyclohexadiene) (PCHD), modification of their finally adopted morphological structure, and a comparison of their behavior as nanoporous or nanorelief composites with the corresponding structures already observed in the literature.[1] The latter case will be reported elsewhere since the results already obtained need further investigation.

PCHD is a very interesting polydiene due to its improved thermal, chemical, and mechanical properties. It can be dehydrogenated to poly(phenylene) (PPP), a highly conductive polymer, either by tetrachloro-1,4-benzoquinone (*p*-chloranil) or by halogenation followed by pyrolysis. It can also be converted to poly(cyclohexylene) (PCHE) by homogeneous or heterogeneous hydrogenation. PCHE has the highest glass transition temperature ($T_g \sim 200°C$ for 1,4-PCHE and $T_g \sim 250°C$ for 1,2 PCHE) among all hydrocarbon polymers, low specific gravity, high heat resistance, high flexural modulus, and other desirable properties.[5]

Natori was the first to report the controlled anionic polymerization of 1,3-CHD with the *n*-BuLi/*N,N,N′,N′*-tetramethylenediamine (TMEDA) initiating system in a 4/5 molar ratio with n-BuLi.[6] The microstructure of the obtained PCHD was almost symmetric for the two isomeric microstructures obtained, being 1,2 and 1,4 respectively.[7] By using the above initiating system, random copolymers of CHD with butadiene, styrene, and isoprene as well as diblock and triblock copolymers of CHD with butadiene or styrene were synthesized.[8] Using the *n*-BuLi/TMEDA initiating system and divinylbenzene, Long and coworkers were able to synthesize PCHD stars,[9] which after hydrogenation produced PCHE stars.[10] 1,4-Diazabicyclo-[2.2.2]octane (DABCO) with *sec*-BuLi was used as another initiating system by Hong and Mays,[11] leading to PCHD with ~90% 1,4 microstructure. With the DABCO initiating system, block copolymers,[12] three-arm star homopolymers, and starblock copolymers of styrene and CHD were prepared.[13] Miktoarm stars with one PCHD arm and two or three poly(butadiene) (PB) arms were also prepared using the same system and were transformed to the corresponding miktoarm stars of PCHE and polyethylene (PE) by complete hydrogenation.[14]

Due to the increased interest in working with such materials, in this article we report only the preparation of the silylated monomer (p-trimethylsilyl styrene) and the synthesis of its corresponding homopolymers as well as copolymers with PCHD, which have not been reported previously in the literature. Molecular and morphological characterization certifies the formation of well-defined, monodispersed, and morphologically well-organized materials with many potential applications.

EXPERIMENTAL SECTION

Materials

All samples were prepared by anionic polymerization using high-vacuum techniques in evacuated, *n*-BuLi washed, and benzene rinsed glass vessels. Thorough information and detailed description of the high-vacuum technique as well as the purification procedures for the monomers (butadiene, isoprene), solvents (benzene, tetrahydrofuran (THF)), and initiator (*sec*-BuLi) to the standards required for anionic polymerization are well known and established.[15] 4-(Trimethylsilyl)styrene or p-trimethylsilyl styrene was synthesized from p-chlorostyrene and chlorotrimethylsilane through a Grignard reaction, under high-vacuum techniques. p-Chlorostyrene was purified in a short-path Pyrex glass apparatus by drying with CaH_2 overnight and finally stored at -20°C in sealed ampules. Magnesium (Aldrich) used in the Grignard reaction was dried in a vacuum oven at 40°C for two days in order to completely remove any traces of humidity prior to use. 1,3-Cyclohexadiene (1,3-CHD, Aldrich, 97%) was stirred overnight under CaH_2 and distilled three times over sodium mirrors in a high-vacuum line. Then it was distilled in a flask containing *n*-BuLi and allowed to react for 30 min at 0°C. The purified 1,3-CHD was finally distilled into calibrated ampules and used immediately or stored at -20°C for a short period of time. 1,4-Diazabicyclo-[2.2.2]octane (DABCO, Aldrich, 98%) was purified by sublimation of the appropriate amount three times under high vacuum in a Pyrex glass apparatus. Finally, the necessary amount of benzene was distilled until proper concentration of the solution was reached.

Instrumentation

Gas chromatography-mass spectroscopy (GC-MS) was adopted for studying the success of the silylated styrenic monomer preparation. The instrument was equipped with a split/splitless injector, and an MDN-5 column (Supelco) was used for separation (30 m × 0.25 mm i.d., 0.25 μm film thickness). The temperature program for the GC-17A interfaced with a QP5000 MS. The GC oven temperature started at 100°C, and after 3 min the column was heated at 10°C/min to 280°C. The total run time was 21 min. The mass spectrometer started its run 3 min after the injection whereby the mass range from 50 to 500 was recorded. The control of the GC-MS system and the evaluation of the chromatograms received were carried out by means of CLASS-5000 Version 1.24 Chromatography Software (Shimadzu Chemical Laboratory Analysis System and Software).

The number-average molecular weights ($\bar{M}_n$) of the precursors and the final products higher than 15,000 g/mol were measured with a Gonotec membrane osmometer (MO) Osmomat 090 at 35°C. Toluene, dried with CaH_2, was used as the solvent. Square-root plots were used in order to minimize the curvature due to the third virial coefficient. More details are given elsewhere.[16] In all cases, the correlation coefficient was better than 0.99.

Number-average molecular weights ($\bar{M}_n$) of the precursors lower than 15,000 g/mol were measured with a Gonotec vapor pressure osmometer (VPO) Osmomat 070 at 50°C under vapors of toluene (purified as described above). The instrument was calibrated with a benzyl solution to determine the consistency of the instrument.

A size exclusion chromatograph (SEC), equipped with an isocratic pump (SpectraSystem P1000), column oven (LabAlliance) heated to 30°C, three columns in serial connection (PLgel 5 μm Mixed-C, 300 × 7.5 mm), refractive index (RI, Shodex RI-101), and ultraviolet absorbance (UV, SpectraSystem UV1000) detectors, and THF as the eluent, was calibrated with eight PS standards (M_p: 4,300 to 3,000,000 g/mol). In every case, prior to calculating the polydispersity indices of the unknown materials, a series of standard PS solutions were tested in order to examine the accuracy of the instrumentation.

Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy was used for determining the composition and the isomeric microstructures of the materials and was carried out in $CDCl_3$ at 30°C using a Bruker AVANCE II spectrometer. Data were processed using UXNMR (Bruker) software.

The casting protocol for film preparation was designed to reproducibly prepare bulk films at thermodynamic equilibrium by solvent casting and annealing. Approximately 0.7 mm thick films of the materials were cast from a dilute solution (~5 wt%) in a nearly nonselective solvent (toluene) over a period of one week at ambient conditions. The films were then dried under vacuum for three days at room temperature and finally annealed at 120°C for one week under vacuum. For transmission electron microscopy (TEM) investigation, approximately 50 nm thick sections of the block copolymers were cryomicrotomed at -110°C using a Reichert-Jung FC 4E cryo-ultramicrotome equipped with a diamond knife to avoid mechanical deformation of the resulting thin sections during their collection in 600-mesh copper grids. To increase the mass-thickness contrast, the thin sections were exposed to OsO_4 vapors for 2 h. The stained sections were examined in a JEOL JEM 200CX electron microscope operated at 200 kV in the bright field mode.

Silylated Monomer Synthesis

p-Trimethylsilyl styrene (TMSS) was synthesized from p-chlorostyrene (5.775 g or 41.60 mmol) and chlorotrimethylsilane (3.160 g or 29.12 mmol) through a Grignard reaction, under high vacuum techniques. The magnesium (1.213 g or 49.92 mmol, in a 20% excess from p-chlorostyrene) was activated via 1,2-dibromoethane (1 mL or 11.60 mmol) in excess of THF (40 mL). The completion of the reaction and the successful synthesis of the required TMSS was verified via GC-MS, where traces of the initial reactants were observed. Through the GC-MS technique, we were able to completely comprehend the yield of the reaction, which was estimated to be approximately 75%. In order to obtain the synthesized monomer as pure as possible, fractional distillation was adopted where the remaining reagents and the solvent

(THF) were removed at low temperatures (< 100°C). By increasing the temperature slightly (up to 135°–140°C) using an oil bath, we obtained a pale yellow-colored liquid, which through the GC-MS observation lead to a molecular weight of 161 g/mol (~95%). This value is lower than the originally expected 176 g/mol for the TMSS component due to the symmetry of the three methyl groups adjacent to the silicon atom (one is eventually missing). The quantity of the monomer received from the above procedure was further purified with dibutyl magnesium (Bu_2Mg), a standard purifying procedure for styrene.

Diblock Copolymer Synthesis

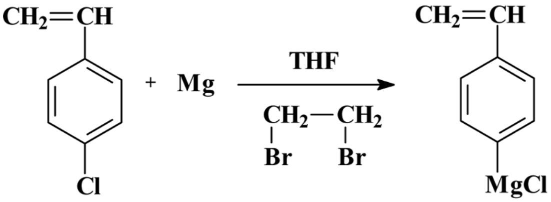
The A-b-B type linear diblock copolymers, where A is poly(p-trimethylsilyl styrene) (PTMSS) and B is poly(1,3-cyclohexadiene) (PCHD), were synthesized by using the monomer sequential addition polymerization technique. The $PTMSS^{(-)}Li^{(+)}$ living chain was synthesized by polymerizing 4.3 g of TMSS (24.3 mmol) with *sec*-BuLi (0.43 mmol) in 150 mL of benzene at room temperature for 24 h. The molecular weight of the living chain was approximately 10,000 g/mol, verified by SEC and VPO experiments. Then DABCO was added, which is essential for the successful polymerization of the CHD monomer. Actually, 0.86 mmol or 3.38 mL of DABCO (diluted in benzene) were added followed by the addition of 4.3 g of CHD (53.5 mmol). The final total molecular weight of the diblock copolymer was approximately 20,000 g/mol. In order to verify whether or not correction factors are needed for the SEC results for both segments, PTMSS homopolymers were synthesized and their average molecular weight per number ($\bar{M}_n$) was calculated with VPO. It was concluded that in both cases no correction factors were needed and the actual molecular weights from SEC and VPO were almost identical.

RESULTS AND DISCUSSION

Monomer Synthesis and Homopolymerization Procedure

The Grignard reaction necessary to synthesize the linking reagent for preparing the first intermediate product is shown in Scheme 1.

The success of the reaction has appeared to be rather crucial for the completion of the polymerization reactions. GC-MS and ^{1}H-NMR studies were employed in order to completely control the final product of the Grignard reaction, after distillation, leading eventually to a large yield (higher than 70%). It should be mentioned that the excess of magnesium (20% more) from the p-chlorostyrene quantity leads to larger yields than initially expected (~60%).

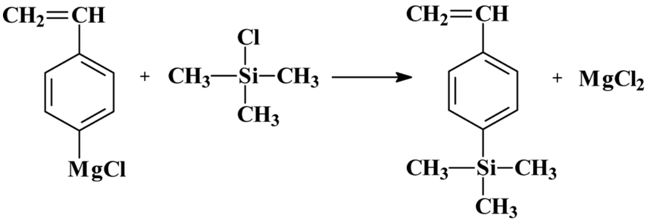


Scheme 1. Preparation reaction of the Grignard intermediate product.

The Grignard reagent was further reacted with the appropriate amount of chlorotrimethylsilane in order to produce the appropriate substituted styrene, as demonstrated in Scheme 2.

As mentioned previously, purification via fractional distillation is useful since it is of major significance to collect the appropriate fraction corresponding to the synthesized silylated styrenic monomer. An aliquot was removed from the reactor and analyzed by GC-MS to study the kinetics of the reaction and verify the preparation of the desired TMSS monomer.

For the synthesis of the PTMSS homopolymers, we followed the typical procedure used for styrene, for *sec*-BuLi as initiator, and benzene as solvent. The only difference observed during the polymerization procedure of TMSS compared to simple styrene was the maintenance of the solution for a longer period of time (24 h) in order to assure the completion of the propagation reaction. Theoretically, the propagation must be somewhat slower than that of styrene due to steric hindrance of the large trimethylsilyl group located in the *para* position of the phenyl group in each monomeric unit. The polymerization was completed giving a very low polydispersity index (I = 1,05) of the homopolymer (PTMSS) and number-average molecular weight ($\bar{M}_n$) of 3,000 g/mol, which was very close to the initially expected one. The difference between the predicted and the actual molecular weights is well within the experimental errors of the characterization methods (SEC and VPO). Larger molecular



Scheme 2. Preparation reaction of the monomer p-trimethylsilyl styrene (TMSS).

Table I. Molecular characteristics of the synthesized homopolymers of poly(trimethylsilylstyrene) (PTMSS)

Sample	Initiating system/ solvent	$\overline{M}_n \times 10^{-3}$ (g/mol)[a,b]	$\frac{\overline{M}_w}{\overline{M}_n}$[c]	$\overline{M}_w \times 10^{-3}$ (g/mol)[d]
PTMSS (1)	sec-BuLi/benzene	3,5[b]	1,02	3,9
PTMSS (2)	sec-BuLi/benzene	10,3[a]	1,03	10,8
PTMSS (3)	sec-BuLi/benzene	24,8[a]	1,06	26,7

[a] MO in toluene at 35°C.

[b] VPO in toluene at 50°C.

[c] SEC in THF at 30°C calibrated with polystyrene standards.

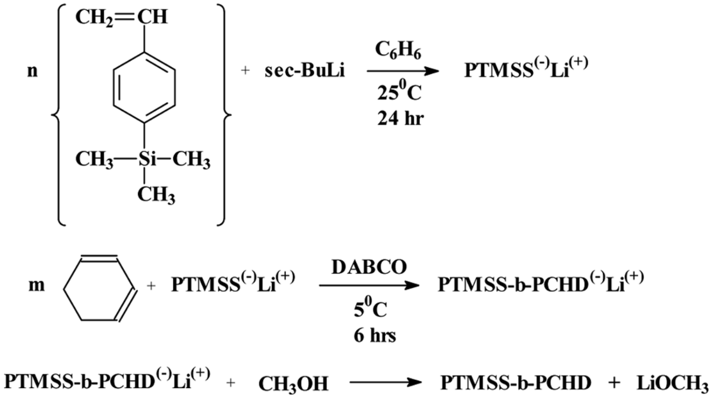
[d] Calculated form the combination of MO/VPO and SEC results.

weights were also prepared, up to 25,000 g/mol, with low polydispersity indices (varying from 1.04 to 1.07). The molecular characterization results of the three synthesized homopolymers are exhibited in Table I. It should be noted that the results from SEC and VPO or MO for the $\bar{M}_n$ values are almost identical. There is a slight difference between them, leading to a corrective factor of 1.04–1.05 for the values given directly from the SEC, which is very small, taking into account the errors given for this characterization technique (±10%).

From the above it is understood that the most difficult procedure was the organic synthesis of the monomer. This was due to the existence of reagents resulting in a coexistence of para products, such as p-chlrostyrene, prior to the purification of the desired TMSS. The use of Bu_2Mg as an additional purifying reagent for TMSS was considered essential for the complete removal of p-chlorostyrene due to the replacement of the $-Cl$ group by Mg, which led to its deactivation. Finally, it should also be noted that TMSS synthesis has already been reported in the literature, but with very low yield (~40%), as well as its homopolymerization via radical polymerization where only intrinsic viscosity measurements are included without any further detailed molecular characterization.[17]

Diblock Copolymer Synthesis

The main purpose of this work was the synthesis of linear diblock copolymers of the PTMSS-b-PCHD type with very low polydispersity index, predictable molecular weight, and desirable isomeric microstructures for the PCHD segments (~90%-1,4 and ~10%-1,2). These copolymers were synthesized by employing the sequential addition of the monomers method, where CHD was always added as the second monomer. All polymerizations were carried out under high vacuum, in *n*-BuLi-washed and



Scheme 3. Synthesis reactions of the diblock copolymers of the PTMSS-b-PCHD type.

benzene-rinsed glass reactors, provided with break-seals and constrictions. *sec*-BuLi was the initiator, benzene the solvent, and DABCO was used as the polar modifier for successful completion of the CHD polymerization in appropriate ratios [*sec*-BuLi]/[DABCO] = 1/2. The reactions used during the synthesis of the PTMSS-b-PCHD copolymers are given in Scheme 3.

SEC chromatograms monitoring the synthesis of a PTMSS-b-PCHD copolymer are shown in Figure 1.

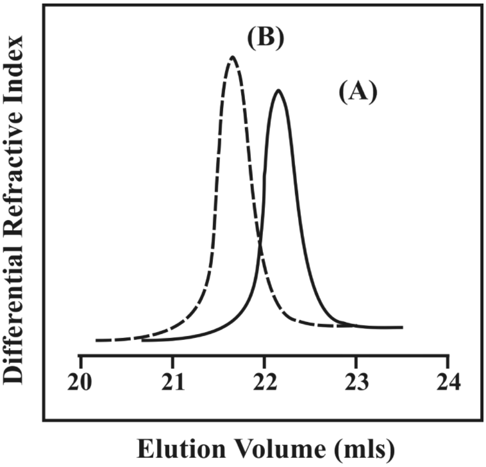


Figure 1. SEC chromatographs of: (A) PTMSS homopolymer with approximate number-average molecular weight (M_n) 25,000 g/mol, (B) PTMSS-b-PCHD diblock copolymer with total number-average molecular weight (M_n) 50,000 g/mol.

Table II. Molecular characteristics of the diblock copolymers of the PTMSS-b-PCHD type

Sample	Initiating system/ solvent	$\overline{M}_n \times 10^{-3}$ (g/mol)[a]	$\frac{\overline{M}_w^{b}}{\overline{M}_n}$	$\overline{M}_w \times 10^{-3}$ (g/mol)[c]	ϕ^{d}_{PTMSS}
PTMSS-b-PCHD (1)	sec-BuLi-DABCO/ benzene	24,5 (11,0)[e]	1,05 (1,04)[e]	27,7 (11,5)[e]	0.46
PTMSS-b-PCHD (2)	sec-BuLi-DABCO/ benzene	35,8 (26,1)[e]	1,07 (1,05)[e]	38,4 (27,5)[e]	0.75

[a] MO in toluene at 35°C.

[b] SEC in THF at 30°C calibrated with polystyrene standards.

[c] Calculated from the combination of MO/VPO and SEC results.

[d] Calculated from ^{1}H-NMR.

[e] Corresponding molecular characteristics for the first PTMSS block.

The $\overline{M}_n$ values for both segments are identical and equal to 25,000 g/mol. Although in some cases minor deactivation (less than 5%) of the first block occurred from the impurities of the polar additive or the second monomer, well-defined diblock copolymers were obtained after fractionation in a solvent/non-solvent system (toluene and methanol respectively). It should be noted that the reaction time for the completion of polymerization for the CHD monomer was approximately 6 h at 5°C and was increased up to 24 h at the same temperature without the observation of different results. The final polymerization time of 6 h, as indicated in Scheme 3, was achieved after kinetic studies, through aliquots taken from the polymerization glass vessel at different times. The molecular characterization results of the two synthesized diblock copolymers are given in Table II.

Structural Characterization of the Diblock Copolymers

TEM micrographs of the two synthesized diblock copolymers are shown in Figure 2.

Staining of the PCHD block was accomplished with OsO_4 vapors since it is commonly known that the specific stainer is the appropriate chemical substance to increase the mass contrast for polydienes during their observation via transmission electron microscopy. The first sample, with volume fraction of PTMSS equal to $\phi_{PTMSS} = 0.46$, exhibited lamellae morphology with black and white regions corresponding to PCHD and PTMSS blocks respectively (Figure 2(a)), while the second sample with $\phi_{PTMSS} = 0.75$ exhibited hexagonally closed packed cylinders of PCHD (black regions) in the white PTMSS matrix (Figure 2(b)). These observations lead to the conclusion that the copolymers of the

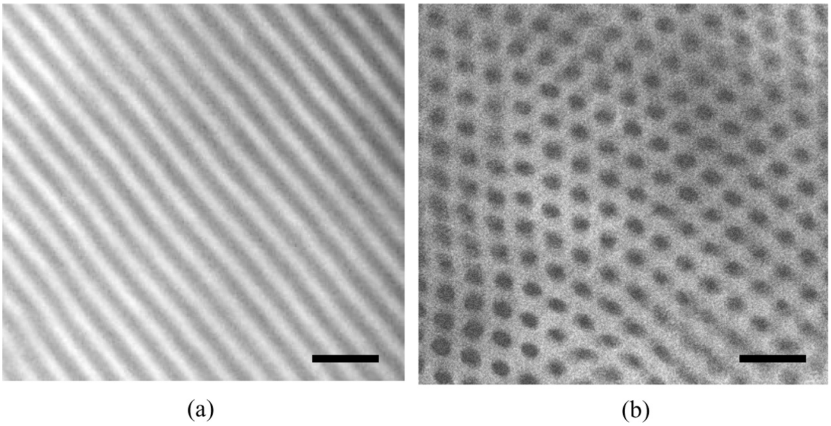


Figure 2. TEM micrographs of two diblock copolymer samples exhibiting (a) alternating lamellae and (b) hexagonally closed packed cylinders of PCHD in a PTMSS matrix. Black regions are PCHD segments due to staining with O_sO_4 vapors. The scale bars at the bottom of each micrograph correspond to 0.8 cm and represent approximately 50 nm.

PTMSS-b-PCHD type behave like the corresponding PI-b-PS type (where PI is polyisoprene and PS is polystyrene) copolymers, which are extensively studied,[18] and their χN versus ϕ phase diagram is very well manipulated (χ is the Flory-Huggins interaction parameter, N the total polymerization degree, and ϕ the volume fraction of one block). Such observations lead to the necessity of synthesizing more diblock copolymer materials of the certain type in order to completely verify this behavior as well as to calculate the χ value between PTMSS and PCHD by small angle X-ray scattering techniques. Finally, it should be mentioned that extensive morphological studies have been performed for corresponding PTMSS-b-PI block copolymers where the molecular weights were much higher than our samples (up to 291,000 g/mol), and the χ parameter was calculated, leading to an order-disorder transition for the sample exhibiting ~152,000 g/mol. By varying the temperature, the disordered state could be reached (200°C) where as at 150°C the ordered state was adopted.[19] Therefore, it is completely understood that the alternation of one block leads to unique differentiation on the self-assembly of the final copolymers, as seen in our case.

CONCLUSIONS

The successful synthesis of p-trimethylsilyl styrene and its homopolymerization and block copolymerization with 1,3-cyclohexadiene is reported.

The molecular characterization results indicated that the homopolymers as well as the diblock copolymers are considered well defined since they exhibit molecular and compositional homogeneity. The structural behavior of the copolymers in bulk is identical to that of the corresponding PI-b-PS diblock copolymers, leading to predictable morphologies by knowing only the volume fraction of one block (ϕ_{PTMSS}).

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