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Synthesis of Well-Defined Polyethylene–Polydimethylsiloxane–Polyethylene Triblock Copolymers by Diimide-Based Hydrogenation of Polybutadiene Blocks

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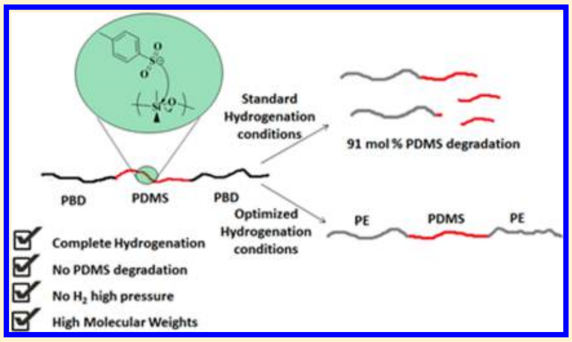
Ⓢ *Supporting Information*



ABSTRACT: Polyethylene, PE, is a crystalline solid with a relatively high melting temperature, and it exhibits excellent solvent resistance at room temperature. In contrast, polydimethylsiloxane, PDMS, is a rubbery polymer with an ultralow glass transition temperature and poor solvent resistance. PE–PDMS block copolymers have the potential to synergistically combine these disparate properties. In spite of this potential, synthesis of PE–PDMS block copolymers has not been widely explored. We report a facile route for the synthesis of well-defined polyethylene-*b*-polydimethylsiloxane-*b*-polyethylene (EDE) triblock copolymers. Poly(1,4-butadiene)-*b*-polydimethylsiloxane-*b*-poly(1,4-butadiene) (BDB) copolymer precursors were synthesized by anionic polymerization, followed by diimide-based hydrogenation. Under the standard hydrogenation conditions established by the work of Hahn, the siloxane bond undergoes scission resulting into significant degradation of the PDMS block. Our main accomplishment is the discovery of reaction conditions that avoid PDMS degradation. We used mechanistic insight into arrive at the optimal hydrogenation conditions, and we established the efficacy of our approach by successfully synthesizing a wide variety of block copolymers with total molecular weights ranging from 124 to 340 kg/mol and PDMS volume fractions ranging from 0.22 to 0.77.

■ INTRODUCTION

Polyethylene (PE) and polydimethylsiloxane (PDMS) are two polymeric materials with significant commercial importance. PDMS is the most important member of the silicone family as it combines a wide range of unique physical properties such as an ultralow glass transition temperature (T_g), high free volume, low surface energy, excellent thermal and oxidative stability, low deep UV absorption, and good resistance to reactive ion etching in the presence of oxygen plasmas. PE on the other hand is a commodity semicrystalline polymer with excellent mechanical properties and exhibits very poor solubility in virtually all common solvents at room temperature. There are numerous reasons to create a single material that embodies the diverse properties obtained separately in PE and PDMS. Such a material can have a wide range of potential applications such as lubricants,[1] adhesives,[2] electronics,[3] nanolithography,[4] microfluidic devices,[5] elastomers,[6,7] and membranes for gas and liquid separations.[6,8] For example, PE–PDMS block copolymers may enable the production of solvent resistant membranes with excellent mechanical properties. The purpose of this paper is to describe a facile approach for the synthesis of model PE–PDMS block copolymers.

The conventional approaches for synthesizing PE and PDMS are very different and incompatible. PE is usually synthesized by metal catalysis (e.g., Ziegler–Natta) while PDMS is usually synthesized by condensation or ring-opening polymerization.[9] This makes the preparation of PE–PDMS block copolymers challenging. A commonly employed route to prepare polyethylene-based block copolymers relies on synthesizing an unsaturated precursor first, most commonly polybutadiene, followed by hydrogenation. A broad range of polyethylene-containing block copolymers have been prepared by this route.[10−15] Interestingly, there are only a few reports in the literature on the synthesis of PE–PDMS copolymers.[16−19] The molecular weights of the PDMS blocks in refs 15–17 range from 0.5 to 8 kg/mol and PE was obtained by high pressure saturation of a polybutadiene precursor using hydrogen gas and a metal catalyst. The same approach was used in reference 20 to hydrogenate polystyrene-*b*-polydimethylsiloxane-*b*-polystyrene with molecular weights ranging from 15 to 32 kg/mol.[20] It is often difficult to use this hydrogenation approach to saturate

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high molecular weight homopolymers and block copolymers (100 kg/mol) because the polymer chains must diffuse through the pores of the catalyst support to interact with the active sites.[21,22]

An alternative metal-free stoichiometric approach for hydrogenation of unsaturated polymers involves the use of diimide (also referred to as diazene) generated *in situ* by thermolysis of *p*-toluenesulfonyl hydrazide.[10,23,24] This approach enables hydrogenation without the use of potentially explosive hydrogen gas at high pressures. In addition, it is possible to use diimide hydrogenation to saturate molecules containing a wide variety of functional groups such as thiols, alkyl halides, and peroxides; conventional metal catalysts are poisoned in the presence of these functional groups. Pioneering work of Hahn has enabled the synthesis of well-defined polyolefins by diimide-based hydrogeation of dienes such as polybutadiene and polyisoprene.[10] The work in ref 10 builds on earlier studies of polydiene hydrogenation.[25] To our knowledge, this approach has not been used to saturate chains containing chemically labile blocks such as PDMS. In this paper, we report on the synthesis of polyethylene-*b*-polydimethylsiloxane-*b*-polyethylene, EDE, triblock copolymers by diimide-based hydrogenation of poly(1,4-butadiene)-*b*-polydimethylsiloxane-*b*-poly(1,4-butadiene), BDB, precursors. The use of standard hydrogenation conditions reported in ref 10 for PBD-containing polymers results in severe degradation of PDMS. It is likely that this is due to nucleophilic attack of the Si–O bond by the *p*-toluenesulfinate anion that is generated by thermolysis of *p*-toluenesulfonyl hydrazide. Herein we report conditions under which the complete saturation of BDB can be carried out with no evidence of PDMS degradation. We established the efficacy of our approach by successfully synthesizing a variety of block copolymers with total molecular weights ranging from 124 to 340 kg/mol and PDMS volume fractions ranging from 0.22 to 0.77. Our results provide some insight into the nature of degradation reactions that can occur in our system, and they suggest that PE-based block copolymers that contain other chemically labile blocks than PDMS may be synthesized by the diimide-based method.

■ EXPERIMENTAL SECTION

Synthetic Methods. *Purifications.* All manipulations were carried out by standard high vacuum techniques and glovebox operations, unless otherwise stated.[26−33] *sec*-BuLi (Aldrich 1.7 M in cyclohexane) was titrated before use by the 1,3-diphenylacetone *p*-tosylhydrazone method to confirm the precise concentration of active species and it was used without any additional treatment. THF was purified by passing through solvent purification columns followed by stirring overnight over finely ground CaH_2 and then stored in a reactor over a Na/benzophenone mixture obtaining the characteristic purple color.[34] Toluene was purified by passing through solvent purification columns followed by stirring overnight over finely ground CaH_2. Finally it was distilled and stored in a reactor over polystyryl lithium obtaining the characteristic red color. Solvents were distilled on the vacuum line prior to use. The purification of hexamethylcyclotrisiloxane, D_3 (gelest 95%), was performed as follows: The appropriate amount of D_3 was melted by heating at 80 °C, put in a flask, diluted by an equal amount of purified cyclohexane, and stirred overnight over CaH_2. Then the solvent along with the monomer was distilled into a flask containing polystyryl lithium. The monomer was in contact with polystyryl lithium for about 2 h at room temperature and then it was distilled into a flame-dried reactor along with the solvent by heating at 80 °C. Finally, the monomer was isolated by distilling cyclohexane to another reactor at room temperature. The reactor containing D_3 was transferred and stored in the glovebox. The purification of 1,3-butadiene (Aldrich, 99%) was performed by drying an appropriate amount of monomer over finely ground CaH_2 overnight, followed by distillation in activated molecular sieves where it remained in contact overnight. Then butadiene was vacuum transferred to a reactor containing *n*-BuLi where it remained with continuous stirring at 0 °C for 1 h. The monomer was distilled in a reactor containing toluene that had been dried as mentioned previously. The monomer was stored at −20 °C in the glovebox and was used within a period of 2 weeks. The linking agent 1,2-bis(dimethylchlorosilyl)ethane (Aldrich) was purified by fractional distillation on the vacuum line and then stored in the glovebox.

Polymerizations. As an example of a polymerization experiment the synthesis of BDB335-78 has as follows: 100 mL of cyclohexane and 10 mL of 1,3 butadiene (0.114 mol), that had been purified and stored as described in the previous section were vacuum transferred in a Schlenk reactor. Subsequently the Schlenk reactor containing butadiene and cyclohexane was transferred in the glovebox where 0.02 mL of *sec*-BuLi (0.000213 mol) were added (target molecular weight 30k). The reactor containing solvent, monomer, and initiator was immediately placed in an oil bath preheated at 50 °C. The reaction was allowed to proceed for 18 h. Then the reactor was transferred in the glovebox and a sample was removed. The sample was quenched by introducing an excess of methanol and was used for characterization purposes (^1H NMR spectroscopy, GPC). Then 26.6 g of purified D_3 (0.120 mol) were introduced (target molecular weight 125k) and the Schlenk reactor was left in contact with the living PBD anions overnight. The THF (dried as mentioned in the previous section) was returned on the vacuum line and 100 mL were vacuum transferred in a graduated ampule. The ampule was transferred in the glovebox and the THF was added in the polymerization reactor (cyclohexane/THF: 50% v/v). The reactor was left at room temperature for 90 min and then was removed from the glovebox and emerged in a chiller with a temperature preset at −20 °C. The polymerization was left for 72 h and then the reactor was transferred in the glovebox where 0.046 g of purified 1,2-bis(dimethylchlorosilyl)ethane (0.000213 mol) were introduced. The coupling reaction was left for 45 min and then excess of trimethylchlorosilane was added. The polymer was precipitated 6 times in methanol and dried under vacuum. Finally, for long-term storage the polymer was dissolved in cyclohexane and butyl hydroxyl toluene (BHT) was added as an inhibitor. Then cyclohexane was removed under vacuum and the polymer/BHT mixture was stored at −20 °C. The volume fractions of the PDMS block of the BDB and EDE copolymers (ϕ_{PDMS}) were estimated using monomer volumes of 0.111, 0.138, and 0.119 nm^3 for PBD, PDMS, and PE respectively.[35]

Hydrogenations. The hydrogenation was carried out in a 1 L three-neck round-bottom flask which was equipped with magnetic stirring, a reflux condenser, a thermometer, and a stopper. The apparatus was supplied with positive pressure of dry argon. Predetermined amounts of BDB block copolymer and *o*-xylene were added, and the mixture was left to stir for 1 h at 60 °C. This resulted in the complete dissolution of the polymer. Predetermined amounts of *p*-toluenesulfonyl hydrazide and tripropylamine were added to the flask and the temperature was raised to the desired set point. The reaction was quenched by precipitating the product in ice cold methanol.

We performed a systematic study of the effect of the concentrations of the reactant, reaction temperature, and reaction time on the final product obtained: Table 2 shows standard conditions taken from ref 10 and optimized conditions that we arrived at after our systematic study.

Preparation of EDE Free-Standing Films. EDE (150 mg) was dissolved in cyclohexane (20 mL) and stirred at 65 °C for a minimum of 5 h. Subsequently the warm solution was poured on a Teflon sheet that was preheated at 65 °C and was placed on a solvent caster. To control the diameter of the films a metal tube with smoothened edges was employed as a template. The cast area was covered with an aluminum foil to slows down solvent evaporation. After solvent removal (approximately 24 h) the film was peeled off the surface and was used for further characterization.

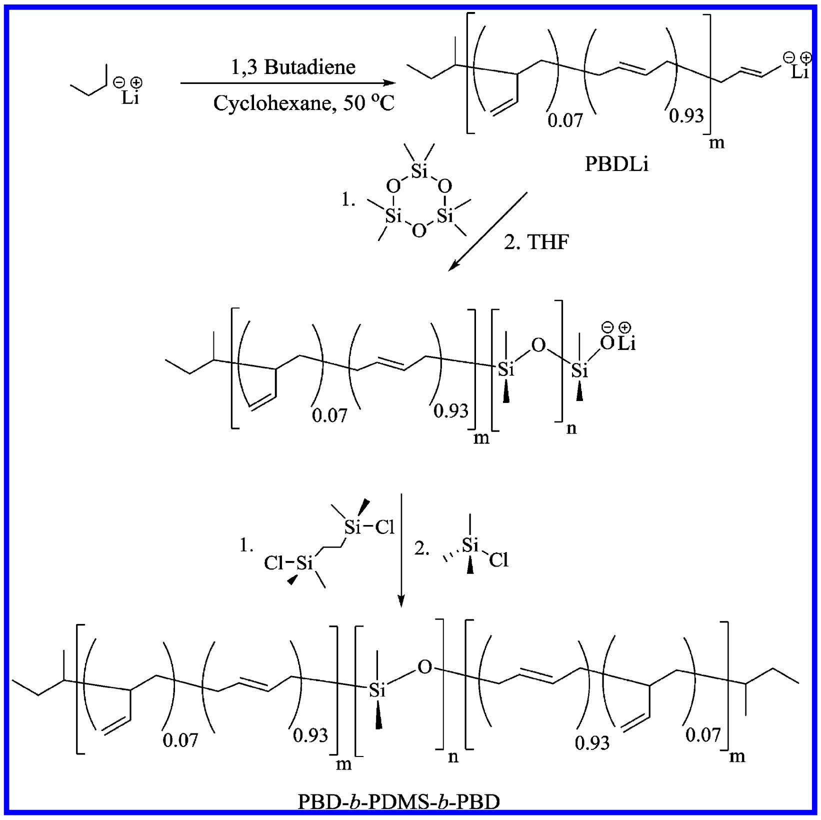

Figure 1. Reaction scheme for synthesis of BDB triblock copolymers via sequential anionic polymerization of 1,3-butadiene and hexamethycyclotrisiloxane and subsequent coupling with 1,2-bis(dimethylchlorosilyl)ethane.

Characterization. *Gel Permeation Chromatography (GPC).* M_n and dispersities, *D*, of the BDB precursors were obtained using a Viscotek TDA 302 GPC system that has a guard column, a set of four Viscotek columns (300 mm ×7.8 mm, T-3000, T-4000, T-5000, and T-6000 columns) and a refractive index detector, with THF eluent (flow rate of 1 mL/min, 35 °C). The instrument was calibrated with polystyrene standards (Agilent Easivials PS-M). The molecular weights of the poly(1,4-butadiene) precursors were calculated based on triple detection experiments.

High Temperature Gel Permeation Chromatography. The hydrogenation products were characterized by gel permeation chromatograph (GPC) using a Malvern Viscotek HT-GPC system with 3 Tosoh GMHh-H(S) HT columns. The samples were analyzed in a mobile phase of 1,2,4-trichlorobenzene with 500 ppm BHT at 145 °C. The polymers were dissolved in the mobile phase for 1 h at 145 °C prior to injection into the system.

Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{1}H NMR measurement was conducted on 500 MHz Bruker DRX 500 spectrometer using deuterated solvents purchased by Aldrich. The solutions for ^{1}H NMR spectra had a polymer concentration of ~10 mg/mL. Polymers post hydrogenation were analyzed at 80 °C to ensure complete solubilization of the polyethylene segments. Spectra were analyzed to determine copolymer compositions as well as hydrogenation and degradation percentages.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). TGA experiments were performed on a "TGA Q20" instrument from TA Instruments under nitrogen flow rate of 100 mL/min. In the first step, the samples were heated from 30 to 110 °C at 10 °C/min, and the temperature was maintained at 110 °C for 1 h. In the second step, the samples were cooled down to 30 °C at 10 °C/min and heated again at 10 °C/min until the temperature reached 600 °C.

DSC experiments were performed on a Thermal Advantage Q200 calorimeter at the joint center of artificial photosynthesis (JCAP), Lawrence Berkeley National Laboratory. Samples were sealed in aluminum hermetic pans. DSC scans consisted of two heating/cooling cycles and were conducted over the range 0−150 °C at a rate of 10 °C/min. The glass transition temperatures (T_g) for EDE32−335, presented in this paper is from the inflection point of the transition in the second heating run.

Small Angle X-ray Scattering (SAXS) and Wide Angle X-ray Scattering (WAXS). Here, 0.1 mm thick EDE samples were prepared solvent casting as described in a previous section. Synchrotron small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) measurements were performed using the 7.3.3 beamline at the Advanced Light Source (ALS, Lawrence Berkeley National Laboratory). At the ALS, the wavelength λ of the incident X-ray beam was 0.124 nm ($\Delta\lambda/\lambda = 10^{-4}$), and a sample-to-detector distance of 4 m was used for the SAXS measurements. The resulting two-dimensional scattering data were averaged azimuthally to obtain intensity versus magnitude of the scattering wave vector q ($q = 4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle). The scattering data were corrected for the detector dark current and the scattering from air and Kapton windows.

RESULTS AND DISCUSSION

Synthesis of Poly(1,4-butadiene)-*b*-polydimethylsiloxane-*b*-poly(1,4-butadiene), BDB. The sequence of reactions used to synthesize the BDB triblock copolymer precursors is shown in Figure 1. The anionic polymerization of 1,3-butadiene was initiated by *sec*-BuLi in cyclohexane at 50 °C in order to obtain predominantly 1,4-polybutadiene (PBD). In this paper we discuss block copolymers made from three different PBD samples ranging in molecular weight from 32 to 66 kg/mol as summarized in Table 1. The anionic ring-opening polymerization (ROP) of D_3 was carried out using a two-step method reported previously.[9] First the D_3 monomer was introduced into the reactor containing living PBD anions and left to react overnight. This is the initiation step and approximately one D_3 monomer is added to each living

Table 1. Molecular Characteristics of the PBD Homopolymers and BDB Triblock Copolymers Synthesized

polymer	precursor	M_n^{exper} (kg/mol)	ϕ_{PDMS}	M_w/M_n
PBD32	–	32	–	1.03
PBD49	–	49	–	1.04
PBD66	–	66	–	1.03
BDB119-43	PBD32	32−55−32	0.43	1.21
BDB156-23	PBD66	66−44−66	0.23	1.19
BDB200-48	PBD49	49−102−49	0.48	1.28
BDB335-78	PBD32	32−271−32	0.78	1.14

chain. Subsequently tetrahydrofuran (promoter) was added to the reaction mixture to give a 50% (v/v) cyclohexane/tetrahydrofuran mixture. This results in propagation which was allowed to proceed for 90 min at room temperature (30−50% monomer conversion). Then the temperature was reduced to −20 °C in order to suppress the undesired side reactions (backbiting and reshuffling reactions) enabling control over the propagation reaction at high conversion of the monomer. The reaction mixture was sampled after 72 h and complete conversion of the monomer was confirmed by ^{1}H NMR spectroscopy. The BDB triblock copolymer was prepared by coupling the living poly(1,4-butadiene)-*b*-polydimethylsiloxanyl lithium polymer chains with 1,2-bis(dimethylchlorosilyl)ethane.

The reaction was run for 45 min and subsequently trimethylchlorosilane was added to terminate any uncoupled polymer chains. As noted in previous studies complete conversion, prior to coupling is essential for obtaining model materials.[9] The characteristics of the four BDB triblock copolymers used in this study are summarized in Table 1. Samples are labeled BDBX-Y where X is the number-averaged molecular weight of the copolymer kg/mol, and Y is the PDMS volume fraction. ^{1}H NMR spectroscopy analysis of the final product was used to calculate the molar ratio between the polybutadiene and polydimethylsiloxane monomeric units (see Figure S1, Supporting Information). The conversion from mole fractions to volume fractions is described in the Experimental Section.

Figure 2 shows GPC traces of a typical PBD precursor (prior to adding D3 monomer) and the BDB triblock copolymer obtained from the corresponding precursor. Both samples show predominantly one narrow GPC peak with clear shift toward higher molecular weights after the addition of the PDMS block and coupling. The dispersity, *D*, of the BDB335-78 was 1.14 which suggests high selectivity toward the ring-opening polymerization reaction at high conversion of the monomer under the conditions specified above. The molecular weights of the BDB copolymers synthesized ranged from 119 to 335 kg/mol, PDMS volume fractions ranged from 0.23 to 0.78, and *D* ranged from 1.14 to 1.28 (Table 1). Dispersity values that we obtained here are larger than those obtained from standard living anionic polymerization indicating that even under optimized conditions, deleterious side reactions have not been completely eliminated.

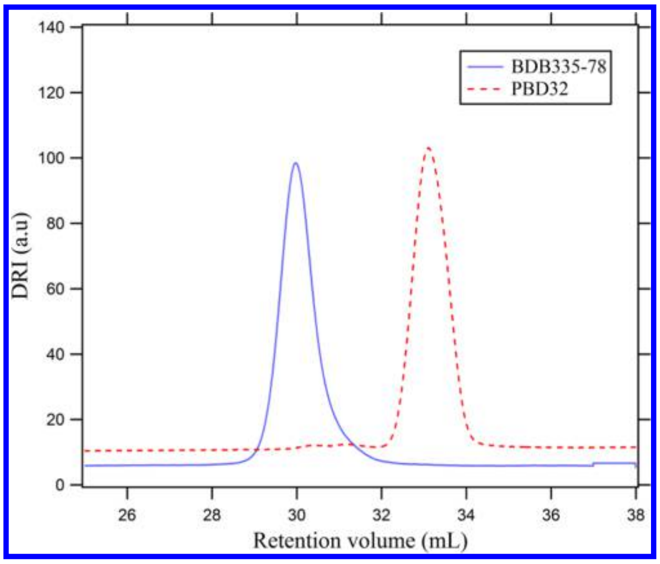

Figure 2. Gel permeation chromatograph of the PBD32 homopolymer (dashed line) and the BDB335-78 triblock copolymer (solid line).

Synthesis of Polyethylene-*b*-polydimethylsiloxane-*b*-polyethylene, EDE, by Hydrogenation. The reactions of this step are outlined in Figure 3 (reactions 1 and 2). In the first reaction, the thermolysis of *p*-toluenesulfonyl hydrazide (TSH) results in the formation of diimide and *p*-toluenesulfinate anion species. Diimide then donates two hydrogen atoms to each double bond of the PBD monomeric units (reaction 2). However, both diimide and *p*-toluenesulfinate anions are capable of participating in side reactions as shown in reactions 3 and 4. In reaction 3, diimide disproportionates to form N_2 and hydrazine. Reaction 4 illustrates the proposed mechanism for degradation of the PDMS block due to nucleophilic attack by the *p*-toluenesulfinate anion formed *in situ* by reaction 1. Our proposal is based on the well-established susceptibility of the siloxane bond in the presence of strong nucleophiles such as the *p*-toluenesulfinate anion.[36] Reaction 4 (Figure 3) results in the formation of PDMS fragments with anionic end groups that in turn self-catalyze PDMS degradation.

The hydrogenation of BDB was initially attempted under the standard reaction conditions reported previously by Hahn.[10] On the basis of this method, 2 equiv of *p*-toluenesulfonyl hydrazide (TSH) and 2 equiv of the tertiary amine are used per equivalent of PBD double bonds. The polymer concentration was 0.2 g/L in *o*-xylene and the reaction was allowed to proceed in refluxing *o*-xylene (135−140 °C) for 4 h. It has been proposed that the need for 100% excess of TSH is due to the high reactivity of diimide and potential side reactions that reduce the active concentration of diimide in solution (e.g., reaction 3 in Figure 3). The hydrophilic impurities in the product were removed by extraction in water (three repeats), the polymer was obtained by precipitation of the remaining organic phase in methanol (three repeats).[10] The characterization of the product by ^{1}H NMR spectroscopy at 353 K in deuterated toluene indicated the hydrogenation was complete by the disappearance of the polybutadiene signals and appearance of the polyethylene characteristic signal at 1.36 ppm. (All ^{1}H NMR spectroscopy of the hydrogenation products were conducted at elevated temperatures to dissolve the polyethylene blocks). The integration of the PDMS methyl protons at 1.03 ppm and the polyethylene protons at 1.36 ppm agreed with the expected molar ratio of the two monomeric units. However, when the same polymer was precipitated in THF (3 repeats), the integrated PDMS signal at 1.03 ppm was suppressed by a factor of about 12 compared to the polymer precipitated in methanol (entry 1, Figure 4). In addition, the polymer precipitated in methanol was a sticky solid while that precipitated in THF was a granular powder. These results suggested two things: (1) Exposure of the BDB precursor to the standard hydrogenation conditions resulted in fragmenta-

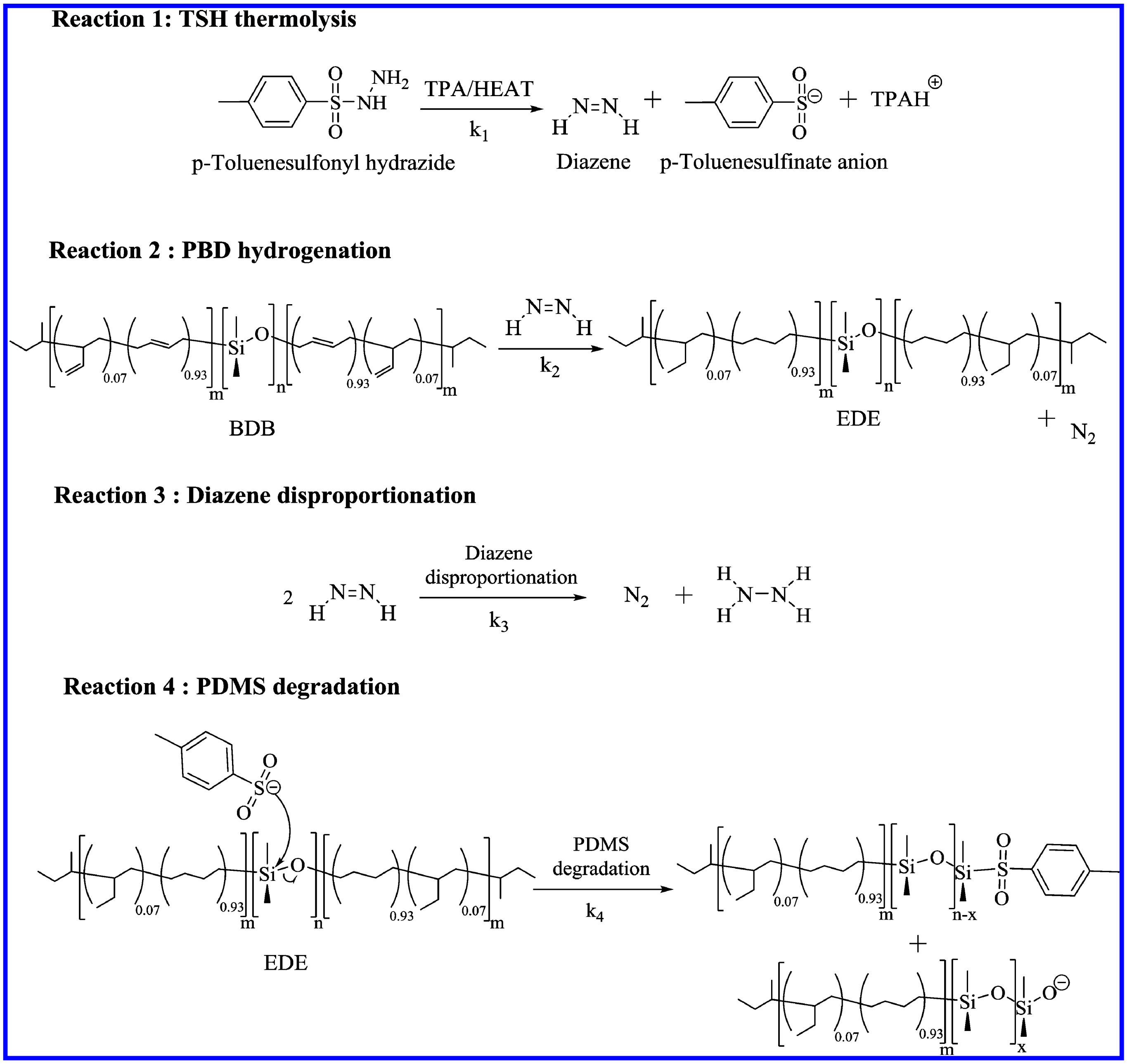

Figure 3. Hydrogenation of BDB via thermolysis of *p*-toluenesulfonyl hydrazide and subsequent side reactions.

tion of the PDMS block. (2) ^{1}H NMR spectroscopy signatures of this fragmentation are masked if the polymer is obtained by standard precipitation in methanol. Obviously, methanol and water are nonsolvents for both PE and PDMS. Therefore, the standard aqueous work up and precipitations in methanol cannot separate PE-rich and PDMS-rich fragments. In contrast, THF is a nonsolvent for semicrystalline PE but a good solvent for PDMS. Therefore, precipitation in THF removes PDMS fragments, providing valuable information regarding the quality of the final product.

In order to further understand the effect of the hydrogenation reaction on PDMS, we carried out a test reaction where we exposed a commercially available PDMS homopolymer with average molecular weight of 63 kg/mol to the standard hydrogenation conditions. The starting material and product were characterized by GPC (see Figure S2). The product showed a significant shift to higher retention time compared to the starting material, indicating the partial degradation of PDMS during the test reaction. It must be pointed out that the scission of PDMS chains during the hydrogenation of BDB not only alters the block ratio between PDMS and PE but also changes the architecture of the final product from ABA type triblock to an AB diblock copolymer resulting in severe alteration of the product's properties.

The addition of large excess of tripropylamine (TPA) as a proton scavenger is key to the efficacy of the hydrogenation procedure developed by Hahn.[10] However, the hydrogenation reaction mixture now contains two nucleophiles, the *p*-toluenesulfinate anion and the tripropylamine. In principle, both nucleophiles could attack PDMS. The susceptibility of the siloxane bond to TPA was tested by performing a blank reaction where the BDB precursor polymer was heated at 135 °C in the presence of only, the weakly nucleophilic TPA, for 4 h (no TSH was present). In this case, ^{1}H NMR and GPC

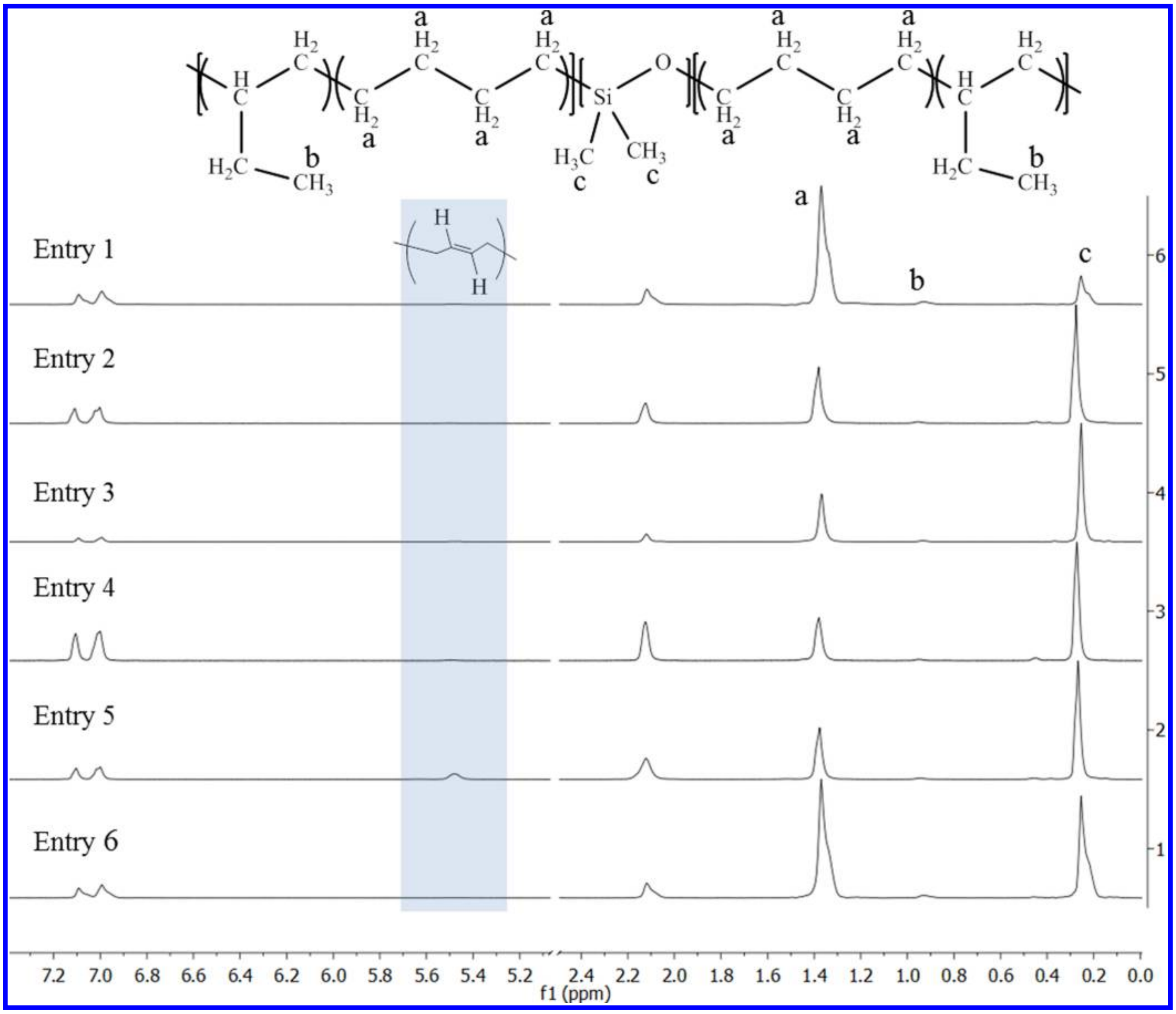

Figure 4. ^{1}H NMR spectra of the hydrogenation products for different reaction conditions described in Table 2 for BDB335-78 (500 MHz, 353 K, toluene-d_8).

Table 2. Molecular Characteristics of the Final Products for Different Hydrogenation Conditions of BDB335-78

entry	*T* (°C)	reaction time (min)	TSH concentration (% wt)	polymer concentration (% wt)	% PBD hydrogenation	mol % PDMS degradation
1	140	240	20	2	>99	91
2	140	240	5	0.5	>99	34
3	115	240	5	0.5	>99	15
4	115	180	5	0.5	>99	0
5	115	180	5	2	79	18
6	115	180	20	2	>99	62

analysis of the purified product showed no evidence of degradation. This result suggests that *p*-toluenesulfinate anion generated by the decomposition of TSH is most likely the species attacking the siloxane bonds. Evidently, maintaining the lowest possible concentration of the *p*-toluenesulfinate anion while efficiently hydrogenating polybutadiene is the key for synthesizing EDE copolymers by this method.

We systematically varied the hydrogenation reaction conditions (reaction temperature, reaction time, and initial concentration of TSH and BDB precursor), and the purified product after THF precipitations was characterized by ^{1}H NMR spectroscopy (Figure 4). The results of six such experiments on BDB335−78 are shown in Table 2. Entry 1 shows results obtained from the standard hydrogenation conditions proposed by Hahn which results in 100% hydrogenation of PBD but in 91% (mol.) degradation of PDMS. Reducing the TSH and polymer concentration by a factor of 4 reduces the PDMS mol % degradation to 34 without affecting hydrogenation, indicating that decreasing the initial TSH concentration slows down the PDMS degradation reaction

Table 3. Characteristics of the EDE Triblock Copolymers Synthesized

polymer	precursor	M_n^{exper} (kg/mol)	M_w/M_n	ϕ_{PDMS}	*d*-spacing (nm)	morphology
EDE124-42	BDB119-43	34−55−34	–	0.42	20	–
EDE187-22	BDB156-23	71−44−71	–	0.22	37	–
EDE209-45	BDB200-48	53−102−53	–	0.45	35	lamellar
EDE340-77	BDB335-78	34−271−34	1.14	0.77	57	–

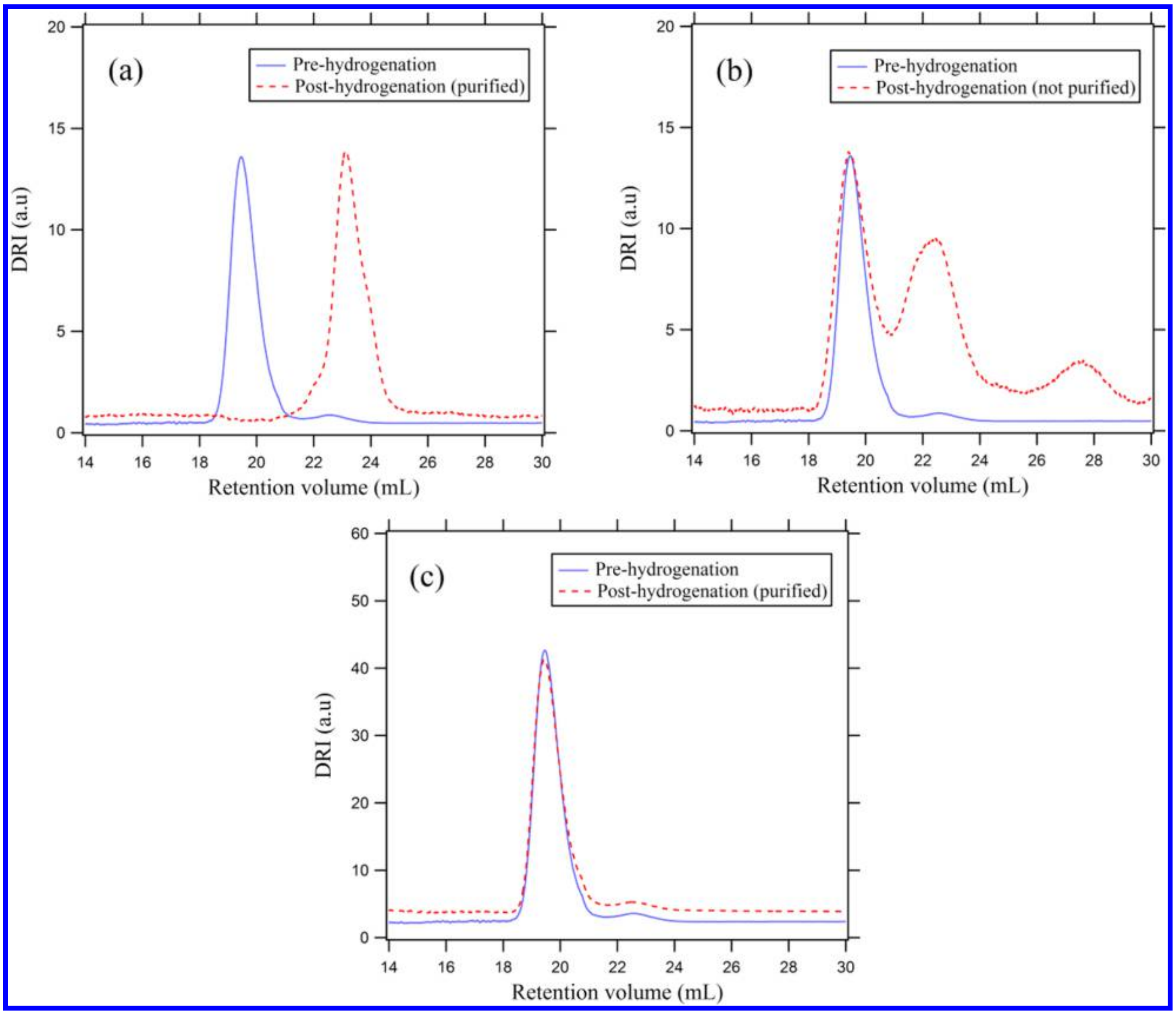

Figure 5. High temperature gel permeation chromatographs of BDB335-78 before hydrogenation (dashed line) and after hydrogenation (solid line) (a) under standard conditions (entry 1, Table 2). (b) under optimized conditions (entry 4, Table 2). (c) under the hydrogenation conditions of entry 6 without purification (entry 6, Table 2).

(reaction 4, Figure 3), which in turn suggests a reduction in the concentration of *p*-toluenesulfinate anion. The thermolysis reaction is known to be first order when carried out with an equimolar amount of TPA.[25] Lowering the temperature slows down the TSH thermolysis which reduces the concentrations of diimide and *p*-toluenesulfinate anions in solution (reducing rate constant k_1 in Figure 3). Comparison of entries 3 and 2 indicates that reducing the reaction temperature to 115 °C also reduces degradation of PDMS without affecting the hydrogenation efficacy. In principle, the reaction rate constant of the PBD hydrogenation, k_2, will also be reduced when the reaction temperature is reduced. However, entry 3 suggests either that the reduction of k_2 is insignificant compared to the reduction in the rate constant of the PDMS degradation reaction, k_4, or/and that k_3 is also reduced, slowing down the rate at which diimide active species disproportionate (note that reaction 3 is second order to diimide concentration while reaction 2 is first order to diimide concentration). In entry 4, the reaction time is reduced from 240 to 180 min with all other conditions identical with those used in entry 3. Under these conditions we observed 0% (mol.) PDMS degradation and 100% PBD hydrogenation. In an attempt to improve the efficiency of the hydrogenation reaction, in entry 5 we increased the polymer to TSH ratio by a factor of 2 with all other conditions identical with those used in entry 4. This results in 18 mol % PDMS degradation and 79% PBD hydrogenation. The incomplete hydrogenation is likely due to the diimide disproportionation reaction and a concomitant reduction in the concentration of the hydrogenation active species. In entry 6, we have increased the TSH concentration by a factor of 4 relative to entry 5. It is evident from Table 2 that this results in a substantial increase in PDMS degradation. Conditions described in entry 4 are thus close to optimal for hydrogenation of PBD blocks in the presence of PDMS. More trials indicated that, for reaction times up to 210 min and by keeping all other conditions identical to entry 4 no PDMS degradation occurred. This suggested that there is a time window of 30 min (from 180 to 210 min) that can give complete PBD hydrogenation and no PDMS degradation. If the reaction is conducted for less than 180 min, the polybutadiene hydrogenation is incomplete, while if the reaction is conducted for more than 210 min, degradation of PDMS starts occurring.

The characteristics of the final EDE copolymers are listed in Table 3; samples are named EDE*X*-*Y* where *X* is the total molecular weight of the copolymer (kg/mol) and *Y* is the volume fraction of the PDMS block. Lower polymer concentrations were used for higher PBD molar fractions.

The conclusions described in the preceding paragraph were supported by high temperature GPC experiments. These experiments also provide further insight into the nature of products formed under the reaction conditions listed in Table 2 and provide support for the proposed reaction 4 in Figure 3. In Figure 5a, we show GPC traces of BDB335-78 before and after hydrogenation using conditions described in entry 1 of Table 2. In this case the hydrogenation product was purified by precipitation in THF which removes PDMS-rich fragments (91% of the sample comprises PDMS-rich fragments). It is perhaps interesting to note that the standard hydrogenation conditions results in complete degradation of triblock copolymer chains; we found a change in peak elution volume from 19.2 to 23 mL. Elution volume of 22.5 mL corresponds to a factor of 2 decrease in average molecular weight (compared to 19.2 mL), suggesting that all of the triblock copolymer chains have been severed to give diblock copolymer fragments that have further degraded. In Figure 5b we show GPC traces of BDB335-78 before and after hydrogenation using conditions described in entry 6 of Table 2. In this case, the hydrogenation product was not purified. Here we see three populations corresponding to hydrogenated triblock copolymers with elution volumes ranging from 18.5 to 21.3 mL, hydrogenated diblock copolymers with elution volumes ranging from 21 to 24 mL, and PDMS fragments with elution volumes ranging from 25.8 to 29.3 mL. In Figure 5c we show GPC traces of BDB335-78 before and after hydrogenation using conditions described in entry 4 of Table 2, the optimized conditions. In this case, the hydrogenation product was purified by precipitations (three repeats) in THF. It is evident that hydrogenation under these conditions results in a molecular weight distribution that is indistinguishable from that of the precursor.

We conclude this section by describing the characteristics of EDE copolymers listed in Table 3. Figure 6 shows SAXS profiles of the EDE membranes at room temperature. The SAXS profiles were isotropic indicating that the membrane preparation process led to the formation of randomly oriented grains. The scattering profile of the nearly symmetric copolymer, EDE209-45, is consistent with that expected from samples with lamellar morphology. The profile contained a primary peak at scattering vector $q = q^* = 0.179\ \text{nm}^{-1}$ and higher order scattering shoulders at the expected locations, $q = 2q^*$ and $q = 3q^*$. The scattering profiles of the other copolymers, EDE124-42, EDE187-22, and EDE340-77 contained primary scattering peaks only. The locations of the primary scattering peaks are indicated by filled triangles in Figure 6. The domain spacing, *d,* of the microphase separated EDE block copolymers was calculated by the equation $d = 2\pi/q^*$. We define normalized periodicity d_n as $d/c(\phi)$, where d is the periodicity of the block copolymer microphases and $c(\phi)$ is a factor accounting for the effect of composition on domain spacing at fixed chain length. We use the theory of Leibler to determine $c(\phi)$ and by definition $c(\phi = 0.5) = 1$.[37] In Figure 7 we plot d_n versus N, the total number of segments per chain based on a reference volume of 0.1 nm^3. The line in Figure 7 represents a least-squares power law fit to the data which gives the scaling, $d_n \sim N^{0.85}$. The observed scaling exponent of 0.85 is consistent with literature reports.[38] SAXS profiles collected at high temperatures, well above the melting temperature of the PE blocks (up to 160 °C), were indistinguishable from the room temperature profiles. Additional characterization results obtained by TGA, DSC, and WAXS are given in the Supporting Information.

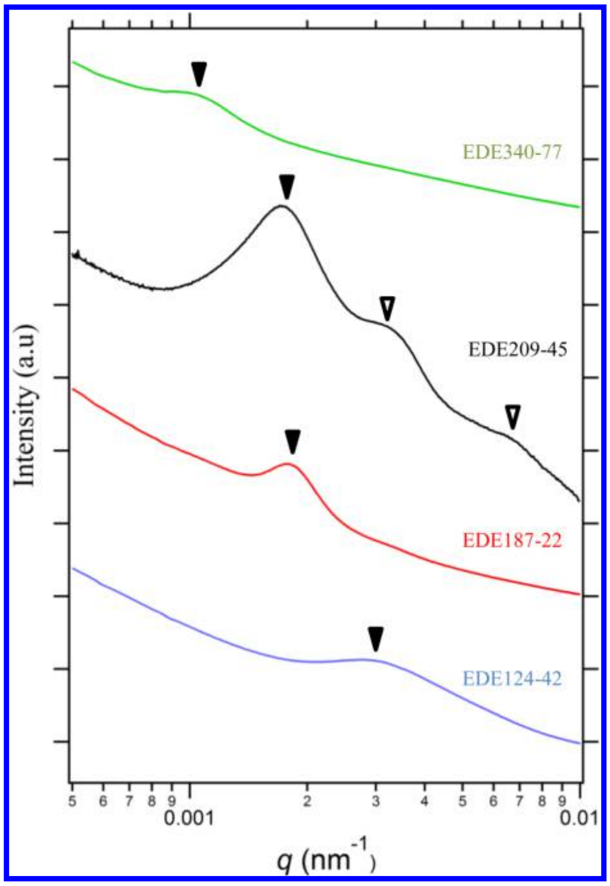

Figure 6. SAXS profiles of microphase separated EDE triblock copolymers collected at 25 °C. Scattering intensity is plotted as a function of the magnitude of the scattering vector, *q*. Filled triangles represent the primary scattering peaks, and the open triangles represent the higher order scattering peaks.

■ CONCLUSIONS

A series of poly(1,4-butadiene)-*b*-polydimethylsiloxane-*b*-poly-(1,4-butadiene) (BDB) triblock copolymers were synthesized by anionic polymerization. The molecular weights of the BDB copolymers ranged from 119 to 335 kg/mol, PDMS volume fractions ranged from 0.23 to 0.78, and dispersities ranged from 1.14 to 1.28. These block copolymers were used to study

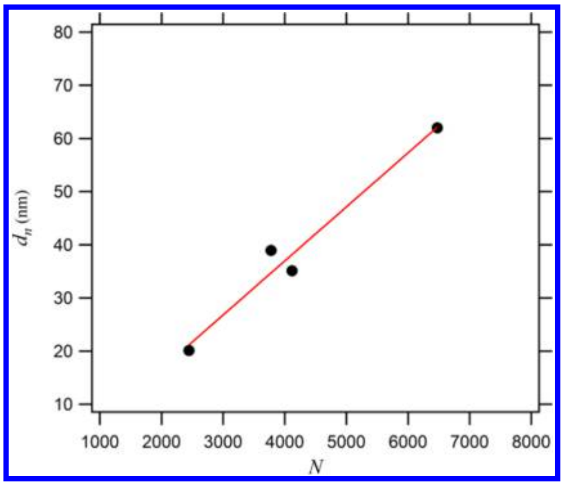

Figure 7. Normalized domain spacing versus the total number of segments per chain based on a reference volume of 0.1 nm^3. Least squares fit is represented by the solid line.

diimide-based hydrogenation of polybutadiene (PBD) in the presence of polydiemthylsiloxane (PDMS). Under standard hydrogenation conditions reported in the pioneering work by Hahn,[10] more than 91% of PDMS degraded. A systematic study of the effect of reaction conditions on the final hydrogenated product suggested that the PDMS degradation was due to nucleophilic attack by the *p*-toluenesulfinate anion species that are generated in situ by the themolysis of *p*-toluenesulfonyl hydrazide. Optimized reaction conditions that led to complete hydrogenation of the PBD blocks without adversely affecting the PDMS block have been identified. This is the first reported synthesis of high molecular weight polyethylene-*b*-polydimethylsiloxane-*b*-polyethylene EDE copolymers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Further characterization results of the synthesized block copolymers obtained by ^{1}H NMR, TGA, DSC and WAXS. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Zolper, T.; Li, Z.; Chen, C. L.; Jungk, M.; Marks, T.; Chung, Y. W.; Wang, Q. *Tribol. Lett.* **2012**, *48*, 355.

(2) Oksman, K.; Lindberg, H. *J. Appl. Polym. Sci.* **1998**, *68*, 1845.

(3) Rosset, S.; Niklaus, M.; Dubois, P.; Shea, H. R. *Adv. Funct. Mater.* **2009**, *19*, 470.

(4) Jung, Y. S.; Ross, C. A. *Nano Lett.* **2007**, *7*, 2046.

(5) McDonald, J. C.; Whitesides, G. M. *Acc. Chem. Res.* **2002**, *35*, 491.

(6) Ozcam, A. E.; Petzetakis, N.; Silverman, S.; Jha, A. K.; Balsara, N. P. *Macromolecules* **2013**, *46*, 9652−9658.

(7) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359.

(8) de Jong, J.; Lammertink, R. G. H.; Wessling, M. *Lab Chip* **2006**, *6*, 1125.

(9) Bellas, V.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **2000**, *33*, 6993.

(10) Hahn, S. F. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 397.

(11) Schmelz, J.; Schedl, A. E.; Steinlein, C.; Manners, I.; Schmalz, H. *J. Am. Chem. Soc.* **2012**, *134*, 14217.

(12) Pitet, L. M.; Zhang, J.; Hillmyer, M. A. *Dalton Trans.* **2013**, *42*, 9079.

(13) Gehlsen, M. D.; Weimann, P. A.; Bates, F. S.; Harville, S.; Mays, J. W.; Wignall, G. D. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 1527.

(14) Bates, F. S.; Fredrickson, G. H.; Hucul, D.; Hahn, S. F. *AIChE J.* **2001**, *47*, 762.

(15) Hucul, D. A.; Hahn, S. F. *Adv. Mater.* **2000**, *12*, 1855.

(16) Almdal, K.; Hillmyer, M. A.; Bates, F. S. *Macromolecules* **2002**, *35*, 7685.

(17) Spanos, C. G.; Ebbens, S. J.; Badyal, J. P. S.; Goodwin, A. J.; Merlin, P. J. *Macromolecules* **2002**, *36*, 368.

(18) Ciolino, A.; Sakellariou, G.; Pantazis, D.; Villar, M. A.; Vallés, E.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1579.

(19) Hahn, S. F.; Vosejpka, P. C. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40*, 970.

(20) Maheshwari, S.; Tsapatsis, M.; Bates, F. S. *Macromolecules* **2007**, *40*, 6638.

(21) Chang, J. R.; Huang, S. M. *Ind. Eng. Chem. Res.* **1998**, *37*, 1220.

(22) Ness, J. S.; Brodil, J. C.; Bates, F. S.; Hahn, S. F.; Hucul, D. A.; Hillmyer, M. A. *Macromolecules* **2002**, *35*, 602.

(23) Hu, T.-S.; Yu, Q.; Wu, Y.-L.; Wu, Y. *J. Org. Chem.* **2000**, *66*, 853.

(24) Smit, C.; Fraaije, M. W.; Minnaard, A. J. *J. Org. Chem.* **2008**, *73*, 9482.

(25) Cusack, N. J.; Reese, C. B.; Risius, A. C.; Roozpeikar, B. *Tetrahedron* **1976**, *32*, 2157.

(26) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211.

(27) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev. (Washington, D. C.)* **2001**, *101*, 3747.

(28) Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Mays, J. *Prog. Polym. Sci.* **2006**, *31*, 1068.

(29) Hirao, A.; Goseki, R.; Ishizone, T. *Macromolecules* **2014**, *47*, 1883−1905.

(30) Uhrig, D.; Mays, J. W. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6179.

(31) Petzetakis, N.; Pitsikalis, M.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 1092.

(32) Kotzabasakis, V.; Petzetakis, N.; Pitsikalis, M.; Hadjichristidis, N.; Lohse, D. J. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 876.

(33) Vougioukalakis, G. C.; Stamatopoulos, I.; Petzetakis, N.; Raptopoulou, C. P.; Psycharis, V.; Terzis, A.; Kyritsis, P.; Pitsikalis, M.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5241.

(34) Ndoni, S.; Papadakis, C. M.; Bates, F. S.; Almdal, K. *Rev. Sci. Instrum.* **1995**, *66*, 1090.

(35) Eitouni, H. B.; Balsara, N. P. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; Springer: Berlin, 2006.

(36) Bassindale, A. R.; Taylor, P. G. In *Organic Silicon Compounds (1989)*; John Wiley & Sons, Ltd.: London, 2004; p 839.

(37) Leibler, L. *Macromolecules* **1980**, *13*, 1602.

(38) Douzinas, K. C.; Cohen, R. E.; Halasa, A. F. *Evaluation of domain spacing scaling laws for semicrystalline diblock copolymers*; Massachusetts Inst. Technol.: Cambridge, MA, 1991.