

Synthesis and characterization of (star polystyrene)-*block*-(linear polydimethylsiloxane)-*block*-(star polystyrene) triblock copolymers

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Summary

(Star polystyrene)-*block*-(linear polydimethylsiloxane)-*block*-(star polystyrene) triblock copolymers were synthesized by making living star-shaped polystyrenes through a convergent living anionic polymerization procedure, followed by ring-opening polymerization of hexamethylcyclotrisiloxane (D_3) then difunctional coupling. The molecular weights of the resulting polymers were characterized by gel permeation chromatography (GPC), multi angle laser light scattering (MALLS) and 1H NMR spectroscopy. Triblock copolymers with relatively narrow molecular weight distributions were obtained.

Introduction

Polydimethylsiloxane (PDMS) is a material that combines many unique properties, such as high chain flexibility, low surface energy, a low glass transition temperature, a low solubility parameter, low absorption in deep UV, excellent thermal and oxidative stability, and good radiation resistance [1]. These properties make PDMS a very attractive material for many applications.

Block copolymers containing PDMS have been studied as new materials because of the capability of incorporating some of the desirable properties of PDMS. Sequential living anionic polymerization of styrene and ring-opening polymerization of hexamethylcyclotrisiloxane (D_3) has been used to prepare well-defined polystyrene-*block*-polydimethylsiloxane (PS-*block*-PDMS) diblock copolymers with a controlled molecular weight and low polydispersity [2-4]. Followed by coupling, these diblocks have been joined together to make triblock copolymers [5-7]. PS-PDMS block copolymers have a pronounced incompatibility between these two blocks compared to other block copolymers [2,3,5,8,9]. The copolymer is very strongly phase separated with a well-defined interface and nearly pure micro domains up to 150 °C, and no experimentally observed order-disorder transition has been found without first going through the thermal decomposition temperature [6].

PS-*block*-PDMS-*block*-PS triblock copolymers are potential thermoplastic elastomer materials, but they also have numerous drawbacks for that application, including poor processibility and poor tensile strengths [10]. The poor processibility, caused by the persistence of the phase separation under the processing conditions, is expected to be improved by increasing the compatibility between the two blocks [6,11,12]. Because star-shaped polymers have increased solubility [13,14], the compatibility between the two blocks can possibly be improved by introducing star branching into the polystyrene block. Introducing branching to the PS blocks is expected to change the compatibility of the PS block with the PDMS block, thus affecting the order-disorder transition, morphology, and improving the processibility.

Star branching has been introduced into polystyrene by a one-pot convergent living anionic polymerization (CLAP) procedure [15-17]. Star-branched polystyrene has been synthesized by slowly introducing a dual functional coupling agent to living polystyrene anions [15,16]. The dual functional coupling agent contains a silyl chloride group that can terminate a living polymer chain and a vinyl group that can add to a living polymer chain to form a new living site. By adding less than the stoichiometric amount of coupling agent to living polystyrene anions, star-shaped polystyrene with a living site at the core can be produced. The resulting living star can initiate a polymerization reaction of styrene monomer to synthesize star-*block*-linear diblock polystyrene [18-21]. Star-*block*-linear-*block*-star triblock (pom-pom) polystyrene has been obtained by difunctional coupling of the living diblock polystyrenes [19,21].

Star branching can be introduced into the PS block of the PS-PDMS block copolymers by a method similar to that used in the synthesis of star-*block*-linear diblock and star-*block*-linear-*block*-star triblock (pom-pom) polystyrene [19,21]. Star-shaped living anionic macroinitiator can be synthesized by introducing a controlled amount of 4-(chlorodimethylsilyl)styrene (CDMSS) to polystyrene living chains. Followed by the sequential addition of D₃ and then a difunctional coupling agent, a (star PS)-*block*-(linear PDMS)-*block*-(star PS) triblock copolymer can be obtained. The purpose of this paper is to describe the synthesis and molecular weight characterization of (star PS)-*block*-(linear PDMS)-*block*-(star PS) triblock copolymers. The resulting material can be used as model samples to study the morphology and the influence of branching on the order-disorder transition of this phase separated copolymer.

Experimental Section

Materials

Styrene (98%), *p*-chlorostyrene (97%), chlorotrimethylsilane (99%), dichlorodimethylsilane (99%), 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) (98%), and hexamethylcyclotrisiloxane (D₃) (98%) were obtained from Aldrich Chemical Company. Reagents were dried over calcium hydride and distilled under argon or under reduced pressure. *sec*-BuLi (1.30 M in cyclohexane) was obtained from Aldrich Chemical company and was used as

received. 4-(Chlorodimethylsilyl)styrene (CDMSS) was synthesized as reported [16], dried over calcium hydride, and distilled under reduced pressure just prior to use. HPLC grade cyclohexane and THF from Fisher Scientific were purified as reported [21]. 1,4-dioxane, methanol, and HPLC toluene from Fisher Scientific were used as received. All glassware, glass syringes, and needles were carefully cleaned and subsequently dried in an oven at 150 °C for 24 hours. Reaction flasks were further flame dried and cooled under argon prior to use. Gastight syringes (Hamilton Co., #1005 and #1010) were washed with a dilute *sec*-BuLi solution followed by washing with dry cyclohexane.

Polymerization

The anionic polymerization of styrene and D₃ was carried out under argon in rubber septum sealed round-bottom flasks containing glass-coated stirbars using syringe transfer techniques.

The typical reaction (e.g., Experiment 1) is as follows: styrene (3.0 mL, 26.1 mmol) and 100 mL cyclohexane were charged into a 250 mL round-bottom flask sealed with a rubber septum, and the flask was pressurized with argon. The solution was titrated with *sec*-BuLi to a pale yellow color before the addition of the required amount of *sec*-BuLi (2.4 mL, 3.1 mmol). The polymerization of styrene was allowed to proceed at room temperature for two hours. An aliquot (5 mL) of the reaction solution was removed and precipitated into argon-purged methanol. THF (3.0 mL) was added to the reaction solution and a mixture of CDMSS in cyclohexane (approximately 0.50 M) was added slowly by using a gastight syringe while the addition rate was controlled by using a syringe pump. 4.2 mL CDMSS/cyclohexane mixture was added over a course of four hours. Thirty minutes after completion of the addition, an aliquot (5 mL) of the reaction solution was removed and precipitated into argon-purged methanol. 15-Crown-5 (0.6 mL, 3.1 mmol) was added to the bulk solution followed by a mixture of D₃ (5.0 g, 22.5 mmol) in 20 mL THF. The typical red color of the polystyryl anions quickly disappeared. The temperature of the solution was raised to 50 °C. After five hours, 40 mL of the reaction solution was transferred by a double-tipped needle into a mixture of chlorotrimethylsilane (1.0 mL, 7.9 mmol) in 10 mL cyclohexane, and the resulting mixture was stirred for three hours. The end-capped (star PS)-*block*-(linear PDMS) diblock copolymer that was obtained was then precipitated into methanol. Meanwhile, 1.0 mL of a 0.33 M mixture of dichlorodimethylsilane (DCDMS) in cyclohexane was slowly added into the bulk of the reaction solution at a rate of 0.04 mL/hour. After completion of the addition, the reaction solution was poured into rapidly stirred methanol. All precipitated samples were isolated by filtration, and then dried to a constant weight at room temperature under vacuum. The yield of this reaction was not measured. ¹H NMR (CDCl₃): δ 0.1 ppm (*s*, 6H, -Si-(CH₃)₂); δ 1.3-2.3 ppm (*m*, 3H, -CH(Ph)-CH₂-); δ 6.4-7.2 ppm (*m*, 5H, Ph-H).

Samples from experiments 3 and 4 were fractionated in order to remove residual polystyrene stars that were prematurely terminated from the addition of protic impurities prior to the initiation and subsequent polymerization of D₃. Toluene/1,4-dioxane mixture (4:1 v/v) was used as the solvent and methanol

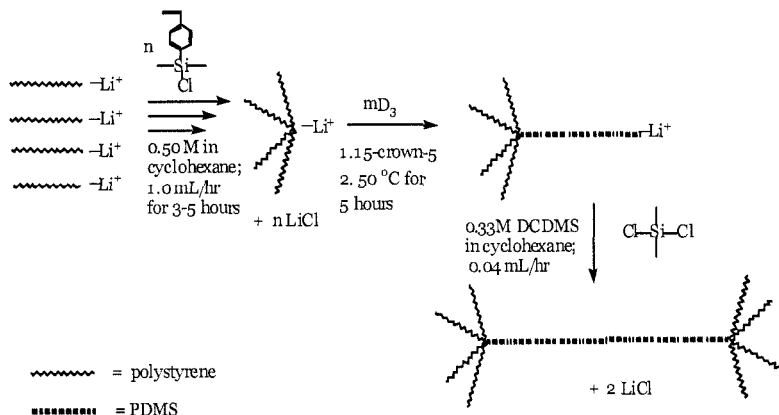
was used as the non-solvent in this procedure. The mass recoveries of these fractionations were over 60%.

Characterization

^1H NMR spectroscopy was performed on samples dissolved in deuterated chloroform on a Chemagnetix CMX Infinity 400 instrument. Molecular weight and molecular weight distributions were characterized by gel permeation chromatography (GPC) performed on a Hewlett-Packard model 1084B liquid chromatograph equipped with two Hewlett-Packard Plgel 5μ Mixed-D columns (linear molecular weight range: 200 – 400,000 g/mol). A calibrated RI (Waters R401) detector and a Wyatt Technology miniDAWN multi-angle laser light scattering (MALLS) detector ($\lambda = 633$ nm, three detector angles: 45° , 90° and 135°) were used. Elutions were carried out at an ambient temperature with THF as the solvent and with a flow rate of 1.0 mL/min. The molecular weight characterization software (Astra 1.5.0b2) was supplied by Wyatt technology. The refractive index increment (dn/dc) used for the polystyrene samples was 0.193 mL/g [16,22]. The dn/dc for the copolymers was determined by the weight average composition determined by ^1H NMR spectroscopy.

Results and Discussion

The synthesis sequence of the (star PS)-*block*-(linear PDMS)-*block*-(star PS) triblock copolymer is shown in Scheme 1. The star-shaped PS macroinitiator was synthesized by slowly introducing CDMSS to living polystyrene chains. (Star PS)-*block*-(linear PDMS) was obtained by the addition of D_3 to the living star-shaped polystyrene. A difunctional coupling agent (DCDMS) was added to the living diblocks to synthesize the triblock copolymer.



Scheme 1. Reaction sequence for the synthesis of (star PS)-*block*-(linear PDMS)-*block*-(star PS). Number of arms in PS star is an average value.

In this work, polystyrene initial chains were synthesized in cyclohexane by

initiating styrene monomers with *sec*-BuLi. A small amount of THF (3% v/v) was added to increase the reaction rate with the CDMSS. The extent of coupling, thus the number of arms as well as the concentration of remaining living anions, was controlled by the total amount of CDMSS added [21]. A series of living star macroinitiators with different arm molecular weight and numbers were prepared. An aliquot of living initial chains and an aliquot of living stars were removed at the appropriate stages of the reaction and each sample was isolated by precipitating in methanol, then characterized by GPC-MALLS to determine the molecular weights and the number of arms. The average number of branching generations (G) and the average number of arms (f) of the living star were calculated as reported [16, 21].

The GPC-MALLS characterization results for the PS initial chains and stars from 4 different experiments are presented in Table 1. The molecular weights of the initial chains are relatively short, 1,170 g/mol, 1,600 g/mol, 2,070 g/mol and 2,070 g/mol, for experiments 1-4, respectively, and the average numbers of the coupled arms in the stars varied from around 2 - 5. For the samples from experiments 1 and 2, the number of coupled arms is only around 2, therefore the resulting copolymers from these experiments are more correctly described as H-shaped [23].

Table 1. Characterization of PS blocks (initial chains and stars)

Exp.	St/BuLi (mmol /mmol)	^a M _n of initial chain (g/mol)/PDI	CDMSS addition rate (mmol/hr)/ BuLi(mmol)	^a M _n of star (g/mol)/ PDI	^b f: Avg. no. of arms
1	8.5	1,170/1.01	0.50/3.12	2,840/1.25	2.3
2	15.0	1,600/1.03	0.25/1.69	3,380/1.20	2.0
3	20.0	2,070/1.01	0.50/2.28	10,300/1.24	4.6
4	20.0	2,070/1.01	0.50/2.28	9,200/1.35	4.1

All reactions were done at room temperature in cyclohexane, the addition of CDMSS (approximately 0.50M in cyclohexane) was completed in the time range of 4-5 hours after 3% v/v THF was added. ^aDetermined by GPC-MALLS; ^bDetermined as reported [16, 21].

15-Crown-5 was added into the solution of living stars to increase the reactivity of the polystyryl anion before the addition of D₃ [6]. THF was added along with D₃ to promote the polymerization [6,24]. The solution quickly changed from the red color of the polystyryllithium to colorless, indicating the formation of the lithium silanolate chain end. The polymerization of D₃ was continued for five hours at 50 °C. Following this reaction time, an aliquot of the reaction mixture was removed to characterize the diblock. In order to stabilize the chain end of the diblock, the diblock was terminated with a trimethylsilyl group by reaction with chlorotrimethylsilane in a cyclohexane mixture.

To the bulk of the reaction mixture, dichlorodimethylsilane was added to couple the diblock chains. The diblocks were joined together by substitution reactions with the silyl chloride groups of dichlorodimethylsilane. In order to achieve the greatest degree of coupling, a dilute solution of dichlorodimethylsilane in cyclohexane was slowly added to the living chains to maintain a deficiency of coupling agent and allow the diblock anions to couple

efficiently.

The GPC elution curves (from RI detector) associated with these experiments are shown in Figures 1-4. As can be seen from these Figures, the progression in molecular weight is as expected. Initial linear chains (a) are coupled by the CLAP technique to form the living stars (b) and the D_3 is effectively polymerized by the star-shaped PS living anionic macroinitiator. The final coupling of the diblock (c) occurs to a high extent by the slow addition of the dilute dichlorodimethylsilane solution to form the triblock copolymer (d), although some low molecular weight contaminants are observed as a high elution volume tail in experiments 1 and 2. Experiments 3 and 4 show a large amount of terminated PS star, presumably due to protic impurities in the THF that was added prior to the addition of D_3 . A simple, one-step fractionation was performed on these samples in order to remove the PS homopolymer impurity (e).

^1H NMR spectroscopy was used to characterize the composition and molecular weight of the triblock samples (Table 2). The composition of the polystyrene and PDMS was obtained by the integration value of the peak areas of the aromatic protons of polystyrene (5 H per repeat unit) and the silyl methyl protons of PDMS (6 H per repeat unit). The molecular weight of the triblock was calculated based on the molecular weight of the PS block from GPC-MALLS and the composition ratio of PS to PDMS.

The characterization of copolymers by GPC-MALLS is a little more problematic than characterization of homopolymers, given that the composition, and therefore the dn/dc , can vary over the elution of the sample [25,26]. The copolymers synthesized in this work, however, were made by living anionic polymerization and should be of a narrow composition. Using the dn/dc of the individual components (0.193 mL/g for PS, and 0.005 mL/g for PDMS [7], and the composition determined by ^1H NMR, the dn/dc of the copolymers were calculated and used for the determination of the molecular weight by GPC-MALLS [22,25].

Table 2. Characterization of triblock copolymers

Exp.	^a Composition (PS/PDMS, wt%)	dn/dc	^c M_n (g/mol) /PDI (GPC-MALLS)	^d M_n (g/mol) (NMR)
1	42/58	0.084	12,100/1.05	13,500
2	47/53	0.093	11,400/1.07	14,400
3	20/80	0.043	74,300/1.07	103,000
4	14/76	0.031	88,000/1.07	131,000

^aBy ^1H NMR; ^bCalculated based on the composition obtained from NMR and the dn/dc of each block. ^cBased on the calculated dn/dc ; ^dCalculated based on the M_n of PS star and compositions of PS and PDMS obtained by ^1H NMR.

Films have been made of these polymer samples. The obtained materials show some characteristics of a thermoplastic elastomer, but qualitatively have poor tensile strengths.

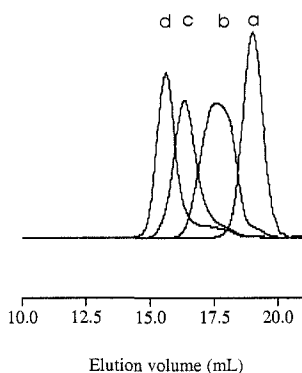


Figure 1. GPC elution curves (RI) demonstrating the molecular weight growth for Experiment 1.

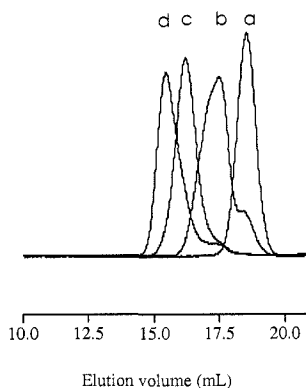


Figure 2. GPC elution curves (RI) demonstrating the molecular weight growth for Experiment 2.

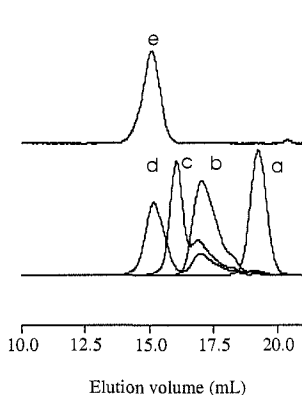


Figure 3. GPC elution curves (RI) demonstrating the molecular weight growth for Experiment 3.

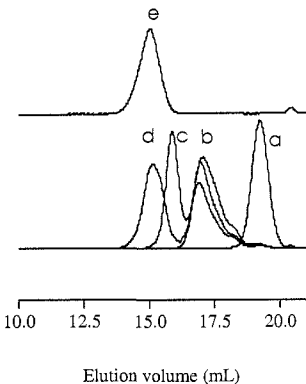


Figure 4. GPC elution curves (RI) demonstrating the molecular weight growth for Experiment 4.

(a) PS initial chain; (b) PS star; (c) (star PS)-*block*-(linear PDMS) diblock; (d) (star PS)-*block*-(linear PDMS)-*block*-(star PS) triblock; (e) purified triblock

Conclusions

Uniquely branched (star PS)-*block*-(linear PDMS)-*block*-(star PS) triblock copolymers were synthesized by the convergent living anionic polymerization (CLAP) of styrene followed by the living anionic ring-opening polymerization of D₃ and difunctional coupling. The progression in molecular weight growth during the synthesis was observed on the GPC elution curves as expected. The chemical compositions and the molecular weights were further characterized by ¹H NMR spectroscopy. The resulting samples are of low polydispersity and displayed thermoplastic elastomer characteristics, but the mechanical properties are relatively poor.

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