

Notes

Self-Assembly Assisted Coupling of End Functional Block Copolymers

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Introduction

In polymer chemistry, living polymerization, especially anionic polymerization, is the most impactful methodology for preparing model block copolymers with a designed molar mass and microstructure.^{1–7} In theory, multiblock copolymers could be synthesized by an alternately sequential addition of different comonomers into a living copolymerization system.^{8–10} In practice, each addition of new monomer will inevitably make some living chain ends dead because of impurities, resulting in a polymer with a broad distribution in chain length. It is very difficult, if not impossible, to fractionate these multiblock chains because their physical properties, such as solubility, are similar. Another limitation of the sequential addition of different comonomers is their compatibility; namely, each added monomer must be sufficiently reactive so that the chain can propagate. Often, a living A block can initiate comonomer B, but a living B block cannot initiate comonomer A. Therefore, the sequential addition method can only be used to make copolymers with a few blocks, such as diblock or triblock copolymers. It is extremely difficult to use this method to prepare long and narrowly distributed multiblock copolymer chains with the block number larger than five.

In another approach, one could, in principle, prepare multiblock copolymers by coupling different precursor polymer blocks capped with extremely reactive ends together in solution.¹¹ However, such a coupling reaction is extremely ineffective when long polymer blocks ($M_w > 10^4$ g/mol) are used because most of the reactive ends are wrapped and hidden inside the polymer chains coiled in good solvent. Moreover, for long precursor polymer blocks, the concentration of the reactive ends is too low to have an effective coupling reaction because the overall polymer concentration cannot be too high. Therefore, the essential problem is how to expose and concentrate the reactive ends of long precursor block

chains and to increase the overall polymer concentration without a significant increase of the solution viscosity.

On the other hand, it is well-known in polymer physics that A–B diblock or A–B–A triblock copolymers with a proper comonomer composition in a selective solvent can self-assemble to form polymeric core–shell-like micelles.^{12–17} Such a self-assembly forces and concentrates the chain end of the soluble block to stay on the periphery of each micelle, which should make the coupling of each two of the reactive ends much easier. Using such a self-assembly assisted polymerization (SAAP) concept, we have so far had a limited success in the preparation of long multiblock copolymers by starting with A–B–A triblock chains.¹⁸ Our experiences have revealed that main difficulties in such a method are twofold. First, we have to remove the solvent in which narrowly distributed precursor A–B–A triblock copolymers chains capped with two reactive ends are prepared and then add a large amount of solvent selectively good for the two A blocks. During this process, some of the chain ends inevitably lose their reactivity because of impurities, such as a trace amount of water and oxygen. Second, the addition of a right amount of linking agent to connect each two of the reactive chain ends is always a problem. Insufficient on excessive amount of linking agent reduces the coupling efficiency. To overcome these difficulties, we recently decided to terminate each anionic end directly with a photosensitive molecule, 7-chlorodimethylsilanoxy-4-methylcoumarin, which can undergo [2 + 2]-photocycloaddition under a UV irradiation of 310 nm. To test this idea, we started with a model precursor diblock polystyrene-*b*-polyisoprene (PS-*b*-PI) copolymer which can self-assemble in *n*-heptane, a poor solvent for the PS block. The self-assembly assisted photocycloaddition of such diblock chains successfully resulted in novel polystyrene-*b*-polyisoprene-*c*-polyisoprene-*b*-polystyrene (PS-*b*-PI-*c*-PI-*b*-PS) “triblock” (B–A–A–B) copolymers.

Experimental Section

Sample Preparation. First, photoreactive coumarin derivative of 7-chlorodimethylsilanoxy-4-methylcoumarin was prepared in the presence of pyridine as the HCl absorbent (Scheme 1). Into 1.06 g (6.02 mmol) of 7-hydroxy-4-methylcoumarin, 30 mL of freshly purified THF and 0.52 mL (6.62 mmol) of pyridine were added and stirred for 10 min at 30 °C, and then, a solution of 0.854 g (6.62 mmol) of dichlorodimethylsilane in 10 mL of THF was slowly dropped in. After 2 h reaction, the mixture was filtrated and purified. Second, the precursor polystyrene-*b*-polyisoprene (PS-*b*-PI) diblock copolymers were synthesized by sequential anionic polymerization of styrene and isoprene. Into a 100 mL Schlenk reactor equipped with a magnetic stirrer, freshly purified 50 mL of THF, 3 mL of styrene, and a calculated amount of *n*-butyllithium solution were injected to start the reaction at –78 °C. After the polymerization was completed, a proper amount of freshly purified isoprene was added, and the reaction was

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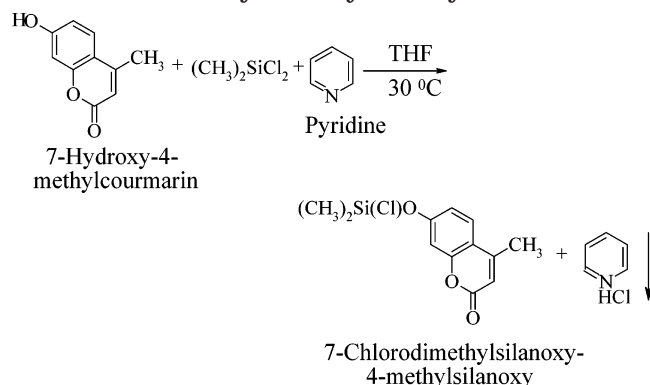
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Table 1. Laser Light Scattering and GPC Characterization of Polystyrene-*b*-polyisoprene Diblock Copolymers in THF, Their Self-Assembled Core–Shell Micellar Nanostructures in *n*-Heptane, and the Coupling Efficiency in the SAAP

characterization of diblock PS- <i>b</i> -PI copolymers											
sample	W_{PS}/W_{PI}^a	structure of PI block ^a		M_w^b (M_w) 10 ⁻⁴ (g/mol)	M_w/M_n^c	$\langle R_h \rangle^d$ (nm)	micellar structure in <i>n</i> -heptane			coupling efficiency ^c (%)	
		1,2- (mol %)	3,4- (mol %)				$M_w^b \times 10^{-6}$ (g/mol)	N_{agg}^b	$\langle R_h \rangle^d$ (nm)		PDI ^d
SI41	4:1	60	40	2.7 (2.8)	1.06	3.7	5.5	203	38.5	1.08	35
SI42	4:2	58	42	3.5 (3.8)	1.08	5.6	5.1	146	27.6	1.01	65
SI44	4:4	60	40	4.5 (4.6)	1.06	7.4	4.0	95	35.0	1.02	46
SI45	4:5	60	40	5.1 (5.3)	1.07	8.6	3.6	71	36.8	1.10	21

^a By ¹H NMR spectroscopy in CDCl₃ at 30 °C. ^b By static laser light scattering. ^c By GPC in THF at 30 °C. ^d By dynamic laser light scattering.

Scheme 1. Synthesis of Photoreactive 7-Chloromethylsilanoxy-4-methylcoumarin



carried at 45 °C for an additional 4 h. The polymerization was terminated by the capture of the anionic end with 7-chlorodimethylsilanoxy-4-methylcoumarin. All manipulations were carried out under an extra-high-pure-grade argon atmosphere. In each step, a portion of the reaction mixture was withdrawn and characterized.

Self-Assembly of PS-*b*-PI. In *n*-heptane, a solvent selectively good for the PI block, such PS-*b*-PI diblock copolymers with a proper comonomer composition can form polymeric core–shell micelles with the insoluble and collapsed PS blocks as the core and the soluble and swollen PI blocks as the shell. The coupling of each two reactive coumarin ends was induced by a photocycloaddition reaction under a UV irradiation of $\lambda_{\text{max}} = \sim 310$ nm. Before the UV irradiation, the solution was degassed with several cycles of vacuum pumping and argon purging so that a possible cross-linking or degradation of the PI block was prevented. The copolymer concentration used was 1.0×10^{-3} g/mL, which is sufficiently low in order to avoid a possible intermicelle coupling reaction.

Laser Light Scattering. A modified spectrometer (ALV/DLS/SLS-5022F) equipped with a multi- τ digital time correlation (ALV5000) and a cylindrical 22 mW UNIPHASE He–Ne laser ($\lambda_0 = 632$ nm) as the light source was used to monitor the self-assembly. Each solution was clarified by passing through a 0.22 μm PTFE filter to remove dust. The stock solution (1 wt %) was first prepared and then diluted to a proper concentration for the LLS measurement. In static LLS, the average radius of gyration ($\langle R_g \rangle$) and the weight-averaged molar mass (M_w) of the micelles were determined, which led to the average aggregation number (N_{agg}) since we know the average molar mass of individual copolymer chains. In dynamic LLS, the Laplace inversion of each measured intensity–intensity time-correlated function in a dilute solution can result in a characteristic line width distribution $G(\Gamma)$. For a purely diffusive relaxation, $G(\Gamma)$ can be converted to a hydrodynamic radius distribution $f(R_h)$ by using the Stokes–Einstein equation.

The average composition and microstructure of PS-*b*-PI diblock copolymers and resultant PS-*b*-PI-*c*-PI-*b*-PS quaterblock copolymers were characterized in CDCl₃ at 30 °C by ¹H NMR spectroscopy (Bruker DPX 300 MHz NMR spectrometer) and by gel permeation chromatography (GPC) (Water 150C

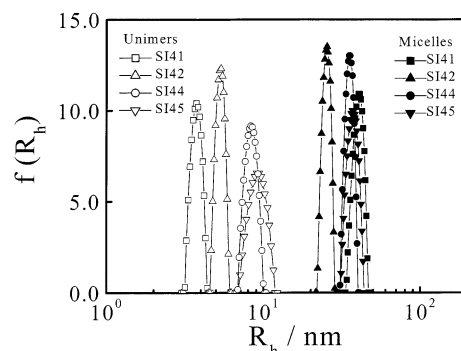


Figure 1. Typical hydrodynamic radius distributions ($f(R_h)$) of four diblock PS-*b*-PI copolymers in THF and their self-assembled micelles in *n*-heptane, when $C = 1.0 \times 10^{-3}$ g/mL and $T = 25$ °C.

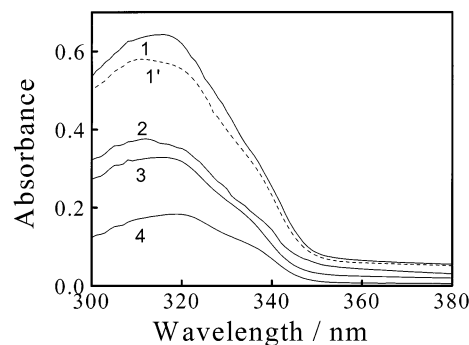


Figure 2. UV spectra of diblock PS-*b*-PI copolymers capped by 7-chlorodimethylsilanoxy-4-methylcoumarin in THF at 25 °C: (1) SI42, without UV irradiation; (1') SI42, after 1 h UV irradiation in THF; (1'') SI42, after 1 h UV irradiation in *n*-heptane; (2) SI41, after 1 h UV irradiation in *n*-heptane; (3) SI44, after 1 h UV irradiation in *n*-heptane.

equipped with a 996 diode-array UV detector) with THF as eluant. The Waters HT-4 column used was calibrated by polystyrene standards with a molar mass range of 2.5×10^3 – 2.0×10^5 g/mol. The extent of the photoreaction was monitored in THF at 30 °C by a UV–vis scanning spectrophotometer (Hitachi U-3300 photodiode) in terms of the change of the maximum absorption of coumarin residues at ~ 310 nm.

Results and Discussion

Four PS-*b*-PI precursor diblock copolymers with an identical PS block ($M_w = 2.26 \times 10^4$ g/mol), but different end-capped PI blocks (PI) ($M_w = 0.57 \times 10^4$, 1.25×10^4 , 2.35×10^4 , and 3.01×10^4 g/mol), were prepared. Their characteristics are summarized in Table 1. The weight-averaged molar mass (M_w) and polydispersity index (M_w/M_n) of four copolymers were in the range of $(2.83\text{--}5.24) \times 10^4$ g/mol and 1.06–1.08, respectively, determined by static LLS and GPC. The low values of M_w/M_n indicate that such prepared copolymers are free

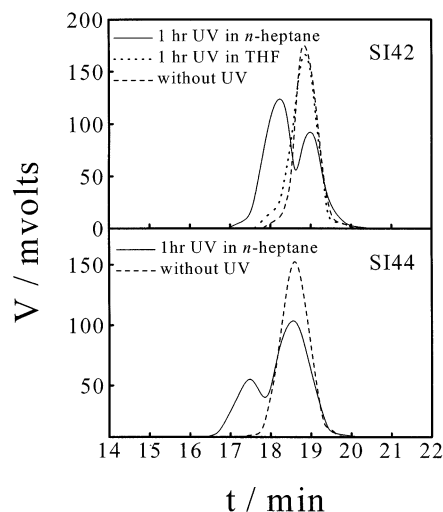


Figure 3. GPC profiles of SI42 and SI44 before and after 1 h UV irradiation in *n*-heptane as well as of SI42 after 1 h UV irradiation in THF without the self-assembly.

of PS homopolymers. The polymerization of isoprene in THF (a polar solvent) results in a mixture of ~60% of 1,2-isomers and ~40% of 3,4-isomers, as revealed by ^1H NMR.

Before the photocycloaddition coupling reaction, the self-assembly of PS-*b*-PI diblock copolymer chains in *n*-heptane was investigated by laser light scattering (LLS). Figure 1 shows typical hydrodynamic radius distributions ($f(R_h)$) of individual PS-*b*-PI diblock copolymer chains in THF as well as their self-assembled core-shell micelles in *n*-heptane. The shifting of the peaks from 3.7–8.6 to 27.6–38.5 nm clearly reveals

the self-assembly of individual diblock copolymer chains, resulting in well-defined narrowly distributed micelles. As shown in Table 1, under an identical adopted micellization condition, the average hydrodynamic radius ($\langle R_h \rangle$) value of the self-assembled core-shell micelles varies with the PI block length. There is a minimum of $\langle R_h \rangle = 27.6$ nm when PS:PI = 4:2. As expected, the aggregation number (N_{agg}) decreases as the soluble PI block length increases because a longer soluble PI block can stabilize a larger surface area of the core so that the copolymer chains have a less tendency to aggregate in *n*-heptane.

It should be emphasized once more that the self-assembly *concentrates* and *exposes* the reactive ends of precursor diblock copolymers on the periphery of such formed core-shell micelles, which greatly increases the coupling efficiency of the photocycloaddition reaction between two coumarin end groups. Such an effect can be clearly viewed in the UV-vis spectrum, as shown in Figure 2. In *n*-heptane, i.e., with the micelle formation, 1 h UV irradiation at $\lambda_{\text{max}} = \sim 310$ nm results in a clear decrease of the absorbance. The decrease is in the order of SI42 > SI44 > SI41. It is helpful to note that the photoreaction only occurs between two very nearby coumarin groups because it involves the orbit overlap of two excited states. In comparison, the irradiation of individual SI42 chains in THF without the micelle formation under the same conditions had much less effect on the absorbance (curve 1 in Figure 2), which clearly reveals the importance of the self-assembly in the coupling reaction.

Figure 3 shows typical GPC curves of two PS-*b*-PI diblock copolymers before and after the photocoupling reaction. The appearance of a peak after the UV

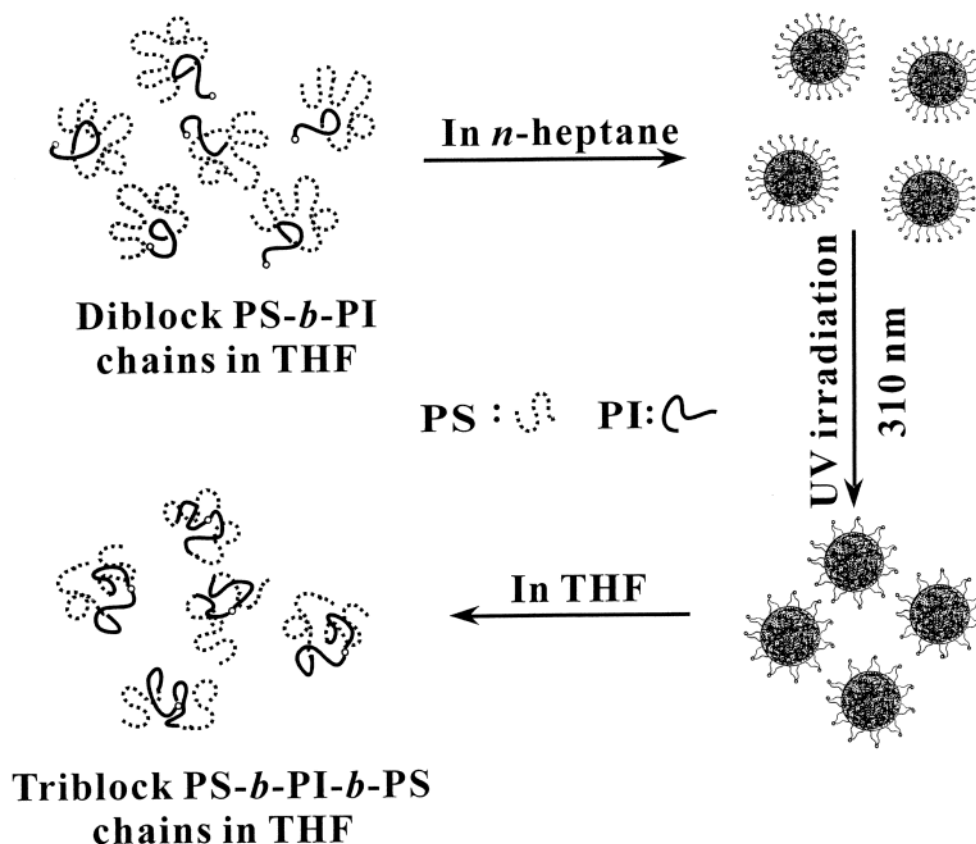


Figure 4. Schematic of self-assembly assisted polypolymerization (SAAP) of PS-*b*-PI diblock chains in a selective solvent solvent, *n*-heptane, under the UV irradiation of ~ 310 nm.

irradiation at a short retention time (i.e., a higher molar mass) with a doubled molar mass ($M_w = 7.2$ and 9.4×10^{-4} g/mol respectively for SI42 and SI44) indicates the formation of longer PS-*b*-PI-*c*-PI-*b*-PS quaterblock copolymer chains. In contrast, the same irradiation of SI42 in THF without the self-assembly resulted in only a slight increase of the molar mass. A deconvolution of the GPC curve shows that ~65% of the diblock chains are coupled together to form triblock copolymer chains. As shown in Table 1, the coupling reaction of diblock copolymer SI42 in the SAAP has the highest efficiency. There is a delicate balance between the self-assembly and the coupling reaction. If the soluble PI block is too long, the reactive end groups are wrapped and hidden inside the coiled PI chains. On the other hand, if the soluble PI block is too short, the self-assembly will be difficult.

Finally, we schematically summarize the principle in Figure 4. It is worth noting that here the two PI-blocks in the resultant triblock copolymer are in the middle. Normally, the PS-block is in the middle of a triblock copolymer made of PS and PI because it is easier to first double-initiate styrene and then to copolymerize isoprene on the anionic end of PS-block. It should be addressed that our final purpose is not to make triblock copolymers. There are classic methods to do it. Our intention is to use this principle to eventually prepare multiblock $-(A-b-B-b-A-c-A-b-B-b-A-)_n-$ copolymer chains by starting with triblock A-B-A chains. We would like to state that the detail of how to couple each two reactive ends can be varied and is not important to the principle of the self-assembly assisted polymerization (SAAP).

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