

# Construction and Properties of Hyperbranched Block Copolymer with Independently Adjustable Heterosubchains

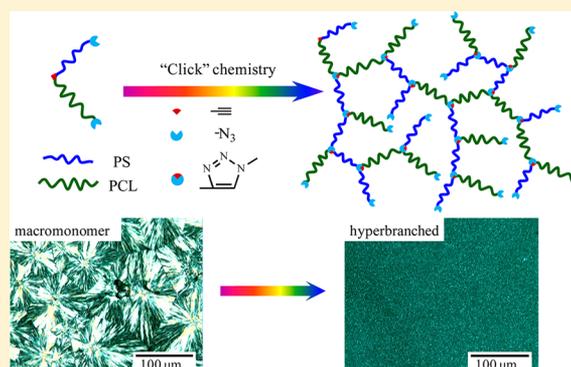
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## Supporting Information

**ABSTRACT:** A trifunctional initiator with one alkyne, one hydroxyl, and one bromine group was used to construct Br-polystyrene-alkyne-poly( $\epsilon$ -caprolactone)-OH (Br-PS- $\equiv$ -PCL-OH) diblock copolymer precursor with one terminal alkyne group located at the junction between the two blocks. Further bromination and azidation substitution of the precursor led to a seesaw-type macromonomer azide-polystyrene-alkyne-poly( $\epsilon$ -caprolactone)-azide (N<sub>3</sub>-PS- $\equiv$ -PCL-N<sub>3</sub>). Subsequently, novel hyperbranched copolymers [HB-(PS-*b*-PCL)<sub>n</sub>] with independently adjustable PS and PCL branching subchains were prepared by “click” chemistry. All of the linear precursors and hyperbranched copolymers were characterized by FT-IR, <sup>1</sup>H NMR, and GPC with triple detectors in detail. It was found that such hyperbranched copolymers are self-similar objects; namely, their intrinsic viscosities ( $[\eta]$ ) are scaled to the weight-average molar masses ( $M_w$ ) as  $[\eta] \sim M_w^\nu$ , where  $\nu = 0.45 \pm 0.01$  and  $0.48 \pm 0.01$  for the longer and shorter PS block, respectively. Moreover, the study on the crystallization behavior of unfractionated and fractionated HB-(PS-*b*-PCL)<sub>n</sub> copolymers indicated both the crystal size and the degree of crystallinity decrease with the PS subchain length and the overall degree of polymerization, and the remaining oligomer and macromonomer components could facilitate the crystallization of the unfractionated sample. Finally, it was found that the degree of crystallinity decreases dramatically when the weight fraction of fractionated hyperbranched copolymer in macromonomer/hyperbranched copolymer blend films exceeds  $\sim 67\%$ , indicating that the uncrystallizable hyperbranched chains may impose some extra restriction on the crystallization of the macromonomer chains.



## INTRODUCTION

Hyperbranched polymers with well-defined long subchains have recently attracted interest due to their unique bulk and solution properties in comparison with hyperbranched polymers with short and rigid subchains,<sup>1–10</sup> such as much higher mechanical strength and different phase morphologies in bulk<sup>3–5</sup> as well as more interesting rheological property<sup>3,11</sup> and self-assembled structures in solution.<sup>7,10</sup> Thus, plentiful research work has been devoted to investigating the structure–property correlation of long subchain hyperbranched polymers. Namely, Hedrick et al. developed a method using AB<sub>2</sub>-type macromonomers with short polymer subchains to synthesize hyperbranched PCL and studied their properties;<sup>12–16</sup> recently, Hutching et al.<sup>5</sup> synthesized complex hyperbranched (co)-polymer architectures by using AB<sub>2</sub>-type polyisoprene and polystyrene as macromonomers and investigated their solid-state morphologies and mechanical properties. However, conventional A<sub>2</sub> + B<sub>3</sub> or Y-type AB<sub>2</sub> approaches always lead to broadly distributed lengths of the subchains between any two neighboring branching points,<sup>3,4,9,17–20</sup> which has hindered the quantitative study of their structure–property correlation.

Previously, using a recently developed B~A~B seesaw-type macromonomer strategy, we prepared different kinds of hyperbranched (co)polymers with uniform subchains, where A and B represent alkyne and azide groups, respectively, and ~ represents a polymer block.<sup>21–24</sup> The scaling relations between their sizes ( $R$ ), intrinsic viscosities ( $[\eta]$ ), and molar masses ( $M$ ) were evaluated;<sup>25</sup> how these hyperbranched chains pass through a small cylindrical pore was studied;<sup>26</sup> and their intrachain folding and interchain association in dilute and semidilute solutions were explored.<sup>10</sup> More recently, Kawaguchi et al.<sup>27</sup> also used a similar approach to prepare a series of hyperbranched poly(L-lactide)s (PLA) and studied how the branching density affects the crystallization of hyperbranched PLA chains.

Those previously studied long-subchain hyperbranched polymers were prepared solely by using either living radical polymerization of vinyl monomers,<sup>21–23,25,26,28–30</sup> such as styrene, methyl methacrylate, and *tert*-butyl acrylate, or ring-opening

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fusion of 100% crystalline PCL.<sup>5</sup>  $W_{\text{PCL}}$  is the weight fraction of PCL in the copolymer which was calculated by <sup>1</sup>H NMR integral.

**Polarizing Optical Microscopy (POM).** The polarizing optical microscopy images were taken by Olympus polarizing microscope with BX51 F system. Each film was prepared by dropping the polymer THF solution with a concentration of 30 mg/mL onto a glass slide and followed by evaporation at room temperature for 24 h.

**Preparation of  $\text{Br-}\left(\text{PCL-OH}\right)_n$  by Ring-Opening Polymerization (ROP).** 0.72 g of initiator (2.2 mmol), 7.72 g of  $\epsilon$ -caprolactone (67.7 mmol), and 0.18 g of  $\text{Sn}(\text{EH})_2$  (0.4 mmol) were added into a 100 mL three-neck bottle, and then 40 mL of anhydrous toluene was added. The mixture was stirred for 5 h at 100 °C under an argon atmosphere. Then the solvent was removed by rotary evaporation, and the product was redissolved in THF. The polymer solution was precipitated into an excess of the mixture of cold methanol/water (3/1, v/v). White solid  $\text{Br-}\left(\text{PCL-OH}\right)_n$  (yield: 7.4 g, 90%) was obtained after drying under vacuum for 24 h.

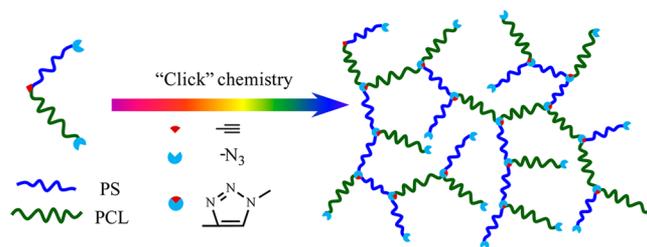
**Preparation of  $\text{Br-PS-}\left(\text{PCL-OH}\right)_n$  by Atom Transfer Radical Polymerization (ATRP).** 1.0 g of  $\text{Br-}\left(\text{PCL-OH}\right)_n$  (0.33 mmol), 3.46 g of St (33.6 mmol), 31 mg of  $\text{Me}_6\text{TREN}$  (0.13 mmol), 54 mg of  $\text{Sn}(\text{EH})_2$  (0.13 mmol), and 2 mL of anhydrous toluene were added into a 15 mL glass tube with a magnetic stirrer. After degassed by three freeze–vacuum–thaw cycles, 5 mg of  $\text{CuBr}$  (0.033 mmol) was added into the tube with a hot funnel, and then the tube was sealed under vacuum. The mixture was stirred for 1.5 h (or 0.5 h to get smaller PS block) at 80 °C in a water bath. Then the tube was rapidly cooled to room temperature. The mixture was diluted with THF and passed through a short neutral alumina column to remove the metal salt. After removing all the solvents by rotary evaporator, the residue was dissolved in THF and precipitated into an excess amount of cold methanol/water mixture (3/1, v/v). White solid  $\text{Br-PS-}\left(\text{PCL-OH}\right)_n$  (yield: 2.1 g, 88%) was obtained after drying under vacuum for 24 h.

**Preparation of  $\text{Br-PS-}\left(\text{PCL-Br}\right)_n$  by Bromination Reaction.** 1.4 g of  $\text{Br-PS-}\left(\text{PCL-OH}\right)_n$  (0.2 mmol), 0.30 g of TEA (3 mmol), and 15 mL of anhydrous DCM were added into a 50 mL three-neck bottle. 2-Bromopropionyl bromide (0.63 g, 3 mmol) dissolved in 5 mL of anhydrous DCM was added dropwise with a constant pressure funnel in 1 h at 0 °C. After 24 h, the solvent was removed. The residue was redissolved in THF. After the removal of insoluble salts by filtration, the filtrate was concentrated by a rotary evaporator. The polymer was precipitated into an excess amount of cold methanol/water mixture (3/1, v/v). Light yellow solid  $\text{Br-PS-}\left(\text{PCL-Br}\right)_n$  (yield: 1.2 g, 85%) was obtained after drying under vacuum for 24 h.

**Preparation of  $\text{N}_3\text{-PS-}\left(\text{PCL-N}_3\right)_n$  by Azidation.** 1.0 g of  $\text{Br-PS-}\left(\text{PCL-Br}\right)_n$  (0.14 mmol) and 0.2 g of  $\text{NaN}_3$  (3.1 mmol) were added into a 50 mL three-neck bottle, and then 18 mL of anhydrous DMF was added. The mixture was stirred for 24 h under an argon atmosphere at room temperature. Then the solvent was removed by rotary evaporation, and the product was redissolved in THF. The polymer solution was precipitated into an excess amount of cold methanol/water mixture (3/1, v/v) after centrifugation. The product  $\text{N}_3\text{-PS-}\left(\text{PCL-N}_3\right)_n$  (yield: 0.85 g, 86%) was light yellow powder after drying under vacuum overnight.

**Preparation of  $\text{HB-(PS-}b\text{-PCL)}_n$  by “Click” Reaction.** As shown in Scheme 2, 0.1 g of  $\text{N}_3\text{-PS-}\left(\text{PCL-N}_3\right)_n$  (0.014 mmol), 15  $\mu\text{L}$  of PMDETA (0.069 mmol), and 0.5 mL of DMF were added into a 2 mL glass tube with a magnetic stirrer. 10 mg of  $\text{CuBr}$  (0.069 mmol) was added into the tube immediately with a hot funnel after degassed by three freeze–vacuum–thaw cycles, and then the tube was sealed under vacuum. The mixture was stirred for 24 h at 60 °C in water bath. After that, the tube was rapidly cooled to room temperature. The mixture was diluted with THF and passed through a short neutral alumina column to remove the metal salt. After removing all the solvents by rotary evaporator, the residue was redissolved in THF and precipitated into an excess of the

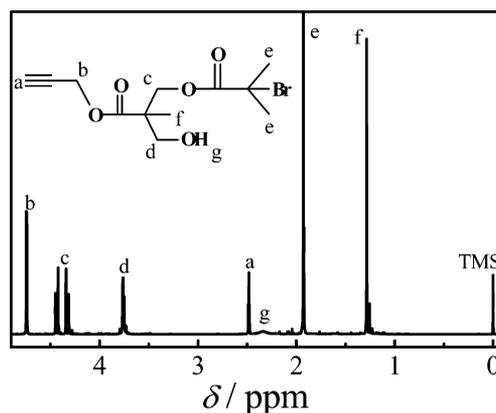
## Scheme 2. Schematic of Topological Structure of $\text{HB-(PS-}b\text{-PCL)}_n$ Prepared via Self-Polycondensation



mixture of cold methanol/water (3/1, v/v). White solid  $\text{HB-(PS-}b\text{-PCL)}_n$  (yield: 68 mg, 68%) was obtained after drying under vacuum for 24 h.

## RESULTS AND DISCUSSION

The preparation of the trifunctional initiator can be found elsewhere.<sup>47</sup> The purity of the initiator was confirmed by <sup>1</sup>H NMR, as shown in Figure 1. Using this initiator, we successively



**Figure 1.** <sup>1</sup>H NMR spectrum of the trifunctional initiator.

obtained precursors  $\text{Br-}\left(\text{PCL-OH}\right)_n$  and  $\text{Br-PS-}\left(\text{PCL-OH}\right)_n$  by ROP of  $\epsilon$ -caprolactone and ATRP of styrene. The absolute degrees of polymerization (DP) of PCL and PS blocks were determined by <sup>1</sup>H NMR. Figure 2 shows that the characteristic peaks located at  $\sim 4.00$  ppm (“d”) and  $\sim 3.65$  ppm (“d’”) are attributed to the protons of  $-\text{CH}_2\text{OOC}-$  and  $-\text{CH}_2-\text{OH}$  on the chain backbone and end of each PCL block, respectively. Therefore, DP of the PCL block was calculated according to the area ratio (A) of the two peaks as

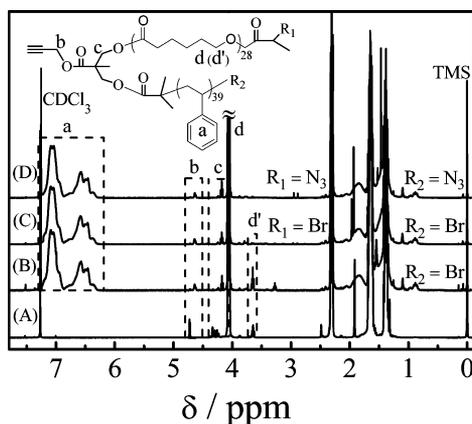
$$\text{DP}_{\text{PCL}} = (A_d + A_{d'})/A_{d'} \quad (3)$$

Similarly, we calculated the DP of the PS block according to the area ratio of the peak (a) and peaks (d and d’) as

$$\text{DP}_{\text{PS}} = (2\text{DP}_{\text{PCL}}A_a)/(5(A_d + A_{d'})) \quad (4)$$

For the sake of convenience, the PCL homopolymers and the PCL-*b*-PS diblock copolymers with different block lengths of PCL and PS are denoted hereafter as  $\text{Br-}\left(\text{PCL-}n\text{-OH}\right)_m$  and  $\text{Br-PS}_m\text{-}\left(\text{PCL-}n\text{-OH}\right)_m$  where *n* and *m* are the DP of PCL and PS determined by <sup>1</sup>H NMR spectroscopy, respectively.

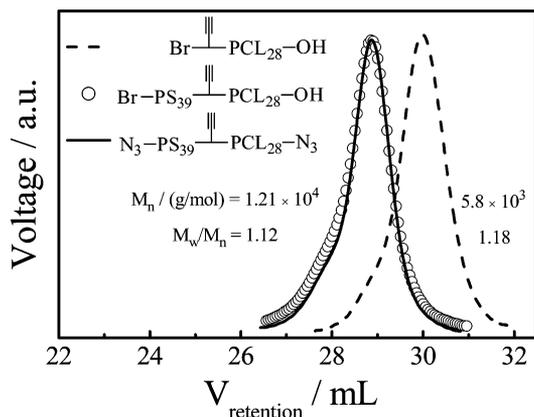
Further conversion of precursor  $\text{Br-PS}_{39}\text{-}\left(\text{PCL}_{28}\text{-OH}\right)_n$  into  $\text{Br-PS}_{39}\text{-}\left(\text{PCL}_{28}\text{-Br}\right)_n$  in a 15-fold excess amount of bromination agent, 2-bromopropionyl bromide, with respect to the hydroxyl



**Figure 2.**  $^1\text{H}$  NMR spectra of (A)  $\text{Br-PS}_{39}\text{-b-PCL}_{28}\text{-OH}$  (B)  $\text{Br-PS}_{39}\text{-b-PCL}_{28}\text{-OH}$  (C)  $\text{Br-PS}_{39}\text{-b-PCL}_{28}\text{-Br}$  and (D)  $\text{N}_3\text{-PS}_{39}\text{-b-PCL}_{28}\text{-N}_3$ .

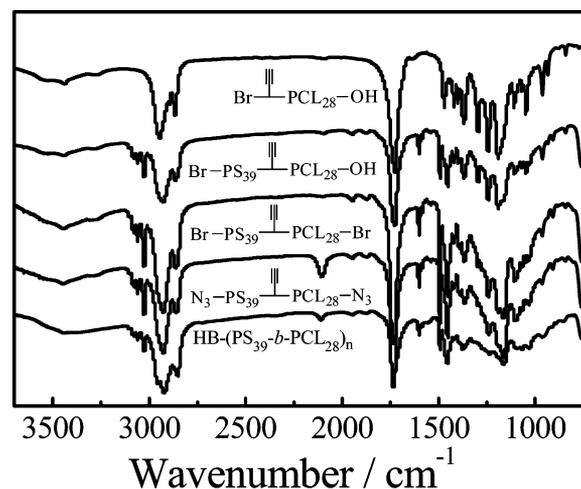
groups is reflected in the disappearance of the proton signals ( $\sim 3.65$  ppm, "d'" in Figure 2) of the  $-\text{CH}_2\text{-OH}$  located at the end of the PCL block. The substitution extent was evaluated to be over 95%. Note that both of the bromine atoms located at the PS and PCL block ends are bonded to secondary carbon atoms, which avoided the possible reactivity difference between the two bromine atoms.

The GPC curves of the prepared linear chain precursors are shown in Figure 3. The polydispersity index ( $M_w/M_n$ ) of the



**Figure 3.** GPC curves of the linear chain precursors  $\text{Br-PS}_{39}\text{-b-PCL}_{28}\text{-OH}$   $\text{Br-PS}_{39}\text{-b-PCL}_{28}\text{-OH}$  and  $\text{N}_3\text{-PS}_{39}\text{-b-PCL}_{28}\text{-N}_3$ .

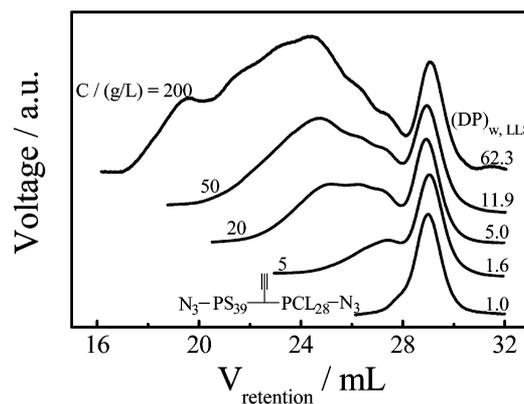
first block  $\text{Br-PS}_{39}\text{-b-PCL}_{28}\text{-OH}$  and the diblock  $\text{Br-PS}_{39}\text{-b-PCL}_{28}\text{-OH}$  was measured to be  $\sim 1.18$  and  $\sim 1.12$ , respectively, indicating that both ROP and ATRP processes were well-controlled. Further substitution of each bromine end by an azide moiety resulted in the final precursor  $\text{N}_3\text{-PS}_{39}\text{-b-PCL}_{28}\text{-N}_3$ . It is well-known that the azidation reaction is extremely effective in polar solvent such as dimethylformamide (DMF) and typically completed within 24 h.<sup>42,43</sup> The successful substitution of the bromines is reflected in the strong  $\text{N}=\text{N}=\text{N}$  asymmetrical stretching vibration ( $\sim 2100$   $\text{cm}^{-1}$ ) (Figure 4). On the other hand, Figure 3 shows no obvious difference between the elution



**Figure 4.** IR spectra of  $\text{Br-PS}_{39}\text{-b-PCL}_{28}\text{-OH}$   $\text{Br-PS}_{39}\text{-b-PCL}_{28}\text{-OH}$   $\text{Br-PS}_{39}\text{-b-PCL}_{28}\text{-Br}$   $\text{N}_3\text{-PS}_{39}\text{-b-PCL}_{28}\text{-N}_3$  and  $\text{HB}(\text{PS}_{39}\text{-b-PCL}_{28})_n$ .

curves of  $\text{Br-PS}_{39}\text{-b-PCL}_{28}\text{-OH}$  and  $\text{N}_3\text{-PS}_{39}\text{-b-PCL}_{28}\text{-N}_3$  indicating no side reaction. In order to find how the PS subchain length and the overall chain molar mass affect the properties of such prepared hyperbranched copolymers  $\text{HB}(\text{PS-}b\text{-PCL})_n$ , we further made another diblock macromonomer ( $\text{N}_3\text{-PS}_{18}\text{-b-PCL}_{28}\text{-N}_3$ ) with an identical PCL block but a shorter PS block. Its characterization results are summarized in Figure S1 of the Supporting Information.

The interchain "clicking" of  $\text{N}_3\text{-PS}_{18}\text{-b-PCL}_{28}\text{-N}_3$  in DMF at  $60^\circ\text{C}$  led to large hyperbranched copolymer chains  $\text{HB}(\text{PS-}b\text{-PCL})_n$ . Figure 5 (also Figures S2 and S3) lists the



**Figure 5.** GPC curves of  $\text{HB}(\text{PS}_{39}\text{-}b\text{-PCL}_{28})_n$  monitored by RI detector, where the signed  $(\text{DP})_{w,\text{LLS}}$  values are calculated from the data collected by the MALLS detector.

characterization results. Note that the difference in the elution curves of  $\text{HB}(\text{PS-}b\text{-PCL})_n$  measured by RI and MALLS detectors, as shown in Figure S2, is due to the fact that the signal from RI detector is proportional to the weight concentration of polymer, while that from MALLS detector is proportional to the weight concentration of polymer multiplied by the weight-average molar mass of polymer. It is known that GPC-RI is not able to effectively distinguish polymer chains with a similar hydrodynamic volume but different configurations.

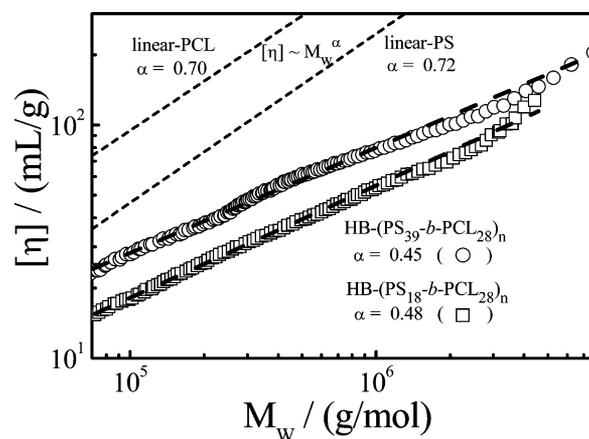
Thus, we used absolute weight-average molar mass ( $M_w$ ) of each hyperbranched copolymer determined by MALLS detector in current study. Furthermore, the self-polycondensation process is described in terms of the average degree of polycondensation (DP), where DP is defined as the number of macromonomers chemically coupled together inside each hyperbranched chain, i.e.,  $(DP)_w = M_{w,hyperbranched}/M_{w,macromonomer}$  and  $(DP)_n = M_{n,hyperbranched}/M_{n,macromonomer}$ , where  $M_{w,hyperbranched}$  and  $M_{w,macromonomer}$  are the weight-average molar mass of hyperbranched copolymers and macromonomers and  $M_{n,hyperbranched}$  and  $M_{n,macromonomer}$  are the number-average molar mass of hyperbranched copolymers and macromonomers, respectively. Hereafter, we will only use the weight-average degree of polycondensation  $[(DP)_w]$ , instead of the number-average one  $[(DP)_n]$  to describe the self-polycondensation process.<sup>21,22</sup>

Figure 5 shows that the interchain “clicking” is promoted in a more concentrated precursor solution. GPC traces of HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> with a shorter PS block length are shown in Figure S4. Similar to our previous work on hyperbranched homopolystyrenes,<sup>26</sup> an obvious peak with a retention volume of 29.1 mL close to that of macromonomer precursor in the elution curve is observed in Figure 5 and Figure S4, presumably attributed to the unreacted macromonomer due to the incomplete functionality of the end group and/or high viscosity of polymer solutions in late stage of self-polycondensation. Moreover, this peak shifts to a higher retention volume by ~0.1 mL after polycondensation process when the concentration of the macromonomer is 200 g/L, indicating the occurrence of intramolecular cyclization. The molecular parameters of all HB-(PS-*b*-PCL)<sub>n</sub> measured by GPC are listed in Tables S1 and S2 in detail. There is no obvious difference of  $(DP)_w$  between HB-(PS<sub>39</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> and HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> chains for a given initial precursor concentration, indicating the PS block length does not affect the reactivity of the azide end group on the PS subchain. Both  $M_w/M_n$  and  $(DP)_{w,MALLS}/(DP)_{w,RI}$  of such formed HB-(PS<sub>39</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> chains increase significantly with the initial precursor concentration (Figure S3), similar to some previous results.<sup>21–23</sup> The successful “click” coupling of precursors N<sub>3</sub>-PS-PCL-N<sub>3</sub> is also reflected in a sharp decrease of the N=N=N asymmetric stretching vibration signal near ~2100 cm<sup>-1</sup>, as shown in Figure 4.

It is well-known that the Mark–Houwink–Sakurada equation can be expressed as

$$[\eta] = KM_w^\alpha \quad (5)$$

where  $[\eta]$ ,  $K$ , and  $M_w$  are the intrinsic viscosity, Mark–Houwink–Sakurada constant, and weight-average molar mass of a polymer, respectively. In principle, the Mark–Houwink–Sakurada parameter  $\alpha$  can reflect the shape and compactness of polymers. More specifically,  $\alpha$  is 0.2–0.5, 0.5, and 0.6–0.8 for branched polymers, linear polymers in theta solvents, and linear polymers in good solvents, respectively.<sup>20,48</sup> Note that for hyperbranched polymers each elution fraction out of GPC column contains polymer chains with a similar hydrodynamic volume but different topologic structures; thus, the parameter  $\alpha$  for hyperbranched polymers is an average value. Previous results showed that the hyperbranched polystyrene chains have a self-similar property; namely, their size ( $R$ ) and intrinsic viscosity ( $[\eta]$ ) in toluene are scaled to their overall weight-average molar masses ( $M_w$ ) and the weight-average subchain molar mass ( $M_{w,s}$ ) as  $R \sim M_w^\gamma M_{w,s}^\phi$  with  $\gamma = 0.47 \pm 0.01$  and

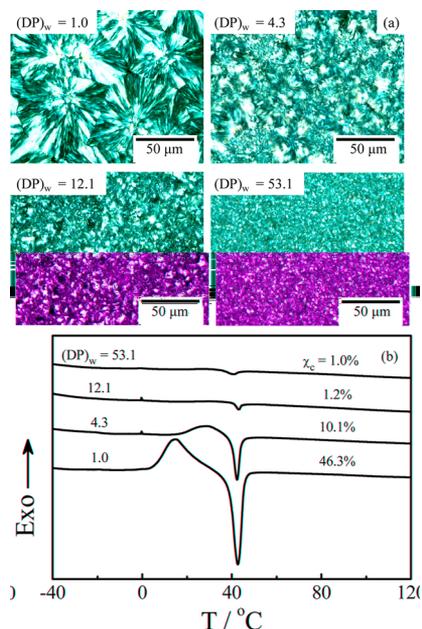


**Figure 6.** Weight-average molar masses ( $M_w$ ) dependence of intrinsic viscosities ( $[\eta]$ ) of HB-(PS<sub>39</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> and HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> in THF. Dashed lines represent weight-average molar masses ( $M_w$ ) dependence of intrinsic viscosities ( $[\eta]$ ) of linear PCL and PS.

$\phi = 0.10 \pm 0.01$ ;  $[\eta] \sim M_w^\nu M_{w,s}^\mu$  with  $\nu = 0.39 \pm 0.01$  and  $\mu = 0.31 \pm 0.01$ .<sup>25</sup> The question here is whether a hyperbranched copolymer chain with two different and alternative subchains still keeps its self-similar character. Figure 6 shows the experimental result about such a  $[\eta]$ – $M_w$  relationship, where we also plot the  $[\eta]$ – $M_w$  relationships for linear PCL and PS (dashed lines) for comparison.<sup>49,50</sup> To the best of our knowledge, there is no theory to predict how  $[\eta]$  is related to  $M_w$  for large hyperbranched copolymer chains in solutions up to now.

Figure 6 shows that for both HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> and HB-(PS<sub>39</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub>  $\log[\eta]$  increases almost linearly with  $\log M_w$ , indicating that their structures remain holding self-similar nature. The least-squares fittings result in  $\nu = 0.48 \pm 0.01$  and  $0.45 \pm 0.01$ , respectively, for HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> and HB-(PS<sub>39</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub>, much smaller than those for linear homopolymers, indicating a hyperbranched chain is more compact than its linear counterpart for a given overall molar mass. On the other hand, Figure 6 shows that  $[\eta]$  of HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> is lower than that of HB-(PS<sub>39</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> for a given  $M_w$ , which is attributed to their different branching densities because shorter subchains lead to a higher branching density. The corresponding scaling laws between the radius of gyration  $R_g$  and molar mass  $M_w$  for HB-(PS<sub>39</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> and HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> are summarized in Figure S5. It is known that the scaling exponent between size and molar mass can also reflect the characteristic of shape and compactness of polymers. The power law exponents are 0.31 for HB-(PS<sub>39</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> and 0.47 for HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub>, which are in accordance with the values of hyperbranched homopolymer PS and PCL,<sup>25,51</sup> indicating compact branched structure.

PCL can be used for biomedical applications because of its excellent biocompatibility and biodegradability. However, its crystallization has an impact on its degradation rate and affects its application. The architectural effect on properties of polymers has been studied by some groups,<sup>5,52–56</sup> including the architecture effect on the crystallization behavior of polymers containing PCL.<sup>52–55</sup> For example, Choi et al.<sup>55</sup> studied the crystallization of three hyperbranched PCLs as well as their linear counterparts with different lengths of homologous PCL segments and different numbers of branching points but similar molecular weights, and they found that the lengths of the linear backbone segments have a positive effect on the crystallization while the numbers of branching points bring opposite effect.



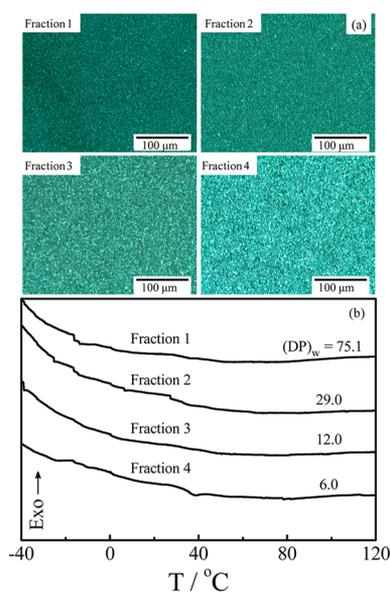
**Figure 7.** Crystalline properties of HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> with different (DP)<sub>w</sub>s: (a) POM photos and (b) DSC curves (10 °C/min) during reheating.

Therefore, we further studied the crystallization of unfractionated HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> with different weight-average molar masses by POM and DSC measurements. Figure 7a shows how the size and shape of the crystalline domain of HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> change with its molar mass. For precursor N<sub>3</sub>-PS<sub>18</sub>-PCL<sub>28</sub>-N<sub>3</sub> ((DP)<sub>w</sub> = 1.0), large integral spherulites were formed, while for large hyperbranched chains with (DP)<sub>w</sub> = 12.1, only few fragmentized crystals appeared; and for even larger hyperbranched chains with (DP)<sub>w</sub> = 53.1, no crystal was observed. The branching effect on the crystallization can be better viewed from the evolution of DSC curves (Figure 7b).

The linear precursor N<sub>3</sub>-PS<sub>18</sub>-PCL<sub>28</sub>-N<sub>3</sub> shows a broad crystallization peak at ~14 °C and a large melting peak at ~44 °C. The endothermic peak (the melting transition) at ~44 °C sharply decreases as the (DP)<sub>w</sub> increases, quantitatively reflecting in a decrease in the degree of crystallinity (χ<sub>c</sub>) from 46.3% to 1.0%, which is similar to the results reported by Kawaguchi et al.<sup>27</sup> for hyperbranched PLA homopolymers. It is interesting to note that a broad exothermic peak attributed to the crystallization is still observable for HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> with (DP)<sub>w</sub> < 12.1, but gradually shifts to a higher temperature as (DP)<sub>w</sub> increases. No exothermic peak can be detected when (DP)<sub>w</sub> ≥ 12.1, indicating the crystallization is completely prohibited due to the constraint of the branching topology. The observed melting transition temperature (T<sub>m</sub> ~ 44 °C) is lower than that of the PCL homopolymer (~64 °C) but similar to those reported by Pan et al.<sup>57</sup> for linear PCL<sub>70</sub>-*b*-PS<sub>24</sub> diblock copolymer (~50 °C). Moreover, no glass transition of linear PS<sub>18</sub> block is detected in both the heating and cooling processes, presumably because the short PS block has a low glass transition temperature (T<sub>g</sub>) that is overlapped with the melting process of PCL.<sup>57,58</sup> In contrast, HB-(PS<sub>39</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> with a longer PS block shows no crystallization in either DSC or POM even for the macromonomer N<sub>3</sub>-PS<sub>39</sub>-PCL<sub>28</sub>-N<sub>3</sub> (Figure S6), revealing that besides using the branching effect, using a longer PS block

can also completely suppress the crystallization of the PCL blocks inside, in consistent with the reported results in the literature.<sup>59,60</sup>

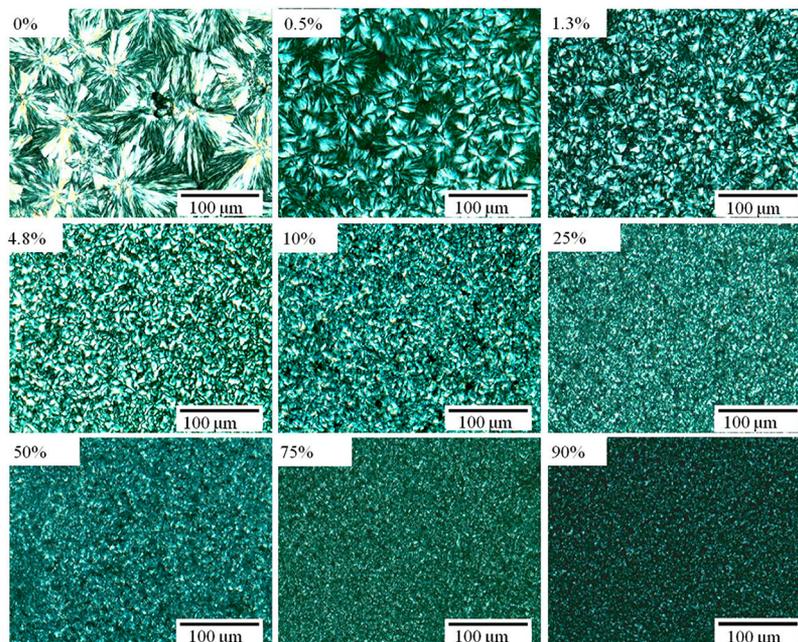
It is worth noting that the conclusions we drew above are established on polymer mixtures with broad polydispersity; as shown in Figure 5, we could draw a more quantitative conclusion with narrowly distributed hyperbranched polymers. Thus, the polydispersed HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> was further fractionated into a set of relatively narrowly distributed samples in a mixed solution of tetrahydrofuran/methanol. The GPC characterization of four selected fractions indicates that the polydispersity index ranges from 1.28 to 2.10, and the detailed characterization results are shown in Figure S7 and Table S3. Both POM and DSC measurements demonstrate that no obvious crystallization behavior was observed for all the fractions, even for the fraction with the smallest (DP)<sub>w</sub> ~ 6.0 (Figure 8),



**Figure 8.** Crystalline properties of four HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> fractions with different (DP)<sub>w</sub>s: (a) POM photos and (b) DSC curves (10 °C/min) during reheating.

indicating that the branching effect originated from only five times of interchain coupling is strong enough to completely suppress the crystallization of PCL blocks. In contrast, the crystallization can be still observed for unfractionated sample with (DP)<sub>w</sub> ~ 12, as shown in Figure 7. Such a discrepancy should be attributed to the existence of some crystallizable components such as linear macromonomers and dimers in the unfractionated mixtures, which also demonstrates that the preparation of narrowly distributed sample is the priority for further quantitative study of structure–property correlation. On the other hand, the complete restriction of crystallization of hyperbranched fraction with a low branching density ((DP)<sub>w</sub> ~ 6) is also due to the introduction of the uncrystallizable PS blocks because the crystallization of hyperbranched PCL homopolymer with a similar branching lengths but a much higher (DP)<sub>w</sub> was still observable in Choi's work.<sup>55</sup>

The above characterization demonstrates that the narrowly distributed hyperbranched fraction and macromonomer are uncrystallizable and crystallizable components in the unfractionated hyperbranched polymers, respectively. Therefore, it is meaningful to further get insight into the effect of one narrowly



**Figure 9.** POM photos of polymer blends of HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>75.1</sub> (fraction 1) and macromonomer  $N_3$ -PS<sub>18</sub>-*b*-PCL<sub>28</sub>-N<sub>3</sub> with different weight fractions (wt %) of HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>75.1</sub>.

distributed uncrystallizable hyperbranched fraction on the crystallization of the crystallizable linear macromonomer. Thus, polymer blends of macromonomer and hyperbranched fraction 1 [HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>75.1</sub>] with different weight fractions (wt %) were prepared for the POM and DSC measurements. Figure 9 shows that the size of the crystallization domain sharply decreases as the weight fraction of hyperbranched fraction 1 increases from 0 to 10%. When the weight fraction reaches 10%, only tiny fragmentized crystals, instead of integrated spherulites, were detected, indicating that the introduction of a small amount of uncrystallizable hyperbranched fraction is enough to significantly affect the crystallization morphology of the PCL blocks. The size of hyperbranched polymer in polymer blend film could be estimated by assuming that the size of hyperbranched polymer is similar to that in theta condition as polymer blend film can be treated as a concentrated polymer solution, in which hyperbranched polymer chains adopt ideal conformation. Considering the difference of the sizes of hyperbranched polymer between in a good solvent and in a theta solvent is small, the average viscometric size ( $\langle R_\eta \rangle$ ) in a theta solvent (or in a polymer blend film) can be extracted from the famous Einstein viscosity relation, modeling the hydrated polymer molecules in terms of equivalent hydrodynamic spheres that would increase the viscosity to the same extent as solid spherical particles of volume  $V_e^{25}$  in a good solvent, i.e.

$$[\eta] = 2.5N_A \left( \frac{V_e}{M_w} \right) \quad (6)$$

where  $[\eta]$  and  $M_w$  are the intrinsic viscosity and weight-average molar mass of the hyperbranched polymer, respectively. Substituting  $V_e = (4/3)\pi R_\eta^3$  into eq 6, we have

$$[\eta] = \frac{10\pi}{3} N_A \left( \frac{R_\eta^3}{M_w} \right) \quad \text{or} \quad R_\eta = \left( \frac{3[\eta]M_w}{10\pi N_A} \right)^{1/3} \quad (7)$$

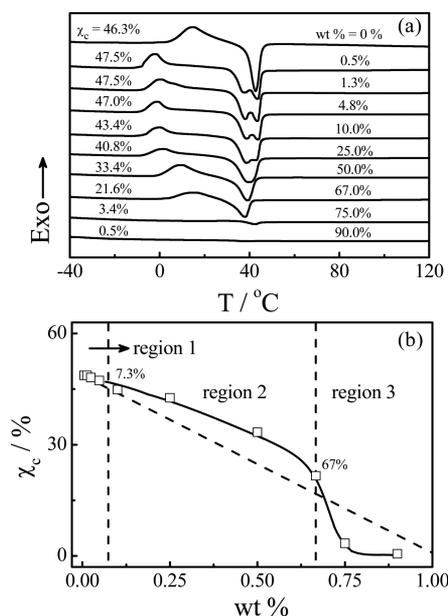
Figure 6 shows that the average intrinsic viscosity of HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>75.1</sub> in THF, a good solvent, is  $\sim 32$  mL/g. Therefore,  $\langle R_\eta \rangle$  of HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>75.1</sub> is calculated to be  $\sim 13$  nm. At a critical weight fraction of hyperbranched polymer (wt %), the whole volume of the blend is filled with hyperbranched polymers; wt % can be evaluated by using

$$\text{wt \%} = \frac{M_w}{\rho N_A \frac{4}{3} \pi \langle R_\eta \rangle^3} \quad (8)$$

where  $M_w$ ,  $\langle R_\eta \rangle$ ,  $\rho$  and  $N_A$  represent the weight-average molar mass, the average viscometric size of hyperbranched polymer, the density of the blend film, and Avogadro's number, respectively. Taking  $M_w \sim 4.07 \times 10^5$  g/mol,  $\langle R_\eta \rangle \sim 13$  nm,  $\rho \sim 1.0$  g/mL and  $N_A \sim 6.02 \times 10^{23}$  mol<sup>-1</sup> into eq 8, wt % can be estimated as  $\sim 7.3\%$ , indicating the hyperbranched polymers start to overlap at wt %  $\sim 7.3\%$  in the blend film and to suppress the free spaces in which large spherulites can form, explaining why only tiny fragmentized crystals were observed when wt % is 10%.

The DSC melting traces of the blends with different weight fractions of HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>75.1</sub> are shown in Figure 10. Figure 10a shows that all the melting peaks are located at the temperature range of 40–50 °C, and some of them contain two melting peaks, presumably due to the melting of the initial crystals grown during the cooling process and the melting of crystals grown during the heating process.<sup>61</sup> Figure 10b shows that the degree of crystallinity decreases as the weight fraction of hyperbranched fraction increases; namely,  $\chi_c$  initially smoothly decreases from  $\sim 47\%$  to  $\sim 21\%$  as wt % increases from 0 to 67% and subsequently drops to 3.4% as wt % reaches to 75%. However, a linear decrease in  $\chi_c$  with wt % is assumed to be observed if only dilution effect is considered, i.e., the dashed oblique line presented in Figure 10b, which is different from what we observed.

It is worth noting that the discrepancy between the transition wt % for the crystal size (wt %  $\sim 10\%$ ) and the degree of crystallinity (wt %  $\sim 67\%$ ) indicates that the crystal size can be



**Figure 10.** (a) DSC curves and (b) degree of crystallinity ( $\chi_c$ ) of polymer blends of HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>75.1</sub> (fraction 1) and macromonomer N<sub>3</sub>-PS<sub>18</sub>-PCL<sub>28</sub>-N<sub>3</sub> with different weight fractions (wt %) of HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>75.1</sub> during reheating, where the scanning rate is 10 °C/min. The dashed oblique line presents the dilution effect of hyperbranched copolymer on the degree of crystallinity.

greatly regulated before a significant change of the overall degree of crystallinity. Combining the results of POM and DSC, the crystallization behavior of the polymer blend may contain three different regions: (1) In the first region (wt % < 7.3%), the hyperbranched polymer cannot fill all the polymer blend as wt % is lower than the critical weight fraction (7.3%), so spherulites can still form but the size of spherulites decreases with the increase in the wt % of the hyperbranched polymer while the degree of crystallinity just decreases slightly. (2) In the second region (7.3% < wt % < 67%), more spaces are occupied as wt % increases, but tiny fragmented crystal can still form because there are abundant but small intrachain spaces for PCL chains to crystallize. (3) In the third region (wt % > 67%), no crystal is detected and the degree of crystallinity sharply decreases to minimum. Such a phenomenon was previously observed in some blend systems where the intercomponent interactions, such as hydrogen bonding<sup>62</sup> or dipole interaction,<sup>63</sup> were introduced into the blend system, which could be explained as the interaction was strong enough to enhance the miscibility of the two components to accordingly completely suppress the crystallization of the crystallizable component at a critical weight concentration. In our case, no specific interaction is assumed to exist between the two components with an identical chemical constituent but only configuration difference; therefore, we would like to attribute this trend to the extra restriction on the crystallization of macromonomer originated from the strong branching interaction of uncrystallizable hyperbranched chains when wt % is ~67%, at which the hyperbranched polymer chains are strongly interpenetrated with each other and result in a highly compact structure. In other words, the interpenetration eliminates all the free volume for the PCL chains to crystallize. This interesting result may provide some useful information for understanding the crystallization behavior of some other polymer blend systems.

## CONCLUSION

In summary, we have developed an approach of combining ring-opening polymerization and atom transfer radical polymerization to construct model hyperbranched copolymers [HB-(PS-*b*-PCL)<sub>n</sub>] with two kinds of controllable and long uniform subchains (PS and PCL) via a trifunctional initiator consisting of one alkyne, one hydroxyl, and one bromine group. Such prepared hyperbranched polymer has a self-similar structure with its intrinsic viscosity ( $[\eta]$ ) scalable to its molar mass ( $M_w$ ) as  $[\eta] \sim M_w^\nu$ , where  $\nu = 0.45 \pm 0.01$  for longer PS block and  $0.48 \pm 0.01$  for shorter PS block. More importantly, we have explored the crystallization behavior of broadly and narrowly distributed HB-(PS-*b*-PCL)<sub>n</sub> copolymers. The results indicate both the crystal size and the degree of crystallinity can be significantly regulated by the PS subchain length and the overall polymerization degree. However, for a given  $(DP)_w$ , the crystallization behavior is much easier to be observed for polydispersed unfractionated samples due to the existence of the crystallizable low-molar-mass components. Finally, the study on the crystallization of polymer blends shows that the degree of crystallinity decreases dramatically when the weight fraction of hyperbranched fractions exceeds ~67%, implying some extra restriction exerted by hyperbranched fraction on the crystallization of the macromonomer. The discrepancy of the transition points of weight fraction between crystal size (~10%) and the degree of crystallinity (~67%) also indicates the crystal size can be greatly regulated before a significant change of the overall degree of crystallinity. It should be emphasized that our synthetic strategy can be applied to not only hydrophobic monomers but also hydrophilic monomers, e.g., methoxy poly(ethylene glycol) methacrylate (POEGMA) and (meth)acrylic acid (PMAA). Such hyperbranched structure may have more potential applications into many bio-related fields. The preparation of other hyperbranched copolymers made of different monomer categories is undergoing.

## ASSOCIATED CONTENT

### Supporting Information

<sup>1</sup>H NMR spectra and GPC curves of macromonomer precursors N<sub>3</sub>-PS<sub>18</sub>-PCL<sub>28</sub>-N<sub>3</sub>, a comparison of  $(DP)_{MALLS}$  and  $(DP)_{RI}$  for HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> and HB-(PS<sub>39</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub>, GPC curves of HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> with different  $(DP)_w$ , GPC curves of HB-(PS<sub>18</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> fractions, POM and DSC studies of crystallization of HB-(PS<sub>39</sub>-*b*-PCL<sub>28</sub>)<sub>n</sub> and GPC data for all the samples used. 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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