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Well-Defined Diblock Macromonomer with a Norbornene Group at Block Junction: Anionic Living Linking Synthesis and Ring-Opening Metathesis Polymerization

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Macromonomers are important precursors for supermolecular construction and have been utilized broadly in the syntheses of branched macromolecular architectures and a variety of polymer materials.[1−6] Two general methods have been used in the preparation of macromonomers: (a) polymerization from a monomer-based initiator[7−13] or chain transfer agent[14,15] and (b) terminal functional group transformation of polymer chains,[16−18] such as end-capping of living polymers,[19−23] to introduce monomer functionalities. The resulting macromonomers typically have a monomer functionality bonded with one polymeric chain. Homopolymer-based macromonomers with in-chain monomer functionalities have been obtained via monomer-based bifunctional initiators or coupling agents, and polymerization of such homopolymerizable macromonomers has produced either brush polymers with relatively high grafting densities[11,12] or graft copolymers with special grafting structures.[19,20] On the other hand, several examples of macromonomers with 1,1-diphenylethylene (DPE) functionalities carrying compositionally different polymeric chains have been reported by Hirao and co-workers.[21−23] These macromonomers were synthesized by end-capping of living anions at the block or star junctions of diblock or miktoarm star copolymers using DPE-based alkyl bromides. Because the DPE group is non-homopolymerizable,[24] these macromonomers would not serve as precursors for brush polymers but were further used for the preparation of asymmetric star copolymers based on anionic living linking chemistry of DPE functionalities.[21−23] Hadjichristidis and co-workers have also used DPE-functionalized macromonomer to prepare miktostar-based macromonomers and graft copolymers.[25] However, to our best knowledge, well-defined diblock macromonomers that possess homopolymerizable monomer functionality at the block junction have not been reported. These macromonomers are of interest because they can be converted into novel "double-brush" copolymers in which each main chain repeat unit carries a diblock graft at the block junction, and potentially the unusual copolymers may further self-assemble into a variety of unique nanostructures. Brush copolymers converted from diblock macromonomers with terminal monomer functionality generally have core−shell morphologies.[9,26]

Herein we report a living linking method for the preparation of such a macromonomer and its transformation into "double-brush" copolymers (Figure 1). The macromonomer synthetic method is based on the terminal functionalization reaction of a living polymer with a monomer-functionalized living linking agent, followed by polymerization of a second monomer initiated by the resulting ω-monomeric macroinitiator. The norbornene (NB) group was selected as the monomer functionality of macromonomer because its high reactivity in ring-opening metathesis polymerization (ROMP) allows for high conversions of macromonomers.[9−11,14−16] Because of the high stability of NB group under typical anionic polymerization conditions as reported by Héroguez et al.,[9,10] and the broad application of anionic living linking chemistry of DPE in the preparation of well-defined complex copolymers,[21−24,27−30] a NB-functionalized DPE agent (**1**) was used as the linking agent to covalently connect NB group to diblock copolymer chain at the block junction. The preparation of **1** was described in our previous publication.[30]

As the first step of the macromonomer synthesis, a poly(styryl-d_8)lithium (**2**) was prepared by anionic polymerization of styrene-d_8 (St-d_8) using *sec*-butyllithium (*s*-BuLi) as initiator in benzene at room temperature ([St-d_8]$_0$:[*s*-BuLi]$_0$ = 10.0). The polymerization was allowed to proceed for 30 min to complete conversion ($DP_{n,calcd}$: 10.0). A small amount of polymerization solution was withdrawn and terminated by methanol. On the basis of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) analysis of the resulting methanol-terminated adduct, **2** was shown to have a M_n of 1250 Da (corresponding to a $DP_{n,MALDI}$ of 10.6) and a low PDI of 1.10 (Figure S1). As the second step of the macromonomer synthesis, addition reaction of a solution of **2** with an excess of **1** (1.27 equiv) was conducted at −78 °C in THF for 1 h to obtain a NB-functionalized poly(St-d_8)-based 1,1-diphenylalkyllithium (**3**). The $-CH_2O(CH_2)_{10}-$ spacer of **1** can reduce unfavorable steric influence on NB group and help to maintain the high ROMP reactivity of the resulting macromonomer. Quantitative formation of **3** was confirmed in a control experiment through a derivative of **3** formed by end-capping of **3** with ethylene oxide, followed by termination with methanol (see Supporting Information for details). As the final step of the macromonomer synthesis, anionic polymerization of 2-vinylpyridine (2-VP) was performed in THF at −78 °C, using **3** as the macroinitiator in the presence of lithium chloride ([LiCl]$_0$:[**3**]$_0$ = 10). To obtain similar lengths of heterochains in the resulting macromonomer **4**, 10.6 equiv of 2-VP relative to macroinitiator **3** was used. Lithium chloride was added to obtain high initiation efficiency and decrease the rate constant ratio of propagation to initiation for anionic polymerization of 2-VP.[31,32] The polymerization was allowed to proceed for 1 h to complete conversion. After the polymerization, the reaction solution was passed through silica gel to remove lithium chloride, followed by precipitated in pentane, to give **4** in 90% isolated yield.

The molecular structure of **4** was verified through its characteristic ^{1}H NMR resonances (Figure 1b, top plot), including resonances of norbornenyl alkene protons *a* and *b* (from **1**) at 6.12, 6.05, and 5.93 ppm, methylene protons *c* and *d* (CH_2OCH_2, from the $-CH_2O(CH_2)_{10}-$ spacer of **1**) at 3.53−2.92 ppm, methyl protons *e* and *f* (from **2**, at the α-end of poly(St-d_8) chain) at 0.78−0.52 ppm, and aromatic protons *g* (from poly(2-VP) chain, on the α-carbon of pyridine nitrogen atom) at 8.66−7.95 ppm. Although the intensity of the resonances of norbornenyl alkene protons *a* and *b* could not be accurately determined due to their overlap with adjacent resonances, the integration area ratio

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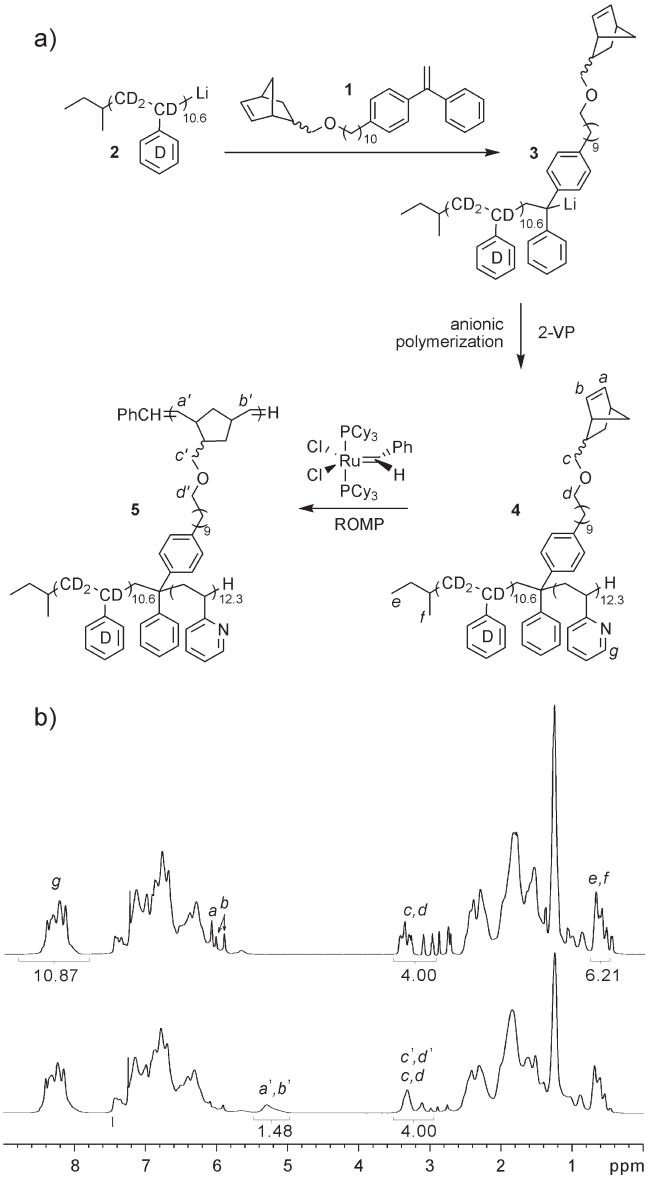

Figure 1. (a) Anionic living linking synthesis and ROMP of novel macromonomer **4**. (b) 600 MHz ^{1}H NMR spectra of macromonomer **4** (top) and its ROMP solution (for entry **5c** in Table 1).

of 4.00:6.21 for resonances of protons *c* and *d* to resonances of protons *e* and *f* agreed with the number ratio of corresponding protons of 4:6 within experimental error, indicating that each macromonomer molecule has quantitatively one poly(St-d_8) chain. Based on the integration area ratio of 4.00:10.9 for resonances of protons *c* and *d* to resonances of protons *g*, a DP_n of 10.9 for the poly(2-VP) chain of **4** was deduced.

MALDI-TOF MS analysis gave molecular weight information on **4**, including a M_n of 2950 Da and a low PDI of 1.08 (Figure 2). Based on a DP_n of 10.6 for the poly(St-d_8) chain of **3**, the $M_{n,MALDI}$ of **4** indicated a DP_n of 12.0 for its poly(2-VP) chain. This $DP_{n,MALDI}$ was in good agreement with the $DP_{n,NMR}$ value of 10.9, and both values were close to the theoretical DP_n value of 10.6 for the poly(2-VP) chain of **4**, suggesting well-controlled anionic polymerization of 2-VP. The low PDI of 1.08 for **4** by MALDI-TOF MS further supports a high initiation efficiency of **3** and a fast initiation relative to propagation in anionic polymerization of 2-VP. Relative to linear polystyrene standards, GPC measurement gave a M_n of 2360 Da and a low PDI of 1.05 for **4**. Its PDI_{GPC} agreed with PDI_{MALDI}. The $M_{n,GPC}$ of **4** was

Table 1. ROMP of Macromonomer 4[a]

		conversion (time)				
entry	$[4]_0/[I]_0$	^{1}H NMR	GPC	$M_{n,calcd}$[b] (kDa)	$M_{n,GPC}$[c] (kDa)	PDI[c]
5a	10	94% (4 h)	94% (12 h)	27.8	11.7	1.15
5b	25	88% (4 h)	88% (12 h)	64.9	20.4	1.13
5c	50	74% (6 h)	77% (12 h)	114	40.6	1.19

[a] Initiator: $RuCl_2(CHC_6H_5)[P(C_6H_{11})_3]_2$; solvent: $CDCl_3$; room temperature. [b] $M_{n,calcd,5} = (M_{n,MALDI,4} \times conv_{GPC} \times [4]_0/[I]_0) + 91$. [c] By GPC relative to linear polystyrenes.

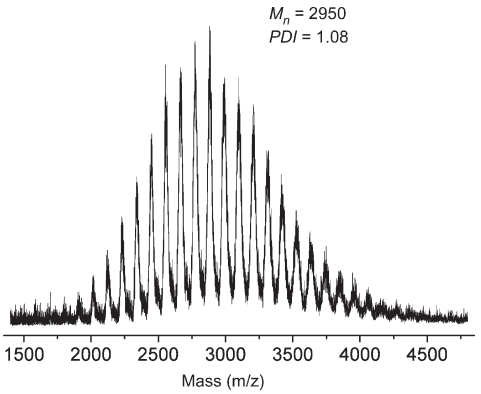

Figure 2. MALDI-TOF MS spectrum of macromonomer **4** (linear mode; matrix: 2,5-dihydroxybenzoic acid).

considerably lower than the correspondent $M_{n,MALDI}$ value as expected for the structure of **4** having a significant side chain at the block junction.

ROMP of macromonomer **4** with its novel structure gave poly(**4**), i.e. **5**, having unique double-brush architecture with each main-chain repeat unit carrying a diblock graft at block junction (Table 1). A series of polymerization experiments of **4** were carried out at room temperature using a commercially available Grubbs' catalyst, $RuCl_2(CHC_6H_5)[P(C_6H_{11})_3]_2$,[33] as the initiator ($[4]_0:[I]_0$ = 10, 25, 50). To monitor readily the ROMP process by ^{1}H NMR spectroscopy, deuterated chloroform was used as the polymerization solvent. With the progress of ROMP, macromonomer **4** was converted into **5**, as indicated by the decrease in intensities of ^{1}H NMR resonances of the norbornenyl alkene protons *a* and *b* of **4** at 6.12, 6.05, and 5.93 ppm, along with the appearance of ^{1}H NMR resonance of the alkene protons *a*′ and *b*′ of poly(NB)-based backbone of **5** at 5.49−5.03 ppm (Figure 1b, bottom plot). The resonance intensities of these alkene protons from **5** were further compared with the entire resonance intensities of methylene protons *c* and *d* from **4** and *c*′ and *d*′ from **5** at 3.54−3.05 ppm to determine conversions of **4**. After 4−6 h of polymerization, high macromonomer conversion (74−94%) was observed by ^{1}H NMR analysis of each trial, although the conversion dropped with increased molar feed ratio of macromonomer **4** to initiator. Then no appreciable increase in macromonomer conversion could be detected with further increase of polymerization time. Finally, all trials were terminated with ethyl vinyl ether after 12 h of polymerization and analyzed by GPC calibrated with linear polystyrenes. Based on the integration area of the GPC peak of **5** relative to the sum of integration areas of both **4** and **5**, GPC analysis of the resulting polymerization solutions confirmed the high conversion of **4** in each trial (Figure 3), and the excellent agreement between GPC measurements and ^{1}H NMR measurements in macromonomer conversion suggests no appreciable occurrence of side reactions for **4** under the ROMP conditions. Well-controlled ROMP behavior of **4** was indicated by the monomodal GPC traces of **5** with low polydispersity values (1.13−1.19). However, the apparent M_n

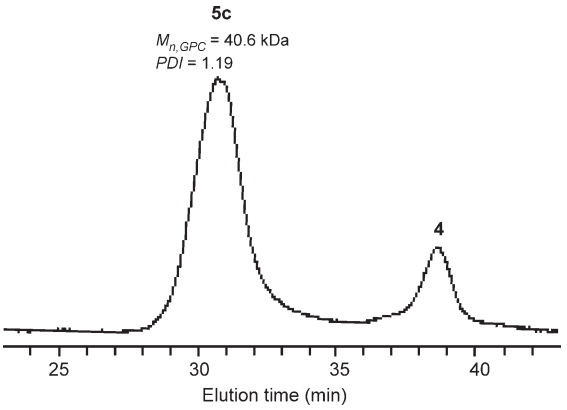

Figure 3. GPC curve for a sample from a ROMP solution of macromonomer **4** (entry **5c** in Table 1).

values of **5** by GPC were only 31−42% of the calculated M_n values ($M_{n,calcd,5} = (M_{n,MALDI,4} \times conv_{GPC} \times [4]_0/[I]_0) + 91$), in agreement with the unusual compactness of densely grafted structure of **5** relative to linear structure of polystyrene standards.[12,14]

In summary, a novel macromonomer with a NB group carrying a diblock copolymer chain at block junction was synthesized by using an NB-functionalized DPE agent as linking agent in anionic polymerization, and its high polymerization reactivity in ROMP was established. The synthetic strategy of the macromonomer via a monomer-functionalized macroinitiator intermediate can be further extended by applying a range of combinations of monomer functionalities and polymerization systems[34] as well as linking chemistry.[35−38] The poly(macromonomer)s derived from such a novel macromonomer possess unique "double-brush" architectures with each main-chain repeat unit carrying two blocks with diverse properties. The macromonomer potentially may also serve as a comonomer for the preparation of a broad variety of grafted architectures with interesting structural features.

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Supporting Information Available: Synthetic and other experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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