

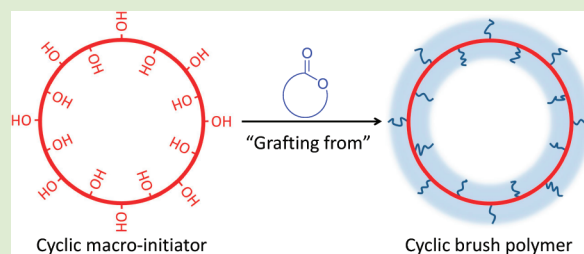
# Cyclic Brush Polymers by Combining Ring-Expansion Metathesis Polymerization and the “Grafting from” Technique

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**S** Supporting Information

**ABSTRACT:** A novel synthetic route to cyclic brush polymers was developed by combining ring-expansion metathesis polymerization (REMP) and the “grafting from” technique. In this approach, ultrahigh molecular weight cyclic polymers with hydroxyl side groups were synthesized first by REMP to form the cyclic macroinitiators. Polyester side chains were then grown from these cyclic macroinitiators by virtue of a triazabicyclodecene-catalyzed cyclic ester ring-opening polymerization to produce the cyclic brush polymers.



Brush polymers have received considerable attention in recent years due to their unique, dense and extended worm-like macromolecular architecture, in comparison with traditional random-coil polymers.<sup>1,2</sup> Over the past few decades, various linear and branched brush polymers have been successfully synthesized;<sup>3–6</sup> however, the preparation of brush polymers with a cyclic macromolecular topology has remained a challenge until now. This is largely due to the difficulty in constructing pure high molecular weight cyclic polymers.<sup>7–9</sup>

To date, there are few reports on the formation of brush polymers that are cyclic in nature. As pioneers in this field, Deffieux and co-workers synthesized cyclic brush polymers by combining the ring-closure approach for the cyclic backbone and the “grafting to” technique.<sup>10–12</sup> Just recently, Laurent and Grayson also reported the preparation of cyclic dendronized polymers via the combination of ring-closure and “grafting from”.<sup>13</sup> However, due to the inherent drawbacks of the ring-closure approach for the synthesis of cyclic polymers, such as the difficulty in obtaining high molecular weight,<sup>14,15</sup> this method is cumbersome. In addition, although the cyclic polymers with high topological purity (>95%) were obtained from click chemistry, the ability to obtain 100% pure cyclic topology remains difficult to guarantee by the ring-closure approach.<sup>16,17</sup> For example, contaminants including linear, figure-eight, and catenane-shaped brush polymer have been observed by atomic force microscopy (AFM).<sup>11,12</sup>

In the past decade, ring-expansion metathesis polymerization (REMP), developed by Grubbs and co-workers, has become a powerful method for preparing cyclic polymers.<sup>14,15,18,19</sup> As is typical of ring-expansion approaches, REMP maximizes the formation of cyclic polymers and avoids interchain reactions at high polymerization concentrations. REMP is unique in that it can also produce cyclic polymers with the highest reported molecular weight, making it the most appropriate candidate for building the long backbone required for subsequent brush formation. However, different from the ring-closure approach, which can provide the resultant cyclic polymers with narrow

polydispersity (<1.1) and varied cyclic structures such as miktoarm polymers,<sup>20–23</sup> the cyclic polymers from REMP have broad polydispersity and less structural variety to date.<sup>14,15,18,19</sup>

By applying REMP to norbornene-based macromonomers, cyclic brush polymers with various polymer side chains were produced by Grubbs and co-workers via the combination of REMP and the “grafting through” technique.<sup>24,25</sup> Although linear brush polymers were occasionally observed by AFM using this method,<sup>25</sup> it was demonstrated that they were caused by mechanical scission of the cyclic backbone during AFM characterization. In this approach, the conversion of macromonomer was limited by the low concentration of polymerizable groups at the end of the chains and high steric hindrance of the bulky macromonomer. This low conversion led to tedious fractionation in order to remove the unreacted macromonomer. Alternatively, by combining REMP and the “grafting to” technique, we previously reported a general method for the preparation of cyclic brush polymers with varied polymer side chains.<sup>26</sup> In this method, REMP provided the cyclic backbone with high purity and large ring size, and the use of click chemistry assured the excellent efficiency for grafting to the short polymer side chains. The topology of the resultant cyclic brush polymers was confirmed by AFM, and no contaminants with any other shapes were observed. However, when the “grafting to” technique was used to attach long bulky polymer side chains, the steric hindrance significantly reduced the grafting density.<sup>27</sup> Furthermore, to obtain a high grafting density, an excess of side chains was typically employed, requiring purification to remove the unreacted side chains.

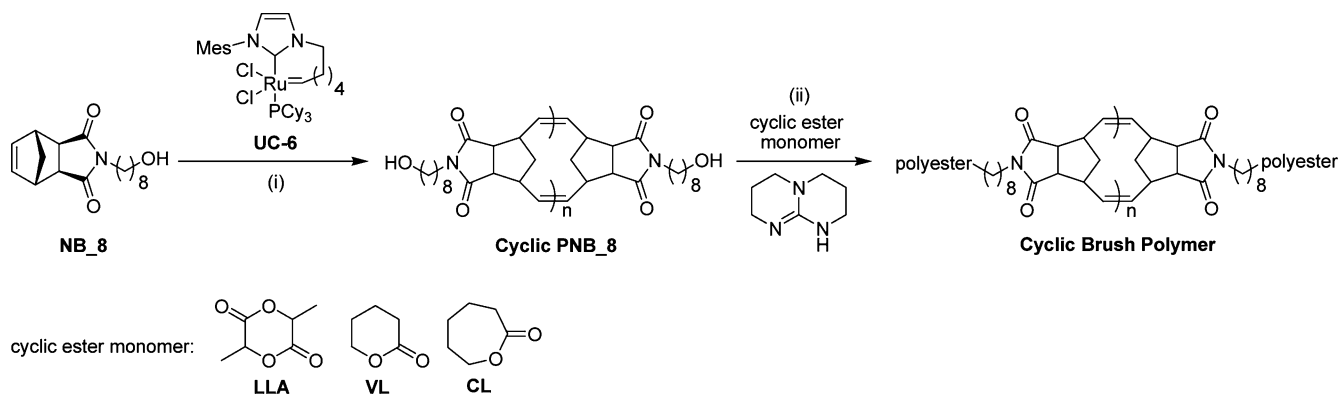
In contrast, “grafting from”, which alleviates the concerns over steric hindrance and tedious purification processes accompanied with the “grafting through” and “grafting to”

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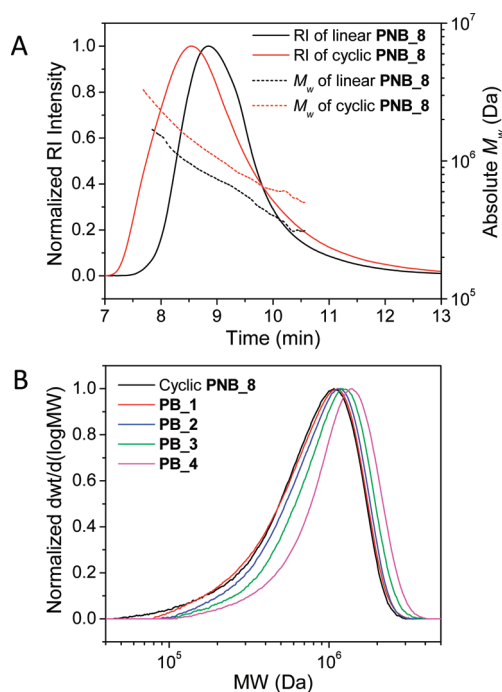


**Figure 1.** Synthetic scheme for the cyclic polymer **PNB<sub>8</sub>** and the corresponding cyclic brush polymers with polyester side chains. (i) Cyclic polymerization was carried out in THF at 55 °C for 12 h. (ii) Brush polymerization was carried out in THF at room temperature and the reaction time varied for each monomer.

strategies, has not been combined with ring-expansion polymerization to prepare cyclic brush polymers to the best of our knowledge. Herein, by combining REMP and the “grafting from” technique, cyclic brush polymers with polyester side chains were prepared. These cyclic brush polymers demonstrate the practical utility of combining REMP with “grafting from”. Both synthetic techniques are highly efficient and extremely versatile, and many chemistry combinations could be employed to give a plethora of new cyclic brush polymers.

Figure 1 shows our general synthetic scheme for the preparation of cyclic brush polymers by combining REMP and the cyclic ester ring-opening polymerization (ROP) to form the cyclic backbone and the polyester side chains, respectively. The cyclic ruthenium-alkylidene catalyst **UC-6**<sup>18,28</sup> was synthesized according to the literature and the related <sup>1</sup>H NMR spectra are shown in Figures S1 and S2. The *exo*-norbornene-based monomer (**NB<sub>8</sub>**) was synthesized by condensation of *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride with 8-amino-1-decanol (see Supporting Information). The corresponding <sup>1</sup>H NMR spectrum (in DMSO-*d*<sub>6</sub>) and peak assignments are shown in Figure S4A. When **UC-6** was used as the catalyst, cyclic **PNB<sub>8</sub>** was obtained by REMP in 12 h at 55 °C (Figure 1i). The <sup>1</sup>H NMR spectrum (in DMSO-*d*<sub>6</sub>) of cyclic **PNB<sub>8</sub>** polymerization solution without purification (Figure S4B) showed the complete disappearance of the peak at 6.30 ppm (peak *a* in Figure S4A) ascribed to  $-\text{CH}=\text{CH}-$  in **NB<sub>8</sub>**, and a new broad peak at 5.35–5.75 ppm (Figure S4B) was observed, belonging to  $-\text{CH}=\text{CH}-$  in cyclic **PNB<sub>8</sub>**. This indicated that the polymerization was carried out with quantitative **NB<sub>8</sub>** conversion. Figure 2A shows the GPC curve of cyclic **PNB<sub>8</sub>** (red) with a monomodal peak shape.

To confirm the cyclic topology of **PNB<sub>8</sub>** formed from **UC-6**, a linear analog was synthesized using the linear ruthenium-alkylidene catalyst **C1** (Figure S3) for comparison. The monomer-to-catalyst ratio was tuned to match the apparent molecular weight of cyclic **PNB<sub>8</sub>**. The apparent and absolute molecular weights of cyclic and linear **PNB<sub>8</sub>** were measured by GPC using a refractive index (RI) detector and a combination of RI and multiangle laser light scattering (MALLS) detectors, respectively. As shown in Table 1, both the cyclic ( $M_{n, \text{apparent}} = 567$  kDa) and linear ( $M_{n, \text{apparent}} = 557$  kDa) **PNB<sub>8</sub>** had similar apparent molecular weights, while the absolute molecular weight of the cyclic **PNB<sub>8</sub>** ( $M_{n, \text{absolute}} = 1090$  kDa) was 1.8 times larger than that of the linear analog ( $M_{n, \text{absolute}} = 602$  kDa). Figure 2A shows the GPC data from the



**Figure 2.** (A) GPC data (from the combined refractive index (RI) and multiangle laser light scattering detectors) for cyclic **PNB<sub>8</sub>** (red) and its linear analog (black): normalized RI detector intensities (solid lines) and absolute  $M_w$  values (dashed lines) vs elution time, where DMF with 0.01 M LiCl was used as the eluent. (B) GPC traces (from a single RI detector) of cyclic **PNB<sub>8</sub>** and the resultant cyclic brush polymers with PVL side chains: normalized differential weight fraction ( $\text{dwt}/\text{d}(\log \text{MW})$ ) vs apparent molecular weight (MW), where DMF with 0.01 M LiCl was used as the eluent and poly(methyl methacrylate) standards were used for calibration.

combined RI and MALLS detectors for both cyclic and linear **PNB<sub>8</sub>**. Across the whole overlapping range in the GPC curves from the RI detector (solid lines), the absolute molecular weight measured from the MALLS detector (dashed lines) for each cyclic **PNB<sub>8</sub>** slice was always higher than that of its linear analog at the same elution time (indicating the same apparent molecular weight). This demonstrated that **PNB<sub>8</sub>** from **UC-6** has a smaller hydrodynamic volume compared to its linear analog, consistent with a cyclic polymer topology. Furthermore, the two absolute molecular weight dashed lines were approximately parallel, and the ratio of the absolute molecular

Table 1. GPC Characterization of Cyclic and Linear PNB\_8

run <sup>a</sup>	GPC-RI <sup>b</sup>		GPC-MALLS <sup>c</sup>	
	$M_{n,apparent}$ (kDa)	PDI	$M_{n,absolute}$ (kDa)	PDI
cyclic PNB_8	567	1.59	1090	1.24
linear PNB_8	557	1.33	602	1.20

<sup>a</sup>For synthesizing cyclic PNB\_8, the initial molar ratio between the monomer NB\_8 and the cyclic catalyst UC-6 was 200/1; for linear PNB\_8, the initial molar ratio between the monomer NB\_8 and the linear catalyst C1 was 1000/1; reaction temperature = 55 °C; reaction time = 12 h. <sup>b</sup>Apparent molecular weight and polydispersity index (PDI =  $M_w/M_n$ ) were determined by GPC with a RI detector; DMF with 0.01 M LiCl was used as the eluent and poly(methyl methacrylate) standards were used for calibration. <sup>c</sup>Absolute molecular weight was determined by GPC with combined RI and MALLS detectors; DMF with 0.01 M LiCl was used as the eluent;  $dn/dc$  for PNB\_8 in DMF with 0.01 M LiCl was measured to be 0.1032 mL/g.

weights between the linear and cyclic PNB\_8 slices at the same elution time was essential constant with a value of 0.7 (Figure S5), which is consistent with previous publications.<sup>14,29–33</sup> This supports the topological purity of cyclic PNB\_8 and indicates that contamination by linear analogs is unlikely.

Cyclic PNB\_8 was designed to have –OH side groups so that it can be used as a macroinitiator to polymerize cyclic ester monomers by ROP (Figure 1ii). This leads to a general method to prepare cyclic brush polymers bearing polyester side chains through the “grafting from” technique. To graft the polyester side chains from the cyclic PNB\_8 backbone, triazabicyclodecene (TBD) was chosen as the catalyst instead of traditional metal catalysts such as Sn(Oct)<sub>2</sub>. TBD, unlike the metal catalysts, allows for the cyclic ester ROP to be performed under milder polymerization conditions, such as room temperature and dilute solutions, as well as significantly faster polymerization kinetics.<sup>34–36</sup> Three cyclic ester monomers were selected to demonstrate this method:  $\delta$ -valerolactone (VL), L-lactide (LLA), and  $\epsilon$ -caprolactone (CL). The corresponding cyclic brush polymers with poly( $\delta$ -valerolactone) (PVL), poly(L-lactide) (PLLA), and poly( $\epsilon$ -caprolactone) (PCL) side chains are described in Table 2.

First, the preparation of the cyclic brush polymers was systematically studied by grafting PVL side chains. Using cyclic PNB\_8 as the macroinitiator, ROP of VL was carried out in THF at room temperature for only 30 min with a TBD catalyst concentration of 1% (molar ratio) relative to VL. The synthesis and characterization of the resultant PVL brush polymers PB\_1, 2, 3, and 4 are included in Table 2, where the VL conversion was calculated by <sup>1</sup>H NMR before purification (Figure S6A). For all four of the feed ratios between the VL monomer and hydroxyl group from cyclic PNB\_8, the final VL conversion after 30 min was 30–40%. When the feed ratio was increased from 1 (PB\_1) to 15 (PB\_4), the apparent molecular weight of the PVL brush polymers increased from 576 kDa (PB\_1) to 1063 kDa (PB\_4). This was also reflected in their corresponding GPC curves shown in Figure 2B, in which, relative to cyclic PNB\_8, the molecular weight distribution traces of the PVL brush polymers shifted in the direction of higher molecular weight from PB\_1 to PB\_4. The monomodal GPC peak shape for cyclic PNB\_8 was maintained for all four PVL brush polymers, regardless of their final molecular weight. In addition, as shown in the full GPC curves for PB\_1–4 after polymerization without purification (Figure S7), lower molecular weight components were not observed. This

Table 2. Synthesis and Characterization of Cyclic Brush Polymers

run <sup>a</sup>	monomer <sup>b</sup>	feed ratio <sup>c</sup>	conv. (%) <sup>d</sup>	$\rho$ (%) <sup>d</sup>	$M_{n,apparent}$ (kDa) <sup>e</sup>	PDI <sup>e</sup>
PB_1	VL	1:1	27	25	576	1.50
PB_2	VL	2:1	34	44	701	1.40
PB_3	VL	7.5:1	42	84	840	1.29
PB_4	VL	15:1	39	Q <sup>f</sup>	1063	1.28
PB_5	LLA	5:1	89	Q <sup>f</sup>	823	1.35
PB_6	LLA	15:1	89	Q <sup>f</sup>	1029	1.29
PB_7	CL	30:1	20	N <sup>g</sup>	917	1.29

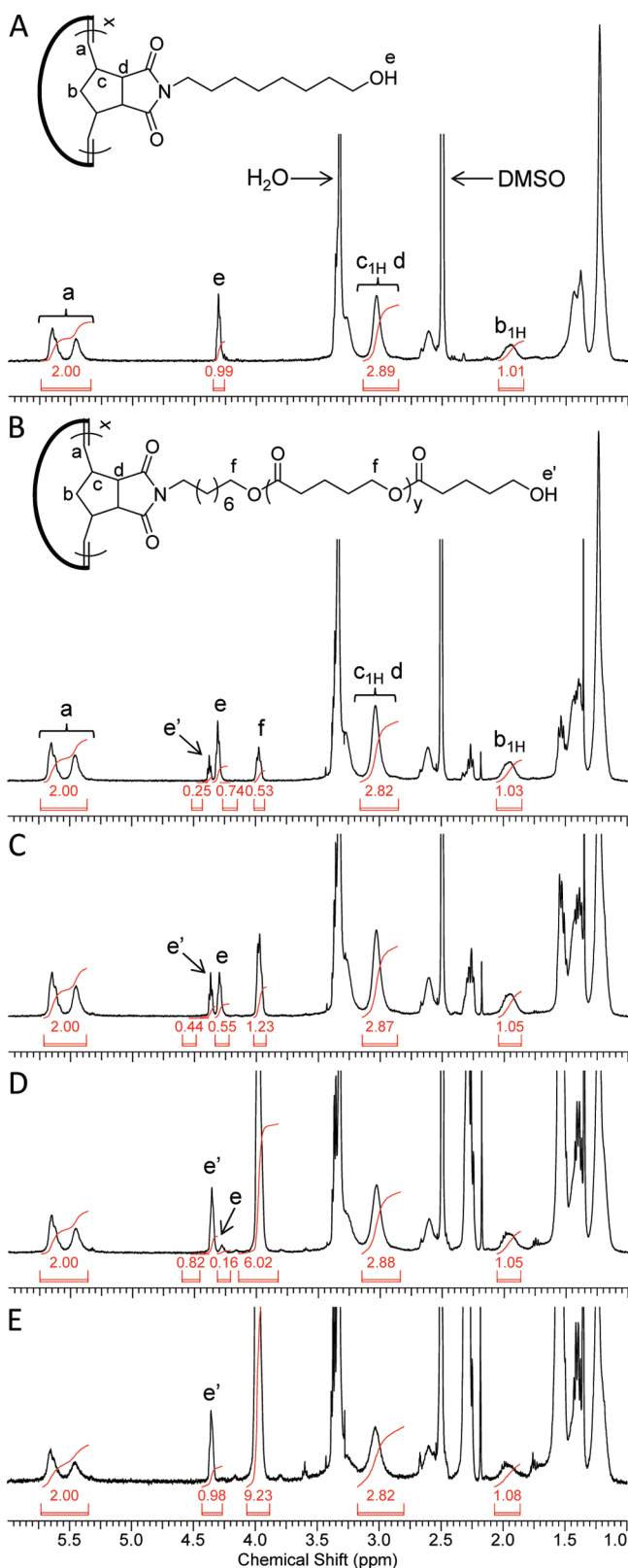
<sup>a</sup>Runs PB\_1–4: cyclic brush polymers with PVL side chains; runs PB\_5,6: cyclic brush polymers with PLLA side chains; run PB\_7: cyclic brush polymer with PCL side chains. <sup>b</sup>Ester monomers used for growing polymer side chains. <sup>c</sup>Initial molar ratio between the ester monomer and the initiating group (–OH) on cyclic PNB\_8. <sup>d</sup>Ester monomer conversion and grafting density ( $\rho$ ) of the polyester side chains were calculated from <sup>1</sup>H NMR. <sup>e</sup>Molecular weight ( $M_{n,apparent}$ ) and polydispersity index (PDI =  $M_w/M_n$ ) determined by GPC with a RI detector; DMF with 0.01 M LiCl was used as the eluent and poly(methyl methacrylate) standards were used for the calibration. <sup>f</sup>Q: quantitative. <sup>g</sup>N: not measured.

demonstrated that all of the PVL chains were grafted on the cyclic PNB\_8 macroinitiator and that there was no backbone scission of the resultant PVL brush polymers into smaller chains during the TBD-catalyzed cyclic ester ROP.

Figure 3 shows the <sup>1</sup>H NMR spectra (in DMSO-*d*<sub>6</sub>) of cyclic PNB\_8 (A) as well as PB\_1–4 (B–E). For all four PVL brush polymers, the characteristic peaks from the cyclic PNB\_8 macroinitiator remained at the same peak positions with the same relative area integrations. This indicated that cyclic PNB\_8 was stable and its chemical structure was preserved through the TBD-catalyzed cyclic ester ROP. From Figures 3B–E, the area ratio between peak *f* (–CH<sub>2</sub>OCO from the PVL side chains) and peak *a* (–CH=CH from the PNB\_8 backbone) was used to calculate the average PVL side chain length (indicated by the average degree of polymerization). When the feed ratio increased from 1 (for PB\_1) to 15 (for PB\_4), the average side chain length increased from 0.27 (Figure 3B) to 4.6 (Figure 3E). This is consistent with the molecular weight increase (Table 2) and the GPC curve shift (Figure 2B), observed from PB\_1 to PB\_4. Furthermore, as shown in Figures 3B–E, the clear peak splitting between the hydroxyl proton from the PNB\_8 macroinitiator (peak *e*) and one at the end of PVL side chain (peak *e'*) was used to monitor the grafting density of the PVL side chains. As the average side chain length increased from 0.27 (B) to 0.62 (C), and again to 3.0 (D), the grafting density increased from 25 to 44%, and again to 84%. When the side chain length was around 5, the grafting density reached approximately 100% (E).

Theoretically, when the “grafting from” technique is used to prepare brush polymers, the molecular topology of the macroinitiator should be inherited by the resultant brush polymers. The above GPC and <sup>1</sup>H NMR analyses have demonstrated that the brush polymers with PVL side chains were successfully obtained using cyclic PNB\_8 as a macroinitiator. In addition, chain scission into pieces, and chemical structure damage of the PNB\_8 backbone were also avoided during the TBD-catalyzed cyclic ester ROP. However, to conclude that the PVL brush polymers maintain their cyclic topology, it is still necessary to eliminate the possibility that the





**Figure 3.**  $^1\text{H}$  NMR spectra for cyclic PNB\_8 (in  $\text{DMSO}-d_6$ ) (A) and the corresponding cyclic brush polymers PB\_1 (B), 2 (C), 3 (D), and 4 (E) with PVL side chains (in  $\text{DMSO}-d_6$ ).

cyclic PNB\_8 backbone was opened into the linear topology after grafting the PVL side chains.

In previously published literature,<sup>14,29–33</sup> for polymers with the same absolute molecular weight, the apparent molecular

weight from GPC of a linear polymer was nearly 1.4 times larger than that of its cyclic counterpart. As shown in Figure 3B, PB\_1 had a short average PVL side chain length of 0.27. In this case, the absolute molecular weight of PB\_1 should be similar to that of its macroinitiator, cyclic PNB\_8. According to the literature, if the cyclic topology of PNB\_8 was opened to become a linear chain after grafting the PVL side chains, the theoretical apparent molecular weight from GPC for PB\_1 would be around 794 kDa, 1.4 times larger than the GPC measured  $M_{n,\text{apparent}} = 567$  kDa for cyclic PNB\_8 (Table 1). However, as shown in Table 2, the GPC measured  $M_{n,\text{apparent}}$  for PB\_1 was only 576 kDa, which is much less than the theoretical 794 kDa but similar to the experimental 567 kDa from cyclic PNB\_8. The similarity between the GPC measured apparent molecular weights of PB\_1 and PNB\_8 can also be seen in their nearly overlapping GPC curves shown in Figure 2B (red and black). Furthermore, even for the brush polymer PB\_2, with an average side chain length of 0.62 (Figure 3C), the  $M_{n,\text{apparent}}$  was measured to be 701 kDa, which is still much less than the theoretical 794 kDa for linear chains. These results are strong evidence that the intact cyclic topology of the PNB\_8 macroinitiator was retained by the PVL brush polymers. As a result, the combination of REMP with the TBD-catalyzed cyclic ester ROP can indeed be used to successfully prepare cyclic brush polymers with polyester side chains.

Encouraged by the success in synthesizing cyclic brush polymers with PVL side chains, we extended ROP to other cyclic brush polymers with PLLA and PCL side chains. For grafting PLLA side chains from the cyclic PNB\_8 backbone, LLA was polymerized in THF at room temperature with a TBD concentration of only 0.5% (molar ratio) relative to LLA. In this situation, the cyclic PLLA brush polymers were obtained in less than 1 min, with a high LLA conversion of approximately 90% regardless of the feed ratio (Table 2, PB\_5 and 6). Figure S8 shows the GPC curves for PB\_5 (red) and 6 (blue), in which, compared to cyclic PNB\_8 (black), the monomodal curve shape was maintained, and the molecular weight distribution traces shifted completely in the direction of higher molecular weight, consistent with the increase in feed ratio. As shown in Table 2, from PB\_5 to 6, the  $M_{n,\text{apparent}}$  increased from 823 kDa to 1029 kDa when the feed ratio was increased from 5 to 15. Figure S9 shows the  $^1\text{H}$  NMR spectra of PB\_5 and 6 in  $\text{CDCl}_3$ , where the area ratio between peak a ( $-\text{CH}=\text{CH}-$  from PNB\_8 backbone) and c ( $-\text{CH}(\text{CH}_3)\text{OH}$  from the PLLA side chains) of approximately 1 indicated a quantitative grafting density regardless of the feed ratio. Additionally, when the feed ratio was increased from 5 to 15, the average PLLA side chain length, calculated from the area ratio between peak b ( $-\text{CH}(\text{CH}_3)\text{O}$  in the PLLA side chain) and peak a ( $-\text{CH}=\text{CH}-$  in the PNB\_8 backbone), increased from 7.6 to 25.

To synthesize cyclic PCL brush polymers, CL was polymerized in THF at room temperature with a TBD concentration of 1.0% (molar ratio) relative to CL. As shown in Table 2 for PB\_7, when the feed ratio was 30, a CL conversion of 20% was obtained after 6 h. From Figure S10, the monomodal GPC curve shape was preserved, and the molecular weight distribution trace shifted completely in the direction of higher molecular weight relative to the macroinitiator, cyclic PNB\_8. Similar to the cyclic PVL brush polymers, the characteristic  $^1\text{H}$  NMR peaks from the cyclic PNB\_8 macroinitiator (Figure S11 A in  $\text{DMSO}-d_6$ ) were also

inherited by PB\_7 (Figure S11 B in DMSO- $d_6$ ), appearing at the same peak positions with the same relative area integrations, which again demonstrated the chemical stability of cyclic PNB\_8 under the TBD-catalyzed cyclic ester ROP conditions. The average PCL side chain length was calculated to be 6.7 from the area ratio between peak *f* ( $-CH_2OC$  from the PCL side chains) and peak *a* ( $-CH=CH-$  from PNB\_8 backbone). However, due to the complete peak inheritance from cyclic PNB\_8, there was no specific proton signal in the  $^1H$  NMR spectrum of PB\_7 that could be used to calculate the grafting density of the PCL side chains.

Finally, the influence of macroinitiator topology (linear vs cyclic) on the formation of the resultant brush polymers was investigated. To demonstrate this, the linear ( $M_{n,apparent} = 720$  kDa, PDI = 1.56) and cyclic ( $M_{n,apparent} = 704$  kDa, PDI = 1.69) PNB\_8 with similar molecular weights and polydispersity were selected as the macroinitiators to prepare the corresponding linear and cyclic brush polymers with PVL side chains. As shown in Figure S12, relative to PNB\_8 macroinitiators, the GPC curves of the resultant brush polymers shifted completely and continuously to higher molecular weight as the reaction time increased, regardless of the PNB\_8 topology. Additionally, for both linear and cyclic PNB\_8 macroinitiators, their monomodal GPC peak shapes were always inherited by the formed brush polymers, regardless of the final molecular weight. This indicated that brush polymers could be successfully synthesized from either the linear or cyclic PNB\_8 macroinitiators, respectively. Further, the kinetics of brush formation was compared under identical conditions. As shown in Figure S13A, the VL monomer conversion was always higher for the linear brush polymers than for the cyclic brush polymers at the same reaction time. Their deviation became more and more obvious as the reaction time increased (corresponding to increased conversion). A similar phenomenon was observed in the relationship between the PVL side chain length and the reaction time (Figure S13B). From Figure S13C, the quantitative grafting density for linear brush polymers was obtained in 20 min, however, it took 30 min for cyclic brush polymers to achieve the same grafting density. This likely stems from the more compact molecular conformation of cyclic polymers versus linear polymers ( $\langle R_g^2 \rangle_{cyclic} = 1/2(\langle R_g^2 \rangle_{linear})$ ).

In conclusion, we developed a general method for the preparation of cyclic brush polymers bearing polyester side chains using the combination of REMP and the “grafting from” technique for the first time. In this novel approach, the exo-norbornene-based functional monomer NB\_8 with an end hydroxyl group was first polymerized by REMP to produce PNB\_8 with a cyclic molecular topology. When the cyclic PNB\_8 is used as a macroinitiator, the polyester side chains were then grown from the cyclic backbone by virtue of TBD-catalyzed cyclic ester ROP. Following the same concept, if the cyclic macroinitiators from REMP were designed to have different initiating sites, such as alkyl bromide or thiocarbonylthio groups, various controlled polymerization techniques like ATRP or RAFT could also be employed with “grafting from” to build cyclic brush polymers. As a result, we expect that our original concept based on the combination of REMP and the “grafting from” technique will become a powerful toolbox for the preparation of cyclic polymer brushes with varied molecular architectures and functionalities.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental section, Figures S1–S13. 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.

## ■ ACKNOWLEDGMENTS

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