# Brush Polymers Containing Semiconducting Polyene Backbones: Graft-Through Synthesis via Cyclopolymerization and Conformational Analysis on the Coil-to-Rod Transition

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Ⓢ Supporting Information

ABSTRACT: Using a grafting-through strategy, brush polymers containing semiconducting polyene backbones were efficiently synthesized by cyclopolymerization for the first time. Macromonomers containing poly(L-lactide) and poly(ε-caprolactone), prepared by living ring-opening polymerization, were polymerized using the Grubbs–Hoveyda catalyst to produce high molecular weight (>0.5 M Da) brush polymers. The brush polymers underwent a unique coil-to-rod transition during the aging of the polymer solution, and this conformational change was supported by UV–vis and size-exclusion chromatography (SEC)–viscometry analysis. In addition, the extended conformation of single chains of the brush polymers could be visualized by atomic force microscopy.
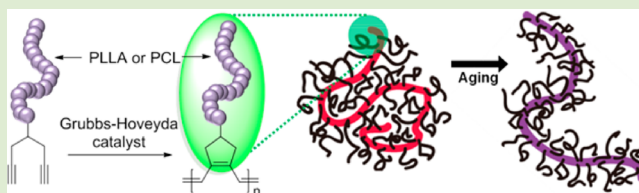
Brush polymers are a unique class of polymers containing densely grafted side chains, which control the polymer's conformation and physical properties via steric repulsion.[1] There are three general strategies for preparing brush polymers: the grafting-from, grafting-onto, and grafting-through methods. Although the grafting-through approach affords many advantages, such as well-defined grafting density and side-chain length, defect-free polymer structures, and even easy access to block copolymer synthesis, the polymerization of macromonomers is still challenging because of the severe steric hindrance imposed between the propagating species and the monomers. For this reason, many brush polymers are preferentially prepared via the grafting-from approach.[2] Recently, ring-opening metathesis polymerization (ROMP) has become one of the most popular methods for the synthesis of brush polymers by the grafting-through approach[3] because the ROMP of norbornenyl macromonomers is highly efficient when a powerful third-generation Grubbs catalyst is used.[4]

The concept of brush polymers has been employed in the synthesis of conjugated polymers to increase solubility, as well as to demonstrate unique optical properties and morphology control.[5] Nevertheless, there have been only a few examples of direct synthesis of conjugated polymers prepared by the grafting-through approach[6] because of the synthetic difficulties arising from severe steric hindrance. Also, these conjugated brush polymers prepared via the grafting-through approach showed only wide band gap (E_g > 3.0 eV) indicating that their conjugation lengths were quite short. To provide a solution to these challenges, we turned our attention to another type of olefin metathesis polymerization, cyclopolymerization.[7] Based on the pioneering work of Schrock and Fox[8] and Buchmeiser et al.,[9] the cyclopolymerization of 1,6-heptadiyne derivatives catalyzed by various transition metals has become an attractive

method for preparing soluble polyenes because even living polymerization is possible in some cases. Recently, we reported highly efficient living cyclopolymerization of 1,6-heptadiynes and 1,7-octadiynes to produce polyenes containing exclusively either five or six-membered ring structures using a third-generation Grubbs catalyst.[10] This cyclopolymerization not only produced soluble semiconducting (with E_g < 2.0 eV) polyenes with narrow polydispersity indices (PDIs), but also provided an efficient route to the synthesis of new diblock copolymers and dendronized polymers containing fully conjugated backbones. Here, we expand the scope of cyclopolymerization to the synthesis of semiconducting conjugated brush polymers grafted by poly(L-lactide) (PLLA) and poly(ε-caprolactone) (PCL). Furthermore, the brush polymers underwent unique conformational changes, which were supported by characterization in both solution and solid states.

To prepare macromonomers for cyclopolymerization, we used living ring-opening polymerization (ROP) of cyclic esters,[11] because polymeric side chains with narrow PDIs would allow the synthesis of final brush polymers having more precise nanostructures. Therefore, a monomer **1** containing 1,6-heptadiyne and an alcohol functional group was used as an initiator for the ROP of PLLA and PCL. Owing to the orthogonal reactivity of alkynes and alcohols, Sn(Oct)$_2$[11a] and methanesulfonic acid catalysis[12] led to the convenient preparation of macromonomers **2** and **3** with narrow PDIs (Scheme 1). Molecular weights of the macromonomers **2** and **3** were determined by end group analysis by ^{1}H NMR, based on

Scheme 1. Synthesis and Cyclopolymerization of Macromonomers

DP (NMR)= 18
M_n (NMR)= 2.72 k
PDI (SEC)= 1.12

DP (NMR)= 26
M_n (NMR)= 3.09 k
PDI (SEC)= 1.20
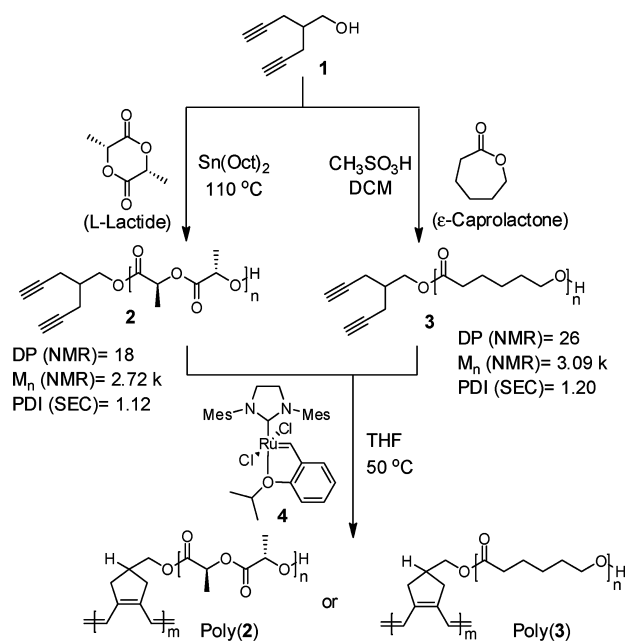
the integration ratio of PLLA or PCL and heptadiyne signals (see Figure S1 in the Supporting Information). Most importantly, end group analysis by MALDI-TOF mass spectrometry confirmed that, even after ROP, both macromonomers retained the heptadiyne functionality that was essential for the next cyclopolymerization (Figure S2).

To investigate the cyclopolymerization of polyester macromonomers, the Grubbs-Hoveyda catalyst (**4**) was added to THF solution of **2** (Scheme 1). With a monomer-to-initiator ratio ($[M]/[I]$) of 100, 90% of **2** was converted into the brush polymer in 1 h at room temperature. The conversions of the macromonomers were confirmed from integration analysis on crude samples by NMR or size-exclusion chromatography (SEC; Figure 1), and the absolute molecular weights of the
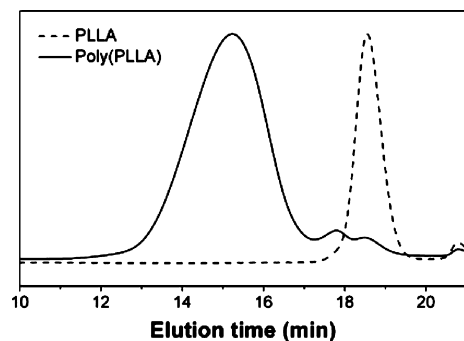

Figure 1. SEC traces of the macromonomer **2** (black line) and crude sample of poly(**2**) (red line).

brush polymers were obtained by multiangle laser light scattering (MALLS) detection. After this initial success in cyclopolymerization, we changed the catalyst to a third-generation Grubbs catalyst bearing 3-chloropyridine to test if living cyclopolymerization would also be possible.[4,10] Gratifyingly, **2** with $[M]/[I]$ of 50 was cyclopolymerized at r. t. to give the brush polymer with M_n of 132k (theoretical M_n: 135k) and narrow PDI of 1.18 although this DP of 50 was too short for

future imaging of polymer single chain due to low aspect ratio of the main back-bone (polyene) to the side-chain (PLLA). Unfortunately, all attempts to achieve living polymerization failed with $[M]/[I]$ of 100, and only brush polymers with broad PDIs (>1.4) similar to the initial case were obtained. Instead of aiming for living polymerization, thermally more stable **4** was used to maximize conversion by increasing temperature to 50 °C (99%, Table 1, entry 1). Under these conditions,

Table 1. Results of Cyclopolymerization at 50 °C

entry	monomer	$[M]/[I]$	time	$M_n{}^a$ (theor.)	$M_n{}^b$	PDI^b	conv.^{c}
1	2	100	1 h	269 k	424 k	1.47	99%
2	2	200	2 h	511 k	453 k	1.51	94%
3	2	300	6 h	604 k	583 k	1.42	74%
4^d	3	100	1 h	346 k	209 k	1.63	99%

^{a}Calculated by this equation: (M_n of macromonomer) $\times$ ($[M]/[I]$ ratio) $\times$ (monomer conversion). ^{b}Determined by THF SEC using MALLS detectors. ^{c}Calculated from the NMR integration of monomers remained. ^{d}Determined by CHCl$_3$ SEC using light scattering detector.

cyclopolymerization with higher $[M]/[I]$ of 200 and 300 was attempted to obtain high molecular weight brush polymers with much lower catalyst loading: the maximum average degree of polymerization (DP), up to 220, was obtained (entries 2 & 3).

Under the same conditions, the other macromonomer **3** also showed good reactivity toward cyclopolymerization; for $[M]/[I] = 100$, full conversion into the brush polymer was achieved within 1 h (entry 4). However, the solubility of poly(**3**) in common organic solvents, such as chloroform and THF, was much poorer than poly(**2**), which made SEC analysis troublesome because it took 2 days to fully dissolve poly(**3**) in chloroform. Although both PLLA and PCL are crystalline polymers, they have different degrees of crystallinity and different physical properties,[13] and their polymer brushes may show different properties as well. Hence, to investigate the solubility issue in detail, differential scanning calorimetry (DSC) analyses on both macromonomers and brush polymers were performed (Figure S3 of the Supporting Information). The crystallinities of the macromonomers were easily calculated as 56% (**2**) and 85% (**3**), by comparison with the reported enthalpy of fusion for the parent polymer crystal. Despite the high crystallinities for both macromonomers, DSC analysis on the brush polymers poly(**2**) and poly(**3**) showed different results. For poly(**3**), a melting temperature (T_m) of 53.0 °C was very similar to that of the macromonomer **3** (58.5 °C), and the enthalpy of fusion did not decrease significantly (114.4 J/g for **3** and 74.7 J/g for poly(**3**)). However, poly(**2**) showed a much smaller enthalpy of fusion (10.3 J/g) at much lower T_m (93.7 °C) than the values for macromonomer **2** (52.5 J/g at 143.5 °C). From these DSC analyses, it was clear that poly(**2**) had low crystallinity, whereas poly(**3**) was significantly more crystalline, which might be reflected in the poorer solubility of poly(**3**) in common organic solvents.

Since the cyclopolymerization produces the fully conjugated polymer structures, careful UV−vis analysis may provide additional information on the polymer conformation. The UV−vis spectrum for the solution of poly(**2**) revealed two distinct vibronic bands with $E_g = 2.0$ eV, indicating that the microstructure of the polymer was regioregular polyenes consisting exclusively of five-membered ring structures (Figure
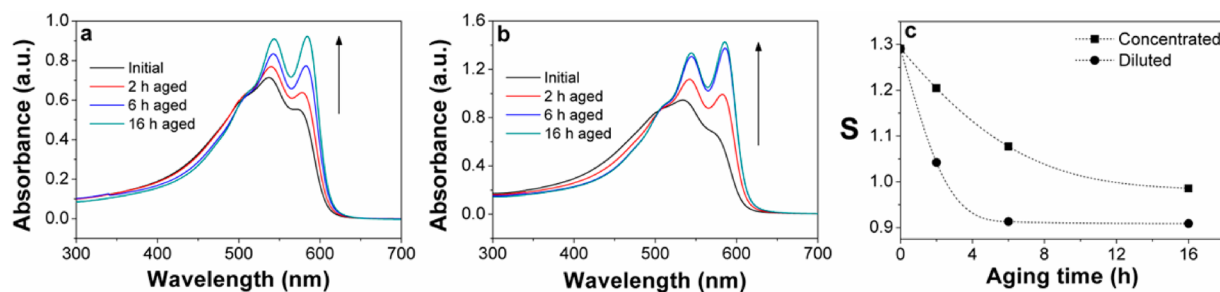
Figure 2. (a) Time-dependent UV−vis spectra of poly(2)$_{190}$ aged in THF solution (2.3 g/L) and (b) in dilute THF solution (0.2 g/L). (c) Comparing the rates of decease in Huang−Rhys factor S for a and b.

2).[9e,10a] This provided strong support for the uniform microstructure of the brush polymers prepared via selective α-addition of the catalyst. Closer inspection revealed that the λ_{max} and the relative intensities of the two vibronic bands changed with time. Compared to the UV−vis spectrum obtained immediately after the synthesis of poly(2), the spectrum from an aged solution showed that λ_{max} was not only red-shifted, but also that the intensity of the first vibronic band at 580 nm (0−0 transition) had significantly increased with aging time (Figure 2a). Since the growth of the intensity for the 0−0 band indicates more coplanar, extended, and stiffer conformations of the conjugated polymers[14] (lower Huang−Rhys factor, S: relative intensity of 0−1 to 0−0 transitions obtained from optical spectra), this observation implied that the conformation of the brush polymers might be undergoing a transformation to a more extended structure over time. This change was certainly not due to the aggregation of the poly(2) because the steric hindrance of the polymeric side chains should prevent any possibility of intermolecular aggregation. In addition, UV−vis analysis in various solvents showed the same trend (see Figure S4 of the Supporting Information for the details). Furthermore, these changes in UV−vis spectra occurred much faster in a dilute solution (0.2 g/L) than in a high-concentration solution (2.3 g/L), confirming that this was not an intermolecular process (Figure 2b and c).

To obtain conformational information on the conjugated polymers, the physics community has commonly used the quantum mechanically derived expression known as the Huang−Rhys factor S.[14b,15] This theory-based Huang−Rhys factor explained the 1D-like conformation for the conjugated polymers at extremely low temperatures and in an aligned solid state, while the conformation of those polymers returned to coil-like structure at room temperature because of entropic factors. However, the correlation of the theoretical Huang−Rhys factor on the polymer conformation has not been supported by chemical methods yet because these extreme conditions were not suitable for typical chemical analysis in solution at ambient conditions. Fortunately, these brush polymers may now be suitable for chemical analysis because they seem to undergo conformational transition at room temperature slowly enough so that reliable time-dependent analysis would be possible (Figure 2). To confirm this conformational change by a polymer chemistry method, we measured the time-dependent shape parameter α, which was obtained by Mark−Houwink−Sakurada plots from SEC−viscometry analysis: a higher α value indicates a more extended or stiffer polymer chain. By comparing α as a function of aging time, we realized that the α values increased from 0.62 (the initial state) up to 0.73 (after 16 h of aging), strongly suggesting

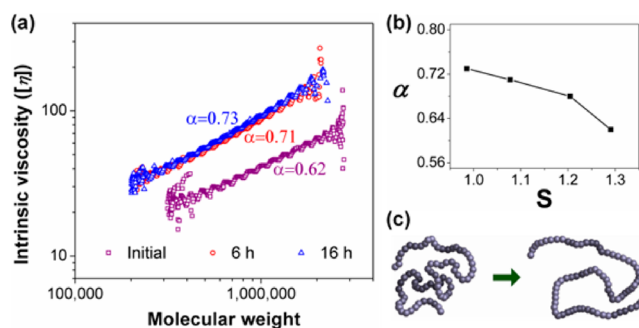that the brush polymers underwent conformational changes to form relatively more extended structures (Figure 3).[16] This

Figure 3. (a) Time-dependent Mark−Houwink−Sakurada plots of poly(2)$_{190}$ in THF (2.3 g/L) confirming the coil-to-rod transition. (b) Correlation between Huang−Rhys factor S and shape parameter α. (c) Graphical scheme for conformational change of poly(2).

coil-to-rod transition[17] on poly(2) is evident because the interpretation of the changes in both the UV−vis spectra and the shape parameter α leads to the same conclusion (Figure 3b).

We believe that the brush polymer with a relatively more extended conformation is thermodynamically more stable than the initial conformation, based on the following two observations. First, UV−vis spectra obtained immediately after the cyclopolymerization conducted at 50 °C with a longer reaction time showed a more intense 0−0 band than that obtained after a shorter reaction time (Figure S5a of the Supporting Information). Likewise, the polymer obtained by the cyclopolymerization at room temperature without aging showed the lowest 0−0 band and required a longer time for the coil-to-rod transition (Figure S5b). In all conditions, molecular weights of poly(2) were similar. These observations conclude that longer reaction time and higher temperature conditions facilitate the conformational change. Second, the changes in both the UV−vis spectra and the α values were irreversible. Even if the aged solution was reprecipitated as a solid and redissolved, the UV−vis spectra and α values remained unchanged (α = 0.72, blue spectrum in Figure S5b). In short, these conformational analyses in solution revealed that the more coil-like kinetic conformation of poly(2) transformed into the more extended rigid-rod-like conformation that was the thermodynamically favored state. This coil-to-rod transition occurred slowly for poly(2) because the sterically demanding grafted side chain slowed down the entire transition process, allowing sufficient time to determine reliable kinetics for the

conformational analysis. We are currently investigating the origin of this coil-to-rod transition.

After obtaining detailed information on the conformation of poly(**2**) in solution, the single chains of the brush polymer were vividly visualized by atomic force microscopy (AFM), as shown in Figure 4. While the imaging of a polymer single chain was
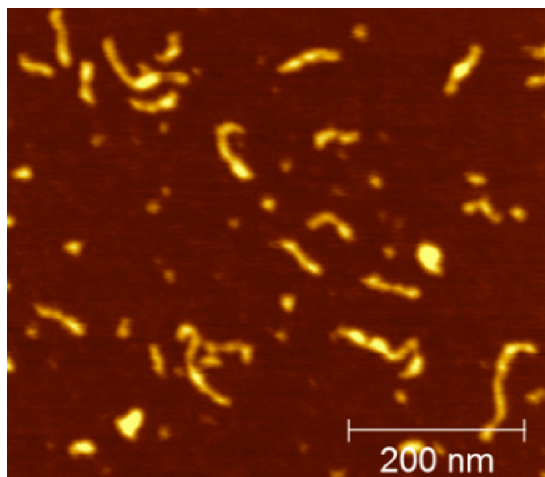

Figure 4. AFM image of poly(**2**) obtained from the aged solution.

more difficult from the just-prepared solution, the extended conformation of the individual brush was observed clearly on mica from the aged solution. Their heights ranged from 0.7 to 1.5 nm because the polymeric side chains were still polydisperse despite the living ROP (PDI of 1.2), and the maximum length was up to 200 nm. The broad dispersity with respect to the length was inevitable due to the large PDI of the brush polymer (>1.4). Some brighter (larger height) but short chains might be due to backbone cleavage in the brush as a result of surface-adsorption-induced chain scission from the brush polymers[18] or the kinetically trapped brush polymers in coil conformation. Unfortunately, single chains of poly(**3**) could not be visualized in the same way, presumably because the high crystallinity and low solubility of poly(**3**) made AFM imaging very difficult.

In summary, the efficient "grafting-through" syntheses of high molecular weight brush polymers having conjugated polyene backbones and PLLA and PCL as side chains were demonstrated by cyclopolymerization using the Grubbs–Hoveyda catalyst. The markedly different solubility of the two brushes was noticed, and using DSC, a simple comparison of the crystallinity of the brushes provided an explanation for it. The PLLA brush polymers in solution showed unique coil-to-rod conformational changes over time, and UV−vis spectra and SEC−viscometry analysis strongly supported this transition. Finally, AFM imaging of single chains further confirmed the extended conformation of the brush polymers. Potentially, this is another example of insulated molecular wire.[10a]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, NMR, IR, elemental analysis, MALDI-TOF, DSC, and UV−vis data for polymers. 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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(16) The α value (0.73) is slightly lower than the theoretical value of the rigid-rod structure (0.8) because the polymeric side chains in brush polymers locally adopt random coil conformations, which lead to lower α values. This is typically observed for the brush polymers, whereas the α values for dendronized polymers containing more densely packed side chains are over 0.8. See: Kim, K. O.; Choi, T.-L. *ACS Macro Lett.* **2012**, *1*, 445.

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