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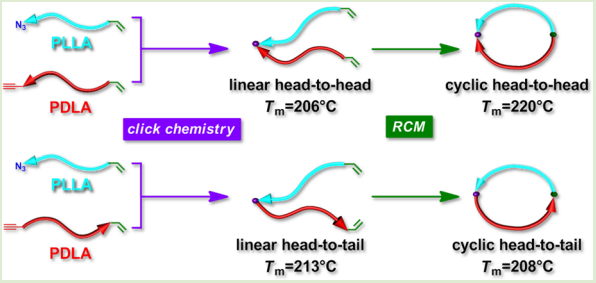
Synthesis of Orientationally Isomeric Cyclic Stereoblock Polylactides with Head-to-Head and Head-to-Tail Linkages of the Enantiomeric Segments

Naoto Sugai, Takuya Yamamoto,* and Yasuyuki Tezuka*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Supporting Information

ABSTRACT: A pair of orientationally isomeric cyclic stereoblock polylactides (PLAs) possessing head-to-head (HH) and head-to-tail (HT) linkages between the poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) segments was synthesized through click chemistry and ring-closing metathesis (RCM) of three asymmetrically functionalized telechelic precursors. Thus, α-ethenyl-ω-azido-PLLA (**2a**) was reacted with α-ethenyl-ω-ethynyl-PDLA (**2b**) and α-ethynyl-ω-ethenyl-PDLA (**2c**) via click chemistry to form ethenyl telechelic stereoblock PLAs with HH and HT orientations (**3a** and **3b**), respectively. The subsequent RCM produced cyclic stereoblock PLAs with the corresponding linking manners (**4a** and **4b**). The effect of the topology on the melting temperature of the series of isomeric linear and cyclic PLAs having the contrastive linking orientations was systematically investigated.



In nature, the assemblies of a pair of polymer chains with a controlled directional arrangement often bring remarkable functionalities. DNA, in which a strand consists of asymmetric sugars connected by phosphodiester bonds and thus has directionality on the polymer chain, is certainly the most typical example. The 3′- and 5′-ends join to form a double helix in an antiparallel orientation, which plays a crucial role for transcription.[1] Moreover, a helix bundle in a protein is composed of parallel and antiparallel orientations of polypeptide α-helices.[2] Such programmed folding of a protein to assemble a tertiary structure with a directional arrangement attracts great interest, and the process is being subject for vigorous studies.[3,4]

Polylactide (PLA), a biodegradable and renewable thermoplastic, is known to form a crystalline ensemble, namely, stereocomplex, through the directional arrangement of a pair of stereoisomeric poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA).[5,6] PLA stereocomplex was reported to show an approximately 50 °C higher melting temperature (T_m) and 60% stronger mechanical strength than that of a homocrystal of a single enantiomer and, thus, is extensively studied for the development as biomass plastic materials.[7−10] The crystal structure of the stereocomplex of high molecular weight PLAs was studied to show that PLLA and PDLA chains are ordered in parallel; the α-ends of PLLA and PDLA point in the same direction, and hence so do the ω-ends (Figure S1a).[11,12] Interestingly, another PLA stereocomplex structure with an antiparallel arrangement, in which the α-ends of PLLA and PDLA are pointing in the opposite direction, was theoretically predicted (Figure S1b).[13,14] While it is argued that an equimolar blend of PLLA and PDLA tends to form the thermodynamically stable crystal in the parallel arrangement with the interaction energy (E_{int}) of −119 kcal/mol,[13] the antiparallel stereocomplex could not be excluded due to the minimal energy difference (E_{int} = −111 kcal/mol)[13] and similarity in the packing.[15] In fact, a statistical mixture of parallel and antiparallel arrangements was also plausible.[14] Hence, further elaborated studies should be of fundamental interest.

We show herein a versatile procedure to designate the directional arrangement of PLLA and PDLA in stereocomplex by taking advantage of a cyclic topology. Thus, cyclic stereoblock PLA **4a**, in which the α-ends of PLLA and PDLA are connected as well as the ω-ends, namely, a head-to-head (HH) arrangement, would form parallel stereocomplex (Figure S1c). In contrast, α−ω,α−ω-connected, or head-to-tail (HT), counterpart **4b** is expected to result in the favored construction of antiparallel stereocomplex on the basis of the geometrical confinement (Figure S1d). In the meantime, a linear stereoblock PLA, regardless of the orientation of HH, HT, or tail-to-tail (TT), may preferentially form thermodynamically stable parallel stereocomplex, as depicted in Figures S1e−g. Thus, **4b** appears to have the unique combination of the orientation and topology to realize antiparallel stereocomplex through the intramolecular ordering of the stereoblock segments. Motivated by these considerations, we synthesized cyclic PLAs having HH and HT linking orientations of the stereoblock segment pair by means of click chemistry and ring-closing metathesis (RCM).[16] Furthermore, thermal analysis by DSC showed that, upon

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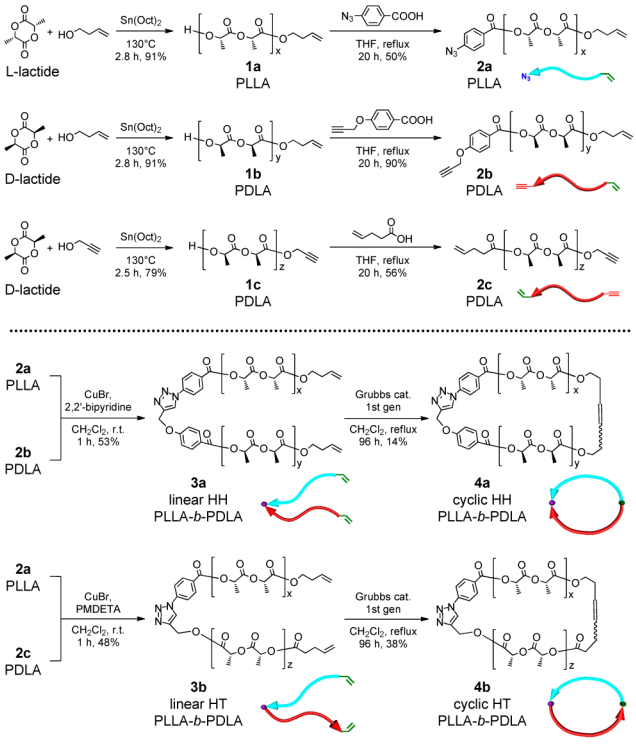
cyclization, the T_m of the HH stereoblock PLA increased by 15 °C, whereas that of the HT counterpart decreased by 5 °C.

Owing to the recent synthetic developments, cyclic PLAs have become obtainable with a well-defined molecular weight and narrow polydispersity,[17] and their differences in properties arising from the topology have subsequently been examined.[18,19] Yin and co-workers first reported the synthesis of oligomeric cyclic PLAs by a resin-supported intramolecular reaction.[20] Later, Dove and co-workers utilized bimolecular cyclization between a maleimidyl-telechelic PLA and dithiol via thiol−ene click chemistry to form cyclic homo and stereoblock PLAs.[21] Notably, ring-expansion polymerization of lactides, which does not require dilute conditions, was developed by Waymouth and co-workers employing an *N*-heterocyclic carbene-catalyzed zwitterionic process to give cyclic homo PLAs in a living fashion.[22−24]

To synthesize the cyclic block copolymers of PLLA and PDLA possessing HH and HT linking orientations, we first polymerized L- and D-lactides separately from designated functional initiators having either an ethenyl or ethynyl group (Scheme 1). Subsequently, the ω-termini were modified to the

Scheme 1. Synthetic Scheme of Cyclic Stereoblock PLAs with the HH and HT Linking Orientations of the Enantiomeric Segments



complementary function of alkene, alkyne, or azide. Thus, PLLA (**1a**) and PDLA (**1b**) with α-ethenyl and ω-hydroxy end groups were prepared by using 3-buten-1-ol as an initiator in the presence of a tin(II) 2-ethylhexanoate, $Sn(Oct)_2$, catalyst.[25−27] Likewise, α-ethynyl-ω-hydroxy-PDLA (**1c**) was synthesized in the same manner from a propargyl alcohol initiator. These products were fully characterized by means of SEC (Figure S2), ^{1}H NMR (Figure S3), IR (Figure S4), and MALDI-TOF MS (Figure S5 and Table S1). The hydroxy termini of **1a**−**c** were esterified with 4-azidobenzoic acid, 4-(propargyloxy)benzoic acid, and 4-pentenoic acid to give α-ethenyl-ω-azido-PLLA (**2a**), α-ethenyl-ω-ethynyl-PDLA (**2b**), and α-ethynyl-ω-ethenyl-PDLA (**2c**), respectively (Scheme 1).[28] Likewise, the formation of these products was confirmed by SEC (Figure 1), ^{1}H NMR (Figures 2 and S6), IR (Figure S7), and MALDI-TOF MS (Figures 3 and S8 and Table S1).

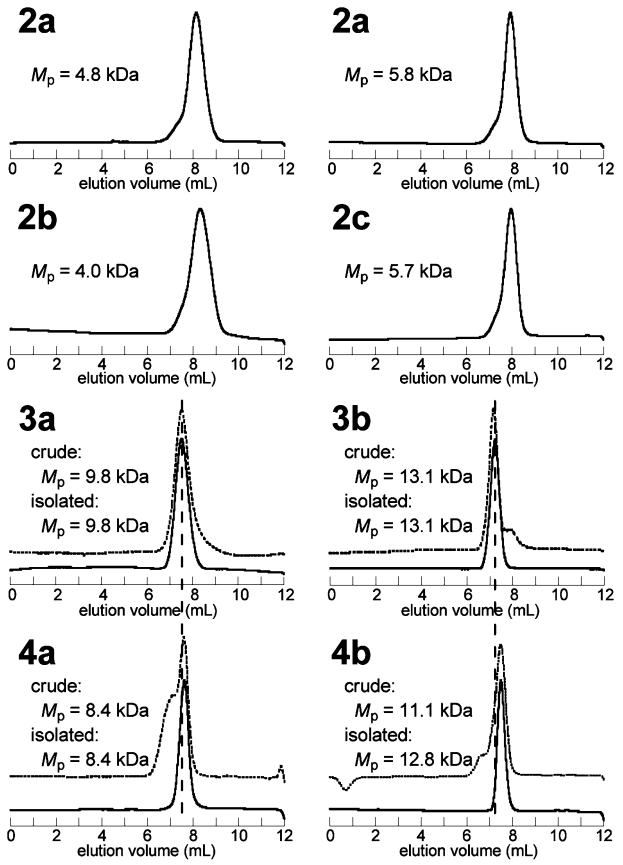


Figure 1. SEC traces of **2a**−**c**, **3a**, **3b**, **4a**, and **4b**: broken line, crude product; solid line, isolated product by preparative SEC.

Azido-functionalized **2a** was subsequently subjected to click chemistry with ethynyl-functionalized **2b** and **2c** to selectively produce ethenyl-telechelic linear stereoblock PLAs with HH (**3a**, M_n(PLLA)/M_n(PDLA) = 56/44) and HT (**3b**, M_n(PLLA)/M_n(PDLA) = 53/47) orientations, respectively (Scheme 1). The mixture of the PLLA and PDLA precursors was poorly soluble in common organic solvents, presumably due to stereocomplexation.[29] After a number of attempts to optimize the reaction conditions, the click chemistry between the enantiomeric prepolymers was found to proceed effectively in CH_2Cl_2 at a concentration of 4.7 or 3.8 mM using 4 equiv of copper(I) bromide.[30−32]

A peak molecular weight by SEC, M_p(SEC), of 9.8 kDa for crude **3a** was consistent with the sum of those precursors **2a** and **2b** (4.8 + 4.0 kDa = 8.8 kDa). Also, the M_p(SEC) of crude **3b** (13.1 kDa) was close to that of corresponding precursors **2a** and **2c** (5.8 + 5.7 kDa = 11.5 kDa). Subsequent isolation was performed by means of preparative SEC fractionation to give **3a** and **3b** in 53 and 72% yield, respectively. SEC traces of the precursors (**2a**, **2b**, and **2c**), crude products (**3a** and **3b**, broken line), and isolated products (**3a** and **3b**, solid line) are also shown in Figure 1.

By comparing the ^{1}H NMR spectrum of **3a** with those of **2a** and **2b** (Figure S6), as well as **3b** with **2a** and **2c** (Figure 2), the

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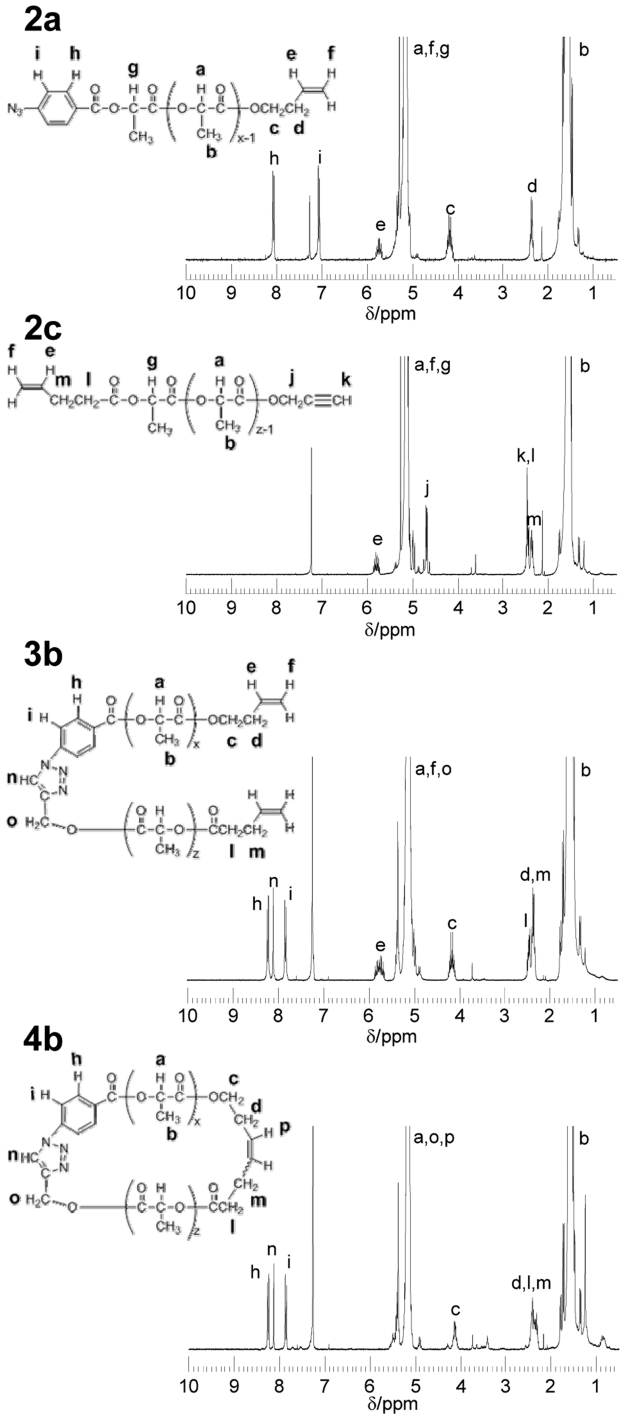

Figure 2. ^{1}H NMR spectra of **2a**, **2c**, **3b**, and **4b**.

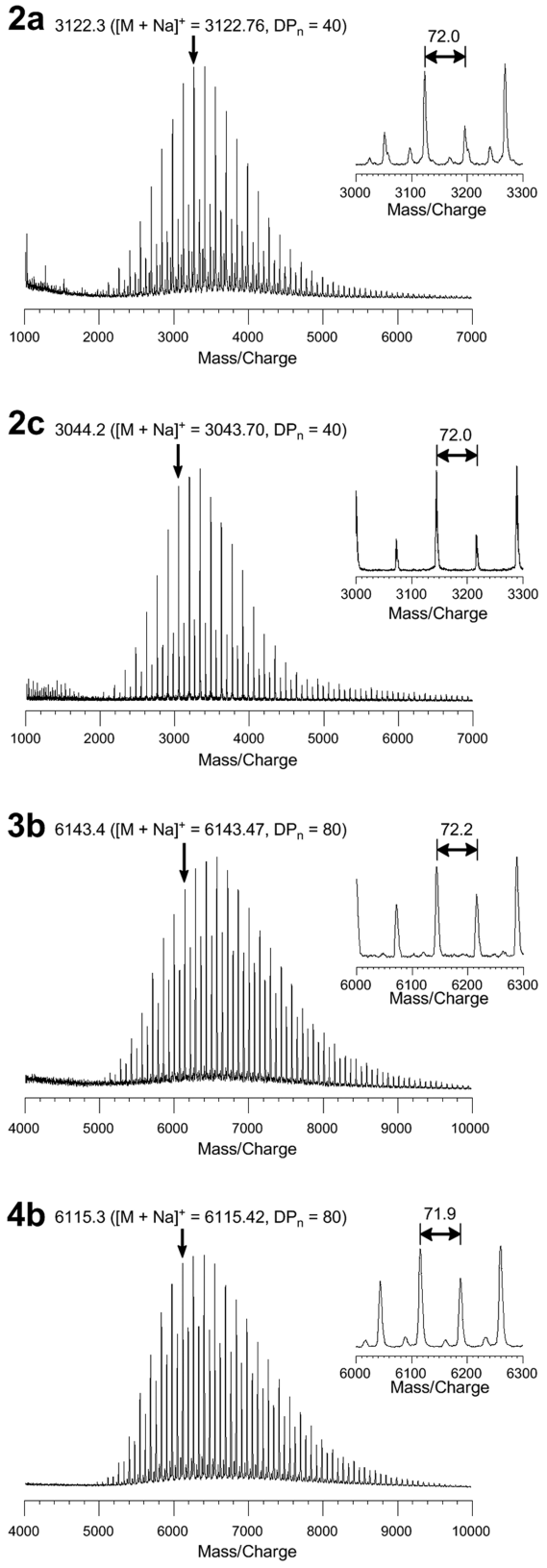

Figure 3. MALDI-TOF mass spectra of **2a**, **2c**, **3b**, and **4b** (DP_n denotes the number of monomer units).

selective reaction between the azido and ethynyl groups was confirmed. Thus, a signal for the ethynyl proton in **2b** (2.53 ppm) and **2c** (2.51 ppm) completely disappeared, and a triazole proton signal emerged at 8.16 and 8.10 ppm in **3a** and **3b**, respectively. Moreover, signals for the azidophenyl protons (7.07 and 8.07 ppm) in **2a** were replaced with those for the phenylene protons adjacent to the 1-position of the triazole ring in **3a** (7.87 and 8.26 ppm) and **3b** (7.83 and 8.22 ppm).

The IR absorbance of the azido group at 2127 cm^{-1} observed in **2a** became scarcely visible in **3a** and **3b**, indicating that the click chemistry proceeded effectively (Figure S7).

The MALDI-TOF mass spectrum of **3a** showed a uniform series of peaks with an interval of 72 mass units for a half of a repeating lactide unit due to the concurrent transesterification during polymerization (Figure S8).[33,34] Each peak exactly

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matched the total molar mass of the repeating units with the linking and terminal structures (Table S1). For example, the observed peak at m/z = 4794.6, which was assumed to be an adduct with Na^+, corresponded to **3a** possessing the expected chemical structure with a DP_n ($x + y$ in the chemical formula in Scheme 1) of 60; $(C_3H_4O_2) \times 60 + C_{25}H_{25}N_3O_5 + Na^+$ = 4794.30 (Figure S8). Furthermore, the sum of the molar masses of **2a** with a DP_n of 30 (2402.2 − [Na^+] = 2379.2) and **2b** with a DP_n of 30 (2413.8 − [Na^+] = 2390.8) is 4770.0, in agreement with that of **3a** with a DP_n of 60 (4794.6 − [Na^+]) = 4771.6) given above (Figure S8). Analogously, in Figure 3, the observed peak at m/z = 6143.4, which was also assumed to be an adduct with Na^+, corresponded to **3b** possessing the expected chemical structure with a DP_n of 80; $(C_3H_4O_2) \times 80 + C_{19}H_{21}N_3O_4 + Na^+$ = 6143.47. The sum of the molar masses of **2a** with a DP_n of 40 (3122.3 − [Na^+] = 3099.3) and **2c** with a DP_n of 40 (3044.2 − [Na^+] = 3021.2) is 6120.5, in agreement with that of **3b** with a DP_n of 80 (6143.4 − [Na^+] = 6120.4) given above (Figure 3). From these results, the structures of the ethenyl-telechelic linear stereoblock PLAs with HH (**3a**) and HT (**3b**) orientations were confirmed.

The cyclization of **3a** and **3b** by RCM was performed under reflux in CH_2Cl_2 at a polymer concentration of 0.2 g/L in the presence of the Grubbs catalyst first generation.[35,36] Crude products (Figure 1 **4a** and **4b**, broken line), which contained intermolecularly metathesized byproducts, were subsequently subjected to preparative SEC fractionation to isolate **4a** and **4b** (Figure 1, **4a** and **4b**, solid line) in 14 and 38% yield, respectively. Noteworthy, the present cyclization process was less effective in comparison with the previous reports on the relevant telechelics of poly(tetrahydrofuran), poly(butyl acrylate)-*b*-poly(ethylene oxide)-*b*-poly(butyl acrylate), and polystyrene-*b*-poly(ethylene oxide)-*b*-polystyrene,[35,37−39] presumably due to the strong interaction between the PLLA and PDLA segments. Applying other types of ruthenium catalysts (Grubbs second generation and Hoveyda-Grubbs first and second generations) and solvents ($CHCl_3$ and toluene) as well as further dilution failed to improve the yield but resulted in low conversion, the formation of byproducts, and decomposition.

The hydrodynamic volume of a polymer, corresponding to the three-dimensional size of a randomly coiled form in a good solvent, has been shown to dependent on the topology.[16,40−43] Based on the SEC traces (Figure 1), the hydrodynamic volume ratios of **4a**/**3a** and **4b**/**3b** were calculated to be 0.86 and 0.85, respectively, in agreement with the previously reported cyclization reactions.[44,45]

The ^{1}H NMR spectra of isolated **4a** and **4b** were compared with their precursors **3a** and **3b**, as shown in Figures S6 and 2, respectively. The signals of the terminal olefinic units in **3a** and **3b** completely disappeared, while the inner olefin signals of the products were not seen due to overlap with those of the mainchain around 5.2 ppm.

The MALDI-TOF mass spectra of the cyclized products and corresponding prepolymers are shown in Figure S8 (**3a** and **4a**) and Figure 3 (**3b** and **4b**). The spectra exhibited a uniform series of peaks with an interval of 72 mass units for a half of a repeating lactide unit, and each peak exactly matched the total molar mass of the repeating units with the linking and terminal structures (Table S1). For example, the observed peak at m/z = 4766.3, which was assumed to be an adduct with Na^+, corresponded to **4a** possessing the expected chemical structure with a DP_n of 60; $(C_3H_4O_2) \times 60 + C_{23}H_{21}N_3O_5 + Na^+$ = 4766.25. Similarly, the observed peak at m/z = 6115.3, which was assumed to be an adduct with Na^+, corresponded to **4b** possessing the expected chemical structure with a DP_n of 80; $(C_3H_4O_2) \times 80 + C_{17}H_{17}N_3O_4 + Na^+$ = 6115.42. Because the cyclization took place by the elimination of an ethylene molecule, the molecular weights of the prepolymer and product should differ by 28 mass units. The experimental difference between the m/z values of **3a** with a DP_n of 60 (4794.6) and **4a** with a DP_n of 60 (4766.3) was 28.3 (Figure S8, Table S1). Analogously, the m/z value of **3b** with a DP_n of 80 (6143.4) and that of **4b** with a DP_n of 80 (6115.3) differed by 28.1 (Figure 3, Table S1). Based on these results, we concluded that cyclic stereoblock PLAs with the controlled linking orientation of the enantiomeric segment pair, **4a** and **4b**, were successfully constructed through RCM of **3a** and **3b**, respectively.

To obtain insights of the effects arising from the topology of the PLAs upon stereocomplexation, DSC measurements were performed on solvent-cast samples of linear stereoblock **3a** and **3b**, cyclic stereoblock **4a** and **4b**, PLLA homopolymer **1a**, and PLLA/PDLA blends **1a**/**1b** and **1a**/**1c** (Figure S12 and Table S2). The PLLA/PDLA blends showed a T_m higher than the PLLA homopolymer due to typical stereocomplexation (**1a**, 148 °C; **1a**/**1b**, 208 °C; and **1a**/**1c**, 216 °C).[46] The T_m of the PLAs with a HH orientation increased from 206 (**3a**) to 221 °C, (**4a**), possibly implying the promoted formation of stereocomplex by the elimination of the free chain ends through the cyclization. Given that stereocomplexation is often hindered by the concurrent formation of homocrystals especially for high molecular weight polymers,[8,47−49] the use of a cyclic HH stereoblock PLA in place of a common linear counterpart[8,9,50−56] should further improve the thermal properties of PLA materials. On the other hand, the T_m of the HT stereoblock PLAs was observed to be marginally decreased from 213 (**3b**) to 208 °C (**4b**) upon cyclization. This could be accounted for by the geometrical restriction of the cyclic topology on the arrangement of the PLLA and PDLA segments in contrast to linear precursor **3b**. Moreover, ethenyl-telechelic linear homo-PLLA (**5a**), ethenyl-telechelic linear homo-PDLA (**5b**), cyclic homo-PLLA (**6a**), and cyclic homo-PDLA (**6b**) were also synthesized (Scheme S1, Figures S9−S11, and Table S1), and the thermal properties of the individual homopolymers and blends were studied (Figure S13 and Table S2). The changes of the melting peaks could be informative to inquire the causes of the effect of the topology.

In conclusion, the synthesis of cyclic stereoblock PLAs was carried out by employing click chemistry and RCM. This process provides a versatile means to control the orientation of the PLLA and PDLA segments in the cyclic structure. Thermal analysis showed that the T_m relies on the topology as well as the linking orientation. The present study would provide new perceptions of stereocomplexation and eventually the functional design of PLA-based materials on the basis of the effect of the topology.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section, schematic representations of PLA stereocomplex, SEC traces (**1a**−**1c**, **5a**, **5b**, **6a**, and **6b**), ^{1}H NMR spectra (**1a**−**1c**, **2a**, **2b**, **3a**, **4a**, **5a**, **5b**, **6a**, and **6b**), IR spectra (**1b**, **1c**, **2a**−**2c**, **3a**, **3b**, **4a**, and **4b**), MALDI-TOF mass spectra (**1a**−**1c**, **2a**, **2b**, **3a**, **4a**, **5a**, **5b**, **6a**, and **6b**), DSC thermograms (**1a**, **1a**/**1b**, **1a**/**1c**, **3a**, **3b**, **4a**, **4b**, **5a**, **5b**, **6a**, **6b**, **5a**/**6a**, **5b**/**6b**, **5a**/**5b**, **6a**/**6b**, **5a**/**6b**, and **6a**/**5b**), and tables for

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mass/charge values (**1a**−**1c**, **2a**−**2c**, **3a**, **3b**, **4a**, **4b**, **5a**, **5b**, **6a**, and **6b**) and melting temperatures (**1a**, **1a**/**1b**, **1a**/**1c**, **3a**, **3b**, **4a**, **4b**, **5a**, **5b**, **6a**, **6b**, **5a**/**6a**, **5b**/**6b**, **5a**/**5b**, **6a**/**6b**, **5a**/**6b**, and **6a**/**5b**). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: yamamoto.t.ay@m.titech.ac.jp; ytezuka@o.cc.titech.ac.jp.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Tsai, C. S. *Biomacromolecules: Introduction to Structure, Function and Informatics*; Wiley: Hoboken, NJ, 2006.
(2) Branden, C. I.; Tooze, J. *Introduction to Protein Structure*, 2nd ed.; Garland Science: New York, 1999.
(3) Anfinsen, C. B. *Science* **1973**, *181*, 223−230.
(4) Dobson, C. M. *Nature* **2003**, *426*, 884−890.
(5) Jamshidian, M.; Tehrany, E. A.; Imran, M.; Jacquot, M.; Desobry, S. *Compr. Rev. Food Sci.* **2010**, *9*, 552−571.
(6) Luckachan, G. E.; Pillai, C. K. S. *J. Polym. Environ.* **2011**, *19*, 637−676.
(7) Fukushima, K.; Kimura, Y. *Polym. Int.* **2006**, *55*, 626−642.
(8) Kakuta, M.; Hirata, M.; Kimura, Y. *Polym. Rev.* **2009**, *49*, 107−140.
(9) Tsuji, H. *Macromol. Biosci.* **2005**, *5*, 569−597.
(10) Yu, L.; Dean, K.; Li, L. *Prog. Polym. Sci.* **2006**, *31*, 576−602.
(11) Okihara, T.; Tsuji, M.; Kawaguchi, A.; Katayama, K.; Tsuji, H.; Hyon, S. H.; Ikada, Y. *J. Macromol. Sci., Part B: Phys.* **1991**, *30*, 119−140.
(12) Sawai, D.; Tsugane, Y.; Tamada, M.; Kanamoto, T.; Sungil, M.; Hyon, S. H. *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45*, 2632−2639.
(13) Brizzolara, D.; Cantow, H.-J.; Diederichs, K.; Keller, E.; Domb, A. J. *Macromolecules* **1996**, *29*, 191−197.
(14) Cartier, L.; Okihara, T.; Lotz, B. *Macromolecules* **1997**, *30*, 6313−6322.
(15) Biela, T.; Duda, A.; Penczek, S. *Macromolecules* **2006**, *39*, 3710−3713.
(16) Sugai, N.; Heguri, H.; Ohta, K.; Meng, Q.; Yamamoto, T.; Tezuka, Y. *J. Am. Chem. Soc.* **2010**, *132*, 14790−14802.
(17) Hoskins, J. N.; Grayson, S. M. *Polym. Chem.* **2011**, *2*, 289−299.
(18) Nasongkla, N.; Chen, B.; Macaraeg, N.; Fox, M. E.; Fréchet, J. M. J.; Szoka, F. C. *J. Am. Chem. Soc.* **2009**, *131*, 3842−3843.
(19) Yamamoto, T.; Tezuka, Y. *Polym. Chem.* **2011**, *2*, 1930−1941.
(20) Chisholm, M. H.; Gallucci, J. C.; Yin, H. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15315−15320.
(21) Stanford, M. J.; Pflughaupt, R. L.; Dove, A. P. *Macromolecules* **2010**, *43*, 6538−6541.
(22) Culkin, D. A.; Jeong, W.; Csihony, S.; Gomez, E. D.; Balsara, N. P.; Hedrick, J. L.; Waymouth, R. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 2627−2630.
(23) Jeong, W.; Shin, E. J.; Culkin, D. A.; Hedrick, J. L.; Waymouth, R. M. *J. Am. Chem. Soc.* **2009**, *131*, 4884−4891.
(24) Shin, E. J.; Jones, A. E.; Waymouth, R. M. *Macromolecules* **2012**, *45*, 595−598.
(25) Shinoda, H.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 6243−6248.
(26) Watanabe, J.; Eriguchi, T.; Ishihara, K. *Biomacromolecules* **2002**, *3*, 1109−1114.
(27) Karanikolopoulos, N.; Zamurovic, M.; Pitsikalis, M.; Hadjichristidis, N. *Biomacromolecules* **2010**, *11*, 430−438.
(28) Yamamoto, T.; Fukushima, T.; Yamamoto, Y.; Kosaka, A.; Jin, W.; Ishii, N.; Aida, T. *J. Am. Chem. Soc.* **2006**, *128*, 14337−14340.
(29) Click chemistry between PDLAs of relevant molecular weight with azido and ethynyl groups did not lead to a significant decrease in solubility.
(30) van Dongen, S. F. M.; Nallani, M.; Schoffelen, S.; Cornelissen, J. J. L. M.; Nolte, R. J. M.; van Hest, J. C. M. *Macromol. Rapid Commun.* **2008**, *29*, 321−325.
(31) Billiet, L.; Fournier, D.; Du Prez, F. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6552−6564.
(32) Hoskins, J. N.; Grayson, S. M. *Macromolecules* **2009**, *42*, 6406−6413.
(33) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F.; Spassky, N.; LeBorgne, A.; Wisniewski, M. *Macromolecules* **1996**, *29*, 6461−6465.
(34) Kadota, J.; Pavlović, D.; Desvergne, J.-P.; Bibal, B.; Peruch, F.; Deffieux, A. *Macromolecules* **2010**, *43*, 8874−8879.
(35) Tezuka, Y.; Komiya, R. *Macromolecules* **2002**, *35*, 8667−8669.
(36) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29.
(37) Hayashi, S.; Adachi, K.; Tezuka, Y. *Chem. Lett.* **2007**, *36*, 982−983.
(38) Adachi, K.; Honda, S.; Hayashi, S.; Tezuka, Y. *Macromolecules* **2008**, *41*, 7898−7903.
(39) Baba, E.; Honda, S.; Yamamoto, T.; Tezuka, Y. *Polym. Chem.* **2012**, *3*, 1903−1909.
(40) Gorbunov, A. A.; Vakhrushev, A. V. *Polymer* **2004**, *45*, 6761−6770.
(41) Gorbunov, A. A.; Vakhrushev, A. V. *Polymer* **2004**, *45*, 7303−7315.
(42) Arrighi, V.; Gagliardi, S.; Dagger, A. C.; Semlyen, J. A.; Higgins, J. S.; Shenton, M. J. *Macromolecules* **2004**, *37*, 8057−8065.
(43) Tezuka, Y.; Fujiyama, K. *J. Am. Chem. Soc.* **2005**, *127*, 6266−6270.
(44) Oike, H.; Imaizumi, H.; Mouri, T.; Yoshioka, Y.; Uchibori, A.; Tezuka, Y. *J. Am. Chem. Soc.* **2000**, *122*, 9592−9599.
(45) Oike, H.; Mouri, T.; Tezuka, Y. *Macromolecules* **2001**, *34*, 6592−6600.
(46) Ikada, Y.; Jamshidi, K.; Tsuji, H.; Hyon, S. H. *Macromolecules* **1987**, *20*, 904−906.
(47) Tsuji, H.; Hyon, S. H.; Ikada, Y. *Macromolecules* **1991**, *24*, 5651−5656.
(48) Tsuji, H.; Hyon, S. H.; Ikada, Y. *Macromolecules* **1991**, *24*, 5657−5662.
(49) Tsuji, H.; Ikada, Y. *Macromolecules* **1993**, *26*, 6918−6926.
(50) Yui, N.; Dijkstra, P. J.; Feijen, J. *Makromol. Chem.* **1990**, *191*, 481−488.
(51) Spassky, N.; Pluta, C.; Simic, V.; Thiam, M.; Wisniewski, M. *Macromol. Symp.* **1998**, *128*, 39−51.
(52) Sarasua, J. R.; Prud'homme, R. E.; Wisniewski, M.; Le Borgne, A.; Spassky, N. *Macromolecules* **1998**, *31*, 3895−3905.
(53) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316−1326.
(54) Masutani, K.; Kawabata, S.; Aoki, T.; Kimura, Y. *Polym. Int.* **2010**, *59*, 1526−1530.
(55) Pounder, R. J.; Stanford, M. J.; Brooks, P.; Richards, S. P.; Dove, A. P. *Chem. Commun.* **2008**, 5158−5160.
(56) Fukushima, K.; Furuhashi, Y.; Sogo, K.; Miura, S.; Kimura, Y. *Macromol. Biosci.* **2005**, *5*, 21−29.