

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/235798255>

Stereocomplexation of Poly(l-lactide) and Random Copolymer Poly(d-lactide-co- ϵ -caprolactone) To Enhance Melt Stability

ARTICLE in *MACROMOLECULES* · APRIL 2012

Impact Factor: 5.8 · DOI: 10.1021/ma202814c

CITATIONS

18

READS

63

3 AUTHORS:



Purba Purnama

Korea Institute of Science and Technology

12 PUBLICATIONS 116 CITATIONS

SEE PROFILE



Youngmee Jung

Korea Institute of Science and Technology

73 PUBLICATIONS 876 CITATIONS

SEE PROFILE



Soo-Hyun Kim

Korea University of Science and Technology

146 PUBLICATIONS 3,280 CITATIONS

SEE PROFILE

Stereocomplexation of Poly(L-lactide) and Random Copolymer Poly(D-lactide-co- ϵ -caprolactone) To Enhance Melt Stability

Purba Purnama,^{†,‡} Youngmee Jung,[†] and Soo Hyun Kim^{*,†}

[†]Biomaterials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

[‡]University of Science and Technology, 113 Gwahangno, Yuseong-gu, Daejeon 305-333, Korea

S Supporting Information

INTRODUCTION

Stereocomplex poly(lactide) (s-PLA) is a poly(lactide) based macromolecule which has been known as one of the choices to enhance the properties of poly(lactides) which is formed from an enantiomeric polymer blend of poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA).^{1–4} The s-PLA has melting temperature (T_m) approximately 50 °C higher than the T_m of either PLLA or PDLA.^{1,4} There are so many reports about s-PLA macromolecules development using linear PLLA and PDLA homopolymers.^{5–8} Moreover, there are also s-PLA macromolecules developments using block copolymer,^{9–15} star-shaped,^{16,17} and cyclic based poly(lactide).¹⁸

The melt processing is regular material processing in industry. Unfortunately, s-PLA from linear high-molecular-weight poly(lactide) has weakness due to limitation of memory to re-form s-PLA after melted (melt stability). Biela et al. reported the star-shaped s-PLA with has 13 arms or more able to completely melt and perfectly reversible due to hardlock-type interactions.¹⁶ The melt stable star-shaped s-PLA requires star-shaped PDLA and PLLA with 13 arms or more. Otherwise, commercial poly(lactide) is mostly in the linear form. Consequently, the star-shaped s-PLA concept is not suitable to apply for commercial poly(lactide). For these reasons, it is necessary to find a new concept for making melt stable s-PLA which can be applied to the commercial poly(lactide). Therefore, we studied about the stereocomplexation of PLLA and random copolymer of poly(D-lactide-co- ϵ -caprolactone) (PDLCL) with small content of ϵ -caprolactone (CL). The addition of small amount of caprolactone in the PDLCL is addressed as soft fragment to accelerate the chain movement of PDLA fragments to interact with PLLA chain after melted and “re-assemble” s-PLA. In this report, we demonstrated for the first time that small caprolactone content in the PDLCL can enhanced the melt stability of s-PLA.

RESULTS AND DISCUSSION

PDLCL copolymers with small content of CL were synthesized by ring-opening polymerization of D-lactide and CL in the presence of stannous octoate and 1-dodecanol (Scheme 1). The structure of PDLCL was analyzed by ¹H NMR which showed methine lactide signals at ~5.14 ppm and methylene CL signals at ~4.1 ppm. Tabel 1 shows the mole fraction of CL in PDLCL, melting point (T_m), also M_n and M_w . On the basis of the result, we successfully synthesized PDLCL with various amount of CL content. The melting point of PDLCL copolymers were between the melting points of PDLA (~180

Scheme 1. Synthesis of PDLCL Copolymer from D-Lactide and CL in Bulk Polymerization

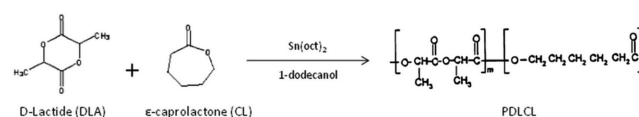


Table 1. Analysis of PDLCL Copolymers Was Produced through Bulk Copolymerization at 140 °C for 24 h

materials	% CL (mol) ^a	CL:LA length ratio ^b	M_n ^c	PDI ^c	T_g (°C) ^d	T_m (°C) ^d
PDLCL 97.5/2.5	2.64	1.0:43.3	164 000	1.90	60.48	166.00
PDLCL 95/5	7.65	1.27:21.9	184 000	1.70	59.9	164.00
PDLCL 90/10	12.74	1.6:13.1	174 000	1.90	54.34	163.41

^aMeasured by ¹H NMR. ^bMeasured by ¹³C NMR.^{20,21} ^cMeasured by GPC. ^dMeasured by DSC.

°C) and PCL (~65 °C) due to the randomization of PDLA and PCL fragments together.¹⁹

The melt stability of s-PLA related to the reassemble of the enantiomeric poly(lactide) chain. The high-molecular-weight linear s-PLA was known has limitation in the ability to re-form after melted. Tsuji and Ikada reported the critical molecular weight (M_w) for the ability restoring s-PLA after melted was about 10 000.⁵ Based on existing reports and in agreement with our works, when high-molecular-weight s-PLA was melted and recrystallized again, a certain portion of homopolymer and s-PLA will exist (see Figure S1). In the first run of DSC analysis, we obtained 100% degree of s-PLA, and it decrease drastically at the second run (about 34.4%). When s-PLA was melted, the homopolymer chains were unzipped; it has much freedom and tends to form homocrystallites.

We successfully generated s-PLA from PLLA and PDLCL random copolymer named s-PLA copolymer with small CL content using supercritical carbon dioxide–dichloromethane (scCO₂-DCM) at 65 °C and 350 bar. The scCO₂-DCM was chosen due to it was proven as effective method to generate high-molecular-weight stereocomplex.²² We denoted s-PLA2.5, s-PLA5, and s-PLA10 for the s-PLA generated from PLLA–

Received: December 30, 2011

Revised: April 16, 2012

Published: April 25, 2012

PDLCL97.5/2.5, PLLA–PDLCL95/5, and PLLA–PDLCL90/10, respectively. As explained elsewhere, the hydrogen bonding ($\text{CH}_3\cdots\text{O}=\text{C}$ interaction) between enantiomeric helical chains of PLLA and PDLA is the driving force for stereocomplexation.^{4,6} The addition of CL fragments in the PDLCL is predicted interrupt the stereocomplexation at certain level and decrease the melting point of s-PLA. As shown in Figure 1a and

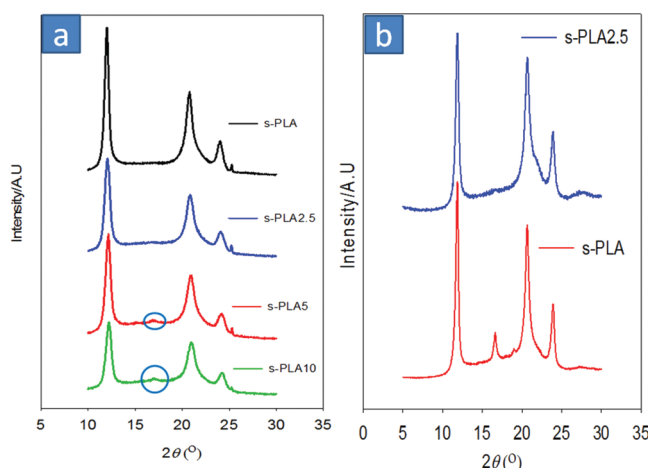


Figure 1. (a) XRD pattern of linear s-PLA and s-PLA copolymer (blends of PLLA and PDLCL random copolymers) were prepared by sc- CO_2 -DCM at 350 bar and 65 °C. (b) XRD pattern of linear s-PLA and s-PLA copolymer (s-PLA2.5) after melted and cooled to room temperature with slow cooling process.

Table 2. Degree of s-PLA and Heat of Melting of the s-PLA Copolymer Compared to Linear s-PLA at First and Second Heating by DSC and XRD

materials	first run		second run	
	deg of s-PLA (%)	ΔH_m (J/g) ^a	deg of s-PLA (%)	ΔH_m (J/g) ^a
s-PLA	100 ^a /100 ^b	70.18	34.4 ^a /69.6 ^b	14.09
s-PLA2.5	100 ^a /100 ^b	64.93	100 ^a /100 ^b	40.80
s-PLA5	99.9 ^a /98.1 ^b	61.92	90.6 ^a /94.0 ^b	31.93
s-PLA10	94.7 ^a /93.6 ^b	37.61	98.0 ^a	40.19

^aMeasured by DSC. ^bMeasured by XRD;^{24,25} sample were prepared as a film using the hot-pressing method.

Table 2, the s-PLA degrees and melting temperature change by increasing CL content on PDLCL. The degree of s-PLA was calculated by X-ray diffraction (XRD) analysis and confirmed by DSC analysis. In order to evaluate the composition of s-PLA and homopolymer, integrated intensity of XRD result was used with the equation^{24,25}

$$I^* = A \int I(2\theta) d\theta \int I(\phi) d\phi \quad (1)$$

with

$$A = (\sin^2 \theta_p \cos \theta_p) / I_p \quad (2)$$

where $I(2\theta)$, $I(\phi)$, θ_p , and I_p represent the integrated intensity in the 2θ direction, integrated intensity in the ϕ direction, peak Bragg angle, and peak intensity in the ϕ direction. Then, the weight fractions (X_c) were calculated with the equation

$$X_c = I^* / (rt \sum |F_{hkl}|^2) \quad (3)$$

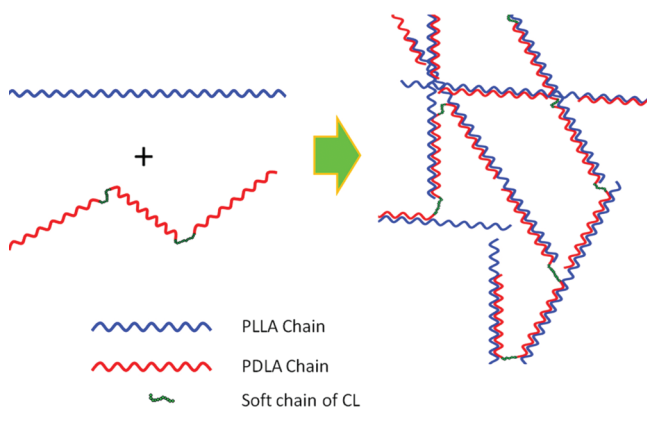
where r , t , and $\sum |F_{hkl}|^2$ represent the X-ray intensity ratio of before and after transmittance, sample thickness, and the structural function of corresponded mirror index parameter.

The degree of s-PLA starts to decrease at s-PLA5 and s-PLA10 which is shown by small homopolymer peak at $\sim 16.8^\circ$ of 2θ . This indicated that at certain level of CL fragment (about $\geq 5\%$) flexible fragments interrupt the interaction (hydrogen bonding) between PDLA fragment and PLLA to form s-PLA copolymer. The DSC data confirmed XRD data as shown in Figure S2. The melting temperatures of s-PLA also decrease by increasing CL contents. The melting temperature of s-PLA2.5, s-PLA5, and s-PLA10 are 222.47, 217.25, and 211.08 °C, respectively. The melting temperature of s-PLA copolymer related to the melting point of its building blocks. For different PDLCL, the melting points of s-PLA slightly decrease by increasing CL fragment on PDLCL which affect to the melting point of PDLCL. The heats of melting for s-PLA containing copolymer are also lower than s-PLA from homopolymer which is likely a consequence of addition of CL fragment.

In this work, we found unique behavior of s-PLA containing small amount of CL. As we expected, the small amount of CL fragment in the PDLCL chains can enhance the ability of restoring stereocomplexes after melted. Let us imagine the s-PLA as zipped pack and homopolymers as unzipped fragments. We evaluated the effect of small amount CL fragment to the melt stability of s-PLA. Figure 1b shows the comparison of linear s-PLA and s-PLA2.5 after melted using XRD analysis. Based on this figure, the addition of CL fragment in PDLCL can improve the melt stability of s-PLA copolymer. For s-PLA2.5, the 2.5% of CL fragment can perfectly preserve the melt stability of s-PLA2.5. The effect of CL fragment addition to the melt stability of s-PLA is summarized in Table 2. In the PDLCL random copolymer, CL fragments distributed randomly with PDLA fragments. We assumed that in this copolymer the PDLA fragment has shorter length compare to PDLA homopolymer due to the presence of CL fragments. Thus, in the concept of s-PLA copolymer, there are two driving force in order to preserve melt stability: the chain mobility and the length of PDLA fragment caused by addition of CL fragment. Increasing CL content means increase chain mobility and shorter PDLA fragments. Increasing chain mobility was caused by methylene groups within CL fragments which acted as soft segments in the copolymer chain.²³ The chain mobility helps the PDLA fragment to confront with PLLA. But at a certain level, the mobility ruins the interaction due to overactive mobility. The length of PDLA fragment related to the easiness of s-PLA formation. The shorter length of PDLA fragment means easier to form s-PLA compare to longer length. So, fundamentally, there is competition between chain mobility and length of PDLA fragment in order to reassemble s-PLA after melted. At s-PLA2.5, the PDLCL2.5 has optimum chain mobility of PDLA fragments which support to reassemble stereocomplex. At s-PLA5, the mobility of PDLA fragment could not covered by length of PDLA fragment to re-form s-PLA5. Shorter chain PDLA covered its overactive mobility to reassemble s-PLA in s-PLA10. Having higher chain mobility and shorter chain of PDLA, it easier to assemble with PLLA chain and form s-PLA. It has better chain arrangement which affect to the higher heat of melting. The DSC analysis also supported the melt stability data (Figure S2b).

The mechanism of the restoring ability of s-PLA copolymer is not clear yet. In star-shaped s-PLA, the neighboring participation occurred by minimize the chain freedom (locking) caused by number of arms.¹⁶ In s-PLA copolymer, the neighboring participation through antiparallel structure caused by increasing chain mobility of PDLA fragment which was affected by a certain content of CL fragment (flexible fragment), as shown in Scheme 2. Increasing chain mobility

Scheme 2. Schematic Structure of s-PLA Copolymer via Antiparallel Reassemble Supported by Soft Fragment of CL



makes PDLA fragments become active to meet with neighboring PLLA. Each PDLA fragments in the PDLCL can meet with different PLLA neighbors. The shorter PDLA fragments facilitate the reassemble of s-PLA easily.

CONCLUSIONS

We proposed new concept to enhance melt stability of s-PLA macromolecules by combining PLLA homopolymer and PDLCL random copolymer, as named s-PLA copolymer. We successfully generated s-PLA copolymer in the sc-CO₂-DCM system. We observed that 2.5% is the optimum CL fragment content. At this level, it does not interrupt the interaction between PLLA and PDLA chain to obtain high-degree of s-PLA. Otherwise, the addition of CL fragments into PDLA chain can enhance the melt stability of s-PLA copolymer by neighboring participation through increasing the chain mobility of PDLA and segmentation of PDLA chain. The melt stability is important point for s-PLA macromolecules development due to the use of thermal processing for various applications. The s-PLA copolymer has better melt stability compared to the linear s-PLA.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Tel +82-2-958-5343; Fax +82-2-958-5308; e-mail soohkim@kist.re.kr.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was supported by the National Research Foundation of Korea Grant funded by the Korea Government (MEST), NRF-2010-C1AAA001-0028939.

REFERENCES

- (1) Ikada, Y.; Jamshidi, K.; Tsuji, H.; Hyon, S. H. *Macromolecules* **1987**, *20*, 904–906.
- (2) Murdoch, J. M.; Loomis, G. L. Du Pont de Nemours & Co. US Patent 4,719,246, 1988.
- (3) Murdoch, J. M.; Loomis, G. L. Du Pont de Nemours & Co. US Patent 4,766,182, 1988.
- (4) Tsuji, H. *Macromol. Biosci.* **2005**, *5*, 569–597.
- (5) Tsuji, H.; Ikada, Y. *Macromolecules* **1993**, *26*, 6918–6926.
- (6) Sarasua, J.-R.; Rodriguez, N. L.; Arraiza, A. L.; Meaurio, E. *Macromolecules* **2005**, *38*, 8362–8371.
- (7) Brizzolara, D.; Cantow, H.-J. *Macromolecules* **1996**, *29*, 191–197.
- (8) Cartier, L.; Okihara, T.; Lotz, B. *Macromolecules* **1997**, *30*, 6313–6322.
- (9) Pensec, S.; Leroy, M.; Akkouche, H.; Spassky, N. *Polym. Bull.* **2000**, *45*, 373–380.
- (10) Fukushima, K.; Chang, Y. H.; Kimura, Y. *Macromol. Biosci.* **2007**, *7*, 829–835.
- (11) Tsuji, H.; Yamamoto, S.; Okumura, A.; Sugiura, Y. *Biomacromolecules* **2010**, *11*, 252–258.
- (12) Tsuji, H.; Shimizu, K.; Sakamoto, Y.; Okumura, A. *Polymer* **2011**, *52*, 1318–1325.
- (13) Portinha, D.; Belleney, J.; Bouteiller, L.; Pensec, S.; Spassky, N. *Macromolecules* **2002**, *35*, 1484–1486.
- (14) Kim, S. H.; Nederberg, F.; Zhang, L.; Wade, C. G.; Waymouth, R. M.; Hedrick, J. L. *Nano Lett.* **2008**, *8*, 294–301.
- (15) Kang, N.; Perron, M.-E.; Prud'homme, R. E.; Zhang, Y.; Gaucher, G.; Leroux, J.-C. *Nano Lett.* **2005**, *5*, 315–319.
- (16) Biela, T.; Duda, A.; Penczek, S. *Macromolecules* **2006**, *39*, 3710–3713.
- (17) Tan, B. H.; Hussain, H.; Lin, T. T.; Chua, Y. C.; Leong, Y. W.; Tjiu, W. W.; Wong, P. K.; He, C. B. *Langmuir* **2011**, *27*, 10538–10547.
- (18) Shin, E. J.; Jones, A. E.; Waymouth, R. M. *Macromolecules* **2011**, in press.
- (19) Brostrom, J.; Boss, A.; Chronakis, I. S. *Biomacromolecules* **2004**, *5*, 1124–1134.
- (20) Kasperczyk, J.; Bero, M. *Makromol. Chem.* **1993**, *194*, 913–925.
- (21) Hiljanen-Vainio, M.; Karjalainen, T.; Seppala, J. *J. Appl. Polym. Sci.* **1996**, *59*, 1281–1288.
- (22) Purnama, P.; Kim, S. H. *Macromolecules* **2010**, *43*, 1137–1142.
- (23) Hiljanen-Vainio, M. P.; Ovara, P. A.; Seppala, J. V. *J. Biomed. Mater. Res.* **1997**, *34*, 39–46.
- (24) Furuhashi, Y.; Imamura, Y.; Jikihara, Y.; Yamane, H. *Polymer* **2004**, *45*, 5703–5712.
- (25) Furuhashi, Y.; Kimura, Y.; Yamane, H. *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45*, 218–228.