디메틸에테르 초임계 유체를 이용한 고분자량 폴리락티드 스테레오 콤플렉스의 제조

굴나즈비비[*,**] · 정영미[**] · 임종주[*] · 김수현[**,***,†]

*동국대학교 화공과, **한국과학기술연구원 생체재료연구단, ***고려대학교 KU-KIST 대학원
(2014년 9월 10일 접수, 2014년 10월 30일 수정, 2014년 11월 9일 채택)

A Faster Approach to Stereocomplex Formation of High Molecular Weight Polylactide Using Supercritical Dimethyl Ether

Gulnaz Bibi[*,**], Youngmee Jung[**], Jong Choo Lim[*], and Soo Hyun Kim[**,***,†]

*Department of Chemical and Biochemical Engineering, Dongguk University-Seoul,
3-26 Pil-Dong, Chung-Gu, Seoul 100-715, Korea
**Biomaterials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea
***KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 136-701, Korea
(Received September 10, 2014; Revised October 30, 2014; Accepted November 9, 2014)

초록: 초임계 유체 기술을 이용한 폴리락티드 스테레오 콤플렉스 제조는 폴리락티드의 열적 및 기계적 물성을 향상시키는 좋은 방법이다. 이 연구에서는 초임계 유체인 디메틸에테르를 이용하여 고분자량 폴리락티드를 높은 수율로 100% 스테레오 콤플렉스화를 시켰다. 폴리락티드에 대한 디메틸에테르의 높은 용해성은 이 공정의 핵심요소로 250 bar, 70 ℃, 1.5시간에 반응이 종료되었다. 폴리락티드의 스테레오 콤플렉스 연구는 압력, 온도, 시간, 농도 및 분자량을 변화시키며 진행하였다. 스테레오 콤플렉스화는 온도와 압력이 증가할 때 높아졌다. 분자량 20만 이상인 PLLA와 PDLA는 6%의 디메틸에테르에서 100% 스테레오 콤플렉스화가 이루어졌다. 스테레오 콤플렉스화 정도는 DSC 및 XRD를 통해 이루어졌다. 또한 DSC 및 TGA 분석을 통해 융점이 50 ℃ 이상 높아진 폴리락티드가 얻어졌음을 확인하였다.

Abstract: Engineering the polylactide via stereocomplexation with supercritical fluid (SCF) technology paved way to fabricate polymers with enhanced thermal and mechanical properties. We aimed to establish a SCF medium with excellent solubility for PLA without any additional solvent/co-solvent. We, therefore, employed supercritical dimethyl ether to synthesize 100% stereocomplex polylactide from high molecular weight homopolymers with an excellent yield. The remarkable solubility of the homopolymers in dimethyl ether is the key for quick conversion to s-PLA. This study proves a rapid synthesis route of dry s-PLA powder with sc-DME at 250 bar, 70 ℃ and 1.5 h, which are reasonably achievable processing parameters compared to the conventional methods. The degree of stereocomplexation was evaluated under the effect of pressures, temperatures, times, homopolymer-concentrations and molecular weights. An increment in the degree of stereocomplexation was observed with increased temperature and pressure. Complete conversion to s-PLA was obtained for PLLA and PDLA with $M_n \sim 200$ kg·mol^{-1} with a total homopolymer to total DME ratio of 6:100% w/w at prescribed reaction conditions. The degree of stereocomplexation was determined by DSC and confirmed by XRD. Considerable improvement in thermo-mechanical properties of s-PLA was observed. DSC and TGA analyses proved a 50 ℃ enhancement in melting transition and a high onset temperature for thermal degradation of s-PLA respectively.

Keywords: fast stereocomplex, dimethyl ether, high molecular weight polylactides, supercritical fluid technology.

Introduction

The term bio-plastics refers a class of biocompatible[1] as well biodegradable[1] polymers. Polylactides (PDLA, PLLA) are nat-

urally reproducible, nontoxic and biodegradable examples of this class. They have a broad range of application both in bio-medical and environment. For vast applications, polylactide are engineered to enhance their hydrolytic resistance, thermal and mechanical properties via stereocomplex formation.[2] The term polylactide stereocomplex (s-PLA) implies a hydrogen bond interaction of PDLA and PLLA enantiomers forming a

stereoregular complex polymer with enhanced physical properties than the parent polymers.[2,3]

The s-PLA is also used in biodegradable films, fibers, hydrogels and microspheres.[3,4]

The s-PLA formation can take place either in the presence[5] or in absence of solution.[6-9] Recently fewer efforts have been made for stereocomplex formation using supercritical fluid technology.[10-12] Although, sc-CO$_2$ is considered to be a favorite solvent in SCF processes due to its low critical parameters, however, it is not a good solvent for dissolving polar biodegradable polymers.[13-15] It requires an additional organic solvent[16] which must be completely removed for biomedical applications.

The solubility of the homopolymer is the most important factor in obtaining excellent degrees of s-PLA formation. The solution casting process has limitations of a perfectly dissolved PDLA and PLLA homopolymer mixture besides the long period of solvent evaporation. The direct melt blending process of PDLA/PLLA for s-PLA formation is not desirable for high temperature requirement.[12] In the case of s-PLA generated from high molecular weight homopolymers particularly, the degree of stereocomplexation is not appreciable using these methods.[17-20] For these reasons, SCF technology provides an alternative strategy for fabrication of s-PLA from high molecular weight polylactides. Simple tuning of the density by varying the temperature and pressure enables broad application to supercritical fluids.[21]

A suitable supercritical fluid solvent is required to dissolve the polymers at relatively moderate conditions.[22] We employed dimethyl ether as the SCF for s-PLA synthesis because it is an excellent solvent for polylactides firstly and is expected to result in faster stereocomplexation. Secondly, it does not need any additional co-solvent being sufficient alone to dissolve polylactides effectively.

A considerable research work has been devoted to dimethyl ether (DME) over the past few decades due to both environmental issues and economic impact of fuel.[23-27]

DME is a volatile organic compound (VOC). However, it is quite non-hazardous for being nonmutagenic, noncarcinogenic, nonteratogenic, and nontoxic. Wuebbles et al.[28] reported that the global warming potential of DME is lower than that of carbon dioxide, methane, and dinitrogen oxide, demonstrating its ecofriendliness. However, it is flammable[29,30] and, thus, safety precautions must be followed when handling DME. sc-DME has been used to synthesize high molecular weight L-polylactide and its microspheres.[31] Recently, DME has been utilized

successfully as a solvent for dispersion polymerization of N-vinylcarbazole (NVCA)[32] and 2-hydroxyethyl methacrylate (HEMA).[33,34] The solubility of a wide range of monomers and the insolubility of most polymers in DME leads to its use in the dispersion polymerization of several monomers. Its critical parameters are T_c=126.9 ℃ and P_c=54 bar.

The cloud point determines a complete dissolution of a polymer in the supercritical fluid. Lee and Mc Hugh[35] and Hasch et al.[36] reported the phase behavior of poly(ethylene-co-methacrylic acid) and poly(ethylene-co-methyl acrylate) copolymers in DME.

The cloud point experiments reported by Kuk et al.[37] investigated the LCST phase behavior of D, L-PLA in DME and DME + CO$_2$ mixtures. DME was observed to be a high quality solvent for the D, L-PLA.

The use of sc-DME for s-PLA formation is a promising technique to address the time requirements, processing parameters and solubility issues of s-PLA homopolymers. We established comparatively moderate processing conditions and faster progress to give 100% stereocomplex formation without any additional solvent. To the best of our knowledge, we are the poineers to report s-PLA formation using sc-dimethyl ether.

We measured the degree of s-PLA formation while investigating the effects of various variables such as the homopolymer molecular weight, concentration, pressure, temperature, and time. The purpose of our study was to employ sc-DME to get 100% stereocomplexation of high molecular weight PLLA/PDLA homopolymers at a faster rate and at easily achievable processing parameters without adding any other solvent or co-solvent.

Experimental

Materials. PDLA (M_n=229705 g/mol, M_w=391668 g/mol, PDI=1.705) and PLLA (M_n=228124 g/mol, M_w=448682 g/mol, PDI=1.890) were synthesized by bulk polymerization in Biomaterial Research Center, KIST. Chloroform (Daejung Chemicals & Metal with a purity >99.5%), dimethyl ether (Sigma-Aldrich, purity 99.9%) and N$_2$ (Shin Yang Oxygen Industry, minimum purity 99.9%) were used as received.

Stereocomplex Formation. PDLA and PLLA with 1:1 weight ratio were added to a 50 mL stainless steel high-pressure reactor equipped with magnetic stirrer and electrical heating mantle. The weight ratio of total polymer to total sc-DME was 5:100. The reactor was purged with nitrogen for 5 min

and vacuumed at 40 °C for 1 h. The reactor was connected to a DME feed system. The reactor was filled with compressed DME to 120 bar at 30 °C and then gradually heated to 70 °C to achieve a pressure of 250 bar. The s-PLA formation was allowed to proceed for the predetermined times (1.5 h) and the reactor was chilled with ice-acetone mixture after the reaction had finished. DME was allowed to evaporate after opening the reactor. The homopolymers concentrations, molecular weight, pressures, temperature, and time were also varied.

Characterization. The degree of s-PLA formation was measured by a modulated differential scanning calorimeter (modulated DSC 2910, TA Instrument). The heating rate was fixed at 10 °C/min. X-ray diffraction spectra were registered with a X-ray diffractometer Rigaku D/Max 2500 composed of Cu Kα(λ=1.54056 Å, 30 kV, 100 mA) source, a quartz mono-chromator, and a goniometric plate. Thermogravimetric analysis (TGA) was conducted on a Hi-Res TGA 2950 (TA Instrument) under N_2 flow. For mechanical properties, we made a film using the pressure instrument equipped with a heating block (250 °C) and polyimide vacuum bag. The mechanical properties were measured on an Instron apparatus. The specimen size was 20×5 mm, and the thickness was 170 μm. The distance between the supports was 10 mm, and the extension rate was 3 mm/min.

Results and Discussion

We investigated the formation of s-PLA using sc-dimethyl ether. We evaluated homopolymers with different concentrations, molecular weights and processing parameters (pressure, temperature, and time) to determine the optimum processing conditions. In our experiments, the optimum conditions of sc-DME processing were sc-DME at 70 °C and 250 bar for 1.5 h.

The final shape of the stereocomplex is a fine powder, which is useful for further applications such as molding, blending and nano-fabrication etc. The reactor was chilled with an ice-acetone mixture, as DME has a high vapor pressure at room temperature. After chilling, the reactor was safely opened and DME was simply evaporated slowly, leaving the dry powder behind. DME has a dipole moment of 1.3D.[38] Therefore, PDLA and PLLA homopolymers are efficiently dissolved in sc-DME. Typical lower critical solution temperature (LCST) phase behavior for the PLA-sc-DME system was reported by Kuk *et al.*[37] The LCST phase behavior of PLA in sc-DME demonstrates the miscibility of the polymers in sc-DME at temperatures below the critical temperature of DME. The

cloud point pressure was as low as 14 MPa even at 393.15 K, indicating that DME is an excellent solvent for polar PLA.[37] The solubility of the PLA homopolymers increases with increasing temperature and hence the pressure of the medium, which meets the cloud point. The cloud point indicates the change of the system from a single (homogeneous) phase to a double (heterogeneous) phase and is defined as the phase boundary as the pressure is reduced.

The single phase of the homopolymer-sc-DME becomes turbid at the cloud point. The s-PLA is precipitated out and stays suspended in this fluid until the crystallization progresses and is completed. The turbidity turns to the heterogeneous s-PLA-sc-DME state as the non-soluble s-PLA is completely formed. The hydrogen bonding (CH_3 and O=C interaction) is the driving force for the nucleation of PLA stereocomplex crystallites.[3] Due to the very low boiling point of DME (-24.81 °C), it evaporates at a high rate at room temperature so that it is possible to immediately obtain a fine dry powder product, as shown in Figure 1.

The helical conformation and crystal structure of PDLA and PLLA change when s-PLA crystallites are formed, which causes the X-ray diffraction pattern of s-PLA to differ from that of its homopolymers.[39] For PDLA and PLLA homopolymers, diffraction peaks (Figure 2(a)) were observed at 2θ values of 16.6° and 19.09°, respectively. Three diffraction peaks were observed for the s-PLA formed by sc-DME at 2θ values of 11.16°, 20.68° and 23.4°.

The stereocomplex enhances the thermal properties of homopolymers. The s-PLA has a T_m of 227.7 °C, which is 50 °C higher than the T_m of PLLA or PDLA (Figure 2(b)). Rapid solubility of the PDLA/PLLA mixture allows free mobility to the homopolymer chains in the fluid.[40] Polar inter-
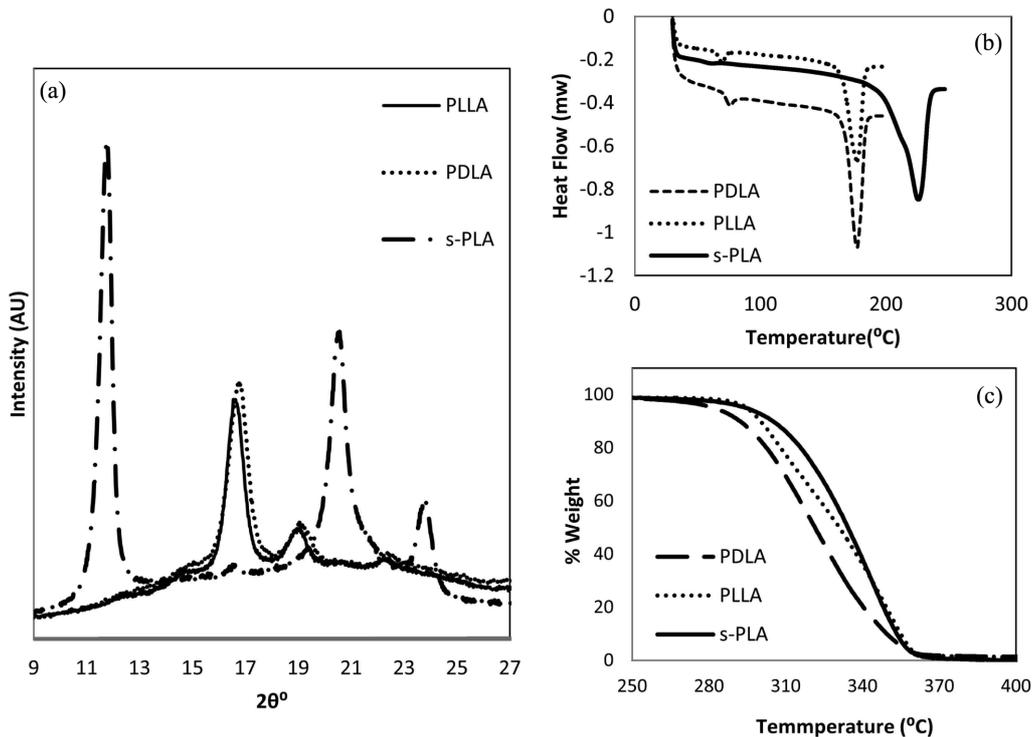

Figure 1. Appearance of the dry s-PLA powder.

Figure 2. Comparison of PLLA, PDLA and s-PLA by (a) XRD; (b) DSC; (c) TGA analyses.

actions developed between the ester carbonyl group of polyester and methoxyl group (CH$_3$-O) of sc-DME, favoring rapid solvation. The higher solubility of the PLA homopolymers is the key to fast stereocomplex generation. Mobile chains are coiled around each other due to van der Waals interactions and the decrease of entropy favors the crystallization of PLA. The degree of crystallinity affects the thermal transition of polymers. It has been observed that the molecular weight does not affect either crystal formation or the final degree of crystallinity, however, the crystallization rate of PLA decreases with increasing molecular weight. These results are consistent with the differential scanning calorimetry (DSC) results, which showed a broad exothermic crystallization peak for the higher molecular weight PLA.[41]

The s-PLA was more strongly bound by the crystal network and had a slightly decreased motion compared to PLA.[39] The s-PLA formed by sc-DME showed a single peak at 227.7 °C obtained as 100% stereocomplex at 250 bar and 70 °C. These results are consistent with the X-ray diffraction analysis results (Figure 2(a)).

The s-PLA formation with SCF technology has alleviated the thermal degradation problems caused by the lower degrees of stereocomplexation (especially in the case of high molecular weight PLA) formed from solid state polycondensation and

melt blending processes. Fukushima and Kimura[9] reported that the solid-state polycondensation process can result into a latent s-PLA with thermal properties similar to those of its homopolymer.[17,18]

The stereocomplex was found to be more thermally stable than the parent homopolymers, as shown in Figure 2(c). Table 1 shows that s-PLA has a high onset temperature of thermal degradation, which indicates the thermal stability of s-PLA synthesized by sc-DME. The strong interactions between the L-lactide and D-lactide chains are responsible for retarding this thermal degradation.[42]

The s-PLA formed by sc-DME had better mechanical properties than the homopolymers. The mechanical properties of s-PLA are shown in Table 1. The elongation at break and tensile strength values increased by almost 58% compared to the neat

Table 1. Onset Temperature of Thermal Degradation and Mechanical Properties of the Homopolymers and s-PLA

Material	Onset temperature (°C)	Elongation at break (%)	Tensile strength (MPa)	Young's Modulus (GPa)
PDLA	293	2.4	14.61	1.38
PLLA	294	2.6	19.2	1.42
s-PLA	310	3.8[a]	47.7[a]	1.67[a]

[a]The degree of stereocomplexation after hotpress was 73%.

homopolymers. Young's modulus also increased as compared to the neat homopolymers, which was caused by the high degree of s-PLA. The free mobility of the homopolymer chains was restricted once converted into the stereocomplex. In other words, van der Waals interactions between homopolymer chains reduce the amorphous domains, increasing the hard crystalline regions which, in turn, make the stereocomplex mechanically strong as compared to the parent homopolymers.

As explained previously, the optimum conditions for s-PLA formation by sc-DME were determined by varying the processing parameters, including homopolymer molecular weight, concentration, pressure, temperature, and time.

We used high molecular weight polylactides ($M_n > 200000$ g/mol) to evaluate many variables related to s-PLA formation. We determined the degree of s-PLA formation by comparing the ΔH_m of the melting point of s-PLA (227.7 °C) and that of homopolymers (177.9 °C). The solubility of polylactide homopolymers in a supercritical fluid is the most important factor in making a stereocomplex. The different degrees of s-PLA formation resulted from the varying extent of solubility of PLA in sc-DME. Several reports have been published regarding the cloud point of polylactide in supercritical fluids.[21,22,37] The cloud point pressure has been characterized as a function of temperature, solvent composition, and polymer molecular weight.[21,22,37]

Although the SCF remains a single phase, its density can easily be "tuned" from gas to liquid values merely by changing the pressure of the fluid. We varied the pressure from 100 to 350 bar to investigate the effect of pressure on s-PLA formation (Figure 3). At low pressure (100 bar), we obtained 34%
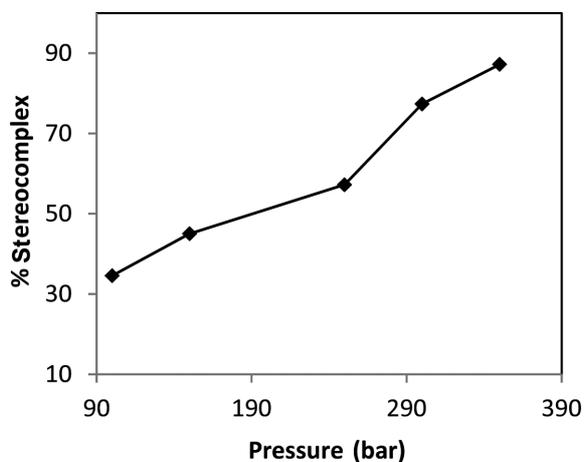
s-PLA, which increased linearly with increasing pressure to 45% at 150 bar, 57% at 250 bar, 77% at 300 bar and 87% at 350 bar. The temperature was held at 65 °C for 2 h in these experiments. The obvious increase of the density of the sc-fluid at elevated pressures can be attributed to the increasing solubility of the polymer.

Lim et al. reported that the increase of solubility correlates high solvent density at higher pressures.[42] These results suggest that the degree of s-PLA formation is dependent on density. The high degree of s-PLA formed was in good agreement with the appreciable polar interactions developed between homopolymers, PLLA, PDLA and the polar solvent sc-DME (dipole moment 1.3 D).

We evaluated the effects of temperature in a series of s-PLA processing experiments conducted at temperatures ranging from 40 to 100 °C at 250 bar for 2 h. Increasing the temperature resulted in increased s-PLA formation, which then decreased beyond the optimum temperature (Figure 4). Polymers are dissolved in sc-DME even at 40 °C, resulting in a 30% stereocomplex conversion. Increasing the temperature to 70 °C enabled the formation of 100% s-PLA. The cloud point was reached under these conditions where the system was single phase and completely dissolved both homopolymers. The degree of s-PLA formation was 59% at 50 °C, 94% at 60 °C, and 100% at 70 °C.

Lee and Kuk[21] reported this condition to be the fluid to liquid-vapor phase transition. At higher temperatures, 100 °C for example, the degree of s-PLA formation decreased (85%). This condition was below the cloud point because increasing temperature decreased the solvent density, which is related to solubility. It is noteworthy that sc-DME proved to be such a
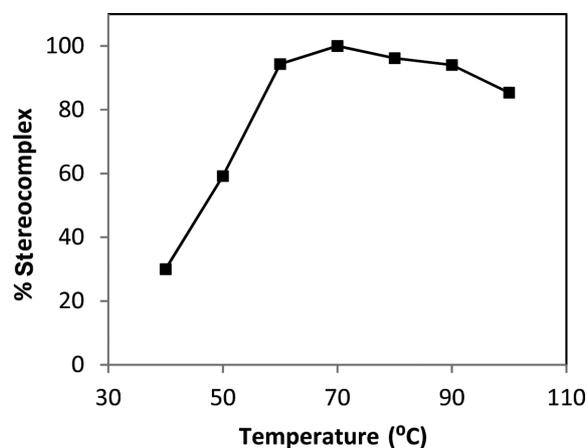

Figure 3. Effect of pressure on s-PLA formation using sc-DME (65 °C, 2 h).

Figure 4. Effect of temperature on s-PLA formation using sc-DME (250 bar, 2 h).
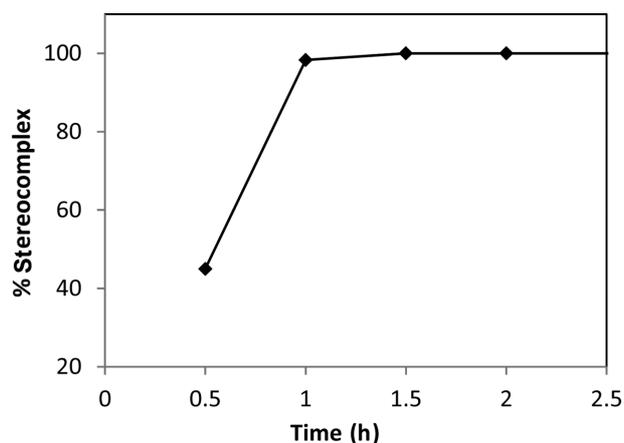
Figure 5. Effect of time on s-PLA formation using sc-DME (70 °C, 250 bar).
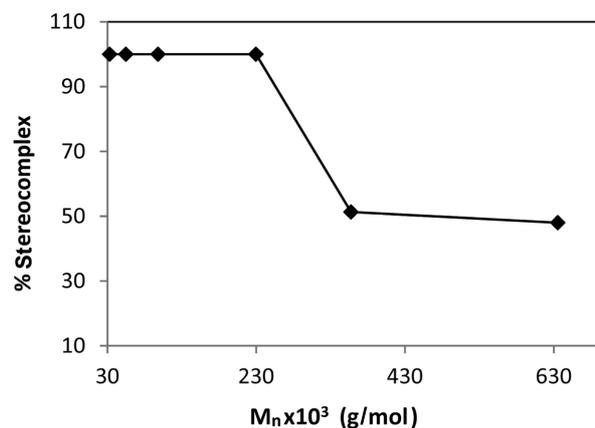

Figure 6. Effect of molecular weight on s-PLA formation using sc-DME (250 bar, 70 °C, 1.5 h).

perfect sc-fluid for PLA stereocomplex formation that even at elevated temperatures; it is capable of dissolving PLA to an appreciable extent. Increasing the pressure and temperature was necessary to maintain the solvent density of the polymer solution in the single-phase region.

Monomer dissolves faster than a macro-structured polymer. By varying the processing time, the minimum time to effectively dissolve the polymers was obtained. As evident from Figure 5, the degree of s-PLA formation at 30 min, 1 h, and 1.5 h was 45, 98, and 100%, respectively, while it remained 100% at 2, 5, and 10 h. The faster solubility of the homopolymers contributes to rapid availability for s-PLA crystallization. This is a beneficial property of sc-DME for which the stereocomplex formation of PLA progressed at faster rates with an appreciable percentage conversion. We obtained 100% stereocomplex formation in 90 min during the time variation

experiments.

The effect of the molecular weight (M_n ~100000 to ~600000 g/mol) of the homopolymers on the degree of stereocomplexation was evaluated under the same processing conditions. Table 2 summarizes the effects of different molecular weights on the degree of stereocomplexation. In the case of the 100% stereocomplex, only one T_m and one ΔH_m were obtained.

In Table 2, four pairs of PLLA and PDLA homopolymers are shown with their GPC and DSC analyses. The degree of stereocomplexation was excellent (100%) up to M_n ~200000 g/mol, as shown in Figure 6. When the molecular weight was increased to M_n~400000 g/mol, the degree of stereocomplexation decreased to 50% under the chosen processing parameters. This can be explained on the basis of the cloud point. The increasing molecular weight of the

Table 2. Effect of Different Molecular Weight Homopolymers on Degree of s-PLA

Homopolymers**	Homopolymer GPC-Analysis		DSC Analysis*				% Stereocomplex
	M_n (g/mol)	PDI	T_m^1 (°C)	T_m^2 (°C)	ΔH^1 (J/g)	ΔH^2 (J/g)	
D1	97980	2.2		222.6	-	77.3	100
L1	94893	2.1	-				
D2	229705	1.7		228.01	-	65.6	100
L2	228124	1.8	-				
D4	357484	2.5	175.7	226.8	32.9	34.7	51.3
L4	407401	2.13					
D6	635413	2.11	186	230	35.6	33.5	48
L6	620935	2.13					

*In the DSC Analysis column, superscripts 1 and 2 represent the thermal parameters of the homopolymers and stereocomplexes, respectively.
**D1/L1 are a pair of homopolymers of similar molecular weight. Likewise, D2/L2 to D6/L6 were paired up respectively for studying the effect of different molecular weights on the degree of stereocomplexation (%).

Table 3. Effect of Different Homopolymer Concentrations on Degree of s-PLA

s-PLA	H.Poly:DME	T_m^1 (°C)	T_m^2 (°C)	ΔH^1 (J/g)	ΔH^2 (J/g)	Stereocomplex (%)
St-5%	5:100	-	228.0	-	65.6	100
St-6%	6:100	-	226.6	-	61.8	100
St-7%	7:100	168.7	226.0	18.0	27.8	60.6
St-8%	8:100	172.2	227.2	38.1	26.6	41.9
St-9%	9:100	170.6	227.4	33.2	27.8	45.5
St-10%	10:100	171.7	227.6	41.7	21.3	33.8

*In the DSC analysis column, superscripts 1 and 2 represent the thermal parameters of the homopolymers and stereocomplexes, respectively.
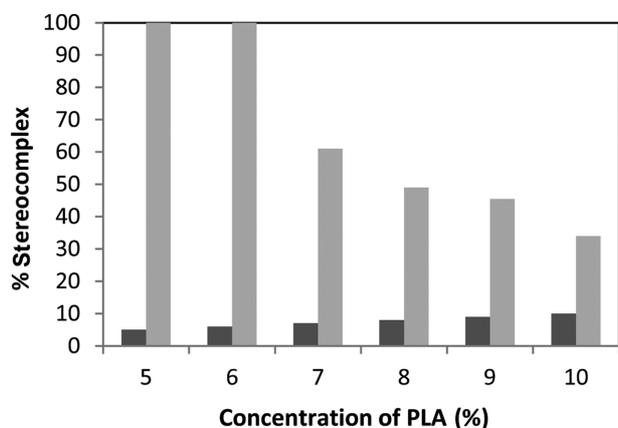

Figure 7. Effect of PLA concentration on s-PLA formation using sc-DME (250 bar, 70 °C, 1.5 h). The short black bars represent the total homopolymer (PDLA, PLLA) to total DME concentrations (%w/w) and the long grey bars represent the degree of stereocomplexation (%).

polymers reduced the single-phase region, elevating the cloud point pressure of the PLA-sc-DME system and therefore, decreasing the solubility of the polymers.[37] This, in turn, lowered the conversion of PLA to s-PLA. We believe that, in order to dissolve the high molecular weight PLA completely, a higher density of sc-DME is required.

To investigate the effect of the homopolymer concentration on s-PLA formation, we varied the ratio of total homopolymer to total sc-DME (% w/w) from 5:100 to 10:100 at 250 bar and 70 °C for 2 h. The degree of stereocomplexation with various homopolymer concentrations was determined by DSC analysis, as shown in Table 3. Single T_m and ΔH_m values were obtained for 100% stereocomplex formation whereas incomplete conversions appear as two melting peaks.

The maximum degree of stereocomplexation was found at a concentration of 6% w/w of the polymers at the chosen processing parameters. Figure 7 shows the effect of homopolymer concentration on the degree of stereocomplexation. In Figure

7, the short black bars represent the total homopolymer (PDLA, PLLA) to total DME (%w/w) concentrations and the long grey bars represent the degree of stereocomplexation (%). Approximately 50% s-PLA could be obtained with a 10% w/w total homopolymer concentration. We assumed that at 250 bar and 70 °C, the density of sc-DME was not high enough to dissolve high concentrations of polymers. In order to meet the cloud point, an increment of the pressure is necessary. The increased concentration of the polymers requires a higher density of sc-DME to result in complete dissolution to yield 100% stereocomplexation.

Conclusions

By comparing the degree of s-PLA formation and thermo-mechanical properties, it was found that, compared to conventional methods, SCF technology is an effective method of synthesizing s-PLA from high molecular weight polylactides. Synthesizing s-PLA using sc-DME is a novel supercritical fluid technique for high molecular weight PLA. Taking into account the processing parameters of 250 bar, 70 °C and 1.5 h, we demonstrated that the sc-DME process occurs at a much faster rate compared to trivial SCF-stereocomplex synthesis (e.g., the sc-CO_2-dichloromethane system). In addition, sc-DME solely is sufficient to dissolve PLA at all temperatures below the T_c of sc-DME. Hence no additional solvent or co-solvents are required for sc-DME-s-PLA processing.

We succeeded in forming stereocomplex polylactide using sc-DME from high molecular weight polylactide homopolymers (M_w > 200000 g/mol), which is difficult to achieve otherwise.

The current processing parameters (250 bar, 70 °C and 1.5 h) along with homopolymer molecular weights of M_n ≥200000 g/mol with total homo:DME 6%w/w were sufficient to yield 100% stereocomplexation at excellent yield.

The sc-DME-s-PLA process generates a fine dust-like dry product which can feasibly be used for further applications e.g. molding, melting or nano-fabrication. The dimethyl ether has a b.p. (-24.81 ℃) which is considerably lower than room temperature. We assume that at room temperature, it will be easier to transfer the s-PLA containing sc-DME to other vessels. This method is promising for the development of a continuous process for s-PLA synthesis. This will have broad applications in sc-DME-polar biopolymer fields.

References

1. S. H. Kim, Y. Jung, S. I. Kim, and J. I. Lim, *Polym. Korea*, **37**, 411 (2013).
2. Y. Ikada, K. Jamshidi, H. Tsuji, and S. H. Hyon, *Macromolecules*, **20**, 904 (1987).
3. H. Tsuji, *Macromol. Biosci.*, **5**, 569 (2005).
4. H. J. Kang, Y. H. Kim, S. H. Kim, and S. W. Chun, *Polym. Korea*, **24**, 656 (2000).
5. S. H. Kim, Y. H. Kim, and W. J. Kim, *Polym. Korea*, **24**, 431 (2000).
6. M. Spinu, U.S. Patent 5,317,064, (1994).
7. K. Fukushima and Y. Kimura, *Macromol. Symp.*, **224**, 133 (2005).
8. K. S. Anderson and M. A. Hillmyer, *Polymer*, **47**, 2030 (2006).
9. K. Fukushima and Y. Kimura, *J. Polym. Sci., Part A: Polym. Chem.*, **46**, 3714 (2008).
10. P. Purnama and S. H. Kim, *Macromolecules*, **43**, 1137 (2010).
11. S. H. Kim, Y. Jung, and M. K Kang, *Macromol. Res.*, **21**, 1036 (2013).
12. S. H. Kim, D. H. Yoon, S. Y. Kim, and B. Prabowo, *Polym. Korea*, **35**, 284 (2011).
13. P. Purnama and S. H. Kim, *Polym. Int.*, **61**, 939 (2012).
14. E. Reverchon, G. D. Porta, I. De Rosa, P. Subra, and D. Letourner, *J. Supercrit. Fluids*, **18**, 239 (2000).
15. J. M. Lee, B. C. Lee, and S. J. Hwang, *J. Chem. Eng. Data*, **45**, 1162 (2000).
16. J. D. Abraham, K. Joseph, and M. W. David, Editors, *Handbook of Biodegradable Polymers*, CRC Press, Boca Raton, 1998.
17. H. Tsuji, F. Horii, M. Nakagawa, Y. Ikada, H. Odani, and R. Kitamaru, *Macromelecules*, **25**, 4144 (1992).
18. H. Tsuji, A. Mizuno, and Y. Ikada, *J. Appl. Polym. Sci.*, **76**, 947 (2000).
19. H. Tsuji, S. H. Hyon, and Y. Ikada, *Macromelecules*, **24**, 5651 (1991).
20. H. Tsuji and Y. Ikada, *Polymer*, **40**, 6699 (1999).
21. M. A. McHugh and V. J. Krukonis, *Supercritical Fluid Extraction: Principles and Practice*, 2nd Ed., Butterworth-Heinemann, Boston, MA, 1994.
22. B. C. Lee and Y. M Kuk, *J. Chem. Eng. Data*, **47**, 367 (2002).
23. B. Herman, *Aerosol Spray Rep.*, **33**, 385 (1994).
24. S. Bobbo and R. Camporese, *J. Chem. Thermodynam.*, **30**, 1041 (1998).
25. D. B. Bivens and B. H. Minor, *Int. J. Refrig.*, **21**, 567 (1998).
26. D. A. Good, Y. Li, and J. S. Francisco, *Chem. Phys. Lett.*, **313**, 267 (1999).
27. D. J. Wuebbles, A. Jain, J. Edmonds D. Harvey, and K. Hayhoe, *Environ. Pollut.*, **100**, 57 (1999).
28. D. A. Good, J. S Francisco, A. Jain, and D. J. Wuebbles, *J.Geophys. Res.*, **103**, 2818 (1998).
29. J. Wu, Z. Liu, J. Pan, and X. Zhao, *J. Chem. Eng. Data*, **49**, 32 (2004).
30. T. A. Semelsberger, R. L. Borup, and H. L. Greene, *J. Power Sources*, **156**, 497 (2006).
31. S. H. Kim, Y. D. Park, and S. Y. Kim, *Macromol. Symp.*, **249-250**, 515 (2007).
32. K. S. Oh, W. Bae, and H. Kim, *Polymer*, **48**, 1450 (2007).
33. K. S. Oh, W. Bae, and H. Kim, *Eur. Polym. J.*, **44**, 415 (2008).
34. K. S. Oh, W. Bae, and H. Kim, *Ind. Eng. Chem. Res.*, **47**, 5734 (2008).
35. S.-H. Lee and M. A. McHugh, *Polymer*, **38**, 1317 (1997).
36. B. M. Hasch, S. H. Lee, and M. A. McHugh, *J. Appl. Polym. Sci.*, **59**, 1107 (1996).
37. Y.-M. Kuk and B.-C. Lee, *J. Chem. Eng. Data*, **46**, 1344 (2001).
38. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th Ed., McGraw-Hill, New York, 1987.
39. K. Fukushima and Y. Kimura, *Polym. Int.*, **55**, 626 (2006).
40. H. J. Choi, K. H. Lee, and J. Kim, *Polym. Korea*, **24**, 358 (2000).
41. H. J. Kang, Y. H. Kim, S. H. Kim, and S. W. Chun, *Polym. Korea*, **24**, 333 (2000).
42. Y. Fan, H. Nishida, Y. Tokiwa, and T. Endo, *Polym. Degrad. Stabil.*, **86**, 197 (2004).