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Printing of Stereocomplexes

# Rapid Fabrication of Polylactide Stereocomplex Using Layer-by-Layer Deposition by Inkjet Printing**

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Layer-by-layer (LbL) assembly is the stepwise deposition of interactive polymers to produce ultrathin polymer films by alternate immersion (dip-coating) of the substrates into polymer solutions.[1] In general, electrostatic forces, hydrogen bonds, van der Waals forces, or combinations of these interactions are available as the driving forces for LbL assembly. The LbL technique enables the preparation of advanced composites with excellent properties that are not attainable by other procedures. However, it is a time-consuming process of repetitive dipping cycles and rinsing steps to remove nonspecifically adsorbed polymers, and it produces chemical waste, which generally limits the practical applications of the LbL technique.[2] Recently, inkjet printing has become an important technology in the field of defined deposition of inorganic or organic materials.[3] The advantages of inkjet printing include small (picoliter) yet accurate drop volumes, highly controlled ink-drop placement (patterning), and high-frequency continuous operation. Therefore, this method has received increased attention for the fabrication of well-defined polymer structures from several kinds of dilute solutions.[4] Thus, inkjet printing techniques should be potentially applicable to the formation of polymer complexes through various interactions on any substrate.

A polymer stereocomplex is formed between two complementary stereoregular polymers. The main interaction resulting in the complexation is suggested to depend on the structural fitting between the polymer chains or between lateral functional groups with van der Waals contact.[5] There have been previous studies on complex formation in enantiomeric polylactides (PLAs), isotactic/syndiotactic poly(methyl methacrylate)s (PMMAs), isotactic PMMA/syndiotactic poly(methacrylic acid), and poly($\gamma$-benzyl L-/D-glutamate) in the form of mixed solutions or solid films.[6] In blends of poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA), the two molecular chains interact to form a 1:1 stereocomplex.[7] The PLA stereocomplex has a melting point 50 °C higher than that of the homopolymer. The physical and mechanical properties of the stereocomplex are largely dependent on the level of crystallinity and the solid-state morphology. Thus, an enhancement of the overall stereocomplex crystallization rate of PLAs and the development of a conventional fabrication method for the stereocomplex are matters of concern when PLAs are utilized for various medical and industrial applications. Although many articles on theoretical, structural, and property analyses of the stereocomplexation between PLLA and PDLA have been published, numerous researchers are currently still trying to develop useful fabrication methods, such as casting, melting, and precipitation procedures, for preparing well-stereocomplexed materials.[8]

In a previous study, we reported the stereocomplex formation of enantiomeric PLAs by LbL assembly to produce highly regular, ultrathin polymer films.[9] Since the LbL assembly of the PLAs involved the monolayer deposition of the interacting polymer with a polymer already deposited at each step, almost all of the polymer molecules can potentially participate in the complex, thus indicating a macromolecularly regulated structure. The LbL technique has attracted significant interest as a simple, highly versatile, and reproducible bottom-up approach that has been widely used to prepare nanostructured materials with various functionalities and potential applications. However, since this technique requires a great deal of time for processing, the development of an easier, alternative approach to fabricate polymer complexes is required.

Herein, we demonstrate the rapid fabrication of the PLA stereocomplex using an inkjet printer as a practical method to alternately deposit precise and minute amounts of PLLA and PDLA for the formation of LbL composites without an intermediate rinsing step. We hypothesized that when a precise amount of each PLLA and PDLA organic solution was alternately printed onto a substrate at the same place, dissociation of the homocrystallites and stereocomplex crystallization would occur at the moment of inkjet printing and during solvent evaporation, respectively. This would result in the predominant formation of stereocomplex crystallites by the repeated printing of PLAs. This method not only provides an approach to regulate the formation of PLA stereocomplex, but also gives insight into the future direction of rapid fabrication techniques for crystalline polymers. Furthermore, the control of self-assembly, crystallization, and crystal forms during inkjet printing fabrication will be of great interest in creating specific materials with a wide variety of mechanical, thermal, and optical properties.

The fabrication of PLLA/PDLA composites by the stepwise deposition of enantiomeric PLAs using an inkjet printer was performed as illustrated in Figure 1. Firstly, to test the performance and capabilities of the inkjet LbL system,

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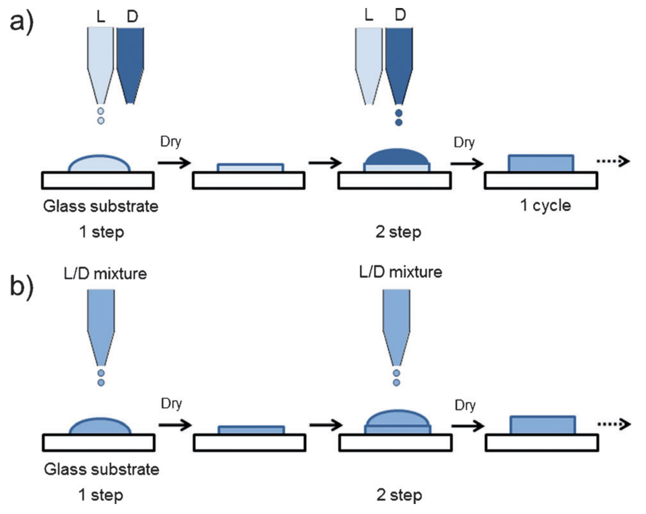

**Figure 1.** Schematic representation of LbL stereocomplex formation of PLAs by the inkjet printing system. a) PLLA and PDLA solutions (both 0.5 mg mL$^{-1}$) in chloroform were alternately printed onto a glass substrate. First, PLLA (L) was printed (1 step), and then the PLLA droplet was dried on the surface at room temperature, and overprinted with PDLA (D) (2 steps = 1 cycle). b) PLLA/PDLA mixed solution (both components 0.25 mg mL$^{-1}$) was printed on the glass substrate (1 step). The next step was performed in the same manner as described above.

a PLLA/PDLA mixture in $CHCl_3$ was printed by changing the discharge steps (2, 5, and 10 steps) of the solution using one nozzle head (the number of droplets printed in every step was kept constant). In this process, the PLLA/PDLA mixed solution was printed first and then overprinted all within a second with the same solution at the desired times (Figure 1 b). The processing time per step ($1 \times 10^5$ droplets) was about 100 s.

The X-ray diffraction (XRD) patterns of the PLAs printed on the substrate are shown in Figure 2 a. Enantiomeric PLLA and PDLA are both crystallizable in an orthorhombic or pseudo-orthorhombic unit cell with a $10_3$ helical conformation (α form).[7b] It has been reported that the racemic mixture forms the stereocomplex of PLLA and PDLA by the alternate packing of β-form $3_1$ helices of the opposite absolute configuration (left- versus right-handed, respectively), side by side with van der Waals contact.[10] The PLA stereocomplex displays XRD peaks at $2\theta$ values of 12, 21, and 24°. As a result, by changing the step numbers (the amount of PLAs discharged), the relative intensities of the peaks at $2\theta = 12$, 21, and 24° increased with increasing step number, thus indicating that the amount of PLA stereocomplex increased, whereas single crystals of the PLA homopolymers did not form at any step. The data from the FTIR spectra also showed the same tendency (Figure 2 b). In the case of printed PLLA alone, the diffractions were observed at $2\theta$ values of 17 and 19°, which are characteristic of PLA homocrystallites (α form; data not shown). The thicknesses of the PLA composites (3 mm$^2$) increased with increasing step number. The thicknesses for 2, 5, and 10 printing steps were 220, 600, and 980 nm, respectively.

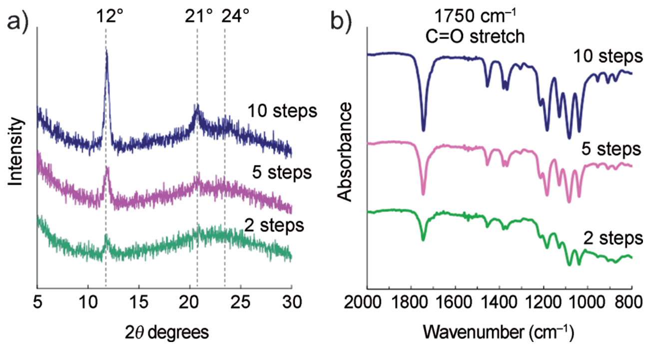

**Figure 2.** XRD patterns (a) and FTIR spectra (b) of PLA composites prepared by inkjet printing as described in Figure 1 b. $1 \times 10^5$ droplets (containing 0.5 μg PLLA and 0.5 μg PDLA) of the PLLA/PDLA mixed solution (both components 0.25 mg mL$^{-1}$) per step were printed on the glass substrate. The step was repeated a total of 2, 5, and 10 times. Spectra are shown offset for clarity.

In the next step, we investigated the effect of the discharge cycle number for the in situ formation of the PLA stereocomplex using each PLA solution. The conditions of the inkjet printing of PLAs are shown in Table 1. Each PLLA and PDLA (L-D LbL) or PLLA/PDLA mixture (L/D mix) was printed by changing the number of droplets and the discharge steps/cycles. Under these conditions, the final amount of printed PLLA or PDLA on the substrate reached the same value. The total amounts of printed PLLA and PDLA on the substrate were both 5 μg. The fabrication time of L-D LbL-2, -3, -4, and -5 was about 15, 20, 60, and 500 min, respectively.

**Table 1:** Inkjet printing conditions of PLAs.

| Sample | PLLA [mg mL$^{-1}$] | PDLA [mg mL$^{-1}$] | Droplet number | Steps | Cycles |
|---|---|---|---|---|---|
| L-D LbL-1 | 0.5 | 0.5 | $5 \times 10^5$ | 2 | 1 |
| L-D LbL-2 | 0.5 | 0.5 | $5 \times 10^4$ | 20 | 10 |
| L-D LbL-3 | 0.5 | 0.5 | $5 \times 10^3$ | 200 | 100 |
| L-D LbL-4 | 0.5 | 0.5 | $5 \times 10^2$ | 2000 | 1000 |
| L-D LbL-5 | 0.5 | 0.5 | $5 \times 10^1$ | 20000 | 10000 |
| L/D mix-1 | 0.25 | 0.25 | $1 \times 10^6$ | 1 | – |
| L/D mix-2 | 0.25 | 0.25 | $1 \times 10^5$ | 10 | – |
| L/D mix-3 | 0.25 | 0.25 | $1 \times 10^4$ | 100 | – |
| L/D mix-4 | 0.25 | 0.25 | $1 \times 10^3$ | 1000 | – |

Figure 3 a shows the XRD patterns of PLA composites prepared by the alternate deposition of PLLA and PDLA solutions. The XRD pattern of PLA composites for one cycle of printing (L-D LbL-1) shows the two main peaks at $2\theta = 12$ and 17°, which correspond to the stereocomplex crystal and the α-form homocrystal, respectively. The composite prepared with one cycle of printing formed both α-form homocrystals and stereocomplex crystals. In contrast, no diffraction peak of the homocrystallites was observed in the XRD patterns of samples with increased cycle numbers. The diffraction peaks at $2\theta$ values of 12, 21, and 24° representing typical stereocomplex crystals were observed in L-D LbL-2, -3, -4, and -5. This finding indicates that the composites are exclusively composed of PLA stereocomplex crystallites, not

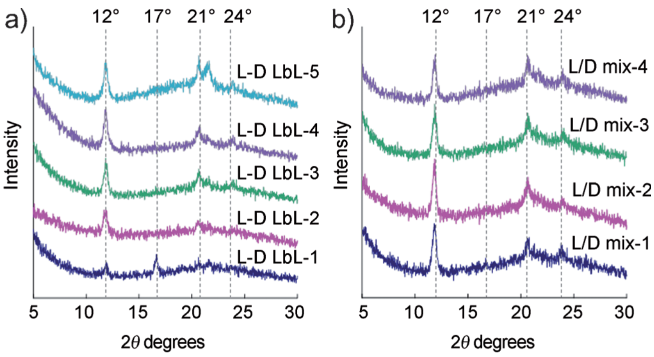

***Figure 3.*** Effect of the printing cycle number on the formation of PLA stereocomplex using the inkjet printing system. a) XRD patterns of PLA composites prepared by the alternate deposition of PLLA and PDLA solutions as described in Figure 1 a. The conditions of the inkjet printing of the PLAs are shown in Table 1. b) XRD patterns of PLA composites prepared from PLLA/PDLA mixed solutions as described in Figure 1 b. The diffraction peaks at $2\theta = 12$, 21, 24, and 17° correspond to the stereocomplex crystal and homocrystal. Spectra are shown offet for clarity.

homocrystallites. More interestingly, the peak intensities derived from the stereocomplex were increased from L-D LbL-1 through -5, which suggests that the degree of crystallinity of the stereocomplexes increased with the cycle number of alternate depositions of PLAs. Therefore, multiple inkjet passes can definitely improve the PLA crystal structure. The thicknesses of stereocomplexes prepared by alternate depositions of PLAs were about 1 μm. The thickness values did not depend on the step number. In contrast, the mean roughness ($R_a$) gradually increased from 55 to 210 nm with increasing cycle number. In addition, PLA composites prepared by the inkjet printing of a PLLA/PDLA mixed solution showed only three peaks ($2\theta = 12, 21$, and 24°) corresponding to the β-form stereocomplex (Figure 3 b). However, no effect of the printed cycle number on stereocomplex crystallinity was observed.

It is well known that no significant stereocomplex formation takes place in the case of mixing two diluted PLLA and PDLA solutions, but both racemic and homopolymer crystallization occur during the course of solvent evaporation because of the changing solution concentration. It was reported that the critical lowest concentration at which the stereocomplex crystallization of PLAs occurs was lower than that for homocrystallization.[11] Therefore, during the course of solvent evaporation, the polymer concentration first reaches the critical level of stereocomplex crystallite formation, and then that of homocrystallite formation. Importantly, upon dilution with solvent following the additional steps, the homocrystallites redissolve but the stereocomplex crystallites are more stable against the same solvent. In this study, in the PLA droplets printed on the substrate, solvent evaporation elevates the polymer concentration of the solution from an initial concentration. Moreover, the printed solutions predominantly dissolve the homopolymer crystallites formed on the substrate. Therefore, the alternate repeated printing of PLAs causes droplet discharge, homocrystallite dissolution, solvent evaporation, and stereocomplex formation in a repeating fashion, thus enhancing the stereocomplex crystallization. However, the process was disadvantageous in fabricating a smooth surface structure on a substrate.

Izquierdo et al. reported the preparation of polyelectrolyte LbL films by dipping versus spraying the respective solutions on a substrate.[2b] The fabrication of films by spraying was fast (250 times faster than dipping) and led to films (thickness about 50 nm) with small surface roughness (about 1 nm), but rinsing steps were needed for the fabrication of structurally controlled films. In our previous study, PLA stereocomplexes were prepared by the stepwise LbL assembly (dipping) of PLLA and PDLA from their acetonitrile solutions on a solid substrate.[9a] A substrate was immersed into both PLA solutions alternately at an immersion time of 15 min and concentrations of 10 $\text{mg}\,\text{mL}^{-1}$. After 12 assembly steps, the amount of formed stereocomplex and mean roughness were 2.7 $\mu\text{g}\,\text{cm}^{-2}$ and 15 nm, respectively. The time of the LbL process per two steps (one cycle) was about 30 min. One disadvantage of the technique is the rather long time required to assemble two interactive polymers on a substrate. In the case of inkjet printing, the processing time per cycle was only 3–90 s, depending on droplet number. A significant remediation of processing time by inkjet printing can be found (approximately 20–600 times faster than the dip-coating method).

In summary, inkjet printing technology has been successfully used for PLA stereocomplex formation on a substrate. PLA stereocomplex composites were fabricated on a substrate by combining two technologies: the LbL deposition of polymers and inkjet printing. The LbL technique involves the simple, alternate immersion of a substrate into two interactive polymer solutions. In each immersion and washing step, the adsorbed polymer is insolubilized and stabilized by polymer complex formation on the substrate, which results in a stable ultrathin film. This concept of stepwise deposition generates the hypothesis that the fabrication of various kinds of polymeric materials on a substrate by the self-assembly of polymers is possible if the precise amount of polymer solution necessary for nano/microstructure formation can be transferred alternately to a surface without a large excess, and that the solvent evaporation behavior during the deposition process can be controlled. We experienced a significant improvement in production time with the use of inkjet LbL assembly as compared to the traditional dip-coating LbL technique. Processing times should be significantly enhanced with advanced printing systems and automation. To the best of our knowledge, this is the first report of stereocomplex fabrication using an inkjet printing system. The control of the crystallization factors allows the design of a variety of materials with desirable properties.

In conclusion, we have demonstrated that the fabrication of stereocomplexes by inkjet printing is an excellent method for controlling the amount, thickness, and structure of printed polymers. The technique is time-efficient and cost-effective and can easily be automated. Using this approach, advanced polymeric materials consisting of stereocomplexes with superior performance will be obtained. Further research on applications to other polymers using the inkjet printing system is now in progress.

## Experimental Section

PLLA and PDLA were synthesized by ring-opening polymerization as previously described.[9a] PLLA (0.5 mg mL$^{-1}$; $M_n = 2400$, $M_w/M_n = 1.67$) and PDLA (0.5 mg mL$^{-1}$; $M_n = 2400$, $M_w/M_n = 1.67$) were dissolved in chloroform. PLLA, PDLA, or PLLA/PDLA 1:1 (w/w) mixed solutions were printed on a glass substrate using an inkjet printer (Cluster Technology Co., Ltd.; pulse conditions: voltage 10 V, frequency 1000 Hz). The inkjet printer was equipped with a single-nozzle drop-on-demand piezoelectric print head (PulseInjector), a two-axis motorized positioning system, and a USB camera aligned with a light-emitting diode for visualization of the droplet ejection. Single droplets with volumes of 20 pL were printed on demand from the nozzle, which had a diameter of 25 μm. A total of 10 pg of polymer was contained in one droplet. The total amount of polymer deposited on the substrate was controlled by changing the droplet number per step. The vertical separation between the nozzle and the substrate was typically 10 mm. The solvent of the droplet was evaporated from the surface at room temperature (1 step), and then overprinted with the solution (1 cycle; Figure 1).

The XRD patterns of the printed PLA composites were obtained from a RIGAKU RINT2000 apparatus. $Cu_{K\alpha}$ radiation ($\lambda = 0.154$ nm) was used as the X-ray source and the patterns were measured at 40 kV and 200 mA with a Ni filter. The samples were examined at $2\theta = 5$–$30°$. The Fourier transform infrared (FTIR) spectra of the PLA composites were obtained by the attenuated total reflection (ATR) method using a PerkinElmer Spectrum 100 FTIR spectrometer. The thickness and the mean roughness ($R_a$) of the printed PLA composites were measured by laser microscopy (VK-9700, KEYENCE).

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