

# Helical Phase Driven by Solvent Evaporation in Self-Assembly of Poly(4-vinylpyridine)-*block*-poly(L-lactide) Chiral Block Copolymers

Tsai-Ming Chung, Hsiao-Fang Wang, Tao Lin, Yeo-Wan Chiang\*,

Yi-Chun Chen, Bao-Tsan Ko\*, Rong-Ming Ho\*

## Supporting Information

### Synthetic Procedures for P4VP-PLLA BCPs\*

**Table S1.** Characterization of representative P4VP-PLLA BCPs\*.

**Figure S1.** TEM micrographs of (a) P4VP23-PLLA09 ( $f_{\text{PLLA}}^v=0.25$ ), (b) P4VP12-PLLA06 ( $f_{\text{PLLA}}^v=0.29$ ) and (c) P4VP15-PLLA09 ( $f_{\text{PLLA}}^v=0.33$ ).

**Figure S2.** WAXD patterns of as-cast P4VP-PLLA samples from dichloromethane and PLLA homopolymer.

**Figure S3.** TEM micrographs of solution-cast P4VP16-PLLA05 ( $f_{\text{PLLA}}^v=0.23$ ) from dichloromethane ( $V_{\text{CH}_2\text{Cl}_2}^{25^\circ\text{C}} = 342 \text{ mmHg}$ ) solution at  $25^\circ\text{C}$  (a) before and (b) after long-time annealing at  $110^\circ\text{C}$ .

**Figure S4.** TGA heating curve of solution-cast P4VP19-PLLA05 ( $f_{\text{PLLA}}^v=0.23$ ) from 1,2-dichloroethane ( $V_{\text{C}_2\text{H}_4\text{Cl}_2}^{20^\circ\text{C}} = 61 \text{ mmHg}$ ) solution at  $20^\circ\text{C}$ .

**Synthetic Procedures for P4VP-PLLA BCPs\*.** The procedures for synthesis were carried out under a dry nitrogen atmosphere. The solvents and deuterated solvents were purified by distillation before utilization.  $\text{AlMe}_3$  (2.0 M in toluene), 2,2'-ethylidenebis-(4,6-di-*tert*-butylphenol) (EDBP- $\text{H}_2$ ), and 2, 2-dimethyl-1, 3-pentadiol were purchased and used without further purification. N, N, N', N'', N''-Pentamethyl-diethylenetriamine (PMDETA, Aldrich, 99%) and CuBr (Aldrich, 99+%) were used as received. L-lactide (L-LA) was recrystallized before used. 4-Vinylpyridine (4-VP, Acros, 99+%) was distilled from  $\text{CaH}_2$  under reduced pressure.  $[\text{Al}(\mu\text{-EDBP})\text{Me}]_2$  was synthesized according to the previously reported literature.<sup>1</sup>  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Mercury-400 (400 MHz) with chemical shifts given in ppm from the internal TMS by using  $\text{CDCl}_3$  as a deuterated solvent. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. The GPC measurements were performed on Hitachi L-7100 or Water system equipped with a differential Bischoff 8120 RI detector using THF or DMF (HPLC grade) as an eluent. Molecular weight and molecular weight distributions were calculated using polystyrene as a standard.

**Preparation of Double-Headed Initiator,  $\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{OC(=O)-CHCl}(\text{CH}_3)$ . (DHI4-Cl)** An ice cold solution (0 °C) of 2, 2-dimethyl-1,3-pentadiol (15.6 g, 0.15 mole) in diethyl ether (200 mL) was added slowly to an

2-chloropropionyl chloride (3.8 g, 0.03 mol). After all of the solution was added, the mixture was stirred for 3 h. The mixture was washed by water to remove free 2,2-dimethyl-1,3-pentadiol. The organic layer was dried over  $\text{MgSO}_4$  and the volatile was removed to obtain a colorless liquid. Yield: 4.70 g (81%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): q, 1H,  $-\text{CHCl}(\text{CH}_3)$ ; 4.02 (m, 2H,  $-\text{CH}_2\text{O}-$ ); 3.34 (s, 2H,  $-\text{CH}_2\text{OH}$ ); 2.02 (s, 1H,  $\text{CH}_2\text{OH}$ ); 1.67 (d, 3H,  $-\text{CHCl}(\text{CH}_3)$ ); 0.92 (s, 6H,  $-\text{C}(\text{CH}_3)_2-$ ).

#### **Synthesis of Al Catalyst Containing Double-Headed Initiator, Al-DHI4-Cl.**

A rapidly stirred solution of  $[\text{Al}(\mu\text{-EDBP})\text{Me}]_2$  (0.96g, 1mmol) in toluene (20ml) was added to  $\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{OC}(=\text{O})\text{CHCl}(\text{CH}_3)$ , DHI4-Cl (0.39g; 2mmol). The reaction mixture was stirred at 25 °C for 10 h resulting in a white precipitate formed. The volatile materials were removed under vacuum, and the residue was washed with pentane twice and then dried under vacuum giving a white solid (Al-DHI4-Cl). Yield: 0.7g (53 %).

#### **Ring-Opening Polymerization (ROP) of L-LA Catalyzed by Al-DHI4-Cl.**

A typical ROP procedure was exemplified by the synthesis of PLLA-35 (the number 35 indicates the designed  $[\text{M}]_0/[\text{I}]_0$ ). L-LA (5.04g, 35 mmol) was added to a rapidly stirred solution of Al-DHI4-Cl (0.13g, 0.2 mmol) and DHI4-Cl (0.156g, 0.8 mmol) in toluene (2.5 mL). The reaction mixture was stirred at 110 °C for 48 h resulting in an increase in viscosity. After the reaction was quenched by the addition of excess 0.35

N acetic acid solution. The polymer was precipitated in methanol to give white solids.

Yield: 4.80 g (95%).  $M_n(\text{GPC}) = 8200$ ;  $\text{PDI} = 1.12$ ;  $M_n(\text{NMR}) = 5400$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 5.13 (q,  $-\text{OCH}(\text{CH}_3)\text{C}(=\text{O})-$ ); 4.32 (m,  $-\text{C}(=\text{O})\text{CHCl}(\text{CH}_3)$ ); 3.97 (m,  $-\text{OCH}_2\text{C}(\text{CH}_3)_2-\text{CH}_2\text{O}-$ ); 1.55 (d,  $-\text{OCH}(\text{CH}_3)\text{C}(=\text{O})-$ ); 0.97 (s,  $-\text{OCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}$ ).

#### **P4VP-PLLA BCPs\* Synthesized by Atom Transfer Radical Polymerization**

**(ATRP) of 4-vinylpyridine (4-VP) Using PLLA-Cl as the Macroinitiator.** In a typical ATRP experiment, the poly(L-lactide) macroinitiator (PLLA-Cl,  $M_n(\text{NMR}) = 5400$ ,  $\text{PDI} = 1.12$ ; 0.54 g, 0.1 mmol), 4-VP (1.9 mL, 18 mmol), catalyst CuBr (1.0 mol equiv to PLLA-Cl, 14.3 mg, 0.1 mmol), DMF (1.0 mL) and PMDETA (10.0 mol equiv to CuBr, 0.21 mL, 1.0 mmol) were introduced into a previously dried Schlenk flask in a drybox. The polymerization was performed under nitrogen at 50 °C for 17 h. The produced polymers were then dissolved in  $\text{CH}_2\text{Cl}_2$  (80 ml) and then passed through a short alumina column to remove the catalysts. After concentrating  $\text{CH}_2\text{Cl}_2$  solution (~30 ml left), the diblock copolymers were recovered by precipitation into pentane (150 ml) and dried in vacuum at room temperature. The molecular weight distribution ( $M_w/M_n$ ) of the P4VP-PLLA BCP\* was determined by GPC and the numbers of L-LA repeating units ( $n$ ) versus 4VP repeating the units ( $m$ ) were determined by  $^1\text{H}$  NMR analysis.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 8.31, 6.37 (br, *Ph*, P4VP);

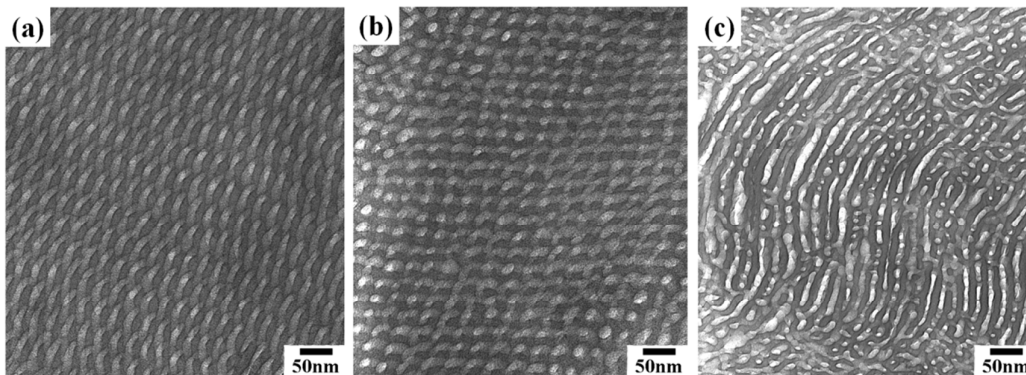
5.14 (q, -OCH(CH<sub>3</sub>)C(=O)-); 1.56 (d, -OCH(CH<sub>3</sub>)C(=O)-); 1.74~1.38 (br, CH<sub>2</sub>CH + CH<sub>2</sub>CH).

**Table S1.** Characterization of representative P4VP-PLLA BCPs\*.

Code	$M_n$ ,P4VP (kg/mol) <sup>1</sup>	$M_n$ ,PLLA (kg/mol) <sup>1</sup>	$M_n$ ,total (kg/mol)	$M_w/M_n$ <sup>2</sup>	$f_{\text{PLLA}}^v$	Morphology
P4VP13-PLLA11	13.2	10.5	23.7	1.24	0.42	L
P4VP15-PLLA09	15.7	9.1	24.8	1.26	0.33	L
P4VP12-PLLA06	11.7	5.6	17.3	1.19	0.29	H*
P4VP23-PLLA09	23.6	9.1	32.7	1.20	0.25	H*
P4VP16-PLLA05	15.5	5.4	20.9	1.17	0.23	H*
P4VP28-PLLA09	27.7	9.2	36.9	1.21	0.22	H*
P4VP19-PLLA05	18.9	5.4	24.3	1.10	0.20	HC

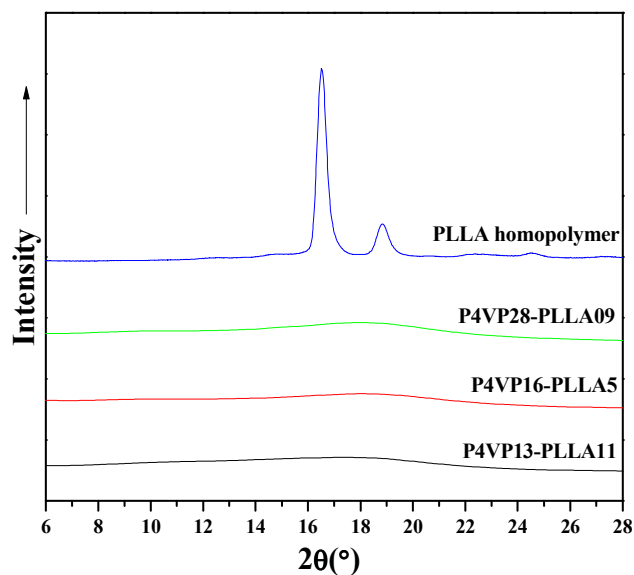
<sup>1</sup> $M_n$ , P4VP and  $M_n$ , PLLA were characterized by proton nuclear magnetic resonance (<sup>1</sup>H NMR). <sup>2</sup>Polydispersity index ( $M_w/M_n$ ) was determined by gel permeation chromatography (GPC) by using standard calibration. All samples were prepared by solution casting from dichloromethane solution (10 wt%)

The self-assembled morphologies for the P4VP-PLLA BCPs\* with the volume fractions of PLLA at 0.25, 0.29 and 0.33 were shown in Figure S1. As shown, the H\* phase can be observed in P4VP23-PLLA09 ( $f_{\text{PLLA}}^v=0.25$ ) and P4VP12-PLLA06 ( $f_{\text{PLLA}}^v=0.29$ ) BCPs\*, whereas the lamellar morphology (L) is obtained in the P4VP15-PLLA09 ( $f_{\text{PLLA}}^v=0.33$ ). Clearly, the phase boundary between L and H\* is between 0.33 and 0.29, which is significantly different to PS-PLLA. Note that the phase boundary of PS-PLLA is at about 0.4.



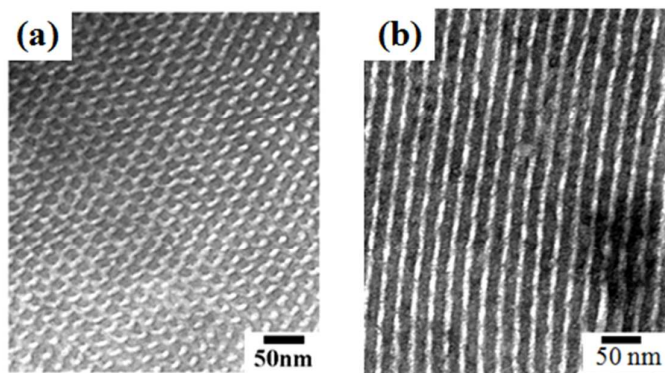
**Figure S1.** TEM micrographs of (a) P4VP23-PLLA09 ( $f_{\text{PLLA}}^v=0.25$ ), (b) P4VP12-PLLA06 ( $f_{\text{PLLA}}^v=0.29$ ) and (c) P4VP15-PLLA09 ( $f_{\text{PLLA}}^v=0.33$ ).

The crystallization events of the solution-cast samples are strongly dependent upon the evaporation conditions. To investigate whether crystallization occurs or not after solution casting, the WAXD experimental results were conducted (Figure S2). On the basis of the WAXD results, the slow evaporation did have the possibility to promote the crystallization event in the PLLA homopolymer. Nevertheless, owing to the confinement effect, the crystallization event in the P4VP-PLLA BCPs\* is not significant to change the self-assembled morphologies from casting.



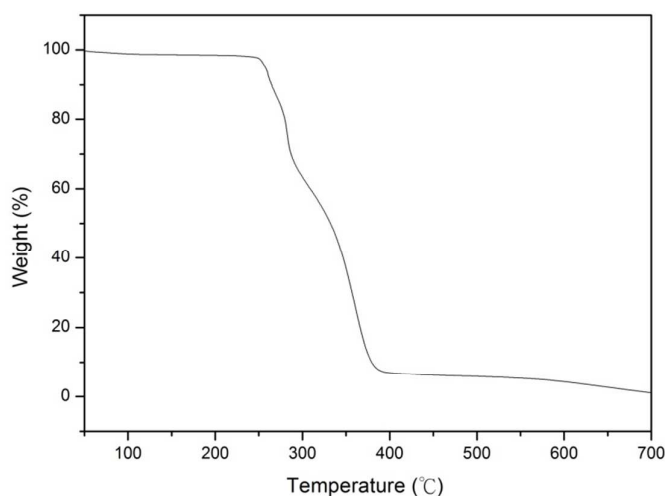
**Figure S2.** WAXD profiles of as-cast P4VP-PLLA samples from dichlorometane and the PLLA homopolymer.

Except for the solvent-evaporation-induced phase transition in this study, the thermal-induced phase transition from metastable  $H^*$  phase to stable HC phase can also be found. As shown in Figure S3, a phase transition from the metastable  $H^*$  phase to the stable HC phase can be observed after long-time annealing at  $110^\circ\text{C}$  in the P4VP-PLLA. As a result, the  $H^*$  phase in the P4VP-PLLA is therefore referred as a metastable phase.



**Figure S3.** TEM micrographs of solution-cast P4VP16-PLLA05 ( $f_{\text{PLLA}}^v=0.23$ ) from dichloromethane ( $V_{\text{CH}_2\text{Cl}_2}^{25^\circ\text{C}} = 342 \text{ mmHg}$ ) solution at  $25^\circ\text{C}$  (a) before and (b) after long-time annealing at  $110^\circ\text{C}$ .

After drying in a vacuum oven at  $65^\circ\text{C}$  for three days, the solvents should be greatly removed. Consistently, on the basis of the TGA result (Figure S4), the weight loss of solvent is extremely low. Therefore, the effect of the residual solvents in the self-assembled morphologies of the P4VP-PLLA BCPs\* should be insignificant.



**Figure S4.** TGA heating curve of solution-cast P4VP19-PLLA05 ( $f_{\text{PLLA}}^v=0.23$ ) from 1,2-dichloroethane ( $V_{\text{C}_2\text{H}_4\text{Cl}_2}^{20^\circ\text{C}} = 61 \text{ mmHg}$ ) solution at  $20^\circ\text{C}$ .



## References

- (1) Ko, B.-T.; Chao, Y.-C.; Lin, C.-C. *Inorg. Chem.* **2000**, 39, 1463-1469.