Electronic Supplementary Material (ESI) for Polymer Chemistry.

Tailoring the Crystallization of Poly (L-lactide) via Structural Optimization of Hydrogen-Bonding Segments with Different Aliphatic Spacer Length

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Support information

Molecular structure of OXA-n and $PLLA_{OXA-n}$

The ^{1}H NMR spectrum of OXA-2 and OXA-4 are shown in Figure S1(a-b), and the specific data are as follows: ^{1}H NMR (400 MHz, DMSO) δ 8.52 (t, 2H), 4.72 (t, 2H), 3.46 (q, 4H), 3.22 (q, 4H) and ^{1}H NMR (400 MHz, DMSO) δ 8.70 (t, 2H), 4.39 (t, 2H), 3.38 (q, 4H), 3.13 (m, 4H), 1.45 (m, 8H). The specific data of the PLLA, $PLLA_{OXA-2}$ and $PLLA_{OXA-4}$ (5×10^4 g/mol, Figure S1(c-e)) are as follows: ^{1}H NMR (400 MHz, DMSO) δ 4.28, 2.82, 1.43, ^{1}H NMR (400 MHz, DMSO) δ 8.86, 5.48, 5.22-5.14, 4.12, 3.38, 1.53-1.32 and ^{1}H NMR (400 MHz, DMSO) δ 8.76, 5.46, 5.20, 4.21-4.06, 3.14, 1.52-1.26. The ^{1}H NMR spectrum of the PLLA, $PLLA_{OXA-2}$, $PLLA_{OXA-4}$ and $PLLA_{OXA-6}$ (M_n ~ 30.0 kg/mol) are shown in Figure S1(f-i) and the specific data are as follows: ^{1}H NMR (400 MHz, DMSO) δ 4.28, 2.82, 1.43, ^{1}H NMR (400 MHz, DMSO) δ 8.88, 5.47, 5.22-5.14, 4.232, 3.37, 1.53-1.28, ^{1}H NMR (400 MHz, DMSO) δ 8.77, 5.48, 5.20, 4.24-4.08, 3.12, 1.52-1.26 and ^{1}H NMR (400 MHz, DMSO) δ 8.63, 5.39, 5.15, 4.14-4.02, 3.10-3.00, 1.58-1.55, 1.53-1.40 1.30-1.08.

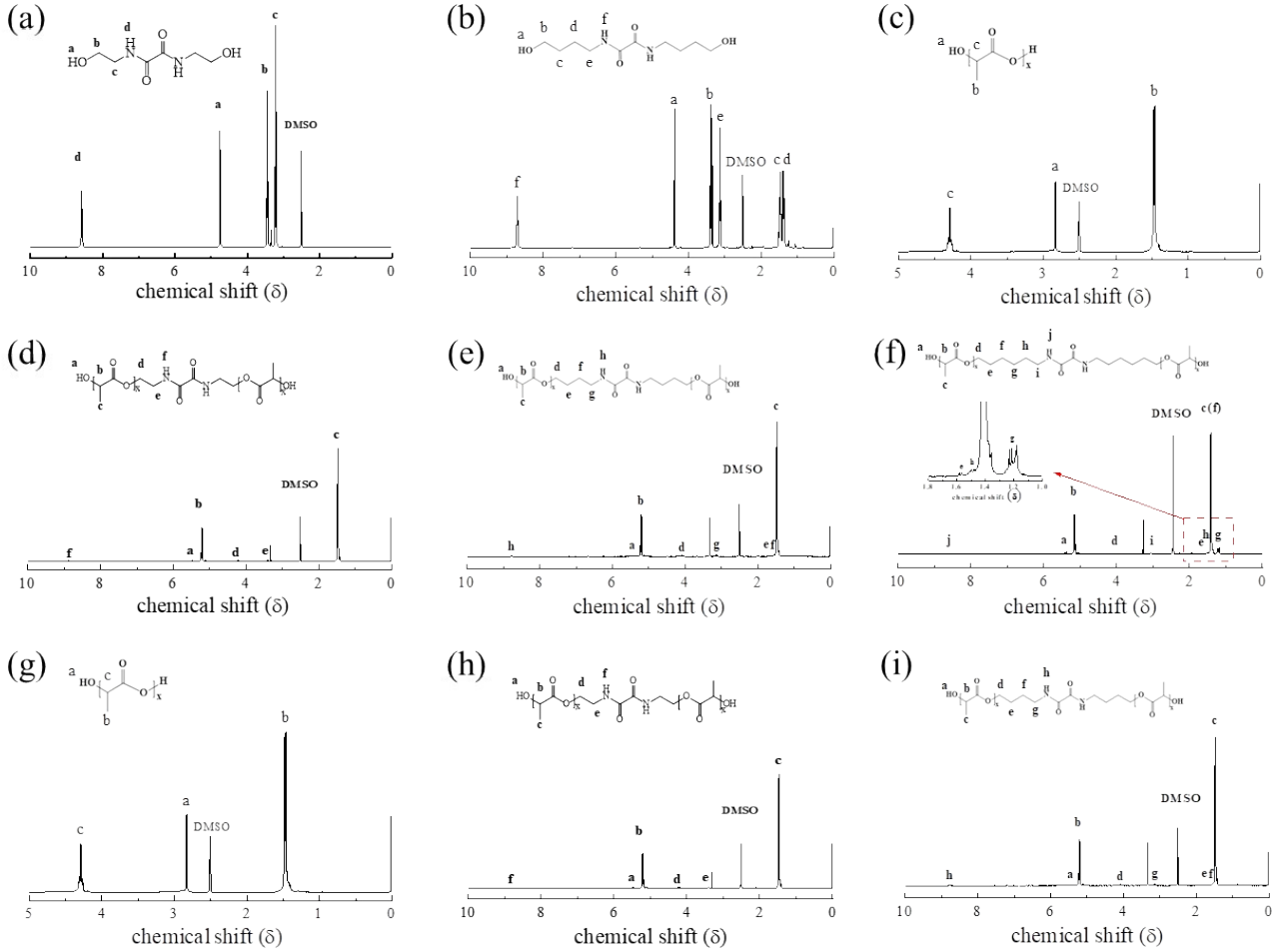

Figure S1. ^{1}H-NMR spectrum of (a) OXA-2 (b) OXA-4 (c) PLLA (M_n ~ 50.0 kg/mol) (d) $PLLA_{OXA-2}$ (M_n ~ 50.0 kg/mol) (e) $PLLA_{OXA-4}$ (M_n ~ 50.0 kg/mol) (f) PLLA (M_n ~ 30.0 kg/mol) (g) $PLLA_{OXA-2}$ (M_n ~ 30.0 kg/mol) (h) $PLLA_{OXA-4}$ (M_n ~ 30.0 kg/mol) and (i) $PLLA_{OXA-6}$ (M_n ~ 30.0 kg/mol) in DMSO

The molecular weight (M_n and M_w) and polydispersity index (PDI) of PLLA and $PLLA_{OXA-n}$ (M_n ~ 30.0 kg/mol) were characterized by gel permeation chromatography (polystyrene standard), and the results are shown in Table S1.

Table S1. The molecular weight and polydispersity index of PLLA and $PLLA_{OXA-n}$ obtained via GPC

Samples	M_n ($g \cdot mol^{-1}$)	M_w ($g \cdot mol^{-1}$)	Polydispersity index (PDI)
PLLA	32150	56380	1.75
$PLLA_{OXA-2}$	31280	59290	1.90
$PLLA_{OXA-4}$	39800	70640	1.77
$PLLA_{OXA-6}$	34240	40090	1.17

Note: M_n is the number average molecular weight and M_w is the weight average molecular weight.

Figure S2 show the cooling and subsequent heating DSC curves of PLLA and $PLLA_{OXA-n}$ (M_n ~ 30.0 kg/mol). And the thermal parameters of the PLLA and $PLLA_{OXA-n}$ calculated from the non-isothermal crystallization and the subsequent melting DSC curves are shown in Table S2.

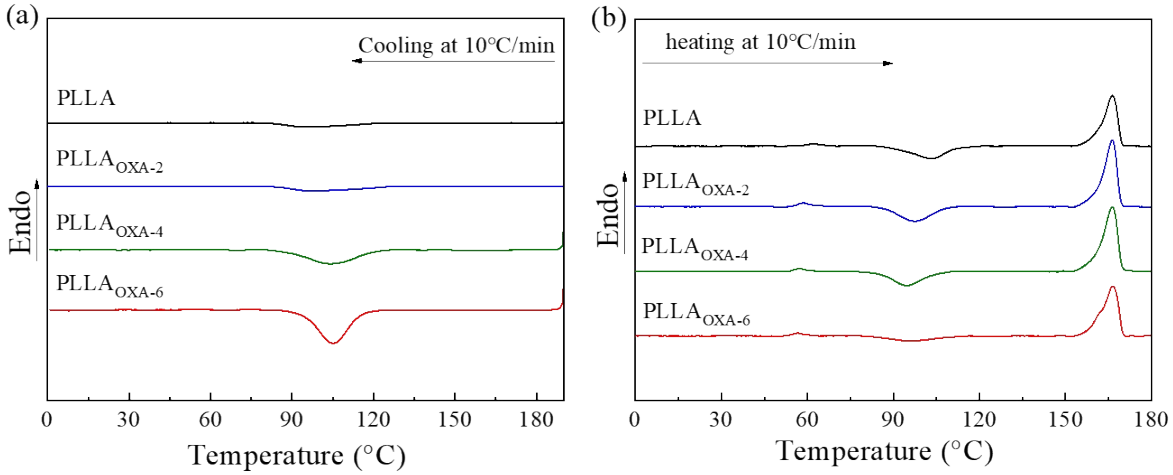

Figure S2. (a) cooling and (b) subsequent heating DSC curves of PLLA and $PLLA_{OXA-n}$ (M_n ~ 30.0 kg/mol)

Table S2. Non-isothermal crystallization parameter of PLLA and $PLLA_{OXA-n}$ (M_n ~ 30.0 kg/mol)

Samples	T_{cc} (°C)	$\triangle H_{cc}$ ($J \cdot g^{-1}$)	T_m (°C)	$\triangle H_m$ ($J \cdot g^{-1}$)	T_c (°C)	$\triangle H_c$ ($J \cdot g^{-1}$)	X_c (%)
PLLA	103.3	16.3	166.5	30.5	96.1	7.1	7.6
$PLLA_{OXA-2}$	97.5	19.5	166.4	33.1	98.5	14.2	15.3
$PLLA_{OXA-4}$	94.9	15.6	166.6	34.4	104.3	24.5	26.4
$PLLA_{OXA-6}$	95.8	7.9	166.6	30.4	104.9	36.4	38.8

Note: T_c is the crystallization temperature, ΔH_c is the crystallization enthalpy, T_{cc} is the cold crystallization temperature, ΔH_{cc} is the cold crystallization enthalpy, T_m is the melting temperature, ΔH_m is the melting enthalpy, X_c is the crystallinity, and X_c is calculated from the DSC data by $X_c = \Delta H_c / (\omega * \Delta H_m^0) \times 100\%$, where ΔH_m and ΔH_c are melting and crystallization enthalpies of PLLA, respectively, ω is the weight proportion of the PLLA in the $PLLA_{OXA-n}$, while the ΔH_m^0 = 93.6 J/g is the melting enthalpy of PLLA with a crystallinity of 100%.

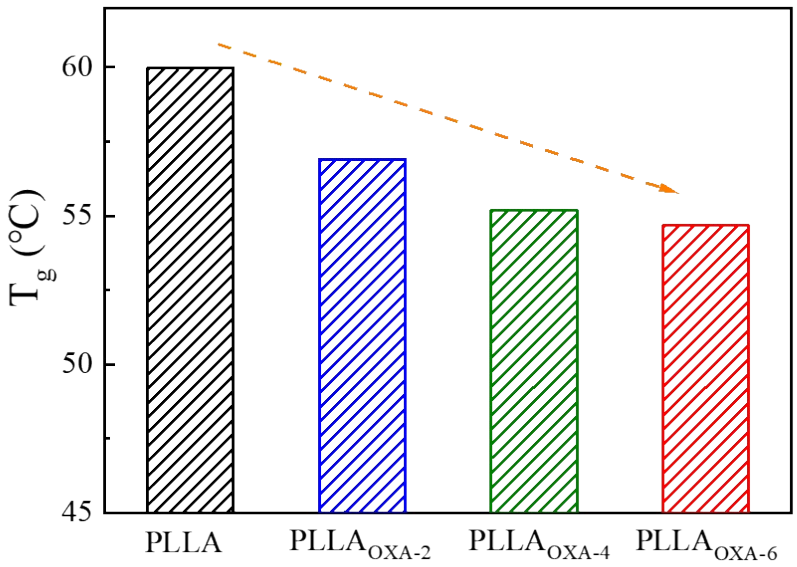

Figure S3. The glass-transition temperature (T_g) of PLLA and $PLLA_{OXA\text{-}n}$ (M_n ~ 30.0 kg/mol)