Supplementary information for "The isothermal crystallization kinetic of poly(ethylene glycol)-*block*-poly(L-lactide) block copolymers (PEG-PLLA): Effect of block lengths of PEG and PLLA"

Yun Chen,<sup>a</sup> Liying Wang,<sup>a</sup> Weishuo Chen,<sup>a</sup> Channa Zhong,<sup>a</sup> Shuangcheng Li,<sup>a</sup> Jun

Shao,\*a, b Gao Lic and Haoqing Hou\*\*a, b

<sup>a</sup> College of Chemistry & Chemical Engineering and Nanofiber Engineering Center of

Jiangxi Province, Jiangxi Normal University, Nanchang, 330022, China.

<sup>b</sup> Key Lab of Fluorine and Silicon for Energy Materials and Chemistry of Ministry of Education, Jiangxi Normal University, Nanchang, 330022, China.

° Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied

Chemistry, Chinese Academy of Sciences, Changchun 130022, China.

specimen	$T_{\rm c}$ (°C)	lnK	t <sub>1/2</sub> (min)	n
PLLA <sub>21</sub>	90	-4.50	5.61	2.26
	100	-3.60	2.25	3.38
	110	-1.42	1.17	3.24
	120	-3.90	4.13	2.39
	130	-7.61	10.42	3.01
	140	-8.94	18.47	2.91
	90	-5.08	8.36	2.19
	100	-3.32	3.09	2.45
PLLA <sub>43</sub>	110	-1.93	1.53	3.34
	120	-4.19	5.36	2.31
	130	-7.19	8.56	3.11
	90	-5.27	6.87	2.49
PLLA <sub>73</sub>	100	-4.01	3.52	2.71
	110	-3.49	3.11	2.45
	120	-4.98	4.87	2.93
	130	-7.34	8.79	3.05
	70	-4.87	1.67	5.32
	80	-1.24	0.77	5.61
MPEG <sub>4</sub> -PLLA <sub>22</sub>	90	0.10	0.61	5.32
	100	0.32	0.63	4.57

Table S1. The lnK,  $t_{1\!/\!2}$  and n values calculated from DSC.

	110	-1.8	1.21	3.73
	120	-4.02	2.58	3.42
	130	-6.54	6.10	3.29
	140	-14.40	19.88	4.27
	70	-14.23	5.22	5.95
	80	-5.57	1.88	5.46
	90	-2.26	0.96	5.36
	100	-0.63	0.81	4.25
$MPEG_4$ -PLLA <sub>42</sub>	110	-2.31	1.37	3.74
	120	-4.81	3.34	3.32
	130	-8.15	9.50	3.30
	140	-9.08	21.54	2.83
	70	-28.63	6.80	9.97
	80	-8.82	2.35	6.48
	90	-3.55	1.44	4.57
	100	-1.63	1.09	3.77
MPEG <sub>4</sub> -PLLA <sub>62</sub>	100 110	-1.63 -2.31	1.09 1.45	3.77 3.56
MPEG <sub>4</sub> -PLLA <sub>62</sub>	100 110 120	-1.63 -2.31 -4.77	1.09 1.45 3.68	<ul><li>3.77</li><li>3.56</li><li>3.50</li></ul>
MPEG <sub>4</sub> -PLLA <sub>62</sub>	100 110 120 130	-1.63 -2.31 -4.77 -7.27	1.09 1.45 3.68 8.98	<ul><li>3.77</li><li>3.56</li><li>3.50</li><li>3.06</li></ul>
MPEG <sub>4</sub> -PLLA <sub>62</sub>	100 110 120 130 140	-1.63 -2.31 -4.77 -7.27 -9.61	1.09 1.45 3.68 8.98 32.73	<ul><li>3.77</li><li>3.56</li><li>3.50</li><li>3.06</li><li>2.60</li></ul>
MPEG <sub>4</sub> -PLLA <sub>62</sub>	100 110 120 130 140 70	-1.63 -2.31 -4.77 -7.27 -9.61 11.01	1.09 1.45 3.68 8.98 32.73 0.14	3.77 3.56 3.50 3.06 2.60 14.21

	90	9.37	0.15	10.09
	100	6.51	0.22	7.87
	110	1.15	0.51	5.10
	120	-2.63	1.45	4.08
	130	-6.68	6.96	3.11
	70	-13.99	4.09	6.77
	80	-3.63	1.76	3.99
	90	-0.79	0.83	4.35
	100	1.06	0.51	5.21
$PEG_4$ -PLLA <sub>40</sub>	110	-1.14	0.96	4.07
	120	-4.25	2.39	3.69
	130	-8.51	8.38	3.57
	140	-6.90	32.40	1.88
	70	-33.77	13.56	9.53
	80	-9.07	6.10	4.24
	90	-4.77	2.46	3.91
	100	-2.457	1.32	4.03
PEG <sub>4</sub> -PLLA <sub>67</sub>	110	-3.397	1.92	3.60
	120	-5.56	4.92	3.09
	130	-9.57	19.66	2.98
	140	-8.97	40.30	2.29
PEG <sub>10</sub> -PLLA <sub>19</sub>	70	-0.38	0.44	9.26

	80	1.28	0.42	7.65
	90	-0.80	0.74	4.96
	100	-1.05	0.86	4.33
	110	-2.88	1.69	3.51
	120	-5.47	4.20	3.20
	70	-2.37	0.89	6.00
	80	2.54	0.52	10.78
	90	-1.84	0.92	4.98
	100	-2.11	1.19	4.03
$PEG_{10}$ - $PLLA_{40}$	110	-2.86	1.69	3.52
	120	-4.52	3.17	3.36
	130	-6.66	6.08	3.35
	140	-9.61	36.11	2.56
	70	-15.91	4.09	7.46
	80	0.01	2.65	6.58
	90	-3.11	2.09	3.93
	100	-3.09	1.81	3.58
PEG <sub>10</sub> -PLLA <sub>69</sub>	110	-3.61	2.10	3.59
	120	-5.67	4.39	3.31
	130	-7.26	10.90	2.79
	140	-11.58	33.38	3.06
PEG <sub>20</sub> -PLLA <sub>20</sub>	60	10.30	0.13	20.26

	70	8.32	0.18	11.73
	80	6.29	0.22	9.21
	90	3.90	0.30	6.86
	100	-0.80	0.82	4.09
	110	-3.95	2.93	3.05
	60	2.62	0.21	8.67
	70	2.80	0.27	6.89
	80	2.95	0.33	7.67
	90	0.83	0.498	5.10
$PEO_{20}$ - $PLLA_{41}$	100	0.87	0.56	4.45
	110	-1.76	1.37	3.10
	120	-3.65	2.86	2.93
	130	-7.55	8.19	3.19
	60	-5.52	1.85	5.45
	70	-1.83	0.87	5.44
	80	0.01	0.55	6.58
	90	-1.03	0.80	4.70
PEG <sub>20</sub> -PLLA <sub>62</sub>	100	-0.85	0.84	4.26
	110	-2.61	1.42	3.99
	120	-5.05	3.35	3.48
	130	-9.11	14.45	3.12
	140	-6.58	26.47	1.90



Fig. S1. (a) The isothermal thermograms, (b) the relative crystallinity as a function of crystallization time (t), and (c) the plots of  $\ln[-\ln(1-X(t))]$  versus  $\ln(t)$  of PLLA<sub>43</sub> at various crystallization temperatures.





Fig. S2. (a) The isothermal thermograms, (b) the relative crystallinity as a function of crystallization time (t), and (c) the plots of  $\ln[-\ln(1-X(t))]$  versus  $\ln(t)$  of PLLA<sub>73</sub> at various  $T_{c}s$ .



Fig. S3. The isothermal DSC thermograms (a), relative crystallinity curves (b), and the  $\ln[-\ln(1-X(t))]$  versus  $\ln t$  (c) of MPEG<sub>4</sub>-PLLA<sub>42</sub>.



Fig. S4. The isothermal DSC thermograms (a), relative crystallinity curves (b), and the  $\ln[-\ln(1-X(t))]$  versus  $\ln t$  (c) of MPEG<sub>4</sub>-PLLA<sub>62</sub>.





**Fig. S5.** The isothermal crystallization curves (**a**), relative crystallinity curves (**b**), and the  $\ln[-\ln(1-X(t))]$  versus  $\ln t$  (**c**) of PEG<sub>4</sub>-PLLA<sub>40</sub> for different  $T_c$ s.



**Fig. S6.** The isothermal crystallization curves (**a**), relative crystallinity curves (**b**), and the  $\ln[-\ln(1-X(t))]$  versus  $\ln t$  (**c**)of PEG<sub>4</sub>-PLLA<sub>67</sub> for different temperatures.



**Fig. S7.** The isothermal crystallization curves (**a**), relative crystallinity curves (**b**), and the  $\ln[-\ln(1-X(t))]$  versus lnt of PEG<sub>10</sub>-PLLA<sub>19</sub> (**c**) for different  $T_{c}$ s.





**Fig. S8.** The isothermal crystallization curves (**a**), relative crystallinity curves (**b**), and the  $\ln[-\ln(1-X(t))]$  versus  $\ln t$  (**c**) of PEG<sub>10</sub>-PLLA<sub>40</sub> for different temperatures.



**Fig. S9.** The isothermal crystallization curves (**a**), relative crystallinity curves (**b**), and the  $\ln[-\ln(1-X(t))]$  versus  $\ln t$  (**c**) of  $PEG_{10}$ -PLLA<sub>69</sub> for different temperatures.



Fig. S10. The isothermal crystallization curves (a), relative crystallinity curves (b), and the  $\ln[-\ln(1-X(t))]$  versus  $\ln t$  (c) of  $PEG_{20}$ -PLLA<sub>20</sub> for different temperatures.





Fig. S11. The isothermal crystallization curves (a), relative crystallinity curves (b), and the  $\ln[-\ln(1-X(t))]$  versus  $\ln t$  (c) of  $PEG_{20}$ -PLLA<sub>40</sub> for different temperatures.

**Fig. S12.** The isothermal crystallization curves (**a**), relative crystallinity curves (**b**), and the ln[-ln(1-X(t))] versus lnt (**c**) of PEG<sub>20</sub>-PLLA<sub>62</sub> for different temperatures.



Fig. S13. The lnK for PLLA<sub>21</sub>, MPEG<sub>4</sub>-PLLA<sub>22</sub>, PEG<sub>4</sub>-PLLA<sub>19</sub>, PEG<sub>10</sub>-PLLA<sub>19</sub> and PEG<sub>20</sub>-PLLA<sub>20</sub>.



Fig. S14. The lnK for PLLA<sub>73</sub>, MPEG<sub>4</sub>-PLLA<sub>62</sub>, PEG<sub>4</sub>-PLLA<sub>67</sub>, PEG<sub>10</sub>-PLLA<sub>69</sub> and PEG<sub>20</sub>-PLLA<sub>62</sub>.