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## **Supporting Information**

## Biodegradable poly(lactide-co-glycolide-co-ε-caprolactone) block copolymers - evaluation as

## drug carriers for a localized and sustained delivery system

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**Figure S1.** Proton Nuclear Magnetic Resonance (<sup>1</sup>H-NMR) spectra after 4 weeks *in vivo*. Crude mixture; (a) before degradation, (b) 50K  $L_1G_1C_8$ , (c) 50K  $L_2G_2C_6$ , (d), 50K  $L_3G_3C_4$ , (e) 90K  $L_4G_4C_2$ , (f) 50K  $L_4G_4C_2$ , (g) 20K  $L_4G_4C_2$ .



**Figure S2.** Gel permeation chromatograph (GPC) charts of poly(lactide-co-glycolide-co- $\epsilon$ -caprolactone) (PLGC) and poly(lactic acid-co-glycolic acid) (PLGA)in vitro. (a) 20K L<sub>4</sub>G<sub>4</sub>C<sub>2</sub>, (b) 50K L<sub>4</sub>G<sub>4</sub>C<sub>2</sub>, (c) 90K L<sub>4</sub>G<sub>4</sub>C<sub>2</sub>, (d) 20K PLGA, (e) 50K PLGA, (f) 90K PLGA, (g) 50K L<sub>3</sub>G<sub>3</sub>C<sub>4</sub>, (h) 50K L<sub>2</sub>G<sub>2</sub>C<sub>6</sub>, and (i) 50K L<sub>1</sub>G<sub>1</sub>C<sub>8</sub>.

Polymer	<i>T</i> <sub>g</sub> (°C) <sup>a</sup>	$T_{\rm m}$ (°C)	$\Delta H$	X <sub>c</sub> <sup>b</sup>
$20K L_4G_4C_2$	9	-	-	-
50K $L_4G_4C_2$	12	-	-	-
90K $L_4G_4C_2$	3	-	-	-
50K L <sub>3</sub> G <sub>3</sub> C <sub>4</sub>	-8	-	-	-
$50 \text{K L}_2 \text{G}_2 \text{C}_6$	-26	-	-	2.5
50K L <sub>1</sub> G <sub>1</sub> C <sub>8</sub>	-49	-	-	7.8
20K PLGA °	46	76	0.4	-
50K PLGA	50	85	0.6	-
90K PLGA	52	87	3.2	-

**Table S1**. Thermal properties of poly(lactide-co-glycolide-co-ε-caprolactone) (PLGC) block copolymers.

<sup>a</sup> Measured by differential scanning calorimeter (DSC)

 ${}^{b}X_{c}$  was calculated as the ratio of the crystalline peak areas to the total areas under the scattering curve

<sup>c</sup> PLGA: poly(lactic acid-co-glycolic acid)