Supporting Information for the manuscript
Tuning the properties of polycaprolactone-based fibers by using polyethylene oxide and polycaprolactone block copolymers

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PCL homopolymer synthesis

The molecular weight of PCL homopolymers synthesized by ring-opening polymerization can be controlled by tuning the monomer (e-caprolactone, M) to initiator (n-hexanol, I) ratio (M/I). In Figure SI-1 is shown the degree of polymerization of PCL homopolymers, obtained from GPC molecular weight measurements as a function of M/I ratio. As can be seen, as M/I ratio is increased, the degree of polymerization of PCL also increases (r^2= 0.88).

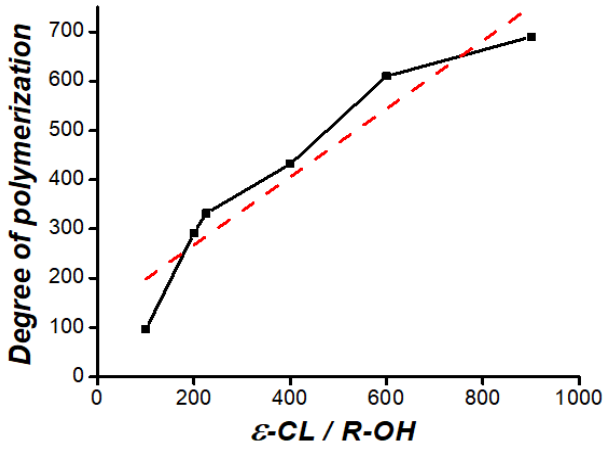

Figure SI-1. Relationship between M/I ratio and degree of polymerization of PCL homopolymers

The synthesized polymers also were characterized by ATR FT-IR, and the results are shown in Figure SI-2. In these spectra, characteristic stretching and bending vibrations for $mPEO_m$ and PEO_m-*b*-PCL_n are observed. A signal appears at

724 cm^{-1} corresponding to the bending of the PCL chain. An intense vibrational signal is observed at 1700 cm^{-1} in the PEO_m-*b*-PCL_n copolymers, associated with the carbonyl stretching vibration of PCL, and the signal at 1929 cm^{-1} is associated with the hydrogen chain stretching vibration of PCL.

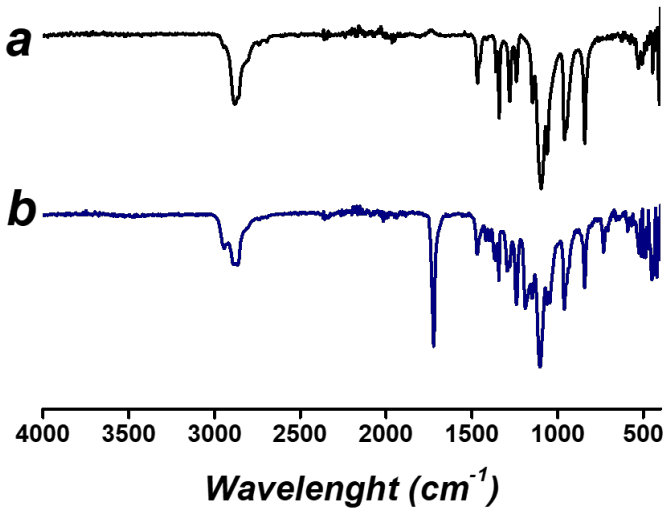

Figure SI-2. FT-IR spectra of $mPEO_m$ having a molecular weight of 10000 g/mol (a), and the corresponding PEO_m-*b*-PCL_n block copolymer synthesized with a M/I ratio of 100 (b).

Molecular weight estimation by ^{1}H-NMR.

The corresponding degree of polymerization of PEO (DP_{PEO}), PCL (DP_{PCL}), and number molecular weight (M_n), have been calculated using an integral method of ^{1}H-NMR resonance peaks, by comparing the proton peak intensity of the repeating units with a known moiety, usually and end-group with a known number of protons.[1] The area or intensity of a proton resonance peak of a given species is proportional to the amount of these species present in the sample, which implies that the area of *i*th peak (A_i) is proportional to the number of molecules of species *i* (N_i) with molecular weight M_i, according to equation 1:

$$A_i = kN_iM_i \qquad (1)$$

where *k* is a constant of proportionality. Rearranging,

$$k = \frac{A_i}{N_i M_i} \quad (2)$$

Considering the ^{1}H-NMR resonance peaks of two moieties *x* and *y*, equation 2 can be transformed in:

$$k_x = \frac{A_x}{N_x M_x} \quad (3)$$

$$k_y = \frac{A_y}{N_y M_y} \quad (4)$$

If $k_x = k_y$ in a given polymer, equations 3 and 4 can be rewritten as follows,

$$\frac{A_x}{N_x M_x} = \frac{A_y}{N_y M_y} \quad (5)$$

where A_x is the area or intensity of the ^{1}H-NMR resonance peak of moiety *x*; N_x is the number of repeating units of moiety *x*; M_x is the number of protons of moiety x; A_y is the area or intensity of the ^{1}H-NMR resonance peak of moiety *y*; N_y is the number of repeating units of moiety *y*; and M_y is the number of protons of moiety *y*. Equation 5 can be rearranged as,

$$N_x = \frac{A_x M_y N_y}{A_y M_X} \quad (6)$$

where N_x can be used to calculate the degree of polymerization of any repeating unit. M_n can be calculated by using the following equation:

$$M_n = nM_0 + M_e \quad (7)$$

where *n* is the number of repeating units or degree of polymerization; M_0 corresponds to the molecular weight of one repeating unit, and M_e corresponds to the molecular weight of terminal groups.

References

(1) Izunobi, J. U.; Higginbotham, C. L. Polymer Molecular Weight Analysis by 1 H NMR Spectroscopy. *J. Chem. Educ.* **2011**, *88* (8), 1098–1104. https://doi.org/10.1021/ed100461v.