Supporting Information

Crystallization Behavior of Crystalline/Crystalline Polymer Blends Under Confinement in Electrospun Nanofibers of Polystyrene/Poly(ethylene oxide)/Poly(ε-caprolactone) Ternary Mixtures

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Figure S1. Variation of normalized heat of fusion with PCL composition, as ascertained from DSC measurements, in as-casted and electrospunned PS/PCL blends. The respective value for neat PCL sample has been represented with the dashed blue line. C denotes cast film whereas N denotes nanofiber samples.



Figure S2. DSC cooling (a) and heating (b) curves of PEO/PCL cast films after first heating upto 90°C



Figure S3. DSC melting curves of PS/PEO/PCL nanofibers after cooling to pre-decided crystallization temperature from 90°C. (a) N-S80E15L05, (b) N-S80E10L10, (c) N-S80E05L15. The figure clearly shows that the crystallization peak above 25°C is solely due to the heterogenous nucleated crystallization of PEO since the subsequent heating curve only depicts the PEO melting behavior. The heterogeneous nucleated crystallization of PCL between 0-10°C leads to the observed melting behavior of PCL on subsequent heating. The homogenous nucleated crystallization of PCL (between 0 - -10° C) and that of PEO (between $-20 - -30^{\circ}$ C) is revealed from the increase in the heat of fusion of respective melting peaks.



Figure S4. WAXD profiles of electrospun PS/PEO/PCL (80/10/10) blend nanofibers (N-S80E10L10) obtained after crystallization at different temperatures. The samples were crystallized at the temperatures mentioned after annealing at 90°C. The WAXD profiles shows that the crystallization nucleation process at 31°C could be solely attributed to PEO crystallization. The heterogeneous crystallization of PCL is visible from the diffraction peak of PCL at 4°C. Subsequent homogenous nucleated crystallization of PCL and PEO at -10°C and -24°C, respectively, is revealed from the increased intensity of the diffraction peaks.



Figure S5. SEM micrographs of electrospun PS/PEO/PCL (90/05/05) blend nanofibers



Figure S6. SAXS (a, b) plots of PS/PEO/PCL blends obtained after isothermal crystallization at - 20°C (a) cast film samples; (b) nanofiber samples. The complete absence of scattering peak in nanofiber samples is due to lower degree of crystallinity and the absence of coherently stacked lamellae in the ternary blend nanofibers.