Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Influence of Chain Topology on Polymer Crystallization: Poly(ethylene oxide) (PEO) Rings vs. Linear chains.

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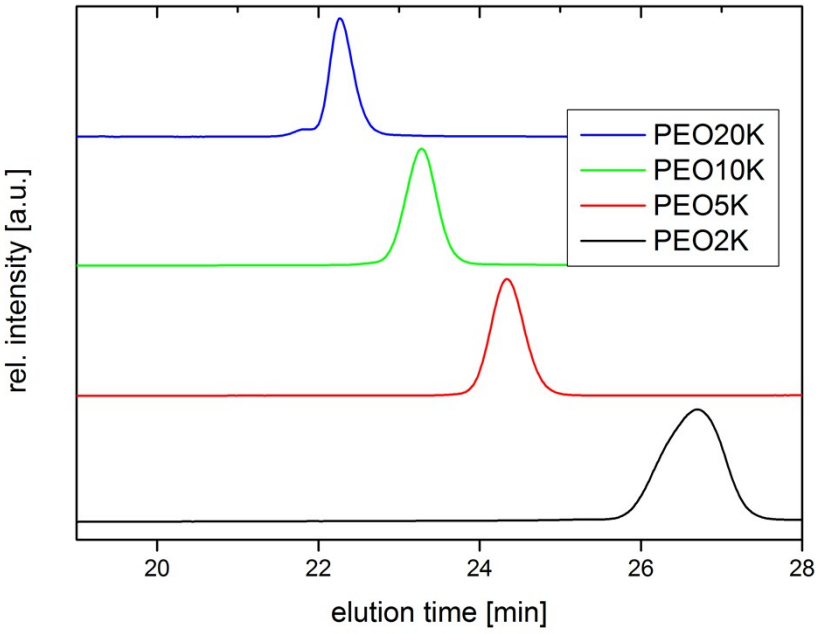

Figure S1. SEC traces of the purified ring polymers. In the elugram of sample PEO20K the small shoulder to the left of the main signal shows the presence of a smaller quantity of linear polymer.

(a) Thermodynamics- DSC

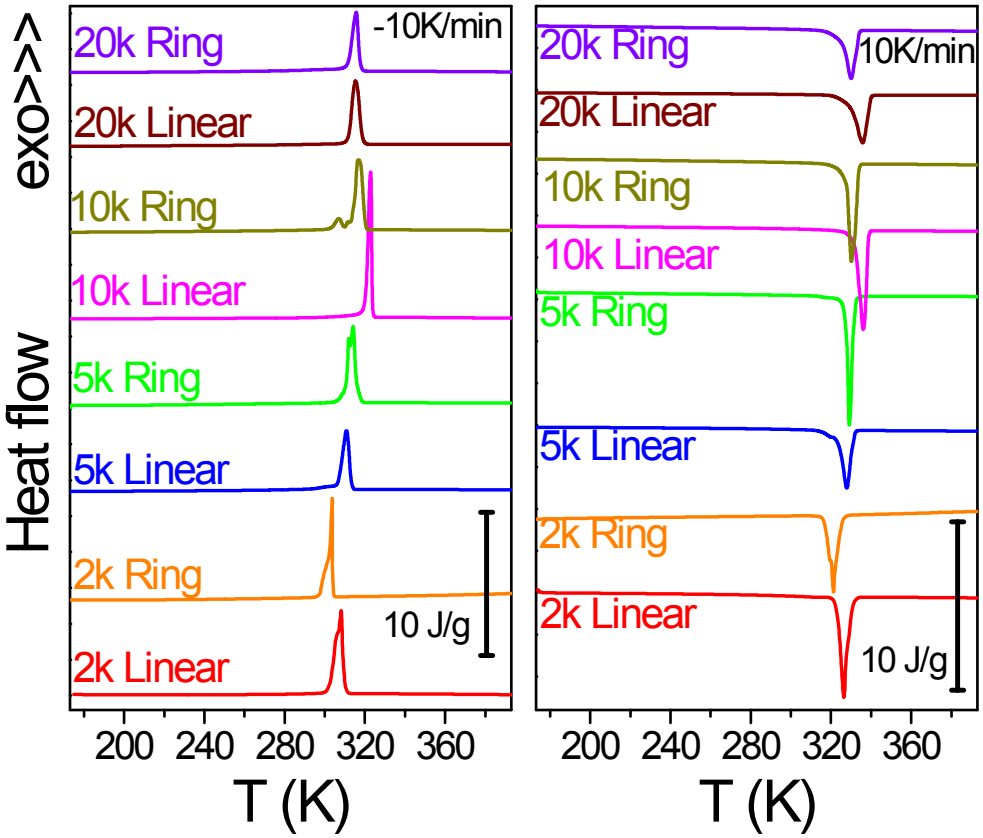

Fig. S2. DSC traces of linear and ring PEO samples obtained on cooling (left) and subsequent heating (right) with 10 K/min. In general, rings melt at a lower temperature.

(b) Structure SAXS

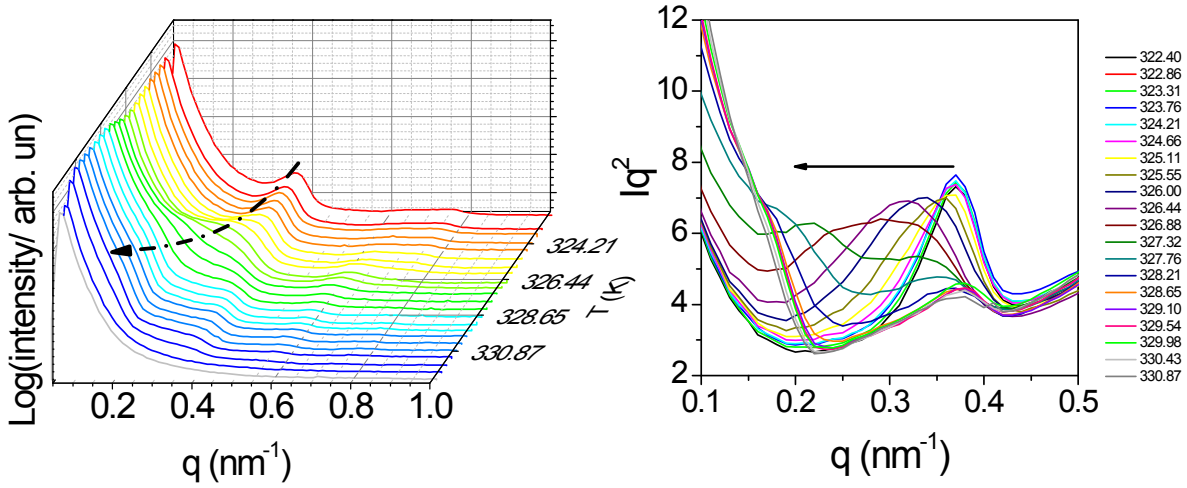

Fig. S3. SAXS patterns of L5k PEO obtained on heating following isothermal crystallization at 322 K. The corresponding Lorentz-corrected patterns are also shown (the corresponding temperatures are indicated in the inset).

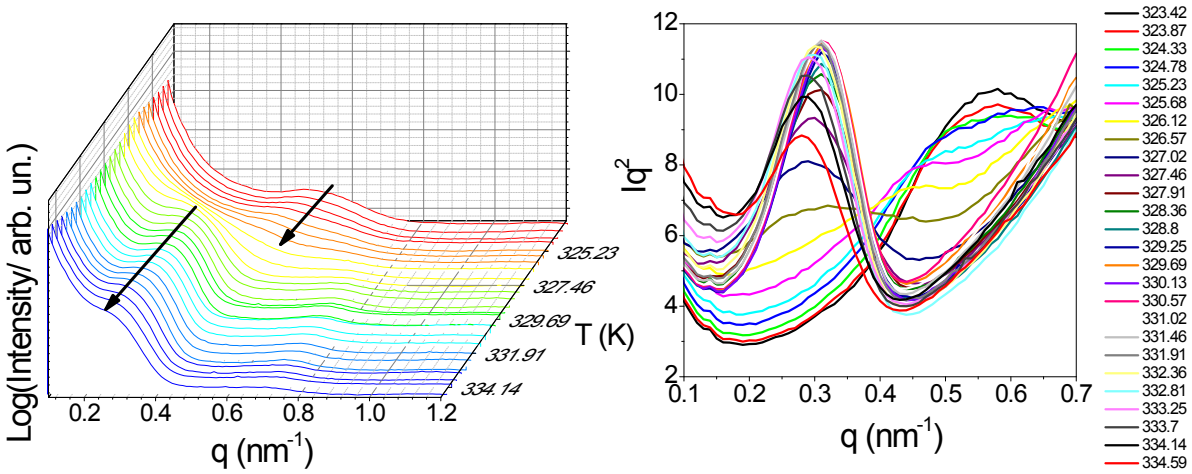

Fig. S4. SAXS patterns of R5k PEO obtained on heating following isothermal crystallization at 323 K. The corresponding Lorentz-corrected patterns are also shown (the corresponding temperatures are indicated in the inset).

In order to obtain detailed structural information, the background- and Lorentz corrected scattering curves were further analyzed with respect to the correlation function analysis. The electron density correlation function, $K(z)$, was obtained from the inverse Fourier transformation of the intensity distribution, $I(q)$, as follows:

$$K(z) = \frac{\int_0^\infty I(q)q^2 \cos(qz)dq}{\int_0^\infty I(q)q^2 dq}$$

Here z denotes the location measured along a trajectory normal to the lamellar surfaces. This analysis allows obtaining directly the long spacing, d, and interlamellar amorphous layer measured along the lamellar normal (d_a). The crystalline lamellar thickness is then obtained as $d_c=d-d_a$. This type of analysis was made for R5k crystallized at the higher temperature (*i.e.* at 325 K) and heated to 333 K and the result is shown in Fig. S5. The interplay between the peaks at lower and higher q's at temperatures precludes a similar analysis at the lower temperatures (321 K and 323 K).

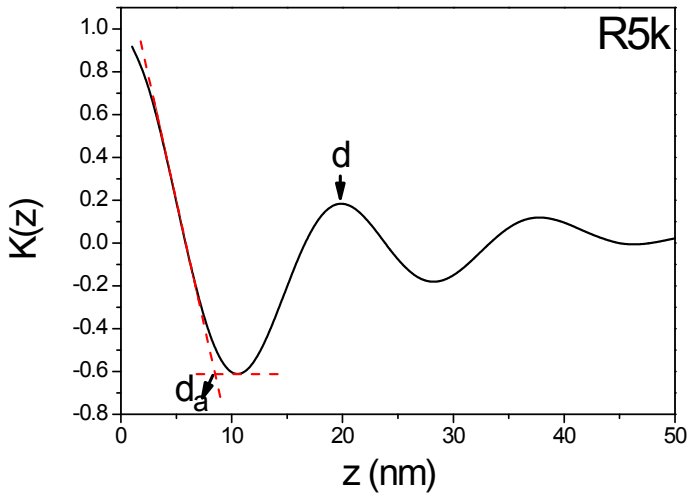

Fig. S5. Correlation function curve for R5k crystallized at 325 K and heated with 0.15 K/min to 333 K. The long spacing, d (~20 nm), and interlamellar amorphous layer thickness, d_a (~8 nm) are shown.

(c) Segmental dynamics - DS

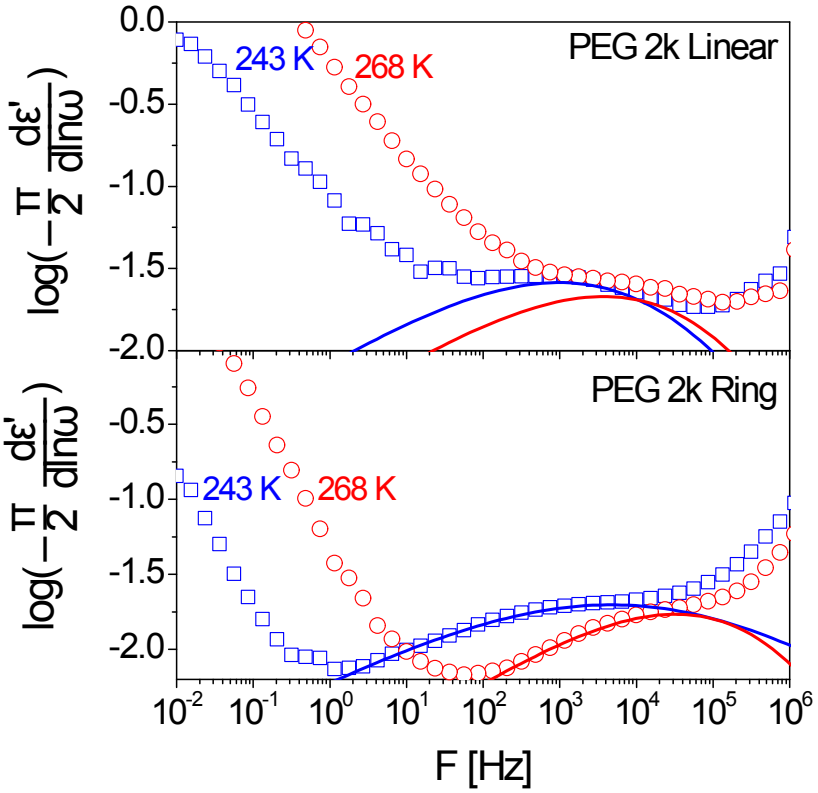

Fig. S6. Representative fits of the segmental relaxation times of L2k and R2k at 243 K and 268 K (lines) using the derivative approach. The low-frequency HN slope, *m* is 0.34 and 0.23 for L2k and R2k, respectively.

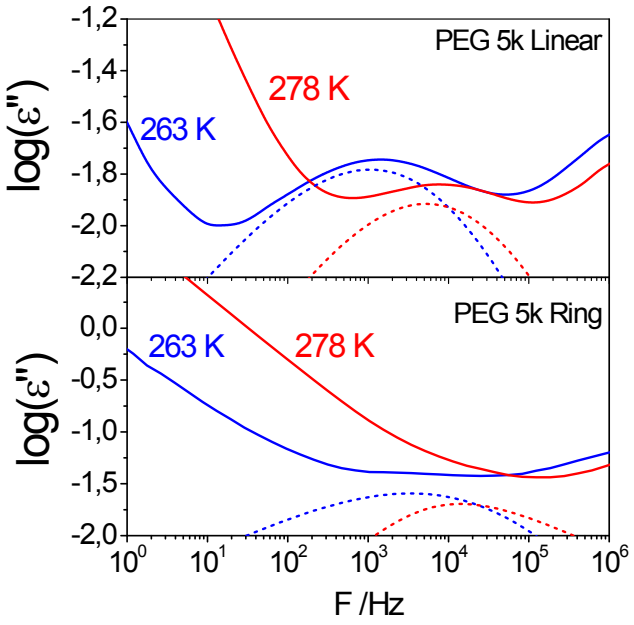

Fig. S7. Representative fits of the segmental relaxation times of L5k and R5k at 263 K and 278 K (lines) using dielectric loss data. The low-frequency HN slope, *m* is 0.46 and 0.13 for L5k and R5k, respectively.