Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

for

Synthesis, Crystallization, and Molecular Mobility in Poly(ε-caprolactone) Copolyesters of Different Architectures for Biomedical Applications Studied by Calorimetry and Dielectric Spectroscopy

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(S1) Thermogravimetric analysis

Thermogravimetric measurements were performed on a Pyris 1 TGA thermal analyzer (Perkin Elmer, USA) with a Pt sample-pan. Samples employed weighted about 5 mg (balance accuracy 0.0001 mg). The specimens were heated from ambient (room) temperature to 600°C at a rate of 20 K/min in N_2 (>99.9%) atmosphere of 20 mL/min constant flow. Mass was recorded versus temperature while the thermograms were treated using the Pyris Manager Software, accompanying the instrument.

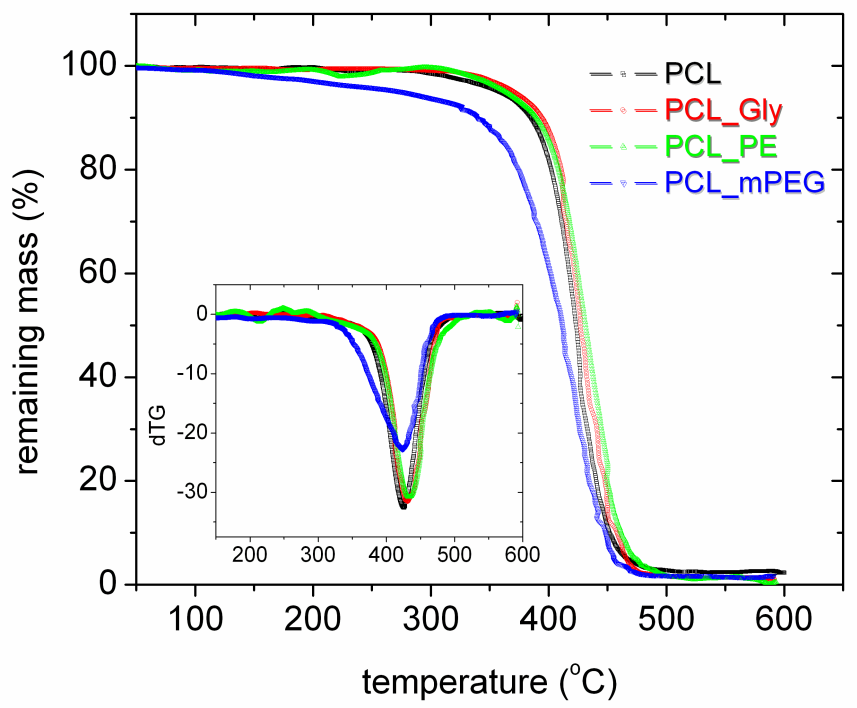
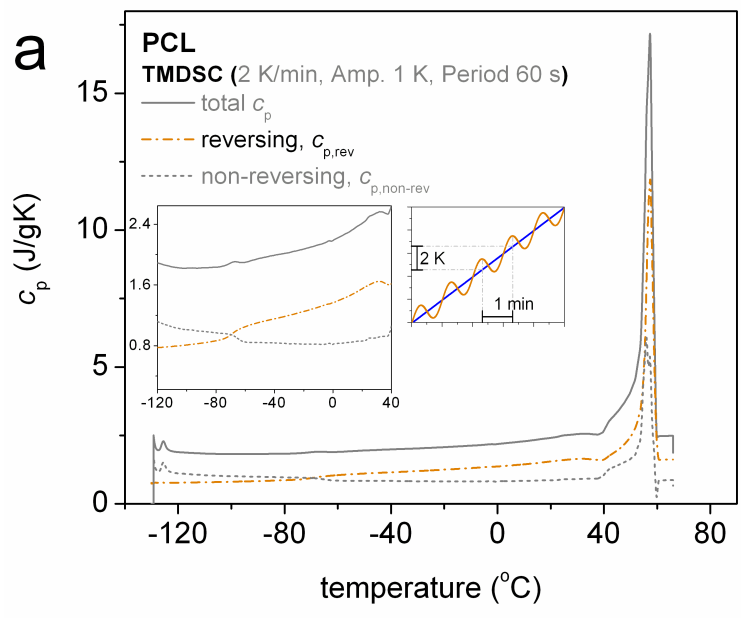


Figure S1. TGA thermograms, namely the remaining mass against temperature upon heating, for all samples described on the plot. The inset shows the same data in the form of derivative thermogram (dTG).

(S2) Overall TMDSC scans



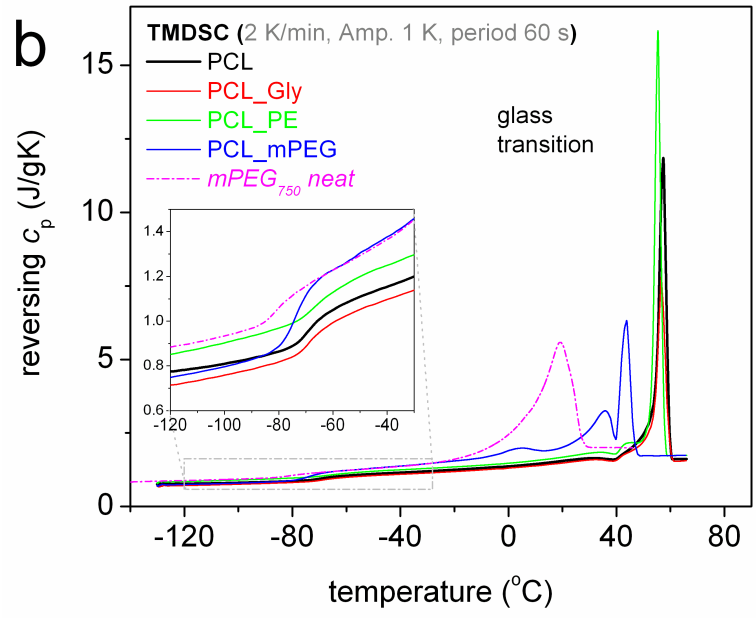


Figure S2. (a) Overall Temperature Modulation DSC thermograms of heat capacity, c_p, (total, reversing and non-reversing terms) for PCL sample under the measurement conditions described on the plot. (b) Comparative TMDSC thermograms for all samples in terms of reversing c_p.

(S3) Thermally stimulated depolarization currents (TSDC)

TSDC is a special dielectric technique in the temperature domain characterized by high sensitivity and high resolving power, the latter arising from its low equivalent frequency (10^{-4}–10^{-2} Hz) [Van Turnhout, J. *Thermally stimulated discharge of electrets*; in *Electrets*, Sessler, G.M., Ed.; Springer: Berlin, 1980; Vol. 33, p 81]. TSDC measurements were carried out in a TSDC Novocontrol setup (Novocontrol GmbH, Germany) on same as those described above for the BDS measurements on sandwich–like capacitors (~50 μm thickness and 20 mm in diameter). The sample-capacitor was inserted between the, placed in a Novocontrol TSDC sample cell and polarized by an electrostatic field V_p = 100 V at polarization temperature T_p for time t_p = 5 minutes. With the field still applied, the sample was cooled down to –150 °C (cooling rate 10 K/min, under nitrogen flow), sufficiently low to prevent depolarization by thermal energy, then short-circuited and reheated up to 20 °C at a constant heating rate, b = 3 K/min. Temperature was controlled to better than 0.5 K by means of a Novocontrol Quatro liquid nitrogen cryosystem. The discharge currents generated during heating were measured as a function of temperature with a programmable Keithley 6517B electrometer of high sensitivity.

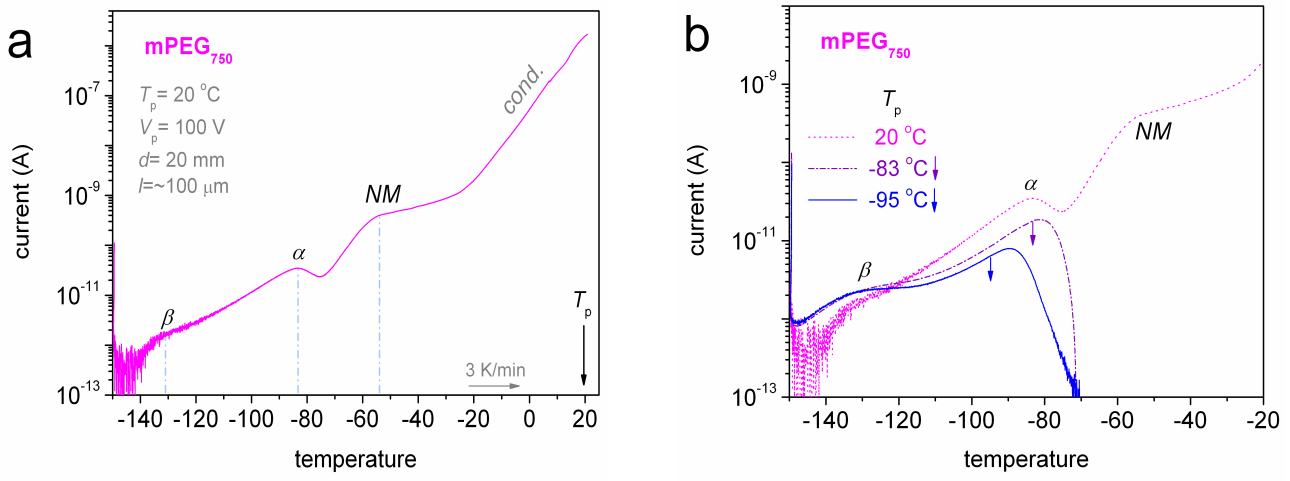


Figure S3. TSDC thermograms for neat mPEG$_{750}$ at different T_p, indicated being the main relaxation peaks recorded.

(S4) Analysis of the XRD data

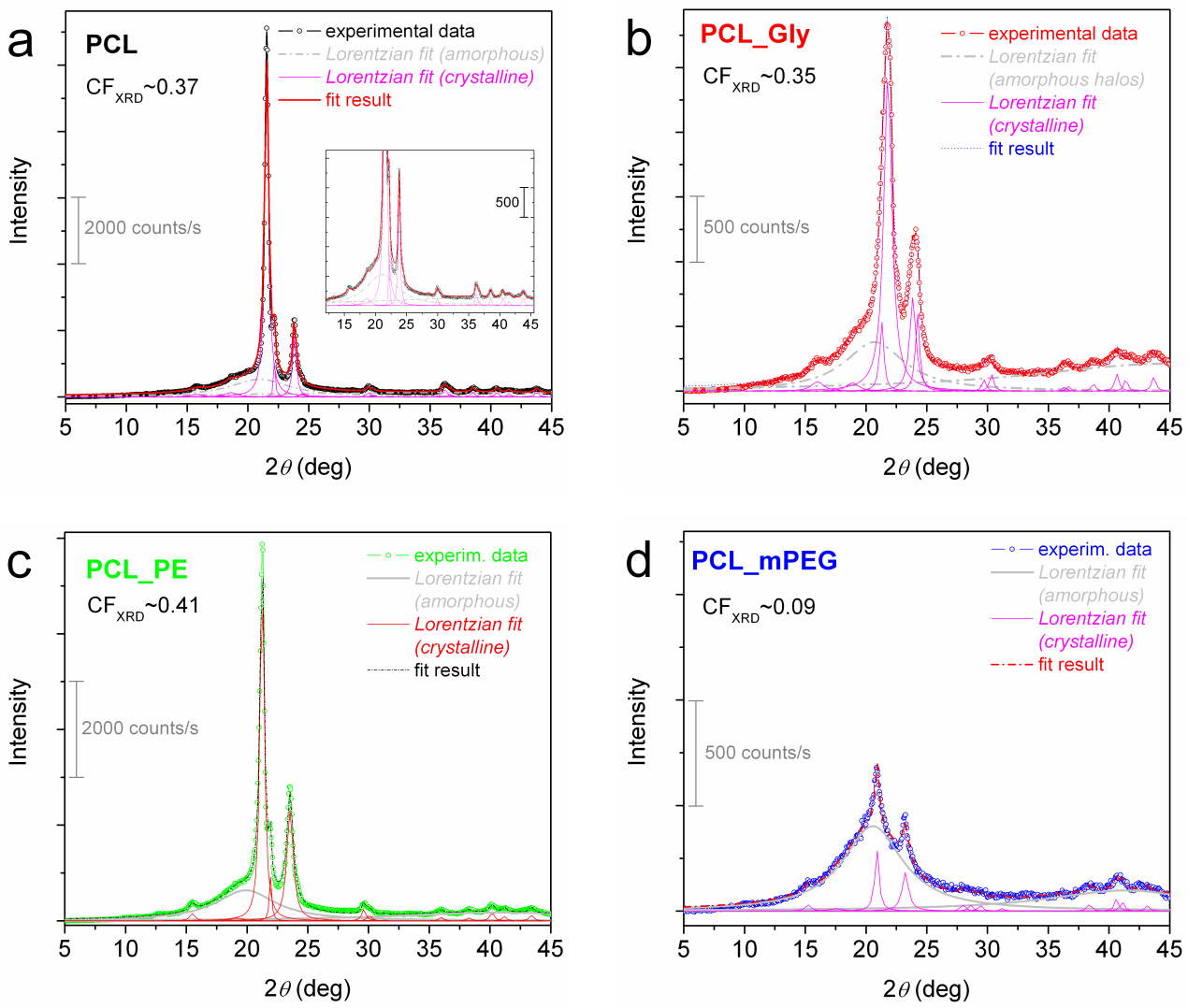


Figure S4. Analysis of the XRD spectra in terms of Lorentzians for all samples (a) PCL, (b) PCL_Gly, (c) PCL_PE and (d) PCL_mPEG. Included are the values for the estimated crystalline fraction, CF_{XRD}.

(S5) Dielectric strength, Δε, for the overall molecular dynamics

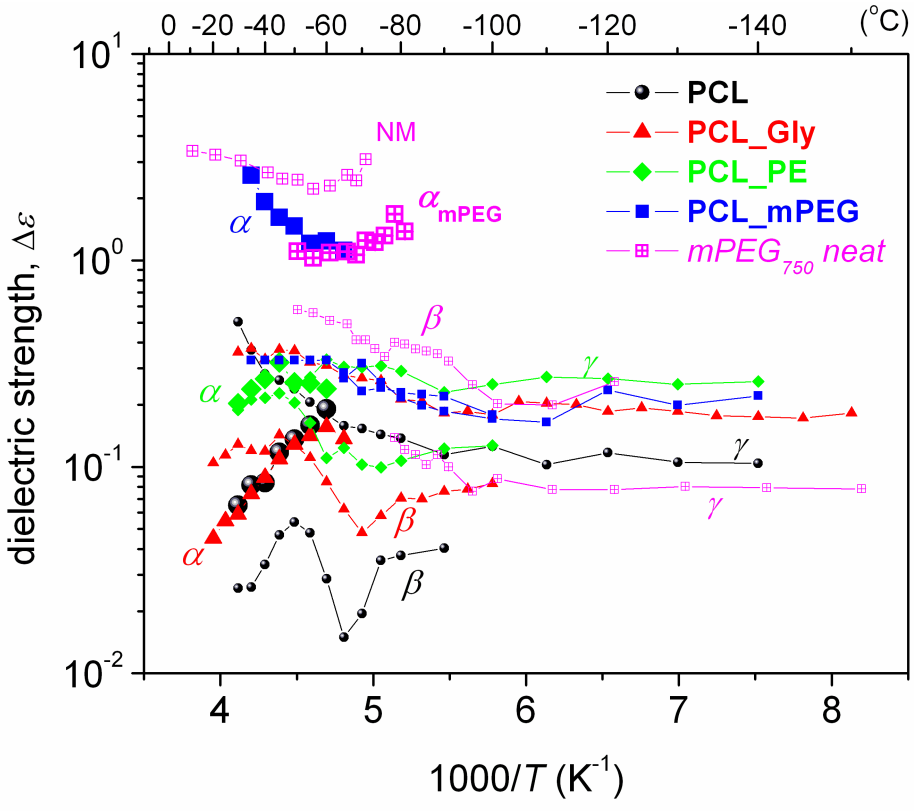


Figure S5. The reciprocal temperature, 1000/*T*, dependence of the relaxation dielectric strength, Δ*ε*, for all samples studied here, a description being given on the plot. The type recorded dynamics (*γ*, *β*, *α*, NM) is indicated along the corresponding data and the used symbols are in accordance with those given in the main article.