

Supporting Information

Tailoring the morphology in partially and fully miscible mixtures of PEEK and PEI

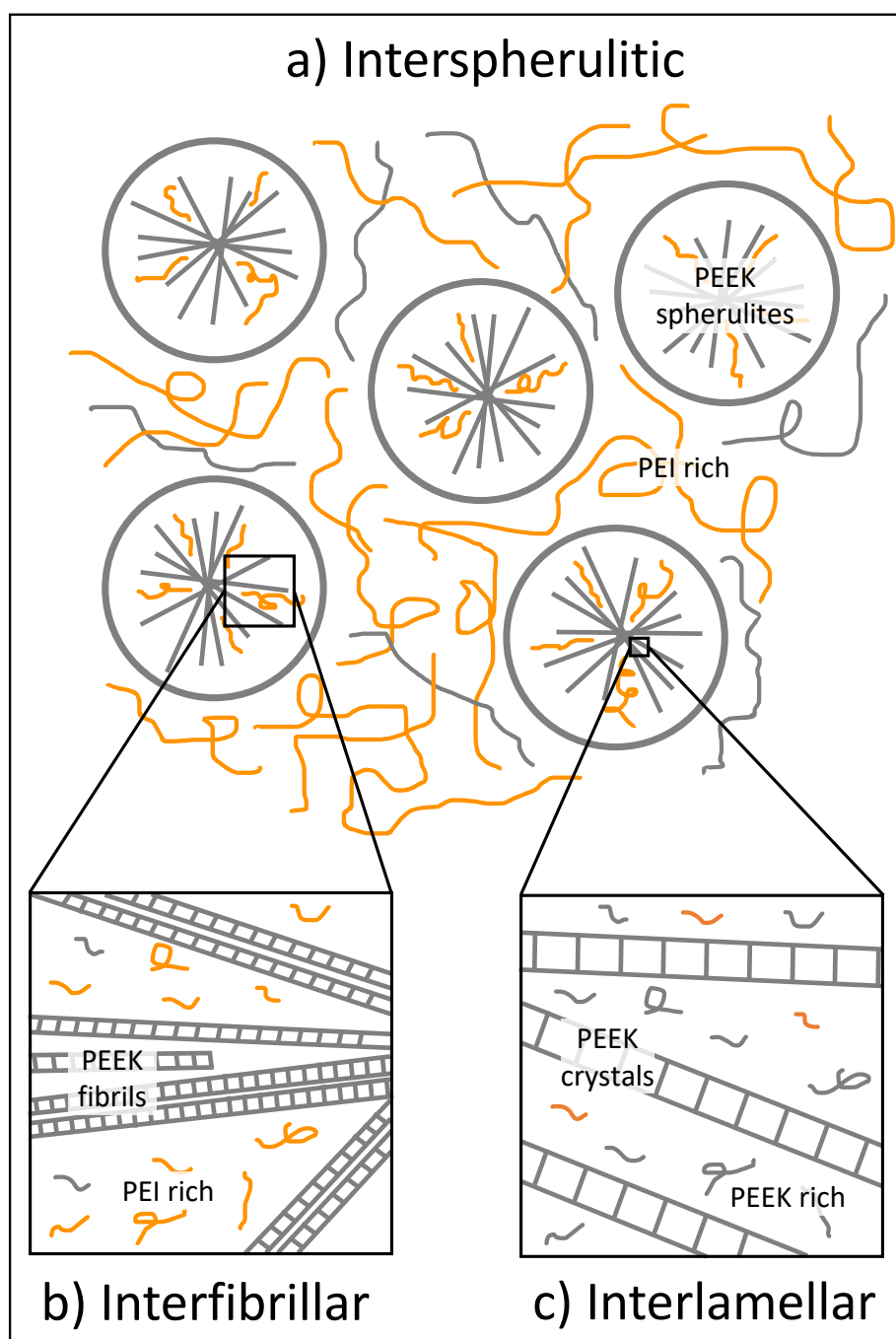
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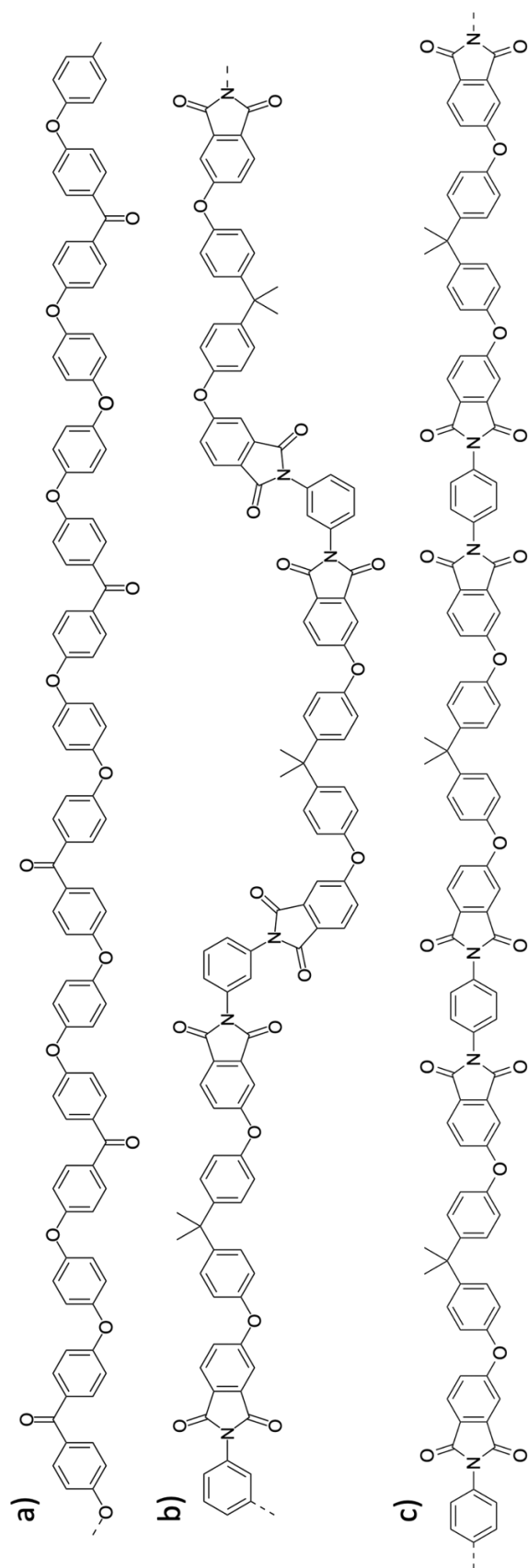
1) Segregation modes of PEI in PEEK/PEI blends



Scheme S1: The different possible segregation modes of PEI concerning PEEK's crystallization.

The segregation of PEI has been reported to occur between PEEK crystalline lamellae, and/or fibrils, and/or spherulites – respectively designated as interlamellar, interfibrillar, and interspherulitic segregation, as illustrated in **Scheme S1**.

2)Molecular structures



Scheme S2: Molecular structures of a) PEEK; b) *meta*-PEI; and c) *para*-PEI

3) DSC thermograms

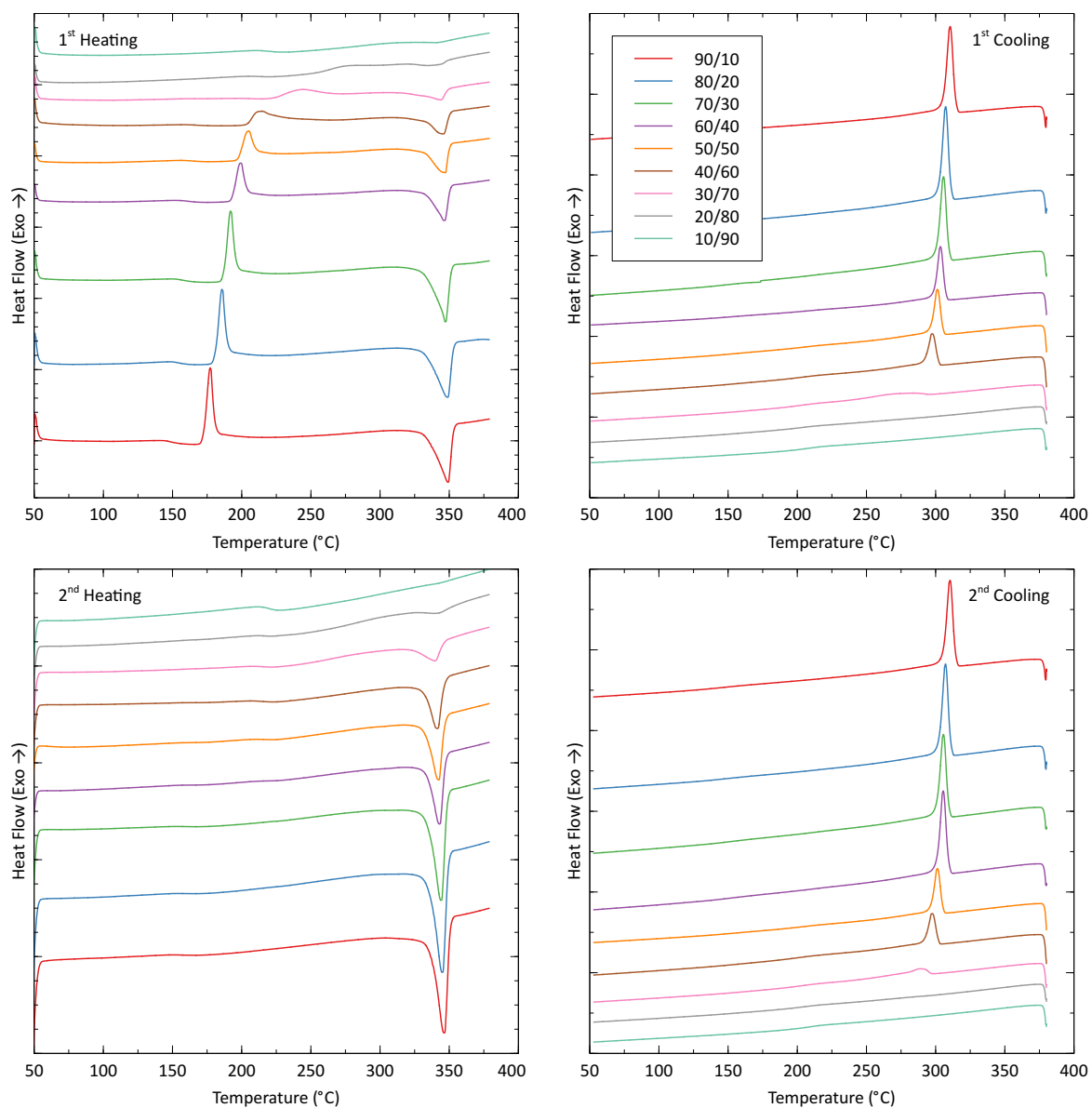


Figure S1: DSC thermograms (10°C/min) for the whole composition range for the PEEK/*p*-PEI quenched system.

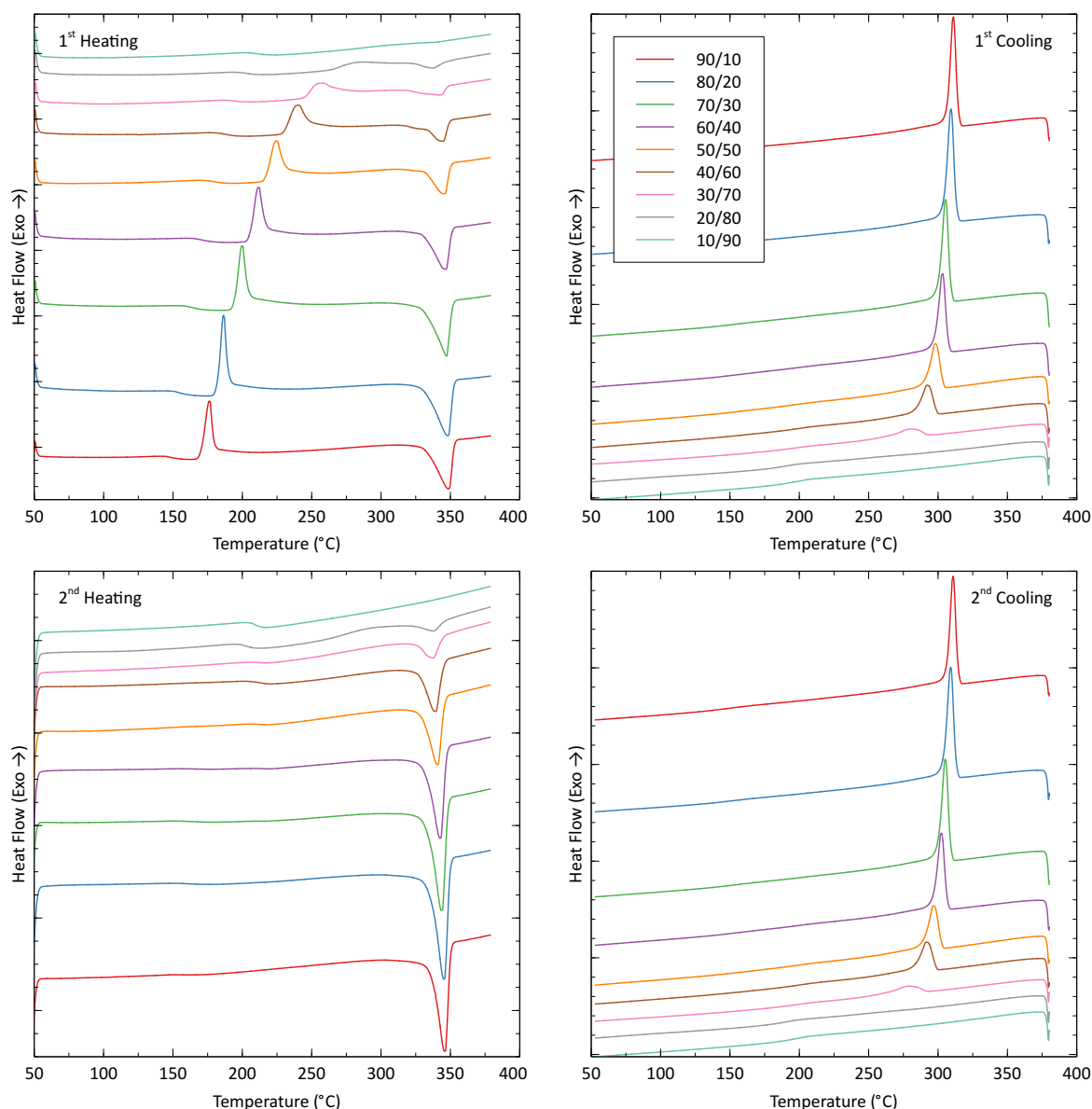


Figure S2: DSC thermograms (10°C/min) for the whole composition range for the PEEK/*m*-PEI quenched system.

4) Breaking thread method

The zero-shear rate viscosities (η_0) of 210 ± 60 Pa.s for PEEK, and 432 ± 55 Pa.s for *p*-PEI₂ (Ultem CRS 5011), were obtained at 375 °C following the procedure described in section 2.8 of the Materials and methods of the article. However, because of the apparition at low frequencies of a sharp increase in complex viscosity, the identification of a zero-shear rate viscosity from the Newtonian plateau for the *p*-PEI₂ proved difficult. Hence, some

complementary frequency sweep tests were performed at different temperatures (300, 320, 340, and 360 °C) to monitor the evolution in the Newtonian plateau for the complex viscosity. This work led to two primary conclusions: (1) First, deviations from the plateau value at low frequencies were observed for test temperatures exceeding 320 °C (see **Figure S3**). This phenomenon is attributed to the partial thermal degradation of the *p*-PEI_2 samples during the experiments at high temperatures; (2) Secondly, an empirical power-law relationship was identified and links the plateau value of the complex viscosity with the test temperature (see **Figure S4**).

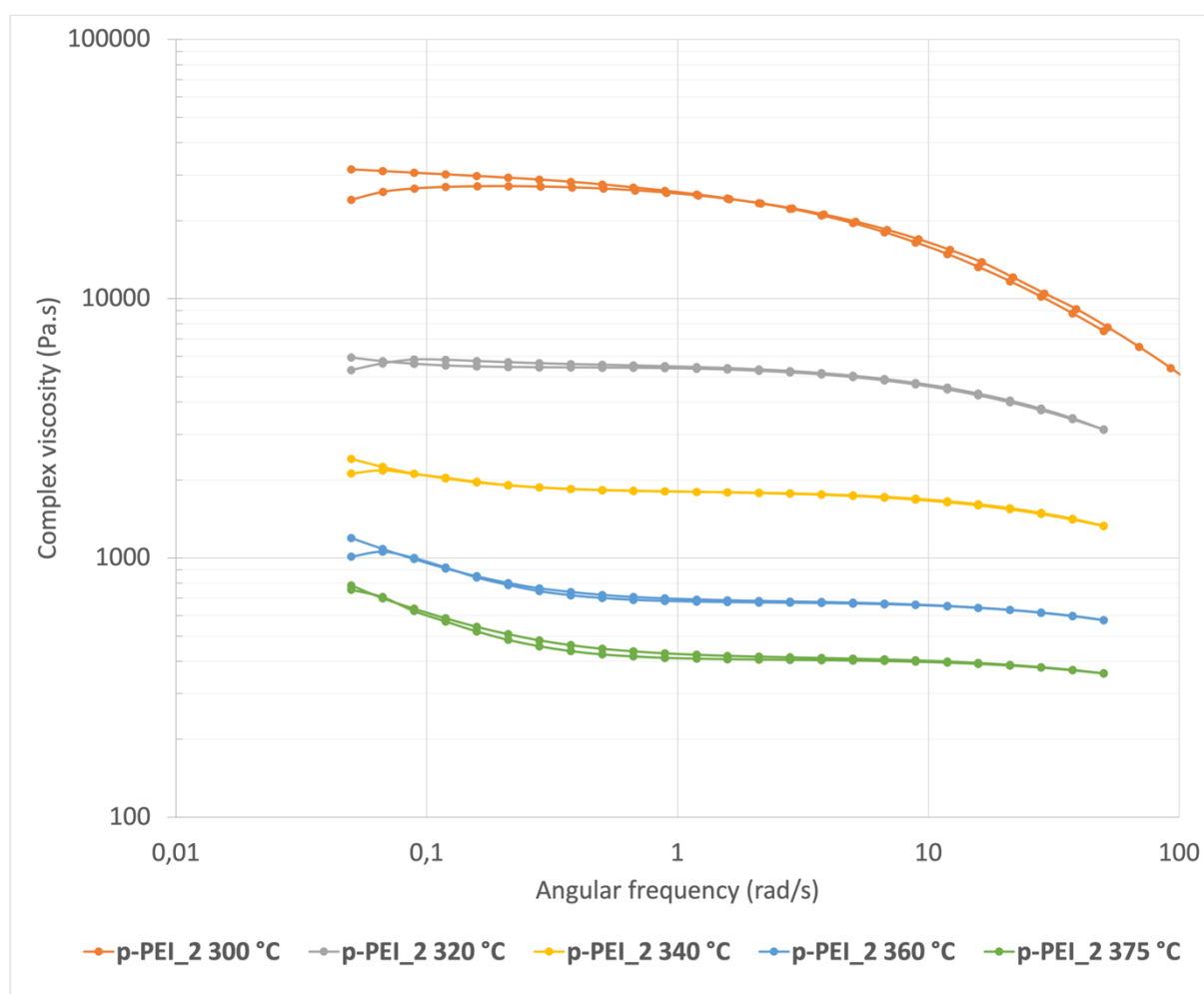


Figure S3: Frequency sweep tests performed at different temperatures (300, 320, 340, 360, and 375 °C) for the *p*-PEI_2 (Ultem CRS 5011).

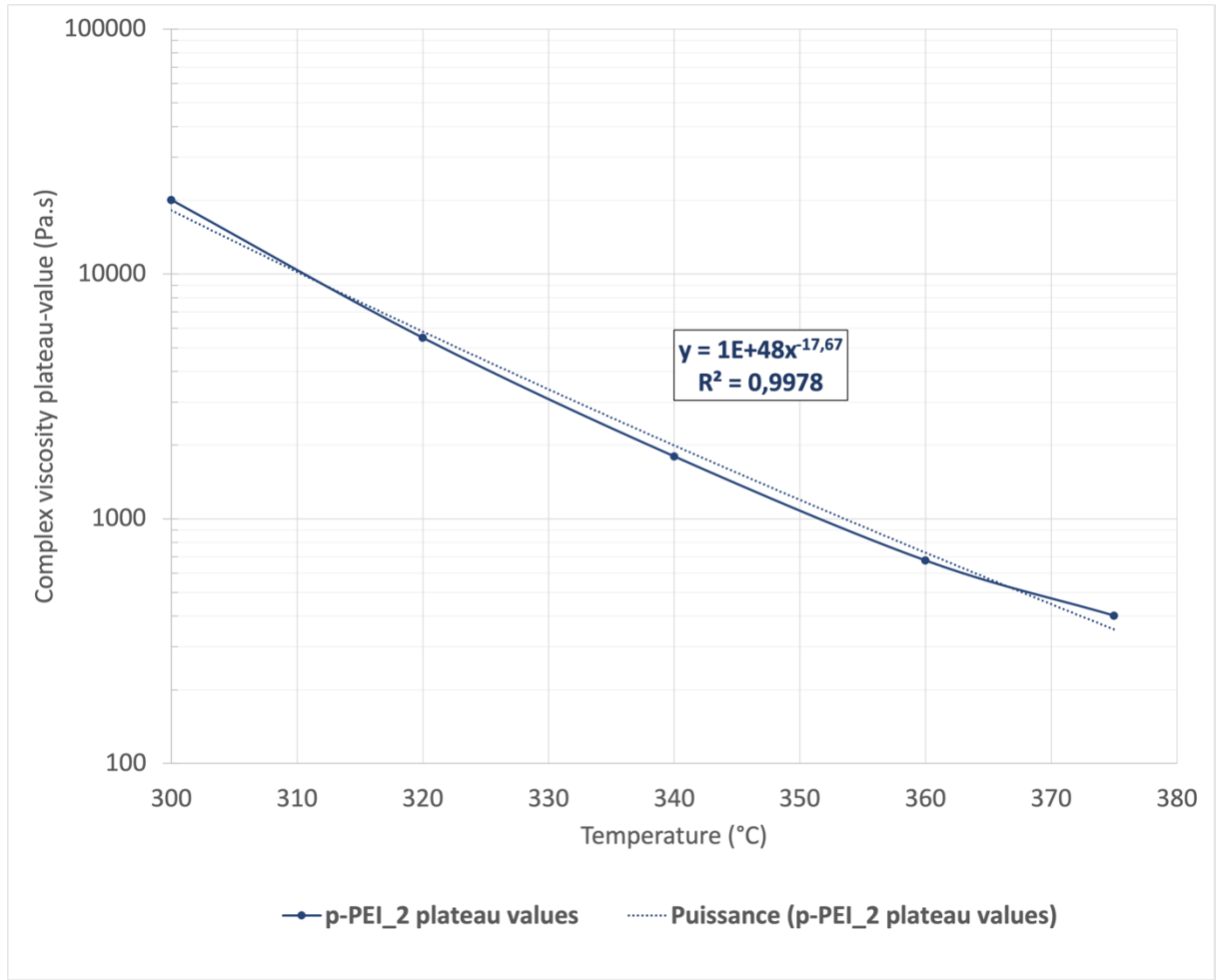


Figure S4: Empirical power-law relationship between the plateau value of the complex viscosity and the test temperature for *p*-PEI₂.

Furthermore, at 375 °C, the difference in the value of complex viscosity between the maximum observed at low frequencies (at 0.05 rad/s = 800 Pa.s) and the Newtonian plateau (at 3.75 rad/s = 404 Pa.s) corresponds to roughly 400 Pa.s. However, doubling the *p*-PEI₂ η_0 value does not affect the interfacial tension value much. This is because the omega (Ω) parameter in Equation 10, which depends on the viscosity ratio between the two polymers, partly compensates for the increase in η_0 of *p*-PEI₂, resulting only in a small increase in the calculated interfacial tension, from 0.14 ± 0.04 mN/m to 0.18 ± 0.05 mN/m.

5) Gravimetric analysis

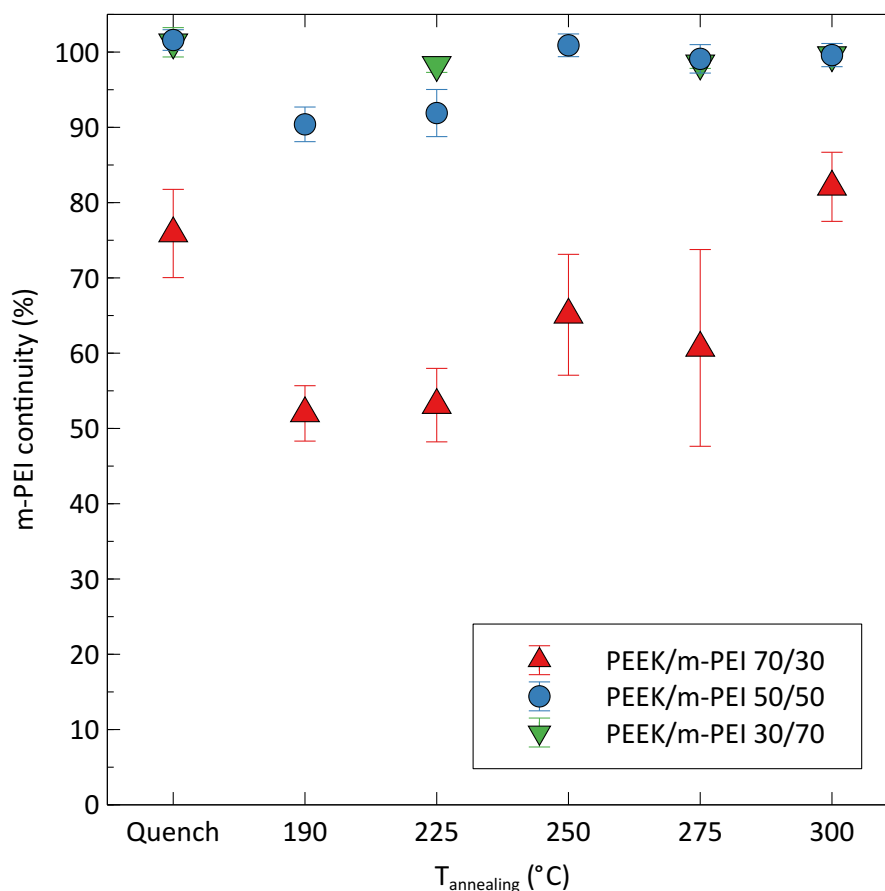


Figure S5: *m*-PEI continuity measured by gravimetric analysis as a function of annealing temperature for three PEEK/*m*-PEI compositions.

Figure S5 presents the continuity of the *m*-PEI phase for three different PEEK/*m*-PEI compositions, annealed at five different temperatures. As already observed in Figure 3 of the article, by increasing the amount of *m*-PEI in the blend we can observe that its continuity is increased too. Interestingly, for each composition under study, the first two temperatures of annealing (190°C and 225°C) always result in lower extraction yields (e.g. *m*-PEI continuity) compared to the quenched blend and annealed blends at higher temperatures. Since these two temperatures are well under and just above the T_g of *m*-PEI, one hypothesis is that the *m*-PEI does not possess enough molecular mobility and gets trapped in between PEEK lamellae or fibrillae when the latter crystallizes. Because crystalline PEEK is less permeable to the solvent

than amorphous PEEK, *m*-PEI is hence less accessible to the follow-up attack by the solvent. Above those temperatures, *m*-PEI displays higher chain mobility and gets expelled in between PEEK spherulites which allows for a higher extraction yield compared to the two previous temperatures. Finally, the quenched state seems to always present nearly equal *m*-PEI continuity compared to the three higher annealing temperatures, suggesting a subtle balance between *m*-PEI expulsion from PEEK crystals and the protection to solvent attack/diffusion offered by these same crystals.

6) PEEK/*m*-PEI 30/70 annealed at 275 and 300 °C

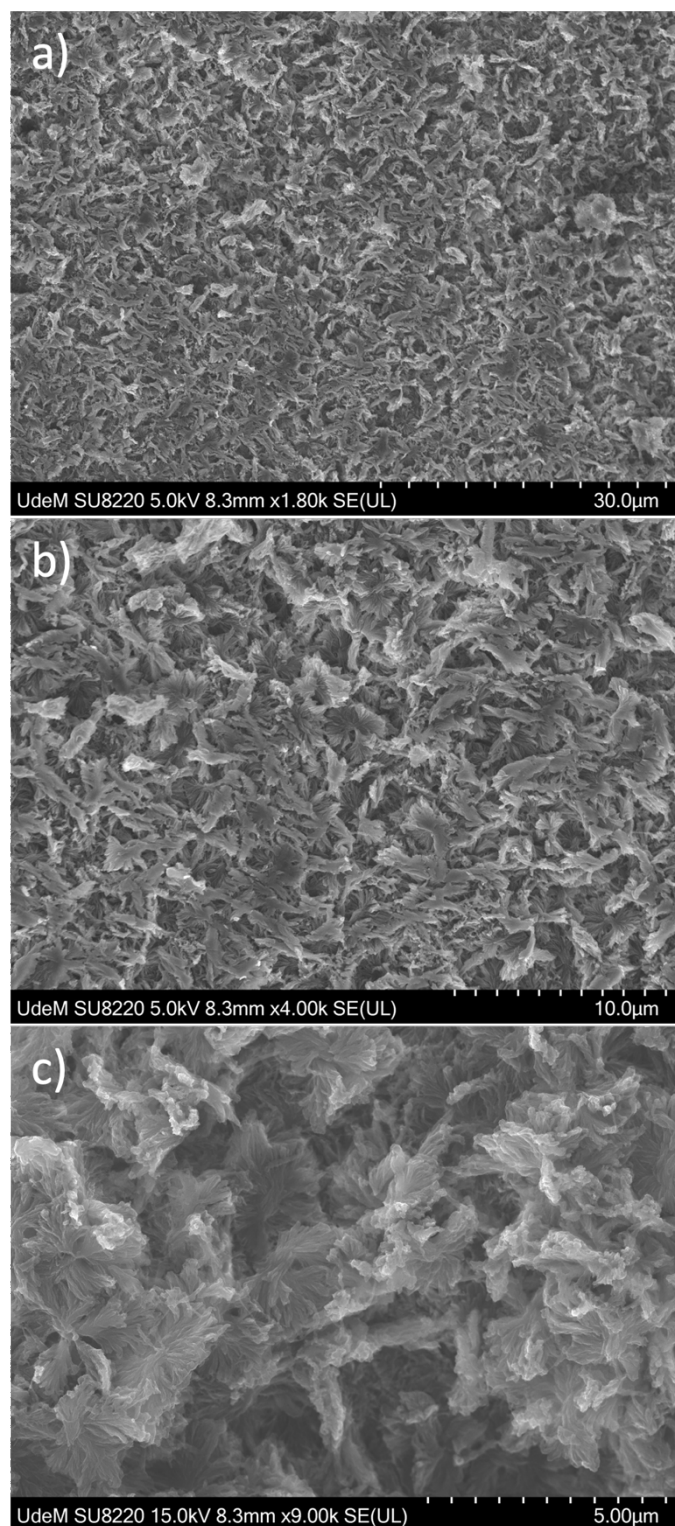


Figure S6: SEM micrographs of PEEK/*m*-PEI 30/70 annealed at 275 °C for 5 min. a) magnification 1 800x; b) magnification 4 000x; c) magnification 9 000x.

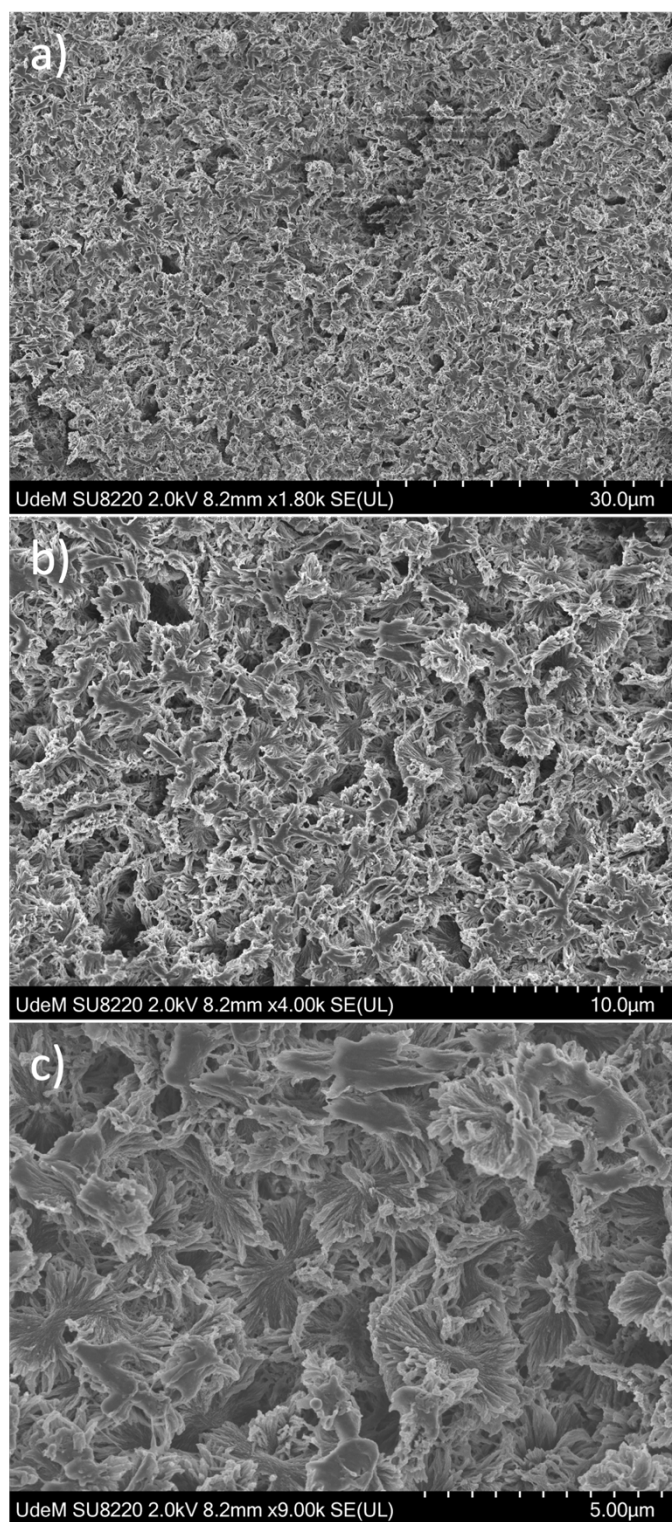


Figure S7: SEM micrographs of PEEK/*m*-PEI 30/70 annealed at 300 °C for 5 min. a) magnification 1 800x; b) magnification 4 000x; c) magnification 9 000x.

7) PEEK/*p*-PEI_2 50/50 blend

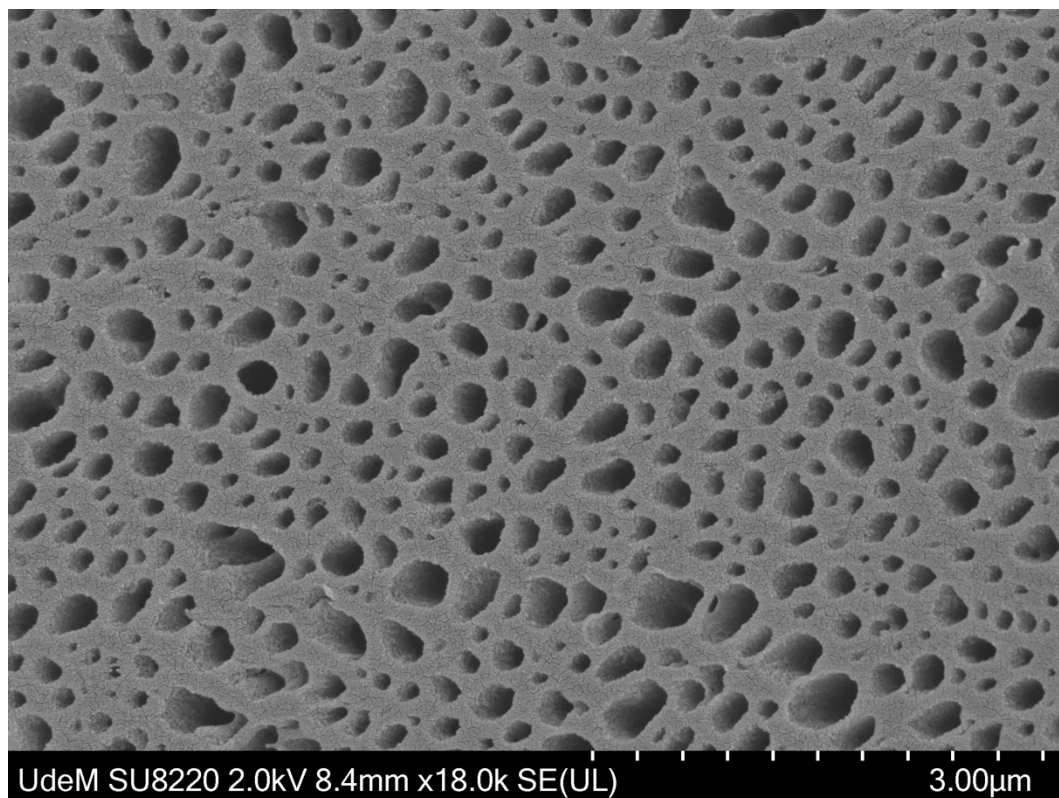


Figure S8: SEM micrograph of PEEK/*p*-PEI_2 50/50 quenched blend, displaying a phase-separated microstructure similar to the PEEK/*p*-PEI system.