SUPPLEMENTARY INFORMATION

Nanostructured Ethylene-Styrene Copolymers

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I. ANALYSIS BY HIGH TEMPERATURE GEL PERMEATION CHROMATOGRAPHY.



I.1. HT GPC analysis iPS-*b*-iP(E-*alt*-S) diblock copolymers 2–5 of Table 1.

Fig. S1. GPC chromatograms at 135 °C of: a) sample **2**, b) sample **3**, c) sample **4** and d) sample **5** of Table1.

II. TEMPERATURE RAISING ELUTION FRACTIONATION.



II.1. TREF analysis of sample 6.

Fig. S2. Plot of TREF fractions for sample 6.



Fig. S3. ¹³C NMR spectra of: a) sample **6**; b) TREF fraction collected at 30 °C containing the sample 6 (signals highlighted in red) and pentaerythritol *tetrakis*(3-(3,5-di*-tert*-butyl-4-hydroxyphenyl)propionate) (added to the eluent as stabilizer); c) TREF fraction collected at 130 °C containing pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate).

III. ANALYSIS BY DIFFERENTIAL SCANNING CALORIMETRY.



III.1. Thermal behaviour of sample 2 annealed at 100 °C for 5 min.

Fig. S4. DSC trace of sample 2 annealed at 100 °C for 5 min: 1st run (blue curve) and 2nd run (red curve).

IV. ATOMIC FORCE MICROSCOPY ANALYSIS.



IV.1. AFM analysis of sample 1 of Table 1.

Fig. S5. Height (a) and phase (b) 2D TM-AFM micrographs of sample 1 of Table 1 corresponding to the 3D micrographs in Fig. 5a.

IV.2. AFM analysis of sample 2 of Table 1.



Fig. S6. Height (a) and phase (b) 2D TM-AFM micrographs of sample 2 of Table 1 corresponding to the 3D micrographs in Fig. 5b. Dimension distribution analysis (c) of iPS domains in Figure (b) performed with Nanoscope Analysis v1.40 r2sr1 software from Bruker as shown in Figure (d).

IV.3. AFM analysis of sample 3 of Table 1.



Fig. S7. Height (a) and phase (b) 2D TM-AFM micrographs of sample **3** of Table 1 corresponding to the 3D micrographs in Figure 5c.

IV.4. AFM analysis of sample 4 of Table 1.



Fig. S8. Height (a) and phase (b) 2D TM-AFM micrographs of sample 4 of Table 1 corresponding to the 3D micrographs in Figure 5d.



Fig. S9. Height (a and c) and phase (b and d) TM-AFM micrographs a iPS-*b*-iP(E-*alt*-S) diblock copolymer sample 4, illustrating the large scale formation of bicontinuous phases.

IV.5. AFM analysis of sample 6 of Table 1.



Fig. S10. Height (a) and phase (b) 2D TM-AFM micrographs of sample 6 of Table 1 corresponding to the 3D micrographs in Figure 5e. c) Dimension distribution analysis of iP(E-*alt*-S) domains in Figure (b) performed with Nanoscope Analysis v1.40 r2sr1 software from Bruker as shown in Figure d.

IV.6. AFM analysis of iPS homopolymer.



Fig. S11. Height (a) and phase (b) 2D TM-AFM micrographs of a thin film of iPS homopolymer (sample 7) corresponding to the 3D micrographs in Figure 5f.





Fig. S12. Height (a and c) and phase (b and d) TM-AFM micrographs of a solution blend of iPS homopolymer and iP(E-*alt*-S) alternate copolymer sample 1 (50:50 by weight), illustrating the large scale raw phase separation.





Fig. S13. SAXS patterns of samples reported in Table 1.