Supporting Information

Porous Polystyrene Monoliths prepared from in Situ Simultaneous Interpenetrating

Polymer Networks: Modulation of Morphology by Polymerization Kinetics

Petra Utroša,[†] Ema Žagar,[†] Sebastijan Kovačič, $*^{\dagger,\ddagger}$ and David Pahovnik $*^{\dagger}$

[†]Department of Polymer Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

[‡]Faculty of Chemistry and Chemical Engineering, Laboratory for Organic and Polymer Chemistry and Technology, University of Maribor, Smetanova 17, 2000 Maribor, Slovenia

*Corresponding authors. E-mail addresses: sebastijan.kovacic@ki.si (S. Kovačič) and david.pahovnik@ki.si (D. Pahovnik)

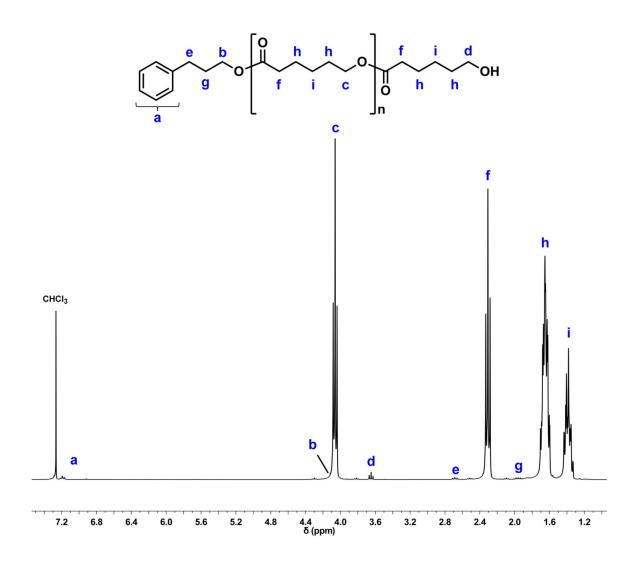


Figure S1. ¹H NMR spectrum of PCL synthesized in solution.

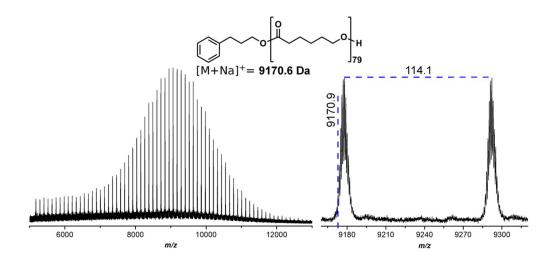


Figure S2. MALDI-TOF mass spectrum and its enlarged region with denoted measured monoisotopic signals for the PCL synthesized in solution.

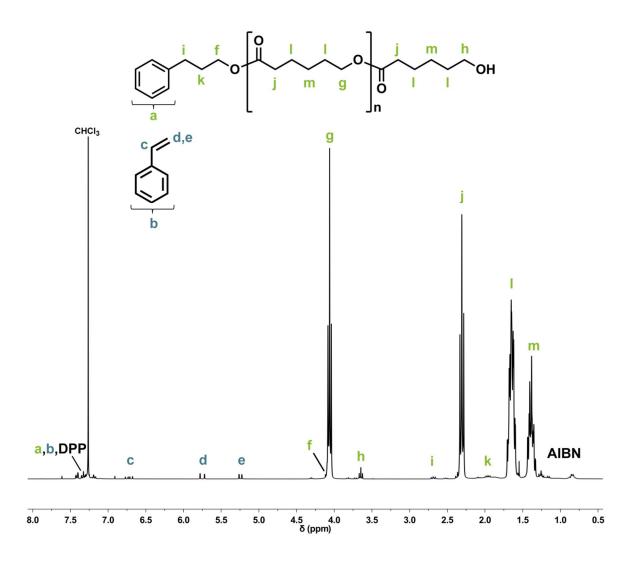


Figure S3. ¹H NMR spectrum of the chloroform extract of the $IPN_{0.5}$. The extract consists mainly of PCL, while the DPP, minute amount of styrene monomer, and degradation products of AIBN are also present.

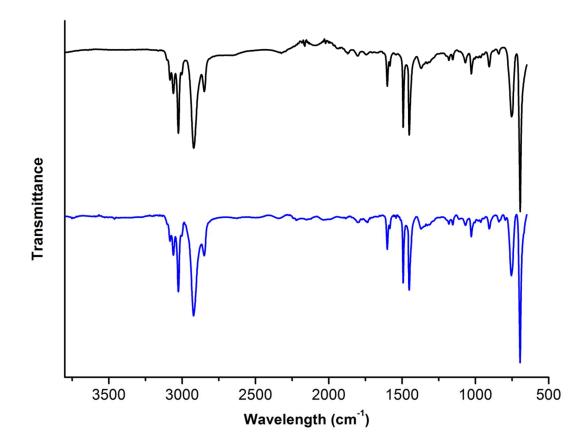


Figure S4. FT-IR spectra of PS framework obtained after extraction of PCL from the $IPN_{0.5}$ with chloroform (bottom) together with PS prepared in bulk (top). The absence of PCL carbonyl stretching band at 1720 cm⁻¹ confirms that the copolymerization of CL and styrene or grafting of CL on PS did not take place.

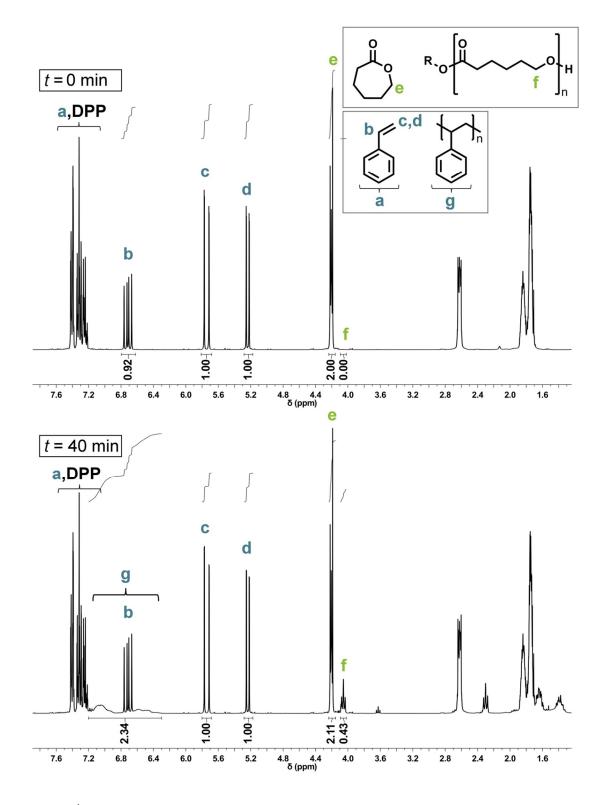


Figure S5. ¹H NMR spectra of aliquots withdrawn during polymerization of styrene and CL mixture in the presence of 0.5 wt % DPP. Top spectrum was recorded at the beginning of reaction and bottom spectrum was recorded after the reaction time of 40 minutes.

The conversion of CL was calculated using Equation (1):

$$x(CL) = \frac{A_{\rm f}}{A_{\rm f} + A_{\rm e}} \tag{1}$$

where *x*(CL) stands for the CL conversion, while A_f and A_e are the integrals of the signals for PCL ($\delta(f) = 4.06$ ppm) and CL ($\delta(e) = 4.22$ ppm), respectively.

Because the broad signal of PS partially overlaps with the signals of styrene and DPP, the conversion of the styrene monomer was calculated by comparison of the signal integrals of the CL, PCL, and styrene using the Equations (2) and (3):

$$r = \frac{2A_{\rm d}}{A_{\rm e} + A_{\rm f}}$$
(2)
$$x(PS) = \frac{r^0 - r}{r^0}$$
(3)

where *r* is a ratio between styrene and (CL + PCL) in the reaction mixture at time *t*, r^0 is a ratio between styrene and (CL + PCL) in the reaction mixture at t = 0 min, while A_d , A_e , and A_f are the integrals of the signals for styrene ($\delta(d) = 5.22$ ppm), CL ($\delta(e) = 4.22$ ppm), and PCL ($\delta(f) = 4.06$ ppm), respectively, at time *t*.

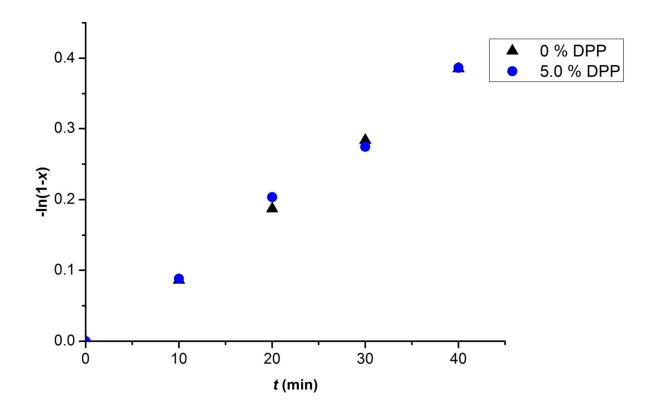


Figure S6. The kinetics of FRP of styrene performed in the bulk in the presence and absence of DPP.

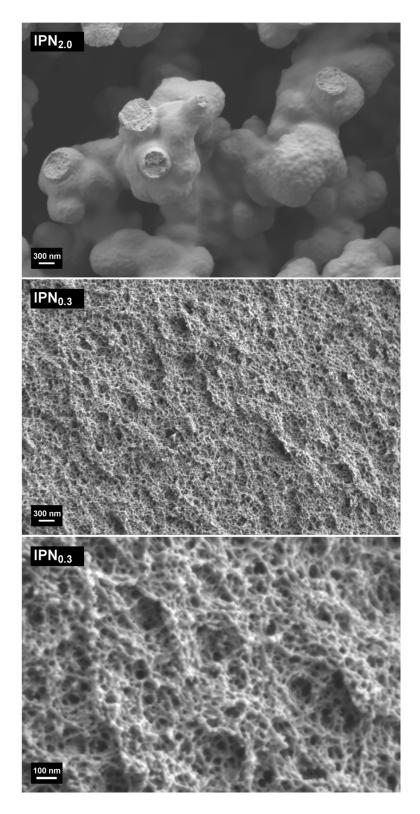


Figure S7. SEM micrographs of the *in situ* simultaneously synthesized IPNs after the removal of PCL.

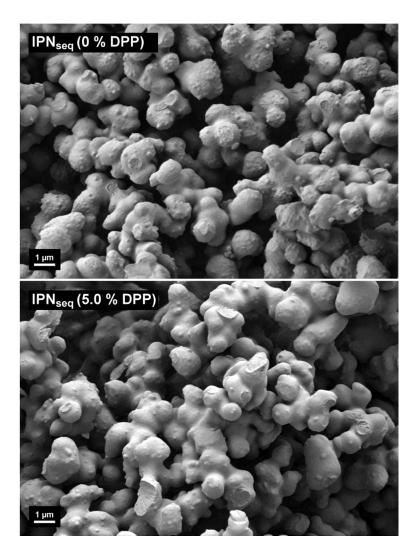


Figure S8. SEM micrographs of the sequentially synthesized IPNs in the presence of 0 wt % (top) and 5.0 wt % of DPP (bottom).

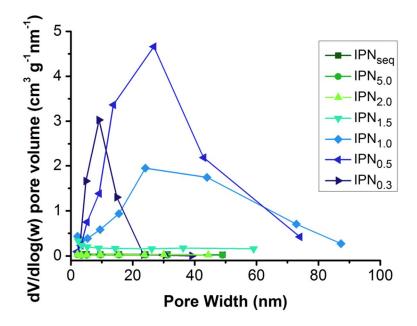


Figure S9. Pore size distribution based on BJH analysis of the nitrogen desorption data.

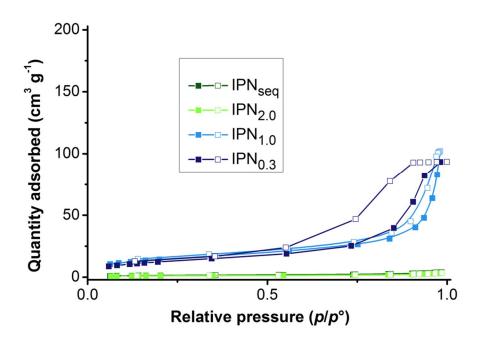


Figure S10. Isotherms from nitrogen adsorption (\blacksquare) and desorption (\Box) measurements of the porous PS frameworks obtained after hydrolysis of PCL from the IPNs.