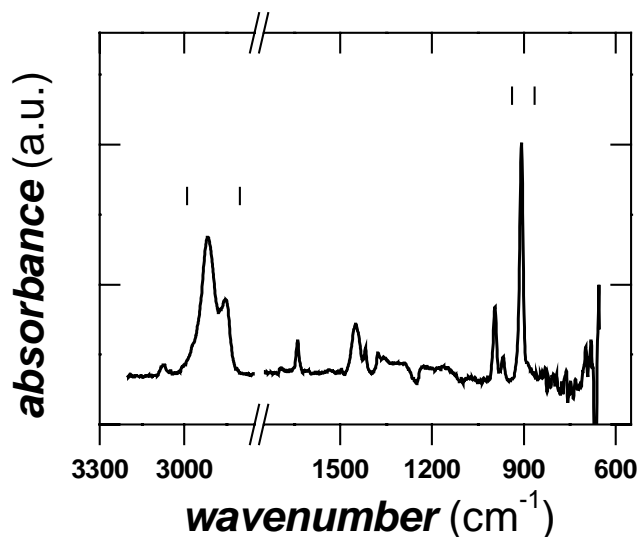


Supporting Information to:

## **Influence of 1,2-PB matrix cross-linking on structure and properties of selectively etched 1,2-PB-*b*-PDMS block copolymers**

### **1. Comparison of cross-linking degree of the block copolymer with homo-polymer.**

Following a suggestion from one of the reviewers, a series of samples with varying cross-linking degree was prepared from a 1,2-PB homopolymer ( $M_n=7800$  g/mol and polydispersity index 1.04). The cross-linking conditions were the same as for the samples derived from the 1,2-PB-*b*-PDMS block copolymer described in the paper. The concentration of double bonds was tentatively determined by FT-IR, on the basis of the areas under the  $2917\text{ cm}^{-1}$  and the  $908\text{ cm}^{-1}$  peaks, as illustrated in Figure S1. The first is related to stretching vibrations of C-H bonds on saturated carbons and the second to out of plane C-H bending vibrations on unsaturated carbons.



**Figure S1.** FT-IR spectrum of a cross-linked 1,2-PB homopolymer (see table S3) with the peak area regions indicated. The peak-area between  $2990\text{ cm}^{-1}$  to  $2805\text{ cm}^{-1}$  was taken as proportional to the concentration of H-C(saturated) bonds, while the peak-area between  $940\text{ cm}^{-1}$  and  $868\text{ cm}^{-1}$  is proportional to the concentration of H-C(unsaturated) bonds.

This procedure is expected to be less accurate than the one used for the calculation of double bond concentration during the cross-linking of the 1,2-PB-*b*-PDMS block copolymer. In that case the  $1261\text{ cm}^{-1}$  peak from the  $\text{CH}_3$  bending vibration in PDMS was used as an internal standard. The main reason for the poorer accuracy is that there are different types of saturated carbons expected to be produced from the reaction of free radicals to double bonds during the cross-linking reaction. As already discussed in

another publication (ref. [14] in the paper) intramolecular reactions mainly produce 6-cycles on the main chain, while intermolecular reactions (cross-linking) produce open branched chains. The C-H vibrations from these two kinds of structures are expected to have slightly different absorbance at similar IR-wavelengths. At the moment we don't have any clue on the relative abundance of the two structures, therefore we rely on the assumptions of equal absorbance for each saturated C-H and the 1:1 correspondence between newly formed saturated C-H and disappeared of unsaturated C-H in the course of the cross-linking reaction. The data on swelling ratio and the calculated network strand length as calculated from the Flory model are summarized in Tables S1 – S3.

**Table S1.** Data on the fraction of consumed double bonds and swelling of the block copolymer samples with different cross-linking degrees.

<b>Cross-linked 1,2-PB-PDMS</b>				
<b>Sample</b>	Fraction of consumed double bonds based on the internal standard method	Swelling ratio in toluene	$M_c$	$1/N_c$
<b>X 0.11</b>	0.11	3.60±0.03	5522	0.010
<b>X 0.15</b>	0.15	2.13±0.04	1230	0.044
<b>X 0.34</b>	0.34	1.60±0.02	478	0.113
<b>X 0.41</b>	0.41	1.42±0.01	305	0.177
<b>X 0.52</b>	0.52	1.28±0.01	196	0.275
<b>X 0.58</b>	0.58	1.26±0.02	183	0.296
<b>X 0.62</b>	0.62	1.20±0.01	143	0.377
<b>X 0.82</b>	0.82	1.15±0.01	113	0.477

**Table S2.** Data on the fraction of consumed double bonds and swelling of the block copolymer samples with different cross-linking degrees after etching.

<b>Etched cross-linked 1,2-PB-PDMS</b>					
<b>Sample</b>	Fraction of consumed double bonds based on assumption that etching does not affect double bonds	Swelling ratio in toluene	Swelling ratio after taking volume of PDMS out	$M_c$	$1/N_c$
<b>E-X 0.11</b>	0.11	4.59±0.12	4.21	8348	0.006
<b>E-X 0.15</b>	0.15	3.25±0.44	2.87	2962	0.018
<b>E-X 0.34</b>	0.34	1.87±0.08	1.49	368	0.147

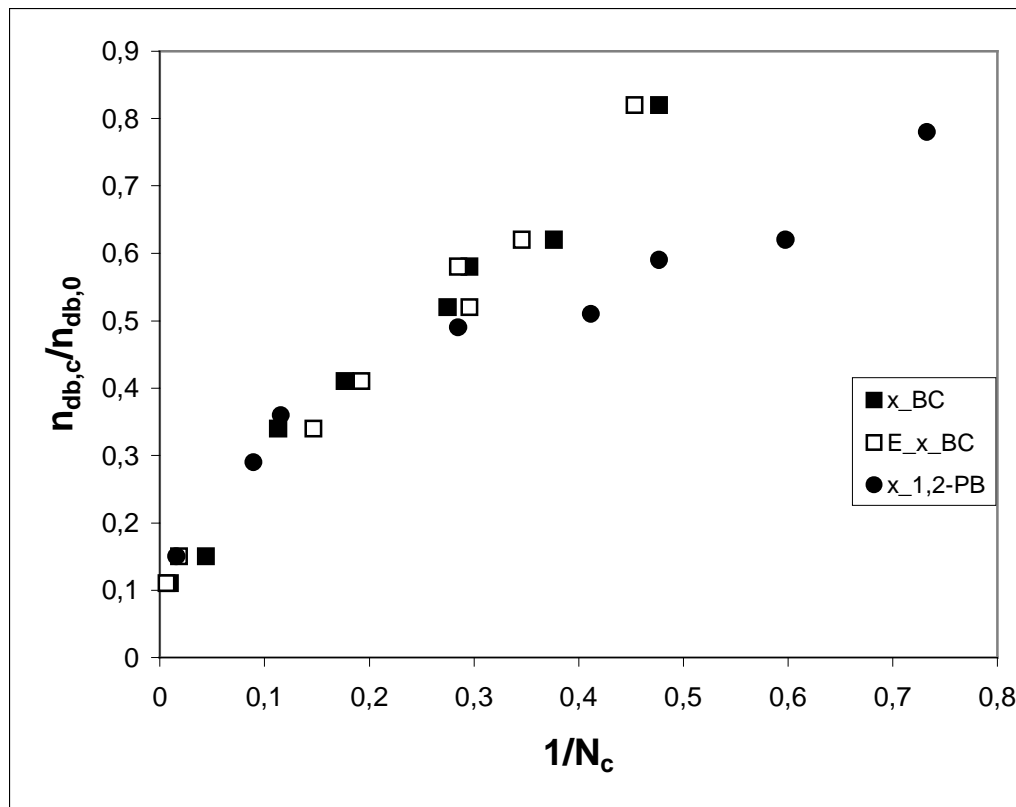
<b>E-X 0.41</b>	0.41	1.77±0.01	1.39	280	0.193
<b>E-X 0.52</b>	0.52	1.64±0.02	1.26	183	0.296
<b>E-X 0.58</b>	0.58	1.65±0.03	1.27	189	0.285
<b>E-X 0.62</b>	0.62	1.60±0.03	1.22	156	0.346
<b>E-X 0.82</b>	0.82	1.54±0.04	1.16	119	0.453

**Table S3.** Data on cross-linking conditions, consumed double bonds and swelling for the homopolymer 1,2-PB.

<b>Cross-linked 1,2-PB homopolymer</b>							
<b>Sample</b>	Cross-linking conditions			Fraction of consumed double bonds Based on the area of two peaks (2990-2805/940-868 cm <sup>-1</sup> )	Swelling ratio in toluene	M <sub>c</sub>	1/N <sub>c</sub>
	conc. ( $n_{\text{DCP}}/n_{\text{db},0}$ )	temp (°C)	time (h)				
<b>x-1</b>	0.002	140	1	0.15	3.02±0.04	4130	0.013
<b>x-2</b>	0.004	140	1	0.29	1.71±0.02	716	0.075
<b>x-3</b>	0.001	140	2	0.36	1.59±0.02	552	0.098
<b>x-4</b>	0.008	140	1	0.49	1.27±0.01	219	0.246
<b>x-5</b>	0.01	140	1	0.51	1.18±0.02	150	0.359
<b>x-6</b>	0.002	140	2	0.59	1.15±0.02	129	0.418
<b>x-7</b>	0.008	140	2	0.62	1.11±0.01	103	0.527
<b>x-8</b>	0.02	140	2	0.78	1.08±0.01	83	0.650

The concentration of the peroxide initiator (DCP) was chosen equal relative to the concentration of double bonds in the two cases of block- and homo- polymer.

Figure S2 is a plot of the results from the Flory model for the block copolymer and the homopolymer. The coincidence between the two systems in the lower range of cross-linking degree is remarkable. The deviations in the high range of the cross-linking degree ( $1/N_c > 0.4$ ) are not relevant in the context of the Flory model, as the network strands in this range are way too short to be treated from the statistical assumptions at the basis of the Flory model. Notice that the average chain length in this range is 1.5 – 2.5 monomer units! All in all the comparison supports a direct correlation between the fraction of consumed double bonds and the cross-linking degree.

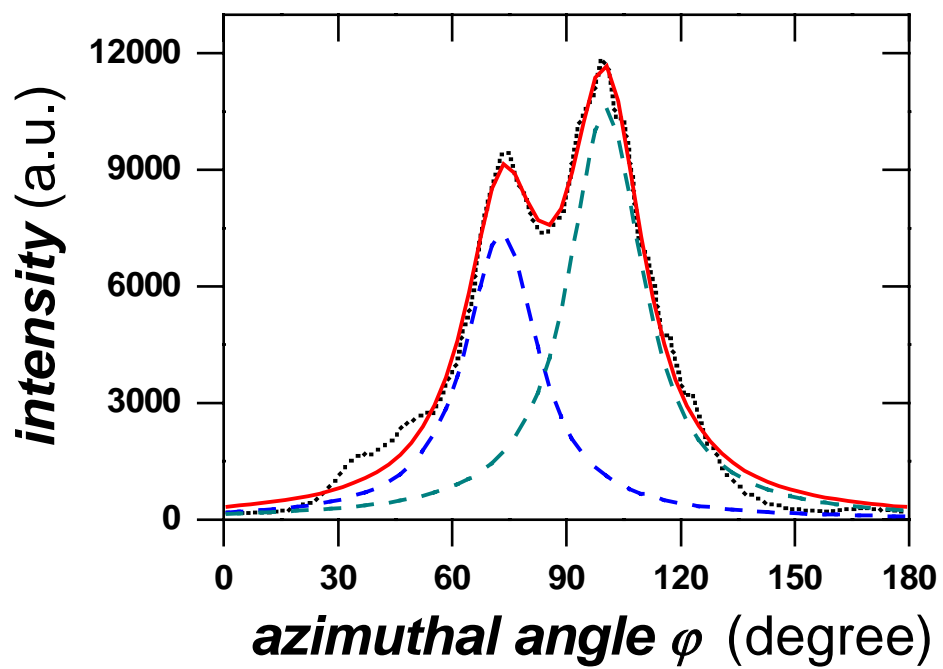


**Figure S2.** Fraction of consumed double bonds against the inverse of the degree of polymerization of network strand as calculated from the Flory model. Comparison of results on the cross-linked block copolymer before (filled squares) and after (open squares) etching, and the cross-linked 1,2-PB homopolymer (filled circles).

## 2. Cylinder alignment parameter of nanoporous shear aligned sample E-x 0.62.

The azimuthal SAXS profile at  $q^*$  is shown in the Figure S3. The values of the azimuthal angle on the x-axes are chosen such that the shear direction lays at  $0^\circ$ . The profile is evidently bimodal and it has been fitted by two Lorentzian curves, also shown on the plot. The Lorentzians peak at  $74^\circ$  and  $100^\circ$ , respectively. At the moment we don't know the precise reason for this double alignment, which is expected to relate to the flow geometry within the extruder. The alignment parameter  $F_2$  was calculated for each of the two directions separately and for the overall scattering profile.

The procedure of calculation followed a scheme first used by de Gennes (*The Physics of Liquid Crystals*, 1973, Oxford University Press) as adopted to block copolymer systems by Sakurai, S. et al (*Macromolecules* **2001**, 34, 3672).



**Figure S3.** The SAXS scattering profile at  $q^*$  (dotted line) as a function of the azimuthal angle  $\phi$  and its fit as a sum (red line) of two Lorentzians (segmented blue and green lines). The shear direction is at  $0^\circ$  ( $180^\circ$ ).