Influence of 1,2-PB Matrix Cross-Linking on Structure and Properties of Selectively Etched 1,2-PB-*b*-PDMS Block Copolymers

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ABSTRACT: A series of samples with varying cross-linking degree were prepared from the same 1,2-polybutadiene-*b*-polydimethylsiloxane (1,2-PB-*b*-PDMS) diblock copolymer precursor. The stability of nanopores generated after PDMS cleaving depends on the cross-linking degree of 1,2-PB. The swelling ratio of the cross-linked samples in toluene was converted into a degree of cross-linking following the Flory scheme; a simple relation between the Flory cross-linking degree and the fraction of consumed double bonds during the cross-linking reaction followed. The structure of the block copolymer at different stages of preparation was characterized by small-angle X-ray scattering (SAXS). In addition, scanning electron microscopy (SEM) gave direct images of the nanoporous polymer structure. Nanocavities are accessible to methanol, and observations of methanol uptake were combined with structural information from SAXS. This permits a classification of the bulk cross-linked and etched polymers into three groups: collapsed, traced, and nanoporous materials.

Introduction

Polymeric nanoporous materials derived from block copolymers offer great technological promise due to their many potential applications as, e.g., size selective separation membranes, sensors, substrates for catalysis, templates for electronic devices, and depots for controlled drug delivery. The mutual repulsion between two blocks in the copolymer molecule provides for microsegregation on the nanometer length scale. One block of the molecules can be removed selectively by chemical etching,[1−4] UV irradiation,[5] or thermal treatment.[6] As a result, nanoscopic pores are generated in a polymer matrix, provided that the matrix has sufficient mechanical stability.

The most common nanoporous polymers are prepared from materials where the matrix block remains in the glassy state.[4,6−8] Obviously, such materials do not need chemical modification of the matrix phase such as cross-linking because the phase is mechanically stable as a glass. But these glassy-matrix materials will typically lack thermal stability and resistance to solvents, which will limit their use in many specific applications, where high temperatures or the presence of solvent are unavoidable. Nanopores will collapse as the temperature approaches the glass transition of the matrix materials,[9] and obviously the matrix dissolves when exposed to solvents.

A nanoporous material of a chemically cross-linked matrix will be advantageous for many applications. However, only a limited number of cross-linked materials have been studied to date.[10−14] Cross-linking the matrix phase increases the thermal and mechanical stability and also improves resistance to solvents. We have recently demonstrated the preparation of a cross-linked nanoporous polyisoprene (PI) material, by first cross-linking the PI block, followed by etching the PDMS block in a PI-*b*-PDMS block copolymer precursor.[11] We have refined the procedures for creating nanoporous materials with cross-linked matrices and recently submitted a first report on the creation of cross-linked nanoporous 1,2-polybutadiene (1,2-PB).[14]

1,2-PB-*b*-PDMS diblock copolymers are a very attractive source of cross-linked nanoporous polymers. They can be prepared in a highly controlled way by living anionic polymerization, the 1,2-PB block is easily amenable to cross-linking, and the PDMS block can be quantitatively and selectively removed. Since 1,2-PB has a glass transition temperature below 0 °C, the cross-linking degree plays a key role in the stability of the nanopores. In this paper we focus on the influence of the cross-linking degree on the bulk properties of the 1,2-PB material derived from a single block copolymer precursor. A series of 1,2-PB samples result from cross-linking to different degrees, followed by selective etching. The chemical composition of these samples is determined by FT-IR and Raman spectroscopies. SAXS studies are undertaken to elucidate the nanostructure, supported by SEM observations on selected etched samples. Finally, we show how simple experiments of methanol uptake can be used to study the porosity and give valuable morphological information.

Experimental Section

Synthesis of 1,2-PB-*b*-PDMS. The 1,2-PB-*b*-PDMS diblock copolymer precursor was synthesized by sequential living anionic polymerization in tetrahydrofuran (THF). *sec*-Butyllithium was used as initiator. The polymerization of 1,3-butadiene was performed at -20 ± 3 °C for 3 h. Then hexamethylcyclotrisiloxane, D_3, was added to the reactor, and the temperature was raised up to 0 °C. The polymerization of D_3 took 3 days before termination with chlorotrimethylsilane.

Solvent Casting. 1,2-PB-*b*-PDMS samples were dissolved in THF, and the solutions were poured into Petri dishes. The solutions were left for 3 days to evaporate slowly under a slight flow of argon at room temperature.

Shear Alignment. One of the 1,2-PB-*b*-PDMS samples was aligned through a homemade extrusion device with a rectangular die. A film with 0.5 mm thickness and 10 mm width was obtained by pressing the block copolymer through the die.

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Table 1. Cross-Linking Conditions and Characteristics of Cross-Linked Samples; M_c Values Calculated from Eq 1 Are Listed in the Last Column

	cross-linking conditions			double bond ratio ($n_{db,x}/n_{db,0}$)[b]			
sample	concn ($n_{DCP}/n_{db,0}$)[a]	temp (°C)	time (h)	from FT-IR	from Raman	equilibrium swelling ratio[c] in toluene	$M_{c,Flory}$[d] (g/mol)
X 0.11	0.004	140	1	0.89	0.90	3.60 ± 0.03	5522
X 0.15	0.002	140	1	0.85	0.80	2.13 ± 0.04	1230
X 0.34	0.001	140	2	0.66	0.63	1.60 ± 0.02	478
X 0.41	0.008	140	1	0.59	n.m.[e]	1.42 ± 0.01	305
X 0.52	0.01	140	1	0.48	n.m.	1.28 ± 0.01	196
X 0.58	0.002	140	2	0.42	0.37	1.26 ± 0.02	183
X 0.62	0.008	140	2	0.38	n.m.	1.20 ± 0.01	143
X 0.82	0.02	140	2	0.18	0.20	1.15 ± 0.01	113

[a] n_{DCP} is moles of DCP molecules, and $n_{db,0}$ is moles of double bonds in virgin material. [b] $n_{db,x}$ is moles of double bonds in cross-linked material. [c] Equilibrium swelling ratio is the mass ratio between equilibrium swollen and dry sample. [d] $M_{c,Flory}$ is the average molecular weight between neighboring cross-links as calculated from the Flory scheme (see text). [e] Not measured.

Cross-Linking of 1,2-PB. Dicumyl peroxide (bis(α,α-dimethylbenzyl) peroxide) (DCP), from Merck, was used as received for the cross-linking of 1,2-PB. The cross-linker was codissolved with the block copolymer in THF in 0.1−2% molar amounts (n_{DCP}) relative to the moles of the double bond ($n_{db,0}$) in the mother polymer. The ratio ($n_{DCP}/n_{db,0}$) was one of the parameters varied in order to obtain differently cross-linked samples. The other parameter was the reaction time. The solutions were left under an argon flow, and the solvent evaporated overnight. The cross-linking of the solvent cast blends was conducted under argon at 140 °C for 1−2 h in a homemade gastight steel cylinder.

Etching of PDMS. 1.0 M tetrabutylammonium fluoride (TBAF) in THF from Aldrich was used as cleaving reactant for PDMS. Cross-linked samples were stirred for 36 h in a volume of THF solution containing 5 times molar excess TBAF relative to PDMS repeating unit. Afterward, the samples were washed by fresh THF and methanol for 24 h before drying under an argon flow at room temperature.

Chromatography and Spectroscopy. The molecular weight (MW) of 1,2-PB-*b*-PDMS was determined by a combination of size exclusion chromatography (SEC) and ^{1}H NMR, as described in detail in ref 14. The chemical composition and the number of double bonds surviving after cross-linking and etching of the 1,2-PB−PDMS samples were monitored by Fourier transform infrared FT-IR (Perkin-Elmer Spectrum) and Raman (Renishaw system 3000) spectroscopies. Specimens of 1 cm × 1 cm of 0.5−1 mm thickness were prepared for the measurements.

Rheology. The morphology of the diblock copolymers was investigated by isothermal and temperature-gradient dynamic mechanical measurements on a Rheometrics RS 800 using parallel plate geometry. The results used in this paper refer to temperature gradients of 2.5 °C/min.

Swelling Studies and Pore Accessibility. Swelling behavior of cross-linked and etched samples and pore accessibility of etched samples were investigated by the uptake of either toluene or methanol. Dry samples (25−62 mg) were placed in glass vials containing 15 mL of toluene or methanol and kept under gentle stirring at room temperature. After being submerged for a certain time a fine tissue was used to dry the surfaces of the sample quickly before the sample mass was measured and the sample placed back in the liquid. Data were collected as a function of time as the weighing procedure was repeated. Toluene and methanol uptake measurements were carried out until the mass of the wet sample stabilized and did not change by more than 0.1 mg over 24 h. The swelling ratios at different times were calculated for each sample by the mass ratio between swollen and dry sample.

Small-Angle X-ray Scattering (SAXS). SAXS measurements were done at the Danish Polymer Centre, Risø National Laboratory, using Cu Kα X-rays with a wavelength of $\lambda = 1.5418$ Å. Radiation was generated by a rotating anode operating at 3 kW and focused and filtered (only Cu Kα is selected) by a multilayer X-ray mirror and collimated by three pinholes. The scattered radiation was collected with a 2D position-sensitive gas proportional, delay line detector. 2D data were integrated azimuthally to give 1D scattering profiles of the scattered intensity as a function of the scattering vector $|\mathbf{q}| = (4\pi \sin \theta)/\lambda$, where θ is half the scattering angle (the angle between the direct and scattered beam) and λ is the wavelength of the used radiation.

Scanning Electron Microscopy (SEM). SEM measurements were done on a Zeiss 1540 EsB Gemini instrument at the Center for Microtechnology and Surface Analysis at the Danish Technological Institute. Details on sample preparation and measurement procedure may be found in ref 14.

Results and Discussion

All the cross-linked samples prepared for this study were made from the same "mother" polymer, a 1,2-PB-*b*-PDMS block copolymer with the following properties:

The number-average molecular weight (M_n) was 15.03 kg/mol, as determined by SEC and ^{1}H NMR.[14] The volume fraction of PDMS (f_{PDMS}) was 0.294, and 90.5% of the repeating units in the polybutadiene block were 1,2-units, as determined by ^{1}H NMR spectroscopy. The polydispersity index (PDI) of 1,2-PB-*b*-PDMS relative to PS SEC calibration was 1.22. The order-to-disorder transition temperature was 260 °C as measured by rheology (data not shown). Because of the composition, the 1,2-PB-*b*-PDMS was expected to have a hexagonal cylindrical morphology with PDMS segregated into cylindrical domains, which was supported by SAXS data and the rheology response.[14]

The first step of sample preparation was to produce a series of variously cross-linked samples from the mother block copolymer. Table 1 lists the cross-linking conditions and characterization data for the cross-linked 1,2-PB-*b*-PDMS samples, which are named by the prefix "X" followed by a numeral. For each sample the numeral identifies the ratio between the concentration of double bonds which were consumed during the cross-linking procedure ($n_{db,c}$) relative to the concentration of original double bonds in the 1,2-PB-*b*-PDMS precursor sample ($n_{db,0}$). Below we will explain how this ratio ($n_{db,c}/n_{db,0}$) is measured and how it can be related to the degree of cross-linking.

The cross-linking of 1,2-PB is a chain reaction,[14] which is the reason why only few molar percent of DCP relative to the double bonds is sufficient to generate a well cross-linked network. Generally the trend for the cross-linked samples in Table 1 is that an increased fraction of double bonds is consumed as the cross-linker (DCP) concentration and/or the cross-linking time increases. This is illustrated in Figure 1, where the FT-IR spectra of the original 1,2-PB-*b*-PDMS and samples X 0.11, X 0.41, and X 0.62 are shown. The DCP concentration used in the cross-linking of sample X 0.11 was half of that used for sample X 0.41, and the cross-linking time was 1 h in both cases. The concentration of DCP was the same in the cross-

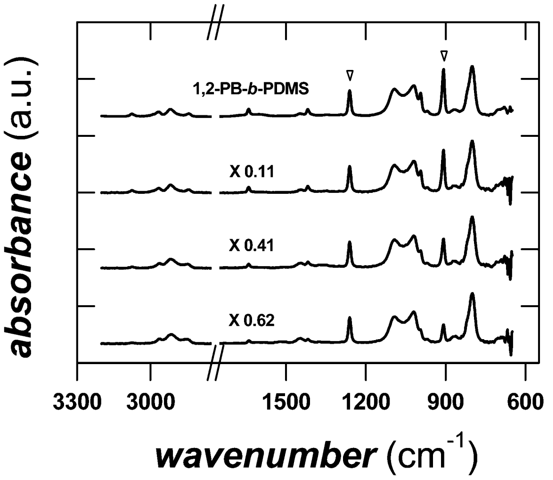

Figure 1. FT-IR spectra of (a) 1,2-PB-*b*-PDMS, (b) X 0.11, (c) X 0.41, and (d) X 0.62. Bottom-up triangles mark the absorption bands at 908 cm^{-1} (out-of-plane C$-$H bending peak in $=CH_2$) and 1261 cm^{-1} (CH_3 bending in PDMS), which were used for the quantification of double bond concentration. The absorbance in the range between 2750 and 1750 cm^{-1} for the all samples is completely flat and omitted for clarity.

linking of X 0.41 and X 0.62, but the cross-linking time of X 0.62 was 2 h. In the case of sample X 0.11 the fraction of consumed double bonds is lower than in the case of sample X 0.15, despite the higher concentration of DCP in the first case (see data on the first two samples in Table 1). This discrepancy at the low end of DCP concentration range is probably due to slight differences in the sample temperature during the cross-linking reaction of the two samples. Another possibility is the presence of different (though very low) oxygen concentrations in the two cases. The important point is that an increased consumption of double bonds correlates to an increased cross-linking degree for all the samples, as will be discussed below in relation to the swelling degree of the samples in toluene.

Two peaks in the FT-IR spectra were selected to quantify the concentration of double bonds in the samples after cross-linking relative to the precursor polymer. The out-of-plane C$-$H bending peak in $=CH_2$ at 908 cm^{-1} represents the double bonds of 1,2-PB, and the CH_3 bending peak at 1261 cm^{-1} represents PDMS (see marked peaks in Figure 1). Separate measurements (not shown) indicate that the cross-linking does not affect the PDMS block which allows us to take the PDMS peak as an internal standard.[11] Therefore, the ratio between the intensities at 908 and 1261 cm^{-1} is directly proportional to the number of 1,2-PB double bonds present in the samples. The ratio of the number of double bonds ("db") in a cross-linked sample ($n_{\mathrm{db,x}}$) relative to the number of double bonds in the mother polymer ($n_{\mathrm{db,0}}$) is easily found by comparison of FT-IR data of cross-linked samples and the unreacted mother polymer. The ratios $n_{\mathrm{db,x}}/n_{\mathrm{db,0}}$ are listed in the fifth column of Table 1, and the fraction of double bonds consumed by the cross-linking, $n_{\mathrm{db,c}}/n_{\mathrm{db,0}}$, is simply $n_{\mathrm{db,c}}/n_{\mathrm{db,0}} = 1 - n_{\mathrm{db,x}}/n_{\mathrm{db,0}}$. The FT-IR results are in good agreement with results obtained by Raman spectroscopy, which are shown in the sixth column of Table 1. Depending on DCP concentration and cross-linking time, the fraction of consumed double bonds varies in the range from 11% to 82%.

Clearly, the swelling ratio of cross-linked 1,2-PB-*b*-PDMS samples in toluene must reflect the cross-linking of the samples. The values of weight equilibrium swelling ratio for the different samples are shown in the seventh column of Table 1. These results show that the equilibrium swelling is dependent on the fraction of consumed double bonds in the cross-linked 1,2-PB matrix. Notice that the swelling ratio is only 1.15 for the sample with the highest cross-linking degree X 0.82. The plot of swelling ratio vs fraction of consumed double bonds is shown in Figure 2.

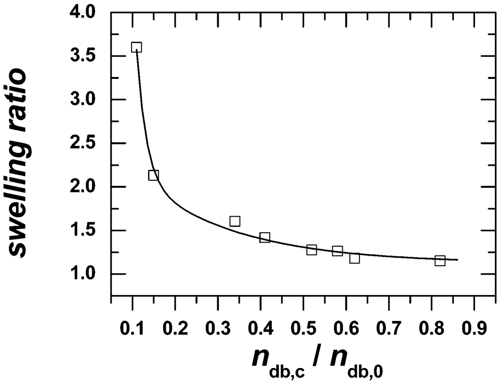

Figure 2. Plot of swelling ratio in toluene vs fraction of consumed double bonds for cross-linked 1,2-PB-*b*-PDMS. The curve is a guide to the eye. The swelling ratio is the mass ratio between equilibrium swollen and dry sample.

The more double bonds consumed during sample preparation, the higher the degree of cross-linking of the resulting network, which physically leads to less swelling of the samples in toluene. Neither the loss of double bonds during cross-linking nor the degree of swelling readily gives us a parameter which describes the molecular structure of the resulting network. In search of such a model parameter we consider the average molecular weight M_c between neighboring network cross-links. Well aware of possible shortcomings of the model as applied to the present situation,[15] we nevertheless attempt to describe the swelling data in the form required by the Flory model.[16] To test the applicability of the model, eight samples of 1,2-PB homopolymer were cross-linked at the same conditions as the block copolymer samples. The swelling degree of the homopolymer as a function of consumed double bonds is similar to that found for the block copolymer, as is reported in the Supporting Information. The Flory model states

$$M_c = -\rho[V_1(\upsilon_2^{1/3} - \omega\upsilon_2)]/[\ln(1 - \upsilon_2) + \upsilon_2 + \chi_{12}\upsilon_2^{2}] \quad (1)$$

where M_c is the average molecular weight between neighboring cross-links, ρ is the overall density, V_1 is the molar volume of solvent (107 cm^3/mol for toluene), υ_2 is the polymer volume fraction at equilibrium swelling, χ_{12} is the solvent$-$polymer interaction parameter (0.47 for toluene$-$1,2-PB[17]), and ω is twice the inverse of the cross-link functionality (here, we take ω as 0, which is the limit for very high cross-linking functionality). Polymer volume fractions at equilibrium swelling can be calculated from the swelling ratios, and values of M_c are listed in the last column of Table 1. The molecular weight between cross-links (the same as a network strand) can easily be transformed into an average degree of polymerization per strand N_c by $N_c = M_c/M$, where M is the molar mass of the PB monomeric unit. Figure 3 shows the dependency of the consumed fraction of double bonds on the inverse of the average polymerization degree per network strand $1/N_c$. This relationship is, to a good approximation, linear, and it serves as a justification for using the fraction of the consumed double bonds in 1,2-PB as a direct measure of the cross-linking degree of this polymer from which we will prepare nanoporous materials (see also the Supporting Information).

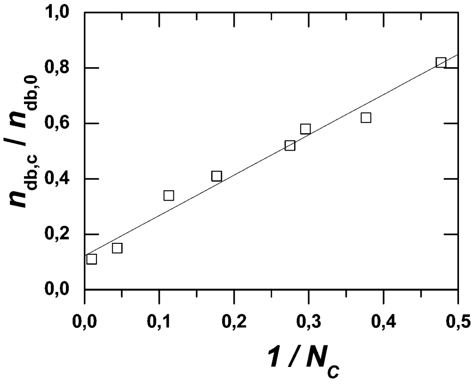

Figure 3. Relationship between the consumed fraction of double bonds and the inverse of the calculated average polymerization degree per network strand $N_{c,\ Flory}$. The equation of the linear fit is $y = 1.45x + 0.12$ with $R = 0.99$.

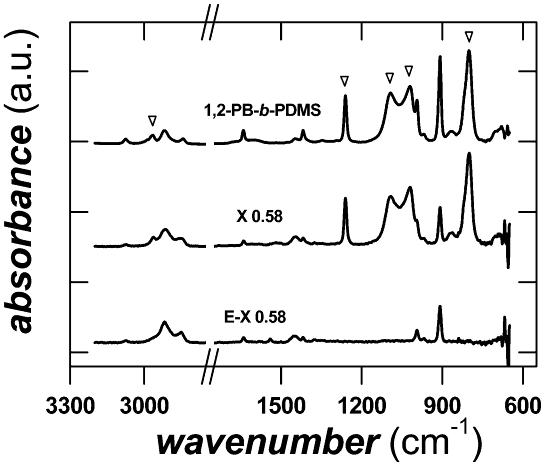

Figure 4. FT-IR spectra of (a) 1,2-PB-*b*-PDMS, (b) X 0.58, and (c) E-X 0.58. Five characteristic peaks of absorbance for PDMS are marked by bottom-up triangles.

The etched samples are named by adding the prefix “E” to the name of the corresponding cross-linked sample. TBAF in THF was used as etching reagent for the cross-linked 1,2-PB-*b*-PDMS samples. FT-IR was used to monitor the chemical composition changes of 1,2-PB-*b*-PDMS after etching. Figure 4 shows a sequence of absorbance spectra on samples illustrating the progression of preparation: the FT-IR spectra of original 1,2-PB-*b*-PDMS, the cross-linked sample X 0.58, and the corresponding etched sample E-X 0.58. The complete removal of PDMS is clearly evidenced by the disappearance of the characteristic absorbance bands for PDMS at the five marked peaks. An accurate determination of the change in double bond concentration as a result of the etching reaction is difficult to obtain alone from the FT-IR spectra of the sample before and after etching. In a separate experiment, a solution of the precursor block copolymer in THF was reacted for 36 h with TBAF, under similar conditions as those applied for the cross-linked samples. No double bonds were observed lost after the reaction, within the ^{1}H NMR accuracy. This was taken as an indication that virtually all of the double bonds in cross-linked 1,2-PB-*b*-PDMS prevail after etching. These remaining double bonds offer the possibility of changing the surface characteristics of pore walls by chemical reactions with other functional groups.[18]

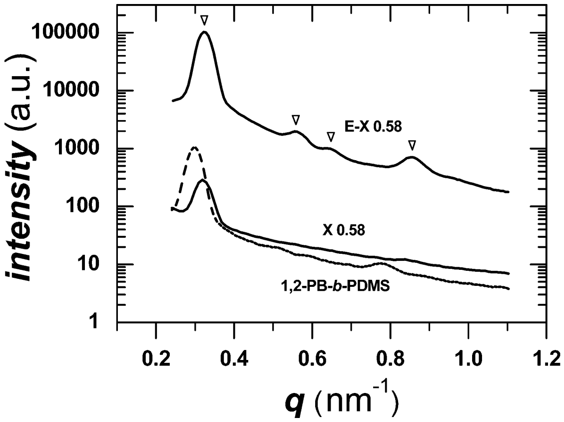

Figure 5. SAXS 1D profiles of (a) E-X 0.58, (b) X 0.58, and (c) 1,2-PB-*b*-PDMS (dashed line) showing the scattered intensity as a function of the scattering vector length *q*. The characteristic peaks for hexagonally packed cylinder morphology are marked (*q*-ratios relative to the principal peak: 1, $3^{1/2}$, $4^{1/2}$, $7^{1/2}$).

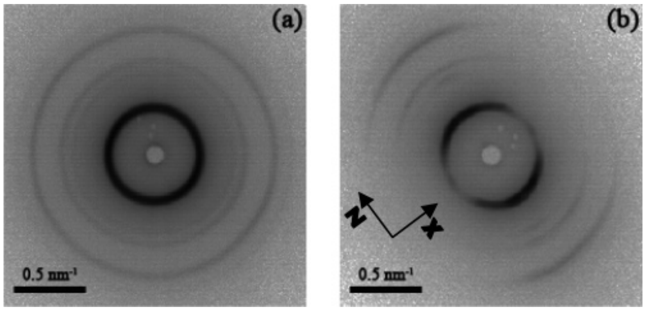

Figure 6. SAXS 2D profiles of (a) solvent-cast sample E-X 0.58 and (b) extruded sample E-X 0.62. The shear direction (**x**) and the neutral direction (**z**) of the extrusion are noted in (b).

Figure 5 shows SAXS 1D profiles of the same series of samples shown in Figure 4, illustrating the progression of preparation. The scattering pattern is consistent with a morphology of hexagonally packed cylinders. Four characteristic peaks are marked in the figure for the etched material. The scattering intensity of the primary peak for the etched sample has increased significantly relative to that of the cross-linked sample. This is due to the removal of PDMS during etching, which causes an increased electron density contrast as a result of PDMS replacement by vacuum ($\rho_e \approx 0$). The data confirm the preparation of nanoporous 1,2-PB with hexagonal cylindrical morphology. Figure 5 also reveals the small length change of the principal scattering vector q^*.

The scattering vector length increases slightly from 0.298 nm^{-1} before cross-linking to 0.319 nm^{-1} after cross-linking and finally to 0.324 nm^{-1} after etching. This corresponds to a domain spacing between principal Bragg planes (d_{10}) of 21.1, 19.7, and 19.4 nm, respectively. The decrease of domain spacing is most pronounced over the cross-linking step. This could be caused by shrinkage of the matrix as a result of the cross-linking.

Figure 6 depicts SAXS 2D profiles of a solvent-cast sample (E-X 0.58, Figure 6a) and a shear-aligned sample (E-X 0.62, Figure 6b). The rings on the scattering patterns illustrate the random orientation of domains of the hexagonal cylinders in E-X 0.58. While the presence of two arcs of reflection with the beam perpendicular to the shear direction (**x**) indicates that there is a preferential orientation of the hexagonal cylinders in E-X 0.62, the arcs of intensity are located along the neutral or vorticity direction (**z**) in the extruded sample. The degree of orientation was characterized by the second order orientation factor, F_2, calculated from the SAXS 2D profile.[3,19] The scattering profile at the principal scattering length q^* as a function of the azimuthal angle was found to be bimodal, with a separation angle of 26° between the two mode maxima. The calculated values of the overall and the two partial orientation

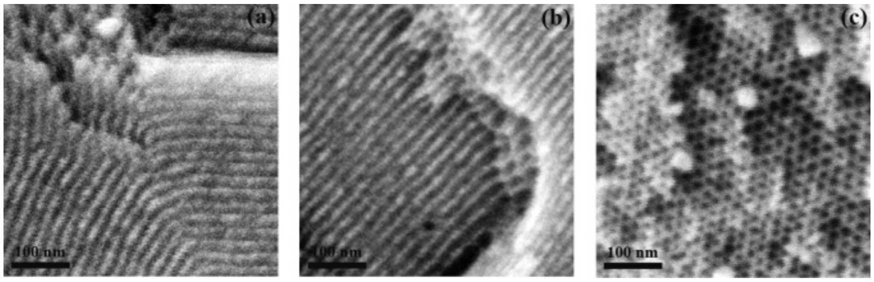

Figure 7. SEM pictures of (a) the solvent-cast sample E-X 0.82, (b) edge-on view of the shear-aligned sample E-X 0.62, and (c) end-on view of the shear-aligned sample E-X 0.62. The micrograph in (a) displays different orientations of the hexagonal domains.

Table 2. Data on Solvent Uptake, SAXS, and SEM Measurements for Etched 1,2-PB Samples

sample	equilibrium swelling ratio in toluene	equilibrium methanol uptake[a] (vol %)	d_{SAXS}[b] (nm)	d_{SEM}[c] (nm)	r_{SEM}[d] (nm)
E-X 0.11	4.59 ± 0.12	1 ± 1	no peak	n.m.[e)]	n.m.
E-X 0.15	3.25 ± 0.44	1 ± 1	no peak	n.m.	n.m.
E-X 0.34	1.87 ± 0.08	12 ± 2	17.6 ± 0.1	n.m.	n.m.
E-X 0.41	1.77 ± 0.01	18 ± 2	17.7 ± 0.1	n.m.	n.m.
E-X 0.52	1.64 ± 0.02	30 ± 1	18.9 ± 0.1	no porosity[f]	no porosity[f]
E-X 0.58	1.65 ± 0.03	29 ± 1	19.4 ± 0.1	n.m.	n.m.
E-X 0.62	1.60 ± 0.03	29 ± 1	19.3 ± 0.2	19.9 ± 1.7	4.7 ± 1.3
E-X 0.82	1.54 ± 0.04	29 ± 2	19.5 ± 0.2	18.2 ± 3.0	5.0 ± 1.0

[a] Volume fraction of methanol uptake. [b] Principal domain d_{10} spacings from SAXS. [c] Principal domain d_{10} spacings from SEM. [d] Pore radius from SEM. [e] Not measured. [f] No porosity observed by SEM.

factors were 0.62, 0.72, and 0.73, respectively (for more details see the Supporting Information).

Figure 7 shows SEM pictures of the solvent-cast sample E-X 0.82 (Figure 7a) and the shear-aligned E-X 0.62 (Figure 7b,c). The SEM micrographs cover roughly sample areas of 0.4 μm^2 and show directly the evidence for nanoporous structure in both samples. It is possible to observe a change in cylinder axis direction (a kink) of the solvent-cast sample in Figure 7a. On the other hand, the shear-aligned sample in Figure 7b showed a unique orientation of cylindrical channels. The same good alignment was observed in the micrometer length scale as the sample was shifted hundreds of microns inside the microscope. Figure 7c is an end-on SEM micrograph of the same shear-aligned sample, clearly showing hexagonally packed pores. Being 2D projections of the surface of a 3D body, SEM pictures like those shown in Figure 7 give a realistic image of alignment on flat areas of the observed surface at micron length scale. The overall alignment at macroscopic length scales is more appropriately characterized by SAXS as discussed in the previous paragraph. It was not possible to observe any porosity from the SEM of sample E-X 0.41. The samples with lower cross-linking degree were not analyzed by SEM (see Table 2).

The remaining part of this report presents a detailed discussion of the effect of cross-linking degree on X-ray scattering and solvent uptake of the etched 1,2-PB samples listed in Table 2.

The swelling ratios of the etched samples in toluene are listed in the second column of Table 2. It is clear that the swelling behavior of the etched samples follows the same tendency as that of the cross-linked samples in Table 1. The ratio between the swelling ratios for the lowest and highest cross-linked samples is roughly 3, which is similar to the corresponding ratio for the cross-linked samples in Table 1. Furthermore, all swelling ratios for the etched samples are larger than those for the corresponding cross-linked ones. This is expected as the cavities formed after the PDMS cleaving allow for higher toluene uptake.

Figure 8 illustrates the trend of the SAXS profiles from the etched samples with different cross-linking degrees. The two top profiles in Figure 8 show the scattering of samples E-X 0.82 and E-X 0.52 and display similar features as the SAXS profile shown for sample E-X 0.58 in Figure 5. The SAXS profile for sample E-X 0.62 (not shown) also shows the same features. These scattering profiles represent scattering from nanoporous materials, with a strong principal peak of scattering and some higher-order reflections. The lower profile in Figure 8 shows the scattering of sample E-X 0.15. This profile does not show any evidence for structured features that can be detected by SAXS. This suggests that there is no nanoporous structure and that the sample is collapsed during etching. Most probably, the 1,2-PB matrix is not cross-linked sufficiently to counteract the tendency of surface area minimization after the removal of PDMS. The remaining profile in Figure 8 represents the scattering of sample E-X 0.41 and shows a weak principal peak at $q^* = 0.355$ nm^{-1}. The scattering intensity of the primary peak for sample E-X 0.41 is increased by ~1 order of magnitude, comparing it to the scattering from its related cross-linked sample X 0.41 (data not shown). This is much less than the expected increase in scattering strength due to the greater contrast factor as mentioned above for the nanoporous polymers. The scattering of sample E-X 0.34 showed a principal peak of scattering (data not shown) similar to E-X 0.41. These two samples exhibit scattering which clearly is not indicating a nanoporous structure (as seen in the well-cross-linked samples) because of the relatively weak Bragg peak. On the other hand, the scattering does not resemble the scattering of the collapsed structures (as seen in the very weakly cross-linked samples) because there is still a significant peak in the scattering profile. The structure of these samples must be different from the nanoporous and the collapsed structures. We will return to the discussion of the nature of this structure after the presentation of the methanol uptake in Figure 9.

The fourth column of Table 2 lists the principal d_{10} spacing for all the etched samples as obtained from SAXS measurements. The table shows that the samples have d-spacings from 17.6 to 19.5 nm depending on the degree of cross-linking and suggests that within a range of 10% it is possible to change the domain lattice spacing via cross-linking. The fifth column of Table 2 lists the principal d_{10} lattice spacings of samples E-X 0.62 and E-X 0.82 from SEM micrographs. They show good

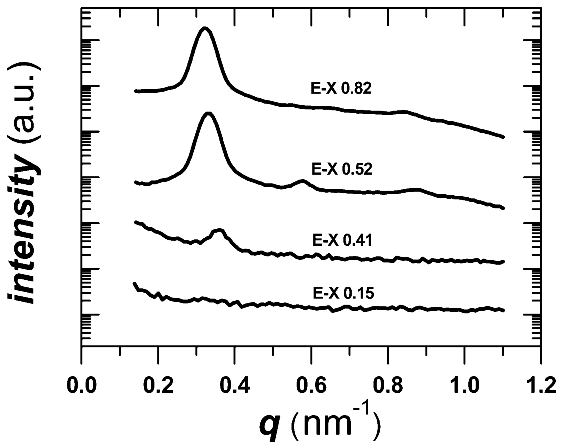

Figure 8. SAXS 1D profiles of four different etched samples with different cross-linking degree. The plots have been shifted vertically to ease comparison.

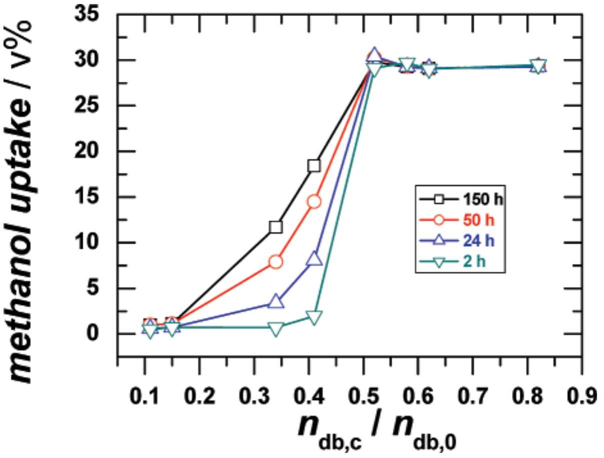

Figure 9. Volume fraction of methanol uptake for etched samples with varying cross-linking degrees after four different times (2, 24, 50, and 150 h).

agreement with the data obtained by SAXS. The pore radii obtained from SEM for these two samples are shown in the last column of Table 2.

Methanol uptake was used to investigate the porous properties of the etched samples. The volume fraction of the methanol uptake was calculated from the following expression: $V_{mu}/V_0 = (m_{mu}/0.791)/(m_{mu}/0.791 + m_e/0.902)$, where V_{mu} is the volume of methanol uptake (mu), V_0 is the original volume of the mother block copolymer, m_{mu} is the mass of methanol uptake, 0.791 g/cm^3 is the density of methanol, 0.902 g/cm^3 is the density of 1,2-PB,[20] and m_e is the mass of the dry etched sample. The values for the equilibrium methanol uptake are listed in the third column of Table 2.

Figure 9 shows the time-resolved data for methanol uptake of the different samples with varying cross-linking degree. Methanol was chosen on the basis of two reasons: First, being a nonsolvent for 1,2-PB, it would permit to fill the nanopores without swelling the bulk of the polymer. Second, having a surface contact angle with 1,2-PB less than 90°, the capillary forces would permit methanol to actually penetrate the nanopores.[14] The four sets of data shown in Figure 9 correspond to the uptake after four different contact times with methanol: 2, 24, 50, and 150 h. The samples follow three different behaviors: (i) Samples with high cross-linking degree (data with $n_{db,c}/n_{db,0} > 0.5$) show a saturated amount of methanol uptake at all plotted times. This saturation appeared for times shorter than 10 min (data not shown). (ii) Samples in the middle segment of cross-linking degree (data with $0.3 < n_{db,c}/n_{db,0} < 0.45$) show an increasing methanol uptake with time over the 150 h time span. (iii) Samples of lowest cross-linking degree (data with $n_{db,c}/n_{db,0} < 0.2$) do not take up more than few volume percent of methanol in the time span of 150 h. The volume fraction of methanol uptake for the samples in the first group is around 30%. This figure is close to the volume fraction of PDMS (29.4%) in the precursor block copolymer. These data indirectly prove that the PDMS was removed by TBAF and that pores exist in the etched samples. The uptake of methanol for the samples in the second group is a slow process. Both a thermodynamic equilibrium (related, e.g., to slight lowering of interfacial energy in the presence of methanol compared to the surface energy of the dry samples) and a kinetic argument relying on the diffusion barriers for methanol in the PB matrix could be at the basis of such a process.

The three sample categories described here also followed different sinking behavior. Samples E-X 0.11 to E-X 0.41 sank down to the bottom of the vial immediately after soaking in methanol, while E-X 0.52 to E-X 0.82, which could take up methanol to the expected limit, floated on the surface of methanol for about 30 s before sinking down to the bottom. This observation suggests a test procedure which may be used as a rapid indicator of nanoporosity for dry samples. Because of the existence of pores, the dry nanoporous samples have overall densities smaller than methanol (0.791 g/cm^3); an overall density of roughly 0.7 g/cm^3 is expected for the samples with high cross-linking degree. As a result, such a sample will float in first contact with methanol; it will actually remain floating as long as the quantity of methanol penetrating into the nanopores does not push the overall density above 0.791 g/cm^3. For the highly cross-linked samples this corresponds to methanol filling more than roughly 1/3 of the pore volume.

A combination of the structural features from SAXS measurements with the behavior diversity during methanol uptake points to a characterization scheme of the differently cross-linked 1,2-PB material. We notice that the samples E-X 0.34 and E-X 0.41 are singled out by both the SAXS scattering and the methanol uptake behavior. FT-IR data (not shown) give evidence that all PDMS is removed from these samples. The SAXS profile hints to the absence of real nanocavities, but the methanol uptake shows that some amount of methanol does indeed penetrate into the sample over time. We speculate that the removed PDMS leaves a trace behind, which may be only a modulation of the PB density in the diblock copolymer after etching with lower density values in the location of the PDMS. This density modulation gives rise to a corresponding electron density modulation which is the cause of scattering SAXS peak and also accommodates penetration of methanol into the sample. We call this intermediate structure a “traced” structure in this polymer system.

Accordingly, the material can take on one of the following three structures: nanoporous, traced, or collapsed. The borderline between the traced and the collapsed states is expected to be solvent-dependent. From unpublished data on polyisoprene nanoporous materials we know that samples in the collapsed state show “wet” nanoporous structure in the presence of toluene.

The nanoporous samples are E-X 0.52 to E-X 0.82, which take up methanol to the saturation level within 10 min. The saturation volume is close to the volume of the removed PDMS microphase. The scattering from the dry samples is strong with intense Bragg peaks.

The traced morphology samples are E-X 0.34 and E-X 0.41, which slowly take up methanol over an extended time span (150 h). The volume of methanol uptake for the sample E-X 0.41 reaches ~60% of the expected maximum limit V_{PDMS}. The SAXS profile from the dry samples shows scattering 1−2 orders of magnitude weaker than the scattering from the dry nanoporous samples.

The collapsed samples are E-X 0.11 and E-X 0.15, which do not take up appreciable volumes of methanol and display no peak in the SAXS profile.

Conclusions

In order to investigate the influence of cross-linking degree on the structure and properties of selectively etched polymers, a series of 1,2-PB-*b*-PDMS with different cross-linking degree were prepared. Thermal scission of peroxides was used to initiate the cross-linking of 1,2-PB. A simple relation between “Flory cross-linking degree” and the fraction of consumed double bonds during the cross-linking reaction was found, based on data on the swelling degree of cross-linked block copolymers in toluene. TBAF was used subsequently for the selective degradation of PDMS. The structure of the polymers in each stage of the preparation procedure was investigated by SAXS. The direct space images of microstructures realized by SEM were in agreement with the morphology as determined by SAXS. The combination of morphological results from SAXS with data on time-dependent methanol uptake suggested the presence of three different structures dependent on the cross-linking degree of the 1,2-PB matrix. In order of increasing degree of cross-linking, we designated these structures as collapsed, traced, and nanoporous.

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Supporting Information Available: Comparison of the cross-linking degree of samples derived from the 1,2-PB−PDMS block copolymer and samples derived from a 1,2-PB homopolymer; orientation factor from the 2D SAXS data on the nanoporous shear-aligned sample E-X 0.62. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(15) The system dealt with in the present paper is a block copolymer system, microphase segregated with only one of the blocks being cross-linked. This is not directly included in the domain of application of the Flory scheme. For the samples with highest cross-linking degree the cross-linking degree is too high, again pushing the system outside the applicability of the Flory scheme. In addition, the 1,2-PB is expected to changes chemical structure (cycle formation on the main chain) during the cross-linking reaction,[14] and this makes the use of a unique interaction parameter questionable. Taken these points into consideration, of course, we have our doubts on whether there is a direct physical meaning related to the calculated network strand M_c. On the other hand, the comparison of the cross-linking data of the block copolymer and a 1,2-PB homopolymer, as derived from the Flory scheme, is quite positive as shown in the Supporting Information.
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