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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. 1,2-polybutadiene-*b*-polydimethylsiloxane (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. The influence of the cross-linking degree on the bulk properties of the 1,2-PB material derived from a single block copolymer precursor was studied.

Cross-linking of 1,2-PB

The first step of sample preparation was to produce a series of variously cross-linked samples from the mother block copolymer by using dicumyl peroxide (DCP) as cross-linker. 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 cross-linking of polymer was conducted under argon at 140 °C for 1-2 h in a homemade gastight steel cylinder. Table 1 lists the cross-linking conditions 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 ($n_{db,0}$).

Table 1. Cross-Linking Conditions of Cross-Linked Samples

Sample	cross-linking conditions	
	conc. ($n_{DCP}/n_{db,0}$)	time (h)
X 0.11	0.004	1
X 0.15	0.002	1
X 0.34	0.001	2
X 0.41	0.008	1
X 0.52	0.01	1
X 0.58	0.002	2
X 0.62	0.008	2
X 0.82	0.02	2

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.

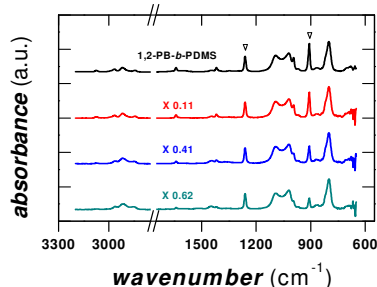


Figure 1. FT-IR spectra of (a) 1,2-PB-*b*-PDMS, (b) X 0.11, (c) X 0.41, and (d) X 0.62.

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 =CH₂ at 908 cm⁻¹ represents the double bonds of 1,2-PB, and the CH₂ 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. 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.

Clearly, the swelling ratio of cross-linked 1,2-PB-*b*-PDMS samples in toluene must reflect the cross-linking of the samples. The plot of swelling ratio vs. fraction of consumed double bonds is shown in Figure 2. 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.

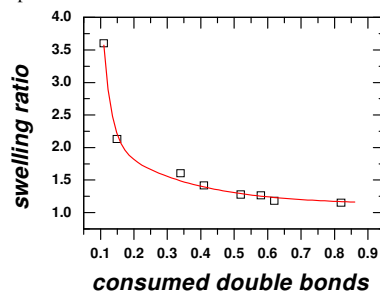


Figure 2. Plot of swelling ratio in toluene vs. fraction of consumed double bonds for cross-linked 1,2-PB-*b*-PDMS. The red curve is a guide to the eye. The swelling ratio is the mass ratio between equilibrium swollen and dry sample.

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. The etched samples are named by adding the prefix "E" to the name of the corresponding cross-linked sample.

SEM micrographs of E-X 0.62 as shown in Figure 3 show directly the evidence for nanoporous structure.

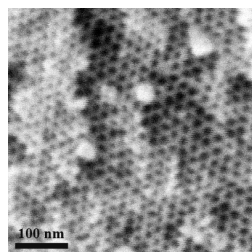


Figure 3. SEM picture of E-X 0.62.

Figure 4 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. 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 4 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. The remaining profile in Figure 4 represents the scattering of sample E-X 0.41 and shows a weak principal peak. This exhibits scattering which clearly is not indicating a nanoporous structure 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 E-X 0.15) 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.

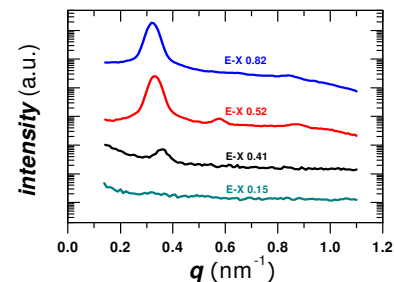


Figure 4. SAXS 1D profiles of four different etched samples with different cross-linking degree. The plots have been shifted vertically to ease comparison.

Figure 5 shows the time-resolved data for methanol uptake of the different samples with varying cross-linking degree. 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. (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.

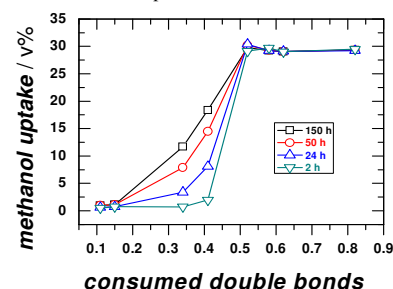


Figure 5. Volume fraction of methanol uptake for etched samples with varying cross-linking degrees after four different times (2, 24, 50, and 150 h).

Conclusions

Degree of 1,2-PB crosslinking determines material properties after etching. 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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