Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2016

RSC Advances

Electronic Supplementary Information

13th March 2016,
DOI: 10.1039/x0xx00000x

Self-assembled structure and relaxation dynamics of diblock copolymers made of polybutadiene and styrene/butadiene rubber

C.A. da Silva,[a,b] H. Budde,[c] M. Menzel,[d] U. Wendler,[c] M. Bartke,[c] M. Weydert,[a] M. Beiner[b,d,†]

Structural investigations on non-crosslinked PB-SBR diblock copolymers

Small - Angle X-Ray Scattering (SAXS) measurements were performed on non-crosslinked samples (without crosslinking additives). Thin films were prepared by pressing small polymer pieces in a frame of 10x30x2 mm^3 with hydraulic pressure of 4 bar, at 160°C for 5 min. SAXS measurements were carried out at room temperature using a pinhole instrument designed by JJ X-rays on a Rigaku rotating anode as radiation source (CuKα, λ = 0.1542 nm) with an Osmic multilayer optics, and a Bruker Hi-Star 2D detector. The scattering angle of the instrument was calibrated using silver behenate as reference material. The accessible q-range was $0.065\ \mathrm{nm}^{-1} \leq q \leq 0.5\ \mathrm{nm}^{-1}$. The sample-to-detector distance was about 1580 mm.

Microphase separated state and morphology of the non-crosslinked diblock copolymers are analyzed by small-angle X-ray scattering (SAXS). SAXS pattern measured at room temperature are shown for all samples under investigation in **Figure A1** (a). The scattering pattern for most of the symmetric PB-SBR diblock copolymers (**Series I**) indicate a well-ordered lamellar morphology formed due to microphase-separation of the soft (PB) and hard (SBR) blocks. The periodicities taken from Bragg's law $d = 2\pi/q_{\mathrm{max}}$ are listed in **Table 1**. Commonly d values in the range 65 ± 15 nm are observed. Note that the higher order peak at $3q_{max}$ is usually well pronounced while the peak at $2q_{max}$ is suppressed, which is a common feature of systems with volume fractions Φ_{SBR} very close to 50% due to the influence of the form factor. The only exception is the block copolymer sample containing only 21 mol% styrene in the SBR block. In this case mainly one peak is observed while higher order peaks are extremely weak or absent. This may indicate that this sample is close to the disordered state at room temperature. This seems to be reasonable for low styrene concentrations in the SBR block where a tendency toward miscibility is to be expected. Note that a certain increase of the peak width is already indicated in case of the sample containing 27 mol% S in the SBR block (in particular for the third order peak). This might be a first hint for reduced long range order and weak segregation.

SAXS pattern for asymmetric diblock copolymers (**Series II**) in the non-crosslinked state are presented in **Figure A1** (b). Although a strong diffraction peak at low q values is present for all samples, morphology information is in most of the cases

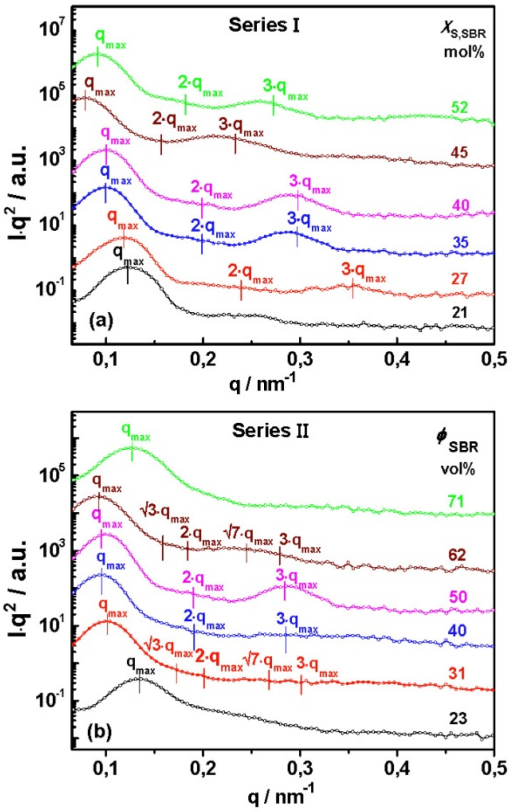

Figure A1. Lorentz-corrected SAXS patterns measured at room temperature for the non-crosslinked **(a)** symmetric (***Series I***) and **(b)** asymmetric (***Series II***) PB-SBR diblock copolymers. The patterns are vertically shifted to the sake of clarity

---

[a] *Goodyear Innovation Center Luxembourg, L-7750 Colmar-Berg, Luxembourg.*
[b] *Martin-Luther-Universität Halle-Wittenberg, Naturwissenschaftliche Fakultät II, D-06099 Halle (Saale), Germany.*
[c] *Fraunhofer PAZ, Value Park A74, D-06258 Schkopau, Germany.*
[d] *Fraunhofer IMWS, Walter-Hülse-Str. 1, D-06120 Halle (Saale), Germany*
† Corresponding author. (Email: mario.beiner@imws.fraunhofer.de).

not available since higher order peaks are either smeared or absent. However, AFM pictures of the corresponding crosslinked samples prepared at 150°C (**Figure 1**) show for various samples (31 vol% ≤ Φ_{SBR} ≤ 62 vol%) a well-defined microphase separated structure. Hence, the absence of higher order peaks in the SAXS pattern for these non-crosslinked samples is probably caused by limited long range order. Expected positions for the higher orders in the SAXS patterns for the different volume fractions are incorporated in **Figure A1** (b). Periodicities for non-crosslinked samples are determined based on the position of the first scattering peak and Bragg's law (**Table 1**).

The periodicities *d* for symmetric samples with styrene contents higher than 27 mol% indicates together with volume fractions close to Φ_{SBR} = 0.5 thicknesses of the individual PB and SBR layers of about 30-35 nm (except the sample containing 45 mol% S showing a slightly larger *d* values due to its higher molecular weight). The periodicities for the asymmetric samples are in the same range (50-70 nm).

SAXS data for crosslinked samples are not useful since the presence of additives like zinc oxide (ZnO) and stearic acid causes strong additional scattering contributions making it impossible to extract information about the block copolymer morphology. As a representative example, **Figure A2** shows acomparison of the SAXS pattern for the PB_{50}-$S^{35}B^{65}R_{50}$ samples in the non-crosslinked (additive-free) and crosslinked state. A decay-like behavior without obvious scattering peaks is observed for the crosslinked sample. This is due to scattering contributions of well dispersed particles masking those of the periodic block copolymer matrix. This phenomenon has already been reported for crosslinked SBR rubbers containing dispersed ZnO particles [I. Morfin, F. Ehrburger-Dolle, I. Grillo, F. Livet, F. Bley, *J. Synchrotron Radiat.* 2006, **13**, 445-521]. As shown on AFM images in Figure 1 the absence of diffraction peaks in the SAXS pattern for the crosslinked samples is definitively not caused by a missing long-range order after the mixing and vulcanization processes. Accordingly, by plotting a Kratky plot like ($I(q)\cdot q^3$ vs. q) it was possible to observe a small shoulder for crosslinked samples at the same q_{max} of its corresponding non-crosslinked sample. This is shown in the insert of **Figure A2** and clearly indicates that domain size was maintained for samples in the strongly segregated state after processing.

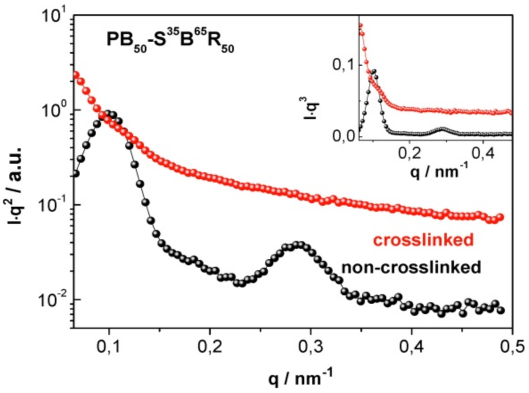

Figure A2. Lorentz-corrected SAXS patterns measured at room temperature for the diblock copolymer sample PB_{50}-$S^{35}B^{65}R_{50}$ in the non-crosslinked (red) and crosslinked (black) states. The inset shows a plot Iq^3 vs. q where the presence of a scattering peak near 0.1 nm^{-1} is indicated for both samples.

Temperature dependence of the shift factors for different α relaxation processes

In order to quantify the temperature dependence of the cooperative α dynamics in pure PB and SBR domains the individual shift factors $(a_T)_{PB}$ and $(a_T)_{SBR}$ are fitted using the Vogel-Fulcher-Tammann (VFT) equation

$$\log(a_T) = \log(a_{T,0}) - \frac{B}{T - T_\infty} \tag{A1}$$

where $a_{T,0}$ is the extrapolated shift factor at infinite temperature, B is the curvature and T_∞ is the Vogel temperature where the extrapolated α relaxation time diverges. Eq.(1) describes quite well the segmental α dynamics in many glass forming materials over a wide temperature range. The VFT parameters for the investigated samples are listed in **Table A1**. Note that only the value of $a_{T,0}$ is dependent on the reference temperature chosen for the master curve construction while the other parameters should be unaffected.

Table A1: VFT fit parameters for crosslinked diblock copolymers in the microphase-separated state and corresponding homopolymers.

	PB phase					SBR phase				
Label	$T_g^{\$}$ °C	$T_\alpha^{10\ rad/s}$ °C	$\log(a_{T,0})$	B K	T_∞ °C	$T_g^{\$}$ °C	$T_\alpha^{10\ rad/s}$ °C	$\log(a_{T,0})$	B K	T_∞ °C
Series I										
PB_{53}-$S^{35}B^{65}R_{47}$	-92.4	-81.5	9.1	200	-107	-25.8	-25.0	15.5	701	-72
PB_{54}-$S^{40}B^{60}R_{46}$	-93.1	-81.7	10.8	315	-114	-18.8	-17.7	15.9	660	-63
PB_{54}-$S^{45}B^{55}R_{46}$	-93.4	-83.0	9.0	195	-108	-9.2	-6.5	14.9	620	-51
PB_{54}-$S^{52}B^{48}R_{46}$	-93.8	-81.3	9.1	220	-107	-2.7	-0.3	19.0	1120	-63
Series II										
PB_{70}-$S^{30}B^{70}R_{30}$	-92.1	-82.3	11.6	298	-111	-35.8	-30.1	13.2	640	-83
PB_{62}-$S^{30}B^{70}R_{38}$	-92.7	-82.6	10.5	266	-111	-33.5	-33.0	14.7	650	-77
PB_{53}-$S^{35}B^{65}R_{47}$	-93.1	-81.5	9.1	200	-107	-25.8	-25.0	15.5	701	-72
PB_{40}-$S^{35}B^{65}R_{60}$	-92.4	-83.8	17.0	760	-131	-23.8	-27.4	14.2	573	-67

\$ taken from DSC scans on non-crosslinked samples