

Structural study on star bottlebrush elastomer under uniaxial deformation

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1 Introduction

Bottlebrush (BB) polymers, in which a backbone chain is densely grafted with side chains, are an attractive class of polymer due to its unique structure and properties. In particular, it combines high flexibility of the chain and low tendency to entangle, making it suitable for the component of ultrasoft materials. Recently, ultrasoft elastomers based on cross-linked BB polymers have been extensively studied to mimic mechanical properties of soft biological tissues. However, BB elastomers are usually synthesized by random copolymerization, which inevitably introduces various defects in the network structure and makes it difficult to predict the network property. In this study, we report the structural study of the BB elastomer with controlled network structure synthesized by end-linking of star-shaped BB polymer.

2 Experiment

The BB elastomer (Fig. 1) was prepared by drying a BB polymer gel synthesized according to our previous work [1]. A dumbbell-shaped test piece was subjected to in situ SAXS measurements coupled with uniaxial tensile testing. The test piece was stretched at a constant rate $d\lambda/dt = 0.001 \text{ s}^{-1}$ where λ is the stretch ratio, during which the SAXS measurements were repeated at 10 s exposure and 40 s interval. The experiments were performed at BL-6A in KEK-PF using a custom-made tensile tester.

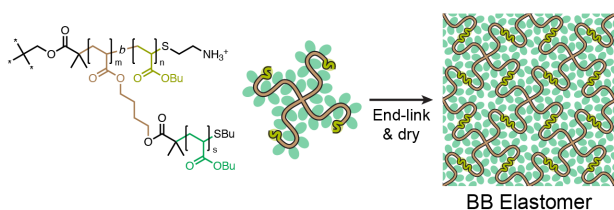


Fig. 1: Preparation of the BB elastomer.

3 Results and Discussion

Fig. 2 shows the stress-strain (SS) curve and the representative 2D SAXS images. The dashed curve represents the prediction of the neo-Hookean model using the observed Young's modulus. The observed stress clearly deviate upward from the model prediction, demonstrating the strain-stiffening behavior characteristic of BB elastomers. Upon examination of the SAXS images, two distinct peaks can be seen as diffuse rings: the high- q peak can be assigned to the interchain correlations among the poly(*n*-butyl acrylate) (PnBA) side chains while the low- q peak was assigned to the interbackbone correlations between the backbone chains of the BB polymer.

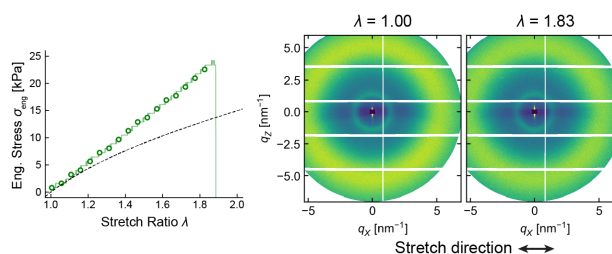


Fig. 2: Stress-strain curve and representative 2D SAXS images during the uniaxial tensile test. The dashed curve indicate the prediction of the neo-Hookean model with the identical Young's modulus.

At first glance, the SAXS image does not show any noticeable changes upon stretching of the elastomer. Therefore, we performed sector-averaging followed by peak deconvolution to extract the intensity profiles of the two peaks as a function of the azimuthal angle β and the stretch ratio λ (Fig. 3). The interbackbone correlation peak shows a concentration of intensity around $\beta = 90^\circ$ (perpendicular to the stretching direction), indicating that the backbone chains are oriented along the stretching direction. Interestingly, the side chain correlation peak does not show any anisotropy up to maximum λ . These results suggest that the strain stiffening is accompanied by the alignment of the backbone chains, caused by steric repulsion among the unoriented side chains.

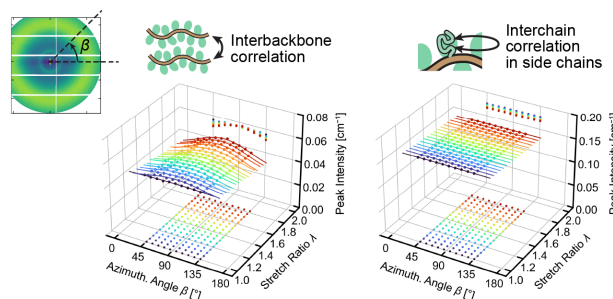


Fig. 3: Peak intensities plotted as a function of azimuthal angle β and stretch ratio λ .

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References

- [1] S. Nakagawa and N. Yoshie, *ACS Macro Lett.* **10**, 186 (2021).

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