

Strain-induced crystallization in noncrystalline homogeneous polymer networks

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1 Introduction

Crosslinked elastomer (rubber) has been an important class of material since the discovery of vulcanization by Goodyear in the mid-19th century. Elastomers find utility in various applications, from car tires to medical appliances, due to their high deformability and elastic nature. Crosslinked polymers are conventionally fabricated either by random inter-chain coupling or random copolymerization of monomers and crosslinkers, both of which inevitably lead to various inhomogeneities in the polymer network structure. The inhomogeneities would deteriorate the mechanical properties of the material. A promising way to achieve more homogeneous network structure is the "module-assembly" strategy, in which the network is constructed by end-linking of monodisperse star-shaped prepolymers[1]. Herein, we report the development and characterization of a tough elastomer synthesized via the module-assembly strategy[2]. By means of the in situ small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) measurements, we have found that the homogeneous network structure led not only to the excellent stretchability but also an unprecedented phenomenon: strain-induced crystallization of noncrystalline polymer chains.

2 Experiment

Fig. 1 shows the synthetic scheme of the elastomer. 4-arm or 3-arm star poly(4-methyl- ϵ -caprolactone) (PMCL) with phenylmaleimide end groups was synthesized and end-linked via thiol-maleimide reaction with a dithiol linker, yielding a gel. Then the solvent was removed from the gel to obtain a solvent-free elastomer. The in situ SAXS/WAXS during uniaxial testing was performed at BL15A2 in KEK-PF using a custom-built tensile tester. A dumbbell-shaped test piece of the elastomer was stretched at a constant speed and the SWAXS data were collected successively during the stretching process.

3 Results and Discussion

The stress-strain curve of the elastomer is shown in Fig. 2. The elastomer showed not only an excellent tensile strength and stretchability but also an unusually abrupt upturn in the stress starting at the stretch ratio of $\lambda \sim 15$, i.e., it showed a significant strain stiffening. Although soft materials such as rubber and biological tissues tend to show strain stiffening, the strain stiffening capability of our elastomer was unprecedented by any other soft materials known to date.

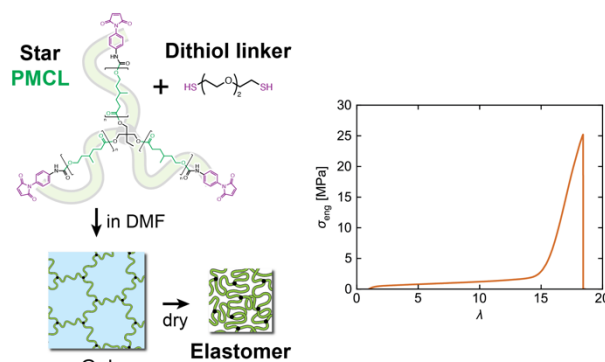


Fig. 1. Synthetic scheme.

Fig. 2. Stress-strain curve of the synthesized elastomer.

We performed in situ X-ray scattering measurements on the elastomer during uniaxial tensile testing. Fig. 3 shows a representative two-dimensional WAXS patterns along the direction perpendicular to the stretching direction. While the WAXS pattern exhibits only an amorphous halo at low stretch ratios, a distinct bright spot appears at high stretch ratios. A one-dimensional WAXS profile at the highest stretch ratio tested ($\lambda = 12.3$) is also shown in Fig. 3. A distinct peak and a shoulder are discernible, which indicate the presence of crystal-like ordered structure. We emphasize here that the main component of our elastomer, PMCL, is a totally non-crystallizable amorphous polymer. We found that even non-crystallizable polymer chains underwent strain-induced crystallization when subjected to extreme strain in a homogeneous network. The strain-induced crystallization should be mainly responsible for the extraordinary strain stiffening capability and tensile strength. We hope that the unique mechanical property of the elastomer will open new application fields of elastomers.

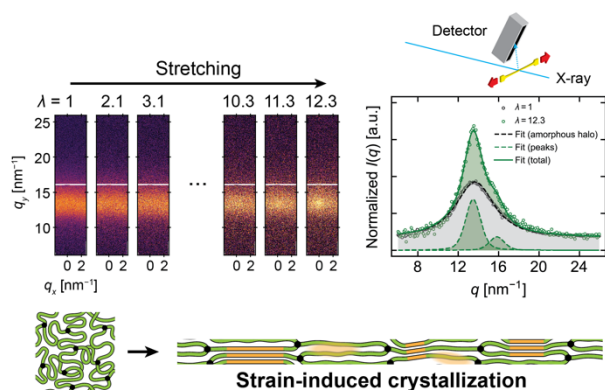


Fig. 3. In situ WAXS analysis of the elastomer during uniaxial tensile testing.

Acknowledgment

This work was supported by JSPS KAKENHI Grant No. 21K14678 and JACI Prize for Encouraging Young Researcher. The author thank Prof. Naoko Yoshie (The University of Tokyo) and Prof. Daisuke Aoki (Chiba University) for their kind help on this research.

References

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