

Study on Polymer Networks Prepared from Star-shaped Vinyl Polymers

Shintaro Nakagawa^{1,*}, Xin Huang¹, and Naoko Yoshie¹¹ Institute of Industrial Science, The University of Tokyo

4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

1 Introduction

Properties of crosslinked polymer networks such as gel and elastomer depend on the homogeneity of the network structure. Polymer networks usually possess a significant level of inhomogeneity due to random nature of crosslinking reaction. Recently, end-linking of monodisperse star-shaped polymers has been proven to be an effective way to prepare highly homogeneous polymer networks. However, most of the studies focus only on a limited kinds of polymer, which may restrict the possible applications. In this study, we developed a versatile method to prepare polymer networks from various kinds of vinyl homopolymers and copolymers and examined their homogeneity and mechanical properties.

2 Experiment

Star-shaped polymers were synthesized by atom transfer radical polymerization (ATRP) of vinyl monomers. The monomers used are *n*-butyl acrylate (BA), (4-hydroxybutyl) acrylate (HBA), (4-trimethylsilyloxybutyl) acrylate (TMSBA), methyl methacrylate (MMA), and styrene (S). The star polymer, having an alkyl bromide group at each chain end, was reacted with a stoichiometric amount of a dithiol linker in the presence of appropriate organic base, which yielded an organogel. For preparation of a dry elastomer, the gel was washed in pure solvents and thoroughly dried in vacuo. The structure of the gels and elastomers were examined by small-angle X-ray scattering (SAXS) measurements performed at BL-6A, KEK-PF.

3 Results and Discussion

We first prepared a gel from four-arm star-shaped PBA. A mixture of star PBA, bifunctional thiol linker, and an organic base turned from solution to gel. This was due to the nucleophilic substitution of bromide chain ends with thiolate. Rheological measurements revealed that the elasticity of the gel was comparable to the theoretical prediction, suggesting the high homogeneity of the network. Fig. 1 shows the SAXS profile of the PBA gel. The linearity in the Zimm representation of the profile indicates that the profile obeys the Ornstein-Zernike function which describes the concentration fluctuations from homogeneous media. Overall, the results strongly suggest that the PBA gel synthesized by our method had relatively homogeneous network structure. The major advantage of our method is that it does not need tedious end-group modifications: the polymer synthesized by ATRP can be directly end-linked. This is because the process uses the alkyl bromide group as the reaction point for both ATRP and subsequent end-linking reaction.

We also explored the applicability of our methods to other vinyl monomers. It was possible to synthesize a gel from PHBA, PTMSBA, or a copolymer of BA and TMSBA in a similar manner as the PBA gel. PMMA and PS, which were other types of common vinyl polymers, could also be made into a gel with a small modification of the original method, where a few BA repeat units were added to the chain ends to improve the reactivity.

As an application of the developed method, we prepared elastomers with homogeneous network structure reinforced by hydrogen bonds (H-bonds). Incorporation of transient bonds into polymeric materials is a key strategy to improve mechanical performances. We aimed to quantify the impact of different kinds of H-bonding groups to the mechanical properties of an identical homogeneous network. Elastomers with randomly embedded hydroxy (OH), urethane (U), or carboxylic acid (COOH) groups were prepared based on a network of a copolymer of BA and HBA. Fig. 2a shows the SAXS profiles of the obtained dried elastomers. There is no appreciable peak or shoulder, suggesting the homogeneity of the network as well as the homogeneous dispersion of the embedded H-bonding groups. The results of the tensile tests of the elastomers are shown in Fig. 2b. The stress clearly improves by introducing H-bonding groups.

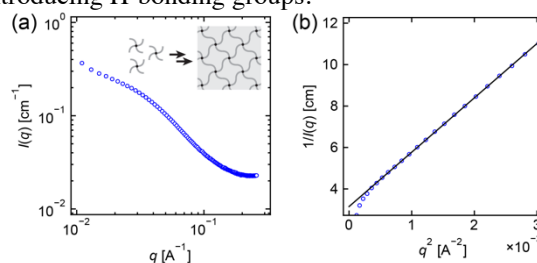


Fig. 1: SAXS profile of the PBA gel.

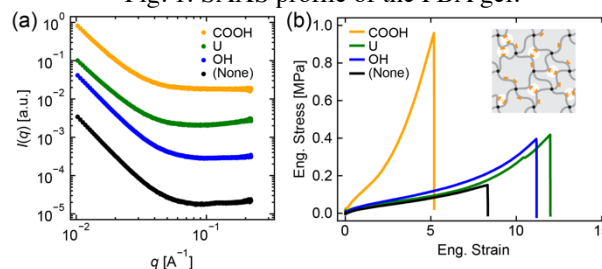


Fig. 2: SAXS profile (a) and stress-strain curve (b) of elastomers containing H-bonding groups.

References

- [1] X. Huang et al. *Angew. Chem. Int. Ed.* **59**, 9646 (2020).
- [2] X. Huang et al. *Macromolecules* **54**, 4070 (2021).

* snaka@iis.u-tokyo.ac.jp