

Photocleavable Regenerative Synthetic Elastomers for the On–Off Switching of Mechanical Properties

Photocleavable and regenerative networks (PRNs) have potential applications for dismantlable adhesives and recyclable elastomeric materials. In this study, we developed PRNs composed of polydimethylsiloxane (PDMS) and photoresponsive hexaarylbiimidazole (HABI) and successfully applied them as a solventless photodismantlable adhesive that can be remotely peeled off with a commercial laser pointer. The uniformity of the internal structure of PRNs at the nanoscale was investigated by synchrotron radiation small-angle X-ray scattering (SAXS) analysis.

Synthetic elastomers with three-dimensional network structures linked by covalent bonds, i.e., network polymers, have been utilized in a broad spectrum of applications, such as in adhesives, tires, sealants, rubbers, and 3D printing materials. While their insolubility and infusibility lead to their excellent thermal and chemical resistance, their durable nature hampers resource recycling once they have been synthesized. Hence, there has been a strong demand to develop synthetic elastomers with stimuli-responsive scissible network structures for a sustainable future, and various stimuli-responsive network polymers have been proposed to date [1]. While most of them utilize heat as an external stimulus, it is generally difficult to apply heat stimulation only at a targeted location of the material. On the other hand, photostimulation has temporal and spatial locality and thus would be preferable for modulating properties of network polymers only at a targeted location at the desired timing [2, 3]. In this context, we previously synthesized cyclic poly(dimethylsiloxane)s (PDMSs) linked with photoresponsive hexaarylbiimidazoles (HABIs) in their molecular chains [4, 5]. HABI undergoes cleavage of the imidazole–imidazole covalent bond upon photostimulation to generate a pair of triphenylimidazolyl radicals (TPIRs), and the generated TPIRs readily recouple into HABI upon terminating photoirradiation [6]. Encouraged by the stability of TPIR even in air, we exploited this photochemistry for the repeatable cyclic–linear topological transformation (TX) of PDMS fluids [5]. However, the development of PDMS elastomers that enable wide-range tuning and dramatic on-off switching of viscoelasticity while retain-

ing the solid state remains a significant challenge.

To this end, we have recently synthesized network PDMSs with HABIs (N) in the chains from star-shaped PDMSs having 2,4,5-triphenylimidazole (lophine) end groups (S) with controlled molecular weight (MW) and narrow dispersity [7], anticipating that better control of MW and dispersity of the parent star-shaped precursors would lead to stiffer networks and more dramatic changes in viscoelasticity upon phototriggered network–star TX of PDMS [Fig. 1 (a) and (b)]. The appearance of the synthesized PDMS network was a transparent yellowish rubbery solid [Fig. 1 (c), top] and it showed a rapid response to photostimulation only in the irradiated region, causing an apparent color change [Fig. 1 (c), top]. The production of TPIRs upon photoirradiation of the PDMS network was validated based on electron spin resonance (ESR) and UV–Vis spectrometric analyses [7]. This supports the progress of the intended photochemistry of HABI [Fig. 1 (a)] and network–star TX [Fig. 1 (b)] only at the photoirradiated regions, and thus the fabrication of photocleavable and regenerative networks (PRNs) has been achieved.

Having confirmed the apparent photoresponse of N, we next compared the small-angle X-ray scattering (SAXS) profiles of N and S. The SAXS profile of S showed an apparent scattering derived from aggregates of end groups [Fig. 2 (a), top (blue curve)] [5]. One possible driving force of the formation of aggregates is the formation of hydrogen bonds (H-bonds) between lophine end groups [Fig. 2 (a), bottom] [8]. In contrast, only a slight broad scattering derived from the correla-

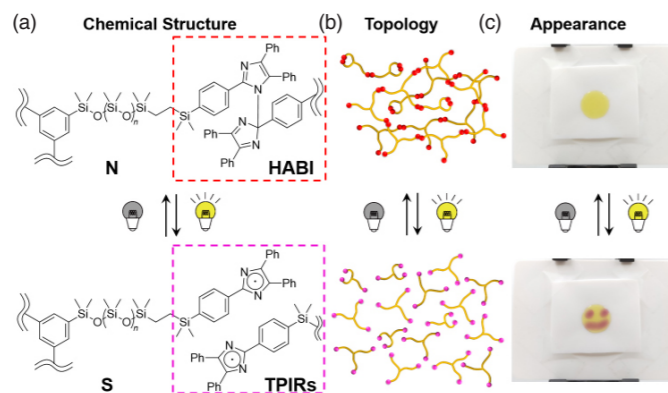


Figure 1: (a) Chemical structures of network PDMS linked with HABIs in the chains and star-shaped PDMS with TPIR end groups produced upon photochemistry of HABI. (b) Schematic illustration of photo-triggered network–star TX. (c) Photographs of rubbery network PDMS without (top) and with (bottom) photoirradiation ($\lambda \sim 410$ nm) on a PTFE sheet.

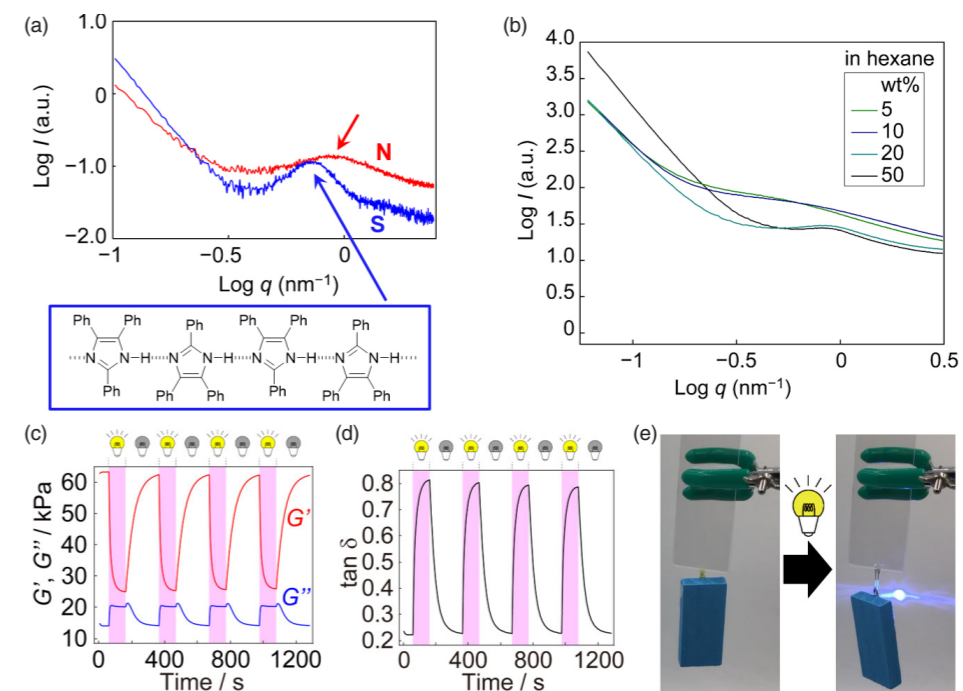


Figure 2: (a) SAXS profiles of S and N recorded at BL-10C in KEK-PF. (b) Concentration-dependent SAXS profiles of N swollen with hexane recorded at BL19B2 in SPring-8. Time-course plots of (c) G' and G'' and (d) $\tan \delta$ upon on–off cycles of photoirradiation to N. The sample was irradiated during the time ranges indicated in pink ($\lambda = 365$ nm). (e) Photographs of a glass slide connected with a wood brick with an N string before (left) and during (right) photoirradiation ($\lambda = 410$ nm).

tion hole [9], which represents the scattering contrast between the main chains and functional groups in a homogeneous state, appeared at the higher q region in the profile of N [Fig. 2 (a), top (red curve)]. Moreover, the formation of network structures within N was confirmed by swelling N with hexane. The SAXS profiles of gels derived from N showed an upward shift of the traces at Log q range roughly between -0.5 and 0 at the concentration of 5 and 10 wt% for hexane [Fig. 2 (b)]. The scatterings that appeared in these profiles are consistent with those of gels formed from star-shaped polymer networks.

We then investigated the photorheological properties of N. Time-course plots of storage and loss moduli (G' and G'') upon on–off cycles of photoirradiation demonstrate a sudden decrease in G' upon photoirradiation (< 1 min) and a subsequent autonomous return upon terminating photoirradiation within 4 min [Fig. 2 (c)]. The change in its solidity was further evaluated by time-course plots of loss tangent ($\tan \delta = G''/G'$), where $\tan \delta$ increased from 0.25 to almost 0.8 [Fig. 2 (d)]. Given that the boundary of solid and liquid is often considered to be $\tan \delta$ of 1 ($G' = G''$) [10–12], these data indicate that photoirradiation induces a hard-to-soft transition of the network while retaining its solidity ($G' > G''$). We finally applied our PRNs as a remotely-controlled photocleavable rubber string by exploiting the on–off switchability of its rheological properties upon photoirradiation. A wood brick was connected to a glass with an N string [Fig. 2 (e), left]. Photoirradiation to the center of the string resulted in elongation [Fig. 2 (e), right] and finally the string broke. It should be noted that these changes

were achieved by a consumer-use blue laser pointer ($\lambda \sim 410$ nm).

REFERENCES

- [1] M. Shirai, *Polym. J.* **46**, 859 (2014); D. J. Fortman, J. P. Brutman, G. X. De Hoe, R. L. Snyder, W. R. Dichtel and M. A. Hillmyer, *ACS Sustainable Chem. Eng.* **6**, 11145 (2018).
- [2] T. F. Scott, A. D. Schneider, W. D. Cook and C. N. Bowman, *Science* **308**, 1615 (2005).
- [3] M. Burnworth, L. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, S. J. Rowan and C. Weder, *Nature* **472**, 334 (2011).
- [4] S. Honda and T. Toyota, *Nat. Commun.* **8**, 502 (2017).
- [5] S. Honda, M. Oka, H. Takagi and T. Toyota, *Angew. Chem. Int. Ed.* **58**, 144 (2019).
- [6] G. R. Coraor, L. A. Cescon, R. Dessauer, A. S. Deutsch, H. L. Jackson, A. MacLachlan, K. Marcali, E. M. Potrafken and R. E. Read, *J. Org. Chem.* **36**, 2267 (1971).
- [7] M. Oka, H. Takagi, T. Miyazawa, R. M. Waymouth and S. Honda, *Adv. Sci.* **8**, 2101143 (2021).
- [8] S. Horiuchi, F. Kagawa, K. Hatahara, K. Kobayashi, R. Kumai, Y. Murakami and Y. Tokura, *Nat. Commun.* **3**, 1308 (2012).
- [9] J. Cortese, C. Soulié-Ziakovic, M. Cloitre, S. Tencé-Girault and L. Leibler, *J. Am. Chem. Soc.* **133**, 19672 (2011).
- [10] H. H. Winter and F. Chambon, *J. Rheol.* **30**, 367 (1986).
- [11] H. H. Winter and M. Mours, "Rheology of Polymers Near Liquid-Solid Transitions" in *Neutron Spin Echo Spectroscopy Viscoelasticity Rheology*, (Springer press, Berlin Heidelberg, 1997) P165.
- [12] T. G. Mezger, "Users of Rotational and Oscillatory Rheometers" in *The Rheology Handbook* edited by U. Sorll, (Vincentz press, Network, 2014).

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