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Light-driven rheological modulation of solventless polymer networks enabled by precisely architected flexible star polysiloxanes

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We report the synthesis and photoresponsivity of precisely designed liquid star-shaped poly(dimethyl siloxane) (PDMS) with anthracene end groups. Owing to the efficient end-linking of the flexible PDMS arms upon the first UV irradiation (λ = 365 nm, UV$_{365}$), the storage modulus (G') increased from 4.7 Pa to 119 kPa ($>25\,000$-fold), and the physical state became a rubbery solid. Subsequent irradiation with UV light at a shorter wavelength (λ = 254 nm, UV$_{254}$) decreased G' toward the photostationary state, and viscoelasticity modulation was achieved between the two photostationary states under solvent-free conditions.

Smart polymers that respond to external stimuli are emerging as versatile materials for a broad spectrum of applications including adhesives, cosmetics, biomedical devices, and soft robotics.[1–5] In particular, photoresponsive polymers have garnered considerable attention for their ability to convert precise, remote, and spatiotemporal optical signals into macroscopic changes in material behavior such as mechanical, morphological, or rheological transformations.[6–9] In this context, polymer networks incorporating coumarin moieties have been widely explored for their ability to undergo efficient and reversible [2+2] cycloaddition, (generally under exposure to UV at a wavelength of 365 nm (UV$_{365}$) to induce dimerization and 254 nm (UV$_{254}$) to trigger photocleavage), thus enabling dynamic tuning of network stiffness, self-healing properties, and stimuli-responsive adhesion.[10–16] Similarly, hexaarylbiimidazole (HABI) derivatives provide another compelling route to photoresponsivity, forming persistent triphenylimidazolyl radicals under UV excitation, which have been harnessed to produce noticeable rheological changes.[17–21] These reversible molecular systems are commonly characterized by the scission and formation of covalent bonds and are clearly distinguished from

other photoresponsive molecules, such as azobenzenes and stilbenes, which have been employed to cause conformational changes in polymer chains on the basis of *trans–cis* photoisomerization.[22–24]

Similar to the coumarin-based photodimerization system, anthracene has also attracted significant attention, in which UV light (>300 nm) induces [4+4] cycloaddition to form small molecular and polymer networks that can be thermally cleaved or exposed to UV light at shorter wavelengths (<300 nm). For small molecules, liquid branched compounds with anthracene moieties and excellent photoresponsivity have recently been reported.[25,26] However, many materials used in industry are polymers, and they are inevitably used owing to social demands, cost, and quality standards. As such, achieving such a responsivity with common polymers is meaningful. In this context, anthracene-based photodimerization systems have also been harnessed in various polymer networks,[27–32] and have been further extended to photodynamic star polymer networks. Indeed, following the pioneering works of Mengel *et al.* in 2001[33] and Zheng *et al.* in 2002,[34] various anthracene-based photodynamic systems for enabling photocontrolled mechanical modulation of hydrogels[35] and ion-gels[36] have been reported, to mention a few. On the surface, coumarin- and anthracene-based photodimerization systems are quite similar, but the anthracene moieties are obviously bulkier and should form more rigid dimers. Hence, when star polymer networks are formed by the dimerization of anthracene, the resulting network should tend to be more rigid and less flexible, leading to dynamic properties different from those of coumarin-based systems. Moreover, in the synthesis of star polymer networks, it has generally been recognized that the uniformity of their star polymer precursors enhances the mechanical properties of the resulting networks.[37,38] However, the limited photoresponse of star polymer networks from their precisely designed precursors suggests the existence of other factors that dictate their photoresponse (Fig. 1a). In contrast, examples of various photoresponsive silicones that exhibit prominent rheological responses[15,20] suggest the importance of polymer chain flexibility and compatibility or miscibility between the polymer chain and the

a Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0385, Japan E-mail: shonda@ms.ifoc.kyushu-u.ac.jp

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(a) Conventional studies

➤ **Presence of solvent fraction**
➤ **Moderate photoresponse**

(b) This work

➤ **Solventless**
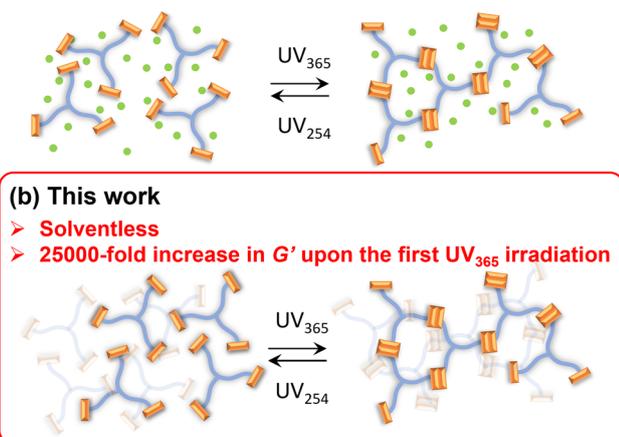➤ **25000-fold increase in G' upon the first UV$_{365}$ irradiation**

Fig. 1 Schematic illustration of (a) conventional design of anthracene-appended polymer networks and (b) precisely architected flexible star-polymer elastomers in this work.

Fig. 2 (a) Synthesis and (b) photo-induced dimerization and dimer dissociation of anthracene-appended star-shaped PDMS.

photoactive group in rheological responses. However, several long-standing problems in the precision synthesis of polysiloxanes through polymerization reactions have hampered further progress in related fields.[39,40] Very recently, these problems have begun to be resolved,[20,39,41] opening up the possibility of synthesizing polymer networks from precisely designed networks using flexible polysiloxane. As silicones are flexible, durable, industrially important, and used in a wide range of applications that are irreplaceable with carbon-based polymers, achieving significant photoswitchability with silicone is not only fundamentally but also industrially significant.

Guided by this research progress and the wealth of aforementioned conventional research on anthracene-appended polymers, here we describe the design and synthesis of novel anthracene-appended star-shaped poly(dimethylsiloxane) (PDMS) with a controlled molecular weight (MW) and narrow dispersity ($Đ$), and its networks. While previous anthracene- and coumarin-based systems typically achieved approximately 100^{36}–1000^{35}-fold increases in the storage modulus (G'), remarkably, the developed anthracene-appended star PDMS realizes a very large initial increase ($>25\,000$-fold) upon the first dimerization and a smaller but reproducible decrease in G' upon subsequent dimer dissociation under solvent-free conditions (Fig. 1b). The large initial response enabled by the marriage of precision manipulation of macromolecular architectures and the flexibility of polysiloxanes demonstrates the potential of the present solventless system for applications requiring finite cycles of tunable properties.

According to the recently developed protocol for the organocatalyzed ring opening polymerization of hexamethylcyclotrisiloxane (D3) initiated from trifunctional silanol (**I3**), three-armed star-shaped PDMS with hydrosilane end groups (**1**: $M_n = 19\,800$, $M_w = 22\,300$, $Đ = 1.13$) was prepared.[41] The star-shaped **1** was then subjected to a hydrosilylation reaction between

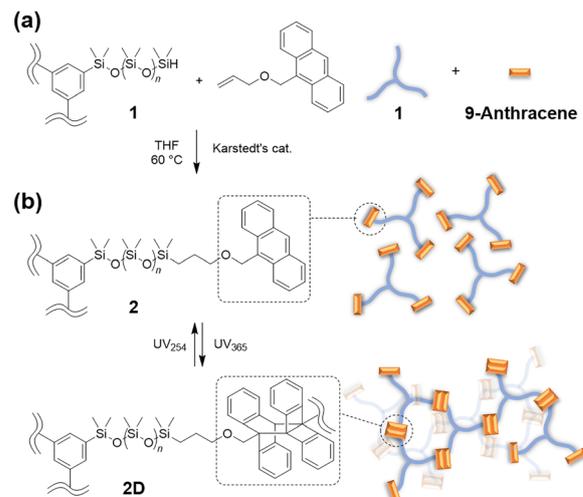9-anthrylmethyl methacrylate in the presence of Karstedt's catalyst (Fig. 2a) to yield three-armed star-shaped PDMS with anthracene end groups (**2**: $M_n = 22\,000$, $M_w = 27\,200$, $Đ = 1.23$), which was thoroughly characterized by the combination of ^{1}H NMR (Fig. S1) and size exclusion chromatography (Fig. S2). Similar to our previous report on coumarin-appended PDMSs,[15] the color was slightly yellowish, reflecting the color of 9-anthrylmethyl methacrylate, and the physical appearance of **2** was a transparent oily liquid, which is advantageous for intended dimerization-induced network formation (Fig. 2b).

The first surprising finding was the sensitivity of **2** to light. As repeatedly reported in previous studies, direct evidence of reversible photodimerization of anthracene in insoluble network materials can be obtained from ultraviolet-visible (UV-VIS) absorption spectra. When UV light at a wavelength of 365 nm (UV$_{365}$) was irradiated to **2** for 1 min, sandwiched between two quartz glass plates with a spacer to achieve a thickness of 0.1 mm, the absorption at 300–400 nm derived from anthracene drastically decreased and almost disappeared within three minutes (Fig. 3a). Unlike in the solution state, network polymeric materials formed *via* the photodimerization of anthracene typically require a long time to proceed. For example, in the case of star-PEG networks, a noticeable amount of anthracene-derived absorption remained even after several hours of UV$_{365}$ irradiation.[34,36] Encouraged by the present UV$_{365}$ response, the same sample was subsequently irradiated with UV light at a wavelength of 254 nm (UV$_{254}$). As a result, the absorption at 300–400 nm almost reached a photostationary state within one minute, and there was a negligible difference after 3 min (Fig. 3b). The precisely controlled star architecture ensures a uniform distribution of anthracene end groups, which contribute to enhance mechanical properties. Moreover, the flexible nature of PDMS likely provide high segmental mobility, enabling rapid migration and kinetically advantageous [4+4] cycloaddition of anthracene end groups even under solvent-free condition.
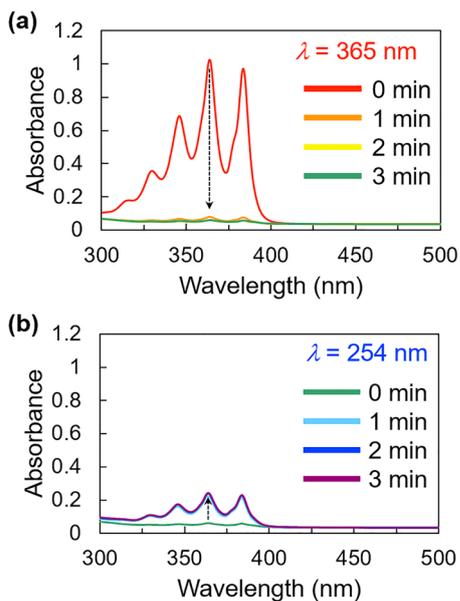
Fig. 3 UV-VIS spectra of **2** sandwiched between two quartz glass slides upon sequential irradiation with (a) UV$_{365}$ and (b) UV$_{254}$.

Next, the reversibility of our material was evaluated by monitoring the UV-VIS absorption spectra as a function of time under alternating UV$_{365}$ and UV$_{254}$ irradiation (Fig. 4). After a significant decrease in absorption during the first UV$_{365}$ irradiation, the absorbance of **2** at a wavelength of 366 nm varied regularly between 0 and 0.2 upon subsequent UV$_{254}$ and UV$_{365}$ irradiation, which is also consistent with previous reports.[34] Given the versatility of silicone itself, the ability to achieve reversibility similar to that reported in previous studies but with a solventless system and an extremely quick response would be appealing for a range of applications.

A surprising finding introduced at the end of this Communication is the photodynamic rheological properties of **2**. Changes in the storage and loss moduli (G' and G'') upon cycles of alternating UV$_{365}$ and UV$_{254}$ irradiation to **2** under solventless conditions at room temperature (25 °C) were investigated. First, the initial G' and G'' (G'_{ini} and G''_{ini}) values were 4.7 Pa and 8.3 Pa, respectively. In general, the magnitude of the
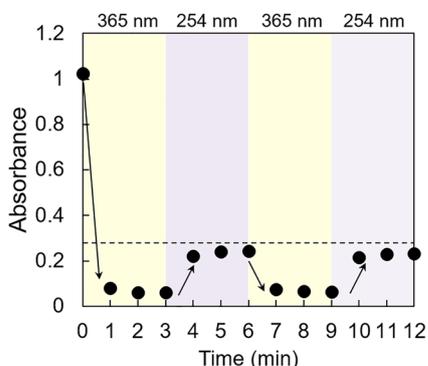

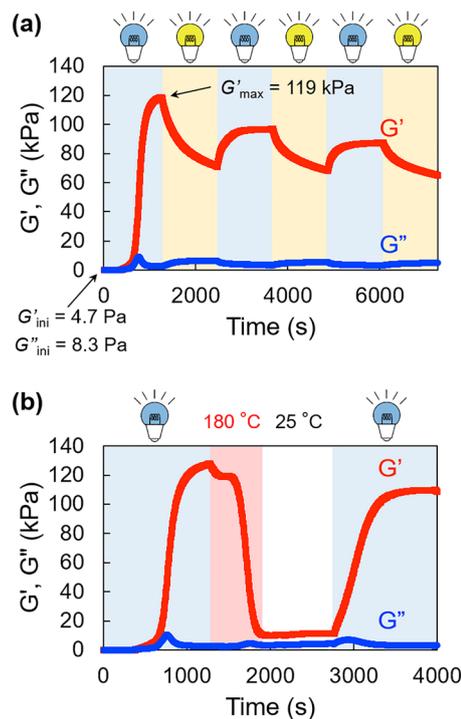Fig. 4 Absorbance of **2** (λ = 366 nm) monitored by UV-VIS spectroscopy upon UV$_{365}$ and UV$_{254}$ irradiation cycles.

Fig. 5 Time-course rheological analysis of **2** upon (a) sequential UV$_{365}$ and UV$_{254}$ irradiation cycles and (b) sequential UV$_{365}$ irradiation, heating to 180 °C, cooling, and UV$_{365}$ re-irradiation.

relationship between G' and G'' is an indicator used to determine solidity ($G' > G''$) and liquidity ($G' < G''$), and the present result again shows an inherent liquidity of **2**. Next, time-dependent plots of G' and G'' upon UV$_{365}$ irradiation revealed a sharp increase in G' (Fig. 5a, left blue-colored region). The G' reached 119 kPa, which is more than 25 000-fold greater than the G'_{ini}, and the change in G'' was obviously less prominent. During UV$_{365}$ irradiation, G' exceeded G'', and the resulting network **2D** (Fig. 2b bottom) became a rubbery solid. When anthracene groups are introduced into side chains, the presence of only a small number of light-responsive groups, less than 1% of the total, causes dimerization-induced crystallization even with very high-MW polysiloxanes.[42] With the developed material, the liquid or rubbery solid state was maintained and no crystalline components were formed throughout the entire process. This noncrystallizable nature is likely due to the presence of anthracene moieties as highly mobile end groups, discouraging crystallization. Upon subsequent UV$_{254}$ irradiation, the G' apparently decreased (Fig. 5a, left orange-colored region) but did not revert back to its initial value. Moreover, a gradual decrease in G' after irradiation with UV light during the cycles of UV$_{365}$ and UV$_{254}$ irradiation was observed (Fig. 5a). In addition to the involvement of photostationary states (Fig. 3a and b), the reversibility may be constrained by irreversible side reactions such as photooxidation and photobleaching of anthracene, which are frequently reported in the photochemistry of anthracene-based compounds. Given that the photoirradiation experiments were conducted under ambient atmospheric conditions, the presence of oxygen and humidity may also influence the photoreversibility. To investigate

this, a predetermined amount of **2** was stored for 24 h under three different conditions: a nitrogen atmosphere ($>$99%, 37 °C), an oxygen-rich atmosphere (95%, 37 °C), and a humidified oxygen atmosphere (95% O_2, 90% relative humidity, 37 °C). However, the differences in storage conditions resulted in negligible variation in the photoresponsivity monitored with a UV-VIS spectrometer, suggesting that the observed behavior is governed mainly by the presence of photostationary states rather than by the aforementioned side reactions. On the other hand, when the UV_{365}-irradiated network **2D** was heated (Fig. 5b, left blue-colored region), G' decreased to 10 kPa, which is comparable to that of G'' (3 kPa) (Fig. 5b, right red-colored region). In addition, G' and G'' remained unchanged upon subsequent cooling to room temperature (Fig. 5b, central white region), but following UV_{365} irradiation, the G' significantly increased to approximately 110 kPa (Fig. 5b, right blue-colored region), demonstrating the manipulability of viscoelasticity by the combination of light and heat stimuli.

In conclusion, we have demonstrated the synthesis of a new class of photoresponsive silicone elastomers derived from precisely designed star-shaped PDMS terminated with anthracene moieties. While photodynamic star polymer networks based on the reversible photodimerization of anthracene terminals are now commonplace materials, the combination of PDMS and anthracene enables extremely amplified responses in terms of rheological properties, with a more than 25 000-fold increase in G' upon the first UV_{365} irradiation. Assisted by the highly flexible nature of PDMS chains, the precisely controlled star architecture allows the formation of a more uniform network structure, likely leading to the present photoresponsivity even under solvent-free conditions. The findings underscore both the opportunities and the limitations of anthracene photodimerization in solvent-free soft materials, and point toward strategies for designing responsive networks, demonstrating how careful selection of photoresponsive molecules and polymers with controlled MW and Đ can be harnessed to amplify their responses to external stimuli. Further systematic studies related to these findings, including MW dependence, synthetic and processing scalability, and durability are currently in progress for extending the generality and practical relevance of the platform in future work.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data underlying this study are available in the published article and its supplementary information (SI). Supplementary information: experimental details, ^{1}H NMR spectrum, Size Exclusion Chromatography traces. See DOI: https://doi.org/10.1039/d5cc04840k.

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