Photocleavable Regenerative Network Materials with Exceptional and Repeatable Viscoelastic Manipulability

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The development of solventless system form modulating properties of network materials is imperative for the next generation sustainable technology. Utilization of photostimulation is important owing to its spatial and temporal locality, yet designing photoresponsive network materials exhibiting repeatable and dramatic change in their properties remains a challenge. Here, the authors report a photocleavable regenerative network (PRN) linked with photoresponsive hexaarylbiimidazoles (HABIs) synthesized from narrow dispersity star-shaped poly(dimethylsiloxane) (PDMSs) having 2,4,5-triphenylimidazole end groups. The use of urea anion as a catalyst for ring opening polymerization (ROP) of cyclic siloxane initiated from silanols enables control of molecular weight and dispersity. The rheological measurements for the synthesized PRNs exhibit drastic changes in storage and loss moduli \( (G' > G'') \) upon photoirradiation in the solid state. This photocontrolled change in viscoelasticity with retaining solidity enables application of PRNs as a remotely-controlled photo-melt adhesive and photo-scissible string. The developed PRNs will enable a wide variety of applications such as industrially important next-generation sustainable adhesive, sealant, and reversibly-deformable 3D printing materials with their spatially and temporally local manipulability, solventless handleability, and excellent reversibility.

1. Introduction

Moldability of polymeric materials undoubtedly contributes to our lives. The soft and viscoelastic nature of polymeric materials enables the formation of various complex shapes. Thermal stimulation has generally been applied for controlling the viscoelasticity of materials, yet expansion of available stimulation is highly desirable.\[1\] The spatiotemporal control possible with focused photostimulation is particularly attractive as a means of modulating the local viscoelasticity of materials. Recently, polyacrylates and polymethacrylates with azobenzene side chains have been shown to change their viscoelasticity upon photoirradiation, relying on the photoisomerization of azobenzenes on side chains.\[2\] The glass transition temperatures \( (T_g) \) of polymers with trans-isomeric side chains were higher than room temperature; trans to cis photoisomerization of side chains upon photoirradiation lowered the \( T_g \)s below room temperature, attaining repeatable change in mechanical properties with the same polymers without solvent. On the other hand, we have synthesized a photocleavable regenerative network (PRN) composed of poly(dimethylsiloxane) (PDMS) linked with photoresponsive hexaarylbiimidazoles (HABIs) in the chains from the corresponding star-shaped precursors with 2,4,5-triphenylimidazole (lophine) end groups.\[3\] Upon photoirradiation, HABI generates a pair of triphenylimidazoryl radicals (TPIRs) and the generated TPIRs undergo recoupling into HABI again by terminating photoirradiation (Figure 1a).\[4\] When elevated temperature to 100 °C, TPIRs produce non-photoresponsive isomers of HABI...
that are not photoresponsive,[5,6] yet this reversible photoreaction proceeds quantitatively at lower temperatures. Owing to the stability of TPIR even under the presence of oxygen,[7] solventless network scission and reformation at room temperature was realized in air; nevertheless, for these very soft materials, the loss modulus ($G''$) remained higher than storage modulus ($G'$) irrespective of photoirradiation.[3] As more uniform networks are known to have superior mechanical properties,[8] we anticipated that better control of molecular weight (MW) and dispersity of star-shaped precursors for the network would lead to stiffer networks and more dramatic changes in viscoelasticity upon photoirradiation.

Herein we show that a urea anion-catalyzed ring opening polymerization (ROP) of cyclic siloxanes initiated from a trifunctional arylsilane core affords star-shaped PDMSs with narrow dispersity that can be capped with HABIs to generate well-defined networks that show dramatic changes upon photoirradiation (Figure 1b). The combination of silanol initiators and a urea anion catalyst[9] for ROP of hexamethylcyclotrisiloxane (D3) enabled the controlled synthesis of PDMSs with narrow dispersity ($D < 1.1$). The subsequent introduction of lophines and oxidation of lophines into TPIRs and their spontaneous coupling into HABIs produced network PDMSs functionalized with HABIs in the chains. Rheological studies revealed dramatic and reversible changes in viscoelasticity upon photoirradiation in the solid state. By taking advantage of properties of the present PRN, we further succeeded in applying our PRN as a remotely-controlled photo-melt adhesive and photo-scissible string.

Figure 1. a) Photochemistry of HABI. b) Schematic illustration of photo-cleavable regenerative network (PRN).

2. Results and Discussion

To identify the optimal conditions for generating well-defined polysiloxanes, we carried out model reactions using dimethylphenylsilanol as an initiator for ROP of D3 with either 1,5,7-triazacyclo[4.4.0]dec-5-ene (TBD)[3,10] or urea anions[9] as catalysts. These studies revealed that the urea anion derived from 1,3-bis(3,5-bis(trifluoromethyl)phenyl)urea, U(4CF$_3$)$_2$ and NaH afforded narrow molecular weights and the optimal reaction rates for polymerizations carried out in batch (Figure S1a, Supporting Information); the ROP of D3 was completed within 30 min (Figure S1b, Supporting Information). Although broadening of dispersity was observed after the 30 min due to equilibrium polymerization, size exclusion chromatography (SEC) showed unimodal traces (Figure S1b, Supporting Information) with narrow dispersities ($D < 1.2$) at monomer conversions $\leq 63\%$ (Figure S1c, Supporting Information).

Next, ROP of D3 initiated from trifunctional silanol ($I_3$) was investigated to generate star polysiloxanes (Figure 2a). The trisilanol $I_3$ exhibits relatively poor solubility in THF; deprotonation of $I_3$ with NaH in THF resulted in the formation of large precipitates (Figure 2b, left). Nevertheless, addition of U(4CF$_3$)$_2$ to this mixture solubilized the ionic species to give a homogeneous solution (Figure 2b, right). SEC monitored through the following ROP of D3 showed unimodal traces having narrow dispersities for conversions $\leq 80\%$ ($\approx 40$ min, Figure 2c,d). The conversion of D3 reached 96% at 60 min although the dispersities increase slightly (Figure 2d). The urea anion catalysts are particularly useful for generating the lower molecular weight polysiloxane stars (Table S1, Supporting Information, entry 1–4). Moreover, the combination of silanols and urea anion catalysts overcomes
the solubility problem derived from mismatch of polarity between initiators, D3, and PDMS. On the other hand, TBD is less effective at solubilizing the I1 initiator and leads to polysiloxanes of broader polydispersities, even for the lower molecular weights \((D = 1.34, M_n = 9200 \text{ Da});\) however, TBD enabled production of high-MW PDMS \((D = 1.35, M_n = 63 300 \text{ Da})\).\(^{10}\)

Having established the control of ROP of D3, we synthesized star-shaped PDMSs with lophine end groups \((P)\) by the end capping reaction with chlorodimethylvinylsilane and subsequent hydroxylation with hydroxilane-appended lophine according to the reported procedure (Scheme S1, Supporting Information).\(^{11}\) Oxidation of lophine end groups into TPIRs and their spontaneous coupling into HABI formed the corresponding network PDMSs (N), that is, PRNs linked with HABIs in the chains (Scheme S1, Supporting Information, bottom). All of these PDMSs were characterized based on \(^{1}H\) NMR (Figure S2, Supporting Information) and SEC (Table S2, Supporting Information). The networks \(N_1\) and \(N_2\) derived from \(P_1\) \((M_n = 7400 \text{ Da})\) and \(P_2\) \((M_n = 11 200 \text{ Da})\), were transparent yellowish films (Figure 3a, left) and showed response to photostimulation only at the irradiated region to change the color into pink (Figure 3a, middle and right), suggesting progress of the intended photochemistry of HABI within the material (Figure 1a). The physical properties of the networks \(N\) depend on the molecular weight of the precursors \(P\). Whereas networks derived from \(P_1\) and \(P_2\) are stable films, the \(N_3\), derived from the higher molecular weight star \(P_3\) \((M_n = 50 400 \text{ Da})\) is a yellowish liquid. Differences in topological inhomogeneity\(^{12}\) between the networks likely affected their physical states. That is, most of the reactions between TPIRs for the higher molecular weight materials were intramolecular and thus it was difficult to construct a long-range network.

The transparency of \(N\) also suggests the inner homogeneity of the material. This is favorable because the formation of aggregates derived from moieties immiscible to polymer chains causes phase separation and would restrain change in the physical properties of PRNs upon photoinitiation. The nanoscale homogeneity of \(N_2\) was validated by small-angle X-ray scattering (SAXS) analyses. The SAXS profile of \(P_3\) showed an apparent scattering derived from aggregates of end groups (Figure S3, Supporting Information, blue line). This scattering pattern is similar to that that appeared for linear PDMSs with lophine end groups. As imidazoles form several types of H-bondings,\(^{13}\) the end groups were probably aggregated within the material by H-bonding between the imidazoles in lophines similar to a previous report.\(^{11}\) However, only a slight broad scattering derived from correlation hole appeared at the higher \(q\) region in the profile of \(N_2\) (Figure S3, Supporting Information, red line). Therefore, the formation of aggregates was inhibited upon forming HABI and the SAXS profile revealed nanoscale homogeneity of \(N_2\). To further validate the formation of network structures within the materials, gels were prepared by swelling \(N_2\) either with hexane or EtOAc and were subjected to SAXS analyses, expecting enhanced contrast of scattering between polymer chain and solvent. Both of SAXS profiles of gels from \(N_2\) showed 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 (Figure S4a, Supporting Information) and with at the concentration of 5 wt% for EtOAc (Figure S4b, Supporting Information). The scatterings appeared in these profiles are apparently different from those of end group aggregation (Figure S3, Supporting Information) but are in good agreement with those of gels formed from star-shaped polymer networks.\(^{14}\) This strongly suggests the construction of the intended covalent bonding network within our PRNs.

The dynamic properties of \(N_s\) upon photoinitiation are intriguing, because the network cleavage and rebonding can occur even in the solid state \(N_s\) (Figure 3b). The formation of TPIRs upon photoinitiation was validated by comparing ESR spectra of \(N_1\) before (Figure 3c, black line) and after (right) photoirradiation (Figure 3c, pink line) by the appearance of the signal at 327 mT, which is identical to the previous report.\(^{10}\) A slight ESR signal appeared before photoirradiation indicates the presence of unreacted TPIRs due to the restricted mobility of polymer chains after forming the network (Figure 3c, black line). Effective consumption of the generated TPIRs upon photoinitiation has been validated by measuring ESR spectra over time, demonstrating that the almost complete disappearance of the ESR signal upon photoirradiation after 20 min (Figure S5, Supporting Information).
a photoresponse similar to that of upon ON–OFF photoirradiation cycles to N1. The sample was irradiated nent. For Information), yet the magnitude of the change was less promi-

described in our previous study. [3] The change in the viscoelastic-
plots of loss tangent (tan \(\delta\)) at the wavelength of 567 nm (\(\lambda\approx 410\) nm) captured from Movie S1, Supporting Information). Time-dependent plots of \(\tan \delta\) upon photoirradiation showed repeated increase and decrease of from 0.25 to almost 0.8 (Figure 4b). Given that the boundary of solid and liquid is often considered by the tan \(\delta\) of 1 (\(G''/G'\)). [15] these data indicate that photoirradiation induces a hard-to-soft transition of the network in the solid state (\(G'' > G'\)). Network \(N_1\) derived from the higher molecular weight precursor \(P_2\), showed a photoresponse similar to that of \(N_1\) (Figure S7a, Supporting Information), yet the magnitude of the change was less prominent. For \(N_3\), derived from the highest MW precursor \(P_3\) (\(M_n = 50\) 400 Da) the response of \(G'\) and \(G''\) to photoirradiation was very small and the material maintained liquid state (\(G' < G''\)) irrespective of photoirradiation (Figure S7b, Supporting Information).

We finally applied our PRNs as a remotely-controlled photomelt adhesive (Movie S1, Supporting Information) and photo-scissible string (Movie S2, Supporting Information) by taking advantage of the dramatic change in rheological properties upon photoirradiation. Thus, \(N_1\) was sandwiched between two glass slides and the set of slides was attached on the wall (Figure 4c, left). Adherence property of \(N_1\) was high enough to maintain the attached state at least for 2 weeks in the experimental period. Photoirradiation caused a loss of adhesion of the network \(N_1\), as the glass slide gradually slid down the plate (Figure 4c, middle) and finally detached (Figure 4c, right). Evidently, the increase of tan \(\delta\) upon photoirradiation to \(N_1\) led to the loss of adhesivity. Further, a wood brick was connected with a glass with a \(N_1\) string (Figure 4d, left). Photoirradiation to the center of the string resulted in elongation (Figure 4d, middle) followed by scission (Figure 4d, right). It should be noted that these changes were achieved by a consumer usage blue laser pointer (\(\lambda \approx 410\) nm).

3. Conclusions

In summary, we have succeeded in synthesizing PRNs linked with HABIs from star-shaped PDMSs with narrow dispersity. The ROP of D3 based on the combination of trifunctional silanol and urea anion enabled control of MW and dispersity. The rheological measurements for the PRNs disclosed that the drastic changes in \(G'\) and \(G''\) upon photoirradiation. We further demonstrated that this photocontrolled change in viscoelasticity with retaining solidity enables utilization of PRNs as the remotely-controlled photo-melt adhesive and photo-scissible string. With their spatially and temporally local manipulability, solventless handleability, and excellent reversibility, our PRNs may find wide applications such as industrially important next-generation sustainable adhesive, sealant, and reversibly-deformable 3D printing materials.

4. Experimental Section

ROP of D3 Catalyzed by Urea Anion: Into a flask was prepared a mixture of U(4CF₃I)2 (145 mg, 0.30 mmol), NaN₃ (7.2 mg, 0.30 mmol), and THF (0.80 mL). To this mixture, I₄ (10 mg, 0.10 mmol for OH groups) and NaN₃ (6.0 mmol), and THF (0.50 mL) was added and stirred at room temperature (25 °C). After 12 min, THF solution (0.50 mL) of benzoic acid (122 mg, 1.0 mmol) was added and the mixture was further stirred for 120 min. An excess amount MeCN was added to the reaction mixture to cause phase separation into PDMS and MeCN layers. The PDMS layer was washed successively with MeCN and MeOH, and dried under reduced pressure to afford a hydroxy-terminated three-armed star-shaped PDMS, which was used for the subsequent end-capping reaction without further purification. Thus, to this PDMS, THF (3 mL) of pyridine (480 µL, 6.0 mmol), and chloromethylvinylsilane (270 µL, 2.0 mmol) was added in this order and the mixture was further stirred for 21 h. The mixture was poured into an excess amount of H₂O/hexane and aqueous layer was separated and extracted with hexane. The combined hexane phase was washed with water, dried over Na₂SO₄, and concentrated to dryness. The obtained crude oily product was washed with MeOH and dried under reduced pressure to afford vinyl-terminated three-armed star-shaped PDMS (S3) as a colorless...
oil. The yield was 540 mg. $^1$H NMR (500 MHz, acetone-$d_6$): δ = 0.07–0.16 (–SiO(CH$_3$)$_2$–), 0.18 (s, –Si(CH$_3$)$_2$CH=CH$_2$), 0.40 (ArSi(CH$_3$)$_2$O–), 0.79 (dd, –Si(CH$_3$)$_2$CH=CH$_2$), 5.96 (dd, –Si(CH$_3$)$_2$CH=CH$_2$), 6.17 (dd, –Si(CH$_3$)$_2$CH=CH$_2$), 7.87 (s, ArH).

ROP of D3 Catalyzed by TBD: Into a flask was prepared a mixture of D3 (100 mg, 0.31 mmol for lophine end groups), TBD (4.1 mL, 30 mmol), Karstedt’s catalyst (0.1 mL), and THF (2 mL). A separately prepared THF solution (20 mL) of D3 (11.1 g, 50 mmol) was added to the mixture and the resulting solution was stirred at 25 °C for 80 min. Pyridine (3.6 mL, 45 mmol) and chlorodimethylvinylsilane (4.1 mL, 30 mmol) was added in this order and the mixture was stirred at room temperature, thus phase separation into PDMS and MeOH layers occurred. The PDMS layer was diluted with a minimum amount of chloroform and concentrated to a colorless oil. The yield was 540 mg.

1H NMR (500 MHz, acetone-$d_6$, δ): 0.07–0.16 (–SiO(CH$_3$)$_2$–), 0.31 (–Si(CH$_3$)$_2$CH=CH$_2$–), 0.40 (ArSi(CH$_3$)$_2$O–), 0.58 (–Si(CH$_3$)$_2$CH=CH$_2$–), 0.78 (–Si(CH$_3$)$_2$CH=CH$_2$–), 7.20–7.85 (ArH), 7.12 (br, –NH). Likewise, PD$_2$ and PD$_3$ were synthesized from S$_2$ and S$_3$, respectively.

Oxidation of Lophines into TPIRs and their Spontaneous Coupling into HABIs: In a typical procedure, into a flask was prepared hexane (100 mL), pyridine (60 mL), an aqueous solution of sodium hypochlorite (60 mL containing potassium ferricyanide (1.33 g, 4.0 mmol) and H$_2$O/hexane and an aqueous layer was separated and extracted with hexane. The combined hexane phases were washed with water, dried over MgSO$_4$, and evaporated using a parallel plate with a diameter of 12 mm at the frequency of 5 Hz at 25 °C.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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