

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201809621 Angew. Chem. 10.1002/ange.201809621

Link to VoR: http://dx.doi.org/10.1002/anie.201809621 http://dx.doi.org/10.1002/ange.201809621

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Topology-Reset Execution: Repeatable Post-Cyclization Recyclization of Cyclic Polymers

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Abstract: Repeatable topological transformation of polymers has been a challenge for realizing modulation of material functions. Here we developed a methodology for repeatedly resetting a cyclic macromolecular architecture to a linear one by photostimulation, namely, topology-reset execution (T-rex) based on photochemistry of hexaarylbiimidazoles (HABI). We synthesized cvclic poly(dimethylsiloxane)s (PDMSs) containing various ring sizes inchain linked with HABI. UV irradiation to the cyclic PDMSs produced telechelic linear PDMSs having triphenylimidazoryl radical (TPIR) end groups and following termination of UV enabled their end-to-end recyclization by the recoupling of TPIRs into HABIs. The cyclic PDMSs also respond to ultrasound to decrease their molecular weights (MWs) by site-specific cleavage of in-chain HABIs and we are able to reset the MWs by following photo-triggered T-rex after all. Furthermore, Trex enables solvent-free switching of rheological properties with retaining liquid character of PDMS. The T-rex approach developed here is versatile, fast, repeatable, and enables switching of material functions at a desired timing.

Progress in organic synthesis and precise polymerization techniques has led to the construction of topologically unique macromolecular architectures (MAs). Although MAs often differentiate their properties, it is generally difficult to repeatedly transform them into other MAs. Accordingly, an ongoing challenge is to develop a methodology enabling repeated transformation of MAs and some commendable studies have appeared.^[1] Such strategies can, in principle, be applicable for repeatable switching of functions with polymeric materials. Compared to other methodologies, repeated transformation of MAs should be advantageous for controlling properties of polymers because it does not require change in chemical composition and molecular weight (MW), control of stereoregularity, use of additives, but is applicable irrespective of the type of polymer backbones. Among various MAs, cyclic polymers are distinct because of their endless nature.^[2] Particularly, repeatable transformation of linear and cyclic MAs in solution state has been studied with sophisticated molecular and reaction designs,^[1e, 3] yet development of a facile and versatile system without using solvent is imperative for extending its concept to practical applications. On the other hand, we have

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recently achieved solvent-free repeatable transformation between network and star MAs with poly(n-butyl acrylate) oligomer and poly(dimethylsiloxane) (PDMS).[4] The chemistry of network scission and reformation relies on photochemistry of hexaarylbiimidazole (HABI), which can be synthesized by oxidizina 2,4,5-triphenylimidazole (lophine) into triphenylimidazoryl radical (TPIR) as an activation step and following spontaneous coupling between the generated TPIRs (Figure 1a, left). HABI undergoes cleavage of the covalent bond between the two imidazoles to generate a pair of TPIRs and their recoupling into HABI again upon ON-OFF of photoirradiation (Figure 1a, left).^[5] This chemistry enables network-star topological transformation and solvent-free isothermal liquidnonliquid conversion of polymeric materials.^[4] Hence, it can be potentially extended to repeatable transformation between various combinations of topologically unique polymers. Herein, we report a methodology for repeatedly resetting a cyclic topological geometry to a telechelic linear one simply by irradiating UV to in-chain HABI-functionalized cyclic PDMSs (Figure 1a, right). The methodology, named "topology-reset execution (T-rex)", enables post-cyclization re-cyclization (PCR) of polymer components by following termination of photoirradiation.

Linear PDMSs were synthesized by ring opening polymerization of hexamethylcyclotrisiloxane initiated from H₂O^[6] and vinyl end groups were introduced by terminating with chlorodimethylvinylsilane (Scheme S1, top). The resulting α, ω divinyl PDMS was then reacted with hydrosilane-functionalized lophine in the presence of Karstedt's catalyst to afford PDMS having lophine end groups (L) (Scheme S1, bottom). Similar to our previous report,^[4] the lophine end groups of **L** were oxidized to produce telechelic linear PDMS with TPIR end groups (L*), where the TPIRs readily coupled into HABIs in the reaction mixture to produce inter- and intra-molecularly reacted PDMS (C_{mix}) (Figure 1b). Comparison of ¹H NMR spectra revealed the complete dissapearance of -NH signal at 11.7 ppm (marked e) visible in the spectrum of L (Figure S1a) after forming HABI (Figure S1b). Moreover, signals derived from methylene protons (marked **b** and **c**) and those from aromatic region became complex. This is due to the possible three combinations of covalent bonds in HABI, i.e., C-N, N-N, and C-C bonds as reported preivously.^[7] SEC of Cmix showed a bimodal trace with a broad dispersity (D), and the trace significantly shifted from the former (Figure 2a) toward higher MW region (Figure 2b). The existence of high MW fraction suggested intermolecular reaction between the generated TPIRs to cause chain extension. On the other hand, peak MW (M_p) of the second highest peak (Figure 2b) decreased in comparison with that of the parent L (Figure 2a). The reduction in M_{p} , i.e., apparent MW indicates intramolecular cyclization as observed in various cyclization reactions.[2b]

In the course of our study, we noticed that C_{mix} was viscous liquid though L was solid (Figure 1b, right). This difference is strange on the surface because C_{mix} has MW larger than L and chemical compositions are quite similiar. IR spectroscopy verified

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the formation of hydrogen bonding (H-bonding) between the lophines within L. Several types of H-bonding between imidazoles are possible and they typically show a broad stretching vibrational band due to N-H...N at 2500-3500 cm⁻¹.^[8] Obviously, IR spectrum of L showed the broad absorption at the relevant wavenumber region (Figure S2a); however, such broad absorption disappeared after forming HABI as proved in the spectrum of C_{mix} (Figure S2b). The formation of H-bonding within L has also been supported by differential scanning calorimetry (DSC) with the endotherm at 82 °C (1.9 J/g) upon heating (Figure S3a). This thermal behavior is in good agreement with that of poly(propylene oxide) having H-bonding end groups reported in the literature.[9] From the DSC of C_{mix} (Figure S3b), it is also apparent that the disappearance of the corresponding endotherm, again demonstrating complete



Figure 1. (a) Conceptual illustration of T-rex and PCR based on photochemistry of HABI. (b) Synthesis of in-chain HABI-functionalized C_{mix} from L and their appearances (right).

conversion of lophines into HABIs. Analogous to thermoplastic elastomers formed by triblock copolymers, linear polymers having H-bonding groups at both chain ends can cause microphase separation.^[10] As was studied in detail, such materials show characteristic patterns in their small-angle x-ray scattering (SAXS) profiles and the profiles can be fitted with Percus-Yevick (PY) model, assuming random placement of aggregates of end groups immiscible to main chain.[11] Indeed, the SAXS profile of L showed a scattering pattern similar to those reported in the above studies (Figure S4a, red line).^[11] The peak scattering vector (q^*) was 1.01, corresponding to an averaged distance ($d = 2\pi dq^*$) of 6.2 nm between two aggregates. The intensity plots were wellfitted with a curve determined by PY model (Figure S4b) and radius of an aggregate of end groups (R) was calculated as 2.5 nm; the d and R well represented the network structure as illustrated (Figure S4c). On the other hand, only a slight broad scattering assignable to correlation hole^[12] appeared in the SAXS of Cmix (Figure S4a, blue line). Taken together, disappearance of H-bonding by forming HABI evidently avoided formation of aggregates and led Cmix homogeneous liquid.

The synthesized **C**_{mix} provides three intriguing features. The first feature is photo-triggered cleavage and reformation of the HABIs embedded in the PDMS backbone. Screening an optimized condition for end-to-end cyclization reaction is generally cumbersome and wasteful. If polymer materials containing various ring sizes produced in the screening process undergo re-cyclization, they do not become wastes. Thus, we initiated a rigorous study of UV irradiation experiments. As was previously validated with ESR and UV–vis spectral studies,

production of TPIRs and their recoupling into HABIs occur at bulk and in solution.^[4] In the present case, while L* showed TPIRderived strong absorbance in the range 450-650 nm with the peak at 568 nm (A₅₆₈) in its UV-vis spectrum, the absorbance completely disappeared from that of C_{mix} (Figure S5). It is remarkable that complete disappearance of absorption indicates no unreacted L* or longer linear PDMS having TPIR end groups exists in C_{mix}. From time-course plots of A₅₆₈ for products after UV irradiation to THF solutions of Cmix (1.0 and 0.1 mg/mL) recorded immediately after terminating UV irradiation (Figure S6), it is disclosed that almost all of TPIRs reverted into HABI within 30 min. Next, SEC of the products after UV irradiation to THF solutions of C_{mix} (10, 5.0, 1.0, and 0.5 mg/mL) showed decrease of the trace at higher MW region with lowering concentration (Figure 2c-g). The higher MW fraction eventually disappeared at the concentration of 0.10 mg/mL and the M_p of the resulting unimodal trace was 3600 (Figure 2g). The M_p ratio compared to that of L was 0.84 (3600/4300), which is similar to the reported values,^[1c, 2b] suggesting production of unimolecularly cyclized PDMS (C_{uni}). The MALDI-TOF mass spectra of L (Figure S7a) and C_{uni} (Figure S7b) showed a series of peaks with an interval of 74 mass units corresponding to the repeating dimethyl siloxane unit. Moreover, each peak exactly matched the total molar mass of the expected chemical structure of L and Cuni. For the former, the peak at the m/z = 2747.85, which is assumed to the adduct with H⁺, corresponds to L possessing the expected chemical structure with a DP_n of 25; (C₂H₆OSi) × 25 + C₅₄H₆₂ N₄OSi₄ plus H^+ equals 2747.88. And for the latter, the peak at the m/z = 2746.22, which is assumed to the adduct with H⁺, corresponds to

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Figure 2. SEC traces of (a) L, (b) C_{mix} , and products after UV irradiation to THF solution of C_{mix} at the concentrations of (c) 10.0 mg/mL, (d) 5.0 mg/mL, (e) 1.0 mg/mL, (f) 0.5 mg/mL, and (g) 0.1 mg/mL, respectively, determined using UV detector. The elution time corresponding to the M_p of L was indicated with the dashed line. SEC traces of (h) a mixture of the products after UV irradiation to THF solutions of C_{mix} at the concentrations of 10.0, 5.0, 1.0, and 0.5 mg/mL, (i) its UV irradiated product (the concentration of the reaction THF solution was 0.1 mg/mL), and (j) the product after further UV irradiation at bulk.

 C_{uni} possessing the expected chemical structure with a DP_n of 25; (C₂H₆OSi) × 25 + C₅₄H₆₀ N₄OSi₄ plus H⁺ equals 2745.87. The molar masses of L and C_{uni} differ by 2 mass units, confirming the elimination of two hydrogen atoms through the activation step (Figure 1a). Hence, unimolecularly cyclized C_{uni} was undoubtedly produced under dilution (Figure 3). We then mixed the remained UV irradiated products (products corresponding to Figure 2c, d, e,



and f) and subjected to SEC analysis. Of course, the SEC trace of the mixed product showed the trace (Figure 2h) similar to that of the parent C_{mix} (Figure 2b). Upon T-rex to its THF solution at the concentration of 0.10 mg/mL, the resulting product showed the SEC trace (Figure. 2i) surprisingly similar to that of C_{uni} (Figure 2g), revealing repeatable nature of T-rex and following PCR process. Moreover, further T-rex for the product without solvent for only 1 min resulted in increase of MW (Figure 2j), demonstrating chain extension under the solvent-free condition (Figure 3). Importantly, all of the above experiments of T-rex were achieved in air by taking advantage of the stability of TPIR against oxygen.^[13]

In the second, Cmix displays response to a mechanical stimulus. Among a wide variety of mechanical responses of polymer materials,^[14] main-chain scission is crucial because it seriously impairs their performance. Ultrasound is often utilized for causing main chain scission and for triggering reaction with compounds responding to mechanical stimuli (mechanophores).^[15] We envisioned that in-chain HABIs in cyclic PDMSs will be sacrificially cleaved into TPIRs upon ultrasound irradiation but will reproduce again. Interestingly, SEC traces of products immediately after ultrasound irradiation to Cmix displayed two distinct changes in their MW: (i) increase of MW in the initial stage (~10 min); and (ii) subsequent gradual decrease into a converged MW (10~120 min). Compared to the SEC curve of Cmix (Figure 4a), initial increase of MW is apparent by the shift of $M_{\rm p}$ toward higher MW region (Figure 4b). About 120% increase of M_p corresponds to the apparent MW ratio between cyclic and linear polymers with the identical absolute MW, suggesting cyclic to linear transformation took place by main chain scission. On the other hand, the latter stage supports further main chain scission (Figure 4c). As was established by conventional studies,



Figure 4. SEC traces of (a) C_{mix} , products after ultrasound irradiation for (b) 10 min and (c) 120 min and (d) a product after further UV₃₆₅ irradiation at the THF concentration of ca. 0.1 mg/mL. Dashed line indicates M_p of the larger fraction at the ultrasound irradiation time of 10 min. Time-course plots of (e) G' and G'' and (f) tan δ upon ON–OFF of UV irradiation to C_{mix} . The sample was irradiated with UV for 3 min during time ranges colored in pink.

ultrasound irradiation causes main chain scission of polymers, yet the response is dependent upon MW; as polymers below their MW thresholds do not respond to ultrasound.^[15] Time-course plots of MW upon ultrasound irradiation indeed resulted in convergence of MW (Figure S8). On the other hand, the SEC traces remained almost unchanged upon ultrasound irradiation to a smaller MW mixture prepared by irradiating UV to THF solution (1.0 mg/mL) of Cmix (Figure S9). These support the existence of a MW threshold similar to the conventional study.^[15] Finally, the ultrasound-irradiated product containing high MW fraction (Figure 4c) was subjected to photo-triggered T-rex under dilution (ca. 0.1 mg/mL). The SEC of the product after UV irradiation (Figure 4d) showed a trace similar to that of Cuni (Figure 2g). Moreover, MALDI-TOF mass spectrum (Figure S7c) showed a series of peaks nearly identical to those of Cuni (Figure S7b). Remarkably, these results demonstrate that ultrasound irradiation does not cause ill-defined main chain scission but cause site-specific and sacrificial cleavage of the covalent bond between the two imidazoles in HABI similar to the mechanophore reported in the literature.^[16] It is also noteworthy that both of mechanical- and photo-stimuli dissociate polymer chains with mechanistically different but complemental principles and we are able to reset the MW of C_{mix} through photo-triggered T-rex in either case.

In the third, UV irradiation to C_{mix} dramatically and repeatedly changes its rheological properties under a solvent-free isothermal condition with retaining liquid character of PDMS. As was expected from flowable characteristic, C_{mix} shows loss modulus (*G*") higher than storage modulus (*G*') in the frequency range of 1–10 Hz (Figure S10). This is typical behavior of liquid materials. Time-course plots of *G*' and *G*" upon ON–OFF cycles of UV irradiation showed their sudden decreases and increases (Figure 4e). Both of *G*' and *G*" repeatedly decreased to converged values within 1 min upon UV irradiation and completely reverted

within 4 min after terminating the irradiation. The response of Cmix is significantly faster than that of previously reported network materials likely owing to its liquid nature, allowing effective diffusion of TPIR end groups within the PDMS matrix.^[4] Moreover, as appeared in time-course plots of loss tangent (tan $\delta = G''/G'$), liquid-like character of the UV irradiated material become further conspicuous; the tan δ increased by the factor of 5 and became almost 8 compared with those of the former ca. 1.6 (Figure 4f). To further clarify the effect of MW on the response of rheological properties upon UV irradiation, we prepared linear PDMS having lophine end groups with longer chain length (L_I, $M_n(NMR)$ = 20000) and cyclic PDMS synthesized therefrom (CI, mix). Shift of $M_{\rm p}$ from L_I (Figure S11a) to C_{I, mix} (Figure S11b) suggests that C_I, mix is composed of about three Lis. The number of components is quite less than the aforementioned C_{mix} (Figure 2b), which is composed of about ten Ls (Figure 2a). Time-course plots of G' and G" upon ON-OFF cycles of UV irradiation to CI, mix showed trends similar to those of C_{mix} but the response was less prominent (Figure S12). This indicates the magnitude of the change in MW upon T-rex is one of the decisive factors in the present system.

In conclusion, we have established the methodology for repeatedly reconstructing cyclic MAs triggered bv photostimulation. Photo-triggered T-rex against in-chain HABIfunctionalized cyclic PDMSs enables reproduction of cyclic PDMSs with a desired mixing state of ring sizes; from the uniform monocyclic to the maximally broad polydispersed state depending on the UV-irradiating condition (diluted, concentrated, or solventfree condition). The in-chain HABIs also enable sacrificial dissociation of polymer chains upon the application of ultrasound. While MW decreases to converge into its threshold upon ultrasound irradiation, further photo-triggered T-rex enables complete dissociation into L* and reverts, for example, back to

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unimolecularly cyclized PDMS under dilution. Moreover, T-rex enables repeatable and dramatic change in rheological properties of PDMS with retaining its liquid character. Given that PDMS is known as an industrially important polymeric material, the concept of T-rex developed here could be useful for applications ranging from lubricants, greases, and adhesives.

Acknowledgements

We are grateful to Mr. Yuichi Shinozaki, Mr. Ryuta Kawanishi, Mr. Ryuuichi Yoshida, and Mr. Sadayuki Tanaka (Anton Paar Japan K.K.) for their kind support for the rheological analyses and to Prof. Robert M. Waymouth (Stanford University) for helpful discussion. Synchrotron radiation-SAXS measurements were performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2017G124 S.H.). This work was supported by JSPS Grant-in-Aid for Scientific Research on Innovative Areas "Discrete Geometric Analysis for Materials Design" (Grant Number 18H04479 S.H.) and JSPS KAKENHI (Grant Numbers 16K14074 S.H., and 16H04032 T.T.)..

Keywords: polymers • cyclic polymers • photochemistry • macromolecular architecture • rheology

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Topology reset execution (T-rex):

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