Photo-Triggered Topology-Reset Execution of Cyclic Polymers for the Tuning of Viscoelasticity

Repeatable topological transformation of polymers has been a challenge for modulating material functions. We synthesized cyclic poly(dimethylsiloxane)s (PDMSs) containing various ring sizes in-chain linked with hexaarylbiimidazoles (HABIs) from linear PDMSs with 2,4,5-triphenylimidazole (lophine) end groups. The physical state of PDMS turned into liquid simply by converting lophines into HABIs from the former solid state of linear PDMS. Based on the photochemistry of HABI, cyclic PDMSs were successfully reset to linear PDMSs having triphenylimidazoryl radical (TPIR) end groups upon photoirradiation, and subsequent termination of photoirradiation enabled recyclization into cyclic PDMSs again. Moreover, photoirradiation of cyclic PDMSs enabled solvent-free switching of rheological properties.

Advances in synthetic polymer chemistry have produced various nonlinear polymers such as cyclic, star, comb-like, and network polymers. There is much interest in studying topology-property relationships because the topology of polymers often dramatically differentiates their properties. An ongoing challenge in this field is to establish a reversible topological transformation system for switching their properties [1–5]. Obviously, it is important to develop a solventless repeatable topological transformation process, but this remains mostly unrealized.

On the other hand, changes in the physical states of materials are a familiar phenomenon in daily life. Such changes between physical states or viscoelasticity are generally caused by heat stimulation. However, materials displaying a change in viscoelasticity including a liquid-solid change upon receiving external stimuli



Figure 1: (a) Photochemistry of HABI. (b) Synthesis of inchain HABI-functionalized C_{mix} and cyclic–linear topological transformation based on photo-triggered cleavage and reformation of HABI

other than heat are rare. The conventional approach to attaining such materials is to use photoisomerizable molecules. Notable examples are isothermal melting and crystallization of multi-azobenzene-containing branched small molecules [6, 7] based on photoinduced phase transition [8] and reversible shift in the glass transition temperature of side-chain azobenzenecontaining polymers [9]. In contrast, we have focused on network materials containing reversibly cleavable and reformable covalent linkings. In particular, we have used the photochemistry of hexaarylbiimidazole (HABI) [10]. HABI undergoes cleavage of the covalent bond between the two imidazoles to generate a pair of triphenylimidazoryl radicals (TPIRs) upon photoirradiation and the generated TPIRs readily recouple into HABI upon terminating photoirradiation [Fig. 1(a)]. Importantly, TPIRs are stable even in the presence of oxygen and thus the photochemistry can be achieved in air [11]. We have used this photoreaction for repeatable transformation of the topologies of polymers and realized phototriggered solvent-free isothermal liquid-nonliquid conversion of network poly(dimethyl siloxane)s (PDMSs) at room temperature [12]. To extend the current frontier of this chemistry, the construction of a simple topological transformation system and nanoscale analysis of these materials for more sophisticated polymer design remain crucial issues to be tackled.

We synthesized cyclic PDMSs linked with HABIs (C_{mix}) from linear PDMSs having lophine end groups (L). The lophine end groups of L were oxidized to produce linear PDMS with TPIR end groups (L*) and subseguent coupling of TPIRs into HABI occurred intra- and inter-molecularly to afford C_{mix} [Fig. 1(b), top]. Although **L** and C_{mix} have guite similar chemical compositions and C_{mix} has a much higher molecular weight, the appearance of L and C_{mix} was completely different; that is, while L was solid, C_{mix} was viscous liquid [Fig. 2(a)]. Related to this, DSC and IR analyses indicated the existence of hydrogen bonding (H-bonding) only in L. We have further analyzed synchrotron radiation small angle X-ray scattering (SAXS) profiles of L and C_{mix} to evaluate the molecular ensemble on a nanoscale. Analogous to thermoplastic elastomers formed by triblock



G' and G' and (d) tan δ of C_{mix} upon ON–OFF UV irradiation cycles (the periods of UV irradiation are colored in pink).

copolymers, linear polymers having H-bonding end groups cause microphase separation. As was studied by SAXS, such materials show scattering derived from end groups. The SAXS profile of L showed a scattering similar to the reported one and the peak scattering vector (q^*) was 1.01, corresponding to an averaged distance of about 6 nm between two aggregates formed by end groups [Fig. 2(b), light blue line]. In contrast, SAXS of C_{mix} showed no aggregates-derived scattering [Fig. 2(b), red line]. It is noteworthy that the simple conversion of lophines into HABIs changes the material to a homogeneous liquid.

By taking advantage of the liquid character of C_{mix}, we conceived of solvent-free repeatable tuning of viscoelasticity upon photoirradiation of C_{mix} while retaining the liquid state. Time-dependent plots of G' and G'' of C_{mix} upon ON-OFF UV (365 nm, 150 mW/cm²) irradiation cycles showed their sudden decrease and increase [Fig. 2(c)]. Both of G' and G'' repeatably decreased to converged values within 2 min upon UV irradiation and reverted within 4 min after terminating irradiation. As shown in the time-dependent plots of loss tangent (tan $\delta = G''/G'$), UV irradiation suddenly increased tan δ from 1.6 to almost 8 [Fig. 2(d)], indicating the UVirradiated product has a more liquid-like character.

Solventless photo-triggered repeatable transformation of cyclic and linear topologies resulted in dramatic changes in the rheological properties of PDMS while retaining the liquid state, which is arguably important for a broad range of applications. The key process here is resetting a polymer topology into that of precursor, and thus we have named this strategy "topology-reset execution (T-rex)" [13]. Work on expanding the T-rex strat-



egy to different combinations of polymer topologies and characterizing unprecedented properties is currently in progress.

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