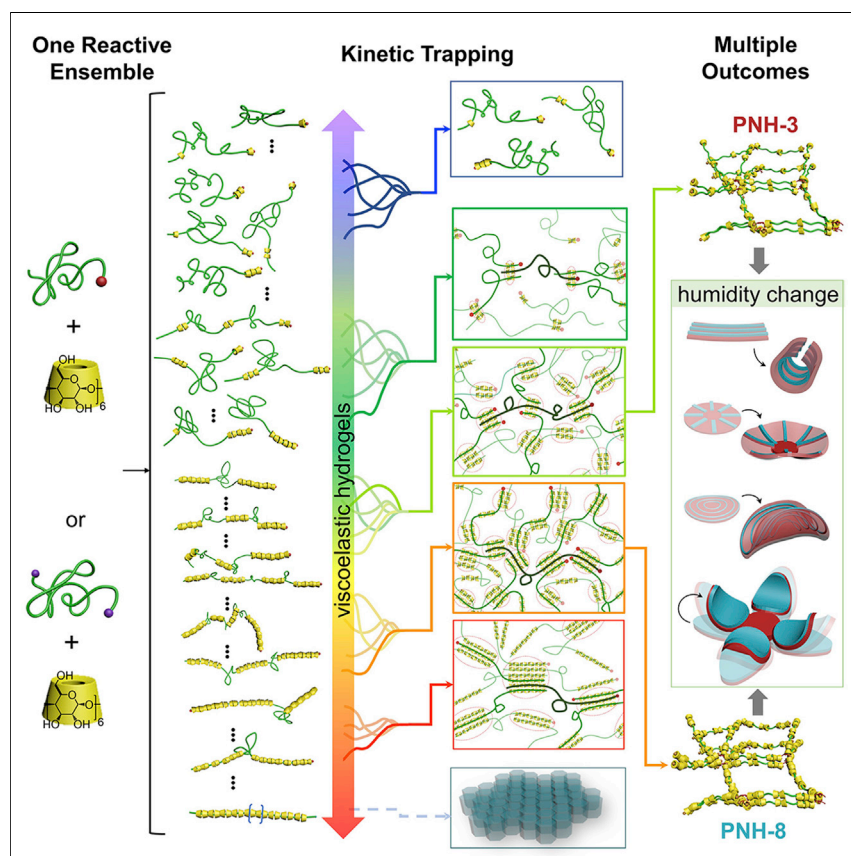


Article

Kinetic trapping of 3D-printable cyclodextrin-based poly(pseudo)rotaxane networks



A concerted kinetic trapping method is demonstrated to capture different α -cyclodextrins and polyethylene glycols-based polypseudorotaxane network hydrogels. Varying the 3D printing temperatures, one hydrogel was diverged to two polyrotaxane networks and fabricated as a moisture-responsive actuator.

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Highlights

The kinetic formation of polypseudorotaxane was navigated synthetically

A series of physically crosslinked networks were kinetically trapped

One reactive ink was diverged into two networks by varied-temperature-3D printing

Packing models of polypseudorotaxanes in the solid-state was corrected



Article

Kinetic trapping of 3D-printable cyclodextrin-based poly(pseudo)rotaxane networks

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SUMMARY

Synthetically trapping kinetically varied (super)structures of molecular assemblies and amplifying them to the macroscale is a promising, yet challenging, approach for the advancement of meta-stable materials. Here, we demonstrated a concerted kinetic trapping design to timely resolve a set of transient polypseudorotaxanes in solution and harness a crop of them via micro-crystallization. By installing stopper or speed bump moieties on the polymer axles, meta-stable polypseudorotaxanes with segmented cyclodextrin blocks were hierarchically amplified into crystalline networks of different crosslinking densities at mesoscale and viscoelastic hydrogels with 3D-printability in bulk. We demonstrated simultaneous 3D-printing of two polypseudorotaxane networks from one reactive ensemble and their conversion to heterogeneous polyrotaxane monoliths. Spatially programming the macroscale shapes of these heterogeneous polyrotaxanes enabled the construction of moisture-responsive actuators, in which the shape morphing originated from the different numbers of cyclodextrins interlocked in these polyrotaxane networks.

INTRODUCTION

Supramolecular assemblies, formed under thermodynamic control, have been advanced as a plethora of architectures with high order¹ and high complexity,² as well as stimuli-responsive behaviors.^{3,4} Meta-stable materials^{5–7} and dissipative systems,⁸ formed under kinetic control, often demonstrate superior properties compared with their thermodynamic counterparts due to the differences in energy between their kinetically trapped and stable states. For example, meta-stable metal alloys, perovskites, organic crystals, and organogels show high strength and ductility,⁵ efficient solar-electric conversion,⁶ high porosity,⁷ and photo-switchability,^{9–12} respectively, giving rise to their kinetically trapped structures and morphologies.

Kinetically varied structures and superstructures, however, are often short-lived, and they converge to their stable states rapidly under thermodynamic control. Conventional approaches to trap these transient kinetic variants for the synthesis of meta-stable materials usually involve large physical changes such as rapid cooling and ultrahigh-pressure treatment.^{13,14} Delicate control of the physical variation is critical in this process, due to the co-existence of multiple kinetic paths.^{15,16} In contrast, synthetically modulating the kinetic process to harness the high-energy states¹⁷ offers better selectivity in trapping the desired meta-stable species. To date, diverting the formation of molecular assemblies chemically into kinetic paths was largely

The bigger picture

Meta-stable polymers hold promise for the development of next-generation intelligent materials due to their positive free energy compared with the stable states. However, conventional development of meta-stable materials heavily relies on preparation methods, i.e., rapid cooling, high-pressure treatment, and controlled diffusion. The lack of understanding and control of these kinetic processes across the nano-to-mesoscale challenges the rational synthesis of meta-stable materials. Herein, we demonstrated a synthetic approach to access polypseudorotaxanes' meta-stable states at the molecular level, navigated their crystallization at mesoscale, effectively amplified their structural features to the macroscale, and spatially programmed them as 3D-printed actuators. Future refinements of the axle polymer and speed bump design will expand the meta-stable states' control and network architectures. We envision fabricating 3D architectures with complex soft robotic motions through this approach.

achieved in solution through the modulation of strong non-covalent interactions.^{8,15,16} Design principles to direct the kinetic assembly process across the nano-to-macroscale remain largely heuristic.

In the exploration of the rational design of meta-stable poly(pseudo)rotaxane materials,¹⁸ we seek to divert the formation and crystallization of α -cyclodextrin (α -CD) and polyethylene glycol (PEG)-based polypseudorotaxanes away from the thermodynamic path (Figure 1A). By installing stopper or threading “speed bumps”^{18–20} on the PEG chain end(s), the kinetic energy barriers¹⁴ for the solution-phase polypseudorotaxanes assembly were raised (Figure 1B). A spectrum of polypseudorotaxanes with segmented α -CD blocks (Figure 2) was kinetically resolved and micro-crystallized, following new kinetic crystallization paths with lower energy barriers (Figure 1B). We discovered that the solution-phase kinetic assembly and micro-crystallization of polypseudorotaxanes is a concerted process, affording meta-stable products as physically crosslinked hydrogels with suitable viscoelasticity for direct-ink-write²¹ (DIW) 3D-printing. By diverging the same reactive ensemble of PEG_{4k}-Nor₂ and α -CD simultaneously into two kinetically trapped polypseudorotaxane hydrogels at two temperatures, we obtained 3D-printed heterogeneous polypseudorotaxane hydrogels with spatially configured shapes and compositions. We permanently fixed these meta-stable polypseudorotaxane networks through post-printing covalent crosslinking, and converted them as polyrotaxane networks. As a result of the different numbers of mechanically interlocked α -CDs in each polyrotaxane network, they demonstrated different responsiveness to humidity changes. We demonstrated that, by varying the macroscale 3D-printing designs, the obtained heterogeneous polyrotaxane monoliths exhibited pre-programmed moisture-responsive actuations.

RESULTS

Molecular design considerations

When α -CDs are threaded onto a short-to-medium chain PEG (smPEG, $M_n < 6$ kDa), the smPEG axle is covered by a tube of consecutively hydrogen-bonded α -CDs,^{22–24} forming crystalline polypseudorotaxane precipitates with constant ethylene glycol (EG): α -CD molar ratios.²⁵ These investigations by others²⁵ and us²⁴ suggest that the threading and translocation energy barriers of α -CDs onto smPEGs are small in solution (Figure 1A), but the energy barrier for polypseudorotaxane crystallization is relatively large (rate determining step). Any kinetic variant of polypseudorotaxane in solution was converged to the stable form before crystallization, thus preventing the isolation of kinetically trapped polypseudorotaxanes.

To access these kinetic variants chemically, the energy barrier for the formation of polypseudorotaxane in solution needs to be raised relative to the energy barrier of micro-crystallization (Figure 1B). We designed two types of energy barriers (Figure 2)—(1) by installing a stopper onto one end of the PEG, the translocation distances²⁶ of α -CDs are elongated compared with bare PEG. The coiled PEG axle acts as a dynamic energy barrier to slow down the translocation of α -CDs. (2) By attaching sterically demanding “speed bumps”¹⁸ onto both ends of the PEG, the threading of α -CDs onto the PEG axle is decelerated. Experimentally, we chose adamantylester (-Ad) as the stopper²⁷ and norbonylester (-Nor) as the speed bump²⁸ (~ 4.7 Å) for α -CDs, respectively. Smaller end groups, including hydroxyl (-OH), acylester (-Ac), and benzoylester (-Bz), were also synthesized as α -MeO- ω -R-PEGs (Figure 1C), which were employed as reference axles.

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<https://doi.org/10.1016/j.chempr.2021.06.004>

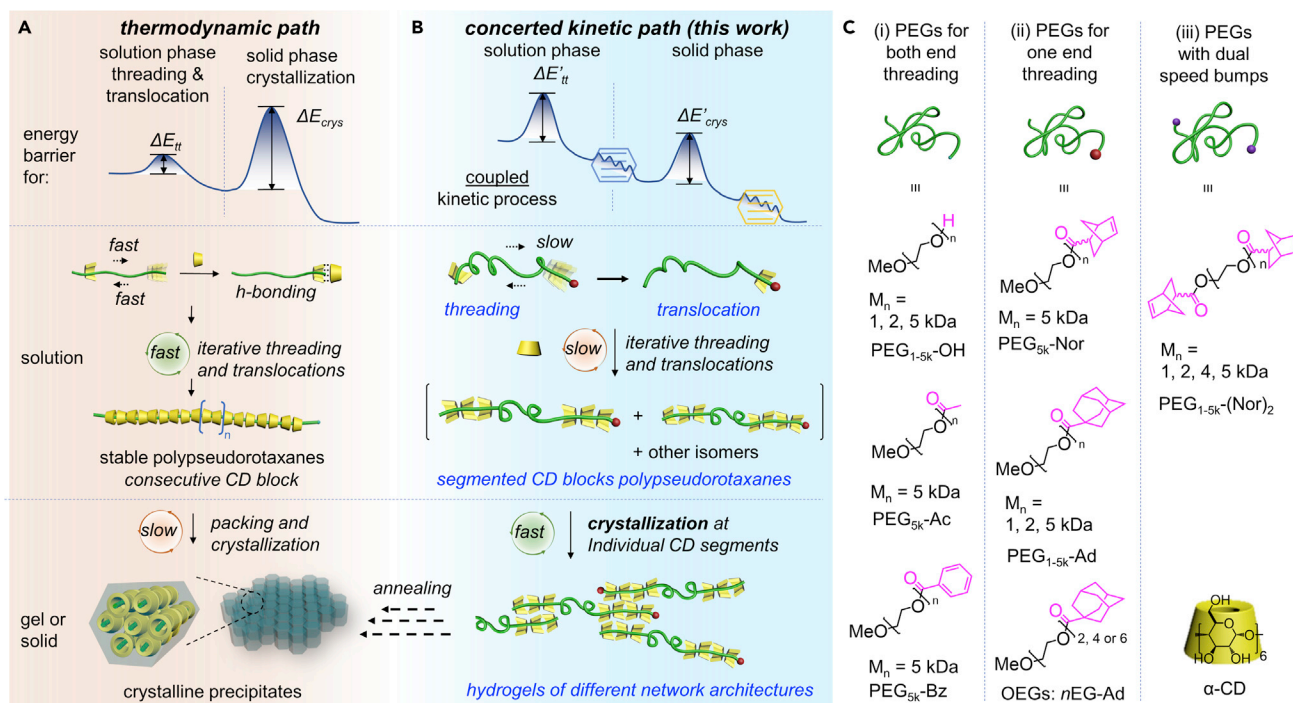


Figure 1. A comparison between the conventional crystalline polypseudorotaxane formation and the concerted kinetic formation of polypseudorotaxane networks via threading-and-crystallization path

(A and B) Energy barriers and graphical representations of the conventional polypseudorotaxanes formation under thermodynamic control (A) and the concerted kinetic formation of meta-stable polypseudorotaxane networks (B). The decelerated threading and translocation of α -CDs on the PEG axle stabilized the otherwise transient polypseudorotaxanes with segmented α -CD blocks, which enabled a new path for kinetic micro-crystallization. (C) PEGs and oligoethylene glycols (nEG-Ad) employed for the formation of α -CD-based polypseudorotaxanes.

Kinetic investigations of meta-stable polypseudorotaxane networks formation

In a PEG_{5k}-OH (1 mM) and α -CD (50 mM) mixture (20°C), α -CDs rapidly threaded onto PEG_{5k}-OH and crystallized as white suspensions. The transmittance²⁹ of the reaction decreased rapidly over time (Figure 3A) due to the increased light scattering (550 nm) of the fast-forming crystalline precipitates. Similarly, the transmittance of reactions of PEG_{5k}-Ac/ α -CD and PEG_{5k}-Bz/ α -CD also decreased quickly upon mixing. In parallel, crystalline PEG_{5k}-OH/ α -CD polypseudorotaxanes formed at different times were collected for ¹H NMR analysis (Figure 3B). The number of α -CDs threaded onto PEG_{5k}-OH was measured to be independent of the reaction time at a constant of 41 ± 1 α -CDs per PEG. These observations are consistent with previous reports,²⁹ indicating the formation of these crystalline polypseudorotaxanes underwent the thermodynamic path.

When PEG_{5k}-Ad (1 mM) was mixed with α -CD (50 mM) at 20°C, the transmittance of the reaction did not change for a long period (~ 100 min, Figure 3C), suggesting that the rate of polypseudorotaxane formation is significantly reduced compared with PEG_{5k}-OH/ α -CD (~ 15 min) in solution. Time-dependent ¹H NMR experiments revealed that the polypseudorotaxane consists of a constant 42 ± 2 α -CDs per PEG_{5k}-Ad (Figure 3B). In the temperature-dependent polypseudorotaxane formation experiments (Figure 3D), the reaction of PEG_{5k}-Ad and α -CD showed "V"-shaped transmittance changes at 25°C and 30°C. This two-stage polypseudorotaxanes precipitation was also confirmed in the time-dependent ¹H NMR experiment (Figure S10). These experiments suggested that, over a period of time, the

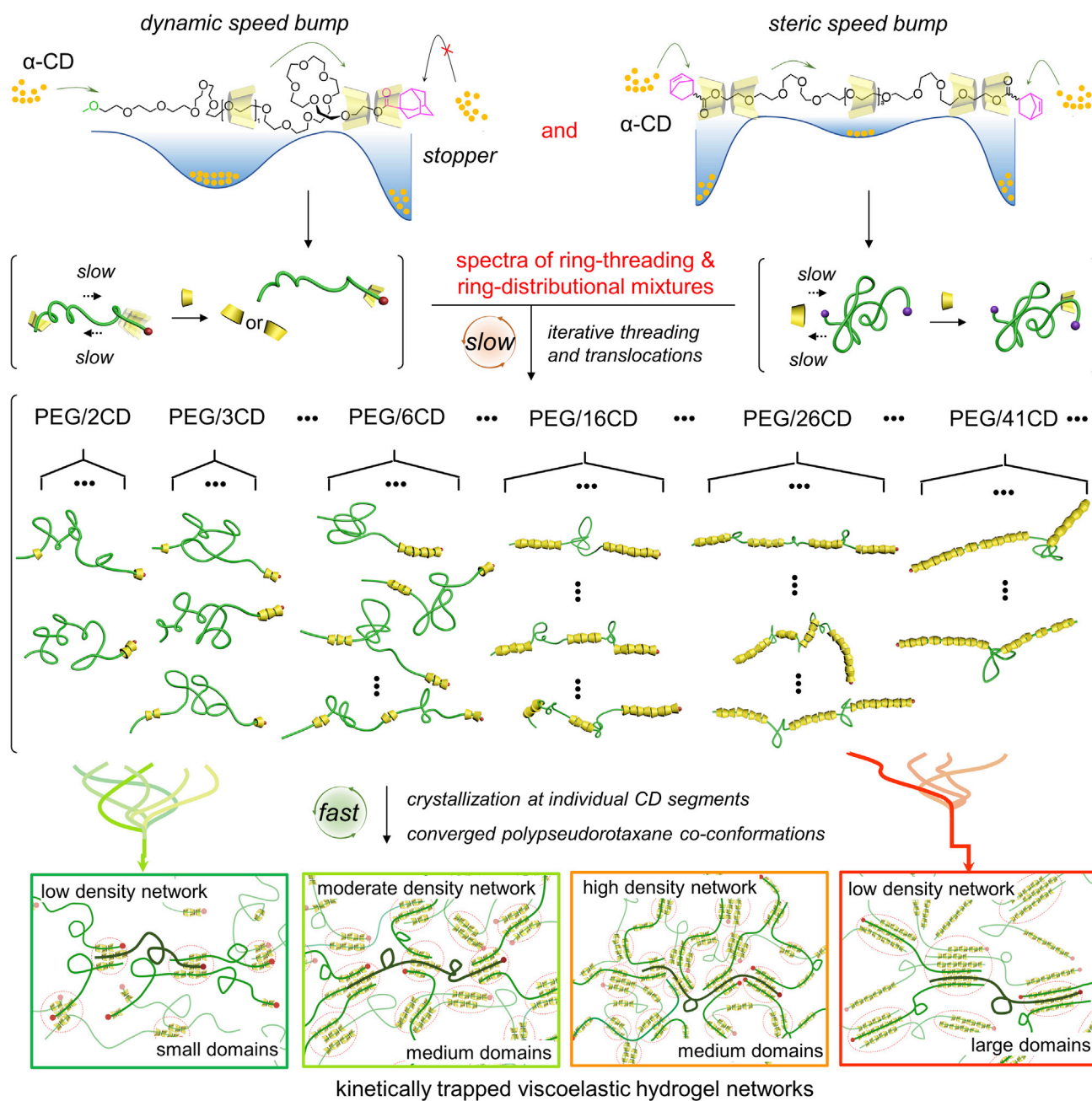


Figure 2. Kinetic trapping of meta-stable polypseudorotaxane networks of different crosslinking densities

Adamantylester and norbonylester end group(s) were installed on PEG axes, creating kinetic barriers to diverge the threading and translocation of α -CDs, resolving a spectrum of polypseudorotaxanes in solution. These polypseudorotaxanes were trapped by kinetic micro-crystallization to afford physically crosslinked crystalline networks of various densities.

accumulated PEG_{5k}-Ad/ α -CD polypseudorotaxanes in solution were not sufficient to allow for continuous crystallization. The rate of the PEG_{5k}-Ad-based polypseudorotaxanes formation in solution and the rate of their crystallization became much more comparable.

The differences in crystallization kinetics between PEG_{5k}-OH/ α -CD and PEG_{5k}-Ad/ α -CD polypseudorotaxanes were investigated by temperature-dependent

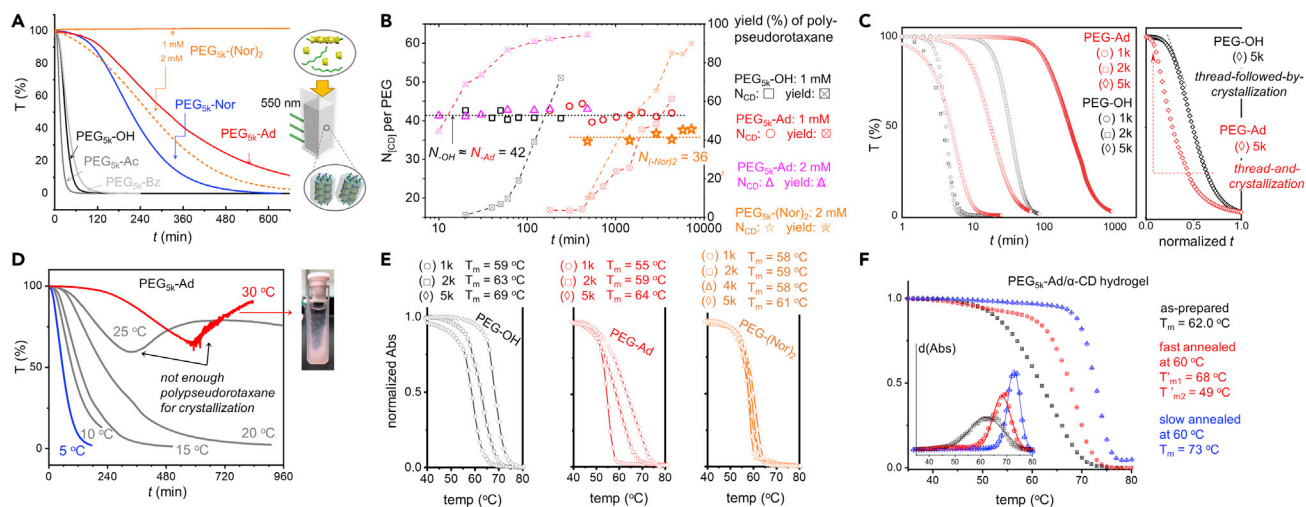


Figure 3. Kinetic investigations of the threading and translocation of α -CDs on polymer axes and the crystallization of polypseudorotaxanes

(A) Time-dependent transmittance of the reactions of α -CD (50 mM, 100 mM for PEG_{5k}-(Nor)₂) and PEG_{5k} (1 mM, 2 mM for PEG_{5k}-(Nor)₂) with different end groups at 20°C. $l = 10$ mm, $\lambda = 550$ nm.

(B) ¹H NMR analysis of the threaded α -CDs per PEG at different times and the measured yields of the polypseudorotaxanes.

(C) Time-dependent transmittance and time-normalized transmittance (right) of the reactions of α -CDs (50 mM) with PEG_{1-5k}-OH, and PEG_{1-5k}-Ad at 20°C, PEG_{1k}, PEG_{2k}, and PEG_{5k} concentrations of 5, 2.5, and 1 mM, respectively, at 20°C.

(D) Time-dependent transmittances of the reactions of α -CD (50 mM) and PEG_{5k}-Ad (1 mM) measured at different temperatures.

(E) Temperature-dependent melting profiles and calculated T_m of polypseudorotaxane aggregates formed by α -CD/PEG_{1-5k}-OH, α -CD/PEG_{1-5k}-Ad, and α -CD/PEG_{1-5k}-(Nor)₂. Heating rate: 1°C/min. $l = 2$ mm.

(F) Melting profiles of a α -CD/PEG_{5k}-Ad polypseudorotaxane hydrogel in its as-prepared form (black), 60°C fast annealed (red) and slow annealed (blue) forms. $l = 1$ mm. Samples were diluted by half to PEG_{5k}-Ad (1 mM) and α -CD (50 mM) for measurements. Inset: fitted T_m .

transmittance experiments (Figures 3D and S11) and their crystallization energy barrier³⁰ difference was calculated as $\Delta E'_{\text{crys}} - \Delta E_{\text{crys}} = -24$ kJ/mol (Figures 1 and S12). The faster crystallization of PEG_{5k}-Ad/ α -CD polypseudorotaxanes was evident in the early onset of transmittance decrease in the time-normalized transmittance spectra (Figure 3C), where the crystallization of PEG-Ad polypseudorotaxanes took place concurrently with the formation of the polypseudorotaxanes in solution, compared with the formation-followed-by-crystallization process in the case of the PEG-OH polypseudorotaxanes. Therefore, the raised energy barrier of PEG_{5k}-Ad/ α -CD polypseudorotaxanes formation in solution and decreased energy barrier of crystallization enabled a concerted threading-and-crystallization process, where the as-formed polypseudorotaxanes were rapidly trapped by crystallization.

Despite PEG_{5k}-OH/ α -CD and PEG_{5k}-Ad/ α -CD polypseudorotaxanes having nearly identical numbers of threaded α -CDs, the large differences of their assembly kinetics in solution and crystallization implied that PEG-Ad/ α -CD polypseudorotaxanes possess very different structures compared with the tubular PEG-OH/ α -CD polypseudorotaxanes.²³ When the first few α -CDs threaded on to PEG_{5k}-Ad, the α -CD/Ad side-on complexation drove these α -CDs to translocate throughout the entire PEG axle to reach the -Ad end. This side-on complexation formation was confirmed as the binding affinity between an oligo-glycol adamantylester 2EG-Ad and α -CD was measured as $K_a = 105$ M⁻¹ at 25°C (Table S2; Figure S16), being larger than the affinity of $K_a = 5$ M⁻¹ for 2EG and α -CD.³¹ Increasing the (EG)₂ moieties to 4EG-Ad and 6EG-Ad resulted in the binding affinities between α -CD and every extended (EG)₂ moiety decreasing gradually (Table S2). When the PEG_{5k}-Ad axle reached 5k Da, the later threaded α -CDs could be segregated kinetically between coiled PEG segments at different locations (Figure 2) in which the coiled PEG axle

acted as a dynamic translocation energy barrier. To confirm this possibility, shorter PEG-OH and PEG-Ad axles (1k and 2k Da) were employed for the time-dependent polypseudorotaxanes formation experiments (Figure 3C). Reducing the axle length from 5k to 2k and 1 kDa, the formation and crystallization between PEG-Ad and PEG-OH polypseudorotaxanes became increasingly comparable, since less segmented α -CD blocks could be kinetically trapped on shorter PEG-Ad axles.

When these polypseudorotaxanes with segmented α -CD blocks crystallized before they reached the thermodynamically preferred tubular co-conformations in solution, these kinetically resolved polypseudorotaxanes were trapped as micro-crystallized meta-stable aggregates. This early crystallization could be attributed to faster diffusion and conformational relaxation³² of the segmented α -CD blocks. To assess the energy differences between the crystallized PEG_{5k}-OH/ α -CD and PEG_{5k}-Ad/ α -CD polypseudorotaxanes, melting curve analyses were carried out (Figures 3E and 3F). The melting points (T_m) were measured to reflect the energy required to extensively break the multivalent hydrogen bonding interactions of the crystalline domain (Table S3; Figures S23 and S24). Compared with a $T_m = 69^\circ\text{C}$ and a narrow melting profile of PEG_{5k}-OH/ α -CD, the lower $T_m = 64^\circ\text{C}$ and broader melting curve of PEG_{5k}-Ad/ α -CD (Figure 3E) suggest that less extensive hydrogen-bonding networks were formed in its crystalline domains. Annealing the PEG_{5k}-Ad/ α -CD polypseudorotaxanes resulted in narrower melting profiles and higher T_m in PEG_{5k}-Ad/ α -CD (Figure 3F). These experiments suggested that the formed PEG_{5k}-Ad/ α -CD polypseudorotaxanes are kinetic products with higher energies compared with their stable states. The broad melting profile of the as-prepared PEG_{5k}-Ad/ α -CD sample suggested that the PEG_{5k}-Ad/ α -CD polypseudorotaxanes were constituted by a dispersed mixture of PEG_{5k}-Ad/ α -CD co-conformers, which converged to the stable conformer during the annealing process. Furthermore, the melting temperature differences between the PEG-Ad/ α -CD and PEG-OH/ α -CD polypseudorotaxanes at shorter PEG axles were smaller (Figure 3E) since the translocation energy barriers for α -CDs are decreased at short PEG axles.

When PEG-(Nor)₂ of different molecular weights were employed as axles, the bulky -Nor end groups reduced the rate of α -CD (de)threading, resulting in fewer threaded α -CDs per PEG_{5k}-(Nor)₂ (a constant of 36 ± 1 α -CDs, Figure 3B). Since the -Nor moieties also formed side-on complexes with α -CDs (Table S2), less dispersed co-conformers of polypseudorotaxanes were trapped kinetically, featuring α -CD blocks at each chain end and the middle of the PEG (Figure 2). This is evident in the narrow melting profiles of PEG_{1-5k}-(Nor)₂/ α -CD polypseudorotaxanes (Figure 3E). Note that higher reactant concentrations are required to form crystalline polypseudorotaxane aggregates, which indicates that the crystallization threshold could be adjusted (i.e., reaction concentrations) to selectively trap polypseudorotaxanes in different kinetic states.

At higher concentrations, PEG_{5k}-Ad/ α -CD polypseudorotaxane ([PEG_{5k}-Ad] = 6 mM) formed much stronger hydrogels compared with PEG_{5k}-OH/ α -CD hydrogels³³ at various EG/ α -CD ratios (Figure 4A). When decreasing the EG/ α -CD ratio from 10:1 to 2:1 (more fed α -CD, I to IV, Figure 4A), the elastic moduli of the hydrogels composed of PEG_{5k}-Ad/ α -CD increased first to a maximum $G' = 0.52$ MPa at EG/ α -CD = 4:1 and then decreased. By changing the fed EG/ α -CD ratio from 10:1 to 4:1, the number of threaded α -CDs increased from 15 to 28 α -CDs per PEG (Table S1). More segmented α -CD blocks were kinetically trapped and crystallized, which increased the crosslinking density of the hydrogel networks to an optimized network density and crystalline domain size (III, Figure 4A). Further changing the EG/ α -CD

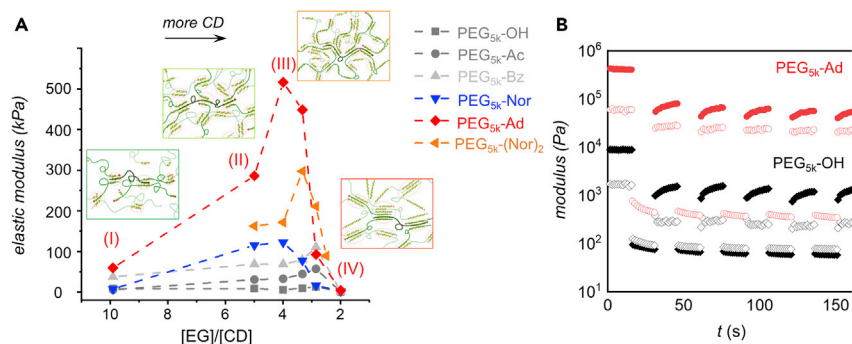


Figure 4. Rheological investigations of kinetically trapped polypseudorotaxane networks

(A) Elastic moduli of polypseudorotaxane hydrogels measured by angular frequency sweeps. Hydrogels were prepared by mixing α -CD (67 to 330 mM) and PEG_{5k}-R (8 mM) at listed EG/ α -CD ratios.

(B) Step-strain rheological profiles of polypseudorotaxane hydrogels composed of PEG_{5k}-OH/ α -CD and PEG_{5k}-Ad/ α -CD at an EG/ α -CD ratio of 4:1. Alternating 0.1% and 100 % strain were applied to the sample every 15 s.

ratio to 2:1, the number of threaded α -CDs increased to 44 α -CDs per PEG (Table S1), which significantly lowered the number of α -CD blocks formed on the PEG axle and reduced the network crosslinking density (IV, Figure 4A). Similarly, a “ Δ ”-shaped elastic moduli variation of hydrogels formed by PEG_{5k}-(Nor)₂/ α -CD were also measured at different EG/ α -CD ratios (Figure 4A). The maximum $G' = 0.30$ MPa of PEG_{5k}-(Nor)₂/ α -CD hydrogel was recorded in EG/ α -CD = 3.3:1, in which an averaged 26 α -CDs were threaded on the axle (Table S1). In great contrast, the elastic moduli of PEG_{5k}-OH/ α -CD polypseudorotaxane hydrogels demonstrated little change at various EG/ α -CD ratios, highlighting the differences of the polypseudorotaxane networks formed under kinetic (PEG_{5k}-Ad/ α -CD and PEG_{5k}-(Nor)₂/ α -CD) and thermodynamic (PEG_{5k}-OH/ α -CD) paths. Step-strain rheological experiments (Figures 4B and S27) showed that both PEG_{5k}-Ad/ α -CD and PEG_{4-5k}-Nor/ α -CD hydrogels exhibited rapid self-healing properties for 3D-printing, but PEG_{5k}-OH/ α -CD hydrogels were not 3D-printable.

Structural analyses of α -CD/PEG polypseudorotaxanes

To structurally verify the segmented α -CD blocks in the kinetically trapped polypseudorotaxanes hydrogels, small-, wide-angle X-ray diffractions (S/WAXS), and scanning electron microscopy (SEM) analyses were carried out. However, the widely adopted parallelly packed PEG/ α -CD polypseudorotaxanes model³⁴ disfavors the crystallization of α -CD blocks of different sizes (Figure S29). We, fortunately, obtained high-quality hexagonal single-crystals of PEG₆₀₀-(OH)₂/ α -CD polypseudorotaxanes (Figure 5A). For the first time, we revealed the molecular details of the crystalline domains. Two co-existing polymorphs of PEG₆₀₀/ α -CD polypseudorotaxanes were consistently discovered as PEG₆₀₀-(OH)₂/6(α -CD) and [(EG)₄/2(α -CD)]_n complexes through a solvent evaporation method. The major polymorph PEG₆₀₀-(OH)₂/6(α -CD) complex (Figure 5A) crystallized into a trigonal P3₂21 space group with $a = b = 23.7877$ Å, $c = 52.0858$ Å. The minor polymorph [(EG)₄/2(α -CD)]_n complex (Figure 5A) crystallized into a P321 space group with $a = b = 23.5446(15)$ Å, $c = 15.7523$ Å. In the PEG₆₀₀-(OH)₂/6(α -CD) complex, there are six α -CDs hydrogen-bonded in a head-to-head and tail-to-tail manner on the PEG axle. The secondary faces of the two α -CDs located at the PEG chain end (blue colored, O●●●O = 6.45 and 6.71 Å, Figure 5A) are hydrogen-bonded via water molecules along the c -axis. In [(EG)₄/2(α -CD)]_n, threaded α -CDs on the PEG are tightly packed

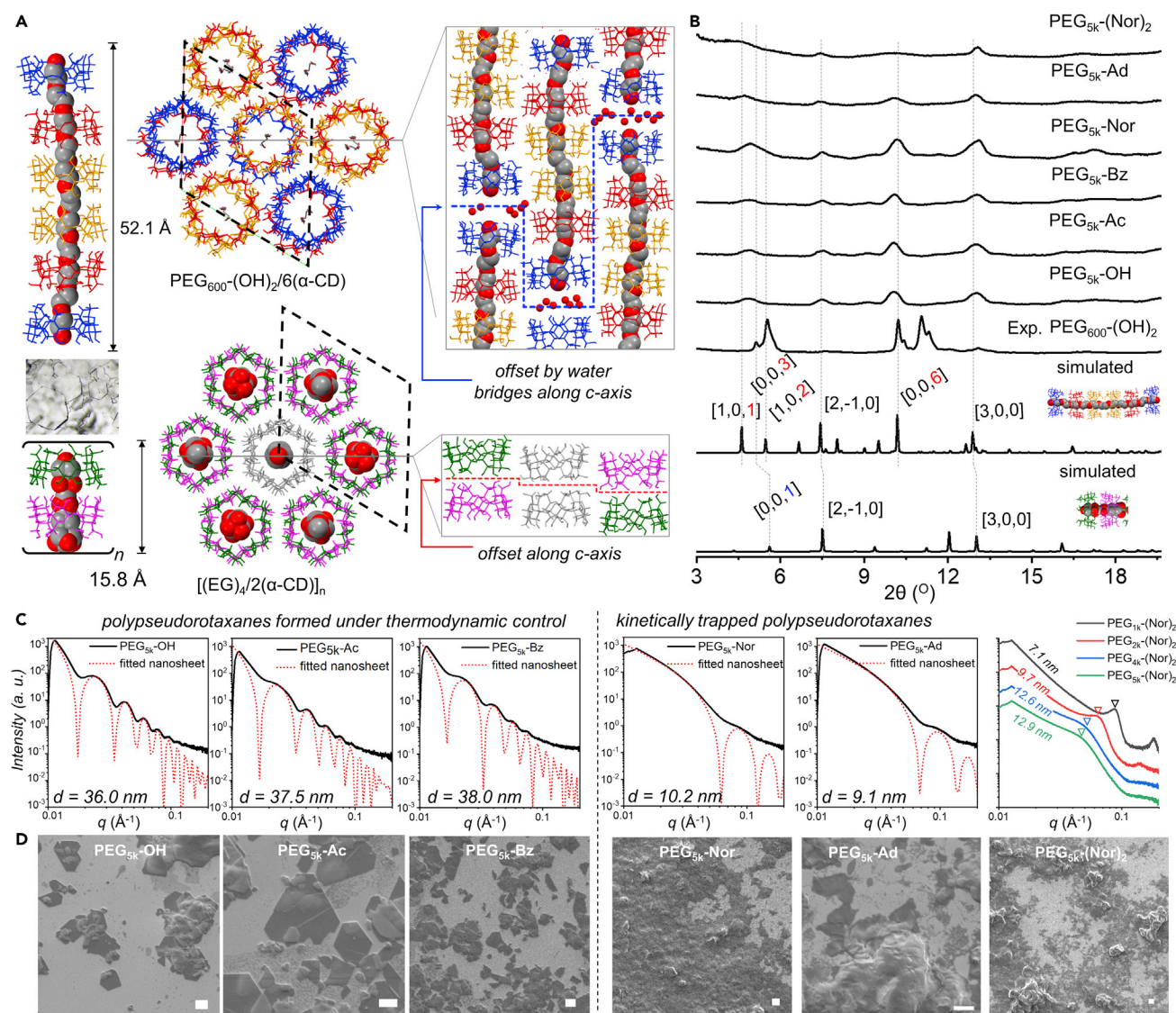


Figure 5. Structural and morphological analyses of $\alpha\text{-CD}/\text{PEG}$ polypseudorotaxanes

(A) Single-crystal structures of two polymorphs of polypseudorotaxane $\text{PEG}_{600}-(\text{OH})_2/6(\alpha\text{-CD})$ and $[(\text{EG})_4/2(\alpha\text{-CD})]_n$. $\alpha\text{-CD}$ s were color-coded to represent different symmetry equivalences.

(B) WAXS profiles of the hydrogels formed by different $\alpha\text{-CD}/\text{PEG}$ polypseudorotaxanes, the crystal sample of $\text{PEG}_{600}-(\text{OH})_2/\alpha\text{-CD}$, and the simulated of $\text{PEG}_{600}-(\text{OH})_2/6(\alpha\text{-CD})$ and $[(\text{EG})_4/2(\alpha\text{-CD})]_n$.

(C) SAXS profiles (solid line) of the hydrogels formed by different $\alpha\text{-CD}/\text{PEG}$ polypseudorotaxanes ($\text{EG}/\alpha\text{-CD} = 3.3:1$) and their fitted curve (dotted line) and thickness. Polypseudorotaxanes are fitted to hexagonal sheet-like form factor, and $\alpha\text{-CD}/\text{PEG}-(\text{Nor})_2$ polypseudorotaxanes are fitted to lamellar form factor.

(D) SEM images of the hydrogels formed by different $\alpha\text{-CD}/\text{PEG}$ polypseudorotaxanes; scale bar, 1 μm .

continuously between two adjacent rings, and the PEG_{600} axes are crystallographically disordered along the c -axis. It is worth noting that the polypseudorotaxanes in both polymorphs were packed unparallel and offset along the c -axis (Figure 5A), which corrected the previously suggested parallel packing models without offsetting.³⁴ The offset packing of polypseudorotaxanes could allow the co-crystallization of size ill-matched $\alpha\text{-CD}$ blocks from different polypseudorotaxanes along the c -axis (Figure S29), similar to those double helices formed by ill-matched DNA base pairs.³⁵

We used experimental and simulated WAXS profiles of PEG₆₀₀-(OH)₂/α-CD polypseudorotaxanes to index the diffraction profiles of the polypseudorotaxane hydrogels. In the PEG_{5k}-OH/α-CD, PEG_{5k}-Ac/α-CD, and PEG_{5k}-Bz/α-CD hydrogels (Figure 5B), similar diffraction peaks with their Miller indices were assigned as 2θ = 5.0° [0, 0, 3], 7.5° [2, -1, 0], 10.1° [0, 0, 6], 13.0° [3, 0, 0], in which *l* is an integral number reflecting different c-axis lengths. In PEG_{5k}-Ad/α-CD hydrogel, the diffraction peaks at 2θ = 5° and 10.1° were broadened, indicating that the c-axis of each crystalline domains in these hydrogels were dispersed. The structural differences of the crystalline domains formed in PEG_{5k}-R/α-CD with different end groups were more pronounced in small-angle X-ray (SAXS) and SEM analyses (Figures 5C and 5D). Clear fringes fitted to the sheet-like form factor of 36.0, 37.5, and 38.0 nm were recorded in PEG_{5k}-OH/α-CD, PEG_{5k}-Ac/α-CD, and PEG_{5k}-Bz/α-CD hydrogels, respectively, with sub-micron sized hexagonal sheet-like observed in SEM (Figure 5D). In contrast, fringes of kinetically trapped PEG_{5k}-Ad/α-CD hydrogels were fitted to a sheet-like thickness of 9.1 nm with much fewer structural features, indicating that the segmented α-CD blocks comprised about 10 α-CDs on average. In the PEG_{2k}-Ad/α-CD hydrogel, diffraction fringes with better structural features were fitted to a sheet-like thickness of 15.8 nm (Figure S40), indicating that the crystalline domains formed using shorter PEG_{2k}-Ad axle are larger and less disordered. SEM analysis showed the annealed sample of PEG_{5k}-Ad/α-CD polypseudorotaxane as micrometer-sized trigonal single-crystals (Figure S45), confirming the structural differences between the kinetic and thermodynamic outcomes. Similarly, the S/WAXS profiles of the PEG_{4/5k}-(Nor)₂/α-CD hydrogels contained fewer structural details. Their structures were suggested as disordered lamellar assemblies by comparing to the clear fringes in shorter chain PEG_{1-2k}-(Nor)₂/α-CD hydrogels (Figures 5C and S41). When α-CDs surmounted the -Nor speed bumps of shorter PEG_{1/2k}-(Nor)₂, they were concentrated locally at each chain end. When the PEG chain lengths were extended to PEG_{4/5k}-(Nor)₂, segmented α-CD blocks at the chain ends and random sites of the chain emerged, which nucleated individually³⁶ to form branched meta-stable crystalline networks (Figure 2).

3D-printing of polyrotaxane network hydrogels

The concerted kinetic trapping of polypseudorotaxane networks enabled the possibility to trap different network architectures from the same reactive ensemble. We chose to trigger an initial temperature difference to the PEG_{4k}-(Nor)₂ and α-CD mixture at high concentrations to kinetically trap two meta-stable polypseudorotaxanes networks of different densities. They were subsequently covalently crosslinked as polyrotaxane networks. Experimentally, a hydrogel ink-1 (Figure 6A) composed of PEG_{4k}-(Nor)₂ (22.5 mM), α-CD (308 mM), tetrathiol crosslinker TTC (11.3 mM), and a photo-initiator was optimized with suitable viscoelasticity for 3D-printing (Figure S48). Ink-1 possesses a high elastic modulus of $G' = 0.70$ MPa at 25°C (Figure 6B). By increasing the reaction temperature, the overall binding affinity between α-CDs and PEG-(Nor)₂ decreased, which dismantled the original crystalline network, dethreaded some α-CDs, and formed a new crystalline network. At 60°C for 1 h, the elastic modulus of ink-1 was reduced to 56 kPa but remained viscoelastic for 3D-printing. After rapid cooling to 25°C, the elastic modulus of ink-1 increased very slowly at ambient conditions (Figure 6B), suggesting that the meta-stable crystalline network formed at 60°C prevented rapid α-CD rethreading at room temperature.

After thiol-ene crosslinking, the polypseudorotaxanes 3D-printed at 20°C and 60°C were converted to polyrotaxane network hydrogels (PNHs) as PNH-8 and PNH-3 (Figure 6C), respectively. An α-CD-free hydrogel PNH-0 was also synthesized in

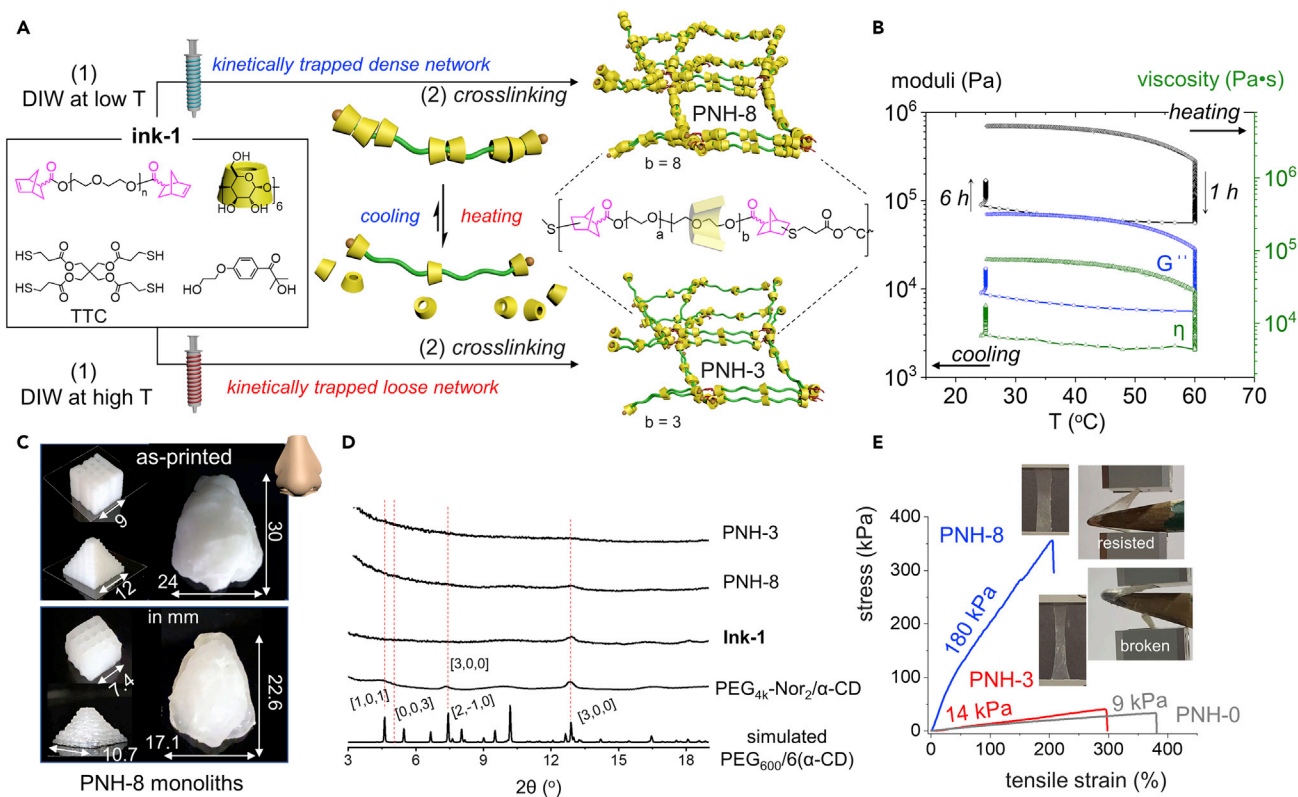


Figure 6. Two 3D-printed polyrotaxane networks obtained from the same reactive polypseudorotaxane hydrogel

(A) Temperature-diverged formation of PNH-3 and PNH-8 after 3D-printing and photo-crosslinking.

(B) Temperature-dependent elastic (black), loss moduli (blue), and viscosity (green) of ink-1, heating and cooling rates set as 3°C and 20°C/min.

(C) As-printed hydrogels and their covalently crosslinked polyrotaxane monoliths.

(D) WAXS profiles of hydrogels PEG_{4k}-(Nor)₂/α-CD, ink-1, PNH-3, and PNH-8.

(E) Tensile stress measurements of PNHs, rate: 0.1 mm/s. Inset: PNHs upon elongation and pencil penetration. PNH-0 was synthesized in a DMF solution in the absence of α-CD.

DMF for reference (Figure S51). The averaged molar ratios of PEG_{4k}-(Nor)₂/α-CD/TTC components in PNH-8 and PNH-3 were revealed by ¹H NMR hydrolysis as 1:8.0 ± 0.7:0.62 ± 0.02 and 1:2.9 ± 0.4:0.67 ± 0.05, respectively (Table S13). The covalent network densities in these PNHs were similar, as suggested by the ratios of PEG_{4k}-(Nor)₂/TTC. There are eight α-CDs per PEG in PNH-8, compared to only three α-CDs per PEG in PNH-3. The WAXS profiles of PNHs were broad (Figure 6D), because fewer interlocked α-CDs and the limited PEG chain diffusion in PNHs reduced their crystalline domain sizes proportionally, compared to the parent ink-1. At the macroscale, Young's moduli of PNH-0, PNH-3, and PNH-8 were measured as 9, 14, and 180 kPa, respectively (Figure 6E). PNH-3 showed slightly enhanced Young's moduli over PNH-0 due to its sparsely distributed hydrogen-bonded crystalline network. PNH-8 was significantly tougher than PNH-3 in the pencil penetration test (Figure 6E; Videos S1 and S2) benefiting from its denser crystalline network formed by more interlocked α-CDs.

The different numbers of interlocked α-CDs in PNH hydrogels gave them different moisture-responsiveness at varied relative humidities (RH). When PNH-3 and PNH-8 were placed in sealed chambers of different RH, PNH-3 swelled to 270% at RH = 58% with significantly reduced Young's moduli (Figure 7A). In comparison, PNH-8 showed better resistance to humidity change, since its denser crystalline network

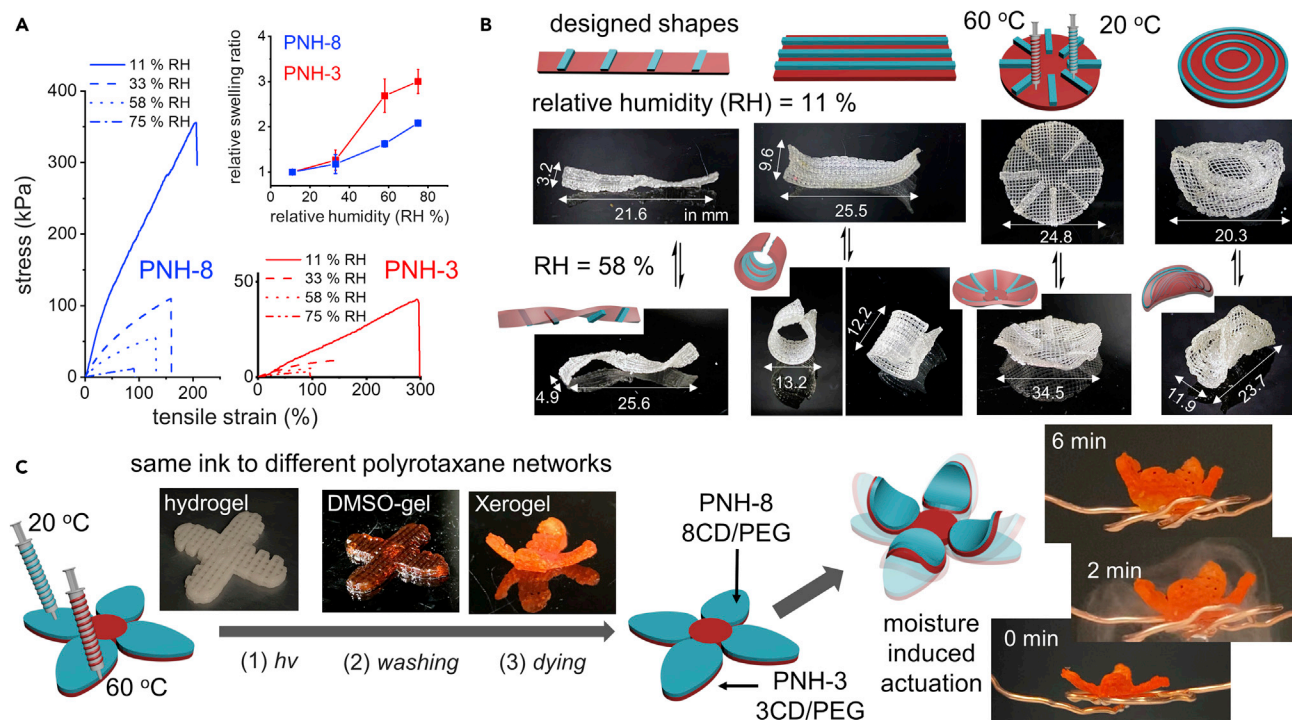


Figure 7. 3D-printed heterogeneous polyrotaxane actuators and their moisture-responsive shape-morphing behaviors

(A) Tensile stress measurements of PNH hydrogels equilibrated at different relative humidity (11%, 33%, 58%, and 75%), respectively, rate: 0.1 mm/s. Inset: relative swelling ratios of PNHs at different relative humidity. The error bars were derived from three individual experiments. (B) Designed dual-material actuator models (top), the fabricated (3D-printing followed by crosslinking and washing) heterogeneous hydrogels at relative humidity 11% (middle), and their morphed shapes in the chamber of relative humidity = 58% (bottom). These heterogeneous hydrogels were fabricated using identical ink-1 printed at 20°C (green) and 60°C (red), respectively. (C) 3D fabrication of a flower model using ink-1 printed at 20°C (green) and 60°C (red) followed by crosslinking. The afforded polyrotaxane flower demonstrated folding motions upon moistening due to the spatial integration of PNH-3 and PNH-8 at the top and bottom layers.

formed by segmented α -CD blocks competed against the osmotic pressure variation upon moisturizing.

By designing the 3D-printing script,³⁷ a series of heterogeneous lattices (Figure 7B) were 3D printed using the 60°C ink-1 (green) and the 20°C ink-1 (red), followed by photo-crosslinking. At a low RH of 11%, the lattices resembled their as-printed shapes (Figure 7B, middle). After being placed in a closed chamber at RH = 58%, they morphed into different shapes as designed (Figures 7B and S60–S64). When ink-1 was 3D-printed into a flower model (Figure 7C; Video S3), its lower section and the core were printed using the 60°C ink-1 and the top section was printed using the 20°C ink-1. After photo-crosslinking, the compositions of the heterogeneous polyrotaxane flower was revealed as PEG_{4k}-(Nor)₂: α -CD ratios of $1:7.6 \pm 0.5$ and $1:3.5 \pm 0.2$ for the top and bottom sections, respectively. The dried flower (Figure 7C) bent slightly inwards due to the higher density of the α -CD crystalline domains in the top section. When this monolith was exposed to moisture, it folded inward in 6 min (Figure 7C; Video S4). During this process, the top layer possessing a denser α -CD crystalline network persisted against osmotic pressure variation, but the bottom layer swelled quickly due to the solvation of its mostly unthreaded PEG and sparse crystalline network. Shape-morphing in response to the relative humidity change enabled the fabrication of environmentally controlled actuators with low energy consumption,³⁸ providing a sustainable solution for the development of smart devices.^{39,40}

DISCUSSION

In summary, our discovery demonstrated a chemical approach to synthesize 3D-printable poly(pseudo)rotaxane materials through a concerted kinetic coupling of polypseudorotaxane formation in the solution phase with their micro-crystallization in the gel phase. Through the installation of sterically demanding end groups on PEG, we created kinetic barriers for α -CDs threading and translocation, and resolved a spectrum of previously transient states in the solution phase. These polypseudorotaxanes with segmented α -CD blocks possess lower kinetic barriers for micro-crystallization, forming polypseudorotaxane hydrogels with different network architectures. We demonstrated that the kinetically trapped PEG-Ad/ α -CD and PEG-Nor₂/ α -CD polypseudorotaxanes form less-ordered α -CD blocks on the PEG axles. Our single-crystal X-ray analysis of PEG-OH₂/ α -CD polypseudorotaxanes corrected the long-standing misunderstanding of the packing models of polypseudorotaxanes. The revealed unparallel packing of polypseudorotaxanes indicated the possibility of forming crystalline domains using length varied α -CD blocks in our kinetic synthesis. Furthermore, we demonstrated a simultaneous variation of polypseudorotaxane network architecture using the same reactive ensemble at different temperatures. After dual-material 3D printing followed by chemical cross-linking, 3D-printed heterogeneous lattices demonstrated moisture responsive actuations, which was enabled by the two polyrotaxane materials possessing different numbers of α -CDs at the nanoscale, different crystalline domains at the mesoscale, and different mechanical properties at the macroscale. Our work not only showcased a concerted kinetic trapping approach capable of synthesizing materials in their higher energy states but also demonstrated a path to use less-ordered molecular assemblies that were previously considered disadvantageous to construct supramolecular polymer materials with superior properties. In addition, we successfully synthesized kinetically stable hydrogels using medium to low molecular weight PEG derivatives (≤ 5 kDa), which overcame a long-standing obstacle in biomedical applications because current stable hydrogels formed by large molecular weight PEG presented problems⁴¹ to be filtered out by human kidneys.⁴²

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Chenfeng Ke (chenfeng.ke@dartmouth.edu).

Materials availability

All unique reagents generated in this study are available from the lead contact without restriction.

Data and code availability

The X-ray datasets generated during this study are available at the Cambridge Crystallographic Data Centre (CCDC) <https://www.ccdc.cam.ac.uk> under deposition numbers 2008413 and 2008415. The 3D printing scripts generated in this study are available from the lead contact.

Time-dependent ¹H nuclear magnetic resonance experiments

To understand the crystallization process and examine the components remaining in the solution phase, time-dependent ¹H NMR experiments were performed on reactions of polypseudorotaxane formed by α -CD (50 mM)/PEG_{5k}-OH (1 mM) or α -CD (50 mM)/PEG_{5k}-Ad (1 mM) in D₂O. D₂O solutions of PEG_{5k}-OH (2 mM) or PEG_{5k}-Ad (2 mM) were added to NMR tubes to acquire their proton resonances. Upon

the addition of α -CD (50 mM), periodic acquisitions (every 10 min for PEG_{5k}-OH and 30 min for PEG_{5k}-Ad) were performed until correspondent polypseudorotaxane formed a hydrogel-like aggregate and broadened the ¹H NMR signal (160 min for PEG_{5k}-OH and 15 h for PEG_{5k}-Ad).

Binding affinities and stoichiometries measurements

The binding affinities and stoichiometries of the complexes formed between Nor-CO₂Na, 2EG-Ad, 4EG-Ad, 6EG-Ad, and α -CD were measured by ¹H NMR titration. D₂O solutions of Nor-CO₂Na or *n*EG-Ad (*n* = 2, 4, 6, 2.0 mM) were titrated with α -CD solutions. The α -CD solutions (20, 40 and 60 mM respectively for *n* = 2, 4, 6) were prepared by dissolving α -CD in a Nor-CO₂Na or *n*EG-Ad (2.0 mM) D₂O solution. The binding constant between Nor-CO₂Na and α -CD was fitted using the algorithms provided by [Supramolecular.org](https://supramolecular.org)⁴³ using a 1:1 binding model. Binding constants between 2/4EG-Ad and α -CD were fitted using the algorithms in a 1:1 binding model and 1:2 binding model (full and additive). The 1:3 binding model for 6EG-Ad and α -CD was accessed using MATLAB provided by literature with a minor adaptation to NMR titration. Job's plots were performed on the complexes formed between 4EG-Ad, 6EG-Ad and α -CD, revealing the formation of 1:2 and 1:3 complexes, respectively. To elucidate the binding affinities between *n*EG-Ad (*n* = 2, 4, 6) and α -CD, and to simplify the binding models as a result of the calculation complexity, we employed several binding models to fit the binding between *n*EG-Ad (*n* = 2, 4, 6) and α -CD, including a full binding model, additive binding model, non-cooperative binding model, and statistical binding model.

Transmittance monitoring of the formation of polypseudorotaxanes

Transmittance monitoring of the formation of polypseudorotaxanes was performed on a Shimadzu UV-vis spectrophotometer (UV-1800) with a Thermal CUBE solid-state cooling system for thermal control between 5.0°C and 90.0°C with temperature precision of 0.1°C, and optical lengths for general turbidity measurements and hydrogel melting experiments were set as 10 and 2 mm, respectively. When α -CDs are threaded onto the PEG axles, less-soluble polypseudorotaxanes are formed and they crystallize as crystalline precipitates. The reaction turned from transparent to opaque. To understand the cascade threading and crystallization kinetic processes, a time-dependent reaction transmission change was monitored by UV-vis light scattering upon the mixing solutions of α -CD and PEG-R from 100% transmittance to less than 1%. In typical time-dependent transmittance monitoring experiments, the reaction cuvette (optical length: 10 mm) was added with PEG_{5k}-R (1, 2 mM for one case of PEG-(Nor)₂, after mixing) with various end groups and α -CD (50, 100 mM for one case of PEG-(Nor)₂, after mixing) at 20°C. The transmittance was monitored at 550 nm, accounting for the size of polypseudorotaxanes for appropriate Rayleigh scattering.²⁹ The data were acquired every 30 s until the transmittance was less than 1%.

Temperature-dependent absorbance profiles

The temperature-dependent absorbance profiles (melting curve) of polypseudorotaxanes hydrogels formed by PEG_{1-5k}-R with various end groups and different molecular weights (PEG-OH or PEG-Ad: 5, 2.5, 1 mM for 1, 2, 5 kDa respectively; PEG-(Nor)₂: 5, 2.5, 1.25, 1 mM for 1, 2, 4, 5 kDa respectively, after mixing) and α -CD (50 mM, 100 mM for PEG-(Nor)₂, after mixing) was analyzed as follows: (1) the absorbance was normalized by defining the largest absorbance as 1.0 and the smallest absorbance as 0. (2) The first derivative of the absorbance profile was calculated quantitatively. (3) The derivatized data points were fitted by a Gaussian

function to generate the fitting parameters as the expected phase transition temperature T_m (melting point) and phase transition temperature variance σ_T .

Annealing of polypseudorotaxanes

The kinetically formed polypseudorotaxanes were annealed at different conditions and the corresponding melting experiments were performed. PEG_{5k} with various end groups (PEG_{5k}-R: 2 or 4 mM, after mixing) and α -CD (100 or 113.6 mM, after mixing) were mixed in reaction vials to form the corresponding polypseudorotaxane hydrogels (EG/CD = 2.2:1 or 4:1) at 20°C and stabilized overnight. The as-prepared samples were heated at 60°C for 1 h and naturally cooled down in the air, or cooled down slowly in a temperature-controlled programmable oven over a period of 16 or 40 h (cooling ramp: 60°C–50°C: 1°C/h, 50°C–20°C: 3°C/h or 60°C–20°C: 1 °C/h). Samples were diluted by half to PEG (1 or 2 mM) and α -CD (50 or 56.8 mM) for each measurement. We employed higher concentrations of reactants to form kinetically generated products for annealing followed by dilution because the higher concentration formed products could not be dissolved at the annealing temperatures.

Rheological measurements

Rheological measurements were performed on a stress-controlled rheometer (TA instruments, DHR-2) with a 20-mm diameter parallel plate geometry and a measuring gap of 1 mm at 20°C. All polypseudorotaxane hydrogel samples were consolidated for at least 12 h at 20°C before the analysis unless otherwise specified. Strain sweep tests were performed to investigate the linear viscoelastic regions of the obtained polypseudorotaxane hydrogels at 25°C. The oscillation strain was increased from 0.01% to 100%. The angular frequency was set at 1 rad/s (frequency = 0.16 Hz). Angular frequency sweep tests were performed to investigate the elastic (storage) and viscous (loss) moduli at 25°C. The angular frequency was increased from 0.1 to 100 rad/s (frequency increased from 0.016 to 15.92 Hz). Based on the results of oscillation strain sweep experiments, the oscillation strain was set at 0.1%. Dynamic step-strain amplitude tests were performed to investigate the self-healing properties of the polypseudorotaxane hydrogels. The oscillation strain applied was 1% and 100% in each cycle at 1 rad/s angular frequency. The duration of strain at each step was 15 s. Steady rate sweep tests were carried out to investigate the shear-thinning behaviors of the polypseudorotaxane hydrogels at 25°C. The shear rate was increased from 1 to 100 s^{−1}. The elastic, loss moduli, and viscosity of ink-1 were measured at a frequency of 1 rad·s^{−1} and a strain of 0.05% between 25°C and 60°C. The temperature-ramp contained a slow heating step from 25°C to 60°C at 3°C/min with an equilibrium time of 60 s for each temperature measurement, an isotherm step at 60°C for 1 h, a fast cooling step from 60°C to 25°C at 20 °C/min, and an isotherm at 25°C for 6 h. To test the self-healing properties of ink-1 at 25°C and 60°C, step-strain tests were performed with alternating 0.1% and 100% strain applied to the samples every 15 s.

Single crystal analysis

Single crystals of PEG₆₀₀/ α -CD polypseudorotaxanes suitable for single-crystal X-ray analysis were obtained by slow evaporation of an aqueous solution of a mixture of PEG₆₀₀-(OH)₂ and α -CD in 1:3 molar ratio (EG/CD = 4.21) over 7 days. Two polymorphs were identified in the same crystallization vial. Data were collected at 20°C in a Rigaku four circle supernova charge-coupled device (CCD) diffractometer with CuK α (λ = 1.54184 Å) radiation or Rigaku Xtalab mini II with MoK α (λ = 0.71073 Å) radiation, working at 50 kV and 12 mA. Data were collected and processed using CrysAlis Pro software.

Wide-angle X-ray analysis (WAXS) and small-angle X-ray analysis (SAXS)

WAXS and SAXS experiments were carried out using a Rigaku NANOPIX instrument with a Hypix-3000 detector. The water dispersions (or hydrogels) of the polypseudorotaxanes were poured into a glass capillary for X-ray measurements (WJM-glass/Muller borosilicate capillary: $\phi = 2.0 \times \text{length} = 80 \text{ mm}$) and used for SAXS and WAXS measurements. The sample-to-detector distance was calibrated with a silver behenate diffraction peak. The sheet-like form factors were fitted to the experimental SAXS profiles in the manuscript using the Igor Macros.⁴⁴

Scanning electron microscope (SEM) imaging

SEM observation was conducted with a JEOL JSM-7800F microscope. The samples for SEM analyses were prepared by dipping a silicon oxide substrate into the water dispersion (or hydrogel) of the polypseudorotaxanes samples.

Tensile tests

Tensile tests were performed on a DHR2 system (TA instruments®, New Castle, DE) with a 50 N load cell following the ATSM D638. Ink-1 was preheated at 60 °C for 1 h and injected into a Teflon mold with a rectangular shape (40 × 8 × 2 mm). The molded samples were photo-crosslinked by UV irradiation ($\lambda = 365 \text{ nm}$) at 20 °C for 30 min, followed by a washing process with an excess of DMSO. Freshwater was introduced to exchange DMSO for 3 times. After washing, the samples were placed in a sealed container with a saturated LiCl solution (relative humidity 11%) at 20 °C for 48 h. The 20 °C sample was prepared similarly without pre-heating. A tensile axial load was applied to the molded sample at a rate of 0.1 mm/s until failure occurred. The Young's moduli of the specimens were calculated by fitting the linear equation of the stress-strain curve before the samples yielded. The elongation process was recorded by a digital camera. Pencil penetration tests were performed using PNH-3 and PNH-8 specimens prepared in the tensile tests. The specimens were fixed by two clamps. A pencil was used to apply pressure to the fixed samples. The process was recorded by a digital camera. Optical images were recorded by a consumer-grade camera.

Preparation of ink-1

PEG_{4k}-(Nor)₂ (90 mg/mL, 22.5 mM), α -CD (300 mg/mL, 308 mM), tetrathiol crosslinker TTC (5.5 mg/mL, 11.3 mM), and photo-initiator Irgacure D-2959 (33.3 mg/mL, 148 mM) were dissolved in H₂O. The reaction mixture was stirred at 60 °C for 30 min, then transferred to a syringe. The ink was cooled naturally to 20 °C and was further consolidated for 48 h before being loaded to the 3D-printer. To analyze the number of threaded α -CDs in ink-1, the hydrogel was quickly diluted by 3-fold with water and the mixture was centrifuged at 7,000 rpm for 2 min. The dilution and centrifugation processes were repeated two additional times. The collected white precipitate was lyophilized for ¹H NMR analysis and the ratio of α -CD to PEG_{4k}-(Nor)₂ was calculated as 12.9:1 (EG/ α -CD = 7.1:1), compared to the feeding ratio of α -CD:PEG = 13.7 (EG/ α -CD = 6.6:1).

3D printing

Ink-1 was loaded into syringes equipped to the BioAssemblybot 3D-printer. The printing scripts were generated by CAD software and Advanced Solution. The printing speed varied between 5–40 mm/s. High-temperature 3D-printing was conducted using BioAssemblybot 3D-printer equipped with a heating nozzle. Before printing, the heating nozzle was preheated at 60 °C for 1 h. The printed monoliths were photo-crosslinked by UV irradiation ($\lambda = 365 \text{ nm}$) at 20 °C for 0.5–1 h, depending on the size of the printed objects. After photo-crosslinking, the monoliths were

immersed in an excess of DMSO until they became transparent. Subsequently, DMSO was decanted and water was added to exchange the solvent. The water bath was refreshed three times. The hydrogel was then immersed in an acetone bath for 2 h and transferred to a heated chamber to remove the acetone quickly, affording the xerogel. To analyze the compositions of polyrotaxane network, dried hydrogel samples prepared at 20°C and 60°C were hydrolyzed in 5% (v/v) NaOD/D₂O until no insoluble residuals were found in the NMR tube. Three samples at each temperature were prepared for ¹H NMR hydrolysis measurements. PEG_{4k}: tetra-SH: α-CD ratios of PNH-8 and PNH-3 were measured as 1:0.62 ± 0.02:8.0 ± 0.7 and 1:0.67 ± 0.05:2.9 ± 0.4, respectively.

Flower model design and 3D-fabrication

A printer equipped with a 60°C and a 20°C nozzle was filled with ink-1. A flower model with a bilayer structure was designed. Its lower section and the core were printed using the heated ink, and its top section was printed using the 20°C ink. The flower model was photo-crosslinked by UV-irradiation (λ = 365 nm) for 1 h. After photo-crosslinking, the monoliths were immersed in an excess of DMSO until the objects became completely transparent. The DMSO was decanted and a rhodamine b (0.2 mM) DMSO solution was added to dye the DMSO-gel for imaging. The DMSO-gel was transferred to an aqueous bath (washed 3 times) and re-dyed using a rhodamine B (0.2 mM) aqueous solution. The hydrogel was then immersed in a rhodamine B (0.2 mM) acetone bath for 2 h and then placed in a heated chamber to evaporate the acetone quickly. To analyze the average number of threaded α-CDs per PEG in the flower model, the samples were hydrolyzed in 5% (v/v) NaOD/D₂O until no insoluble residuals were found in the NMR tube. Three additional samples of each section were prepared and hand-cut for ¹H NMR hydrolysis.

Moisture induced actuation

The dyed xerogel was placed on a copper wireframe. A humidifier was placed 5 cm underneath the frame. Moisture was introduced and the process was recorded by a digital camera.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.chempr.2021.06.004>.

ACKNOWLEDGMENTS

C.K., M.T., and L.L. thank the Beckman Young Investigator Program. Q.L. and L.L. were partly supported by NSF EPSCoR-1757371. J.S. was supported by the NSF DMR-1844920. S.U. and K.I. were supported by JST-Mirai Program grant number JPMJMI18A2; JSPS KAKENHI grant numbers JP19H00907, JP21K14477, and JP19J12840; and OPERANDO-OIL. We thank Dr. Rina Maeda (formerly at the University of Tokyo) for the helpful discussion.

AUTHOR CONTRIBUTIONS

C.K. conceived the idea and wrote the manuscript. K.I. and S.U. assisted in editing. L.L. and M.T. initiated and conducted the polymer synthesis and kinetic studies with assistance from L.Z. Q.L. conducted the 3D printing and materials investigations. S.U. conducted the X-ray and SEM studies. J.S., C.K., S.L., and X.J. conducted the single-crystal studies.

DECLARATION OF INTERESTS

The authors have filed a provisional patent application US 63/021,971 on the 3D-printable polyrotaxanes.

Received: November 11, 2020

Revised: January 12, 2021

Accepted: June 3, 2021

Published: June 29, 2021

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