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Aggregate Engineering in Supramolecular Polymers via Extensive Non-Covalent Networks

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Abstract: Aggregate engineering of non-covalent networks enables thermo-mechanical versatility of supramolecular polymers, particularly the stimuli-responsive phase transitions and intrinsically damage-healing abilities. However, most non-covalent networks are vulnerable at elevated temperatures, which significantly suppress the robustness of supramolecular polymers. Herein, ureidocytosine (UCy) motifs that can form extensive non-covalent networks and thus robust molecular aggregates via multivalent hydrogen bonds and aromatic stackings, are proposed to enable precise programming of the thermo-mechanical versatility. Molecular simulations reveal that the enthalpic contributions from the UCy aggregates play dominant roles to compensate the entropic loss from the redistributions of polymeric spacers and stabilize the non-covalent networks over wide temperature windows. Such aggregate-level strategy offers prospects for applications which require thermo-mechanical versatility of supramolecular polymers, such as 3D printing, microfabrication and damage-healing coating.

INTRODUCTION

Supramolecular polymers^[1-4] assembled from low-molecular-weight monomeric blocks or oligomers through dynamic and reversible non-covalent interactions typically exhibit stimuli-responsiveness^[5-8] and exceptional mechanical properties,^[9-10] such as malleability,^[11-12] reprocessability,^[13-18] recyclability^[19-21] and self-healing.^[22-29] However, most supramolecular polymers suffer from rapid solid-fluid phase transition at elevated temperatures due to cascade dissociation of non-covalent interactions, which imposes limitations on the thermal stability and durability. Oligomeric units are therefore incorporated with non-covalent bonding motifs at high density or at specific linear or branched topologies, in order to facilitate the precise growth of non-covalent networks and the propagation of molecular aggregates.^[30-32] For example, molecular engineering of supramolecular polymers with controllable crystallinity,^[33-35] multiscale non-covalent interactions,^[36-38] or nested assembly feature^[39] have been exploited, which substantially enhance the thermo-mechanical versatility of the supramolecular polymers. However, the recognitions between non-covalent motifs are significantly impeded when they are separated by high-molecular-weight spacers, because the entropic loss caused by the redistributions of the long polymeric spacers cannot be fully compensated by the enthalpic gains from the aggregations of these non-covalent motifs.^[39-41] The understanding on the mechanism of programming and stabilizing non-covalent networks in supramolecular polymers, where the energy landscapes from structural hierarchy and complexity are involved, will lead to a paradigm shift in research methodology but currently remains elusive.

In response to these challenges, we describe here an aggregate engineering strategy that is built upon energy contributions of specific non-covalent networks, for the design of supramolecular polymers with thermo-mechanical versatility. Specifically, a structural minimalistic

ureidocytosine (UCy) motif is synthesized and incorporated into bifunctional polysiloxane (PDMS) oligomers (UCy-PDMS-UCy). The terminated UCy motifs can form extensive non-covalent networks in molecular aggregates, which are interconnected through multivalent hydrogen bonds and aromatic stacking. The enthalpic contributions from the UCy aggregates provide extraordinary driving forces to facilitate the solidification of fluidic PDMS spacers (up to $M_w \approx 27K$), and elevate the solid-fluid phase transition windows of UCy-PDMS-UCy oligomers over 70°C . Notably, the UCy motif can form quadruple hydrogen bonds with another multivalent motif ureidopyrimidone (UPy) to form UCy-UPy dimerization, and the co-assembly of the two motifs with distinct bonding features and aggregation capabilities can significantly extend the tunability on the thermo-mechanical properties in the supramolecular polymers. Such aggregate engineering strategy offers prospects for the applications of supramolecular polymers where thermo-mechanical versatility is required. As a proof of demonstration, the UCy-PDMS-UCy oligomers have been employed as an effective modulator to regulate the thermostability, rheological and mechanical properties of different supramolecular polymers, enabling tunable working windows for 3D printing, microfabrication and damage-healing coating.

EXPERIMENTAL

Materials

$\text{H}_2\text{N-PDMS-NH}_2$ ($M_w \approx 1000, 3000, \text{ and } 5000$) and $\text{H}_2\text{N-PDMS}$ ($M_w \approx 1000$) were purchased from Gelest. $\text{H}_2\text{N-PDMS-NH}_2$ ($M_w \approx 2500, 27000$) were purchased from Sigma-Aldrich. $\text{H}_2\text{N-PDMS-NH}_2$ ($M_w \approx 1250, 1550, 1800, 2000, 8000$) were synthesized according to literature. 2-amino-4-hydroxy-6-methylpyrimidine was purchased from Alfa Aesar. Cytosine, N,N-carbonyldiimidazole (CDI), butyl isocyanate, hexamethylene diisocyanate and other solvents were

purchased from Sigma-Aldrich. All of the chemicals were used as obtained, unless otherwise specified.

General characterization

Solution ^1H NMR spectra were recorded on a Bruker DRX 400 NMR spectrometer in CDCl_3 at room temperature ($20\text{ }^\circ\text{C}$), chemical shifts are reported in ppm relative to tetramethylsilane as an internal standard (^1H). UCy-PDMS-UCy polymers were annealed at $150\text{ }^\circ\text{C}$ for 10 min and thin slices ($\sim 5\text{ }\mu\text{m}$) of the prepared through cryotomy. The semicrystalline properties of the UCy-PDMS-UCy polymers were examined under a polarizing optical microscope (POM, Carl zeiss microscope, Axioplan2 imaging). X-ray diffraction (XRD) patterns were obtained from analysis instrument (Bruker AXS, D2 PHASER). Single-crystal measurements were performed via X-Ray Diffractometer - Single Crystal Analyzer (Oxford GEMINI S Ultra), mounted with a 92 mm diagonal Sapphire CCD detector and co-mounted Enhance (Mo) and Enhance (Cu) X-ray sources. The differential scanning calorimetric (DSC) curves are recorded on TA DSC25. The rheological measurements were performed on a rotational rheometer (Malvern Kinexus Lab+) with a circular 20 mm specimen stage. The samples with thicknesses of ca. 0.7 mm were prepared through stainless steel molding. For frequency sweep, the strain was set as 0.1%. For temperature weep, the frequency and strain was set as 1 Hz and 0.1%, respectively. Nanoindentation tests were performed on a Hysitron UBi1 Nanoindenter, in a displacement-controlled mode.

Computation simulation

The software Material Studio and its Forcite module was used to perform all the simulations. Forcefield COMPASS II was adopted to describe atomic interaction and partial charges. The van der Waals and Coulombic interactions are calculated with a cutoff distance of 18.5 \AA . Flory-

Huggins interaction parameters were obtained from Blend module. SAPT calculations was performed using Psi4, using M062X/6-311G*(GD3) method.

Synthesis of UCy-BI

The UCy-BI was synthesized according to the reaction in Scheme S1. Cytosine (1.1 g; 10 mmol) was dissolved in 10 mL DMSO. Butyl isocyanate (1.9 g; 20 mmol) was added and the mixture was stirred for 24 hrs with N₂ protection at 60 °C. The solution was cooled to room temperature and acetone was added to precipitate the product. The precipitate collected by filtration and washed with acetone. The product was dried under vacuum (yield 90 %). Single crystal structure was obtained by recrystallization in acetic acid.

Synthesis of UPy-BI

The UPy-BI was synthesized according to the reaction in Scheme S1. 2-amino-4-hydroxy-6-methylpyrimidine (1.3 g; 10 mmol) was dissolved in 10 mL DMSO. Butyl isocyanate (1.9 g; 20 mmol) was added and the mixture was stirred for 24 hrs with N₂ protection at 60 °C. The solution was cooled to room temperature and acetone was added to precipitate the product. The precipitate collected by filtration and washed with acetone. The product was dried under vacuum (yield 90 %).

Synthesis of UCy-PDMS-UCy

The UCy-PDMS-UCy polymer was fabricated with similar processes of UCy-PDMS polymer. The synthesis of UCy-PDMS3K-UCy was depicted as an example. First, cytosine (1.1 g; 10 mmol) was dissolved in 10 mL DMSO. CDI (2.5 g; 15 mmol) was added. The mixture was stirred for 24 hrs with N₂ protection at 60 °C. The solution was cooled to room temperature, and the precipitate was collected by centrifugation and washed by acetone. The product was dried under vacuum

(yield 88 %). The product was a white powder (denoted as UCy-CDI). Then, UCy-CDI (1.5 g; 7 mmol) was suspended in 20 mL chloroform, and H₂N-PDMS- NH₂ (2.5 mmol, 7.5 g) was added. The mixture was stirred for 24 hrs with N₂ protection at 60 °C. The solution was cooled to room temperature and the unreacted UCy-CDI precipitate was removed by filtration. 20 mL DMSO was added into the solution, and the chloroform was evaporated by heating at 60 °C. The DMSO was removed by centrifugation, and the product was washed by ethanol for three times to remove imidazole. The product was dried under vacuum (yield 80 %). ¹H NMR (400 MHz, CDCl₃, δ): 10.95 (s, 2H, N-H), 10.18 (s, 2H, N-H), 9.60 (s, 2H, N-H), 8.66 (s, 4H, CH-NH), 8.38 (s, 2H, pyrimidyl), 1.62-1.56 (m, 4H, NH-CH₂-CH₂-), 0.96–0.73 (m, 4H, -CH₂-CH₂-Si), 0.58-0.54 (m, 4H, Si-CH₂), 0.09-0.02 (m, 235H, CH₃-Si).

Synthesis of UPy-PDMS-UPy

The UPy-PDMS-UPy polymer was fabricated with similar processes as described by Meijer and coworkers.^[41] The synthesis of UPy-PDMS3K-UPy was depicted as an example. First, 2-amino-4-hydroxy-6-methylpyrimidine (1.25 g; 10 mmol) was dissolved in 10 mL DMSO. CDI (2.5 g; 15 mmol) was added. The mixture was stirred for 24 hrs with N₂ protection at 60 °C. The solution was cooled to room temperature, and the precipitate was collected by centrifugation and washed by acetone. The product was dried under vacuum (yield 90 %). The product was a white powder (denoted as UPy-CDI). Then, UPy-CDI (1.7 g; 7 mmol) was suspended in 20 mL chloroform, and H₂N-PDMS- NH₂ (2.5 mmol, 7.5 g) was added. The mixture was stirred for 24 hrs with N₂ protection at 60 °C. The solution was cooled to room temperature and the unreacted UPy-CDI precipitate was removed by filtration. 20 mL DMSO was added into the solution, and the chloroform was evaporated by heating at 60 °C. The DMSO was removed by centrifugation, and the product was washed by ethanol for three times to remove imidazole. The product was dried

under vacuum (yield 85 %). ^1H NMR (400 MHz, CDCl_3 , δ): 13.16 (s, 2H, NH), 11.87 (s, 2H, N-H), 10.21 (s, 2H, N-H), 5.79 (s, 2H, aromatic), 2.22 (s, 6H, CH_3 -aromatic), 1.62-1.56 (m, 4H, $\text{NH-CH}_2\text{-CH}_2$), 0.58-0.54 (m, 4H, Si- CH_2), 0.09-0.02 (m, 234H, CH_3 -Si).

RESULTS AND DISCUSSION

UCy motif facilitates extensive non-covalent networks

The UPy motif can form self-complementary quadruple hydrogen bonds, which is reminiscent to the UPy motif.^[43] Different from the UPy motif, the UCy motifs can be interconnected by alternative quadruple and double hydrogen bond arrays, resulting in extensive hydrogen bonding networks (**Figure 1a**). The UCy motif can also form intermolecular aromatic stackings due to its large planar structures,^[44] and the stacking distance in molecular crystal is 3.47 Å (**Figure 1a**), which is inherited from the aromatic stacking of cytosine (3.45 Å, Supplementary Figure S1).^[45]

The UCy motif can drive the formation of the UCy-UPy dimer with quadruple hydrogen bonds, and the free energy cost for the conversion from their homodimer counterparts is almost negligible ($0.71 \text{ kcal mol}^{-1}$) (**Figure 1b**). Decomposition of non-covalent interaction energy via symmetry adapted perturbation theory reveals that the electrostatic interactions play domination roles in stabilizing these quadruple hydrogen bonds (Supplementary Figure S2). The enthalpic and entropic landscapes of UCy-UPy, UCy-UCy and UPy-UPy dimers are similar across wide temperature and pressure ranges (Supplementary Figure S3, S4), indicating random homo- and hetero-dimerization under thermal perturbation.

The UCy-UPy co-assembly combines both the strong UCy-UPy dimerization ($-45.79 \text{ kcal mol}^{-1}$) which is comparable with that of UPy-UPy dimerization ($-51.90 \text{ kcal mol}^{-1}$), and the extensive non-covalent networks which is ascribed to the UCy aggregation, and therefore the UCy-UPy co-

assembly is expected to promote the stabilization and propagation of non-covalent networks.^[46] As a proof of demonstration, UPy-BI and UCy-BI with n-butyl termini were synthesized by condensation reactions (Supplementary Figure S5), and the two molecules can individually assemble into molecular crystals in chloroform with needle-shaped and tabular morphologies (**Figure 1c, e**). In contrast, when the UPy-BI and UCy-BI are mixed at 1:1 molar ratio in chloroform, a distinct crystal morphology can be observed (**Figure 1d**), indicating the conversion of the UCy-UPy co-assembly. X-ray diffraction (XRD) patterns, ¹H-NMR and DSC analysis (**Figure 1f-g**, Supplementary Figure S6) further prove the formation of unique molecular aggregates between UPy-BI and UCy-BI.

Lattice energy calculations from molecular crystal structures are used to reveal possible driven mechanism for the UCy-UPy co-assembly. Estimated from Born–Haber cycle,^[47] UCy motif in molecular crystal presents a lattice energy of $-251.06 \text{ kcal mol}^{-1}$, showing an increase about 65 % than that of UPy motif ($-151.74 \text{ kcal mol}^{-1}$). Compared with the dominant roles of lattice energies in the free energy landscapes of perfect crystals, the contributions of entropy below the melt temperature are subordinate.^[48,49] Therefore, additional enthalpic gains from the extensive non-covalent networks of the UCy motif can be consumed to compensate the energy cost for the dissociation of UPy motifs in molecular aggregates, driven the UCy-UPy co-assembly.

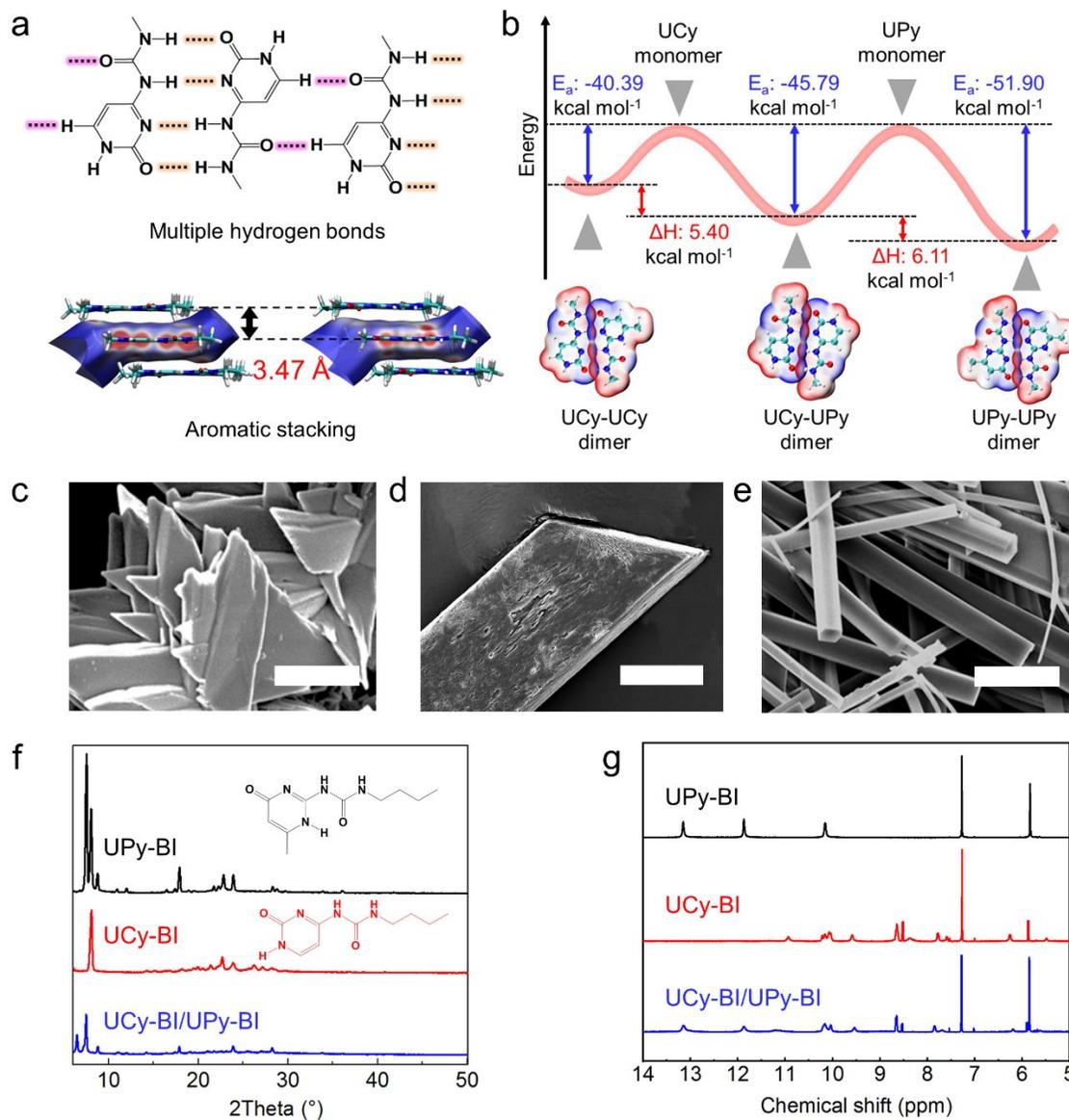


Fig. 1 UCy motif facilitates extensive non-covalent networks. **a)** Multiple hydrogen bonds and aromatic stacking patterns of UCy motifs (weak interactions are presented by Hirshfeld surface, and red regions indicate strong intermolecular hydrogen bonds). **b)** Energy diagram for the dimerization between UCy and UPy motif. Electrostatic potential surfaces overlaps are mapped on the 0.01 e Bohr⁻³ isovalue surfaces (obtained from M062X/6-311G*(GD3) calculations). **c-e)** Crystal morphologies observed from SEM images, including UCy-BI (c), UCy-BI/UPy-BI co-assembly (d), and UPy-BI (e). Scale bar 20 μm. **f)** XRD analysis of molecular crystals, which proves the distinct non-covalent networks. **g)** ¹H-NMR results of homo and hybrid molecular dimers in CDCl₃.

Extensive non-covalent networks and thermo-mechanical responsiveness in UCy-PDMS-UCy oligomers

The UCy motif can be employed as an effective modulator to regulate the thermostability, rheological and mechanical properties of supramolecular polymers. As a proof of demonstration, UCy terminal-bifunctionalized UCy-PDMS-UCy oligomers have been synthesized with PDMS molecular weights from 1K to 27K (**Figure 2a**). Driven by the UCy aggregation, extensive non-covalent networks in UCy-PDMS-UCy oligomers can be constructed (**Figure 2b**). Interconnected UCy aggregates can be observed from polarizing optical images of the cryo-sectioned samples (5 μm thickness) with the molecular weight of PDMS fragment adjusted from 5K (UCy-PDMS5K-UCy), 8K (UCy-PDMS9K-UCy) to 27K (UCy-PDMS27K-UCy) (**Figure 2c-e**).

The UCy aggregates in UCy-PDMS-UCy oligomers enables improved thermostability, and the solid-fluid phase transitions temperatures of UCy-PDMS5K-UCy, UCy-PDMS8K-UCy and UCy-PDMS27K-UCy decreased from 133 to 76°C (**Figure 2f-h**). Decreasing PDMS spacers present sequentially increased modulus for UCy-PDMS-UCy oligomers, and mechanical properties from nanoindentation verify this trend from 4 MPa (UCy-PDMS27K-UCy) to 192 MPa (UCy-PDMS1K-UCy) (Supplementary Figure S7). The hindrances of longer PDMS spacers could suppress the UCy aggregation, and the amorphous UCy-PDMS-UCy oligomers exhibit broad diffraction peaks from XRD measurements (Supplementary Figure S8). The intensity of UCy aggregates in UCy-PDMS-UCy oligomers are evaluated from viscosity activation energies (E_v), and reduced E_v values are measured for longer PDMS chains in UCy-PDMS-UCy oligomers (Supplementary Figure S9).

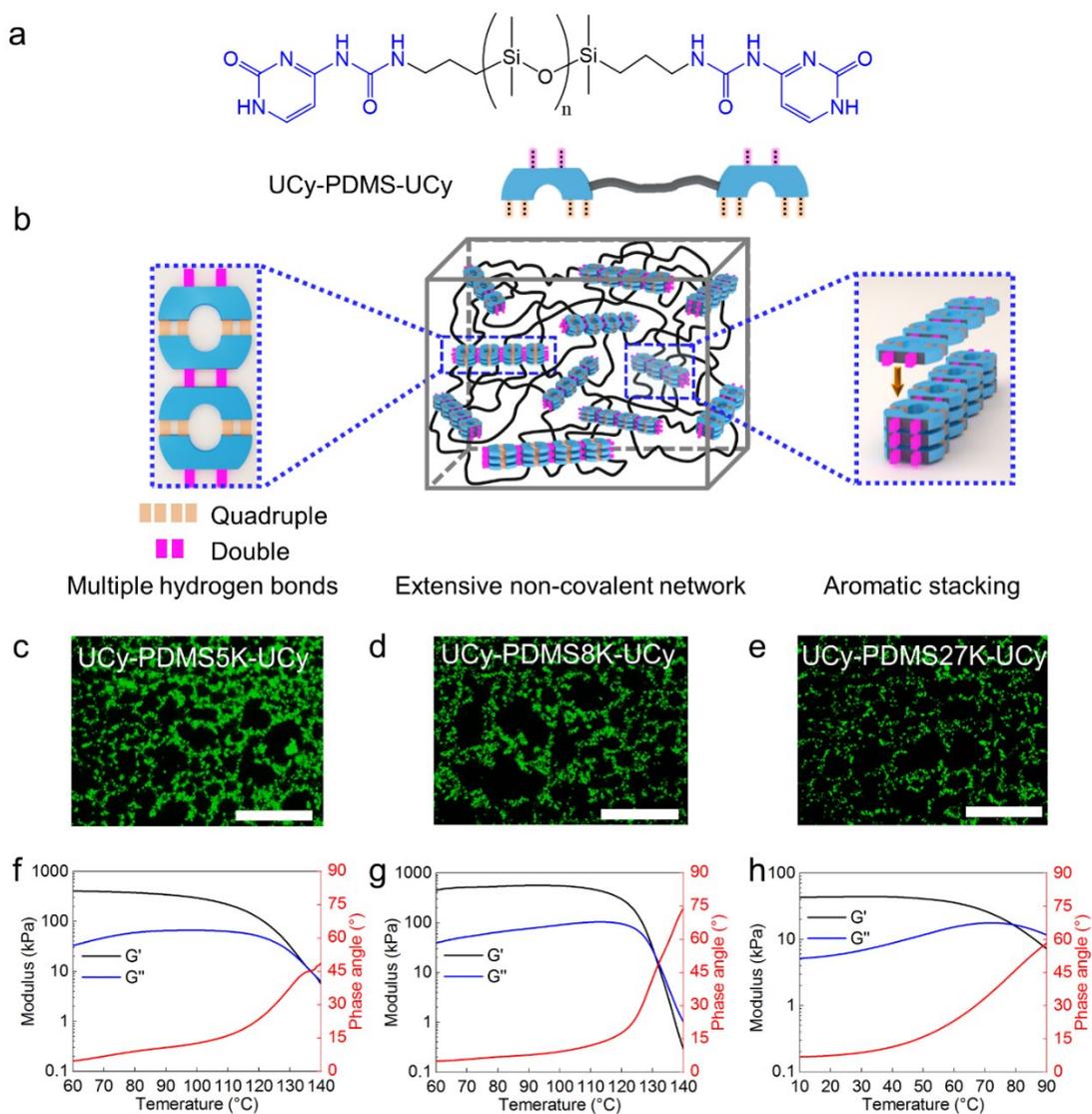


Fig. 2 Extensive non-covalent networks in UCy-PDMS-UCy oligomers. **a)** Molecular structures of UCy-PDMS-UCy oligomers. **b)** Schematic illustration of extensive non-covalent networks of UCy motif, with multiple hydrogen bonds and aromatic stacking. **c-e)** Polarizing optical images of the sectioned sample films (5 μm thickness) of UCy-PDMS-UCy oligomers. Interconnected green regions indicate extensive non-covalent networks of UCy aggregates. Scale bar 100 μm . **f-h)** Rheological temperature sweep of UCy-PDMS-UCy oligomers and phase angle values obtained by oscillatory shear rheology measurements at 1 Hz.

Reprogramming non-covalent network for controlled solid-fluid phase transition

UCy-UPy co-assembly facilitates the reprogramming of extensive non-covalent networks, enabling tunable solid-liquid phase transition of supramolecular polymers (**Figure 3a**). To demonstrate this tunability, UCy-PDMS3K-UCy oligomers are selected as modulators and co-assembled with UPy-PDMS3K-UPy oligomers by UCy-UPy dimerization. Increasing the weighting ratio of UCy-PDMS3K-UCy from 10 to 40 wt % can help reprogram the dispersed UPy stackings into extensive UCy-UPy co-assembly and stackings, resulting in improved rheological properties with higher storage modulus (**Figure 3b**) and complex viscosity (**Figure 3c**). The increased adhesion forces measured from atomic force microscope (AFM) further verify the fluid-solid phase transition of oligomer composites with higher UCy-PDMS3K-UCy contents (**Figure 3d**). As shown in XRD results, the disappearances of diffraction peaks around $10\text{-}15^\circ$ in the co-assembled oligomers is ascribed to the organization of the fluid PDMS chains (**Figure 3e**). The abundant formation of UCy-UPy dimerization in the oligomer composites is revealed from the frequency changes around 1670 cm^{-1} in attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) (**Figure 3f**). Compared with UPy motif, the UCy motif enables effective PDMS chain organization with less temperature and molecular-weight dependency of solid-fluid phase transition (**Figure 3g**, Supplementary Figure S10), indicating consistent and robust reprogramming of non-covalent networks to realize solid-fluid phase transition.

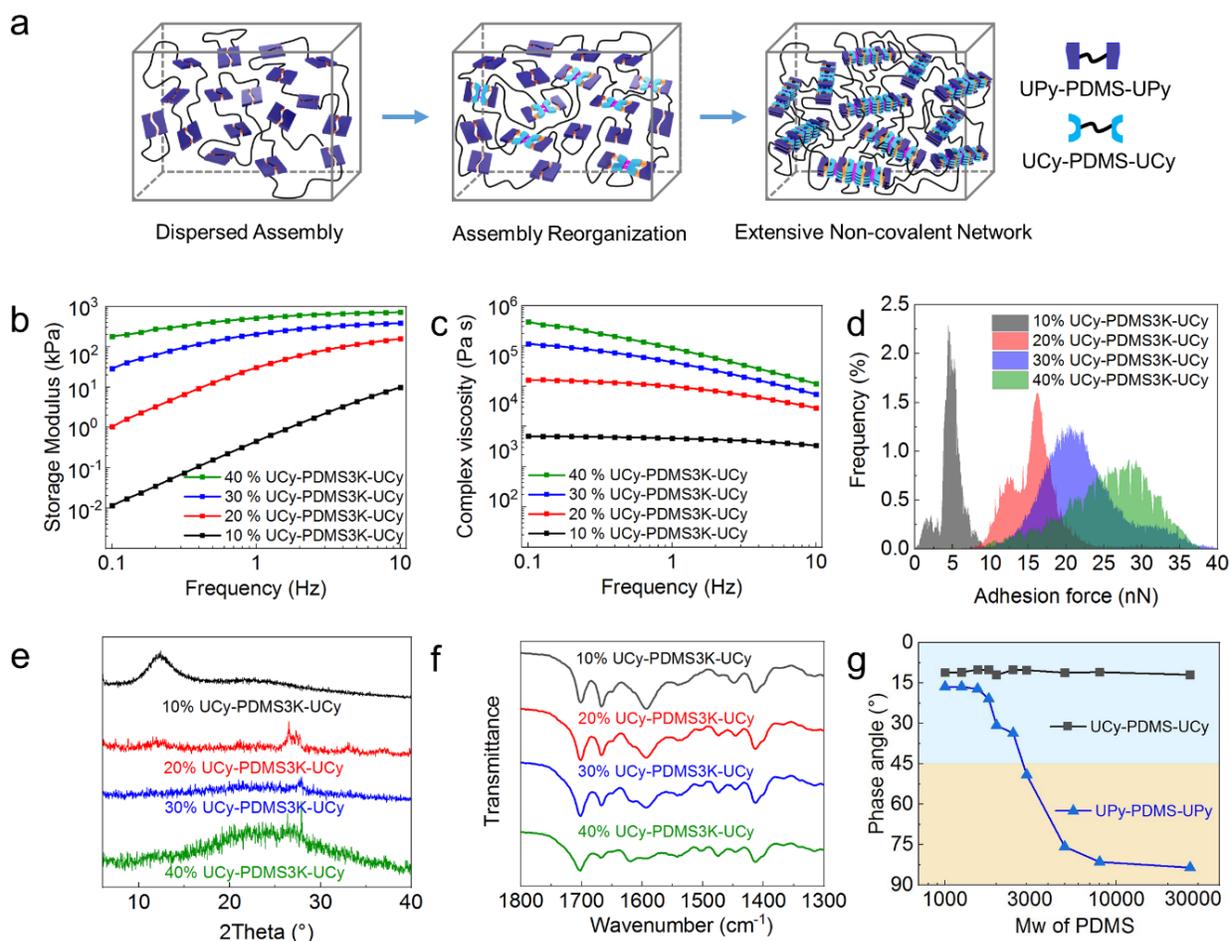


Fig. 3 Non-covalent network reprogramming and thermo-mechanical responsiveness. a)

Schematic illustration of non-covalent networks in UCy-PDMS-UCy/UPy-PDMS-UPy blends, and tunable solid-liquid phase transition from UCy/UPy co-assembly. **b-c)** Storage modulus (b) and frequency-dependence complex viscosity (c) of UCy-PDMS3K-UCy/UPy-PDMS3K-UPy blends. The values are measured at 25 °C. **d)** Distributions of adhesion forces of oligomeric blends at 20°C in air. **e)** X-ray diffraction results of UCy-PDMS3K-UCy/UPy-PDMS3K-UPy blends. **f)** ATR-IR spectra showing UCy/UPy co-assembly. **g)** Phase angle values of UCy-PDMS-UCy and UPy-PDMS-UPy oligomers with different PDMS chain length at 25 °C. Tunable solid-fluid phase transition can be realized from selection among PDMS chain length and temperatures.

UCy-PDMS-UCy oligomers for additive manufacturing

The UCy-PDMS-UCy oligomers present sharp temperature windows of solid-fluid phase transition, which can be applied as potential candidates for 3D printing and microfabrication, which require well-controlled thermo-mechanical responsiveness and working windows. As a proof of demonstration, helix tubes are prepared by extrusion 3D printing, using filaments made from UCy-PDMS3K-UCy oligomer (**Figure 4a**). The 3D-printed tubes can be structurally sustained upon heating to 60°C and 120°C for 2 h (**Figure 4b**), and they are able to support 200 g load without structural rupture (**Figure 4c**). UCy-PDMS3K-UCy oligomers also present anti-swelling properties in solvents such as water and ethanol (Supplementary Figure S11). As a comparison, UCy-PDMS27K-UCy oligomers show lower solid-liquid phase transition temperature around 74°C, and they can be utilized as melt casting materials for molding and microfabrication (**Figure 4d-g**, Supplementary Figure S12).

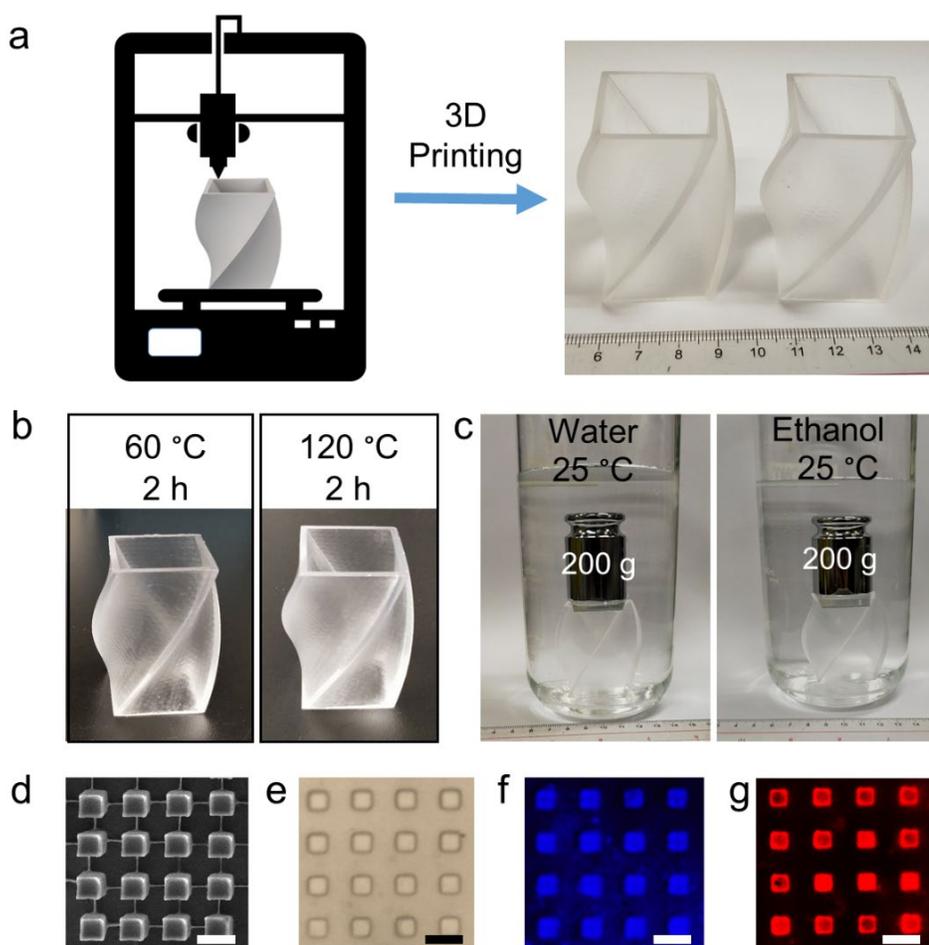


Fig. 4 UCy-PDMS-UCy polymers for additive manufacturing. **a)** Illustration of helix tubes composed of UCy-PDMS3K-UCy oligomer, which are prepared by 3D printing. **b)** Structural stability of helix structures at elevated temperatures for 2 h, including 60 °C and 120 °C. **c)** Structural robustness of helix structures with 200 g load in water and ethanol for 24 h. **d)** SEM images of blank micropattern templates. Scale bar 10 μm . **e)** Optical images of blank micropattern templates. Scale bar 10 μm . **f-g)** Fluorescent images of templates labeled by Coumarin 6 (**f**) and Nile Red (**g**). Scale bar 10 μm .

Tunable damage-healing properties via non-covalent network reprogramming

Coatings composed of UCy-PDMS-UCy and UPy-PDMS-UPy oligomers present tunable thermo-mechanical responsiveness and damage-healing properties at desired temperature. For example, when UCy-PDMS3K-UCy oligomers are mixed with UPy-PDMS3K-UPy oligomers at 30 wt% content, the solid-fluid phase transition temperature of the composite is around 37°C (**Figure 5a**). The coating shows excellent optical transparency when it is casted on glass coverslip at 200 μm thickness (**Figure 5b**). After being cut by a razor blade, the damage of the coating can heal in 5 min at 25°C (**Figure 5c**). At higher UCy-PDMS3K-UCy contents, for example 40 wt%, the UCy-UPy co-assembly will be promoted, which will result in elevated modulus and higher solid-fluid phase transition temperature around 43°C (**Figure 5d**), while the optical transparency is not affected (**Figure 5e**). The temperature and time for the damage healing of the coating becomes 40°C and 10 min (**Figure 5f**). When UCy-PDMS3K-UCy content is further increased to 50 wt%, the solid-fluid transition temperature becomes 65°C, and the damage healing can be realized after melting at 75°C (Supplementary Figure S13). Therefore, the non-covalent network reprogramming can be regulated via UCy-UPy co-assembly, which is effective for tunable thermo-mechanical responsiveness, from highly effective self-healing around room temperature to other desired temperatures.

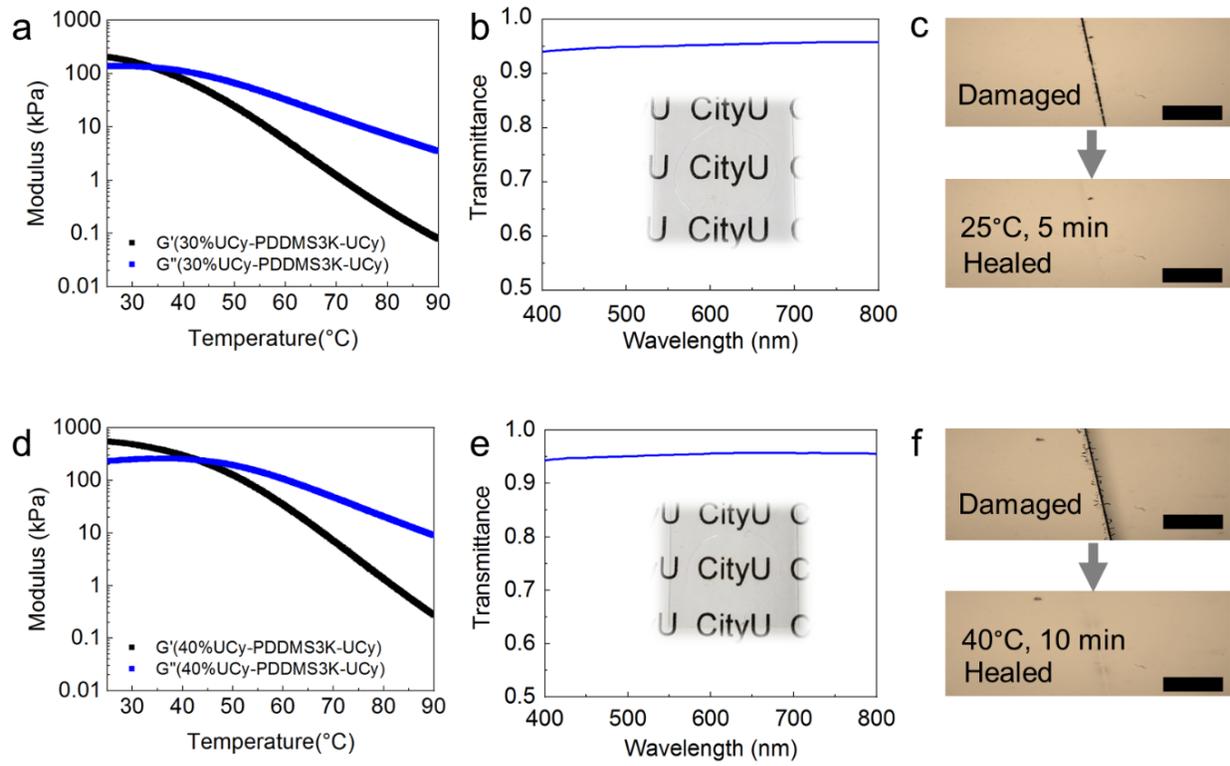


Fig. 5 Tunable damage-healing properties via non-covalent network reprogramming. a)

Rheological temperature sweeping for 30 wt % UPy-PDMS3K-UPy/70 wt % UCy-PDMS3K-

UCy blend. Results are obtained by oscillatory shear rheology measurements at 1 Hz. **b)** Optical

transmittance property of coating on glass coverslip, and **c)** damaged coating healing process

with composition in a). Film thickness 200 μm . Scale bar 10 μm . **d)** Rheological temperature

sweeping for 40 wt % UPy-PDMS3K-UPy/60 wt % UCy-PDMS3K-UCy blend. Results are

obtained by oscillatory shear rheology measurements at 1 Hz. **e)** Optical transmittance property

of coating on glass coverslip, and **f)** damaged coating healing process with composition in d).

Film thickness 200 μm . Scale bar 10 μm .

CONCLUSIONS

Programming thermo-mechanical responsiveness in supramolecular polymers is challenging, due to the limited tunability on the non-covalent networks with structural hierarchy and complexity, as well as the cascade dissociation of the non-covalent networks at elevated temperatures. To address this issue, we describe here an aggregate engineering strategy that the construction of extensive non-covalent networks can significantly improve thermo-mechanical properties of supramolecular polymers. Specifically, the UCy motif has been proposed with extensive non-covalent networks, and there is high enthalpic gain from UCy aggregation which can contribute to the stabilization of the formed non-covalent networks.

Notably, the UCy motif can drive UCy-UPy co-assembly, enabling the reprogramming of the non-covalent network of UPy motif with promoted extensiveness. In this work, the UCy-PDMS-UCy oligomers have been employed as an effective modulator to regulate the solid-fluid phase transition and mechanical properties of UPy-PDMS-UPy oligomers. Such reprogramming capacity can significantly extend the tunability on the thermo-mechanical properties in supramolecular polymers. Moreover, the thermo-mechanical versatility by UCy-UPy co-assembly is successfully exploited for 3D printing, microfabrication and damage-healing coating. We envision that the aggregate engineering strategy for regulating non-covalent networks has potential to broaden the applications of supramolecular polymers.

Supporting Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article.

Competing interests: The authors declare no conflict of interest.

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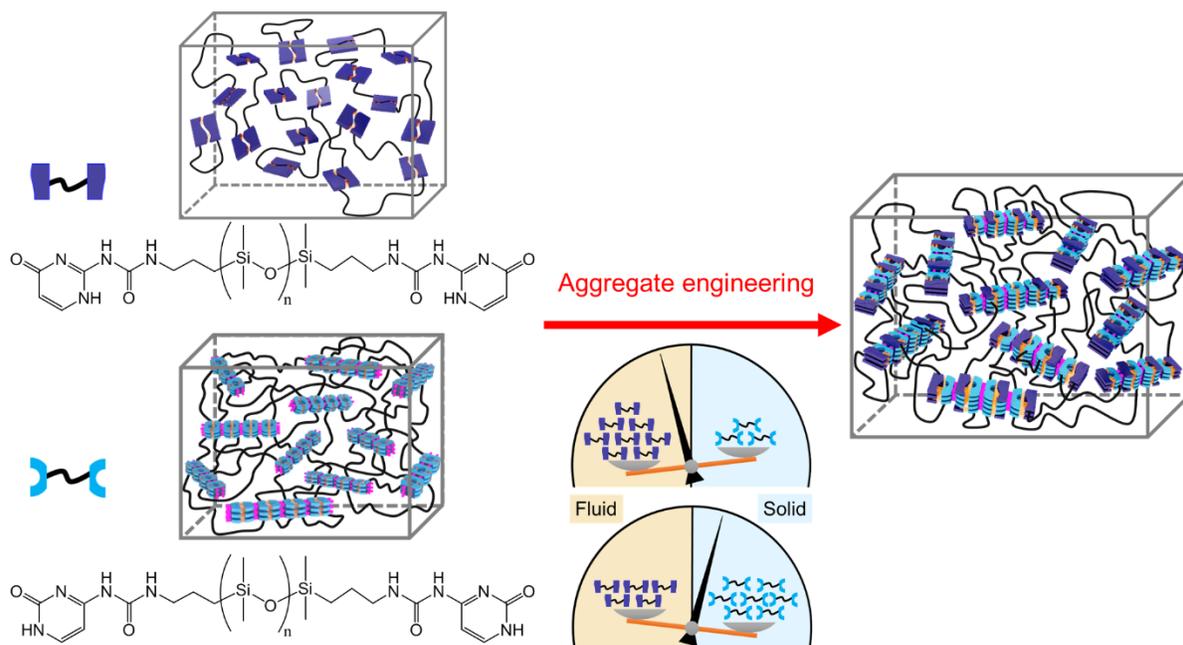
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TOC figure



- An aggregate engineering strategy is proposed to improve the vulnerability of non-covalent networks at elevated temperatures.
- Programming and stabilizing non-covalent networks can be realized in supramolecular polymers.
- Such aggregate engineering strategy offers prospects for the on-demand tunability in thermo-mechanical responsiveness.
- 引入聚集态工程思路，改进非共价网络的稳健性。
- 实现了可控及稳定的非共价网络。
- 有益于力热响应性的按需调控。