Dynamic Bonds Mediate $\pi$-\(\pi\) Interaction via Phase Locking Effect for Enhanced Heat Resistant Thermoplastic Polyurethane

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Electronic Supplementary Information

Abstract  Stimulus-responsive polymers containing dynamic bonds enable fascinating properties of self-healing, recycling and reprocessing due to enhanced relaxation of polymer network with labile linkages. Here, we study the structure and properties of a new type of thermoplastic polyurethanes (TPUs) with trapped dynamic covalent bonds in the hard-phase domain and report the frustrated relaxation of TPUs containing weak dynamic bond and $\pi$-$\pi$ interaction in hard segments. As detected by rheometry, the aromatic TPUs with alkyl disulfide in the hard segments possess the maximum network relaxation time in contrast to those without dynamic bonds and alicyclic TPUs. In situ FTIR and small-angle scattering results reveal that the alkyl disulfide facilitates stronger intermolecular interaction and more stable micro-phase morphology in $\pi$-$\pi$ interaction based aromatic TPUs. Molecular dynamics simulation for pure hard segments of model molecules verify that the presence of disulfide bonds leads to stronger $\pi$-$\pi$ stacking of aromatic rings due to both enhanced assembling thermodynamics and kinetics. The enhanced $\pi$-$\pi$ packing and micro-phase structure in TPUs further kinetically immobilize the dynamic bond. This kinetically interlocking between the weak dynamic bonds and strong molecular interaction in hard segments leads to much slower network relaxation of TPU. This work provides a new insight in tuning the network relaxation and heat resistance as well as molecular self-assembly in stimulus-responsive dynamic polymers by both molecular design and micro-phase control toward the functional applications of advanced materials.

Keywords  Thermoplastic polyurethane; Disulfide bond; Stimuli-responsive rearrangement; $\pi$-$\pi$ Stacking; Phase locked effect

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INTRODUCTION

Stimulus-responsive polymeric materials containing dynamic bonds exhibit interesting adaptive functional properties, such as self-healing\textsuperscript{[1–3]} shape-memory,\textsuperscript{[4,5]} and recyclability/reprocessability.\textsuperscript{[6–8]} Upon external stimulus, the reversible bonds in dynamic undergo either bond break/reformation or exchange reaction to reconfigure the polymer architecture. The smart/functional properties of dynamic polymers are derived from enhanced multiscale molecular/network relaxation in physically or chemically crosslinked polymer networks due to the limited bond life-time of dynamic bonds under external stimulus.\textsuperscript{[9,10]} In the past decade, plenty of dynamic covalent bonds and dynamic reactions, such as Diels-Alder adduct,\textsuperscript{[11–14]} disulfide bond,\textsuperscript{[15–17]} Schiff-base,\textsuperscript{[18–22]} and transesterification,\textsuperscript{[23–26]} to name a few, have been used to fabricate dynamic polymers. The molecular chain mobility and network relaxation kinetics of the dynamic polymers play a critical role in the stimulus-responsive properties. In most homogeneous one-phase dynamic polymers, the network relaxation relies on the intrinsic reaction kinetics and thermodynamics of dynamic bonds. For example, rapid macromolecular dynamics of weak dynamic bonds, such as hydrogen bonding and disulfide bond, were used to achieve fast self-healing and reprocessing.\textsuperscript{[27,28]} Nevertheless, such highly dynamic materials usually suffer from weak mechanical stiffness and strength as well as low-temperature tolerance.\textsuperscript{[29–31]} Recently, heterogeneous or multiphase dynamic polymers have been synthesized to balance self-healing and mechanical properties. For example, Guan and coworkers used the supramolecular block copolymer with hard/soft two-phase morphology and dynamic motifs (such as multihydrogen bonding and metal-ligand interaction) selectively located in the soft phase to afford both advantageous mechanical stiffness and fast healing.
capacity. However, these materials still show limited improvement in mechanical properties due to a large number of weak linkages in the soft domain and suffer from high hysteresis owning to the intrinsic high dynamic of the material.

Thermoplastic polyurethanes (TPUs), as one of the most widely used engineering materials, attract great attention in both industry and academia community. TPUs are multiblock copolymers with thermodynamically immiscible alternating hard segments and soft segments leading to microphase separation. The soft segments of polyester or polyether with a low glass transition temperature \((T_g)\) form the soft domain and accommodate flexibility of TPUs. The hard segments derived from the reaction between diisocyanates and small diol chain extenders form hard domain, which act as physical cross-linking and effective reinforcement to improve the stiffness and toughness of TPUs. In the past years, various dynamic moieties have been incorporated into PU molecular chains to access self-healing/reprocessing and reconfigurable shape memory. Especially, aromatic and aliphatic disulfides were introduced in polyurethanes (PUDS) to achieve both fast healing at mild temperature and mechanical robustness. More recently, our group used the phase-locked dynamic bond design to trap alkyl disulfide kinetically in hard segments with strong hydrogen bonding to fabricate colorless, transparent, robust, and fast scratch-self-healing PUDS. It was found that the hard phase with strong hydrogen bonding and high \(T_g\) can act as a switch to immobilize the weak dynamic bonds below \(T_g\) and readily be activated by heating above the \(T_g\). This kind of kinetically trapped dynamic polymers is a promising candidate for the high-performance smart materials featuring both excellent mechanical properties and tailor-made fast dynamics.

Here, we studied the temperature dependent network relaxation and structure-property relation of PUDS and reported a frustrated relaxation effect of aromatic TPUs with alkyl disulfide and \(n\)-\(\pi\) interaction in hard segments. It is hypothesized that the network relaxation of PUDS is dominated by the thermal stability of the hard domain, which is affected by the interplay between the dynamic bond and micro-phase separation. On the one hand, similar to the conventional idea that dynamic bonds make the polymer chain with weak bonds, dynamic alkyl disulfide can act as weak molecular linkages to accelerate the relaxation of TPUs with hydrogen bonding dominated hard segments; on the other hand, in the aromatic TPUs, we find the dynamic alkyl disulfide as molecular switch would enhance the probability of \(n\)-\(\pi\) stacking between benzene rings and micro-phase separation of hard segment so as to suppress the network relaxation (Scheme 1a). The kinetics interlocking between the weak dynamic bonds and strong molecular interaction in TPU results in a delayed relaxation of the system, i.e. weaker can make stronger (Scheme 1b). A combined characterization of rheology, in situ FTIR and small angle X-ray scattering as well as molecular dynamics (MD) simulation was used to investigate the temperature-dependent intermolecular interaction and micro-phase morphology evolution to elucidate the molecular origin of such unique relaxation effect. Finally, based on this stimuli-responsive rearrangement behavior, some functional applications including as heat resistant material with reprocessing ability are demonstrated.

**EXPERIMENTAL**

**Materials**

Polycaprolactone diols (PCLD, \(M_n\)=3000) was purchased from Perstorp. 4,4′-Methylene diphenyl diisocyanate (MDI) was purchased from J&K Chemical Ltd. Bis(2-hydroxyethyl) disulfide (HEDS, tech. 90%) was purchased from Alfa Aesar. The catalyst dibutyltin dilaurate (DBTDL, tech. 97.5%), the solvent \(N,N\)-dimethylacetamide (DMAc) and 1,6-hexanediol (HDO) were purchased from J&K Chemical Ltd.

**Synthesis of PUDSs**

PUDSs were synthesized according to the method in our previous work via a one-pot two-step protocol (Scheme S1 in the electronic supplementary information, ESI). For the prepolymer synthesis, PCLD was preheated at 70 °C till melt, and fed into a

![Scheme 1](https://doi.org/10.1007/s10118-020-2494-7)

**Scheme 1** The schematic illustration of the process of the stimuli-responsive rearrangement and its molecular origin. (a) Hard segments in TPUs containing aromatic extender with alkyl disulfides. (b) Temperature-dependent micro-phase structure evolution of alkyl disulfide contained in aromatic TPUs from loose \(n\)-\(\pi\) packing at low temperature to enhanced \(n\)-\(\pi\) packing and more stable micro-phase structure at elevated temperature.
250 mL glass flask equipped with mechanical stirrer and a vacuum inlet. The PCLD was stirred under vacuum while heating at 120 °C for 2 h to remove moisture residue and then cooled to 70 °C. To avoid the side reactions (forming cross-linking), MDI was then added into the flask without the catalyst and the mixture was stirred for 2 h under nitrogen protection. DMAc was then added into the flask and the mixture was cooled to 50 °C. HEDS (or HDO, for blank control samples) and the catalyst (DBTDL, 0.5 wt%) were added gradually. The mixture was then further stirred for 2 h. Finally, clear resins with different chemical structures of hard segments were then obtained and named as PUDS-5-M and PUDS-0-M. All the product was not cross-linked which can be completely dissolved in the good solvent as DMAc. The molar ratio of PCLD/MDI/HEDS (or HDO) was 1/5/4. The disulfide content of the samples was calculated using Eq. (1). The disulfide content of the polyurethane with disulfide bonds (PUDS) samples are also shown in Table S1 (in ESI). Films for testing were prepared by casting the resins on Teflon plates, placing them in a fume cupboard for 24 h, and then removing the solvent at 80 °C for 24 h under vacuum. All samples were annealed at 100 °C for 24 h, naturally cooling to the room temperature for the same thermal history condition and better phase separation.

**Synthesis of Model Molecules (Pure Hard Segments)**

For the model compounds synthesis, MDI was fed into a 100 mL glass flask equipped with mechanical stirrer and nitrogen gas seal equipment. HEDS (or HDO), catalyst (DBTDL, 0.2 wt%) and the solvent (DMAc, 30 mL) were then gradually added into the flask and the mixture was stirred for 2 h under nitrogen gas protection. Finally, clear products with different chemical structures were obtained and named as MDI-HEDS and MDI-HDO. The molar ratio of MDI/HEDS (or HDO) was 10/11. All compounds for testing were prepared by casting on Teflon plates, placing them in a fume cupboard for 24 h, and then removing the solvent at 80 °C for 24 h under vacuum. All samples were annealed at 100 °C for 24 h, naturally cooling to the room temperature for the same thermal history condition and better phase separation.

**Characterization**

Gel permeation chromatography (GPC) (DAWN HELEOS, Wyatt, U.S.) tests were employed to study the molecular weight changes of PUDSs performed, where the chloroform was used as eluent and polystyrene served as calibration standard.

Differential scanning calorimetry (DSC) (200, TA Instruments, U.S.) experiments were performed to characterize the film thermal properties from −150 °C to 200 °C at a rate of 10 °C/min under nitrogen flow.

Thermogravimetric analysis (TGA) (8000, PerkinElmer, U.S.) experiments were performed at a linear heating rate of 40 °C/min from 30 °C to 100 °C under nitrogen atmosphere in order to remove the water. Then the samples were heated from 100 °C to 800 °C at the heating rate of 20 °C/min. The first-stage degradation temperatures of the PUDS samples are approximately 300 °C (Fig. S1 in ESI).

In situ small angle X-ray scattering (SAXS) measurements were carried out on a Xenocs 2.0 system (Xenocs SA, France) equipped with a semiconductor detector (Pilatus 300K, DEC-TRIS, Swiss). X-ray radiation with a wavelength of 0.15418 nm was produced by Cu Ka X-ray source (GeniX3D Cu ULD), generated at 50 kV and 0.6 mA. Sample temperature was controlled by a Linkam THMS600E hot stage. The SAXS data were collected at various temperatures (30, 70, 100, 150, 180, 200, 230 °C) and the image acquisition time was 1200 s. The sample-to-detector distance was 2521.07 mm. The one-dimensional (1D) intensity profiles were integrated from background corrected 2D patterns. The thickness of all samples was approximately 1 mm.

Atomic force microscopy (AFM) (Bruker multimode 8, Bruker, Germany) was performed using tap-ping MPP-Ro-tated cantilevers with silicon probes (names: RTESP, orders MPP-11120-10, 40 N/m, 300 kHz, rotated tip). To measure the phase morphology of the PUDS systems, the amplitude set point was adjusted above 250 mV and both the AFM height and phase images were collected at the same time.

Rheology measurements were performed on a stress-controlled rheometer (DHR II, TA instruments, U.S.) in the oscillatory mode with parallel plate fixtures (25 mm diameter). Dynamic storage modulus (G') and loss modulus (G'') over a frequency range of 0.01–600 rad/s were determined with the small-amplitude oscillatory mode at various temperatures. The temperature control was accurate to within 1 °C, and a fixed strain of 1% was used at a given temperature, to ensure that measurements were taken well within the linear viscoelastic range of the materials investigated. All rheological measurements were conducted under a nitrogen atmosphere in order to prevent oxidative degradation of the samples. In order to determine the equilibration time of samples at 0.01 rad/s, the dynamic time sweep with various temperatures were performed for the reference of the waiting time in dynamic frequency sweep experiment. Based on the result, the waiting time in the low frequency region was finally specified as 1000 s.

Fourier transform infrared spectroscopy (FTIR) experiments were performed in order to determine the extent of intermolecular interactions, especially the hydrogen bonds and n-π stacking, in PUDS specimen during isothermal annealing at 100 °C. For the experiment, films suitable for spectroscopic studies were prepared by directly casting 0.2 mg/mL solution in DMAc on the KBr salt plate. They were slowly dried for 24 h in a fume hood until most of the solvent evaporated and then dried at 70 °C for a few days in a vacuum oven. Samples were then stored in a desiccator until used. FTIR spectra were recorded on a Nicolet 6700 spectrometer equipped with a Linkam hot stage (FTIR 600). The spectra were obtained by co-adding 16 scans at a temperature interval of 1 °C during heating process. FTIR experiment was carried out at a heating rate of 10 °C/min from 30 °C to 230 °C for all samples and steadied every 5 °C to scan the curve. The scanned wavenumber range was 650–4000 cm⁻¹. The spectral resolution is 4.0 cm⁻¹. All infrared spectra were baseline corrected. To erase the influence from the sample thickness caused by the temperature variation, the absorbance of all IR bands is normalized by that of 2723 cm⁻¹ band that is assigned to the combination band of CH₃ asymmetric bending vibration and CH bending vibration.

The calculation of the disulfide content of the PUDS-M samples:

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\[ \text{PUDS-M}_{n}\text{PCL}_m \text{MDI}_n \text{HEDS}_m = \frac{2M_g}{M_{\text{PCL}} \cdot n_{\text{PCL}} + M_{\text{MDI}} \cdot n_{\text{MDI}} + M_{\text{HEDS}} \cdot n_{\text{HEDS}}} \times 100\% \]  

where PUDS-M_{n}\text{PCL}_m \text{MDI}_n \text{HEDS}_m denotes the disulfide content of the samples (%); \( M_g \) denotes the relative atomic mass of the sulphur atom; \( M_{\text{PCL}}, M_{\text{MDI}}, \) and \( M_{\text{HEDS}} \) donate the mass fraction of PCL, MDI, and HEDS, respectively; \( n_{\text{PCL}}, n_{\text{MDI}}, \) and \( n_{\text{HEDS}} \) donate the molar ratio of the PCL, the MDI, and the HEDS in the system, respectively.

\(^1\)H and \(^{13}\)C solution NMR spectra were recorded on 400 MHz NMR spectrometers (Avance III 400, Bruker, Germany). Chemical shifts are reported in ppm with either tetramethylsilane or the residual solvent as an internal standard. All anhydrous solvents were dried according to standard procedures prior to use. All chemicals were obtained from commercial sources and used without further purification.

\(^1\)H CP-MAS solid-state NMR spectra were acquired on an AVANCE III 400 spectrometer (Avance III 400, Bruker, Germany) with a frequency of 399.16 MHz for \(^1\)H. All experiments were carried out using a 4 mm probe at a spinning speed of 10 kHz. The chemical shifts were referenced to adamantane at 298 K (\(^1\)H 1.91 ppm). For all cross polarization experiments, the 90° pulse length on protons was 5 μs. The recycle delay was 2 s (D1=2 s). In variable temperature experiment, all temperatures were stabilized for 5 min for each sampling.

For all MD simulations, the all-atom optimized performance for liquid systems (OPLS-AA) force field was used. All the molecules in the present study are in all-atomic structures. The total potential energy is given as a combination of valence terms including diagonal and off diagonal cross coupling terms, and nonbonded interaction terms. For the vDW interactions between different atomic species, we used the standard geometric mean combination rule. Atomic charges were assigned based on the atomic charges specified within the OPLS-AA force field. All of the MD simulations were performed using the GROMACS free software package. The nonbonded potential truncation was performed using the spherical cut off method for Lennard-Jones (PME) summation, with a real space cut off fixed at 1.2 nm. We controlled the temperature using the Berendsen thermostat with a coupling constant of 0.1 ps. All the simulations were run with the fast LINCS algorithm to constrain the bond lengths for the surfactant and water molecules, with the time step of 2 fs. The MD simulations were firstly carried out under isothermal constant volume simulations for 1 ns to equilibrate the system at 300 K based on previous studies. In all simulations, the potential energy attains a relatively constant value after around 300 ps. Then MD simulations were carried out under isobaric constant volume simulations for 1 ns at 1.01x10^5 Pa. Finally, MD run was extended for 4 ns and the trajectory was recorded every 1 ps to analyze the properties.

RESULTS AND DISCUSSION

TPUs Synthesis and Characterization

TPUs with aromatic hard segments were synthesized via a one-pot two-step protocol (Scheme S1 in ESI). Specifically, polycaprolactone diol (PCLD) with a selective molecular weight \((M_w=3000\ \text{g/mol})\) was used as the soft segment in this system, which provides elasticity, flexibility as well as crystallinity to the system. Orthogonal molecular design to control dynamic bonds in hard segments was employed to fabricate a series of TPUs. Aromatic disiocyanate (4,4’-methylenebisphenol disiocyanate, MDI) were used to alter the primary intramolecular interaction of \(n-n\) interaction between hard segments. Small molecule diol of bis(2-hydroxethyl) disulfide (HEDS) was utilized to incorporate alkyl disulfide in the hard segments. For the control samples, 6-hexanediol (HDO) was used as the chain extender instead. All GPC results are shown in Table S1 (in ESI). Compared with the blank control, the incorporation of alkyl disulfide would further decrease the molecular weight of TPU chains. The disulfide content of PUDS is calculated as to be 5.2 wt% according to Eq. (1). The heat resistance of PUDS-5-M (94.9%) is slightly poorer than that of the blank control sample (95.8%) at 300 °C, which may be related to the weak chemical bond (Fig. S1 in ESI). DSC results suggest that all TPUs show a glass transition temperature \((T_g)\) at −20 °C to −40 °C attributed to the soft domain. In addition, MDI based aromatic TPUs with \(n-n\) interaction in the hard segment shows a melting/crystallization transition attributed to the crystallization of hard segments (Fig. S2 in ESI). It is noted that the incorporation of alkyl disulfide enables a higher crystallization temperature and freezing temperature for TPUs, indicating stronger or more ordered \(n-n\) packing. The summary of thermal properties of TPUs samples is shown in Table S2 (in ESI).

Relaxation Characterization via Rheometry

The unique network relaxation of the TPU was evaluated by rheological properties as a function of frequency at different temperatures. A small-amplitude oscillatory shear was used and the frequency \((\omega)\) dependent storage (or elastic) modulus, \(G'\), and the loss (or viscous) modulus, \(G''\) were recorded at a temperature ranging from 40 °C to 220 °C. All the TPU materials show an elastic response at 40 °C as indicated by much higher \(G'\) than \(G''\). A drop-off in the low-frequency modulus, and a cross-over in \(G'\) and \(G''\) at low frequency were observed at elevated temperatures (Fig. S3 in ESI). The low-frequency cross-over temperature is different for comparing samples. As the \(G'\) is much more sensitive to the structure relaxation than \(G''\), the effect of hard segment species on the relaxation behavior of the physically cross-linked network was further evaluated by log-log plots of \(G'\) versus \(\omega\) (Fig. 1). The \(G'\) value of PUDS-5-M is one order of magnitude higher than that of the commercial aromatic TPU at room temperature. All samples were filmed by the casting process at 80 °C, which is lower than the crystallization temperature of the hard segments but higher than the reaction temperature of disulfide bonds. The induction of phase separation at 80 °C is not only related to the solvent volatilization rate, but also strongly dependent on the crystallization behavior of the hard segment of the sample. The aromatic segments in the hard domain of PUDS-S-M have been partially rearranged, leading to a solid structure in the process of casting. At a fixed frequency, \(G'\) value of PUDS-5-M reduces with increasing temperature. It is particularly noteworthy that PUDS-S-M exhibits a \(G'\) plateau with almost unchanged values even at a temperature up to 220 °C, suggesting a fairly stable network structure at elevated temperatures. In addition, during the cooling process from 200 °C to the room temperature, the \(G'\)
value of PUDS-5-M is more than 2 orders of magnitude higher than that of the commercial aromatic TPU (without dynamic bonds) at 200 °C (Figs. 1a and 1b). To further illustrate the reinforcement of the structure by the temperature-response, the PUDS-5-M sample was subjected to the stress relaxation tests at a specific temperature for multiple times. Fig. 1(c) shows that the structure adjustment of the aromatic segments in PUDS-5-M continuously evolves with time at an elevated temperature. The more ordered arrangement of the segments resulted in stronger $n$-$n$ interaction. $\omega_c$ is defined as the frequency of intersection between $G'$ and $G''$. The inverse of $\omega_c$ as a longest characteristic relaxation time of the network ($\tau_c$), i.e. $\tau_c\sim1/\omega_c$, was utilized to quantitatively evaluate the relaxation of the network. The temperature-dependent $\tau_c$ for all TPUs is plotted in Fig. 1(d). It can be seen that, at a $\tau_c$ in the scale of 100 s, PUDS-5-M shows an extremely high relaxation temperature ($T_g$). The relaxation temperature was as high as 220 °C for the alkyl disulfide containing aromatics TPU (PUDS-5-M), which is 70 °C higher than that of PUDS-0-M (150 °C).

The temperature-dependent rheology results were further analysed by time-temperature superposition (TTS) (Fig. S4 in ESI). Using 120 °C as a reference temperature, frequency-dep
dependent $G'$ and $G''$ were shifted to obtain their master curves for all TPU samples. The poor overlapping of the master curves for aromatic TPUs (PUDS-M) is attributed to more obvious heterogeneity due to the micro-phase segregated morphology. PUDS-5-M shows no cross-over of $G'$ and $G''$ on the master curve, indicating an extremely stable network structure at the reference temperature. The dissolution experiment with the solvent of DMAC suggests that PUDS-5-M did not undergo chemical crosslinking during the measurements (Fig. S5 in ESI). It is concluded that the incorporation of the weak alkyl disulfide in aromatic TPUs leads to better $n$-$n$ packing, resulting in extremely long relaxation time and superior thermal stability.

**Microstructure and Micro-phase Characterization via FTIR and SAXS**

To better understand the molecular mechanism of different relaxation behavior for TPUs, the in situ FTIR was used to study the temperature dependence on the intermolecular interaction. The $n$-$n$ stacking is dominant between the short-range ordered aromatic ring structures in aromatic TPUs. The temperature-dependent evolution of $n$-$n$ stacking interactions in TPUs was evaluated by the FTIR spectra (Fig. S6 in ESI). The assignments to the main characteristic bands of TPUs chains are shown in Table S3 (in ESI). It can be seen that, the absorption band at about 3300 and 3500 cm$^{-1}$ correspond to hydrogen-bonded and free N-H group, respectively. A series of specific absorption bands are present in the broad band on 1750–1600 cm$^{-1}$, which reflects different types of H-bond from isocyanate. For example, the

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**Fig. 1**  Rheology characterization of TPUs. Storage modulus ($G'$) versus frequency ($\omega$) dynamic frequency sweep curves of (a) PUDS-0-M and (b) PUDS-5-M samples from 40 °C to 220 °C for various TPUs. (c) Cyclic stress relaxation tests of PUDS-5-M at 200 °C. (d) Representative characteristic relaxation time of different samples versus temperatures.
weak H-bond or free H-bond vibration, disordered and ordered H-bond vibration of urethane carbonyl bands are located at 1745, 1730, and 1705 cm$^{-1}$, respectively. The bands at 1598, 1536, and 1462 cm$^{-1}$ are assigned to the vibration of benzene skeleton from n-n stacking, which exists particularly in TPUs.

The typical temperature variation FTIR spectra of TPUs are shown in Fig. 2(a) and Fig. S7 (in ESI), respectively. The spectrum exhibits some peak shift and area change during heating. For the aromatic TPU, short-range ordered rigid aromatic isocyanate results in strong n-n interactions in hard domains. In particular, the peak position and integrated area of the aromatic skeleton vibrations change with temperature, reflecting the evolution of n-n stacking interactions. Fig. 2(b) shows that both the peak positions and the relative integral area of the characteristic peak (RIA) of disulfide containing TPUs is larger than or equal to those without dynamic bonds at different temperatures. During the heating process, due to the thermal motion of the molecular chain, the position of the characteristic peak would have a blue shift. The less blue shift band peaks and more stable band area in PUDS-5-M sample reveal a more stable intermolecular interaction and microphase structural stability.

The temperature-varied small-angle X-ray scattering (SAXS) analysis was further performed to evaluate the micro-phase separation structure (Fig. 3). In order to melt all the PCL crystals in soft domain, the initial temperature of the step-wise heating process started from 70 °C. The scattering peaking is attributed to the micro-phase of hard domains. The change of scattering peaking and position suggests the evolution of hard domain structure with increasing temperature. When the temperature exceeds the stimuli-response temperature of 70 °C, the exchange of the disulfide bonds is helpful to rearrange the aromatic segments in the hard domain of PUDS-5-M to be more orderly, resulting in a stronger n-n interaction. The scattering peak position in the range of 0.3–0.5 nm$^{-1}$ gradually shifts to a lower q value upon heating until 180 °C, indicating the increase of the domain size. However, when the temperature is further increased (≥180 °C), the intermolecular interaction becomes weaker due to the destruction of n-n interaction, resulting in a gradual dissipation of the hard domain. Therefore, the $d_{\text{max}}$ increases with the increasing temperature, i.e., the q value is decreasing. The decrease of the maximum intensity is related to the weakening of the micro-phase separation. The scattering peak disappearance temperature is below 200 °C for PUDS-0-M. By contrast, the scattering peak maintained up to 230 °C for PUDS-5-M, suggesting much higher stability of hard domain than that of PUDS-0-M. The nanometer-scale morphology of the aromatic TPUs containing disulfide linkages was observed by AFM (Fig.

![Fig. 2](https://example.com/fig2.png)  
**Fig. 2** Temperature dependent intermolecular interaction of TPUs. (a) Typical temperature-dependent transmission FTIR spectra for PUDS-5-M. (b) Typical temperature-dependent peak locations and integral area of n-n stacking for PUDS-5-M and control (PUDS-0-M) sample.

![Fig. 3](https://example.com/fig3.png)  
**Fig. 3** Temperature dependent micro-phase structural evolution characterization of TPUs. Temperature dependent $Iq^2$-q profiles for (a) PUDS-5-M and (b) PUDS-0-M from 30 °C to 230 °C by SAXS.
S8 in ESI). The result suggests that the chemical structure of hard segments has a great effect on both the segment miscible, i.e., the degree of micro-phase separation and hard domain stability. The catalysed alkyl disulfide undergoes exchange reaction at about 60 °C. However, the disulfide linkages in hard segments are kinetically trapped in the hard domain. The dynamic reaction is thus determined by the chain mobility and thermal stability of the hard domain. When the temperature reached the \( T_g \) or \( T_m \) of the hard domain, the dynamic disulfide bonds can be activated and the hard segments could adjust the chain configuration. The alkyl disulfide contained aromatic TPUs show more ordered \( n \)-\( \pi \) stacking in hard domains leading to enhanced thermal stability.

**Validation by Model Hard Segment Molecules**

To further validate the unique slower relaxation by the alkyl disulfide and \( n \)-\( \pi \) stacking in hard segments, model molecules were synthesized to eliminate the restriction effect of the soft segments. The model molecules of MDI-HEDS and MDI-HDO with the similarity to the hard segments of above TPU systems were fabricated (Scheme S2 in ESI). The molecular structure, chemical structure and thermal properties of the model molecules were well characterized by GPC (Table S4 in ESI), NMR (Fig. S9 in ESI), and DSC (Fig. S10 in ESI), respectively. Similarly, the intermolecular interaction of the model molecules was analysed by the characteristic band in FTIR spectrum (Fig. S11 and Table S5 in ESI). Particularly, the temperature dependent microstructure evolution at the molecular scale of the aromatic model compounds with and without alkyl disulfide was evaluated by in situ FTIR (Fig. S12 in ESI).

As shown in Fig. 4(a), with increasing temperature, the overall trend of band shows red shift and the relative integral area (RIA) of the characteristic peak decreases in MDI-HEDS, suggesting enhanced molecular chain mobility at high temperature. There are also several obvious turning points of the peak position and RIA. The initial RIA transition temperature at around 70 °C is near the glass transition as well as the activation temperature of disulfide exchange reaction. The result suggests that more aromatic segments form \( n \)-\( \pi \) stacking due to the local adjustment of molecular chain via the dynamic reaction during heating. In addition, compared with MDI-HDO, MDI-HEDS shows a drastic increase in RIA and obvious band shift at the elevated temperature zone (over 200 °C), indicating enhanced ordered structures. The \( n \)-\( \pi \) stacking in MDI-HEDS is also verified by solid \(^1\)H-NMR. The peak in the range of 6.6–8.0 ppm is the signal from \( n \)-\( \pi \) stacking between aromatic benzene rings. The peak integral shows a jump above 50 °C, suggesting there are indeed strong intermolecular interactions between the aromatic segments (\( n \)-\( \pi \) stacking) in MDI-HEDS (Fig. 4c). By contrast, the MDI-HDO shows a weak change of the signal (Fig. S13 in ESI). Thus, the alkyl disulfide as a dynamic linkage can improve the kinetics of \( n \)-\( \pi \) stacking assembling.

**Fig. 4** Intermolecular interaction, molecular structure, micro-phase structure evolution characterization of model molecules. (a) Comparison of the characteristic peak location and integral area of the stimuli-response (MDI-HEDS) and blank control (MDI-HDO) model samples. (b) \( q^2 \cdot q \) profiles of MDI-HEDS in the process of heating. (c) Temperature-variable solid \(^1\)H-NMR spectra (400 MHz) of MDI-HEDS model compounds. (d) Molecular dynamics modelling of the model molecule of hard segment containing disulfide linkages.
The temperature varied microstructures were also confirmed by SAXS (Fig. 4b and Fig. S14 in ESI). The one-dimension curves for both MDI-HEDS and MDI-HDO show larger peak intensity with the increase of temperature, indicating a higher amount of order structure. Surprisingly, the strong $n$-$n$ packing was still stable up to 250 °C even after the melting of the MDI-HEDS molecules (198 °C) as indicated by the strong scattering peak. However, without alkyl disulfide, MDI-HDO was melted at 186 °C, leading to the disappearance of ordered structure above 180 °C, which is comparable to the result for PUDS-0-M.

The molecular dynamics (MD) simulation was also conducted in order to probe into the thermodynamically stable structures. Obvious parallel displaced face-to-face benzene ring packing exists in the MDI-HEDS and MDI-HDO. As shown in Fig. 4(d), two benzene rings are displayed in the format of ball-stick to highlight their orientation. The vertical distance between two benzene rings is shorter than 0.35 nm which is in the range of $n$-$n$ stacking interaction.$^{[57,58]}$ The vertical distance between the two rings is 0.341 and 0.327 nm for MDI-HEDS and MDI-HDO, respectively. In addition, the translation distance between the centers of each ring is 0.077 and 0.140 nm for MDI-HEDS and MDI-HDO, respectively. These observations indicate that MDI-HEDS has thermodynamically stronger $n$-$n$ interaction than that of MDI-HDO. The analysis of model molecules further highlights the synergic effect of $n$-$n$ stacking and alkyl disulfide bond for the stimuli-responsive rearrangement.

**Recycling/Reprocessing Characterization of the PUDS**

We demonstrate the functional application of the PUDS-5-M system for recycling/reprocessing. Fig. 5 shows the morphology evolution of the two TPU samples when treated at an elevated temperature (hot plate here). As the temperature increases, the polymers will gradually transform from solid-state to melting state and lose the shape. The melting temperature or the viscous flow temperature reveals the relaxation temperature. It can be seen that the control sample (PUDS-0-M) becomes obvious melt at 171 °C whereas the PUDS-5-M shows superior thermal stability without melting up to 212 °C, which is the highest among the reported smart TPUs$^{[38,47,48]}$ and similar to the chemically cross-linked vitrimer. In addition, the novel TPU has excellent recyclability. Two kinds of polymer recycling methods, namely solution recycling using a solvent and bulk recycling by hot compressing, were demonstrated. Fig. S15(a) (in ESI) shows the PUDS-5-M samples can be rapidly dissolved (10 min) in a good solvent (10 wt% DMAc) at room temperature. Despite the excellent thermal resistance, the TPU can be dissolved for solution recovery (Fig. S15a in ESI). In this case, the solution castor coating of the PUDS-5-M solution followed by subsequent evaporation of the solvent can be used to obtain recycled elastomers. The mechanical properties were measured by the tensile test. The TPU containing dynamic bonds shows a tensile strength and fracture strain of 45 MPa and 2500%, which is owing to outstanding amount TPUs containing dynamic chemical bonds. The mechanical property of the recycled material is the same as the original one. It is noted that the current TPU is advantageous over vitrimer, which cannot be readily recycled in a simple solvent. For bulk recycling, the PUDS-5-M sample was reprocessed and recycled by hot compression in a mold at an elevated temperature. Fig. S15(b) (in ESI) shows the thin disk samples by three successive cycles of hot recycling. Typically, a processing time of 10–20 min at around 200 °C is sufficient to produce a recycled sample. The mechanical properties of the sample after several cycles of hot pressing will decrease partially, which may be caused by oxidation during heating (Fig. S16 in ESI).

**CONCLUSIONS**

In summary, the dynamic thermoplastic polyurethane with high thermal resistance, excellent mechanical properties, and rapid recycling capability was fabricated using a phase-locked dynamic bond design. The unique relaxation behavior enabled by weak alkyl disulfide and strong $n$-$n$ stacking is proposed for the first time. It was found that the presence of disulfide bonds in aromatic TPUs results in stronger $n$-$n$ stacking. The kinetics interlocking between the weak dynamic bonds and strong $n$-$n$ interaction in aromatic TPU leads to slow network relaxation. Taking advantage of the unique relaxation behavior owing to the stimuli-responsive rearrangement, thermal stable TPUs with viscous flow temperature over 210 °C were fabricated. This work provides a new insight in tuning the network relaxation and molecular self-assembly in stimulus-responsive dynamic polymers by both molecular design and micro-phase control toward high-performance functional applications.

**Electronic Supplementary Information**

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2494-7.

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REFERENCES

1 Ghosh, B.; Urban, M. W. Self-repairing oxetane-substituted chitosan polyurethane networks. Science 2009, 323, 1458–1460.

2 Cordier, P.; Tournilhac, F.; Soulie-Zlakovic, C.; Leibler, L. Self-healing and thermoreversible rubber from supramolecular assembly. Nature 2008, 451, 977–980.

3 Li, Y.; Sun, J. Self-healing and healable polymeric materials based on polymer complexes. Acta Polymetrica Sinica (in Chinese) 2020, 51, 791–803.

4 Lendlein, A.; Jiang, H.; Junger, O.; Langer, R. Light-induced shape-memory polymers. Nature 2005, 434, 879–882.

5 Zheng, N.; Fang, Z.; Zou, W.; Zhao, Q.; Xie, T. Thermostat shape-memory polyurethane with intrinsic plasticity enabled by transcarbamoylation. Angew. Chem. Int. Ed. 2016, 128, 11421–11425.

6 Christensen, P. R.; Scheuermann, A. M.; Loeffler, K. E.; Helms, B. A. Closed-loop recycling of plastics enabled by dynamic covalent diketoenamine bonds. Nat. Chem. 2019, 11, 442–446.

7 Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-like malleable materials from permanent organic networks. Science 2011, 334, 965–968.

8 Yang, Y.; Pei, Z.; Li, Z.; Wei, Y.; Ji, Y. Making and remaking dynamic 3D structures by shining light on flat liquid crystalline vitrimer films without a mold. J. Am. Chem. Soc. 2016, 138, 2118–2121.

9 Xiang, H. P.; Yuan, Y. J.; Rong, M. Z.; Zhang, M. Q. Room-temperature self-healing and healable polymeric materials based on dynamic covalent assembly of thermosets. J. Am. Chem. Soc. 2012, 134, 7664–7667.

10 Lei, Z. Q.; Xiang, H. P.; Yuan, Y. J.; Rong, M. Z.; Zhang, M. Q. Room-temperature self-healing and healable polymeric materials based on dynamic covalent assembly of thermosets. J. Am. Chem. Soc. 2012, 134, 7664–7667.

11 Pei, Z.; Yang, Y.; Chen, Q.; Terentjev, E. M.; Wei, Y.; Ji, Y. Malleable liquid-crystalline liquid actuators with exchangeable covalent bonds. Nat. Mater. 2014, 13, 36–41.

12 Yu, K.; Shi, Q.; Dunn, M. L.; Wang, T. J.; Qi, H. J. Carbon fiber reinforced thermoset composite with near 100% recyclability. Adv. Funct. Mater. 2016, 26, 6098–6106.

13 Lei, Z. Q.; Xiang, H. P.; Yuan, Y. J.; Rong, M. Z.; Zhang, M. Q. Room-temperature self-healing and healable polymeric materials based on dynamic covalent assembly of thermosets. J. Am. Chem. Soc. 2012, 134, 7664–7667.

14 Deng, J.; Xiang, H. P.; Yuan, Y. J.; Rong, M. Z.; Zhang, M. Q. Room-temperature self-healing and healable polymeric materials based on dynamic covalent assembly of thermosets. J. Am. Chem. Soc. 2012, 134, 7664–7667.

15 Hentschel, J.; Kushef, A. M.; Ziller, J.; Guan, Z. Self-healing supramolecular block copolymers. Angew. Chem. Int. Ed. 2012, 51, 10561–10565.

16 Wang, C.; Wu, H.; Chen, Z.; McDowell, M. T.; Cui, Y.; Bao, Z. Self-healing chemistry enables the stable operation of silicon microparticle anodes for high-energy lithium-ion batteries. Nat. Chem. 2013, 5, 1042–1048.

17 Wang, C.; Liu, N.; Allen, R.; Tok, J. B. H.; Wu, Y.; Zhang, F.; Chen, Y.; Bao, Z. A rapid and efficient self-healing thermo-reversible elastomer crosslinked with graphene oxide. Adv. Mater. 2013, 25, 5785–5790.

18 Sun, C.; Feula, A.; Baker, C. B.; Melia, K.; Merino, H. D.; Hamley, W. I.; Buckley, P. C.; Hayes, W.; Sivior, R. C. A dynamic supramolecular polyurethane network whose mechanical properties are kinetically controlled. Polymer 2017, 133, 143–150.

19 Mozhidehi, D.; Ayala, S.; Cromwell, O. R.; Guan, Z. Self-healing multiphase polymers via dynamic metal-ligand interactions. J. Am. Chem. Soc. 2014, 136, 16128–16131.

20 Berezkin, Z.; Urick, M. In Modern polyurethanes: overview of structure property relationship. ACS Syr. 2013, p. 65–81.

21 Engels, H. W.; Pirki, H. G.; Albers, R.; Albach, R. W.; Krause, J.; Hoffmann, A.; Casselmann, H.; Dormish, J. Polyurethanes: versatile materials and sustainable problem solvers for today’s challenges. Angew. Chem. Int. Ed. 2013, 52, 9422–9441.

22 Xiang, D.; He, J.; Cui, T.; Liu, L.; Shi, Q. S.; Ma, L. C.; Liang, Y. Multiphase structure and electromechanical behaviors of aliphatic polyurethane elastomers. Macromolecules 2018, 51, 6369–6379.

23 Velankar, S.; Cooper, S. L. Microphase separation and rheological properties of polyurethane melts. 2. Effect of block incompatibility on the microstructure. Macromolecules 2000, 33, 382–394.

24 Yu, S.; Zhang, R.; Wu, Q.; Chen, T.; Sun, P. Bio-inspired high-performance and recyclable block-copolymer polyurethane elastomers. Adv. Mater. 2013, 25, 4912–4917.

25 Heo, Y.; Sodano, H. A. Self-healing polyurethanes with shape recovery. Adv. Funct. Mater. 2014, 24, 5261–5268.

26 Liu, W. X.; Zhang, C.; Zhang, H.; Zhao, N.; Yu, Z. X.; Xu, J. Oxime-based and catalyst-free dynamic covalent polyurethanes. J. Am. Chem. Soc. 2017, 139, 8678–8684.

27 Ying, H.; Cheng, J. Hydrolyzable polyureas bearing hindered urea bonds. J. Am. Chem. Soc. 2014, 136, 16674–16677.
