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# Elaborate Fabrication of well-defined side-chain liquid crystalline polyurethane networks with triple-shape memory capacity

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## Tensile test:

The SCLCPU-N films with a dog-bone shape were used for the tensile stress test, using a SANS CMT4104 (SANS Group, China) at a crosshead speed of 35 mm min$^{-1}$ at 25 °C. The thickness and width of the samples were 0.5 mm and 4 mm, and the length of the samples between the two pneumatic grips of the testing machine was 20 mm. At least three times were tested and averaged in each group. Typical engineering stress–strain curve for SCLCPU-Ns are illustrated in Figure S1.

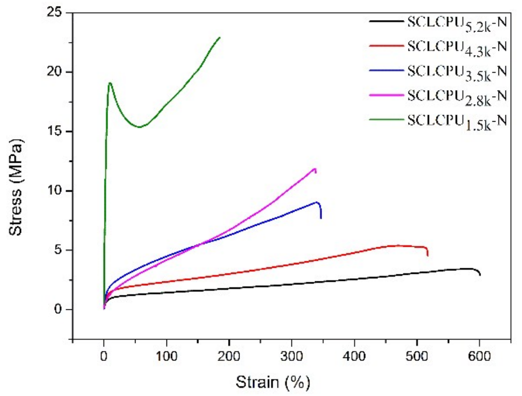


**Figure S1** Typical engineering stress–strain curve for SCLCPU-Ns

## The treatment of peak deconvolution of tan δ curve:

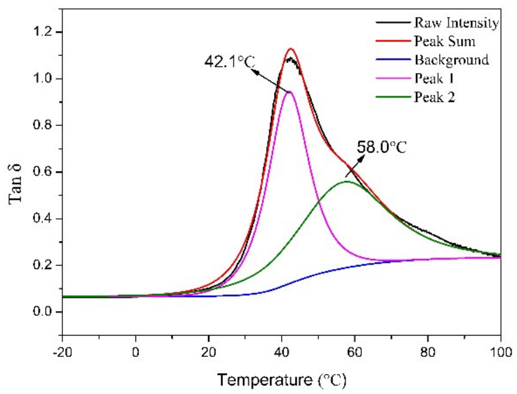


**Figure S2** The peak deconvolution of tan δ of SCLCPU$_{5.2k}$-N.

**The testing program of triple-shape memory effect:**

Considering the $T_g$ and $T_{cl}$ of the networks, the three characteristic programming temperatures $T_{low}$, $T_{mid}$ and $T_{high}$ are sited as $T_g$ -18 °C, $T_g$ + 7 °C and $T_{cl}$ +18 °C, respectively. Taking SCLCPU$_{5.2k}$-Ns as an example, Figure 6 illustrates the typical triple-shape memory behavior of the network recorded by DMA (A) and digital photos of entity in programming and recovery procedures (B).In the programming step, for deformation from S0 to S1, the temperature is kept at 60 °C for 3 min to make sure the sample in isotropic state, and then the sample is stretched from the original strain ($\varepsilon_{S0}$), cooled to 25 °C at 10 °C min$^{-1}$ under constant stress leading $\varepsilon_{S1,load}$. During the cooling step, the sample initially exhibits creep response about 37 °C. The opposite strain response is due to the formation of side liquid crystalline units keep consistent under external stress. The removal of external stress at 25 °C for additional 5 min, results in the first temporary shape ($\varepsilon_{S1}$). The fixing of the shape S1 is realized by the orientation of mesogen in side-chain of network when the temperature is decreased to the $T_{cl}$. For further deformation from S1 to S2, the sample is stretched at 25 °C, and cooled to 0 °C under constant stress resulting in $\varepsilon_{S2,load}$, then unloading the external stress to achieve the second temporary shape ($\varepsilon_{S2}$). The fixing of the shape S2 relies on the vitrification of the backbone of network when temperature is lower than $T_g$.

The recovery process is implemented by heating in two steps at stress free condition. In the first recovery process from S2→S1, the unconstrained strain recovery is drived by heating the sample to 25 °C, and thermally equilibrated for 25 min to arise a stage which denotes as $\varepsilon_{S1,rec}$. Essentially, the stored energy of backbone chains releases when the temperature is beyond the $T_g$, and the shape S1 recovers by entropic elasticity. In the secondly recovery process from S1→S0, the permanent shape is finally obtained by further heating to 60 °C at 10 °C min$^{-1}$, followed by keeping for 25 min. In mechanism also, the recovery in this stage is triggered by contract effect bringing by the disordering of namatic phase while the temperature is above $T_{cl}$. In all, the TSME is proofed in SCLCPU$_{5.2k}$-N.

**TSME of SCLCPU$_{5.2k}$-N under different deform force:**

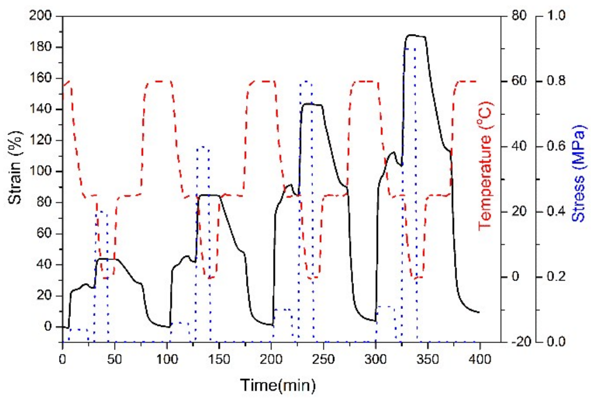


**Figure S3** The cyclics in thermal mechanical analysis of SCLCPU$_{5.2k}$-N with different force recorded by DMA. Solid line: strain; dash line: temperature; short dash line: stress.

**Table S1**. The quantitative triple shape memory properties of $SCLCPU_{5.2k}$-N under different deform force

| Strain (%) | $R_f$(%)[a] | | $R_r$(%)[b] | |
|---|---|---|---|---|
| | S1 | S2 | S2 → S1 | S2 → S0 |
| 43.6 | 91.2 | 99.1 | 84.8 | 100 |
| 85.0 | 91.2 | 99.1 | 85.5 | 98.4 |
| 143.6 | 92.0 | 99.0 | 89.3 | 98.0 |
| 187.8 | 91.8 | 99.0 | 88.8 | 97.0 |