Supplementary Information for

A reconfigurable, healable and recyclable 3D printed orthosis for adolescent idiopathic scoliosis

Xiu-Chong He [a,1], Jian-Cheng Lai [a,c,d,1], Peng-Fei Zheng [b,*], Cheng-Hui Li [a,*]

[a] State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, P. R. China.

[b] Department of Orthopaedic Surgery, Children's Hospital of Nanjing Medical University, Nanjing 210000, Jiangsu Province, China

[c] Beijing Institute of Collaborative Innovation, Beijing 100094, P. R. China

[d] Tachin Technology Co., Ltd., Beijing 100094, P. R. China

* Corresponding authors.

E-mail addresses: chli@nju.edu.cn (C.-H. Li), zhengpengfei@njmu.edu.cn (P.-F. Zheng);

[1] The authors equally contribute to manuscript.

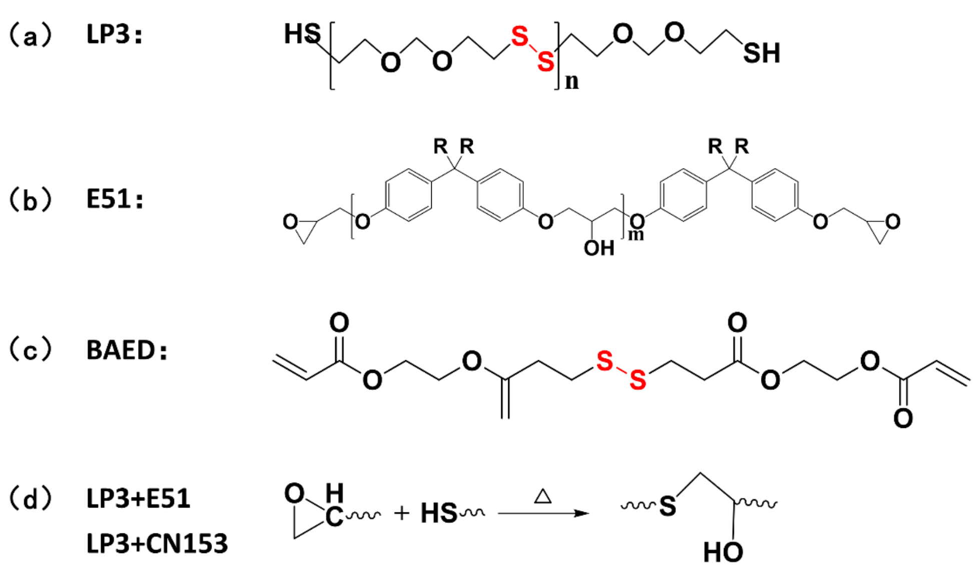

Fig. S1. The molecular structure of these components containing dynamic bonds. (a) The molecular structure of LP3. (b) The molecular structure of E51. (c) The molecular structure of BAED. (d) Reaction of LP3 with E51 or LP3 with CN153.

Excellent exchange ability of S-S bond in Liquid thiol-terminated polysulfide oligomer（LP3）and Bis (2-(acryloyloxy) ethyl) dithiodipropionate（BAED）had been proved.[S1-S2] In this work, we attempt to blend them into 3D printing resin to obtain the characteristics brought by dynamic bonds, as shown in Fig S1. In theory, the prepared 3D printing resin should exhibit characteristics such as self-healing, reprocessing, solubility, and variable stiffness. But in reality, these above characteristics have almost completely disappeared.

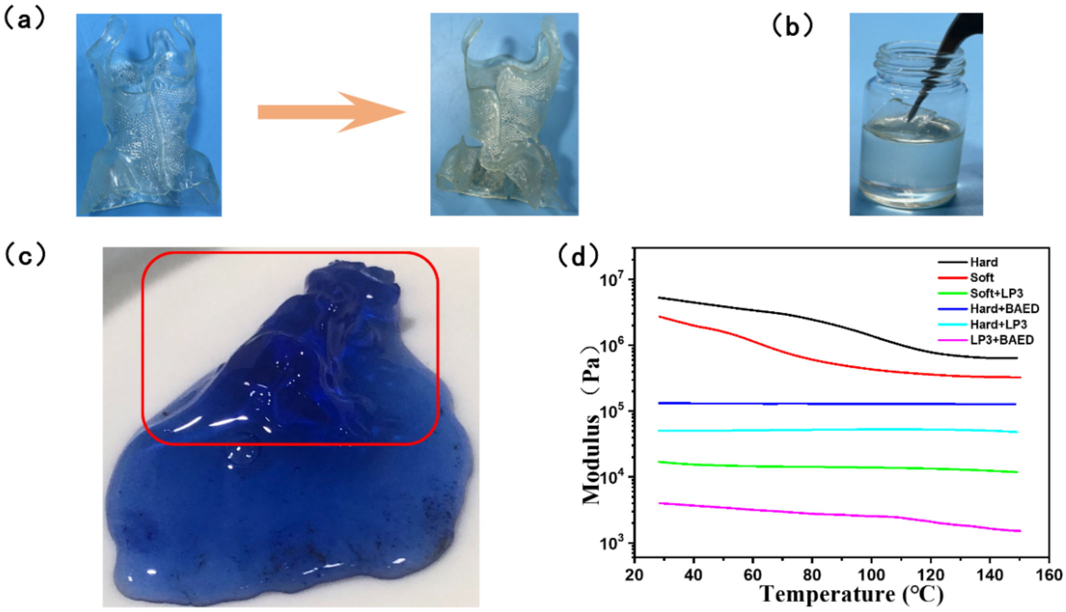

Fig. S2. Properties of 3D printed materials with dynamic bonds. (a) Test the healable property of printed orthoses. (b) Soaked in the mixture of LP3 and acetone (1:1) for 168 h at 80 °C. (c) The reprocessing performance in 150 °C for 60min. (d) Modulus-temperature curves of several 3D printed materials.

It can be seen from Fig. S2 that, despite the addition of a large amount of LP3, the relevant characteristics brought about by dynamic bonding completely disappeared. It is obvious that the sample can not be healed even heated for 24 h (Fig. S2a). But in the thermal curing system, the same reaction between thiol and epoxy functional groups, relying on S-S exchange, it only takes 2 h to be completely healed at 75 °C.[S1] In the thermal curing system, it can be dissolved by soaking in the mixture of LP3 and acetone (1:1) for 24 h. But the 3D printed materials cannot be dissolved even after soaked for 168 h (Fig. S2b). In the original thermal curing system, it can be reshaped by heating at 75 °C for 20 mins. However, in 3D printing, the printed structure (the model inside the red line) was not damaged even heated at 150 °C for 60 mins, making it impossible to reprocess (Fig. S2c). The modulus of these 3D printed models decreases by only two orders of magnitude with the temperature from 28 °C to 150 °C, and there is no sharp drop (Fig. S2d). Whether it is hard or soft resin, there is no variable stiffness performance. These phenomena and data all illustrate that the activity of dynamic bonds in 3D printing materials were inhibited.

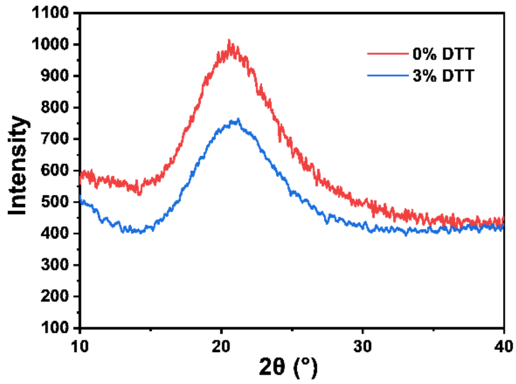

Fig. S3. XRD test of polymers with different DTT content.

Because the 3D printing resin was a mixture of monomers and oligomers, and S-S and S-H caused a complex exchange, the molecular formed an irregular structure. XRD shows that there is no obvious crystal structure**.**

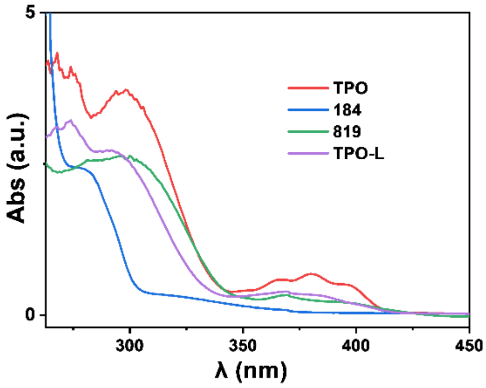

Fig. S4. Ultraviolet absorption spectra of TPO and other UV initiators. The initiator TPO exhibits better absorption in the UV light region. It ensures that 3D printing resins can be quickly cured in UV light.

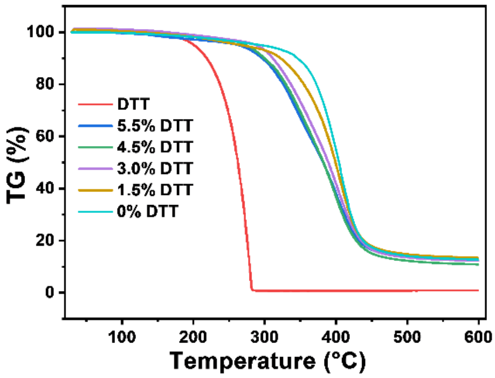

Fig. S5. Thermogravimetric comparison of polymers with different DTT content.

The pure DTT small molecules began to decompose at 165 °C, but after exchanging with LP3, a series of short-chain polymers were formed, and the decomposition temperature increased to 260 °C, and the decomposition temperature increased with the increase of the proportion of macromolecules. This proves that DTT forms a complex exchange with LP3, eventually forming a series of polymers with different chain lengths and dynamic bonds.

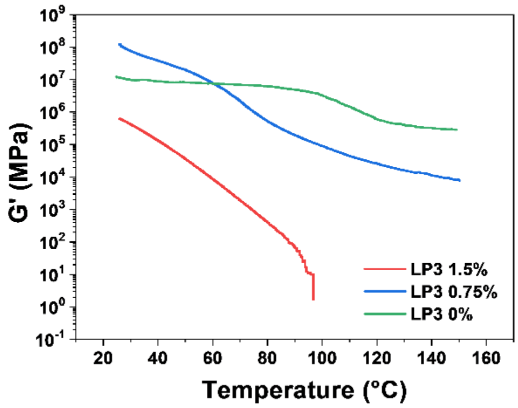

Fig. S6. Effects of LP3 ratio on the modulus-temperature curves.

Without the addition of LP3, the decrease of modulus is very slow under the condition of the existence of DTT, and the modulus at room temperature will be slightly increased. This is because LP3 reacts with epoxy to increase the crosslinking density. When the dosage of LP3 reaches 1.5%, the decreasing rate of modulus increases, but the initial modulus also decreases. It is therefore recommended that no more than 1.5% LP3 may be suitable.

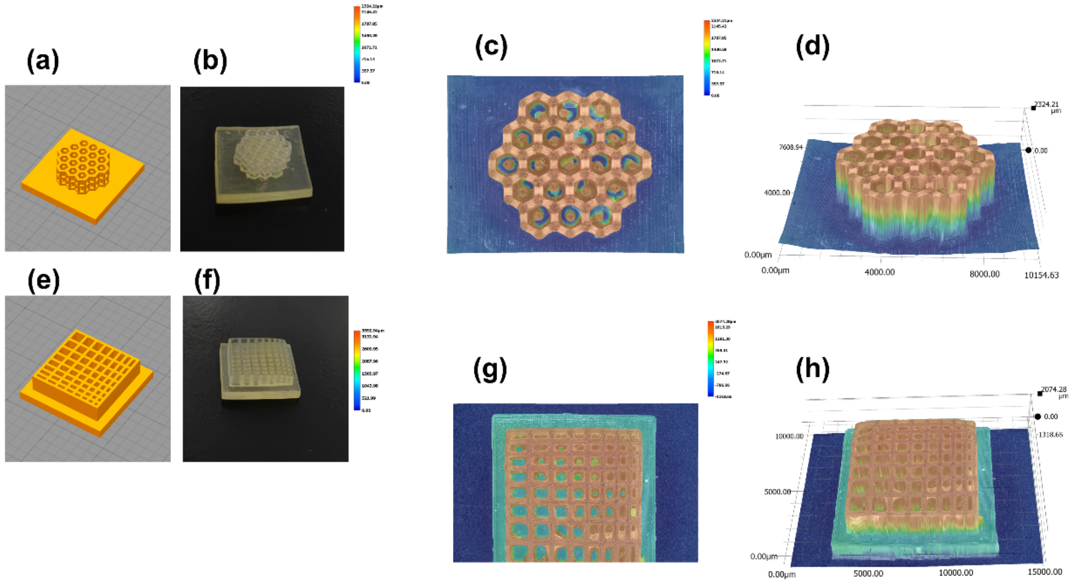

Fig. S7. Other models with complex pattern, printed samples, and the confocal laser testing for them. (a) & (e) Models with complex patterns. (b) & (f) Printed samples. (c) & (g) Top view of the models. (d) & (h) Side view of the models.

Some complex structures are printed (Fig. S7), which show high printing precision and clear microstructure. It is indicated that this resin is suitable for printing various models.

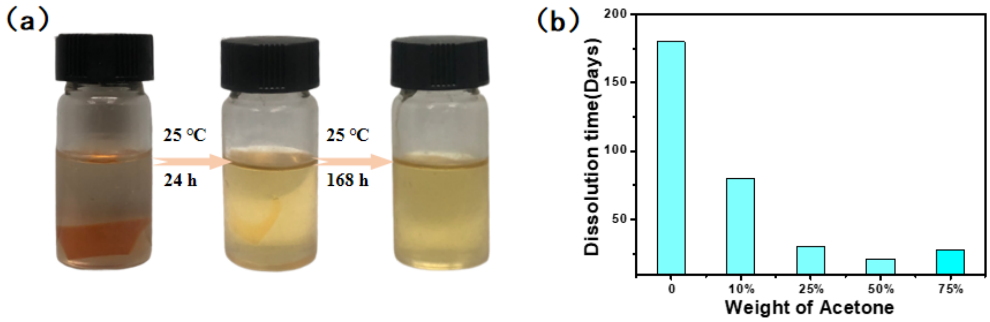

Fig. S8. Solubility of 3D printed materials**.** (a) Dissolution of 3D printed materials in acetone solution containing 50% LP3. (b) The relationship between dissolution time and acetone content.

The printed material can be dissolved in LP3/acetone solution after 168h at 25°C (Fig. S8a). The dissolution time was related to the content of LP3. When the content of LP3 is very low, it hardly dissolves. With the increase of LP3 content, the dissolution rate increases. However, when the content of LP3 exceeds 75%, the dissolution rate will decrease. This is because acetone has the swelling effect, can promote the -SH more easily into the polymer crosslinking network, causing it easier for dynamic exchange (Fig. S8b).

Table S1. The feed ratio of 3D printing resin prepared with conventional methods

Sample	CN153 (g)	LP3 (g)	ACMO (g)	BAED (g)	E51 (g)	TPO (g)	Inhibitor (mg)
Hard	40	0	40	0	0	3	1
Soft	40	0	20	0	20	3	1
Soft+LP3	40	50	20	0	20	3	1
Hard+BAED	40	0	40	50	0	3	1
Hard+LP3	40	50	40	0	0	3	1
BAED+LP3	0	50	50	50	0	3	1

Table S2. The feed ratio of 3D printing resin for comparison in this work.

Sample	CN153 (wt%)	LP3 (wt%)	ACMO (wt%)	DTT (wt%)	CN983 (wt%)	TPO (wt%)	Inhibitor ppm
AA-SS-ACMO-1	80	9	0	3	5	3	10
AA-SS-ACMO-2	60	9	20	3	5	3	10
AA-SS-ACMO-3	30	9	50	3	5	3	10
AA-SS-ACMO-4	9	5	75	3	5	3	10
AA-SS-ACMO-5	2.5	1.5	85	3	5	3	10
AA-SS-CN983-1	34	10	50	3	0	3	10
AA-SS-CN983-2	31	10	50	3	3	3	10
AA-SS-CN983-3	33	5	50	3	6	3	10
AA-SS-CN983-4	30	5	50	3	9	3	10
AA-SS-CN983-5	27	5	50	3	12	3	10
AA-SS-DTT-1	32	10	50	0	5	3	10
AA-SS-DTT-2	30	10	50	2	5	3	10
AA-SS-DTT-3	28	10	50	4	5	3	10
AA-SS-DTT-4	26	10	50	6	5	3	10
AA-SS-DTT-5	24	10	50	8	5	3	10

Supplementary Reference

[S1] W. Gao, M. Bie, F. Liu, P. Chang, Y. Quan, Self-Healable and Reprocessable Polysulfide Sealants Prepared from Liquid Polysulfide Oligomer and Epoxy Resin, *ACS Appl. Mater. Interfaces*, 2017, **9**, 15798-15808.

[S2] L. Zhang, T. Qiu, Z. Zhu, L. Guo, X. Li, Self-Healing Polycaprolactone Networks through Thermo-Induced Reversible Disulfide Bond Formation, *Rapid Commun.*, 2018, **39**, 1800121.