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Digital Light 3D Printing of Biodegradable Elastomers for Personalized Devices

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3D printing has emerged as a transformative technology for both scientific research and industrial applications.[1] In particular, digital light processing (DLP) stands out due to its high printing resolution and excellent surface quality.[2] In combination with computer-assisted design (CAD) and medical imaging, it provides enormous opportunities for personalized medicine, especially for medical implants and devices.[3] However, the fabrication of bioresorbable and elastic medical devices by DLP is challenging due to the difficulty in 3D printing of biodegradable elastomers with desired mechanical properties.[4–6] To tackle this issue, we recently reported a novel 'dual-polymer' resin with tunable crosslinking ability, which enabled digital light printing of biodegradable elastomers with silicone-like mechanical performance.[7]

To obtain biodegradable photopolymers in a liquid state at ambient temperature suitable for DLP printing, we synthesized a series of random copolymers from D,L-lactide (DLLA) and ε-caprolactone (CL) with four-arm structure and varied molecular weight (1200 to 15,000 g mol^{-1}), followed by functionalization with methacrylate groups. To enable the printing of the photopolymers with longer chain length, we designed a customized heating system that allows for DLP printing of the resin at elevated temperature, and thus with lower viscosity. Although the elasticity and maximum strain of the 3D printed elastomers from these polymers can be well tuned by changing the polymer chain length, it is still difficult to achieve desired mechanical strength and Young's modulus at the same time. To further optimize the formulation, we designed a dual-polymer resin by combining the polymer of molecular weight ($M_{n,NMR}$) 15,000 g mol^{-1} (**P1**) with a linear oligomer of $M_{n,NMR}$ 600 g mol^{-1} (**P2**). With a **P1**/*P2* weight feed ratio of 75/25, the resin provided biodegradable elastomers with mechanical performance comparable to that of commercial silicone materials after 3D printing. This resulted from the modified network and enhanced crosslinking density of the dual polymer system. In combination with computed tomography, we successfully applied the polymeric materials to digital light 3D printing of customized airway stents of high resolution. Notably, the stents degraded to soft hydrogels, and when delivered into rabbits' tracheas, they disappeared after 7 weeks, without causing any permanent tissue damage or other side effects. The design of the DLP resin presented here can be expanded to various different types of biodegradable polymers, and exploited in the future to design numerous personalized implants and medical devices as well as tissue scaffolds and drug formulations.

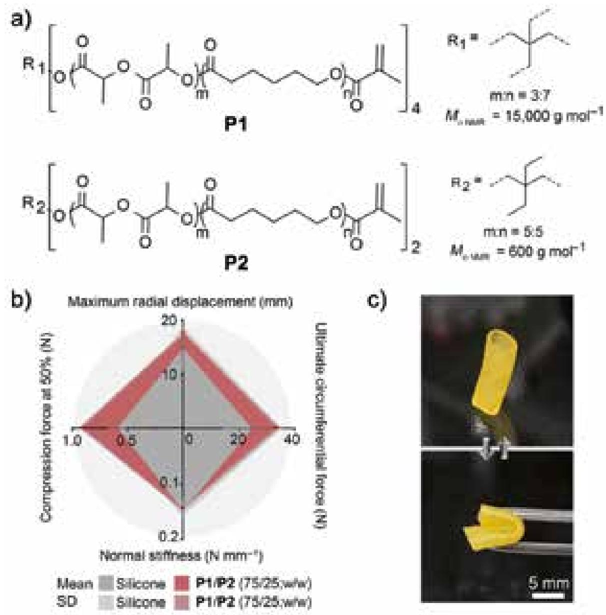

Fig. 1 a) Chemical structures of **P1** and **P2**. b) Mechanical properties of 3D printed biodegradable elastomers from **P1**/**P2** dual-polymer resins and NOVATECH silicone materials. Mean + SD (n = 6). c) 3D printed personalized airway stent based on rabbit airway geometry.[7]

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