

Supporting information

Boronic Ester-Modified Resins: Dual-Function in Micro-Additive Manufacturing and Ceramization

Shuai Zhang*, Jiaming Hu[#], Lukun Wu, Lin Yan, Hao Huang, Jing Li, Xiaobo Wan* and Kai Du

Research Center of Laser Fusion, China Academy of Engineering Physics, Mianyang 621900, PR
China

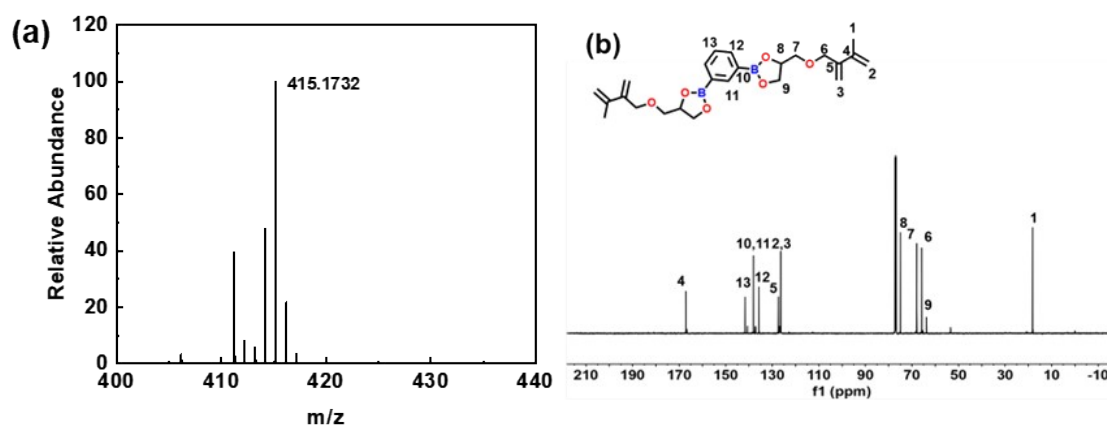
*Corresponding author.

[#]These authors contributed equally to this work and should be considered co-first authors

E-mail address: zhangshuai_scu@126.com (S. Zhang)

1. HRMS and ¹³C NMR test

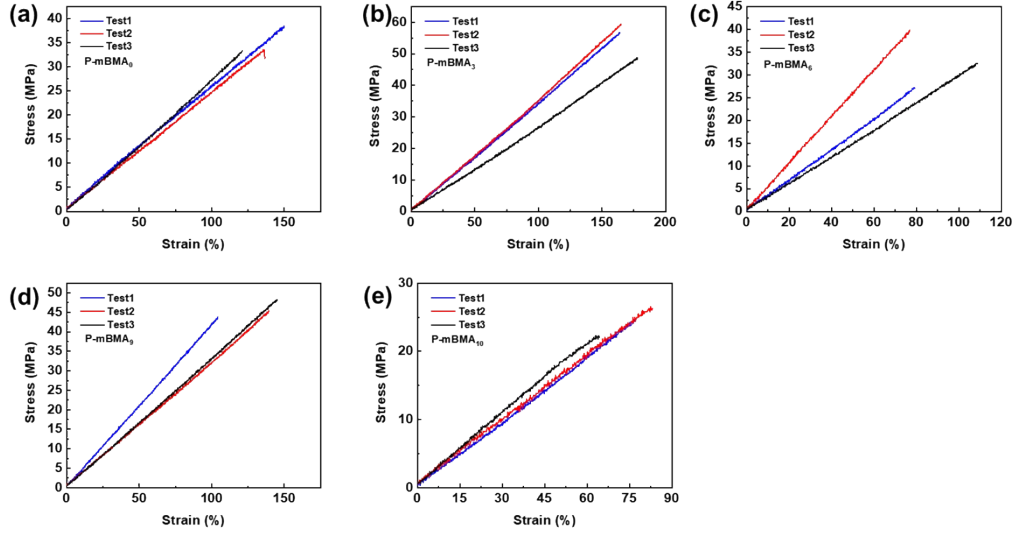
The synthesized monomer was characterized by mass spectrometry and ¹³C NMR spectroscopy, with results shown in Fig S1. HRMS analysis revealed a prominent peak at $m/z=415.17$, corresponding to the protonated molecular ion $[M+H]^+$, which aligns perfectly with the theoretical exact mass for $C_{18}H_{28}B_2O_{10}$ (calc. 415.21). Furthermore, the ¹³C NMR spectrum displayed a complete set of resonance signals that were in full agreement with the predicted chemical environment for each unique carbon atom in the mBBDA structure, thereby providing definitive evidence for the successful synthesis of the target molecule.



S1. (a)HRMS and (b)¹³C NMR spectra of mBBDA

2. Bending test

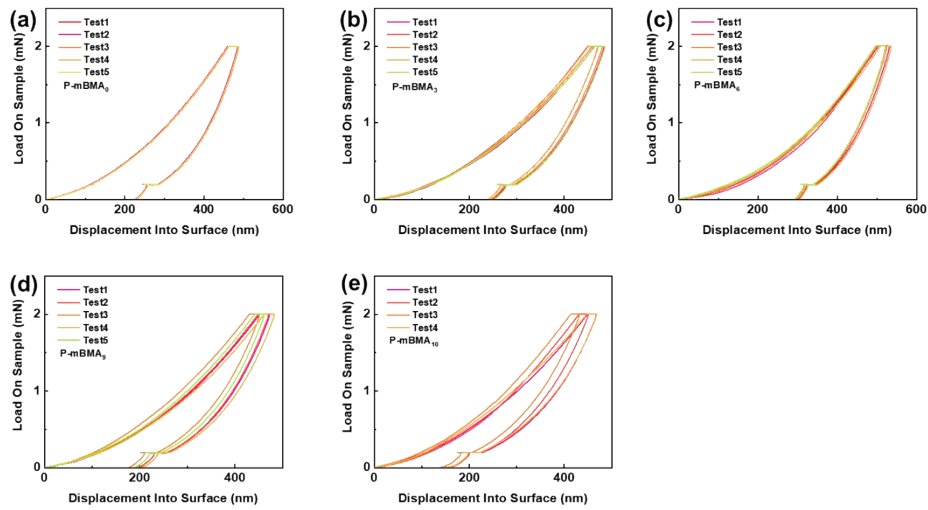
The bending test of resins with increasing mBBDA ratios were characterized. P-mBMA_x resins were injected into PTFE molds and cured under 365 nm UV light for 30 mins. After the irregular samples were polished, their mechanical properties were tested, and the results were shown below.



S2. Bending tests of (a) P-mBMA₀; (b) P-mBMA₃; (c) P-mBMA₆; (d) P-mBMA₉; (e) P-mBMA₁₀.

3. Nanoindentation test of P-mBMA_x

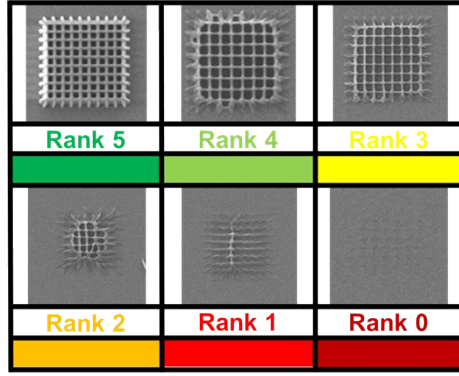
P-mBMA_x resins were cast into a 5mm×5mm×5mm silicone mold, and the molds containing the resins were subjected to polymerization under 365nm UV light. After 30 minutes of UV exposure, fully cured cubic samples were obtained. Two samples of each type of P-mBMA_x photoresist were tested using constant pressing load mode. The constant pressing load mode was set to 2mN. Each test surface underwent more than three tests, and the results were shown below.



S3. Constant load nanoindentation tests of (a) P-mBMA₀; (b) P-mBMA₃; (c) P-mBMA₆; (d) P-mBMA₉; (e) P-mBMA₁₀.

4. Two-photon polymerization printing tests

The rating criteria are shown in Fig. S4: Grade A (indicated by green) earns 5 points, indicating good structure, clear contours, and sharp edges. Grade B (represented as light green) earns 4 points, indicating that the structure is basically intact, but there are slight bends at the edges. Grade C (represented in yellow) earns 3 points, indicating that the structure is basically intact, but there are more obvious bends at the edges. Grade D (represented in orange) earns 2 points, indicating structural deformation, shape change, presence of holes or a large number of curved edges. Grade E (indicated in red) earns 1 point, indicating the presence of significant structural damage, fractures, or unformed areas. Grade F (represented in deep red) scores 0, indicating little or no observed structure. (In supporting information).



S4. grading rules of the zonal assignment method

Comparison of P-mBMA₆ resin two-photon printing performance with other resins.

(a)

$\frac{P_{max}}{mW}$	100	500	1000	2000	4000	6000	8000	10000	20000	30000	40000	50000	60000	70000	80000	90000	100000
5	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
10	5	5	5	5	3	1	0	0	0	0	0	0	0	0	0	0	0
15	5	5	5	5	5	5	5	5	4	3	1	0	0	0	0	0	0
20	5	5	5	5	5	5	5	5	5	4	3	1	0	0	0	0	0
25	5	5	5	5	5	5	5	5	5	5	4	4	2	1	0	0	0
30	0	5	5	5	5	5	5	5	5	5	5	5	5	4	4	3	2
35	0	0	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4
40	0	0	0	5	5	5	5	5	5	5	5	5	5	5	5	5	4
45	0	0	0	0	5	5	5	5	5	5	5	5	5	5	5	5	5
50	0	0	0	0	0	5	5	5	5	5	5	5	5	5	5	5	5

(b)

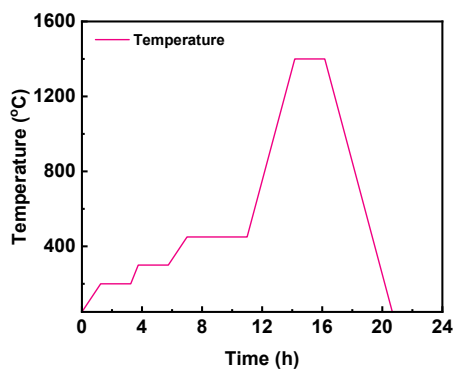
$\frac{P_{max}}{mW}$	100	500	1000	2000	4000	6000	8000	10000	20000	30000	40000	50000	60000	70000	80000	90000	100000
5	5	5	5	1	0	0	0	0	0	0	0	0	0	0	0	0	0
10	5	5	5	5	3	2	1	0	0	0	0	0	0	0	0	0	0
15	5	5	5	5	5	5	5	4	3	3	0	0	0	0	0	0	0
20	0	5	5	5	5	5	5	5	5	5	3	3	3	2	1	0	0
25	0	0	2	5	5	5	5	5	5	5	4	4	3	3	3	3	3
30	0	0	0	3	5	5	5	5	5	5	5	5	4	4	4	4	4
35	0	0	0	1	2	5	5	5	5	5	5	5	5	5	4	4	4
40	0	0	0	0	1	1	2	2	5	5	5	5	5	5	5	5	5
45	0	0	0	0	1	1	1	1	5	5	5	5	5	5	5	5	5
50	0	0	0	0	0	1	1	1	2	2	5	5	5	5	5	5	5

(c)

$\frac{P_{max}}{mW}$	100	500	1000	2000	4000	6000	8000	10000	20000	30000	40000	50000	60000	70000	80000	90000	100000
5	5	4	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
10	5	5	5	5	5	5	4	2	0	0	0	0	0	0	0	0	0
15	5	5	5	5	5	5	5	5	0	0	0	0	0	0	0	0	0
20	5	5	5	5	5	5	5	5	5	0	0	0	0	0	0	0	0
25	5	5	5	5	5	5	5	5	5	5	4	0	0	0	0	0	0
30	0	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
35	0	0	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
40	0	0	0	5	5	5	5	5	5	5	5	5	5	5	5	5	5
45	0	0	0	0	5	5	5	5	5	5	5	5	5	5	5	5	5
50	0	0	0	0	0	5	5	5	5	5	5	5	5	5	5	5	5

S5. Printing qualities of (a) P-mBMA₆; (b) TMPTA; (c) PETA; (d) TMPTA

5. Resin sintering conditions



S6. P-mBMA_x resin sintering conditions.

6. Comparison of resin weight before and after sintering

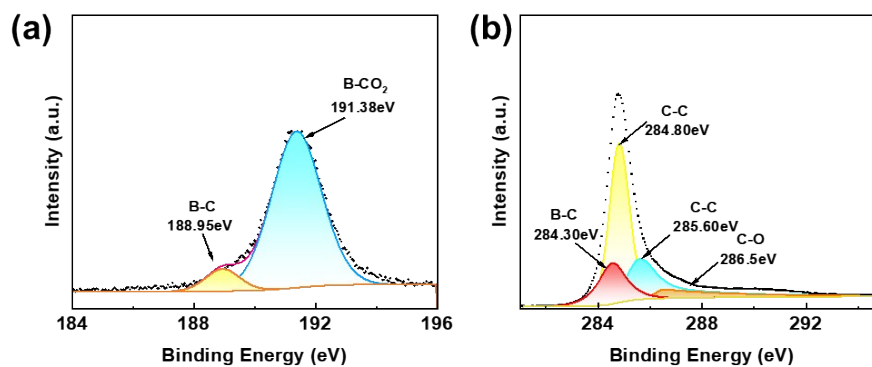
Table S1. Comparison of P-mBMA₆ resin weight before and after sintering

Sample-P-mBMA ₆	1	2	3	4	5
before sintering	0.149	0.147	0.15	0.147	0.155
after sintering	0.032	0.032	0.033	0.032	0.034

Table S1. Comparison of P-mBMA₁₀ resin weight before and after sintering

Sample-P-mBMA ₁₀	1	2	3	4	5
before sintering	0.160	0.158	0.153	0.152	0.15
after sintering	0.021	0.019	0.018	0.018	0.020

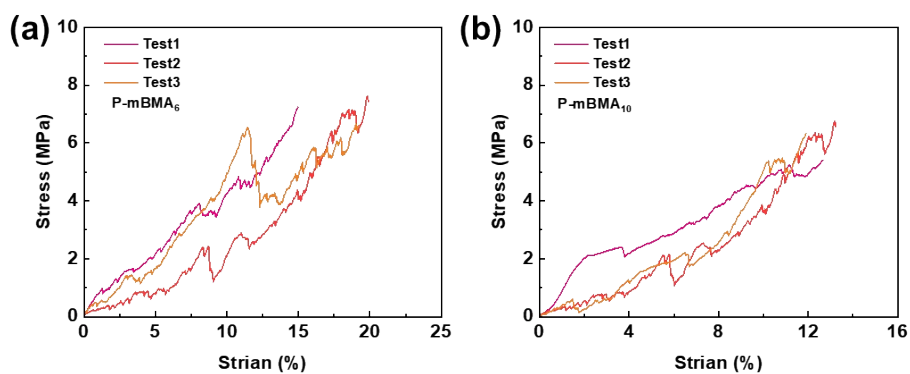
7.XPS test of P-mBMA_x after sintering



S7.XPS of P-mBMA₆ and P-mBMA₁₀ resins after sintering, (a)B1s, (b)C1s.

8. Compressive properties of resin after sintering

P-mBMA_x resins were cast into a 5mm×5mm×5mm silicone mold, and the molds containing the resins were subjected to polymerization under 365nm UV light. After sintering according to the steps shown in Fig. S3, samples were obtained. Three samples of each type were taken for compression tests, and the results were shown below.



S8. Compression curve of (a) P-mBMA₆; (b) P-mBMA₁₀ after sintering.