Supporting Information

Readily Recyclable, High-performance Thermosetting Materials based on a Lignin-derived Spiro Diacetal Trigger

Songqi Ma,[1,*] Jingjing Wei,[1,3] Zhen Jia,[1] Tao Yu,[2] Wangchao Yuan,[1] Qiong Li,[1] Sheng Wang,[1] Shusen You,[1] Ren Liu,[4] Jin Zhu[1,*]

[1] Key laboratory of bio-based polymeric materials technology and application of Zhejiang province, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, P. R. China.

[2] School of Aerospace Engineering and Applied Mechanics, Tongji University, Shanghai 200082, P. R. China.

[3] School of Science, Northwestern Polytechnical University, Xi'an 710064, P. R. China.

[4] School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, P. R. China.

*Corresponding authors: Songqi Ma (email: masongqi@nimte.ac.cn, Tel 86-0574-87619806; Fax 86-0574-86685186), Jin Zhu (email: jzhu@nimte.ac.cn).

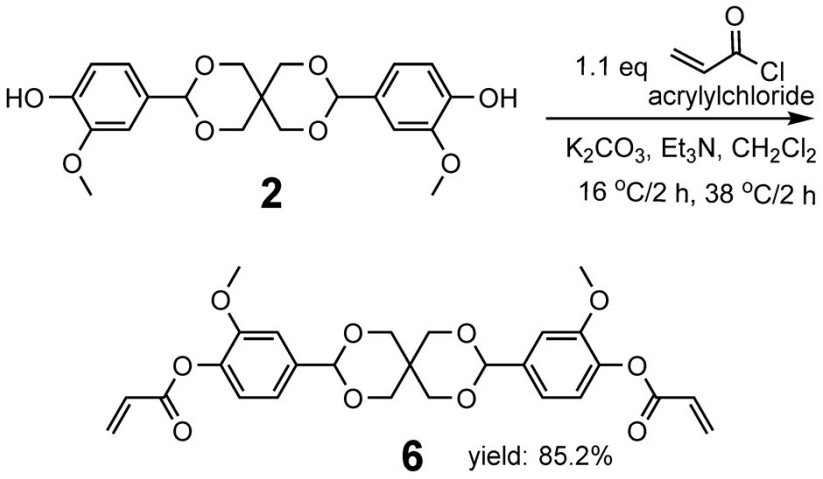
Contents

Synthesis, characterization, degradation of degradable diacrylate (**6**) 2
Scheme S1. Synthetic route of degradable diacrylate **6** from **2**. 3
Figure S1. FTIR spectrum of **2**. 4
Figure S2. FTIR spectrum of **3**. 5
Figure S3. FTIR spectrum of **5**. 6
Figure S4. TOF-MS spectrum of **2**. 7
Figure S5. TOF-MS spectrum of **3**. 8
Figure S6. TOF-MS spectrum of **5**. 9
Figure S7. ^{1}H NMR spectrum of **6**. 10
Figure S8. ^{13}C NMR spectrum of **6**. 11
Figure S9. FTIR spectrum of **6**. 12
Figure S10. TOF-MS spectrum of **6**. 13
Figure S11. ^{1}H NMR spectrum of the DDM cured **3** immersed in 0.1 M HCl solution (acetone/H_2O = 9/1, v/v) at 50 °C for 120 min. 14
Figure S12. Tensile stress-strain curves of the cured **3**. 15
Figure S13. Tensile stress-strain curves of the cured **4**. 16
Figure S14. Appearance of the cured **6** before and after immersing in 1 M HCl solution (THF/H_2O=9/1, v/v). 17
Figure S15. Tensile stress-strain curves of the cured **5**. 18

Figure S16. DMA curves of the cured **5**.....19
Figure S17. The removing process of coating on slide glass with 0.1 M HCl solution (acetone/H_2O=9/1, v/v).20
Table S1. The coating properties of coatings based on **3** and **4**.....21

Synthesis, characterization, degradation of degradable diacrylate (6)

6 was synthesized through acylation reaction between aromatic hydroxyl group of **2** and acrylylchloride. 5 g of **2**, 10 g of anhydrous potassium carbonate (K_2CO_3) and 2.88 g of triethylamine (Et_3N) as the acid-binding agents, 20 mL of dichloromethane (CH_2Cl_2) as the solvent were placed in a round-bottom flask equipped with a constant pressure funnel and a magnetic stirrer, and solution of 6 mL acrylylchloride and 15 mL dichloromethane was added dropwise and reacted at 16 ºC for 2 h, then heated to 38 ºC and reacted for 2 h. The mixture was washed with purified water after being filtrated and dried with anhydrous magnesium sulfate, and 5.4 g of while solid **6** with the yield of 85.2 % was obtained by precipitation with petroleum ether, repeating the process of dissolving with dichloromethane and precipitation with petroleum ether three times, and vacuum drying at 60 ºC for 5 h. The synthetic route is shown in Scheme S1. ^{1}H NMR and ^{13}C NMR spectra of **6** were recorded by an AVANCE III Bruker NMR spectrometer (Bruker, Switzerland) with DMSO-d^6 as solvent, as shown in Figure S7 and S8. FTIR spectrum was examined by a NICOLET 6700 FTIR (NICOLET, America) through the KBr pellet method (Figure S9). TOF-MS spectrum was measured by TripleTOF 4600 Time of Flight Mass Spectrometer (AB Sciex, America) under positive mode using DMSO as the solvent (Figure S10). For the cured **6**, 0.2 g of **6**, 0.3 g of styrene, 1.1 g of butyl methacrylate, 0.4 g of hydroxyethyl methacrylate, and 0.15g of dibenzoyl peroxide were mixed and cured at 80 ºC for 2.5h and 140 ºC for 2 h. The cured **6** (small particles) with the weight of about 80 mg were immersed in vials with 10 mL 1 M HCl solution (THF/H_2O=9/1, v/v). Within 2 h, the cured **6** could be completely dissolved in 1 M HCl solution (THF /H_2O = 9/1, v/v) at 50 °C (Fig. S14)



Scheme S1. Synthetic route of degradable diacrylate 6 from 2.

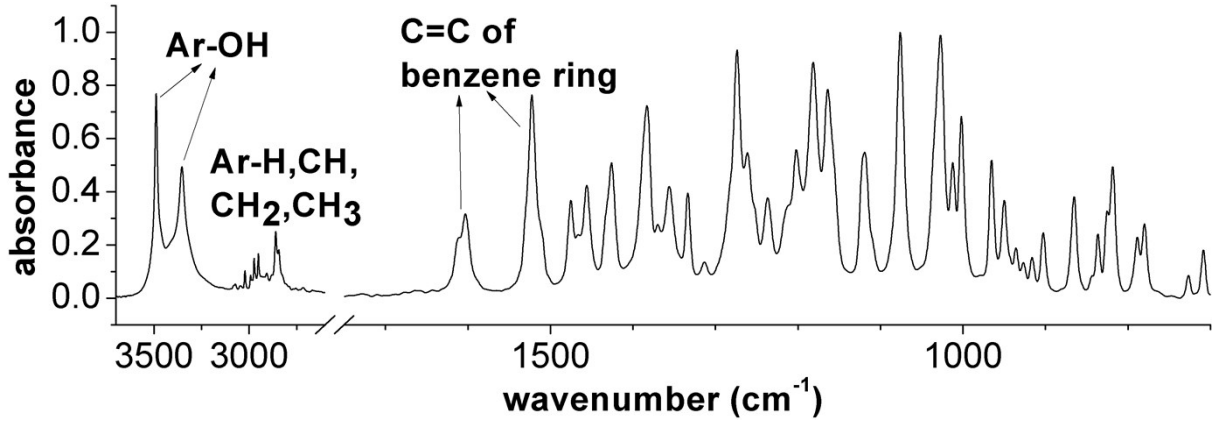


Figure S1. FTIR spectrum of 2.

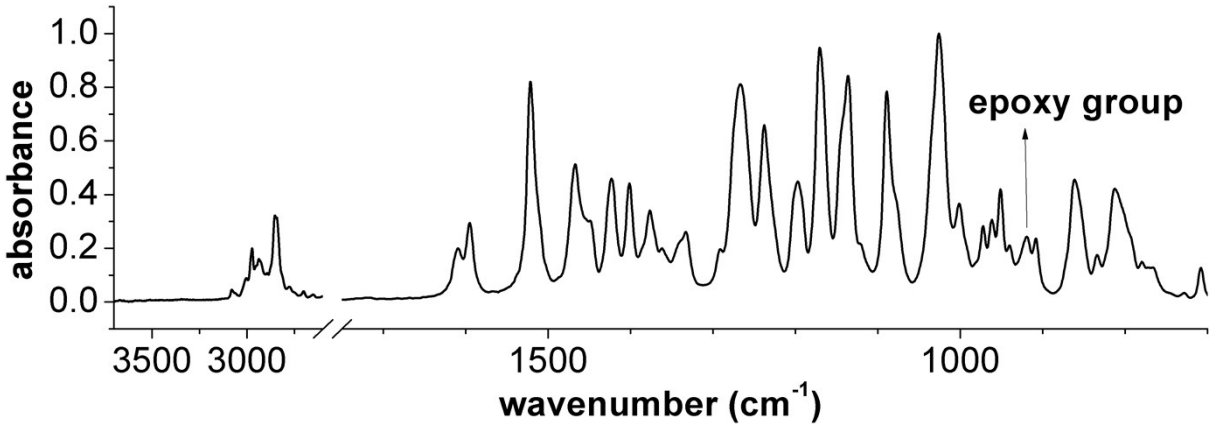


Figure S2. FTIR spectrum of 3.

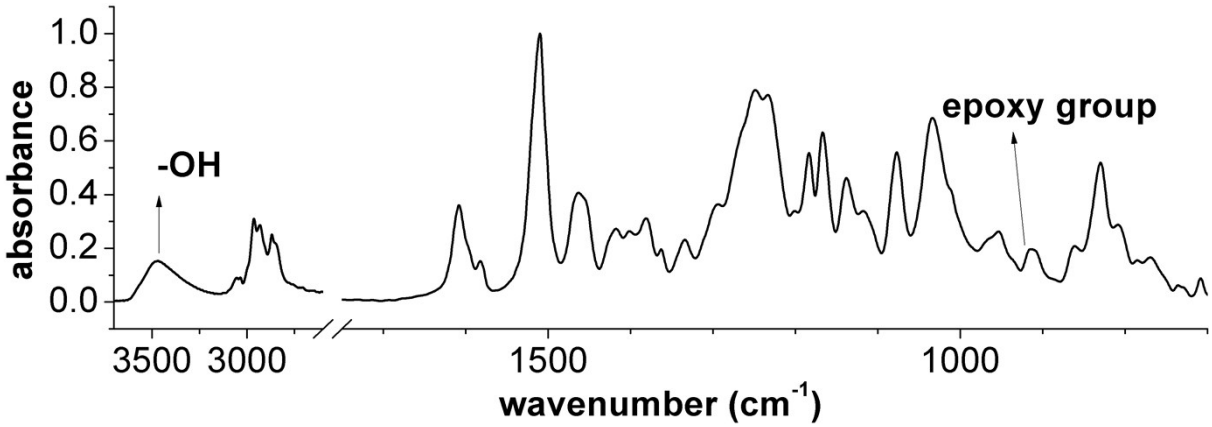


Figure S3. FTIR spectrum of 5.

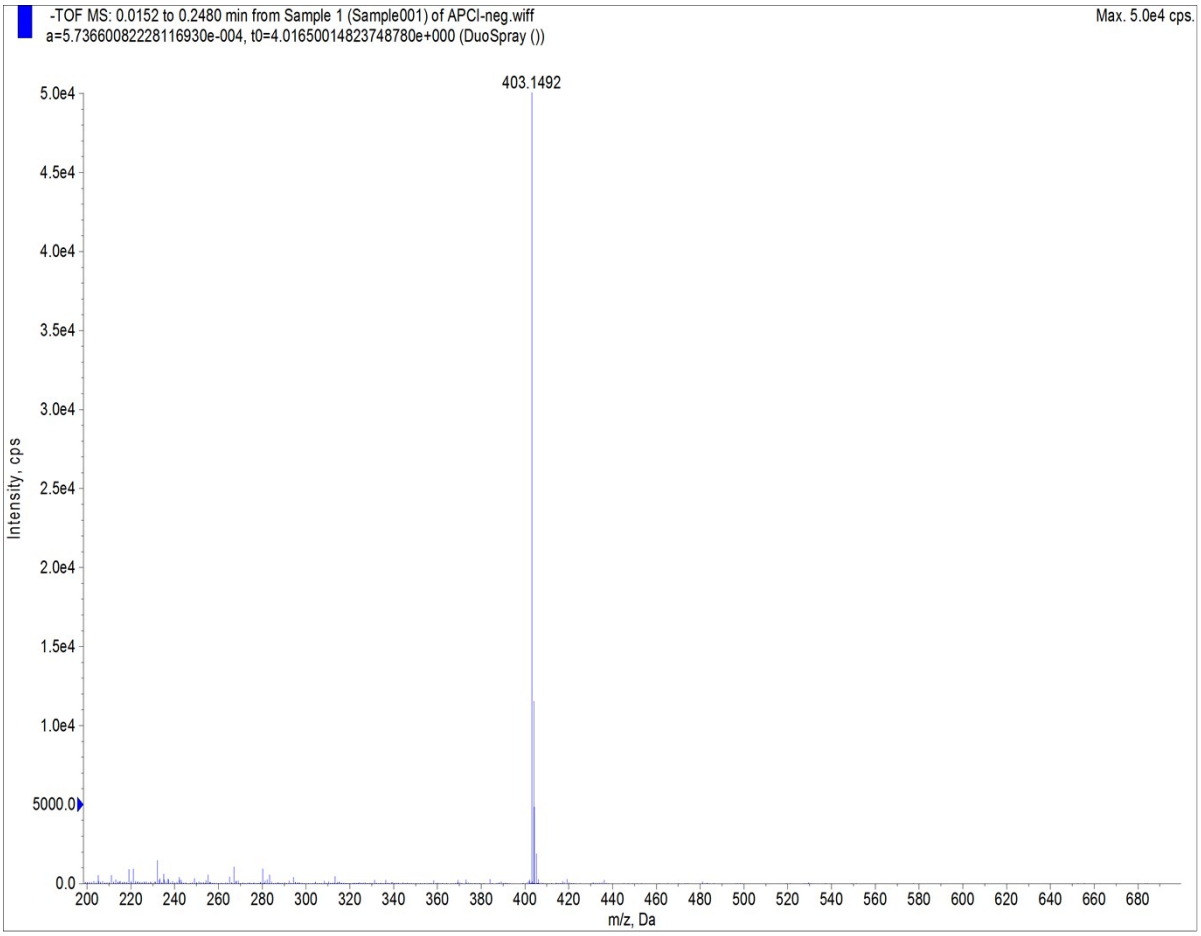


Figure S4. TOF-MS spectrum of 2.

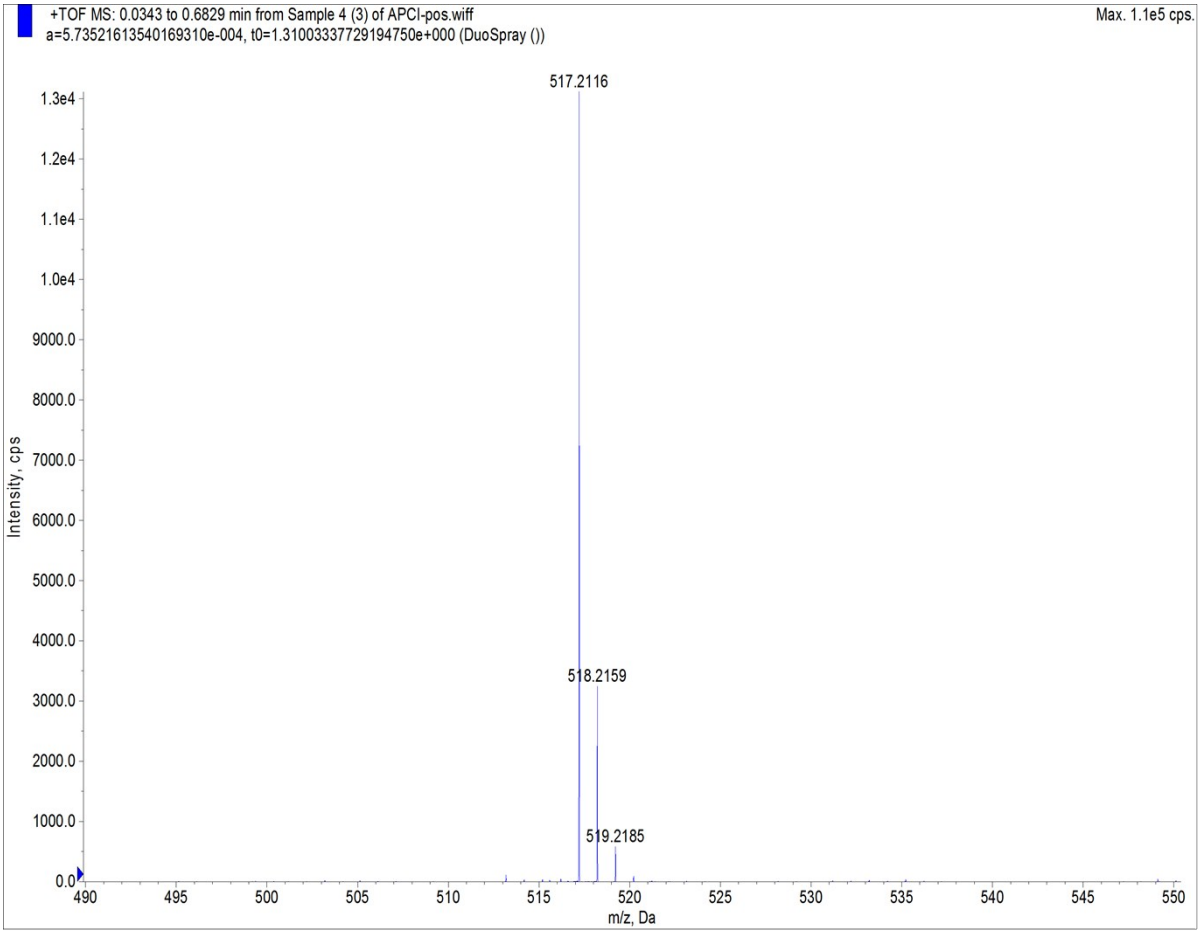


Figure S5. TOF-MS spectrum of 3.

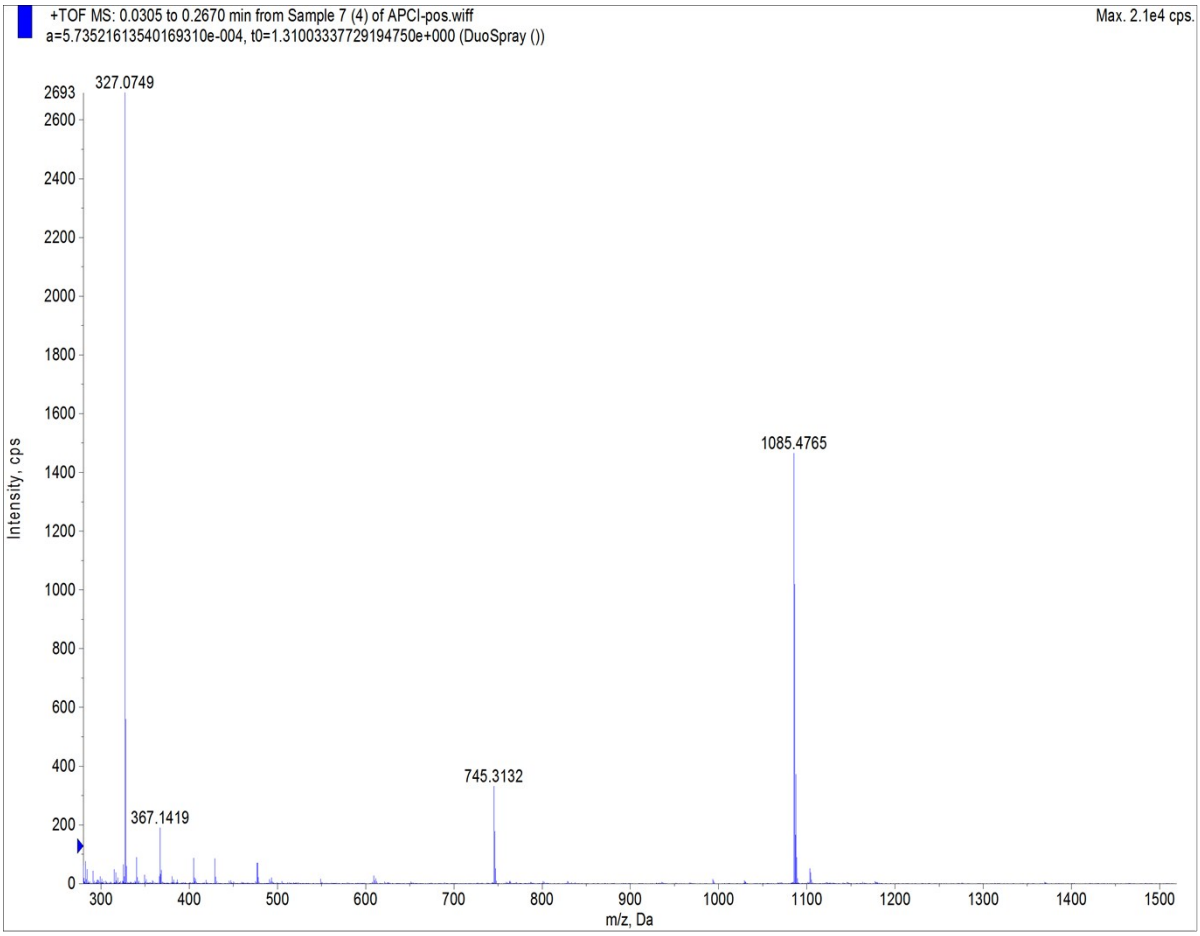


Figure S6. TOF-MS spectrum of 5.

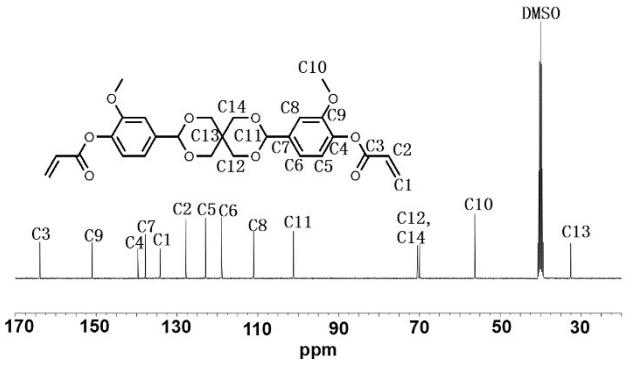


Figure S7. ^{1}H NMR spectrum of 6.

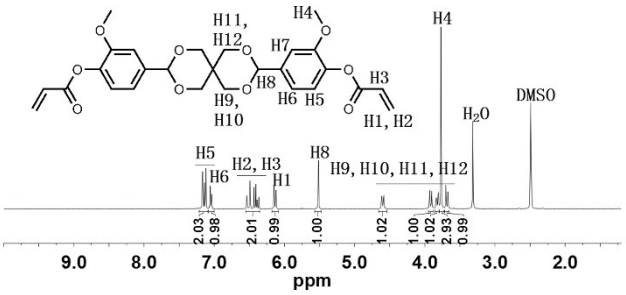


Figure S8. ^{13}C NMR spectrum of 6.

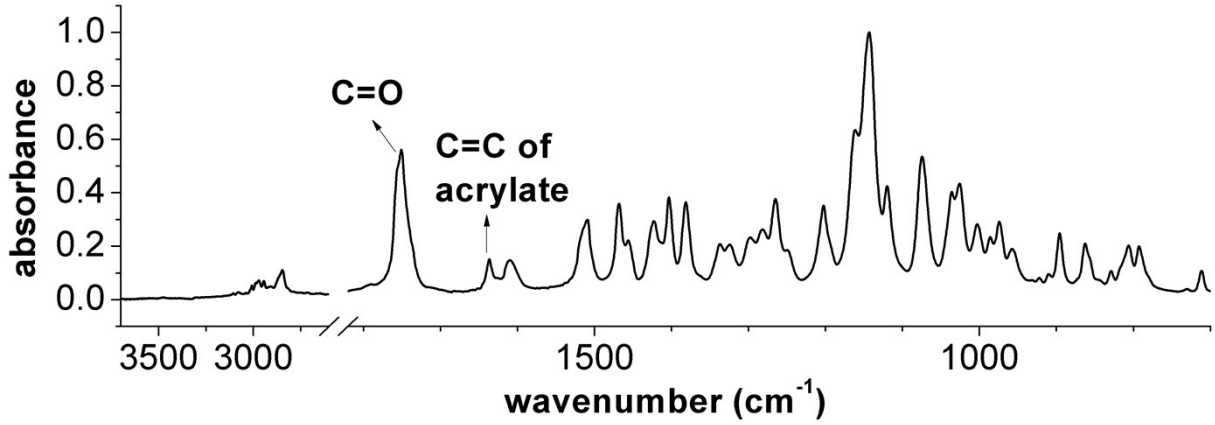


Figure S9. FTIR spectrum of 6.

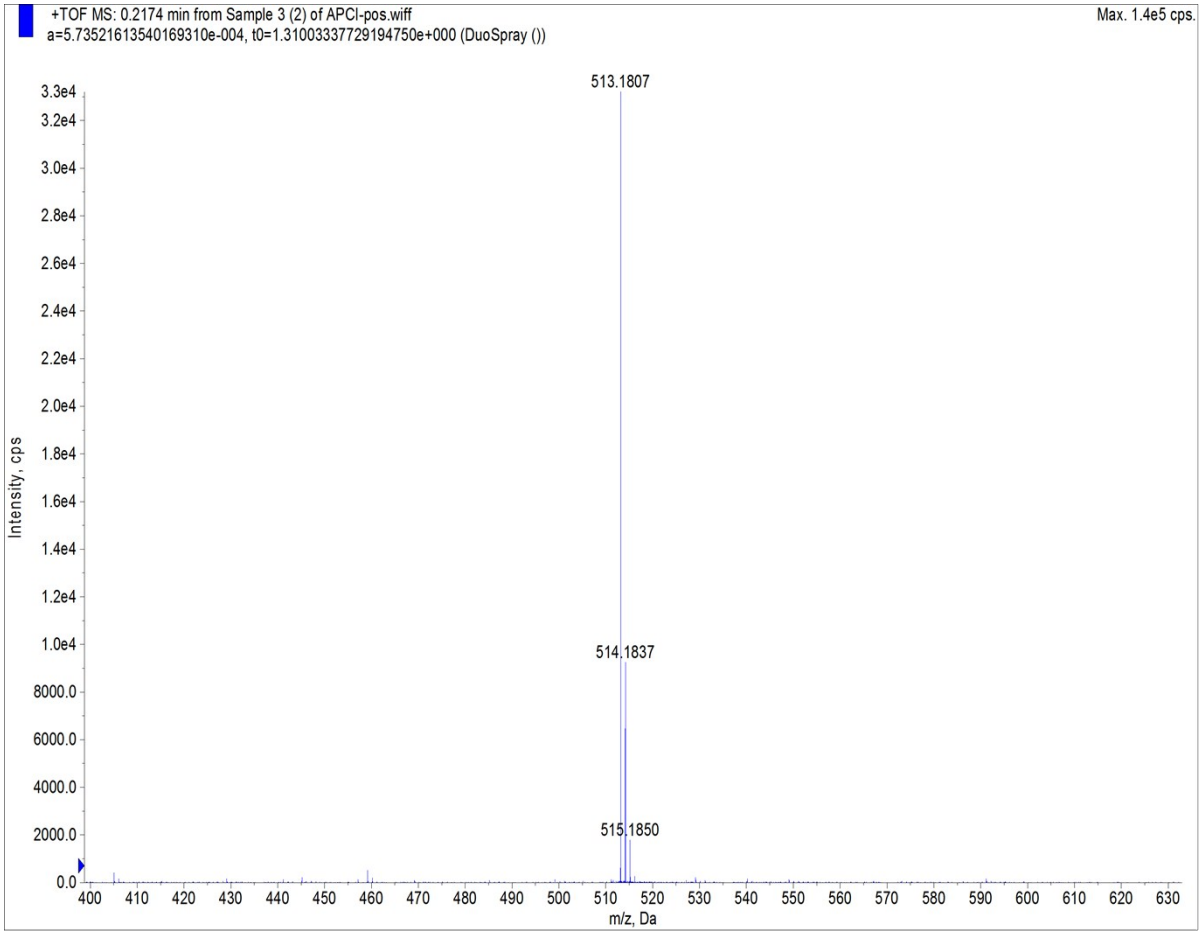


Figure S10. TOF-MS spectrum of 6.

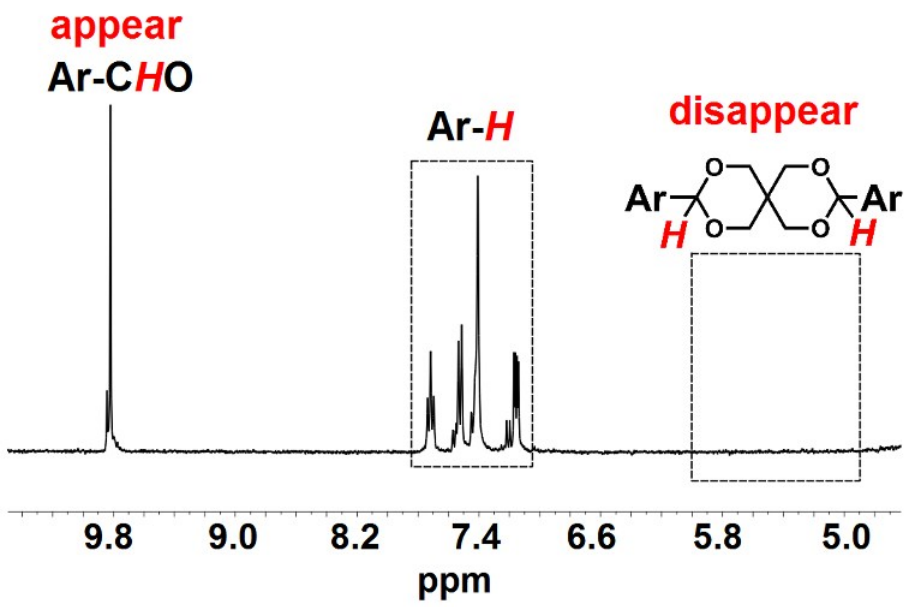


Figure S11. **^{1}H NMR spectrum of the DDM cured 3 immersed in 0.1 M HCl solution (acetone/H_2O = 9/1, v/v) at 50 °C for 120 min.**

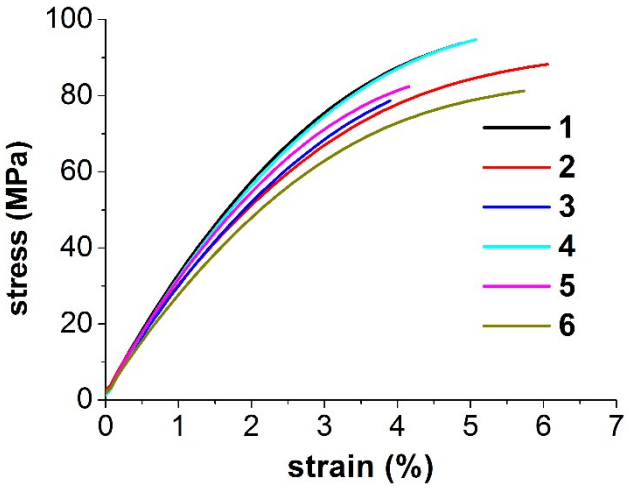


Figure S12. **Tensile stress-strain curves of the cured 3.**

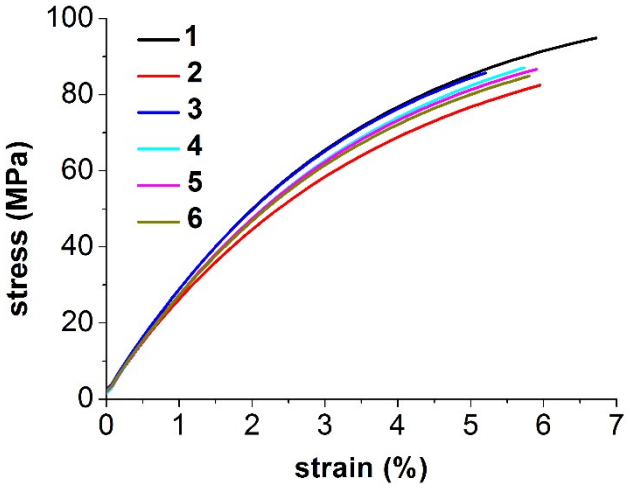


Figure S13. **Tensile stress-strain curves of the cured 4.**

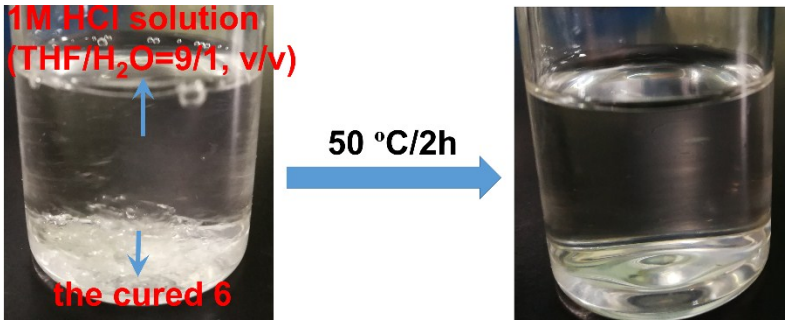


Figure S14. **Appearance of the cured 6 before and after immersing in 1 M HCl solution (THF/H_2O=9/1, v/v).**

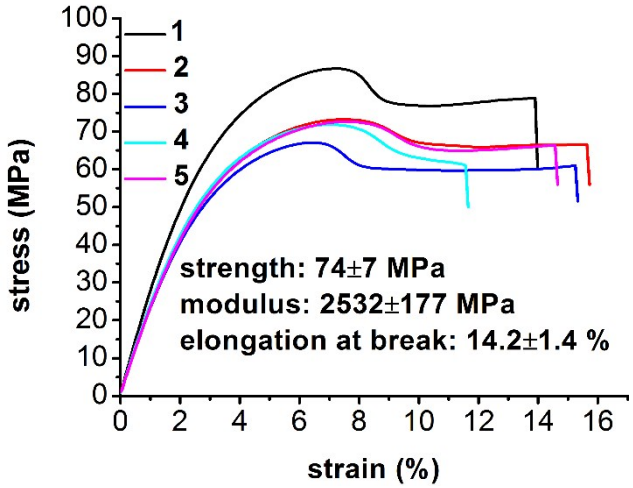


Figure S15. **Tensile stress-strain curves of the cured 5.**

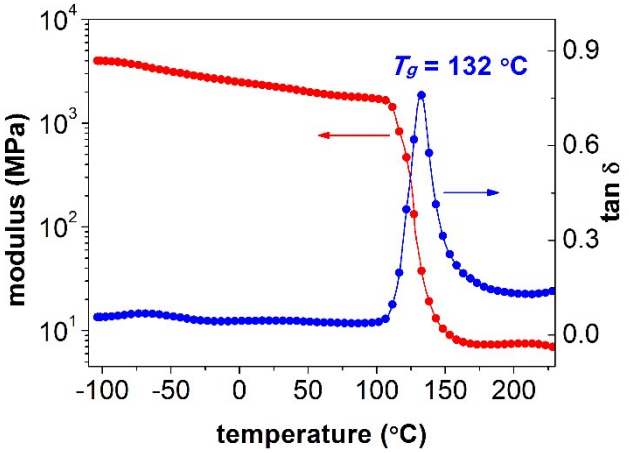


Figure S16. **DMA curves of the cured 5.**

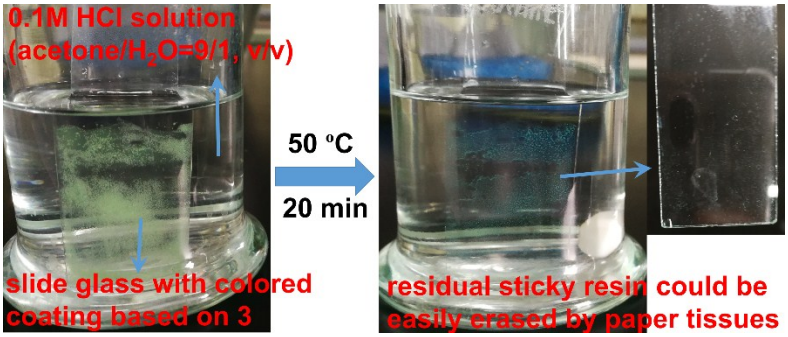


Figure S17. **The removing process of coating on slide glass with 0.1 M HCl solution (acetone/H_2O=9/1, v/v).**

Table S1. **The coating properties of coatings based on 3 and 4.**

sample	thickness	pencil hardness		MEK	mandrel bending
	(μm)	gouge	scratch	double rubs	(elongation at break) (%)
coating based on **3**	61±2	6H	3H	>400	>28
coating based on **4**	58±3	5H	2H	>400	>28