Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

A facile post-modification strategy for carboxylic acid-functionalized UV-responsive pressure-sensitive adhesives.

Chiwon Hwang,[a,b] Jong-Ho Back,[a] Dowon Ahn,[a] Hyun-Jong Paik,[b] Wonjoo Lee[a] and Youngchang Yu*[a]*

[a] *Center for Advanced Specialty Chemicals, Korea Research Instituted of Chemical Technology, Ulsan 44412, Republic of Korea.*

[b] *Department of Polymer Science and Engineering, Pusan National University, Busan 46241, Republic of Korea.*

Table of Contents

Additional Synthetic Details

4-styrenesulfonyl-2-methylaziridine. (StMAz)[1] A 250 mL round bottom flask was charged with sodium 4-vinylbenzenesulfonate (12.5 g, 60.62 mmol), THF (50 mL) and a stir bar. To the resulting solution was added oxalyl chloride (8.2 g, 64.61 mmol) and 2 mL of DMF dropwise at 0 °C. After stirring reaction mixture at 25 °C for 5 h, precipitated NaCl salt was filter and yellowish filtrate which containing **4-styrenesulfonyl chloride** was directly used without further purification to next step. A 250 mL round bottom flask was charged with 2-methylaziridine (3.17 g, 54.56 mmol), trimethylamine (8.28 g, 81.84 mmol), THF (50 mL) and a stir bar. A mixture was stirred to -20 °C, and aforementioned filtrate was added dropwise for about an hour. The reaction was allowed to room temperature and stirred 2 hours. 20 mL of saturated sodium bicarbonate solution was added and the mixture was extracted by washing with 200 mL of THF and 100 mL of water 3 times in the presence of brine solution. Collected organic layer was dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure to afford the desired product as white solid (6.9 g, 64% over 2 steps). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ 7.87 (d, 2H), 7.53 (d, 2H), 6.73 (dd, 1H), 5.88 (d, 1H), 5.42 (d, 1H), 2.82 (m, 1H), 2.60 (d, 1H), 2.02 (d, 1H), 1.23 (d, 3H).

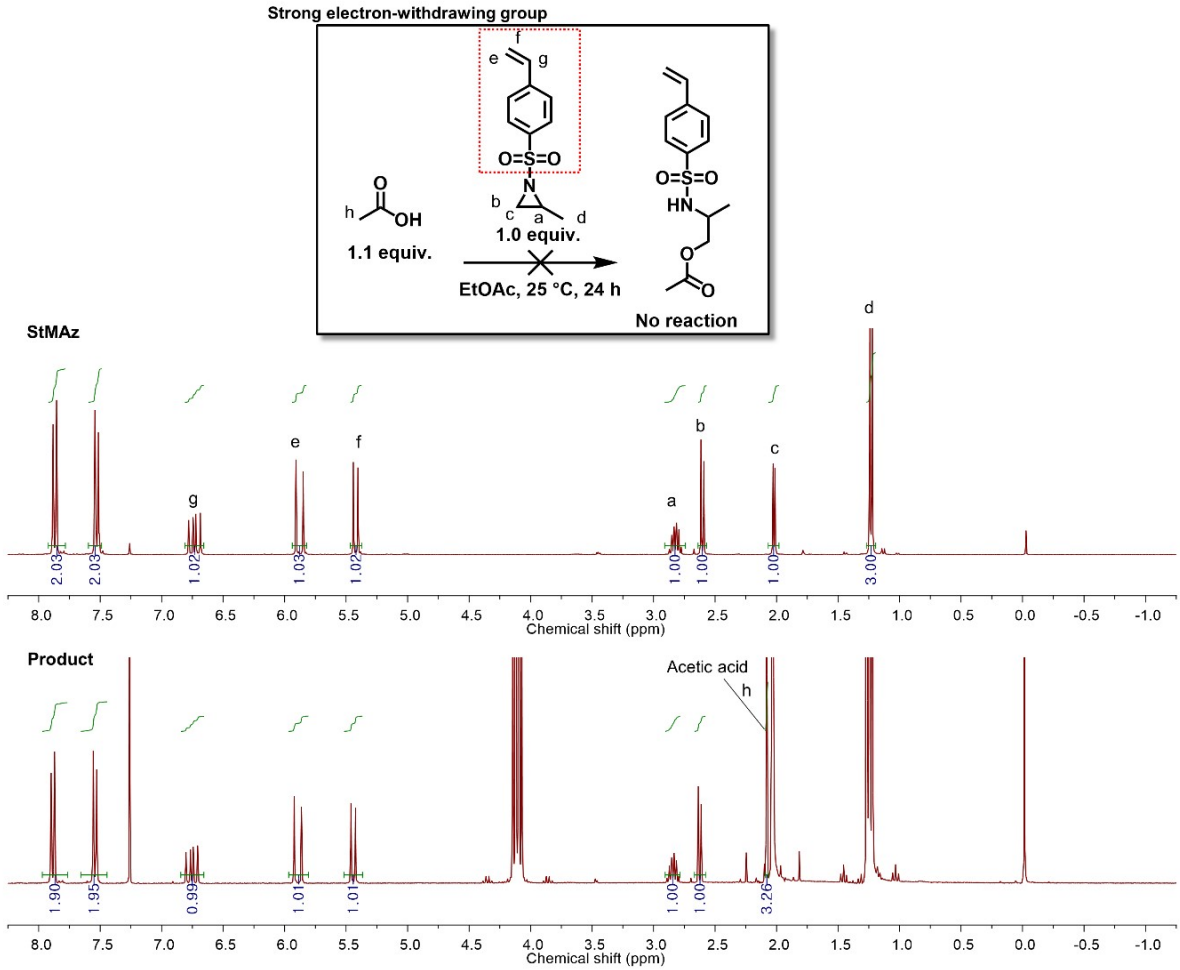

Fig. S1 ^{1}H NMR spectra of reaction between acetic acid and StMAz (4-styrenesulfonyl-2-methylaziridine) at 50 °C for 24 hours. (300 MHz, 298 K, $CDCl_3$)

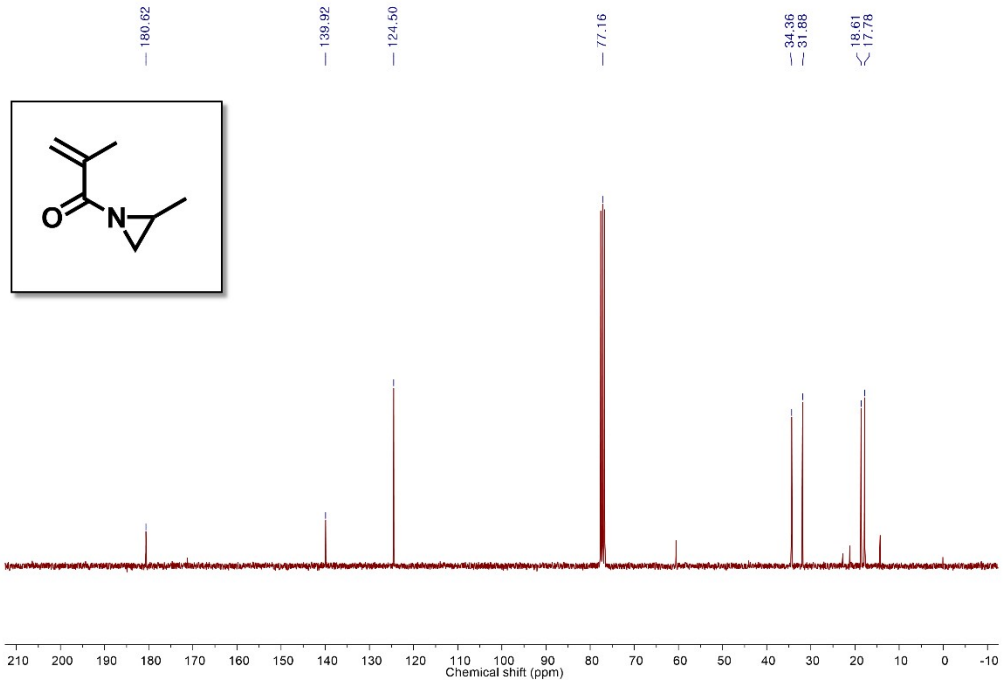

Fig. S2 ^{13}C NMR spectra *N*-methacryloyl-2-methylaziridine (75 MHz, 298 K, $CDCl_3$)

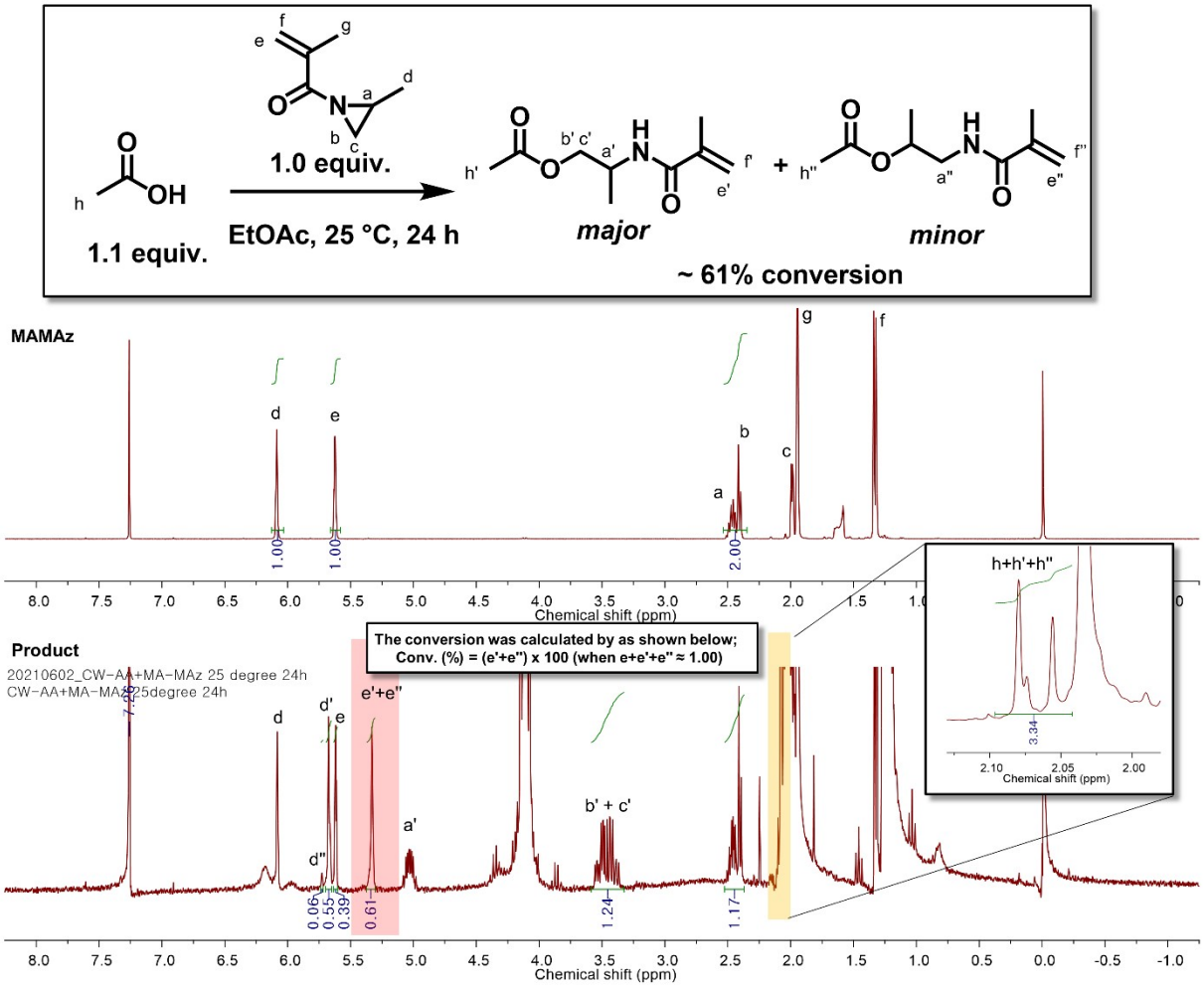

Fig. S3 ^{1}H NMR spectra of reaction between acetic acid and MAMAz at 25 °C for 24 hours. (300 MHz, 298 K, $CDCl_3$)

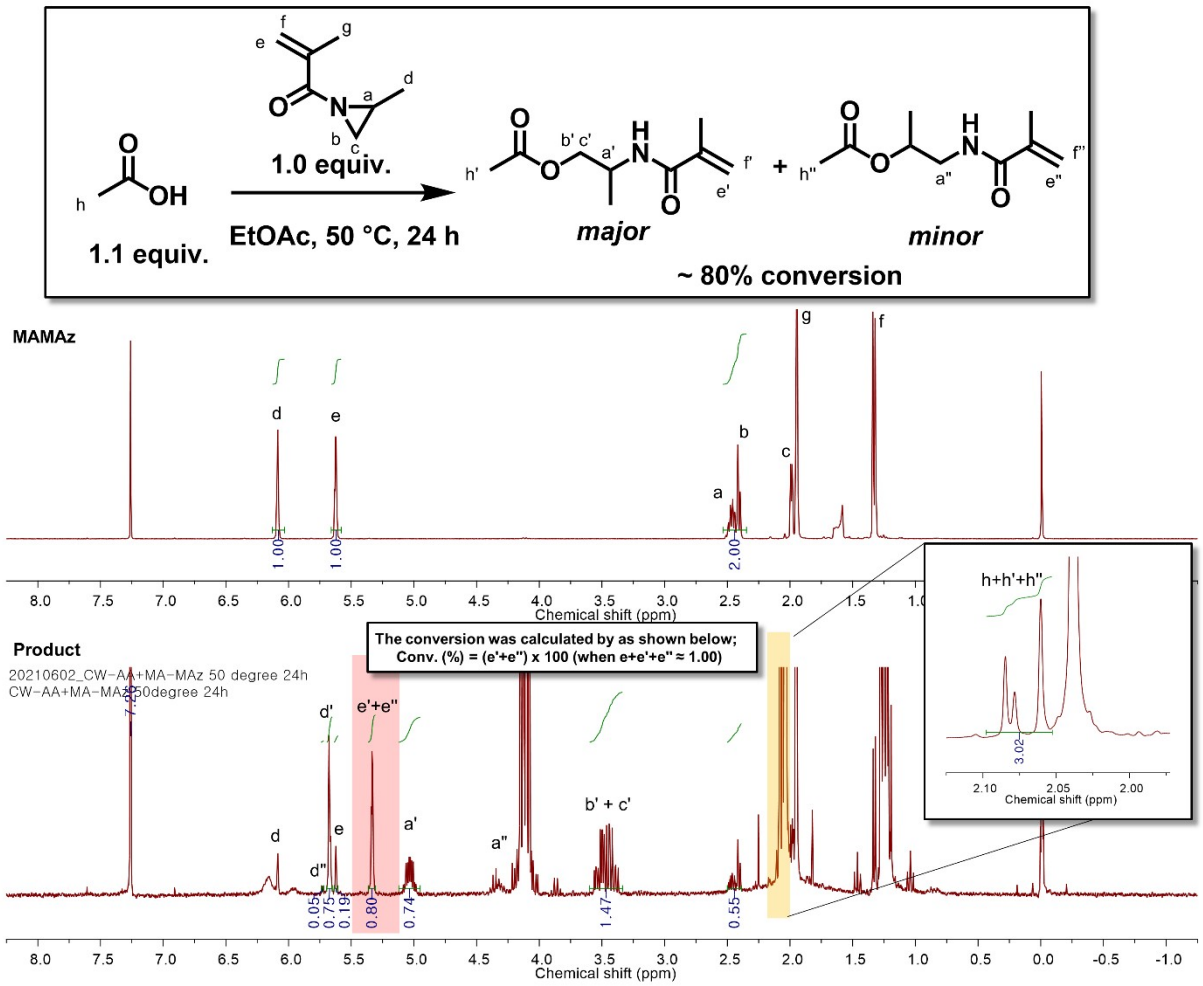

Fig. S4 ^{1}H NMR spectra of reaction between acetic acid and MAMAz at 50 °C for 24 hours. (300 MHz, 298 K, $CDCl_3$)

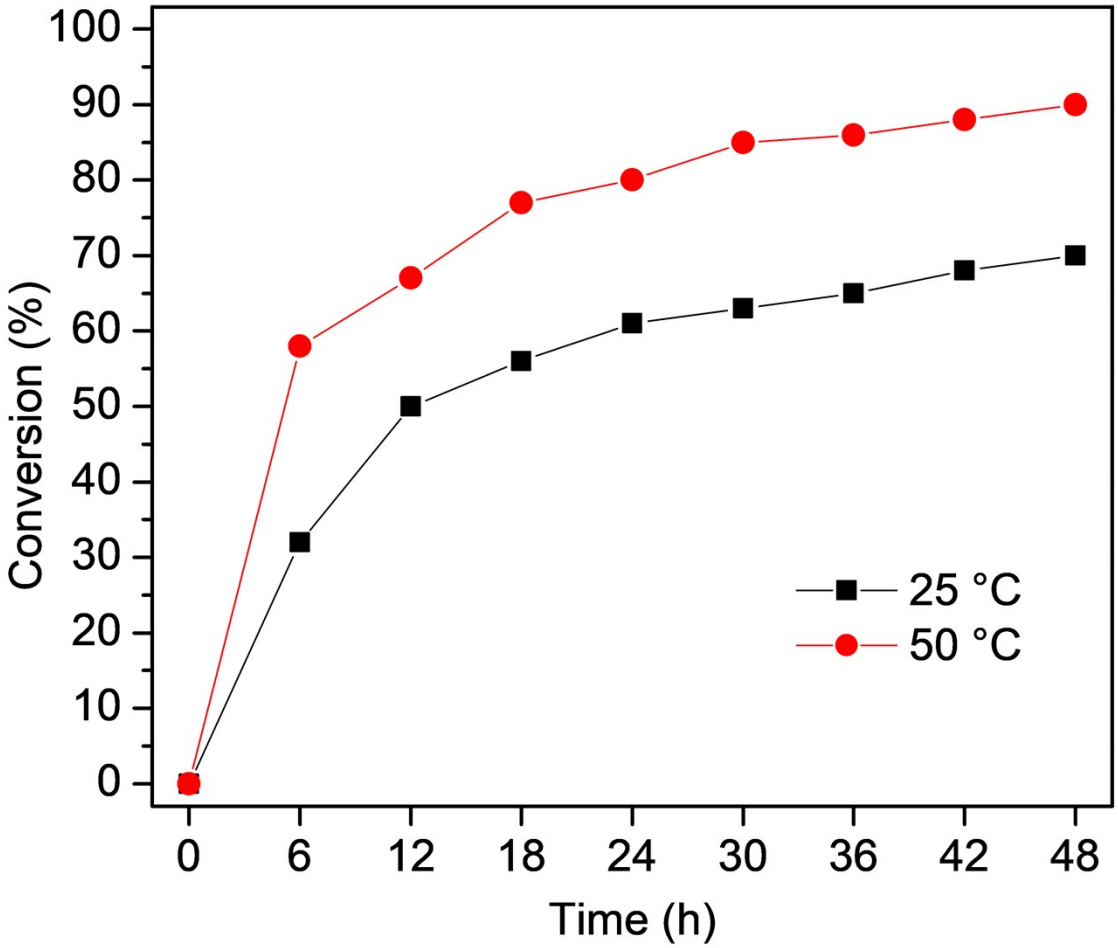

Fig. S5 Reaction kinetics under the modeling test of acetic acid with MAMAz. Conversion was determined by ^{1}H NMR.

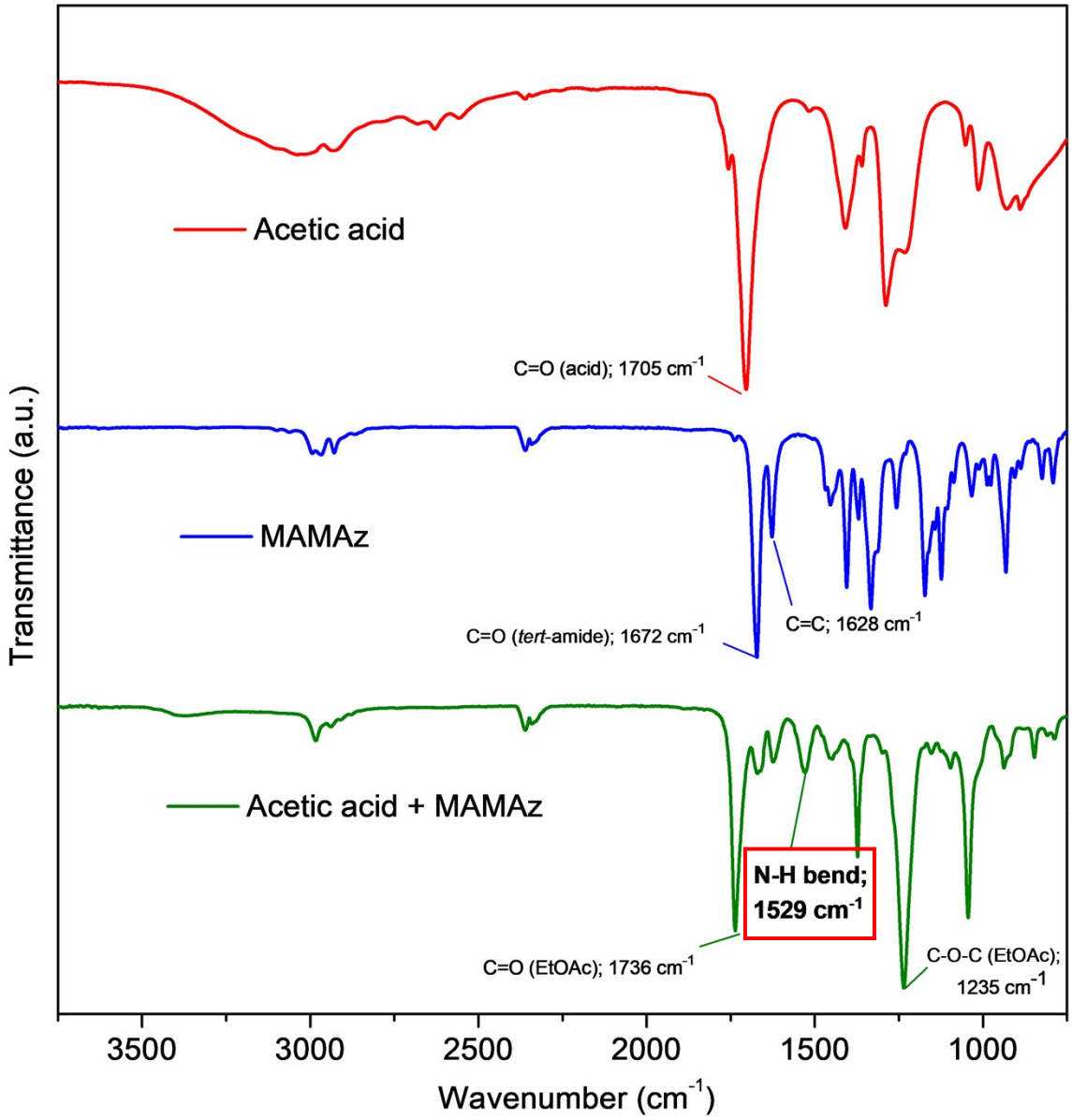

Fig. S6 Integrated IR spectra of reaction between acetic acid and MAMAz at 25 °C for 24 hours.

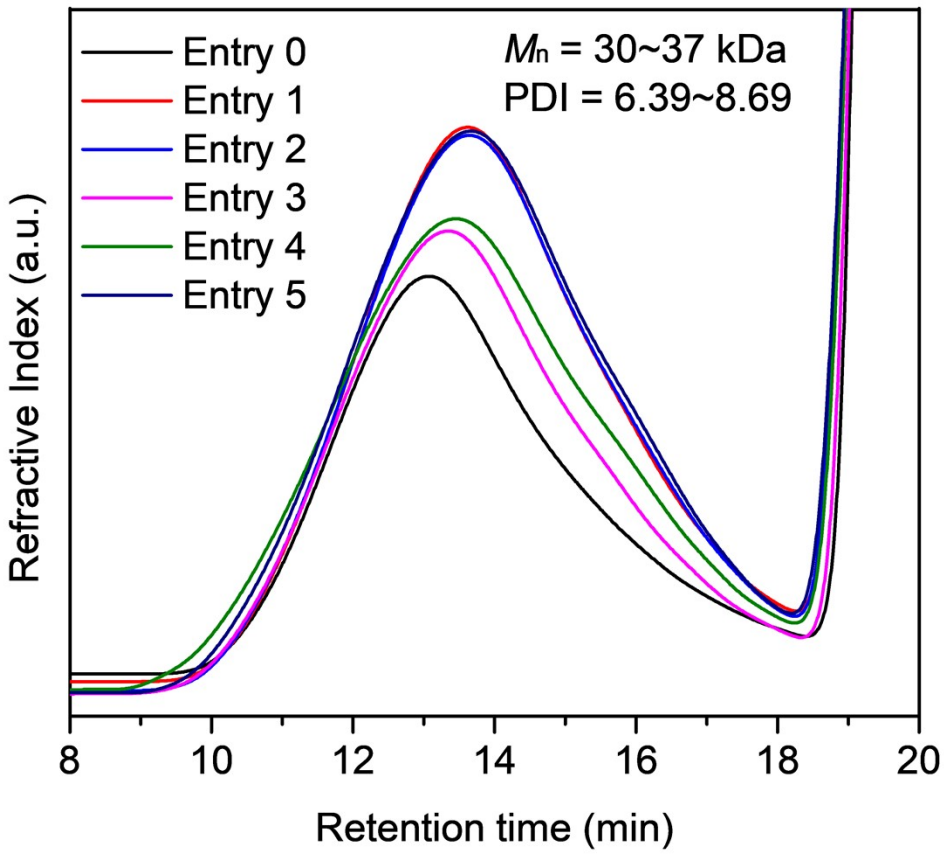

Fig. S7 SEC data recorded for various PSAs (0, 10, 20, 30, 40 and 50 mol % of -COOH substituted; 6 samples)

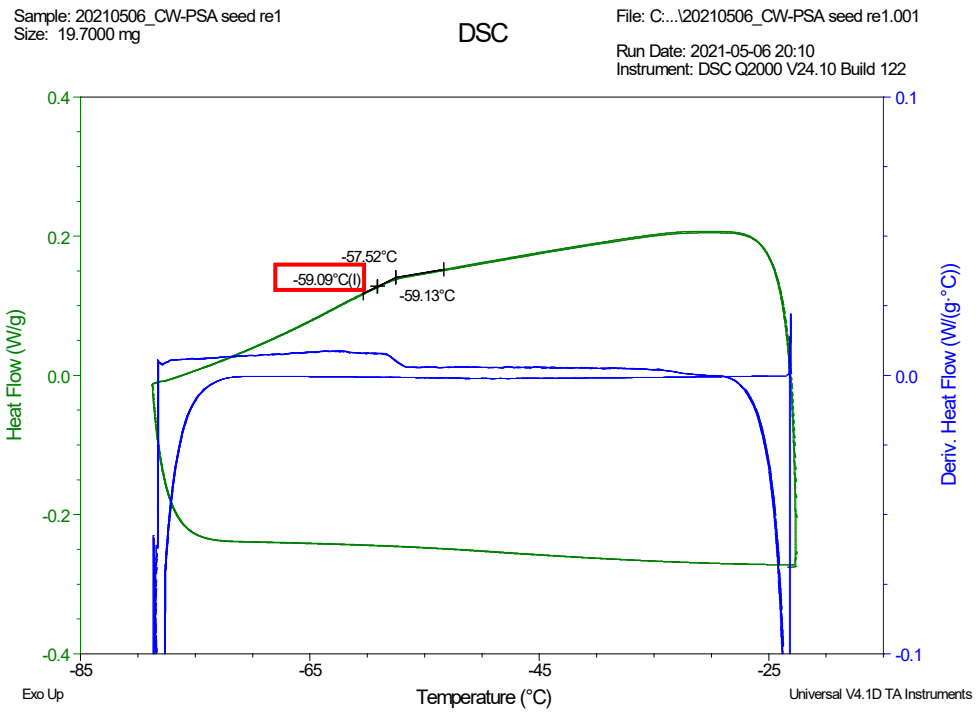

Fig. S8 DSC data recorded for Entry 0 (Original PSA)

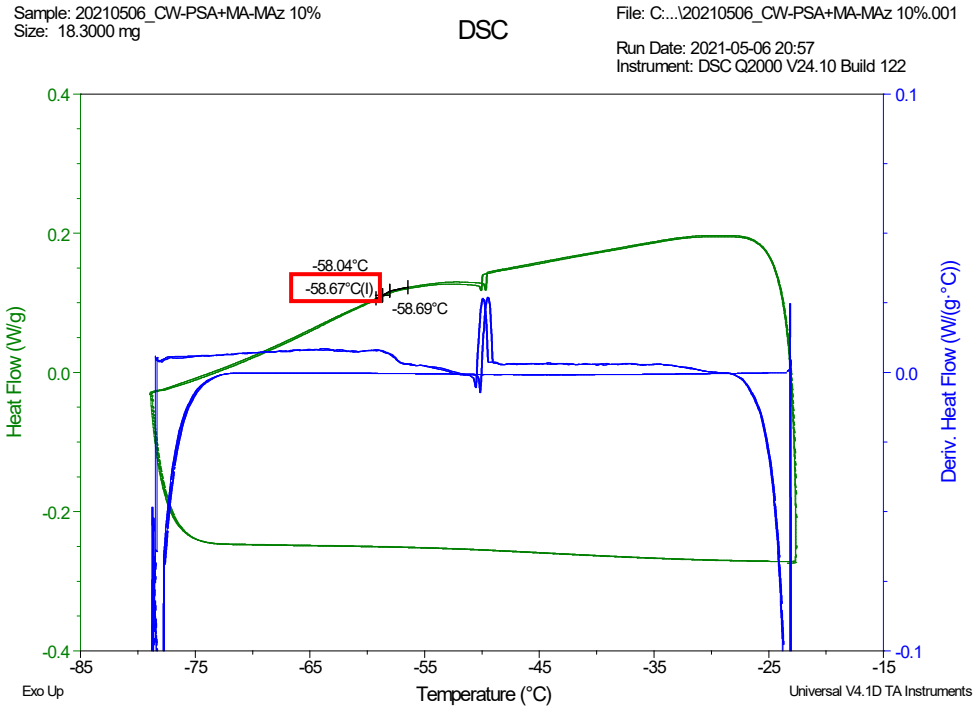

Fig. S9 DSC data recorded for Entry 1 (10 mol % -COOH substituted)

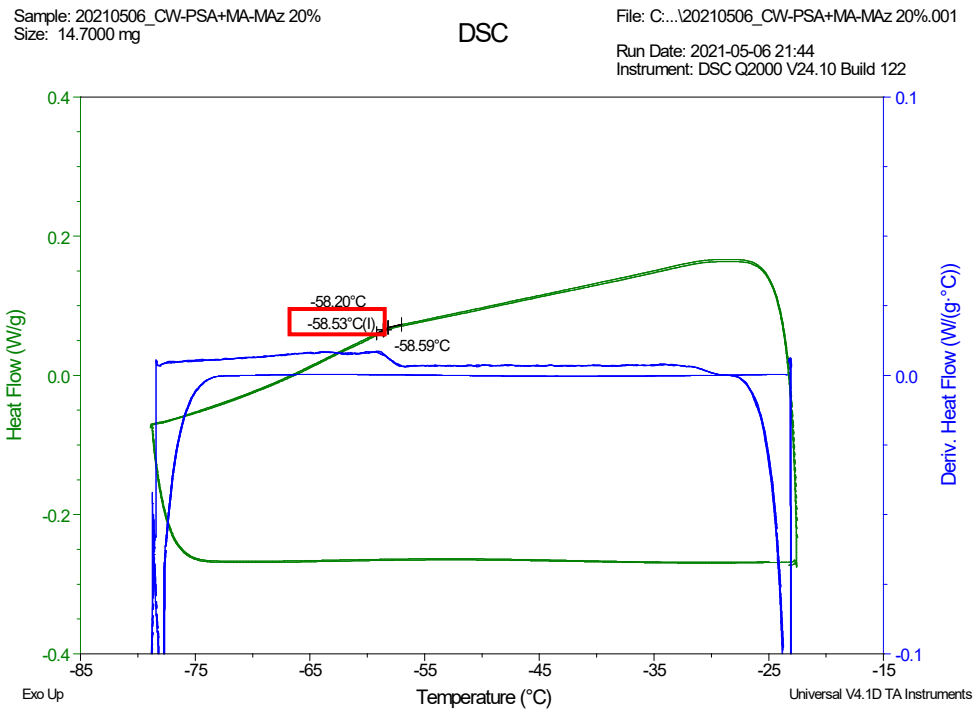

Fig. S10 DSC data recorded for Entry 2 (20 mol % -COOH substituted)

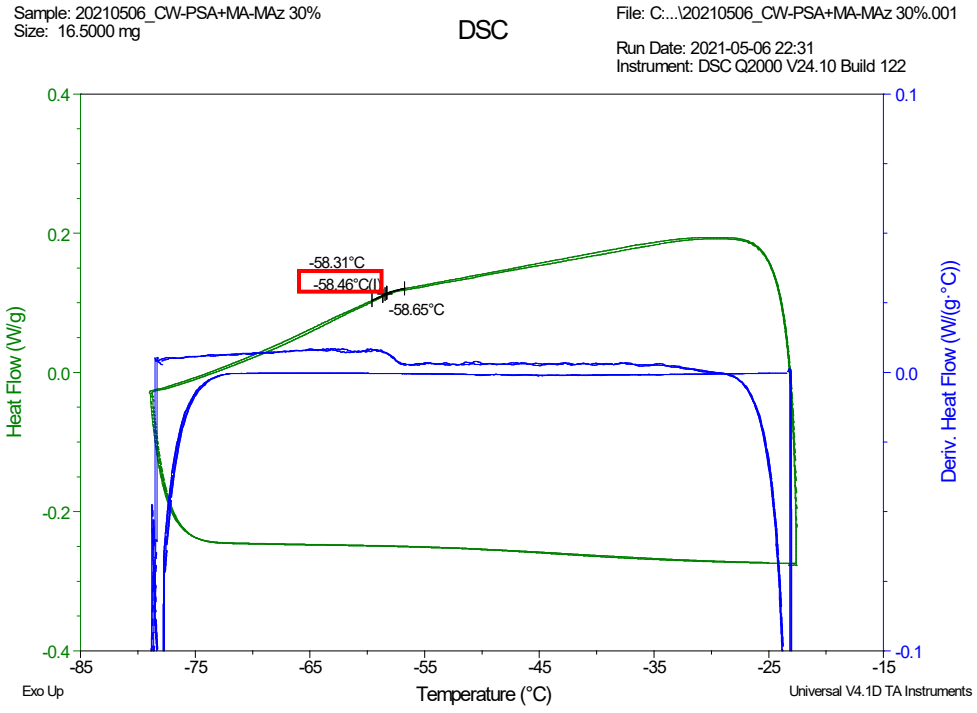

Fig. S11 DSC data recorded for Entry 3 (30 mol % -COOH substituted)

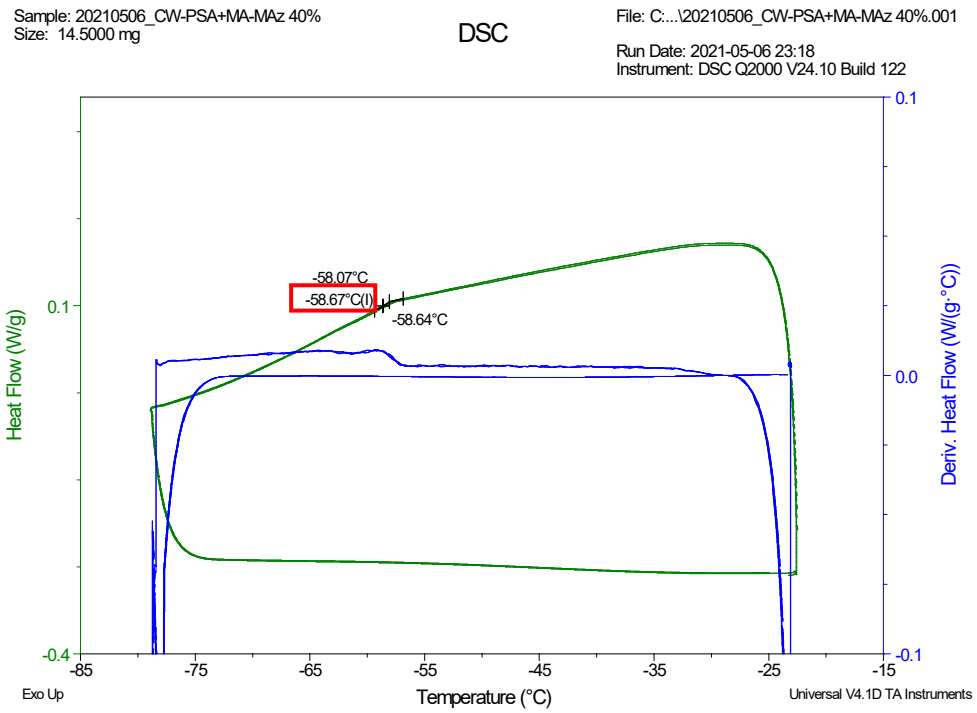

Fig. S12 DSC data recorded for Entry 4 (40 mol % -COOH substituted)

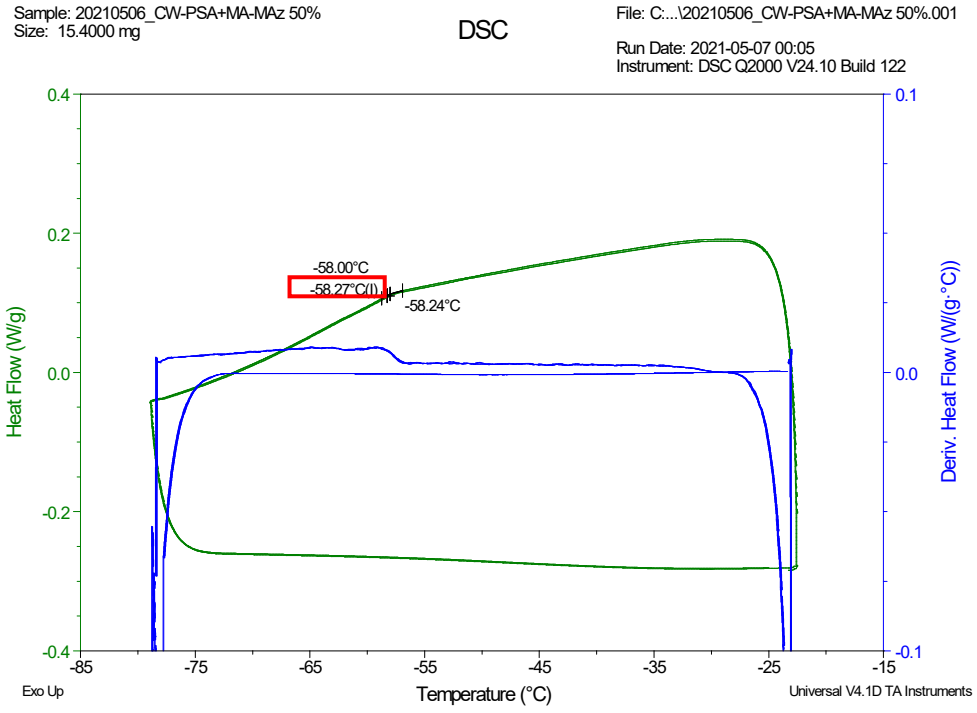

Fig. S13 DSC data recorded for Entry 5 (50 mol % -COOH substituted)

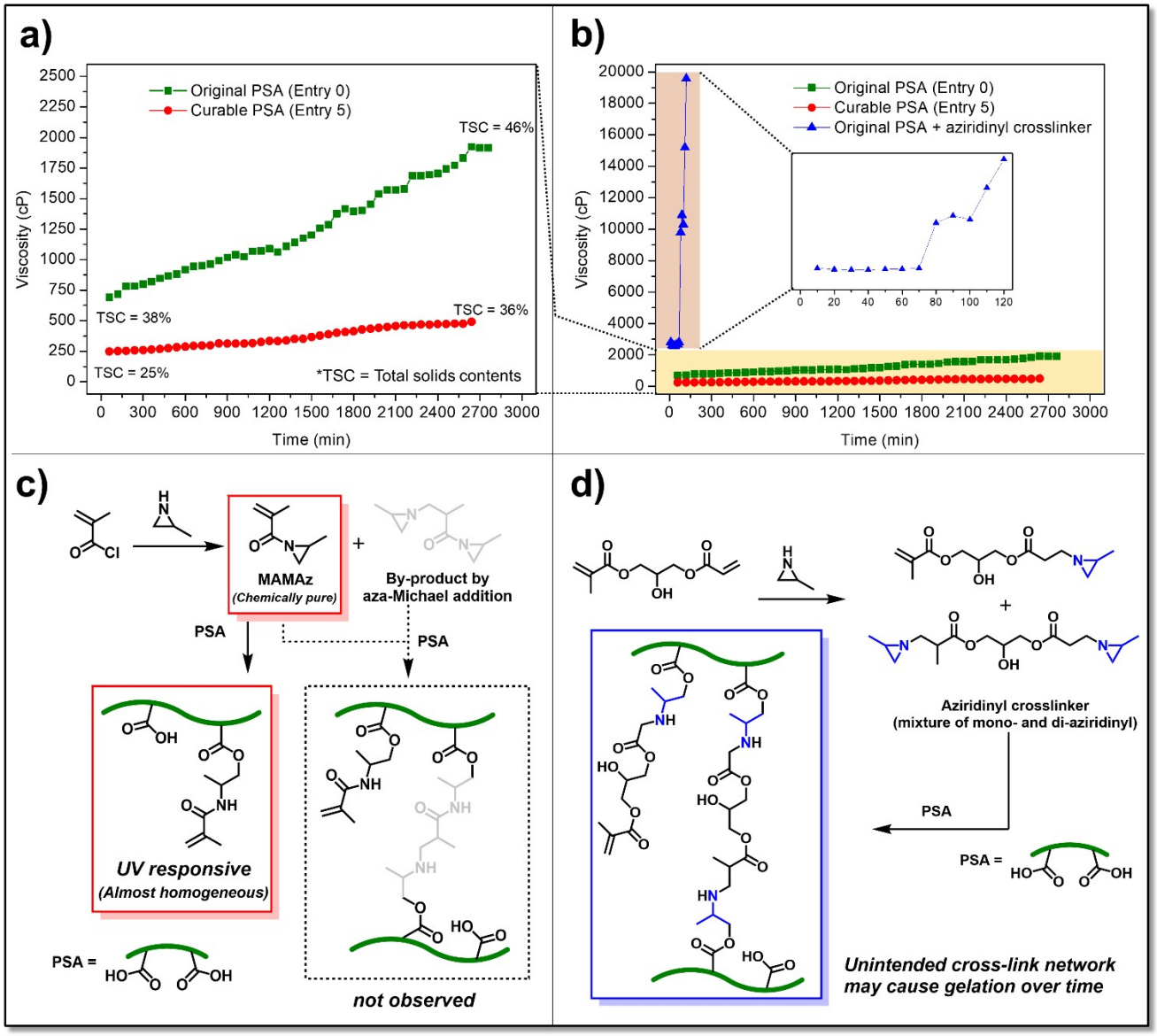

Fig. S14 Real-time viscometer data of **a)** original PSA (Entry 0, green line-dot) and curable PSA (Entry 5; 50 mol % of -COOH substituted, red line-dot) **b)** mixture of original PSA with aziridinyl cross-linker (blue line-dot) which appeared sharp increase of viscosity through unintended gelation. These occurrences were supported by rationalization to ensure pot-life by **c)** proposed mechanism in the presence of MAMAz and **d)** proposed mechanism in the presence of aziridinyl cross-linker.

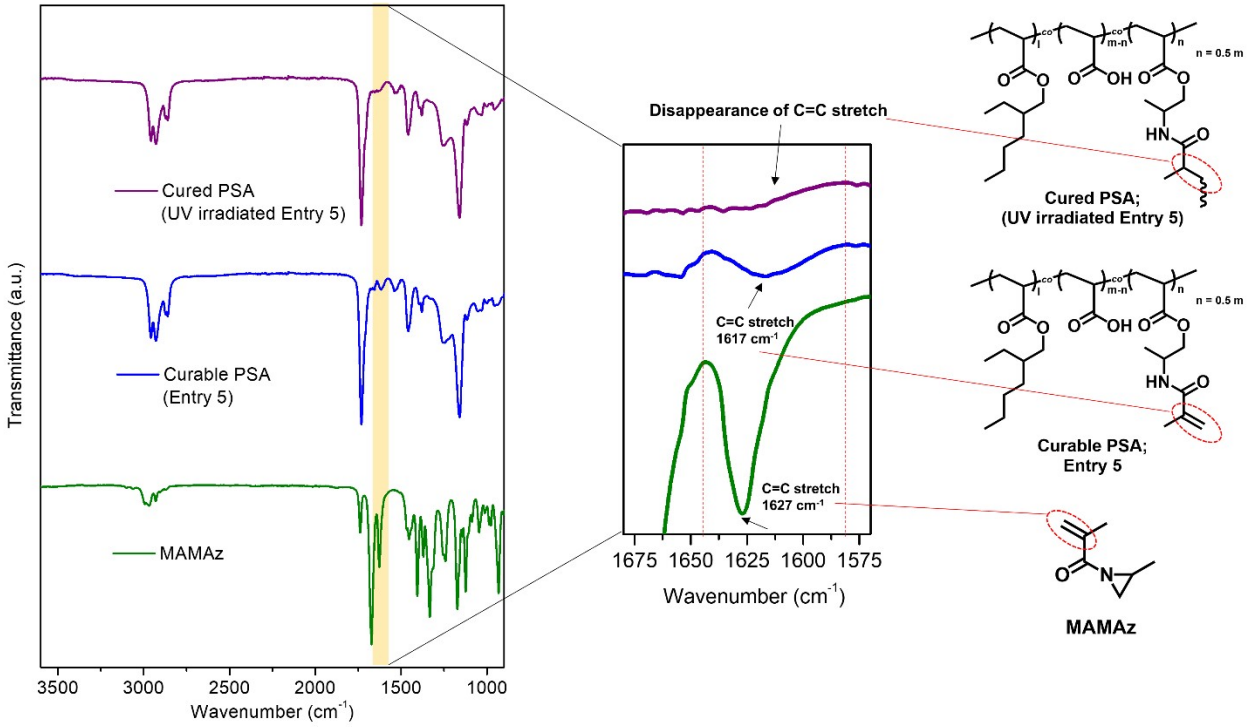

Fig. S15 Integrated FT-IR spectra of MAMAz (bottom), curable PSA (entry 5; 50% of -COOH substituted, middle) and cured irradiated PSA (UV irradiated entry 5, top).

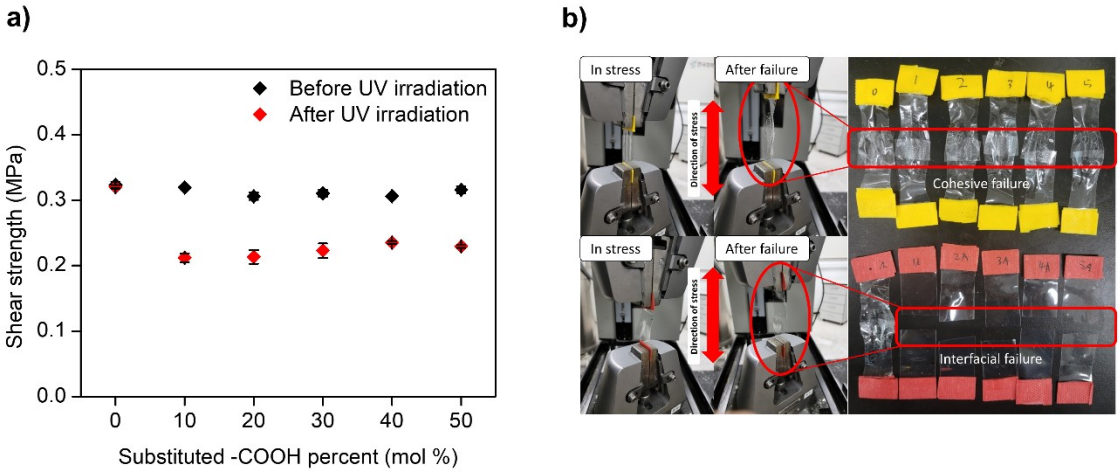

Fig. S16 a) Single lap shear strength test of UV-responsive curable PSAs (entry 0~5; independent 6 samples); b) Images of failure fracture occurrence after shear stress; yellow and red tape-stringed samples represent the PSAs samples as UV irradiation before and after respectively.

References

1) T. Gleede, E. Rieger, T. Homann-Mueller and F. Wurm, *Macromol. Chem. Phys.,* 2018, 219, 1700145.