Supporting Information

for

Enhancing and Toughening Plant Oil-Based Polymeric Materials through Synergetic Supramolecular and Covalent Interactions by Introducing Nucleobase-Functionalized Celluloses

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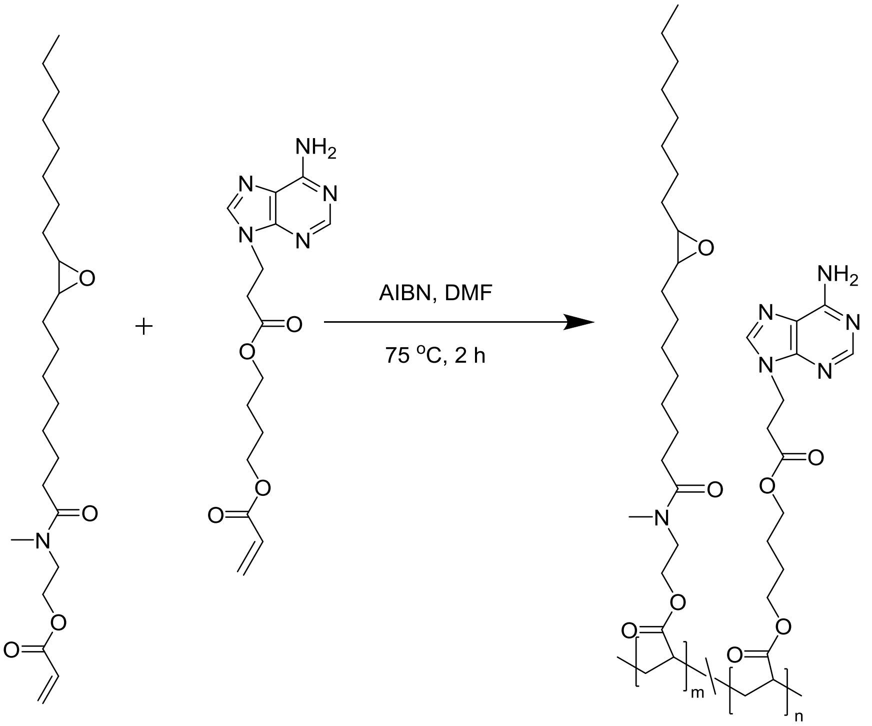
1. Synthetic Procedures

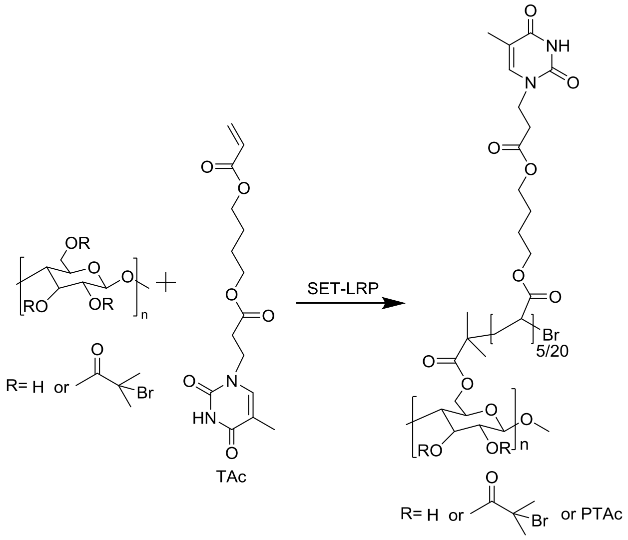
1.1. Synthesis of P(ECO-*co*-AAc) copolymers



Scheme S1. Synthesis of P(ECO-*co*-AAc) copolymers.

The P(ECO-*co*-AAc) copolymers (PA1-5) were synthesized by free radical polymerization with AIBN as the initiator (Scheme S1 and Table 1). The typical synthetic procedure is as follows. For PA5, ECO (3 mmol, 1.2 mL), AAc (3 mmol, 1.05 g), AIBN (0.01 mmol, 1.64 mg) and DMF (4 mL) were added into an ampoule with a stirring bar. The mixture was completely degassed via four freeze−pump−thaw cycles, filled with nitrogen and then immersed in an oil bath at 75 °C for 2 h. The mixture was characterized by ^{1}H NMR spectroscopy and DMF SEC to monitor the conversion. The reaction solution was then precipitated in cold methanol for three times. The purified product was dried under vacuum at room temperature for 24 h and characterized by ^{1}H NMR spectroscopy and DMF SEC (PMMA standards, with 5 mM NH_4BF_4 as eluent).

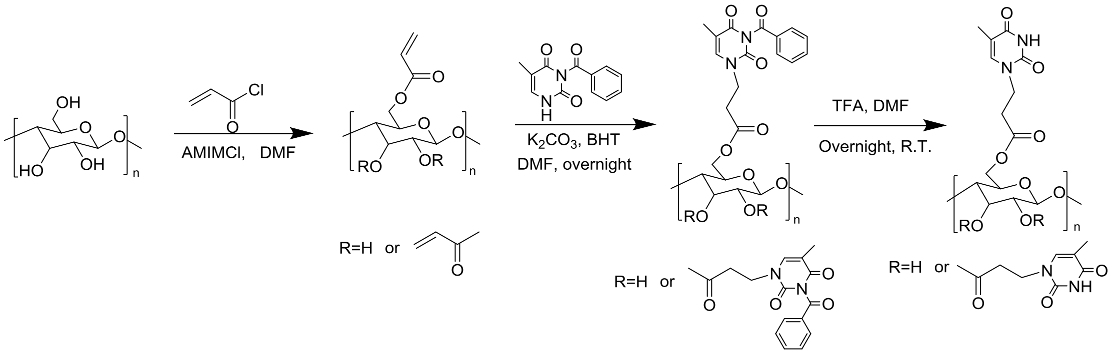
1.2. Synthesis of Cell-*g*-PTAc



Scheme S2. Synthesis of bottlebrush-like cellulose-*grafted*-poly(4-((3-(thymin-l-yl)propanoyl)oxy)butyl acrylate) (Cell-*g*-PTAc) with the variable degree of polymerization (DP).

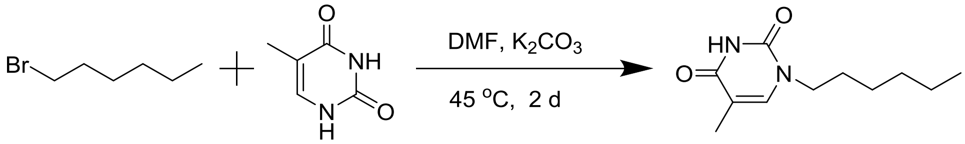
Single electron transfer living radical polymerization (SET-LRP) was used to synthesize Cell-*g*-$PTAc_5$ and Cell-*g*-$PTAc_{20}$. Macroinitiator Cellulose 2-bromoisobutyrylate (Cell-Br) was prepared according to the previous publication.[1] For Cell-*g*-PTAc, the typical synthetic procedures are as follows. For Cell-*g*-$PTAc_{20}$, Cell-Br (0.16 mmol of 2-bromoisobutyrylate, 42 mg), TAc (3. 2 mmol, 1.39 g), $CuBr_2$ (1.6×10^{-3} mmol, 0.35 mg), Me_6TREN (0.014 mmol, 3.75 μL), DMSO (10 mL) and copper wire (with the length of 5 cm) were added into an ampoule. The mixture was thoroughly degassed via 4 times freeze-pump-thaw cycles, back-filled with nitrogen and then immersed into an oil bath at 50 °C for 12 h. The reaction was quenched via exposure to air. Then the mixture was precipitated in cold CH_3OH for three times for purification. The dried Cell-*g*-PTAc copolymers were characterized by ^1H NMR spectroscopy and DMF SEC (PMMA standards, with 5 mM NH_4BF_4 as eluent).

1.3. Synthesis of thymine-*modified*-cellulose (Cell-T)



Scheme S3. Synthesis of acrylate-*modified*-cellulose (Cell-acrylate), 3-benzoylthymine-*modified*-cellulose (Cell-3-benzoylthymine) and thymine-*modified*-cellulose (Cell-T).

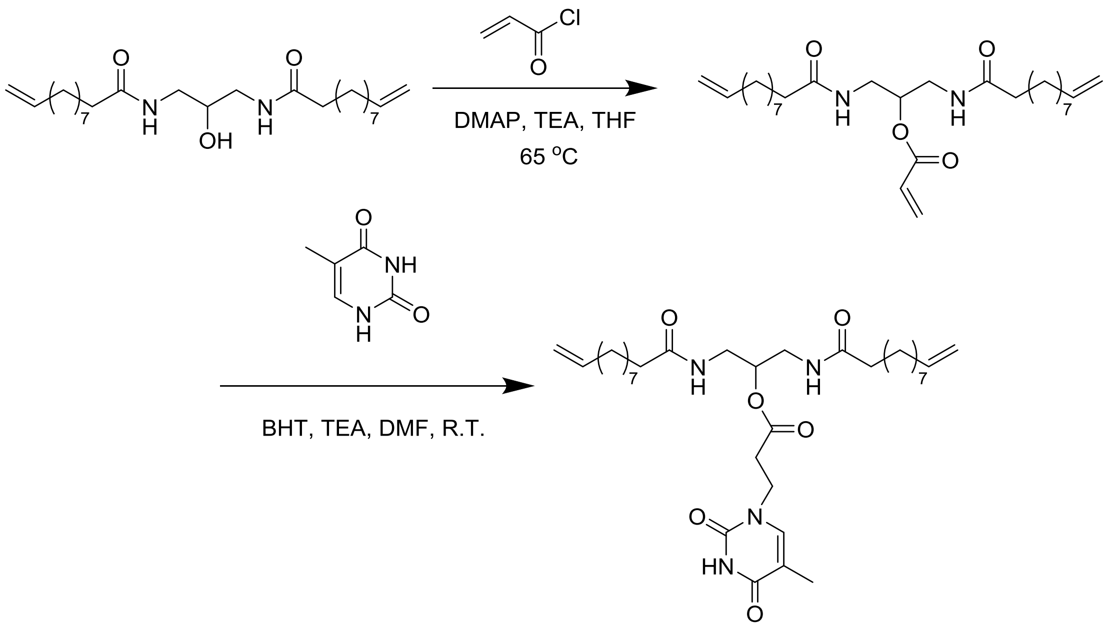
Cell-T was prepared from cellulose as follows (Scheme S3). Firstly, cellulose (MCC, 1.0 g) was dissolved in 25 g AMIMCl at 80 °C under stirring overnight to prepare acrylate-*modified*-cellulose (Cell-acrylate). The residual water in the reaction system was removed under vacuum. Anhydrous DMF (16 mL) was added to the mixture as the cosolvent at 80 °C, then acryloyl chloride (2.0 mL, 2.5 mmol) was added into the mixture in an ice-water bath and the reaction was continued for 18 h. The reaction solution was poured into excessive deionized water (500 mL) for purification. The obtained white powder Cell-acrylate was further washed by deionized water for three times and dried under vacuum for 24 h under ambient conditions. Cell-acrylate was used to prepare 3-benzoylthymine-*modified*-cellulose via an efficient Michael addition reaction. Specifically, Cell-acrylate (1.1 g, 5.0 mmol of acrylate unit), 3-benzoylthymine (1.0 g, 5.0 mmol), BHT (50 mg, 0.23 mmol) and K_2CO_3 (0.69 g, 5.0 mmol) were mixed in 40 mL of DMF and stirred at room temperature for 12 h. The reaction solution was poured into excessive water and methanol for removing unreacted K_2CO_3 and 3-benzoylthymine, respectively. Then, white 3-benzoylthymine-*modified*-cellulose powder was yielded after filtration. To prepare Cell-T, 3-benzoylthymine-*modified*-cellulose (1.0 g) was deprotected in a mixture of TFA/DMF (3:1) (20 mL) under stirring at 50 °C overnight. The excessive TFA was removed under vacuum at 50 °C after the reaction was completed. Then the product was precipitated in methanol for three times and dried overnight at room temperature. The obtained product was analyzed by ^{1}H NMR spectroscopy, FT-IR spectroscopy and DMF SEC, respectively.



Scheme S4. Synthesis of 9-hexylthymine (HeT) as a model molecule of Cell-T.

1.4. Synthesis of 1, 3-di(undec-10-enamido)propan-2-yl acrylate (ACUDA)

N, *N'*-(2-Hydroxypropane-1, 3-diyl)bis(undec-10-enamide) UDA was prepared according to the literature.[2] ACUDA was made by esterification between UDA and acryloyl chloride (Scheme S5). Specifically, UDA (4.23 g, 10 mmol), acryloyl chloride (870 μL, 12 mmol), 4-dimethylaminopyridine (0.50 mmol, 60.0 mg), TEA (10 mmol, 1.4 mL), BHT (40 mg) and THF (20 mL) were added into a 50 mL round-bottom flask. After reacting at 65 °C for 24 h, deionized water (1 mL) and THF (4 mL) were added to the mixture to quench the unreacted acryloyl chloride. The reaction solution was then concentrated to remove the solvents. The evaporation residue was separated using flash column chromatography with EtOAc as the eluent to get white solid powder, ACUDA (3.0 g, yield 63%). ^{1}H and ^{13}C NMR spectra of ACUDA were displayed in Figure S10. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.43 (m, 1H, C*H*=CH-CO-), 6.29 (t, 2H, -N*H*-CO-), 6.10 (m, 1H, CH_2=C*H*-CO-), 5.87 (m, 1H, C*H*=CH-CO-), 5.80 (m, 2H, CH_2=C*H*-CH_2-), 4.98 (m, 2H, C*H*=CH-CH_2-), 4.92 (m, 2H, C*H*=CH-CH_2-), 4.90 (m, 1H, -CH_2-C*H*-OCO-), 3.57 and 3.35 (m, 4H, -NH-CH_2-), 2.21 (t, 4H, -CH_2-CO-NH-), 2.02 (m, 4H, CH_2=CH-CH_2-), 1.62 (m, 4H, -CO-CH_2-CH_2-), 1.28-1.36 (m, 20H, -CH_2-$(CH_2)_5$-CH_2-) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0, 164.2, 138.2, 130.8, 126.8, 113.1, 76.2, 70.4, 37.8, 35.6, 32.8, 28.2, 24.7 ppm.



Scheme S5. The synthesis of 1, 3-di(undec-10-enamido)propan-2-yl acrylate (ACUDA) and 1, 3-di(undec-10-enamido)propan-2-yl thymine (UDA-T).

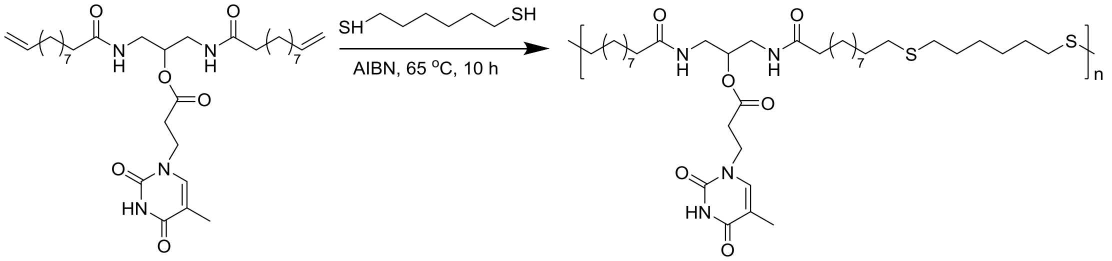
1.5. Synthesis of 1, 3-di(undec-10-enamido)propan-2-yl thymine (UDA-T)

UDA-T was prepared via Michael addition between ACUDA and thymine (Scheme S5). ACUDA (2.86 g, 6.0 mmol,), BHT (180 mg), TEA (840 μL, 6.0 mmol), thymine (630 mg, 5.0 mmol) and DMF (12 mL) were added into a 50 mL round-bottom flask. After reacting at 25 °C for 24 h, the reaction solvent was removed. The residue was purified using flash column chromatography with the mixture of $CHCl_3$ and MeOH (93:7 v:v) to obtain a white solid, UDA-T (2.1 g, yield 70%). ^{1}H and ^{13}C NMR spectra of UDA-T were displayed in Figure S10. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.24 (s, 1H, -CO-N*H*- in pyrimidine), 7.82 (t, 2H, -CO-N*H*-CH_2-), 7.50 (m, 1H, -C*H*=C- in pyrimidine), 5.77 (m, 2H, CH_2=C*H*-CH_2-), 4.98 (m, 2H, C*H*=CH-CH_2-), 4.92 (m, 2H, C*H*=CH-CH_2-), 4.77 (m, 1H, -CH_2-C*H*-OCO-), 3.85 (t, 2H,

-N-CH_2-CH_2-COO-), 3.29 and 3.08 (m, 4H, -NH-CH_2-), 2.65 (t, 2H, -OCO-CH_2-CH_2-), 2.01 (m, 8H, -CH_2-CH=CH_2 and -NHCO-CH_2-CH_2-), 1.73 (s, 3H, -CH_3), 1.46 (m, 4H, -NHCO-CH_2-CH_2-), 1.23-1.32 (m, 20H, -CH_2-(CH_2)$_5$-CH_2-) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0, 170.7, 164.7, 151.3, 142.1, 139.2, 115.0, 108.8, 72.4, 44.2, 40.1, 35.8, 33.58, 33.47, 28.7-29.2, 25.6, 12.3 ppm.

1.6. The polymerization of UDA-T

P(UDA-T) was prepared via thiol-ene step-growth polymerization of UDA-T with 1, 6-hexanedithiol (Scheme S6). Azobisisobutyronitrile (AIBN) was used as a radical initiator. Specifically, UDA-T (0.25 mmol, 151 mg), 1, 6-hexanedithiol (0.25 mmol, 39.5 μL), AIBN (0.0075 mmol, 1.25 mg), and DMF (250 μL) were charged into a 10 mL ampoule. The mixture was thoroughly degassed via 4 times freeze-pump-thaw cycles, back-filled with nitrogen and then immersed into an oil bath at 65 °C for 10 hours. The reaction mixture was diluted with DMF and precipitated in methanol for 3 times. The precipitates were dried under vacuum at 40 °C to obtain P(UDA-T) which was further characterized by ^{1}H NMR spectroscopy and DMF SEC.



Scheme S6. The polymerization of UDA-T via a thiol-ene polymerization to obtain P(UDA-T).

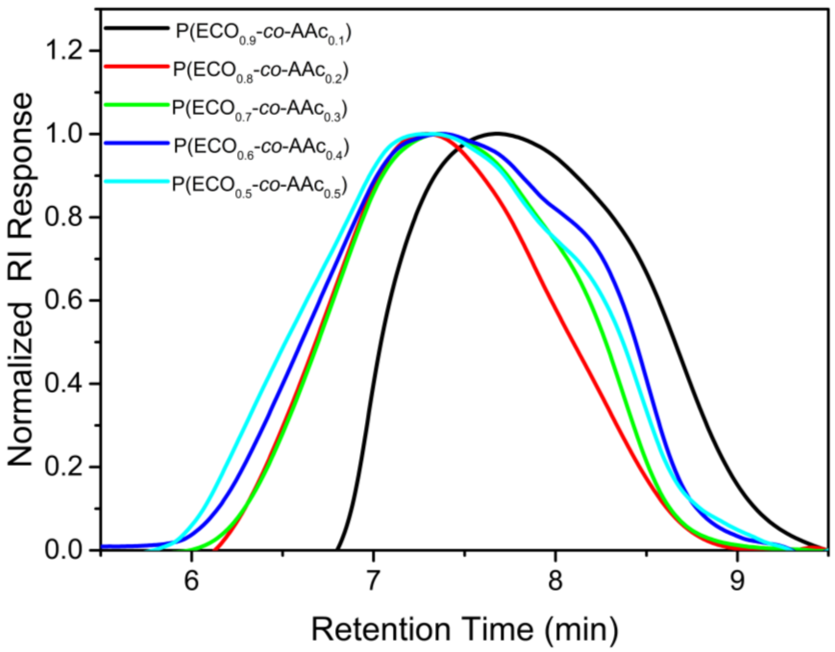


Figure S1. SEC traces of P(ECO-*co*-AAc) copolymers using DMF SEC calibrated with PMMA standards.

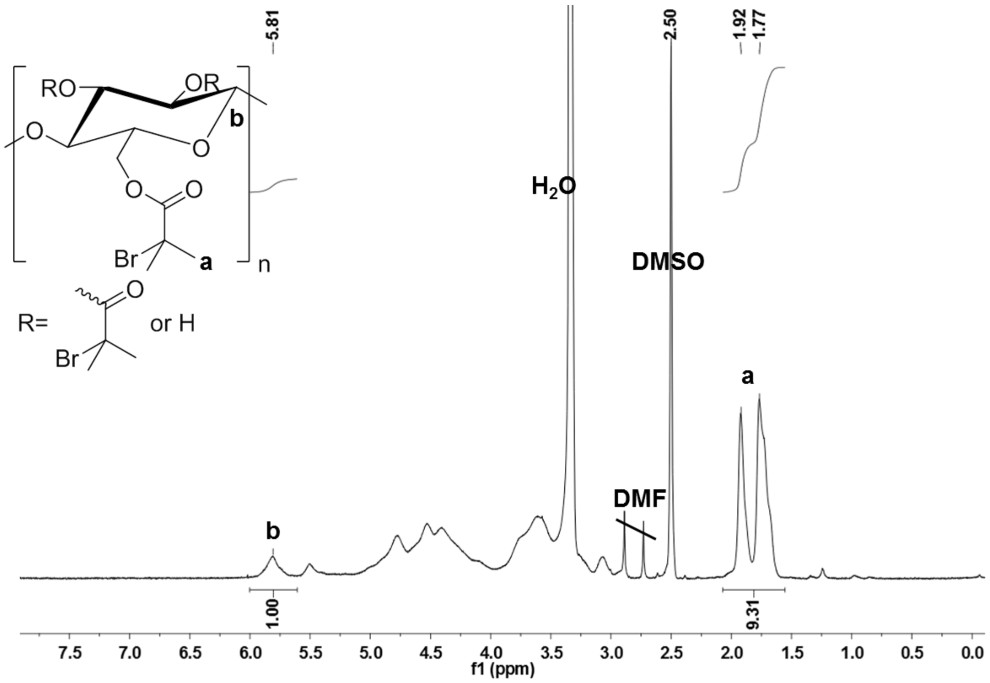


Figure S2. ^{1}H NMR spectrum of cellulose 2-bromoisobutyrylate (Cell-Br) with the degree of substitution of 1.55.

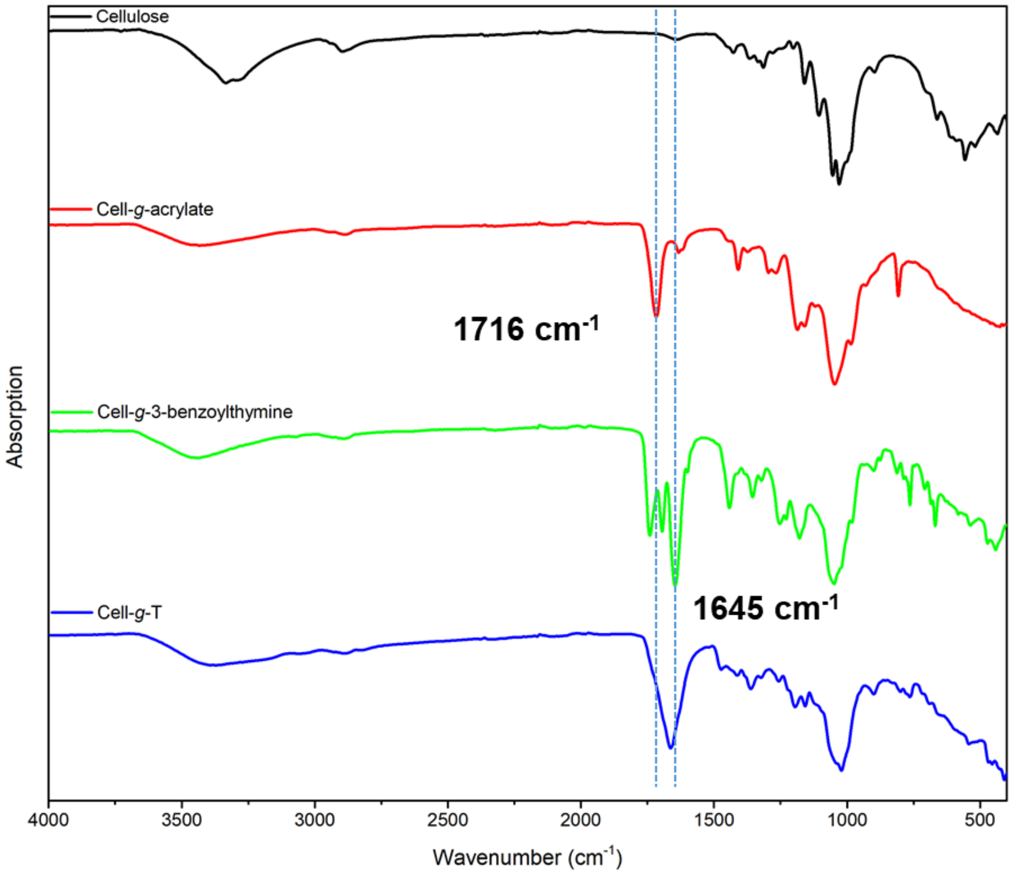


Figure S3. FT-IR spectra of cellulose, acrylate-*modified*-cellulose (Cell-acrylate), 3-benzoylthymine-*modified*-cellulose (Cell-3-benzoylthymine) and thymine-*modified*-cellulose (Cell-T).

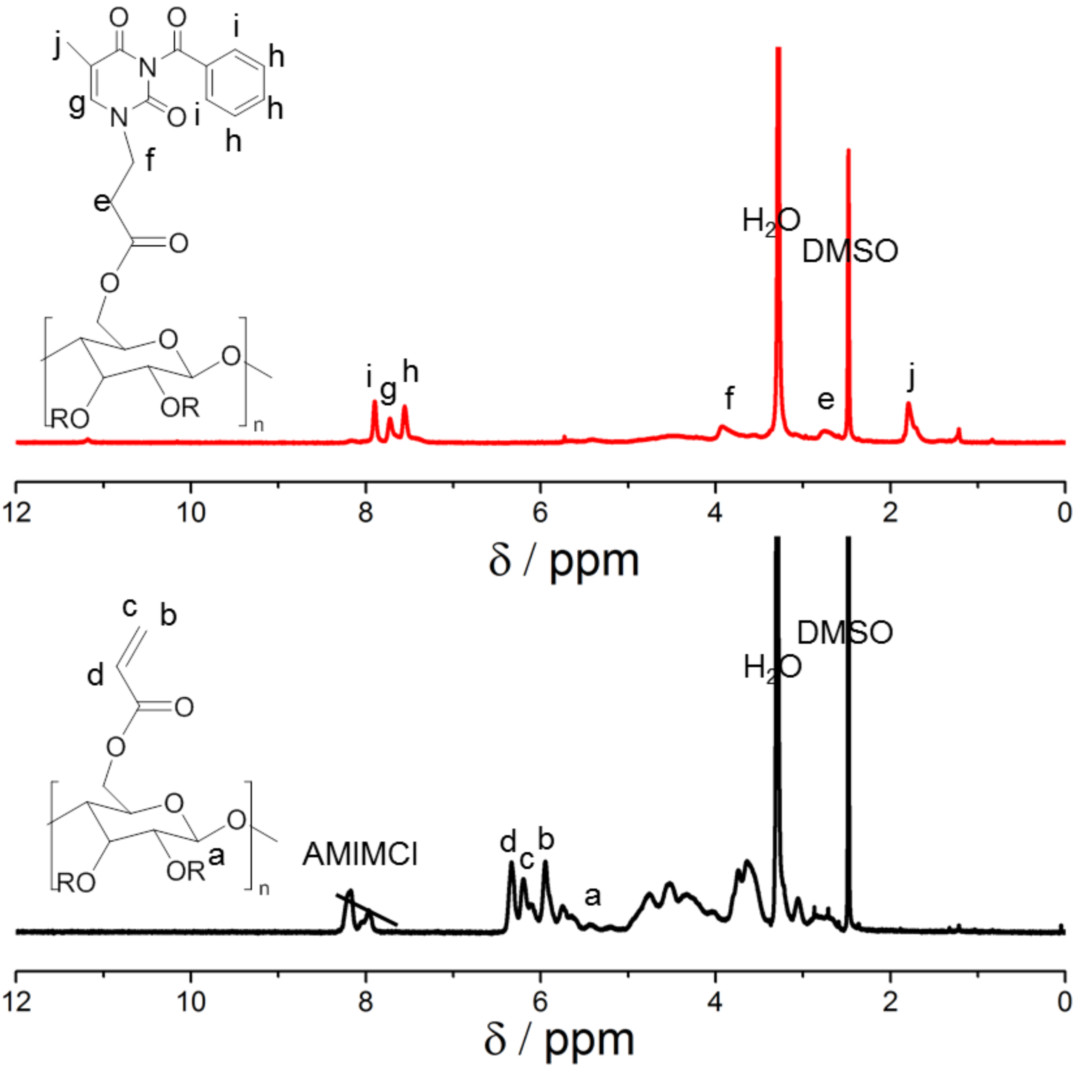


Figure S4. ^{1}H NMR spectra of acrylate-*modified*-cellulose and 3-benzoylthymine-*modified*-cellulose in DMSO-d_6.

Table S1. Compositions and mechanical properties of camellia oil based polymeric blends containing bottlebrush Cell-*g*-PTAc copolymers.

Polymeric Composites	Composition	Young's modulus (MPa)	Tensile strength (MPa)	ε at break (%)	Tensile toughness (10 kJ m^{-3})
PA3/Cell-*g*-PTAc$_5$-5%	P(ECO$_{0.7}$-*co*-AAc$_{0.3}$) + 5wt% Cell-*g*-PTAc$_5$	3.4 ±0.1	1.3 ±0.2	120 ±10	80 ±17
PA3/Cell-*g*-PTAc$_5$-10%	P(ECO$_{0.7}$-*co*-AAc$_{0.3}$) + 10 wt% Cell-*g*-PTAc$_5$	7.3 ±0.1	1.8 ±0.1	210 ±30	272 ±22
PA3/ Cell-*g*-PTAc$_{20}$-5%	P(ECO$_{0.7}$-*co*-AAc$_{0.3}$) + 5 wt% Cell-*g*-PTAc$_{20}$	2.4 ±0.3	1.7 ±0.1	228 ±20	207 ±15
PA3/Cell-*g*-PTAc$_{20}$-10%	P(ECO$_{0.7}$-*co*-AAc$_{0.3}$) + 10 wt% Cell-*g*-PTAc$_{20}$	7.1 ±0.2	1.6 ±0.1	97 ±10	111 ±13
PA4/Cell-*g*-PTAc$_5$-1%	P(ECO$_{0.6}$-*co*-AAc$_{0.4}$) + 1 wt% Cell-*g*-PTAc$_5$	Brittle[a]			
PA4/Cell-*g*-PTAc$_5$-10%	P(ECO$_{0.6}$-*co*-AAc$_{0.4}$) + 10 wt% Cell-*g*-PTAc$_5$				
PA4/Cell-*g*-PTAc$_{20}$-5%	P(ECO$_{0.6}$-*co*-AAc$_{0.4}$) + 5 wt% Cell-*g*-PTAc$_{20}$				
PA4/Cell-*g*-PTAc$_{20}$-10%	P(ECO$_{0.6}$-*co*-AAc$_{0.4}$) + 10 wt% Cell-*g*-PTAc$_{20}$				
PA5/Cell-*g*-PTAc$_5$-5%	P(ECO$_{0.5}$-*co*-AAc$_{0.5}$) + 5 wt% Cell-*g*-PTAc$_5$				
PA5/Cell-*g*-PTAc$_5$-10%	P(ECO$_{0.5}$-*co*-AAc$_{0.5}$) + 10wt% Cell-*g*-PTAc$_5$				
PA5/Cell-*g*-PTAc$_{20}$-5%	P(ECO$_{0.5}$-*co*-AAc$_{0.5}$) + 5 wt% Cell-*g*-PTAc$_{20}$				
PA5/Cell-*g*-PTAc$_{20}$-10%	P(ECO$_{0.5}$-*co*-AAc$_{0.5}$) + 10 wt% Cell-*g*-PTAc$_{20}$				

[a] The sample is too brittle to conduct mechanical tests.

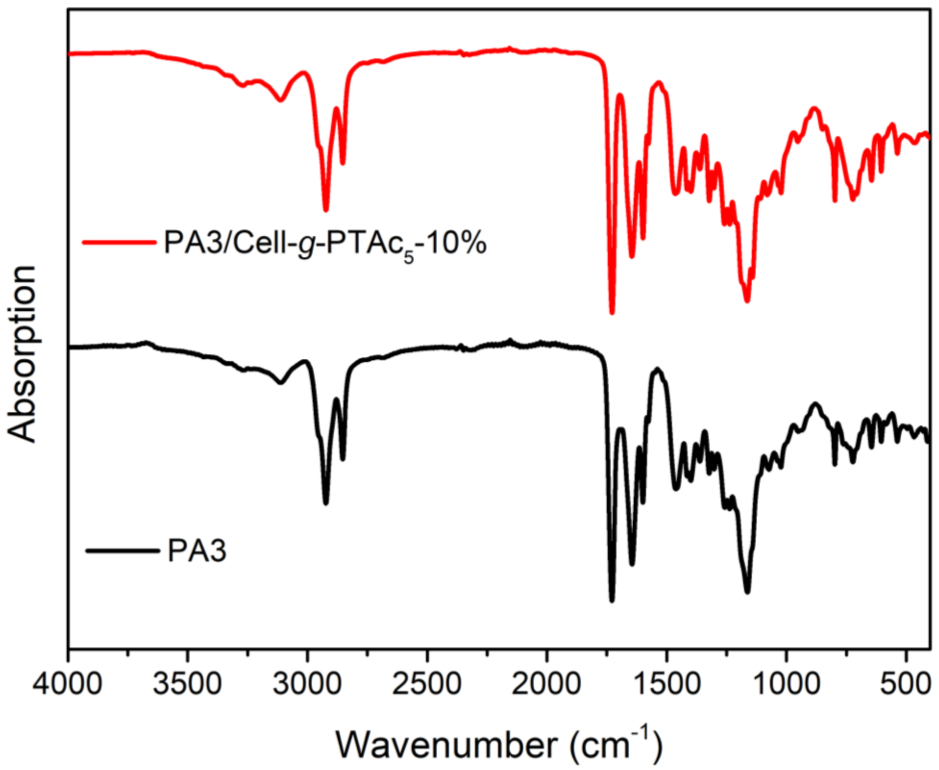


Figure S5. FT-IR spectra of PA3 and the blend PA3/Cell-*g*-PTAc$_5$-10%, showing the weak intermolecular interaction.

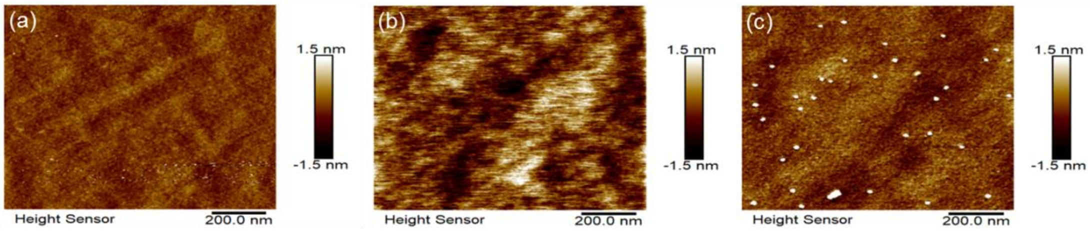


Figure S6. AFM images of (a) PA5, (b) Cell-T and (c) PA5/Cell-T-10% by spin-coating its DMF solution (0.1 mg mL^{-1}) on a silicon wafer, then annealing under a saturated DMF environment at 70 °C for 24 h.

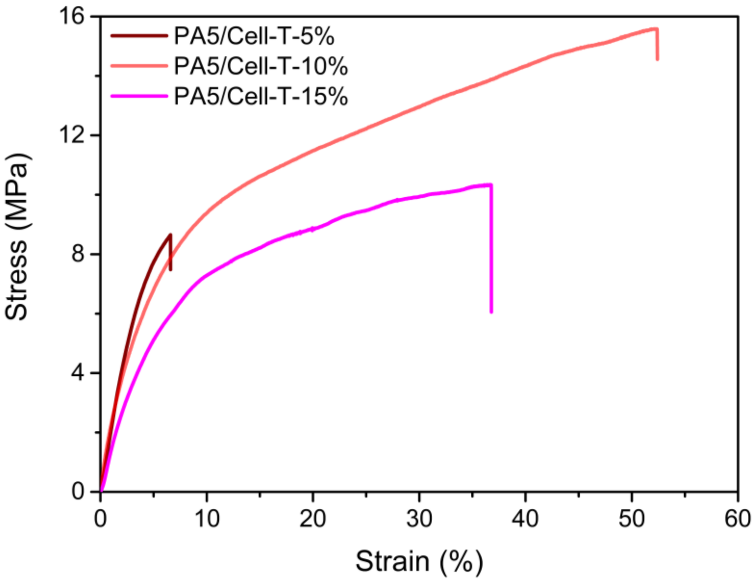


Figure S7. Stress-strain curves of PA5/Cell-T polymeric composites with variable weight ratios.

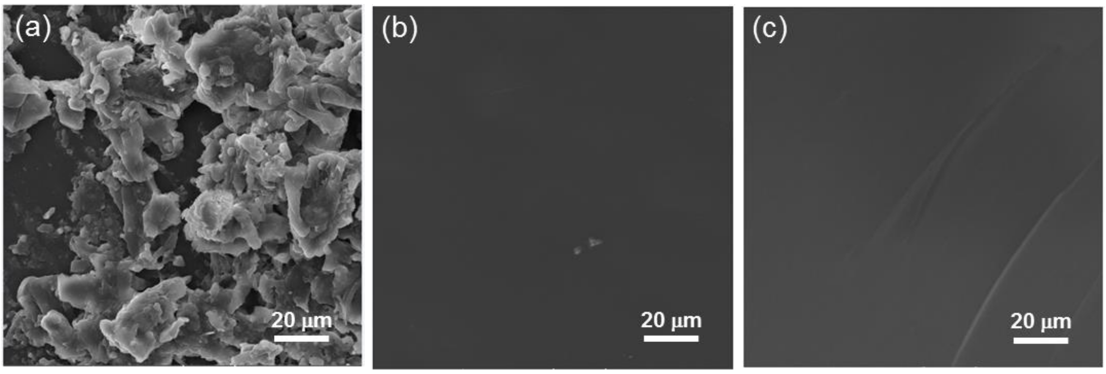


Figure S8. The characterization of PA3-5/Cell-T-10% blends. SEM images display the fractured surface of (a) PA3/Cell-T-10%; (b) PA4/Cell-T-10% and (c) PA5/Cell-T-10%, illustrating good phase compatibility in both PA4/Cell-T-10% and PA5/Cell-T-10%.

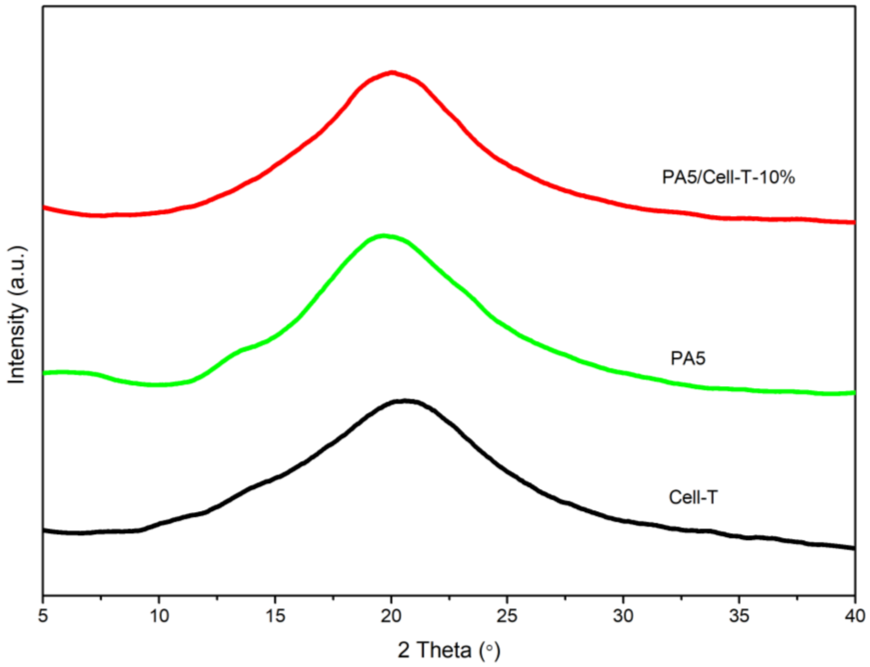


Figure S9. XRD profiles of Cell-T, PA5 and PA5/Cell-T-10%. For clarity, data were shifted vertically by arbitrary factors.

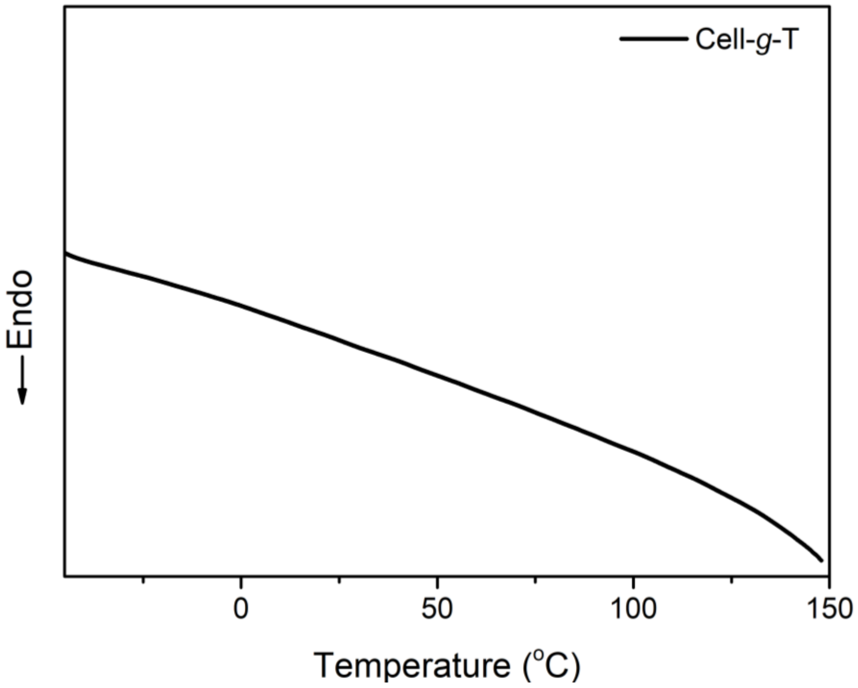


Figure S10. DSC curve of Cell-T, showing no obvious glass transition from -50 to 150 °C.

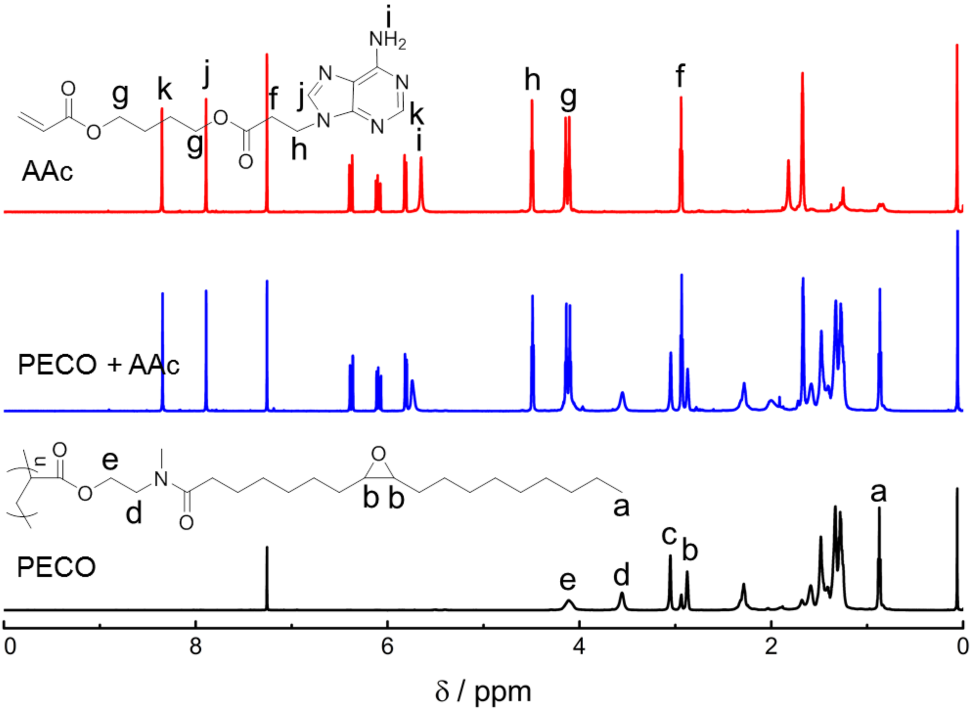


Figure S11. ^{1}H NMR spectra of PECO, AAc and their mixture, demonstrating no ring-opening of epoxy groups in PECO.

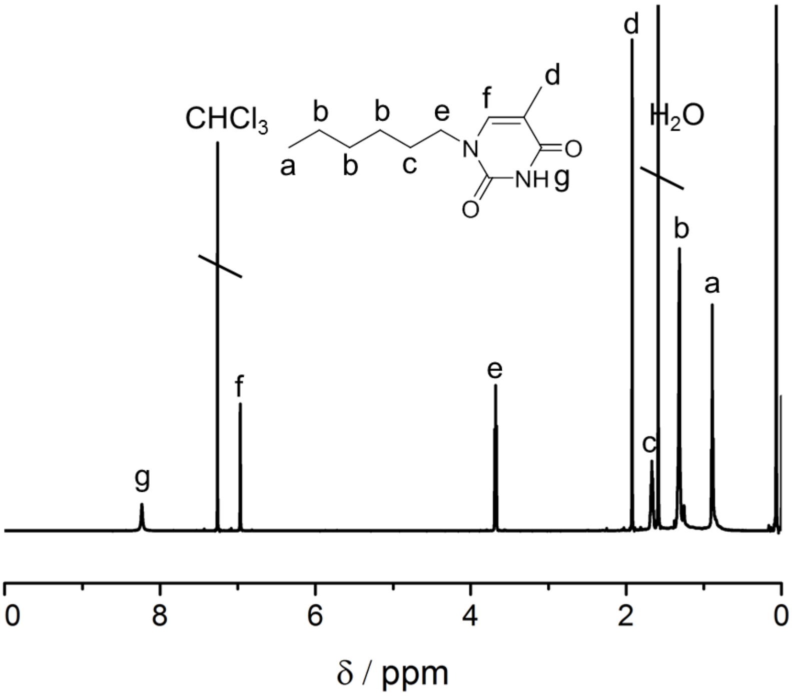


Figure S12. Assigned ^{1}H NMR spectrum of 9-hexylthymine (HeT) in $CDCl_3$.

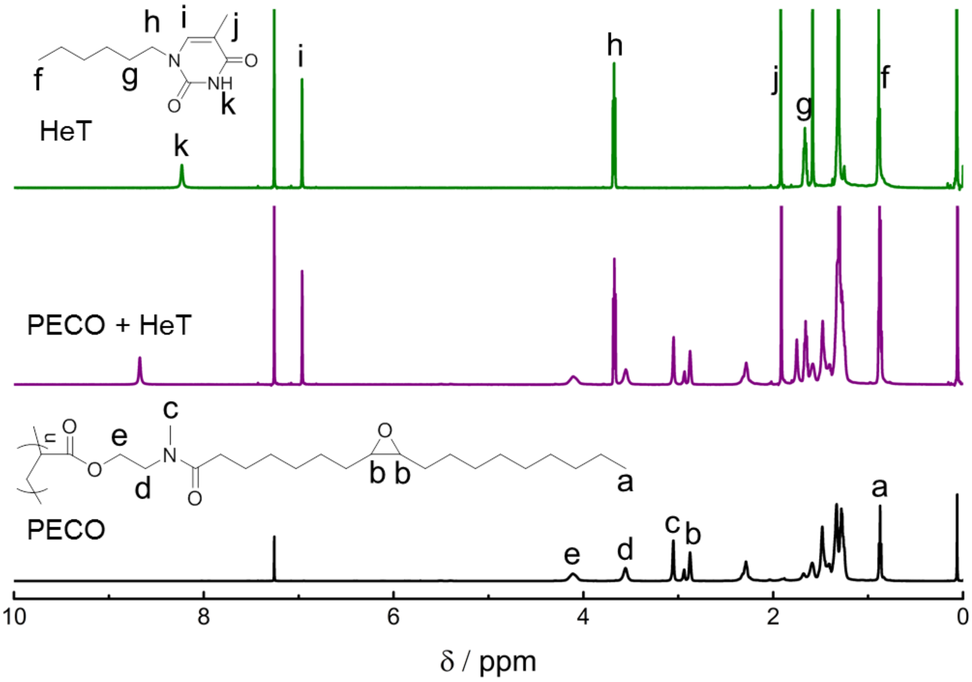


Figure S13. ^{1}H NMR spectra of PECO, HeT and their mixture, demonstrating no ring-opening of epoxy groups in PECO.

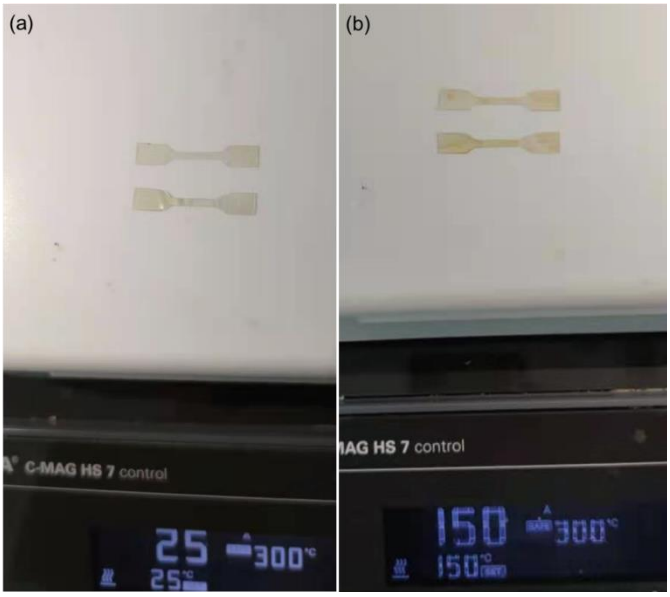


Figure S14. Photographs of PA5/Cell-T-10% at (a) 25 and (b) 150 °C, demonstrating the shape stability at the temperature as high as 150 °C.

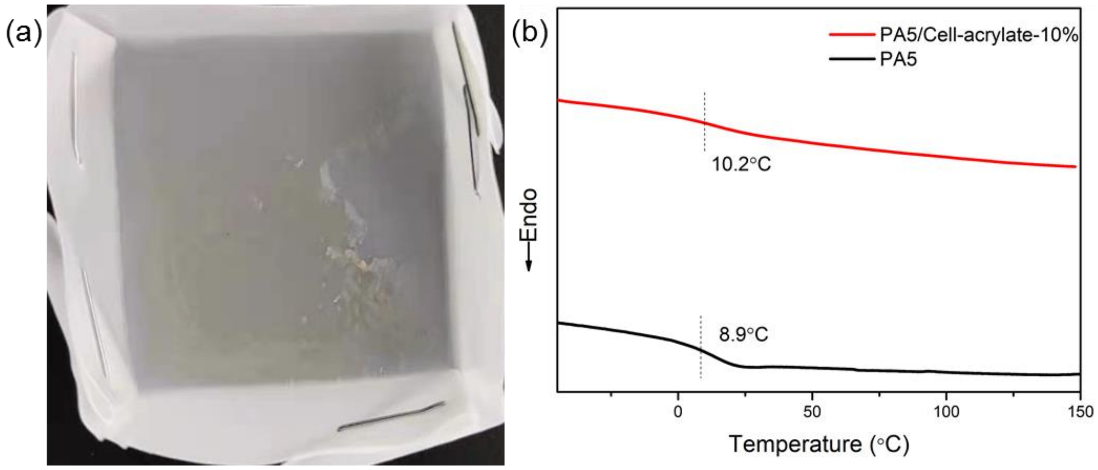


Figure S15. (a) The photograph of PA5/Cell-acrylate-10% showing the incompatibility of the two polymers; (b) DSC analyses of PA5 and PA5/Cell-acrylate-10%, demonstrating the weak intermolecular interaction between PA5 and Cell-acrylate without the complementary nucleobase.

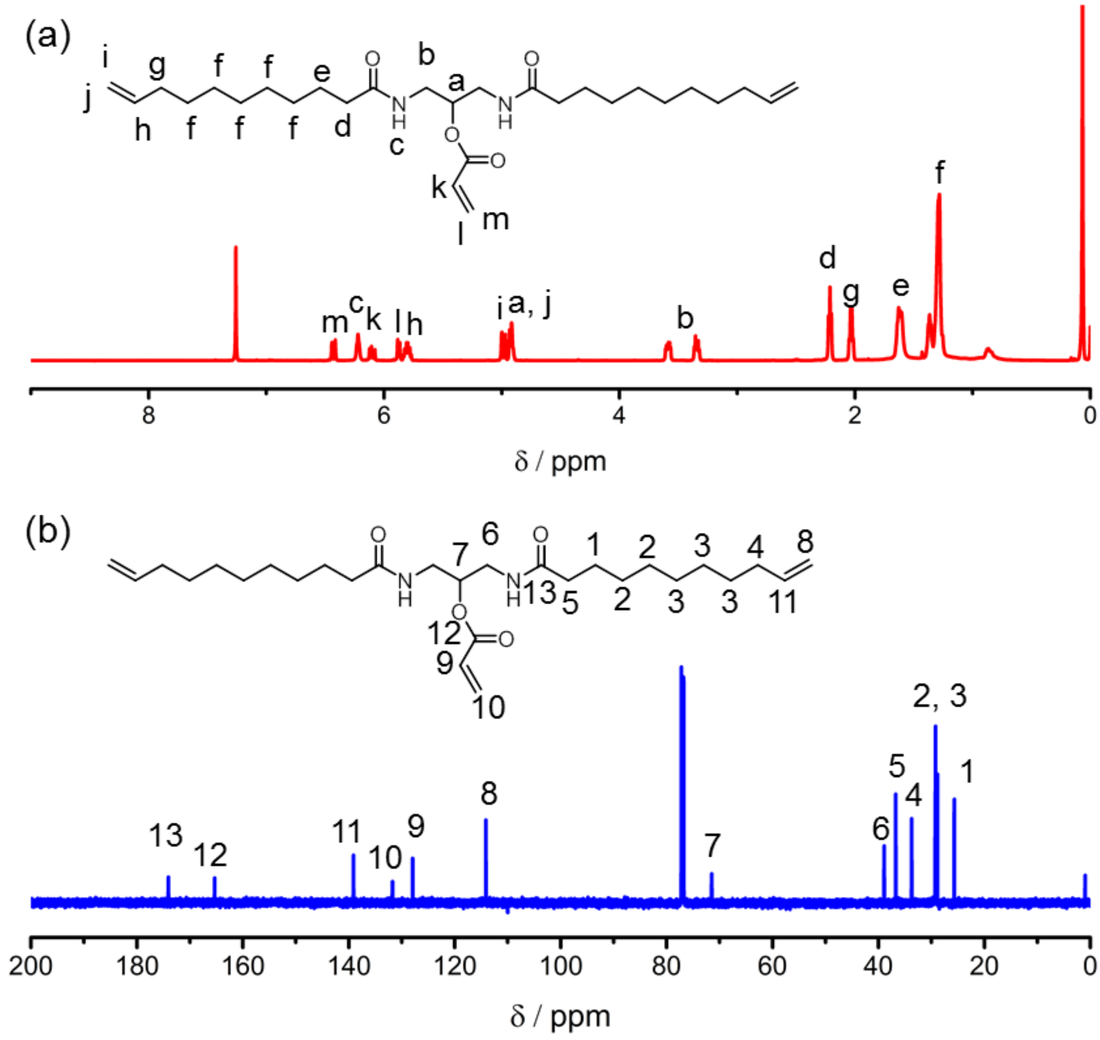


Figure S16. Assigned ^{1}H and ^{13}C NMR spectra of ACUDA in $CDCl_3$.

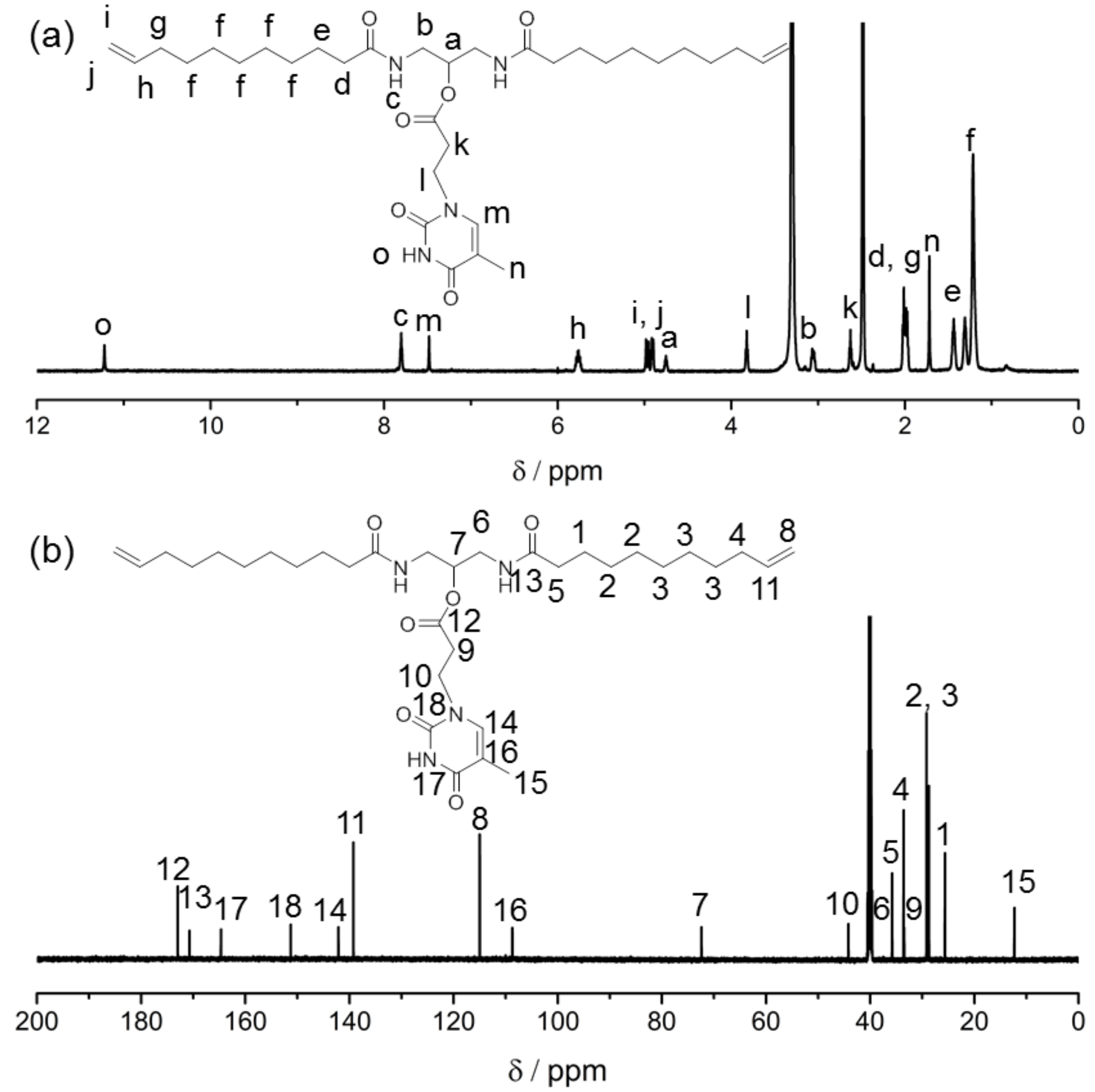


Figure S17. Assigned ^{1}H and ^{13}C NMR spectra of UDA-T in DMSO-d_6.

References

(1) Wang, Z.; Zhang, Y.; Jiang, F.; Fang, H.; Wang, Z. Synthesis and characterization of designed cellulose-graft-polyisoprene copolymers. *Polym. Chem.* **2014**, *5*, 3379-3388.

(2) Song, L.; Zhu, T.; Yuan, L.; Zhou, J.; Zhang, Y.; Wang, Z.; Tang, C. Ultra-strong long-chain polyamide elastomers with programmable supramolecular interactions and oriented crystalline microstructures. *Nat. Commun.* **2019**, *10*, 1315.