Supporting Information

Citric Acid-Modified Cellulose-Based Tough and Self-Healable Composite Formed by Two Kinds of Non-Covalent Bonding

Garry Sinawang, Taka-aki Asoh, Motofumi Osaki, Hiroyasu Yamaguchi, Akira Harada, Hiroshi Uyama*, and Yoshinori Takashima**

E-mail: harada@chem.sci.osaka-u.ac.jp, uyama@chem.eng.osaka-u.ac.jp, and takasima@chem.sci.osaka-u.ac.jp

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1. Experimental details

Materials: The HEA, 12-aminolauric acid, and acryloyl chloride were purchased from Tokyo Chemical Industry Co., Ltd. The γCD was obtained from Junsei Chemical Co. Ltd. The IRGACURE 184 was purchased from BASF Japan Co., Ltd. The cellulose powder, 1,4-dioxane, ethyl acetate, sodium hydroxide (NaOH), hydrochloric acid (HCl), and sodium sulfate (Na_2SO_4) were purchased from Nacalai Tesque Inc. 1-Butyl-3-methylimidazolium chloride was purchased from Sigma-Aldrich Corporation. The 6–acrylamido methylether–γCD (γCDAAmMe)[1] and PAcγCD[2] were prepared according to our previous report. The citric acid (hydrate) was purchased from Fujifilm Wako Pure Chemical Corporation. The CAC was prepared according to previous report.[3] The dimethyl sulfoxide (DMSO)–d_6 was obtained from Merck & Co., Inc. The water used for the preparation of the aqueous solutions was purified with a Millipore Elix 5 system. Other reagents were used without further purification.

Measurements:

NMR spectroscopy: The ^{1}H and ^{13}C spectra were recorded at 500 MHz with a JEOL JNM-ECA 500 NMR spectrometer at 25°C. In all NMR measurements, the chemical shifts were referenced to the solvent values [^{1}H NMR : δ = 0 ppm for tetramethylsilane (TMS) and 2.49 ppm for DMSO–d_6, ^{13}C NMR : δ = 0 ppm for TMS and 39.5 ppm for DMSO–d_6). The ^{1}H field gradient magic angle spinning (FGMAS) NMR spectra were recorded at 400 MHz with a JEOL JNM-ECA 400WB NMR spectrometer. The sample spinning rate was 7 kHz with a relaxation delay of 10 s at 30°C. Chemical shifts were referenced to hydrogen oxide deuterium (HOD) as a standard (δ = 4.79 ppm). The ^{13}C cross-polarization magic angle spinning (CPMAS) NMR was recorded at 75 MHz in the solid state on a Chemagnetics JNM-CMX300W spectrometer with a sample spinning rate of 4.0 kHz at 30°C.

IR spectrometry: The attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) were recorded using JASCO FT/IR-6100 spectrometer in the wavenumber range from 4000 to 400 cm^{-1} in ATR method.

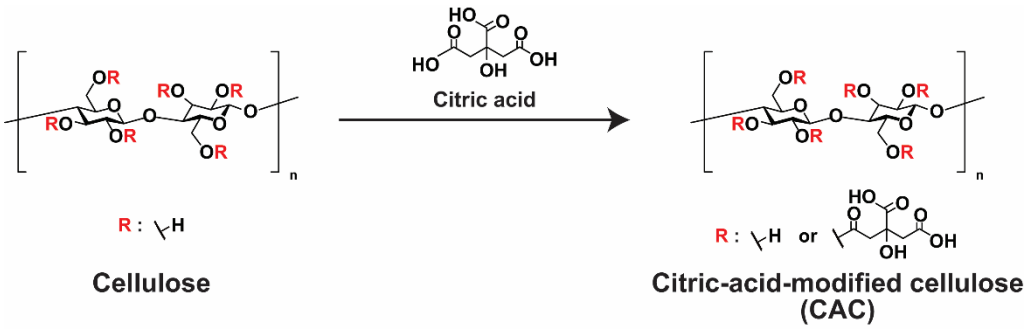
Scanning electron microscope (SEM): SEM images of surfaces were examined with a JEOL JSM-7600F instrument with an accelerating voltage of 2 kV.

Mechanical property measurement: The mechanical properties (fracture energy, Young's modulus, and self-healing) of the CAC-based composites were measured using Autograph AG-X plus (Shimadzu Co.) equipped with a 50 N load cell, at a specific deformation rate (1 $mm \cdot s^{-1}$).

Laser scanning confocal microscope: The laser scanning confocal microscope images were examined using a Keyence Co. VK-X250.

Differential scanning calorimeter (DSC) measurements: Glass transition temperatures (T_g) of the samples were determined by Hitachi High-Technologies Corporation DSC7020 System with a heating rate 10°C/min.

2. Preparation of citric acid-modified cellulose (CAC)



Scheme S1. Preparation of citric-acid-modified cellulose (CAC).

Citric acid-modified cellulose (CAC) were prepared by dispersing 30 g of cellulose in 200 mL deionized water with addition of 1.4 mL 1 M NaOH aqueous solution. The mixture was stirred for several minutes and 90 g citric acid was added. The mixture was heated to 130 ºC for 12 h until all the component completely reacted. After the reaction, the water was evaporated. The supernatant was washed with water until unreacted citric acid was completely removed (pH 7) then followed washing with methanol and acetone. CAC was obtained by evaporating under pressure. CAC was characterized by FTIR measurement. The content of carboxylic acid is 1.8 mmol·g^{-1} (determined by conductivity titration from CAC aqueous dispersion).

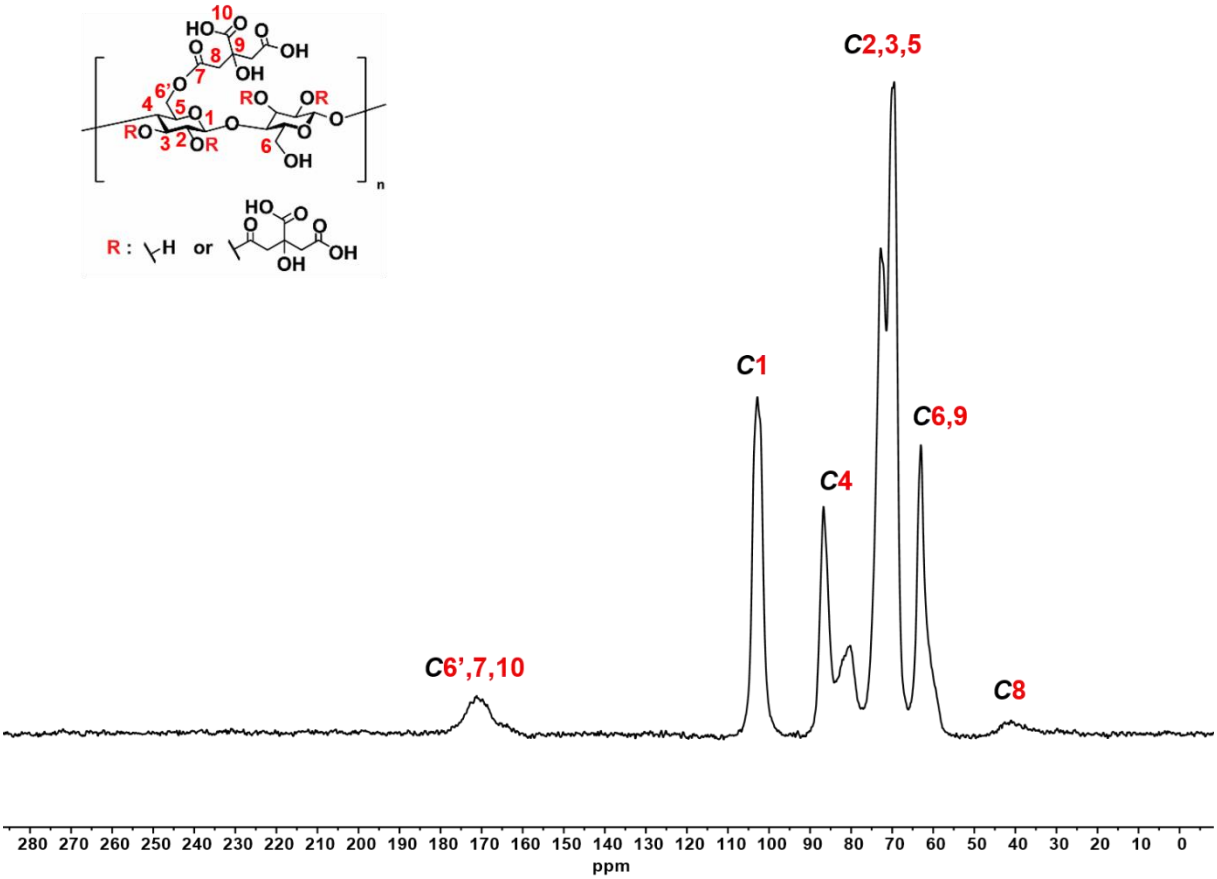


Figure S1. Solid-state ^{13}C CPMAS NMR spectrum of **CAC** (TMS for standard, 75 MHz, 25 ºC, rotation frequency = 7 kHz).

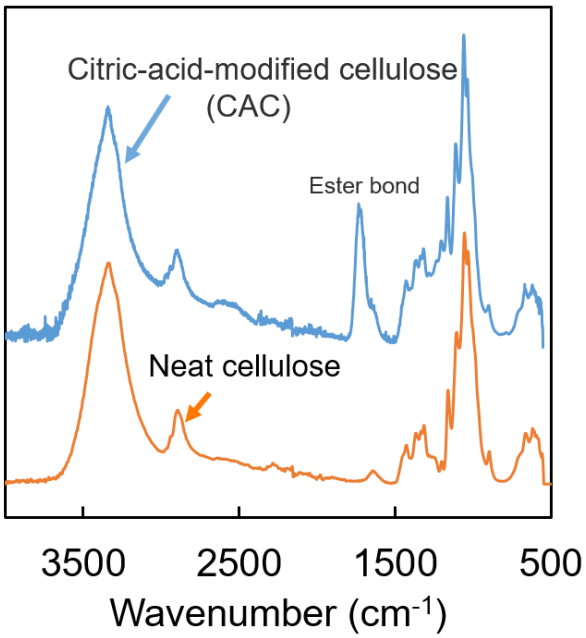
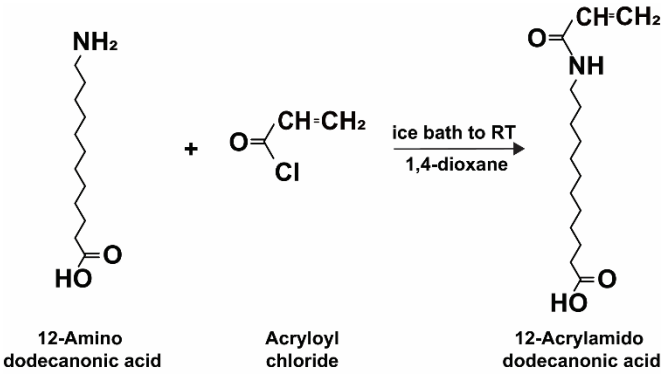


Figure S2. ATR-FTIR spectra of citric acid-modified cellulose (CAC) compared with neat cellulose

3. Preparation of 12-acrylamido dodecanoic acid (Dod)



Scheme S2. Preparation of 12-acrylamido dodecanoic acid (Dod).

12-Aminododecanoic acid (5 g, 323 mmol) and 2M NaOH (2.32 g NaOH in 29 mL water) were dissolved in 1,4-dioxane (0.10 L) and put in ice bath. After the solution was cooled, acryloyl chloride (3.15 g, 35 mmol) was added dropwise. The solution was stirred overnight in room temperature. Next day, HCl was added to solution until pH 2-3 and then the solution was extracted with ethyl acetate. After extraction, the organic phase was filtrated to remove the salt and then extracted again with ethyl acetate. Then, the solution was evaporated and dried at 40 ºC for 24 hours. Yield: 90%.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) of Dod: δ = 11.92 (s, 1H, -N*H*), 7.99 (t, *J* = 5.6 Hz, 1H, -COO*H*), 6.16 (dd, *J* = 17.1, 10.1 Hz, 1H, CH_2CH-), 6.02 (dd, *J* = 17.1, 2.3 Hz, 1H, CH_2CH-), 5.51 (dd, *J* = 10.1, 2.3 Hz, 1H, CH_2CH-), 3.06 (td, *J* = 7.1, 5.7 Hz, 2H, -$NHCH_2CH_2$-), 2.14 (t, *J* = 7.4 Hz, 2H, -CH_2CH_2COOH-), 1.44 (t, *J* = 7.3 Hz, 2H,-$CH_2(CH_2)_{11}CH_2COOH$), 1.37 (q, *J* = 6.8 Hz, 2H,-$CH_2(CH_2)_{11}CH_2COOH$), 1.21 (t, *J* = 2.7 Hz, 14H,-$CH_2(CH_2)_{11}CH_2COOH$).

^{13}C NMR (125 MHz, DMSO-*d*$_6$) of Dod: δ = 175.05, 164.98, 132.44, 125.27, 39.05, 34.20, 29.55, 29.49, 29.46, 29.42, 29.26, 29.07, 26.97, 25.02.

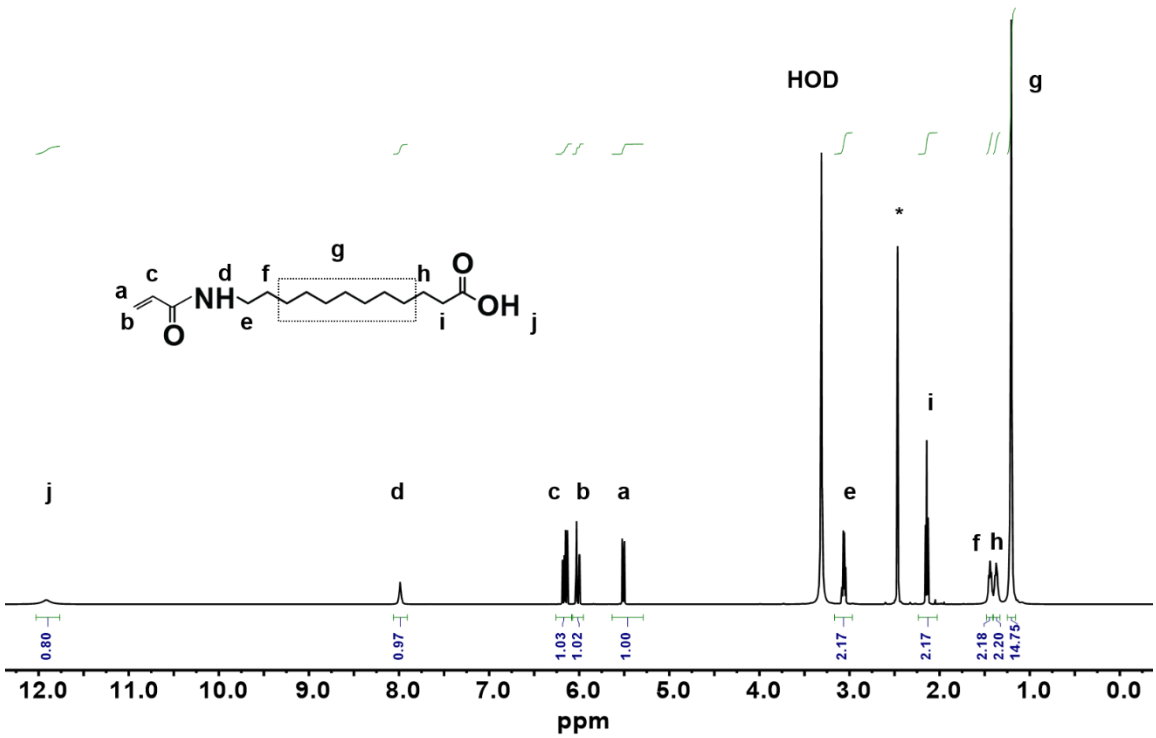


Figure S3. 500 MHz ^{1}H NMR spectrum of Dod in DMSO-d_6.
(TMS for standard, 400 MHz, 25 ºC, rotation frequency = 7 kHz).

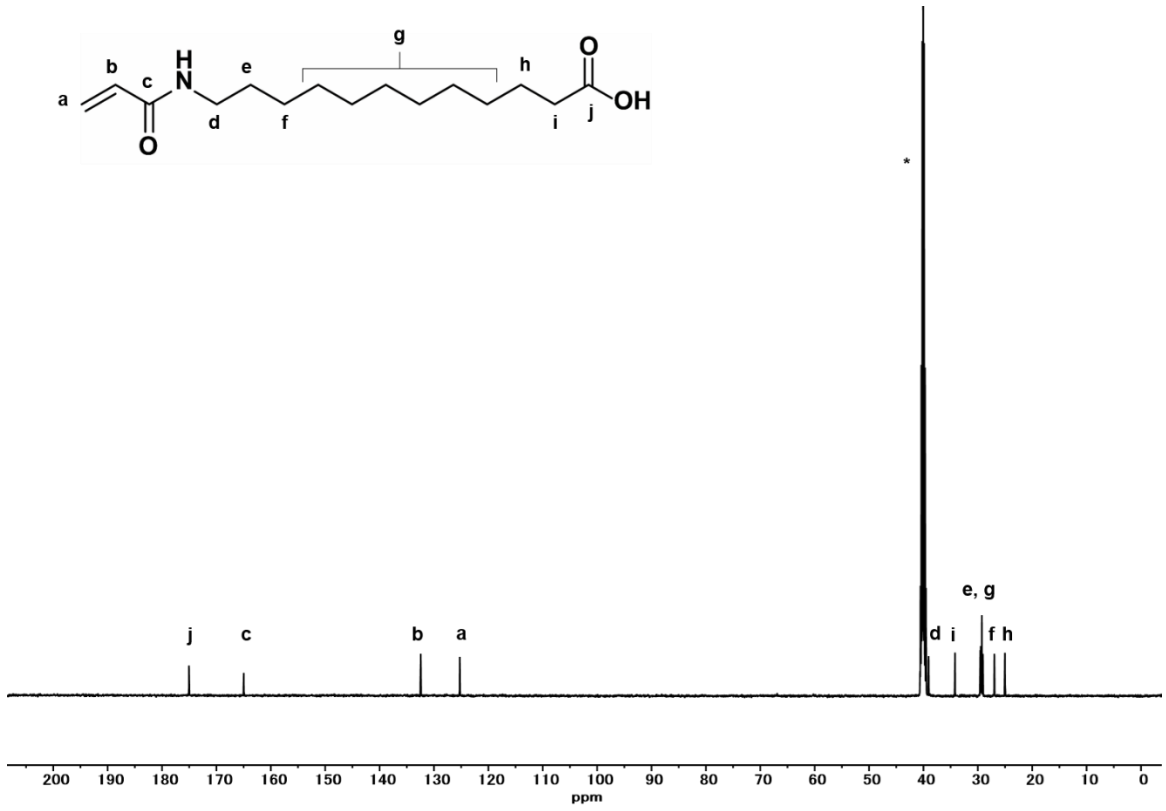


Figure S4. 125 MHz ^{13}C NMR spectrum of Dod in DMSO-d_6.
(TMS for standard, 400 MHz, 25 ºC, rotation frequency = 7 kHz).

4. Preparation of materials

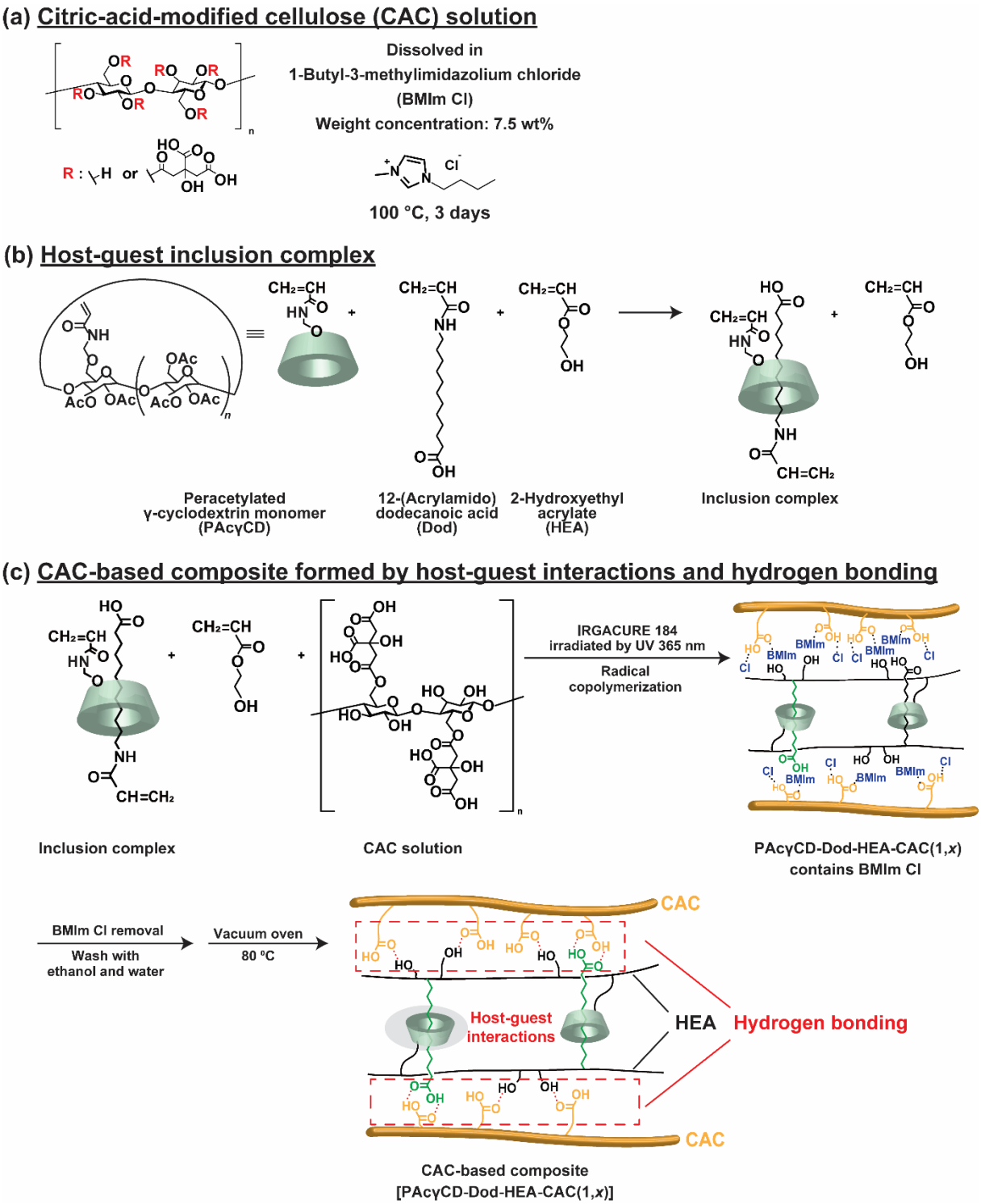


Figure S5. Preparation of CAC-based composite formed by hydrogen bonding and host-guest interactions [PAcγCD-Dod-HEA-CAC(1,*x*)]

Preparation of CAC-based composite **[PAcγCD-Dod-HEA-CAC(1,*x*)]**
CAC solution was prepared by dissolving CAC (1, 3, or 5 wt%) in BMIm Cl at 7.5wt% concentration at 100 ºC for 3 days. PAcγCD (1 mol%) and Dod (1 mol%) were sonicated in HEA (98 mol%) for 90 minutes. CAC solution was added into host-guest inclusion complexes and radical copolymerized using IRGACURE 184 (0.2 mol%) successfully giving CAC reinforced supramolecular materials [PAcγCD-Dod-HEA-CAC(1,*x*)] that still containing BMIm Cl. Then PAcγCD-Dod-HEA-CAC(1,*x*)were washed with ethanol and water to remove remaining BMIm Cl and dried in vacuum oven 80 ºC for 24 h. The notation "1" at PAcγCD-Dod-HEA-CAC(1,*x*) indicates mol% of host guest inclusion complex between PAcγCD and Dod units and "*x*" indicates the wt% of CAC.

Table S1. Preparation of PAcγCD-Dod-HEA-CAC (1,*x*).

(1,*x*)	PAcγCD / g	Dod / mg	HEA / g	CAC / g	IRGACURE 184 / mg
(1,1)	0.41	47	2.0	0.025	7.2
(1,3)	0.41	47	2.0	0.074	7.2
(1,5)	0.41	47	2.0	0.12	7.2

Preparation of polymer without CAC **[PAcγCD-Dod-HEA(1)]**
PAcγCD (1 mol%) and Dod (1 mol%) were sonicated in HEA (98 mol%) for 90 minutes to perform inclusion complex. Then the inclusion complex solution was radical copolymerized using IRGACURE 184 (0.2 mol%) to supramolecular elastomer [PAcγCD-Dod-HEA(1)]. Then PAcγCD-Dod-HEA(1) were dried in vacuum oven 80 ºC for 24 h. The notation "1" at PAcγCD-Dod-HEA(1) indicates mol% of host guest inclusion complex between PAcγCD and Dod units.

Table S2. Preparation of PAcγCD-Dod-HEA(1).

(1)	PAcγCD / g	Dod / mg	HEA / g	IRGACURE 184 / mg
(1)	0.41	47	2.0	7.2

Preparation of host polymer with CAC **[PAcγCD-HEA-CAC(1,5)]**
CAC solution was prepared by dissolving CAC (5 wt%) in BMIm Cl at 7.5wt% concentration at 100 ºC for 3 days. PAcγCD (1 mol%) was sonicated in HEA (99 mol%) for 10 minutes. CAC solution was added into PAcγCD-HEA solution and radical copolymerized using IRGACURE 184 (0.2 mol%) successfully giving CAC reinforced materials [PAcγCD-HEA-CAC(1,5)] that still containing BMIm Cl. Then PAcγCD-HEA-CAC(1,5)were washed with ethanol and water to remove remaining BMIm Cl and dried in vacuum oven 80 ºC for 24 h. The notation "1" at PAcγCD-HEA-CAC(1,5) indicates mol% of PAcγCD units and "5" indicates the wt% of CAC.

Table S3. Preparation of **PAc*γ*CD-HEA-CAC(1,5)**.

x	PAcγCD / g	HEA / g	CAC / g	IRGACURE 184 / mg
5	0.41	2.0	0.12	7.1

***Preparation of guest polymer with CAC* [Dod-HEA-CAC(1,5)]**
CAC solution was prepared by dissolving CAC (5 wt%) in BMIm Cl at 7.5wt% concentration at 100 ºC for 3 days. Dod (1 mol%) was sonicated in HEA (99 mol%) for 10 minutes. CAC solution was added into Dod-HEA solution and radical copolymerized using IRGACURE 184 (0.2 mol%) successfully giving CAC reinforced materials [Dod-HEA-CAC(1,5)] that still containing BMIm Cl. Then Dod-HEA-CAC(1,5) were washed with ethanol and water to remove remaining BMIm Cl and dried in vacuum oven 80 ºC for 24 h. The notation "1" at Dod-HEA-CAC(1,5) indicates mol% of Dod units and "5" indicates the wt% of CAC.

Table S4. Preparation of **PAcγCD-HEA-CAC(1,5)**.

x	Dod / mg	HEA / g	CAC / g	IRGACURE 184 / mg
5	47	2.00	0.11	7.1

***Preparation of linear polymer with CAC* [HEA-CAC(5)]**
CAC solution was prepared by dissolving CAC (1 and 5 wt%) in BMIm Cl at 7.5wt% concentration at 100 ºC for 3 days. CAC solution was added into HEA and radical copolymerized using IRGACURE 184 (0.2 mol%) successfully giving CAC reinforced materials [HEA-CAC(5)] that still containing BMIm Cl. Then HEA-CAC(5) were washed with ethanol and water to remove remaining BMIm Cl and dried in vacuum oven 80 ºC for 24 h. The notation "5" indicates the wt% of CAC.

Table S5. Preparation of **HEA-CAC(1,5)**.

x	HEA / g	CAC / g	IRGACURE 184 / g
5	2.0	0.10	7.0

***Preparation of CAC-based composite with guest unit without carboxyl group* [PAcγCD-DAA-HEA-CAC(1,5)]**
CAC solution was prepared by dissolving CAC (5 wt%) in BMIm Cl at 7.5wt% concentration at 100 ºC for 3 days. PAcγCD (1 mol%) and DAA (1 mol%) were sonicated in HEA (98 mol%) for 90 minutes. CAC solution was added into host-guest inclusion complexes and radical copolymerized using IRGACURE 184 (0.2 mol%) successfully giving CAC reinforced supramolecular materials [PAcγCD-Dod-HEA-CAC(1,*x*)] that still containing BMIm Cl. Then PAcγCD-Dod-HEA-CAC(1,*x*)were washed with ethanol and water to remove remaining BMIm Cl and dried in vacuum oven 80 ºC for 24 h. The notation "1" at PAcγCD-Dod-HEA-CAC(1,*x*) indicates mol% of host guest inclusion complex between PAcγCD and Dod units and "*x*" indicates the wt% of CAC.

Table S6. Preparation of PAcγCD-DAA-HEA-CAC (1,5).

x	PAcγCD / g	DAA / mg	HEA / g	CAC / g	IRGACURE 184 / mg
5	0.41	42	2.0	0.12	7.2

Preparation of CAC-based composite with main chain without hydroxyl group **[PAcγCD-Dod-EA-CAC(1,5)]**

CAC solution was prepared by dissolving CAC (5 wt%) in BMIm Cl at 7.5wt% concentration at 100 ºC for 3 days. PAcγCD (1 mol%) and DAA (1 mol%) were sonicated in HEA (98 mol%) for 90 minutes. CAC solution was added into host-guest inclusion complexes and radical copolymerized using IRGACURE 184 (0.2 mol%) successfully giving CAC reinforced supramolecular materials [PAcγCD-Dod-HEA-CAC(1,*x*)] that still containing BMIm Cl. Then PAcγCD-Dod-HEA-CAC(1,*x*)were washed with ethanol and water to remove remaining BMIm Cl and dried in vacuum oven 80 ºC for 24 h. The notation "1" at PAcγCD-Dod-HEA-CAC(1,*x*) indicates mol% of host guest inclusion complex between PAcγCD and Dod units and "*x*" indicates the wt% of CAC.

Table S7. Preparation of PAcγCD-Dod-HEA-CAC (1,5).

x	PAcγCD / g	Dod / mg	EA / g	CAC / g	IRGACURE 184 / mg
5	0.48	55	2.0	0.13	8.3

Preparation of CAC-based composite with no carboxyl and hydroxyl group **[PAcγCD-DAA-EA-CAC(1,5)]**

CAC solution was prepared by dissolving CAC (5 wt%) in BMIm Cl at 7.5wt% concentration at 100 ºC for 3 days. PAcγCD (1 mol%) and DAA (1 mol%) were sonicated in HEA (98 mol%) for 90 minutes. CAC solution was added into host-guest inclusion complexes and radical copolymerized using IRGACURE 184 (0.2 mol%) successfully giving CAC reinforced supramolecular materials [PAcγCD-Dod-HEA-CAC(1,*x*)] that still containing BMIm Cl. Then PAcγCD-Dod-HEA-CAC(1,*x*)were washed with ethanol and water to remove remaining BMIm Cl and dried in vacuum oven 80 ºC for 24 h. The notation "1" at PAcγCD-Dod-HEA-CAC(1,*x*) indicates mol% of host guest inclusion complex between PAcγCD and Dod units and "*x*" indicates the wt% of CAC.

Table S8. Preparation of PAcγCD-DAA-EA-CAC (1,5).

x	PAcγCD / g	DAA / mg	EA / g	CAC / g	IRGACURE 184 / mg
5	0.48	49	2.0	0.13	8.3

5. NMR characterization of materials

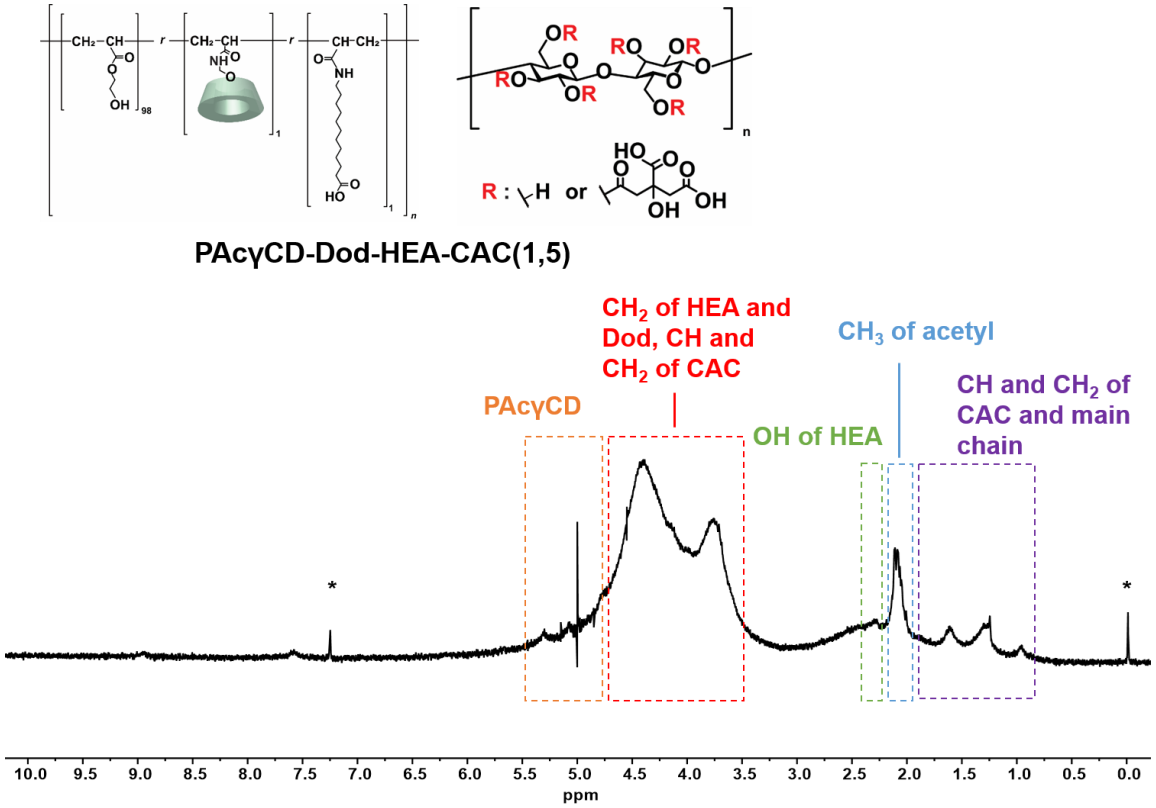


Figure S6. Solid-state ^{1}H FGMAS NMR spectrum of **PAcγCD-Dod-HEA-CAC(1,5)** (TMS for standard, 400 MHz, 25 ºC, rotation frequency = 7 kHz).

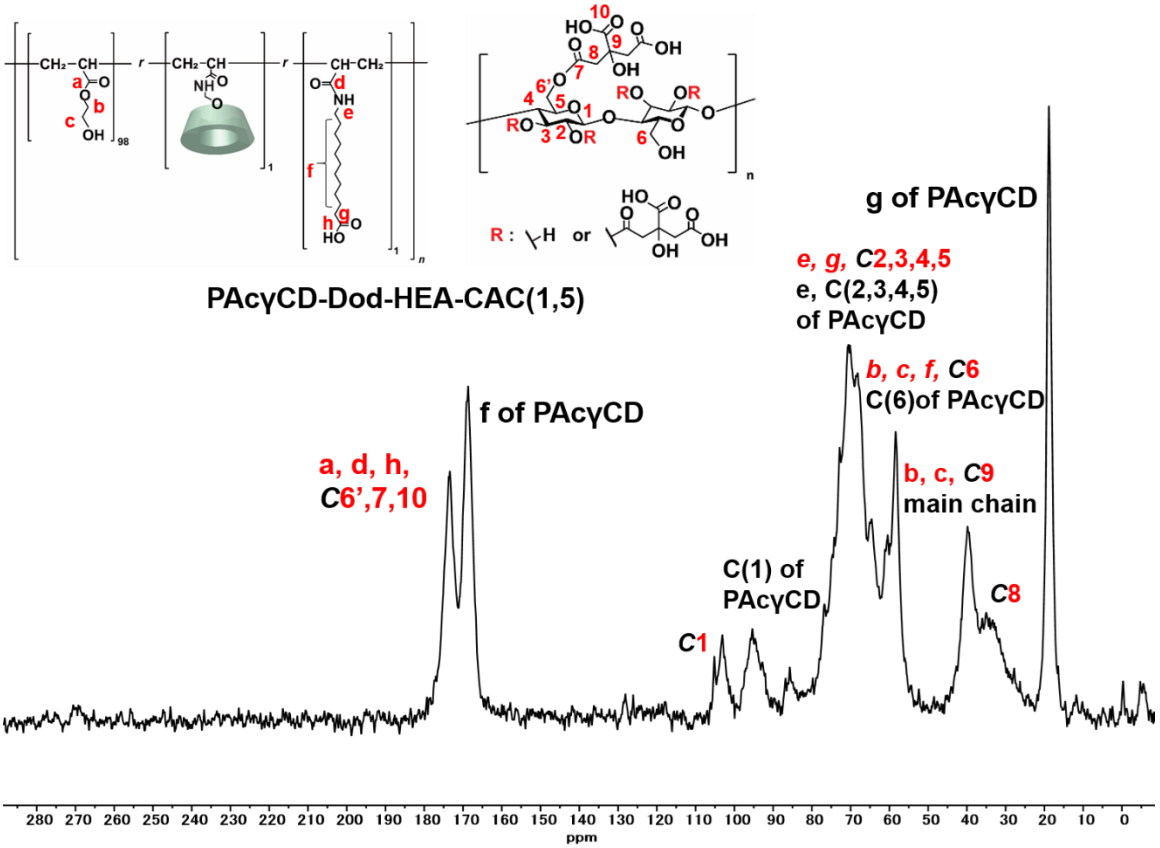


Figure S7. Solid-state ^{13}C CPMAS NMR spectrum of **PAcγCD-Dod-HEA-CAC(1,5)** (TMS for standard, 75 MHz, 25 ºC, rotation frequency = 7 kHz).

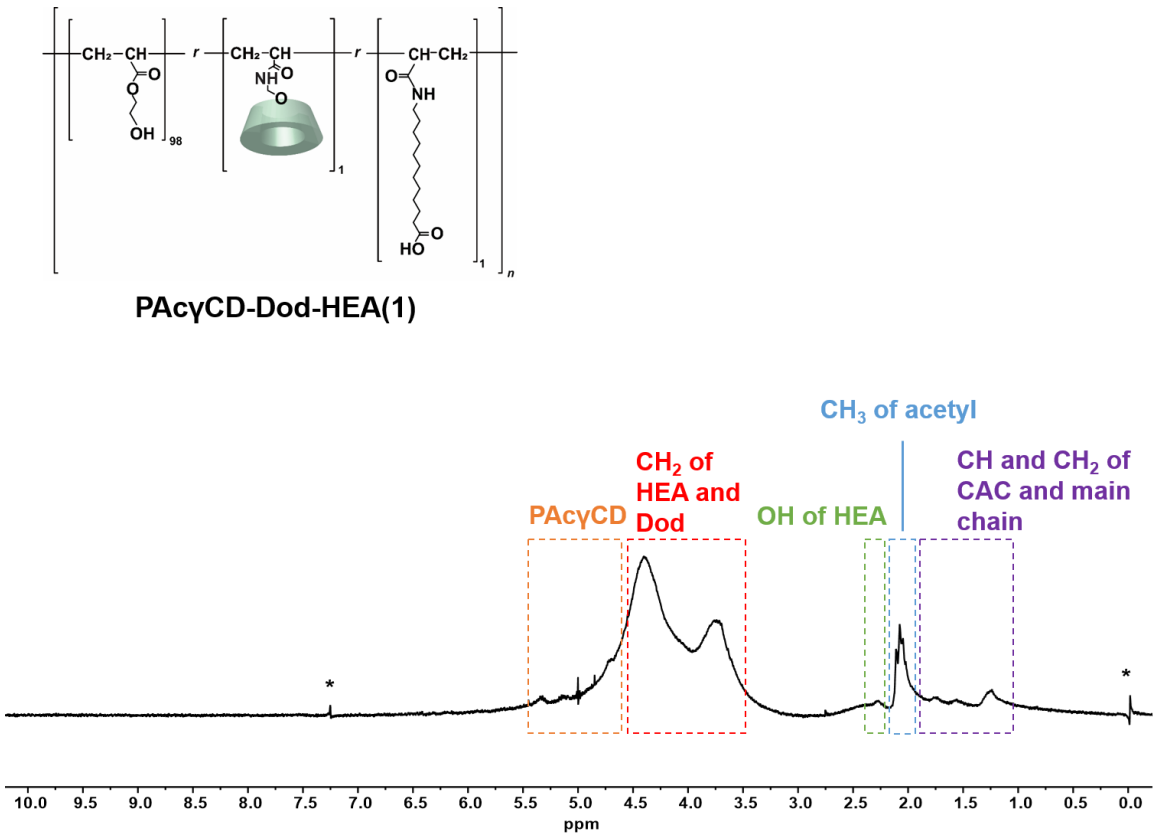


Figure S8. Solid-state ^{1}H FGMAS NMR spectrum of **PAcγCD-Dod-HEA(1)** (TMS for standard, 400 MHz, 25 ºC, rotation frequency = 7 kHz).

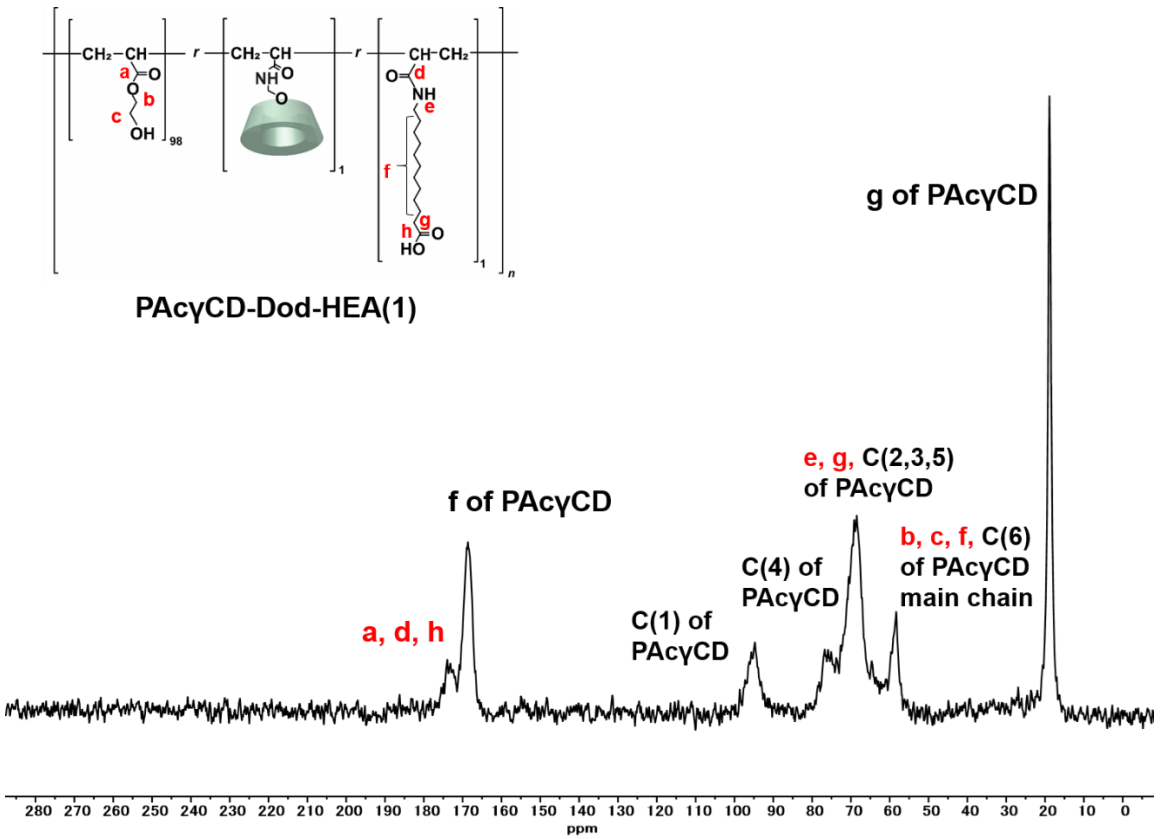


Figure S9. Solid-state ^{13}C FGMAS NMR spectrum of **PAcγCD-Dod-HEA(1)** (TMS for standard, 75 MHz, 25 ºC, rotation frequency = 7 kHz).

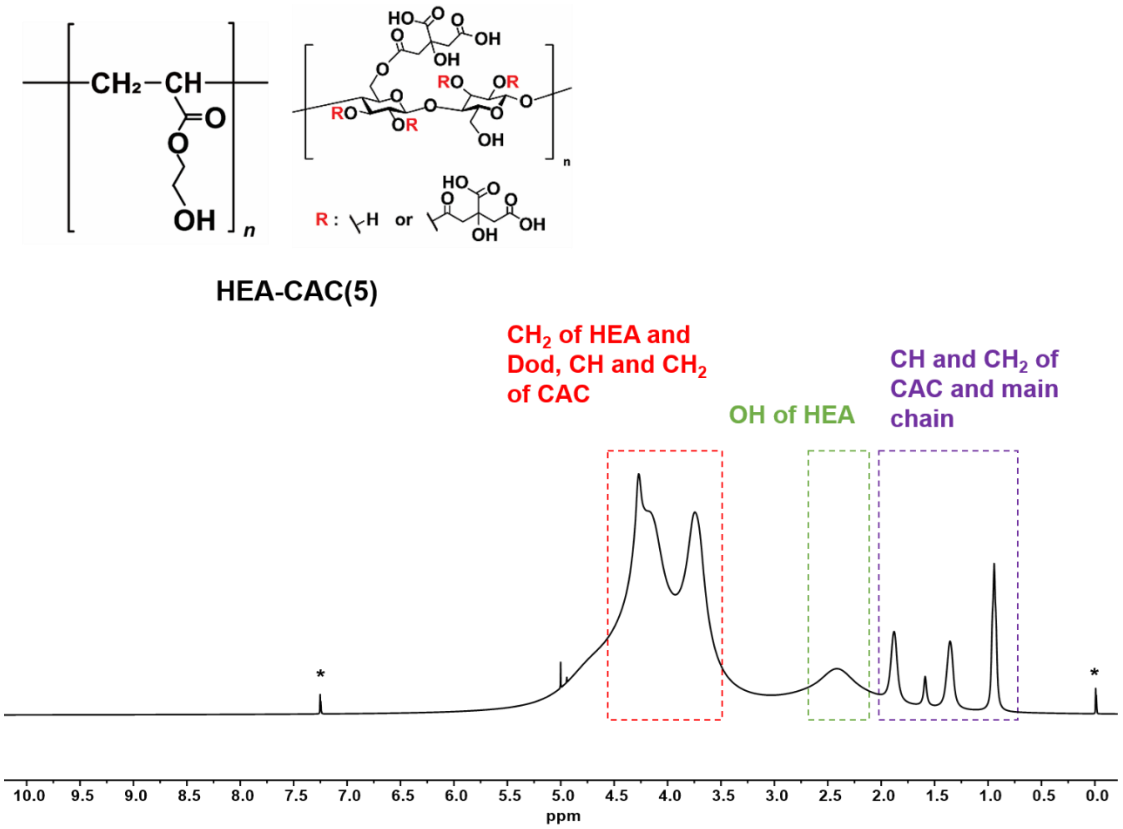


Figure S10. Solid-state ^{1}H FGMAS NMR spectrum of **PAcγCD-HEA-CAC(1,5)** (TMS for standard, 400 MHz, 25 ºC, rotation frequency = 7 kHz).

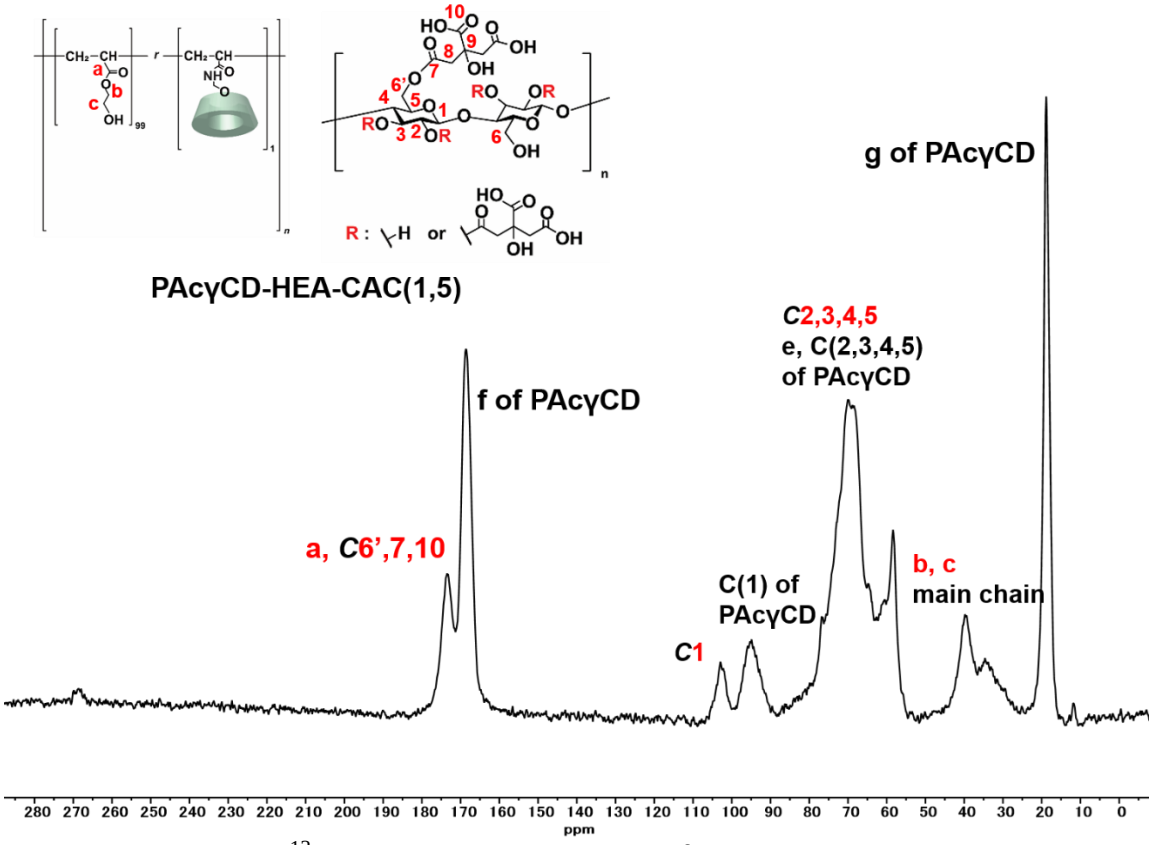


Figure S11. Solid-state ^{13}C CPMAS NMR spectrum of **PAcγCD-HEA-CAC(1,5)** (TMS for standard, 75 MHz, 25 ºC, rotation frequency = 7 kHz).

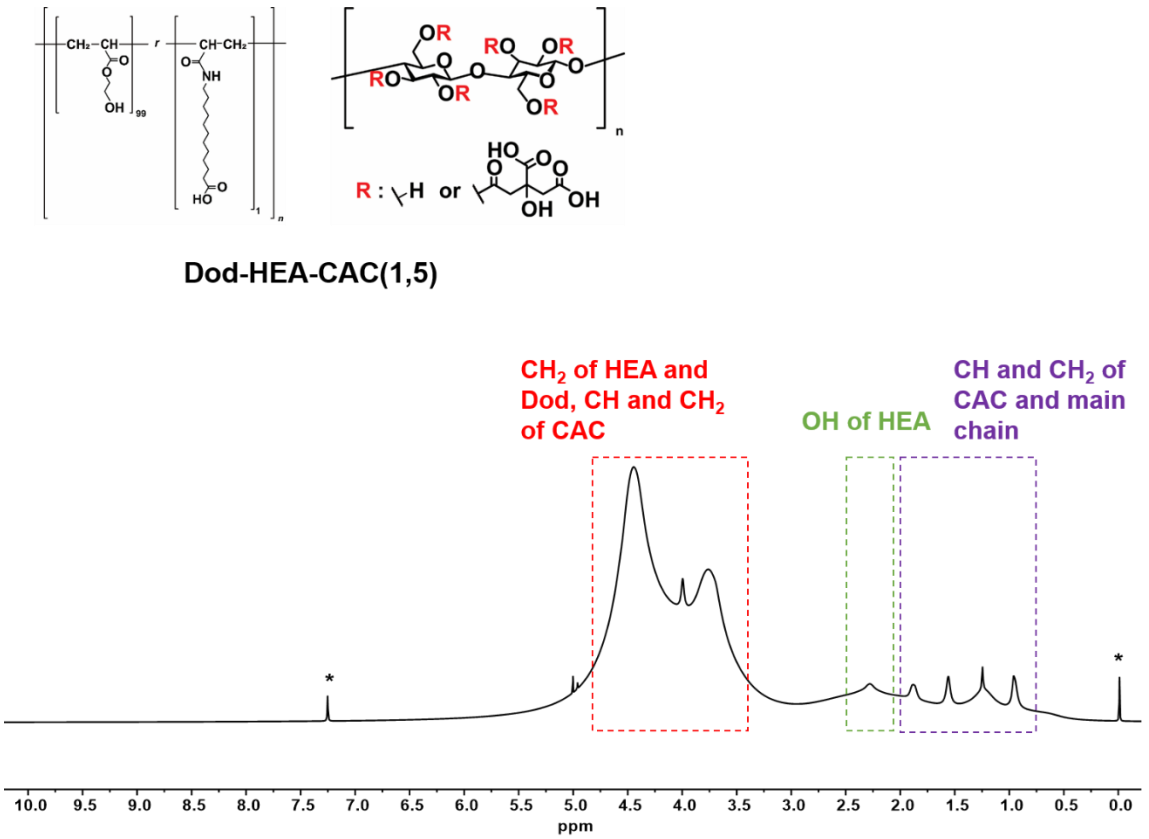


Figure S12. Solid-state ^{1}H FGMAS NMR spectrum of **Dod-HEA-CAC(1,5)** (TMS for standard, 400 MHz, 25 ºC, rotation frequency = 7 kHz).

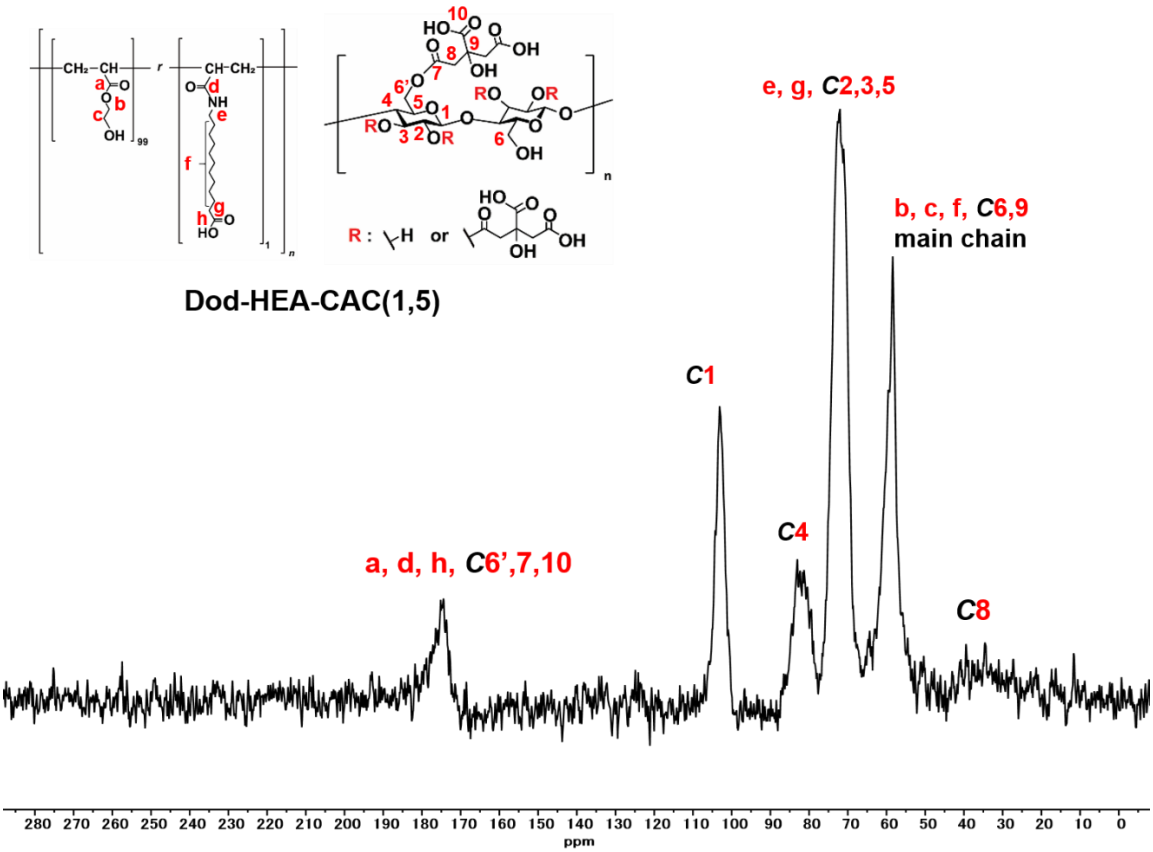


Figure S13. Solid-state ^{13}C CPMAS NMR spectrum of **Dod-HEA-CAC(1,5)** (TMS for standard, 75 MHz, 25 ºC, rotation frequency = 7 kHz).

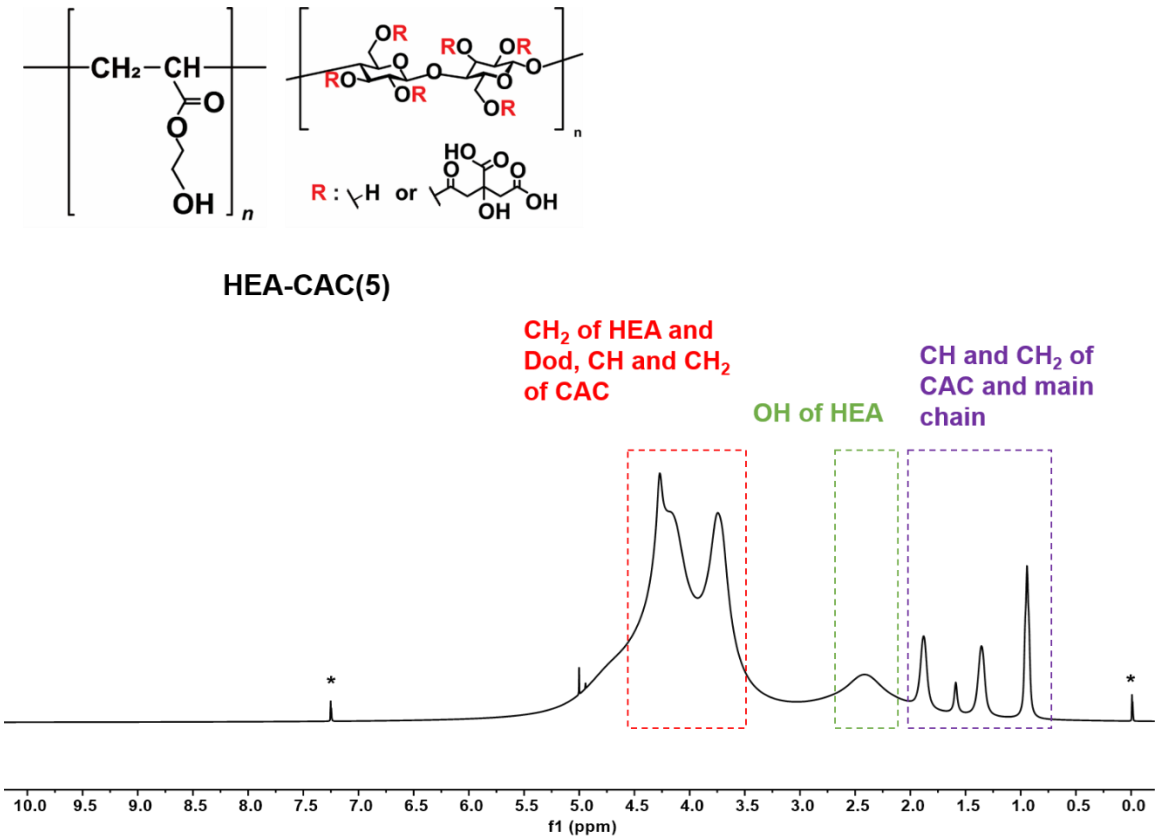


Figure S14. Solid-state ^{1}H FGMAS NMR spectrum of **HEA-CAC(15)** (TMS for standard, 400 MHz, 25 ºC, rotation frequency = 7 kHz).

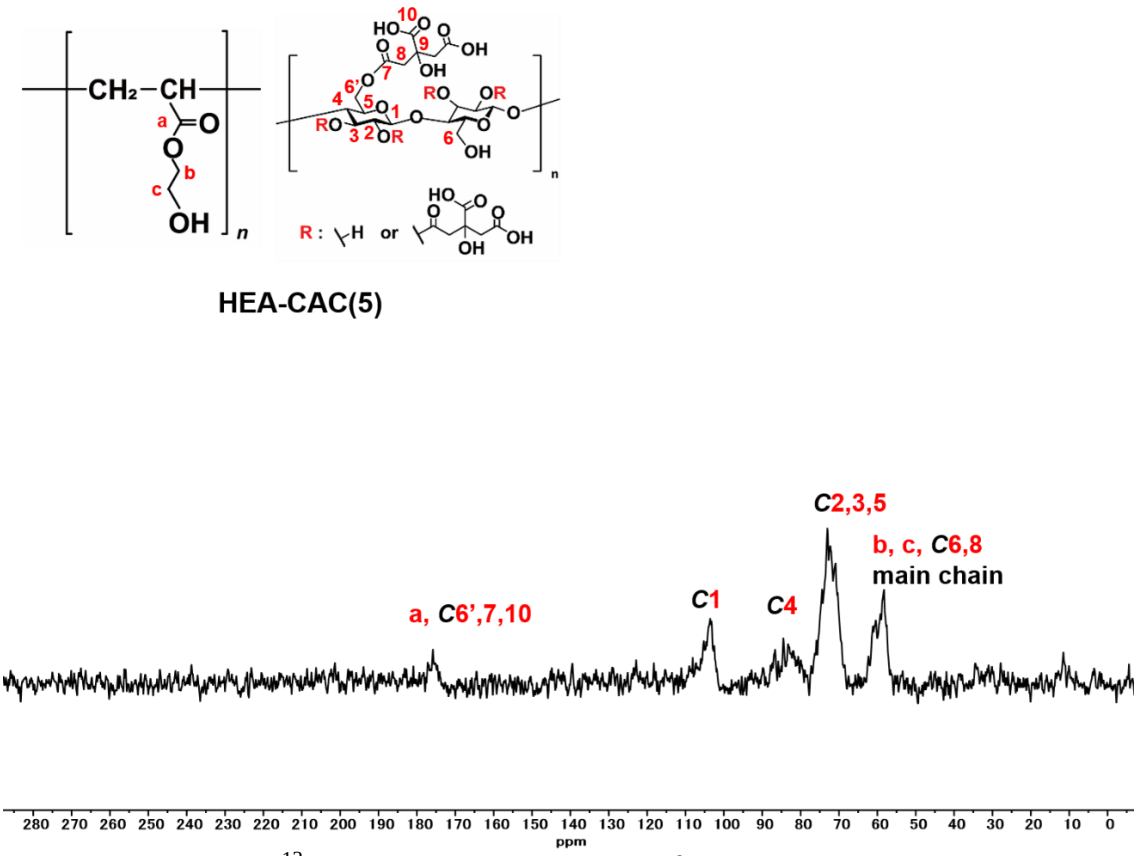


Figure S15. Solid-state ^{13}C CPMAS NMR spectrum of **HEA-CAC(15)** (TMS for standard, 75 MHz, 25 ºC, rotation frequency = 7 kHz).

6. FTIR of materials

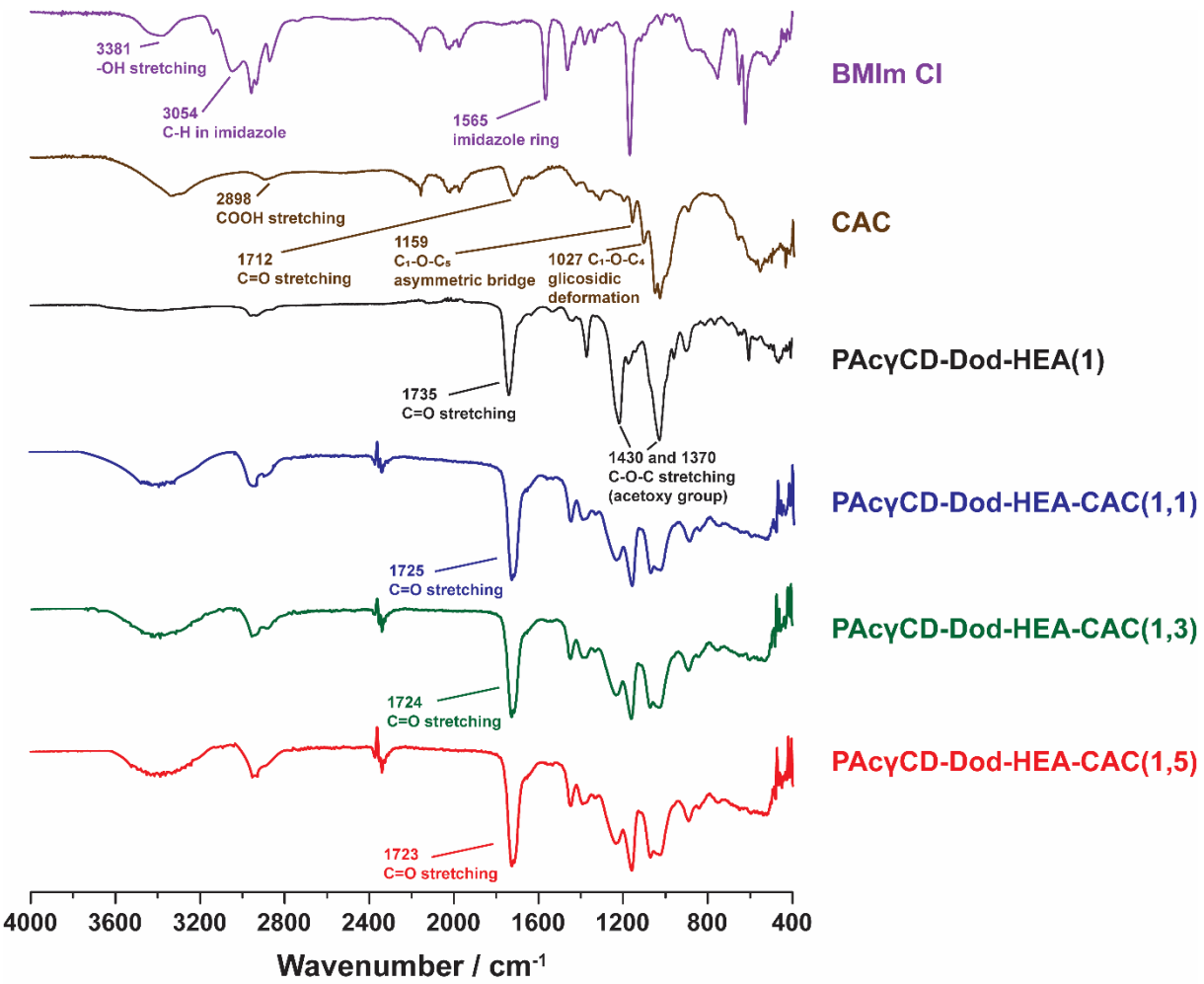


Figure S16. Attenuated Total Reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) of 1-butyl-3-methylimidazolium chloride (BMIm Cl), citric acid-modified cellulose (CAC), supramolecular elastomer [PAcγCD-Dod-HEA(1)], composite with 1 wt% CAC [PAcγCD-Dod-HEA-CAC(1,1)], composite with 3 wt% CAC [PAcγCD-Dod-HEA-CAC(1,3)], and composite with 5 wt% CAC [PAcγCD-Dod-HEA-CAC(1,5)].

7. Cyclic tensile test measurement

Cyclic tensile tests were measured using Autograph AG-X plus (Shimadzu Co.). Test pieces were continuously stretched and recovered without interval. Maximum strains were set to 100%, 200%, 300%, 400%, 500%, 600%, 700%, and 800% at deformation rate of 1 mm·s^{-1} in tests for both PAcγCD-Dod-HEA-CAC(1,5) and PAcγCD-Dod-HEA(1).

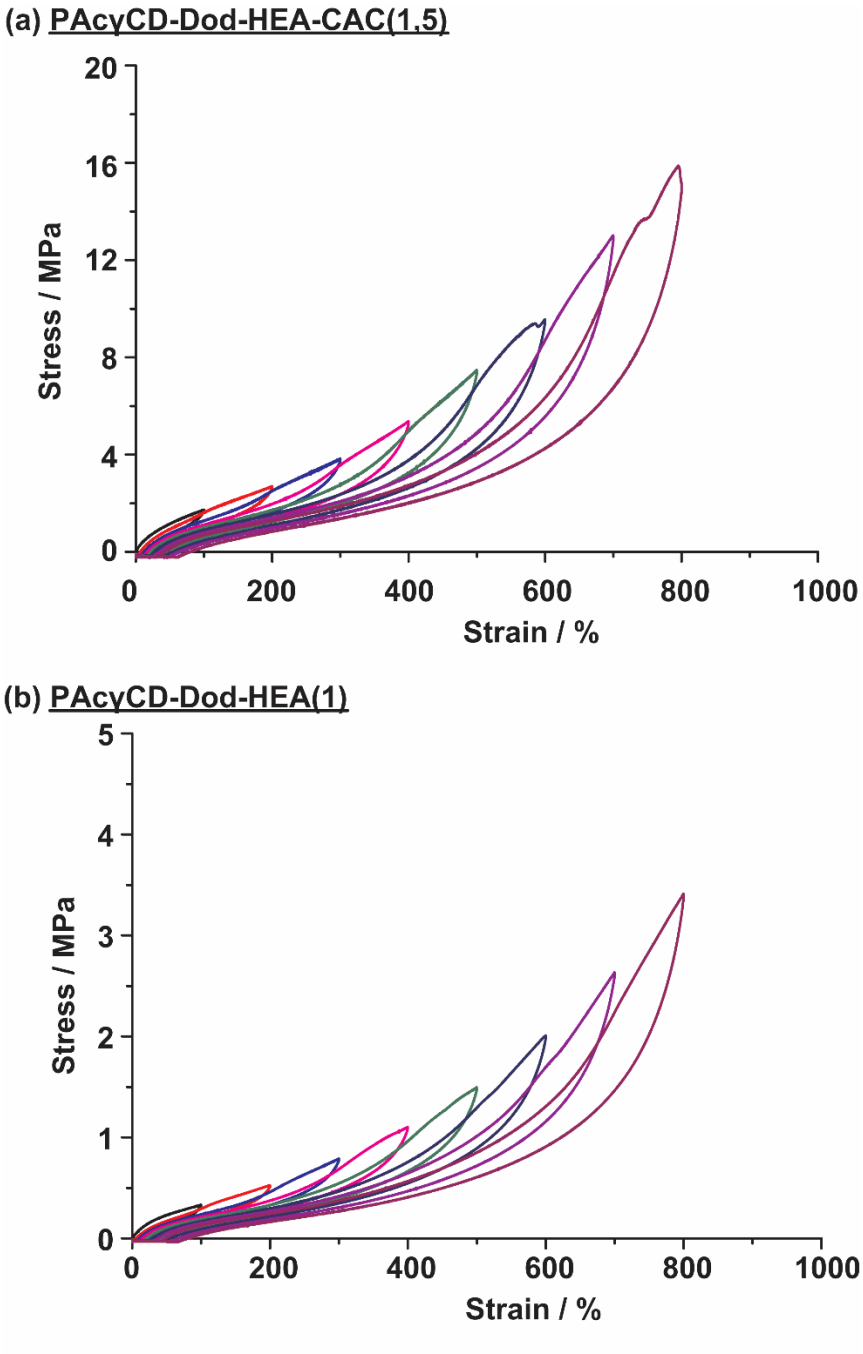


Figure S17. Cyclic tensile test of (**a**) PAcγCD-Dod-HEA-CAC(1,5) and (**b**) PAcγCD-Dod-HEA(1).

8. Creep and stretch recovery measurement

Creep recovery measurement was performed using Autograph AG-X plus (Shimadzu Co.). Stress applying to the test pieces was held at 500 kPa for both PAcγCD-Dod-HEA(1) and PAcγCD-Dod-HEA-CAC(1,5) at 1 hour. Then, the stress was released and strain recovery of the test pieces was recorded as a length of test pieces.

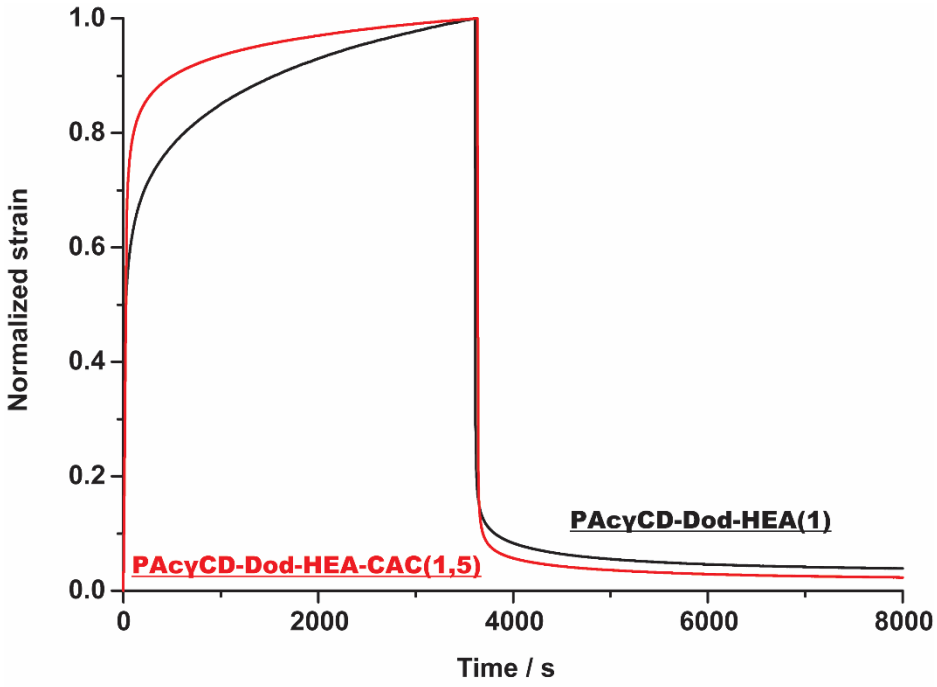


Figure S18. Creep recovery test for PAcγCD-Dod-HEA(1) and PAcγCD-Dod-HEA-CAC(1,5). Stress applying to the test pieces was held at 500 kPa for 1 hour then released.

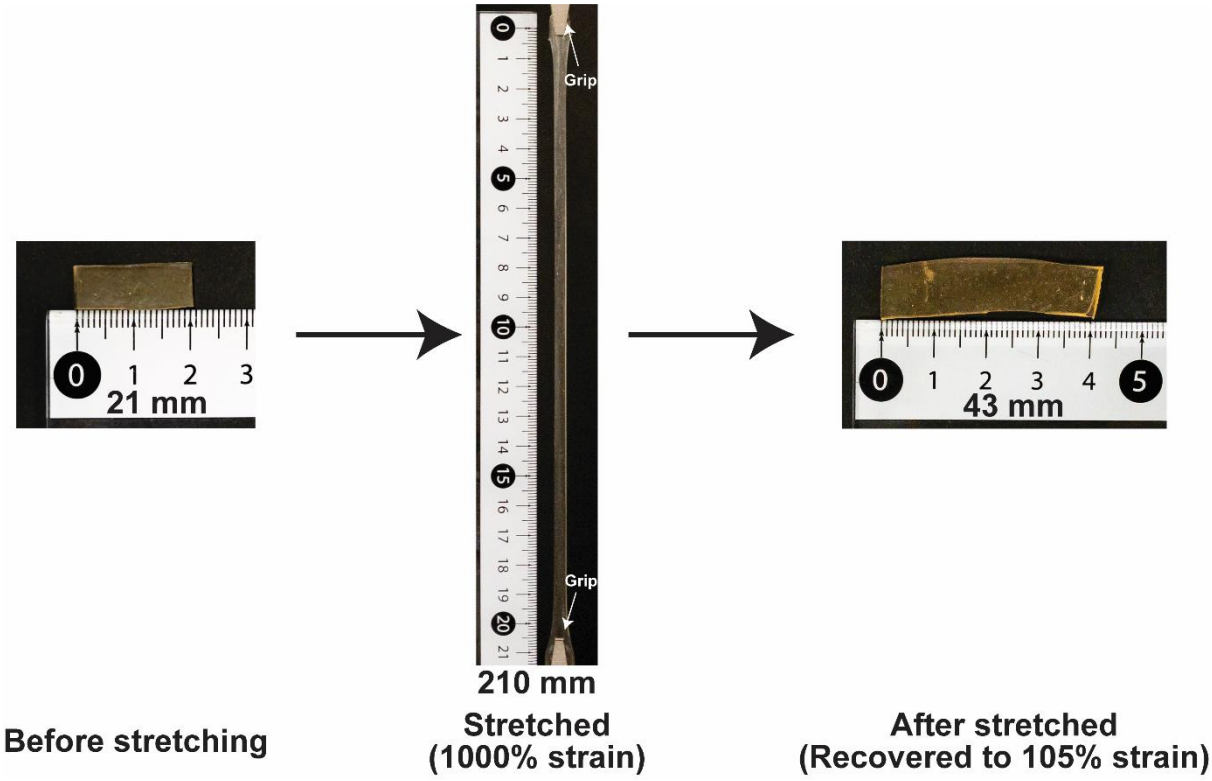


Figure S19. Stretch and recovery test for PAcγCD-Dod-HEA-CAC(1,5).

9. Time dependency self-healing ratio calculation

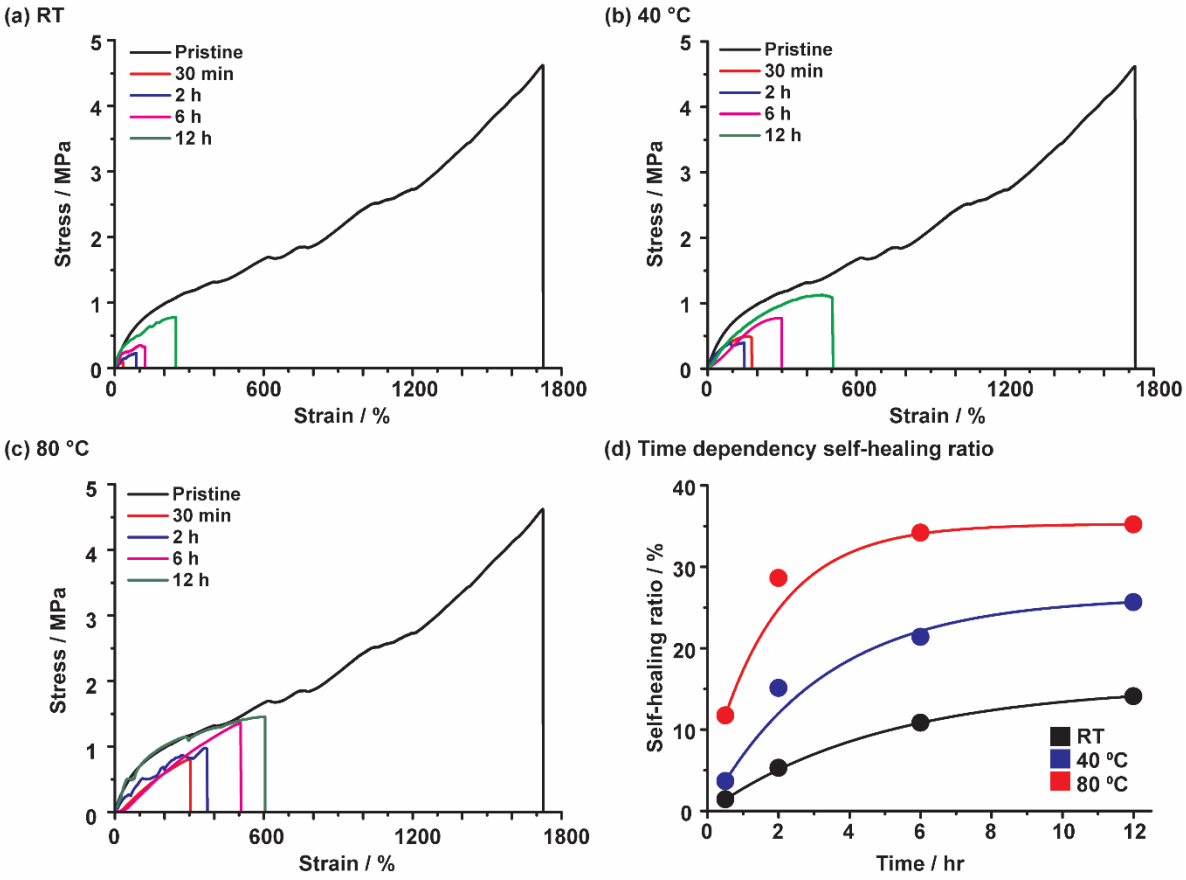


Figure S20. Stress strain curve of PAcγCD-Dod-HEA(1) for self-healing ratio calculation at (**a**) RT, (**b**) 40 ºC, and (**c**) 80 ºC. (**d**) Time dependency self-healing ratio of PAcγCD-Dod-HEA(1).

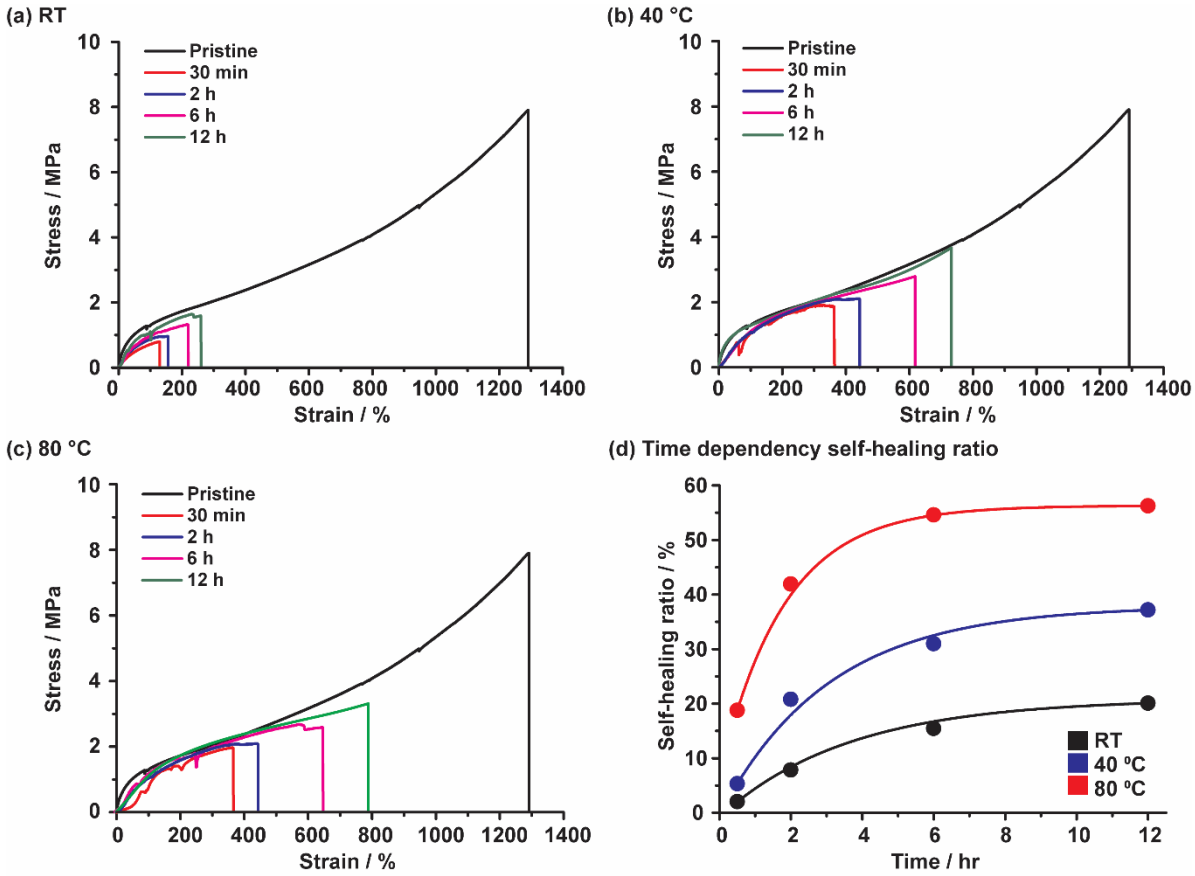


Figure S21. Stress strain curve of PAcγCD-Dod-HEA-CAC(1,1) for self-healing ratio calculation at (**a**) RT, (**b**) 40 ºC, and (**c**) 80 ºC. (**d**) Time dependency self-healing ratio of PAcγCD-Dod-HEA-CAC(1,1).

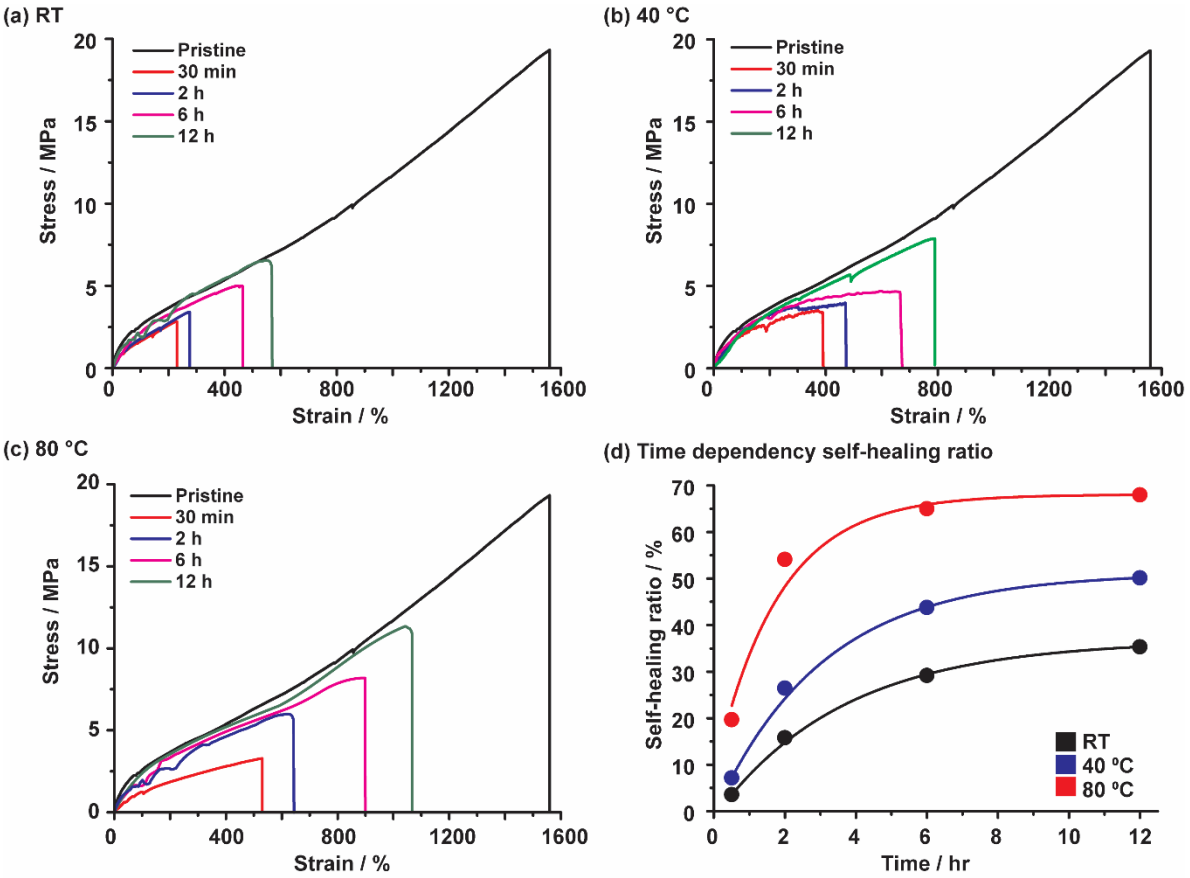


Figure S22. Stress strain curve of PAcγCD-Dod-HEA-CAC(1,3) for self-healing ratio calculation at (**a**) RT, (**b**) 40 ºC, and (**c**) 80 ºC. (**d**) Time dependency self-healing ratio of PAcγCD-Dod-HEA-CAC(1,3).

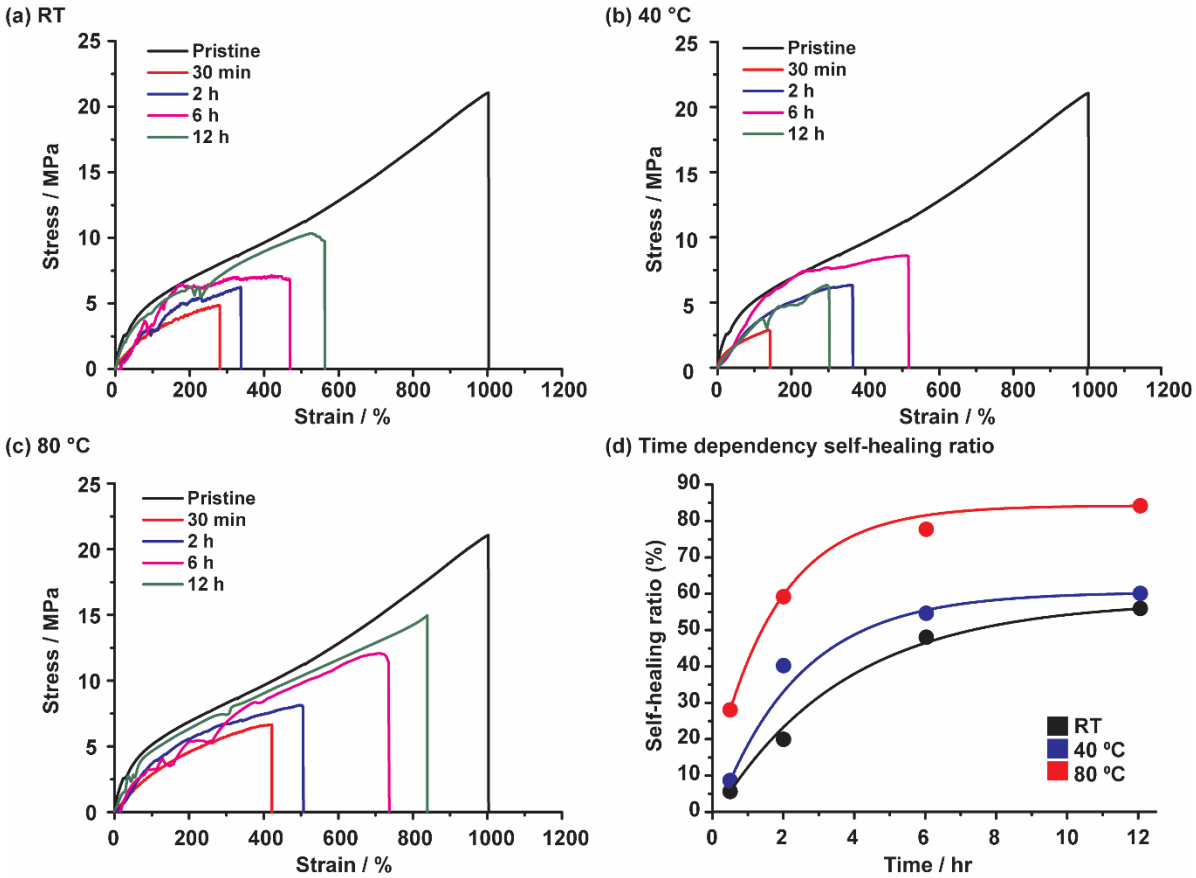


Figure S23. Stress strain curve of PAcγCD-Dod-HEA-CAC(1,1) for self-healing ratio calculation at (**a**) RT, (**b**) 40 ºC, and (**c**) 80 ºC. (**d**) Time dependency self-healing ratio of PAcγCD-Dod-HEA-CAC(1,5).

10. DSC curve of materials

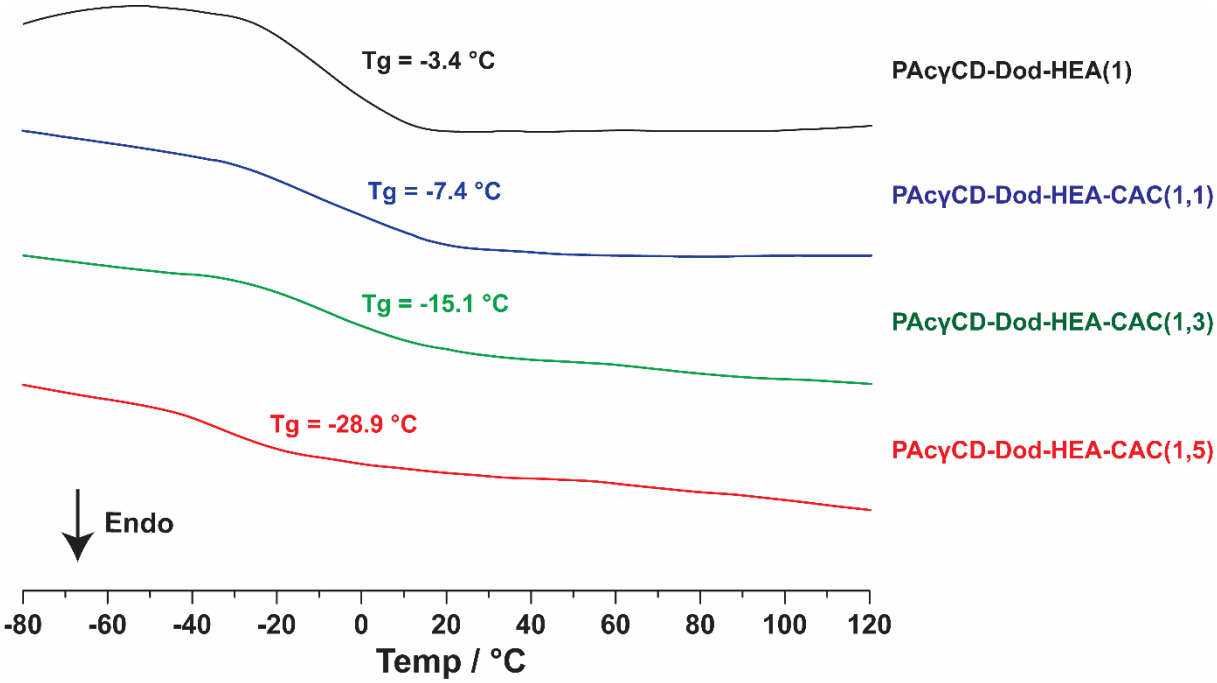


Figure S24. DSC curve for supramolecular elastomer [PAcγCD-Dod-HEA(1)], composite with 1 wt% CAC [PAcγCD-Dod-HEA-CAC(1,1)], composite with 3 wt% CAC [PAcγCD-Dod-HEA-CAC(1,3)], and composite with 5 wt% CAC [PAcγCD-Dod-HEA-CAC(1,5)].

11. Laser scanning confocal microscope

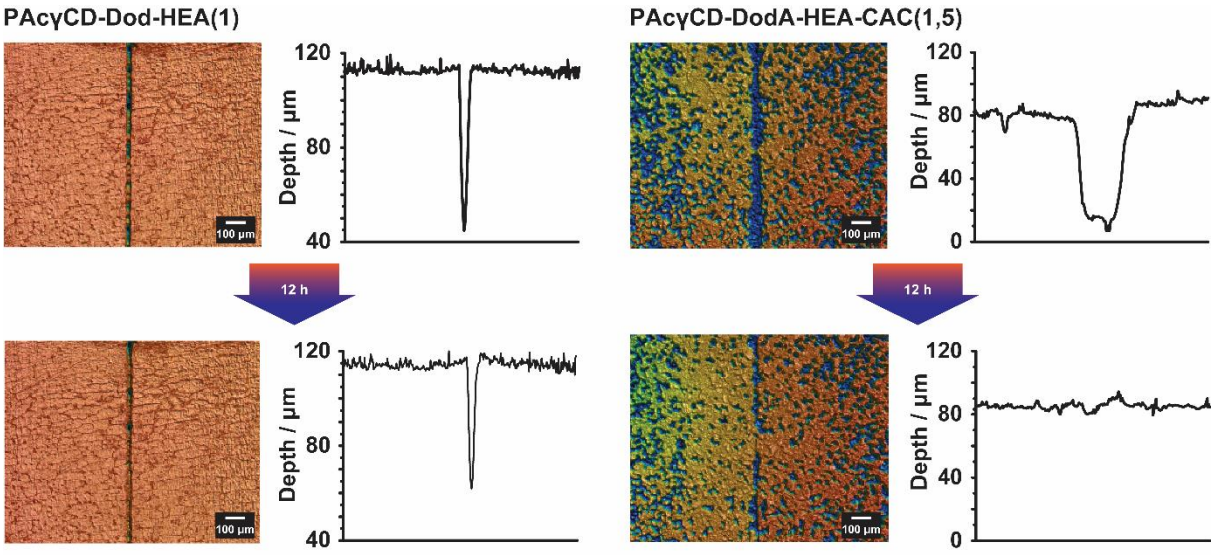


Figure S25. Laser scanning confocal microscope and depth profile of PAcγCD-Dod-HEA(1) and PAcγCD-Dod-HEA-CAC(1,5) at 80°C after reattached for 12 hours.

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1. Takashima, Y.; Sawa, Y.; Iwaso, K.; Nakahata, M.; Yamaguchi, H.; Harada, A., Supramolecular Materials Cross-Linked by Host-Guest Inclusion Complexes: The Effect of Side Chain Molecules on Mechanical Properties. *Macromolecules* **2017,** *50*, 3254-3261.
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