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Supporting Information

2 Cysteine Derivative Enabled Ultrafast Thiol-ene Reaction to Scalable 3 Synthesis of Fully Bio-based Internal Emulsifiers for Super Tough 4 Waterborne Polyurethanes.

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21 Experimental Details

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23 Materials

24 Castor oil (CO, OH number: 164 mg KOH g⁻¹) and castor oil derivative (OH number: 208 mg KOH g⁻¹)

25 ¹) were purchased from Fuyu Chemical Company (China). *N*-acetyl-L-cysteine (NAC), L-cysteine

26 ethyl ester hydrochloride (CEEH), L-cysteine (LCY), L-cysteine methyl ester hydrochloride (CMEH),

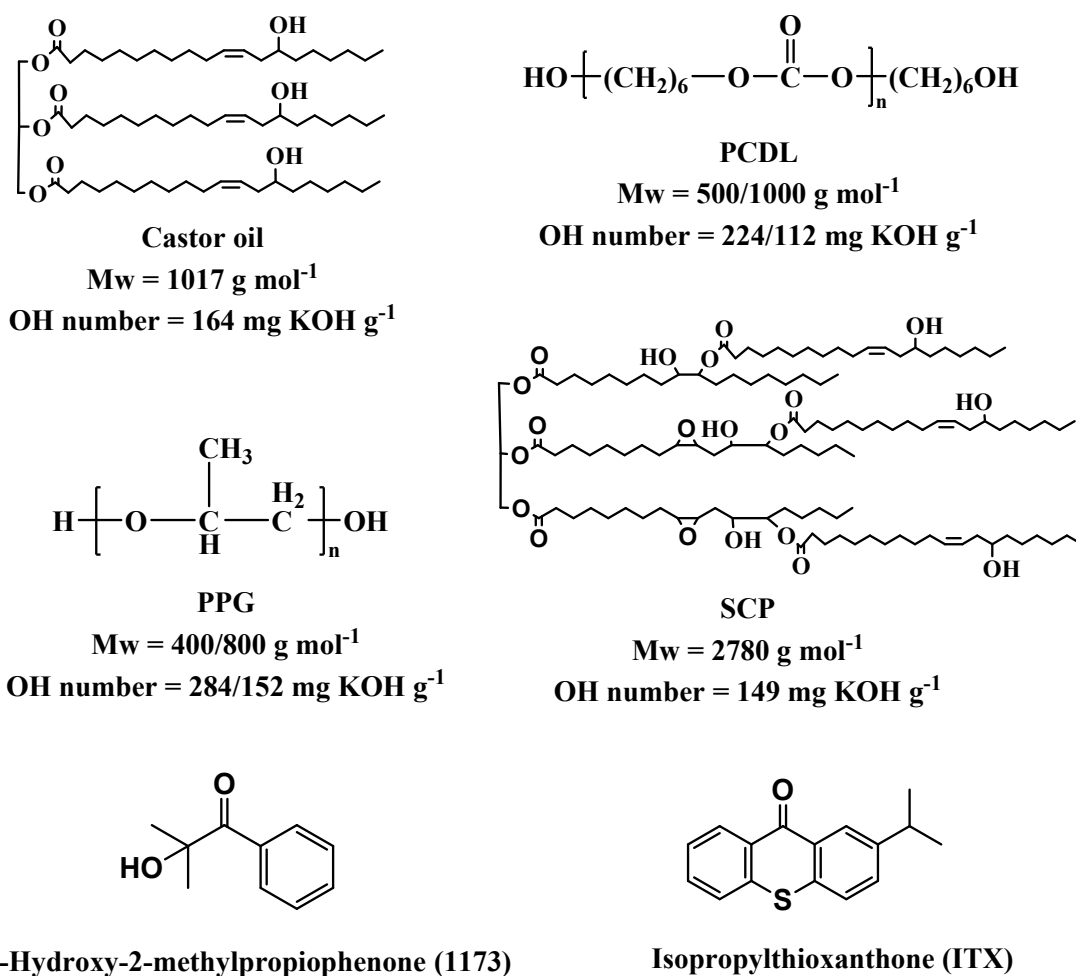
27 thioglycolic acid (MP), acetic anhydride, dichloromethane, chloroform, petroleum ether, and 5,5-

28 dimethyl-1-pyrroline N-oxide (DMPO) were provided by Sigma-Aldrich (USA). Polypropylene

29 glycol with the relative molecular weight of 400/800 g mol⁻¹ (PPG, Mw = 400/800 g mol⁻¹) was

1 bought from Jining Huakai Resin Co., Ltd (China). Polycarbonate diol (PCDL, Mw = 500/1000 g
 2 mol⁻¹) was obtained from Asahi Kasei Corporation (Japan). The chemical structure of the polyols
 3 mentioned above was shown in **Fig. S1**. 2-mercaptoethanol (ME) was provided by Alfa
 4 AesarChemicals Co., Ltd (China). Isopropyl thioxanthone (ITX) was obtained from Shanghai
 5 Curease Chemical Co., Ltd (China). 2-Hydroxy-2,2-dimethylacetophenone (1173) was provided by
 6 Ryojichem Co., Ltd (China). Isophorone diisocyanate (IPDI) was bought from Wengjiang Chemical
 7 Reagent Co., Ltd (China). Dibutyltin dilaurate (DBTDL) was obtained from Fuchen Chemical
 8 Reagent Factory (China). Methyl ethyl ketone (MEK) was provided by Tianjin Hongda Chemical
 9 Reagent (China). Triethylamine (TEA), anhydrous magnesium sulfate (MgSO₄), citric acid, and
 10 ethyl acetate were obtained from Aladdin Reagent (China). Absolute ethanol was bought from
 11 Tianjin Damao Chemical Reagent (China). All chemicals were used as received without further
 12 purification.

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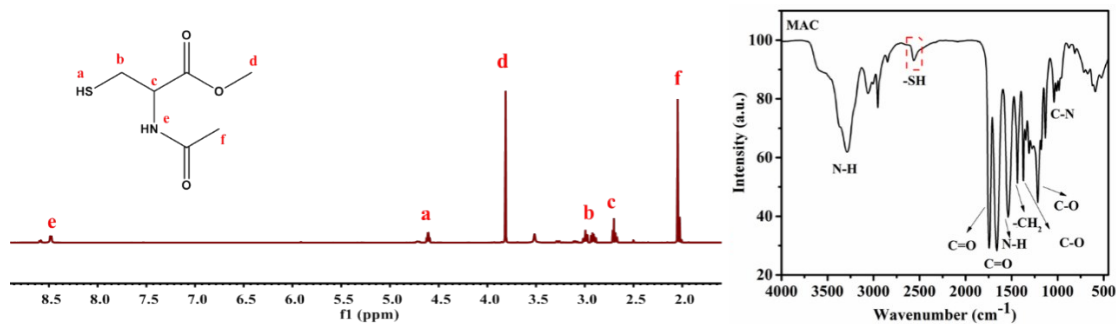
15 **Figure S1.** Representative structure of polyols and photoinitiators used in this study.

1

2 **Synthesis of cysteine derivative: methyl acetylcysteinate (MAC)**

3 The thiol of methyl acetylcysteine (NAC) was synthesized by a one-pot method. L-cysteine methyl
4 ester hydrochloride (1.0 M) and acetic anhydride (1.1 M) in dichloromethane (10.0 mL per 1.0 g
5 CMEH) were thoroughly mixed in a round-bottomed flask kept in an ice bath. Triethylamine (1.7
6 mL per 1.0 g CMEH) was added dropwise and then stirred at room temperature for 1 h. The
7 mixed solution was neutralized by citric acid (10.0 wt. %) and washed subsequently by saturated
8 NaCl aqueous solution, NaHCO₃ aqueous solution (5.0 wt. %), and saturated NaCl aqueous
9 solution. The final product solution was dried with anhydrous MgSO₄ and the solvent was
10 evaporated leading to a white solid. The solid was diluted in chloroform and recrystallized with
11 petroleum ether. Other green alternative solvents could be considered as a replacement of
12 dichloromethane and chloroform, such as γ-valerolactone, ethyl acetate, 2-
13 methylethyltetrahydrofuran. The recrystallization step was tried by using 2-methylethyltetrahydrofuran
14 and petroleum ether, and identical result was obtained. In addition, the isolation mixture of 2-
15 methylethyltetrahydrofuran and petroleum ether could be used for next batch. The structure of
16 MAC was characterized by ¹H NMR and FT-IR (**Figure S2**).

17



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19 **Figure S2.** ¹H NMR and FT-IR spectra of MAC.

20

21 **Synthesis of internal emulsifiers (NACCO) from castor oil and thiol NAC**

22 The internal emulsifiers were prepared by the thiol-ene reaction between castor oil and thiol
23 NAC in a custom-made photochemical reactor (**Scheme 1**). Firstly, the appropriate ratios of NAC,
24 CO, and photoinitiator (4.0 wt. %) were dissolved in absolute ethanol and added to quartz tubes.
25 The reaction proceeded for the reported times under UV irradiation with a power of 350 W. The
26 solution was extracted with ethyl acetate and washed by distilled water repeatedly after the
27 reaction and dried with anhydrous magnesium sulfate. The product was filtered and subjected to

1 rotary evaporation to remove ethyl acetate, before being dried at 45 °C under vacuum overnight
 2 to get the resulting internal emulsifier NACCO. To investigate the effects of photoinitiator, time,
 3 and molar ratios on the efficiency of the process, three photoinitiator conditions (1173, ITX, and
 4 no photoinitiator), six reaction times (5 min, 10 min, 15 min, 20 min, 25 min, and 30 min), and six
 5 molar ratios (1:1, 2:1, 3:1, 4:1, 5:1, and 6:1) were tested. The samples obtained were named
 6 NACCO-p, NACCO-T, and NACCO-m, where p, T, and m are photoinitiator, time and molar ratio
 7 respectively. **Scheme 1** and **Table S1** show the specific reaction conditions tested for the
 8 preparation of internal emulsifiers.

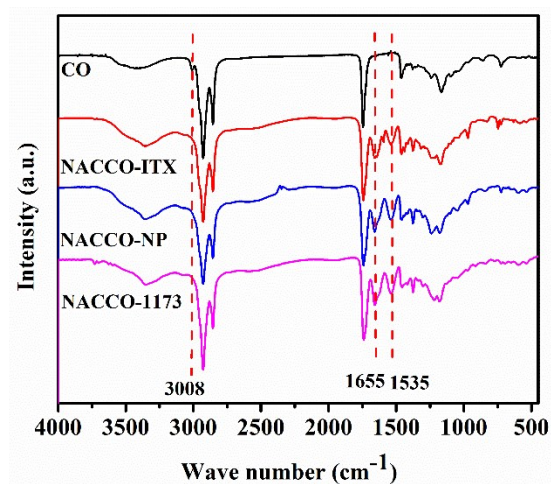
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11 **Table S1.** Molar ratios of starting materials and reaction times tested

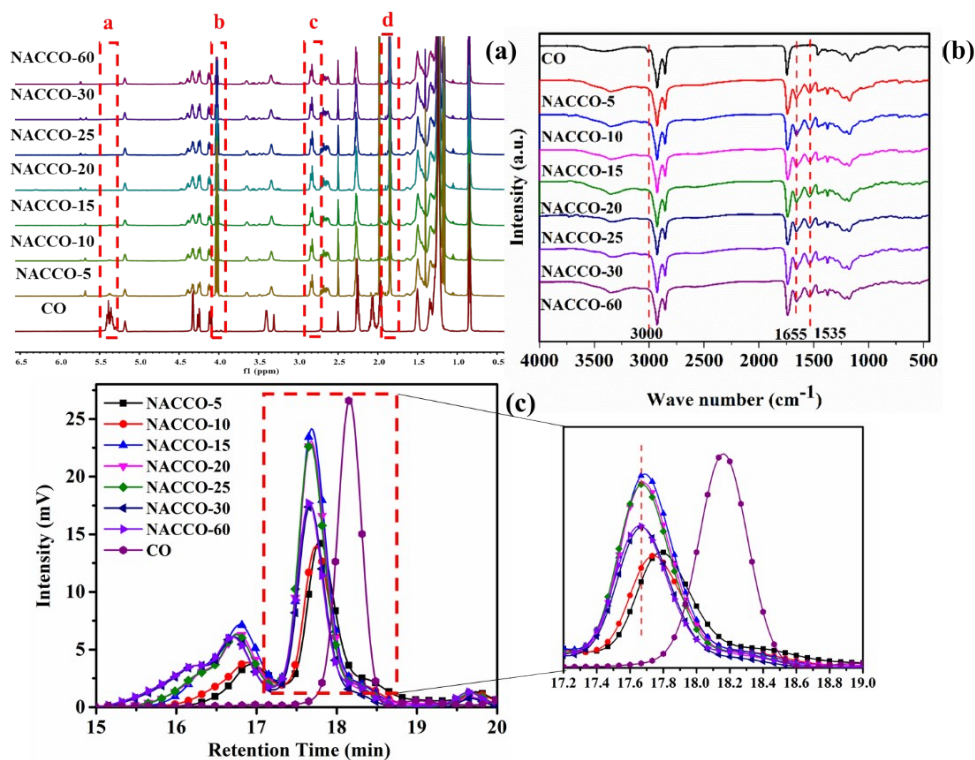
| Sample | Molar ratio | Photoinitiator | Time (min) |
|------------|-------------------------------------|----------------|------------|
| | -SH ^a : C=C ^b | | |
| NACCO-1173 | 6 : 1 | 1173 | 60 |
| NACCO-ITX | 6 : 1 | ITX | 60 |
| NACCO-NP | 6 : 1 | NP | 60 |
| NACCO-5 | 6 : 1 | 1173 | 5 |
| NACCO-10 | 6 : 1 | 1173 | 10 |
| NACCO-15 | 6 : 1 | 1173 | 15 |
| NACCO-20 | 6 : 1 | 1173 | 20 |
| NACCO-25 | 6 : 1 | 1173 | 25 |
| NACCO-30 | 6 : 1 | 1173 | 30 |
| NACCO-1:1 | 1 : 1 | 1173 | 20 |
| NACCO-2:1 | 2 : 1 | 1173 | 20 |
| NACCO-3:1 | 3 : 1 | 1173 | 20 |
| NACCO-4:1 | 4 : 1 | 1173 | 20 |
| NACCO-5:1 | 5 : 1 | 1173 | 20 |

12 ^a SH = mol equivalents of thiols, ^b C=C = mol equivalents of castor oil.

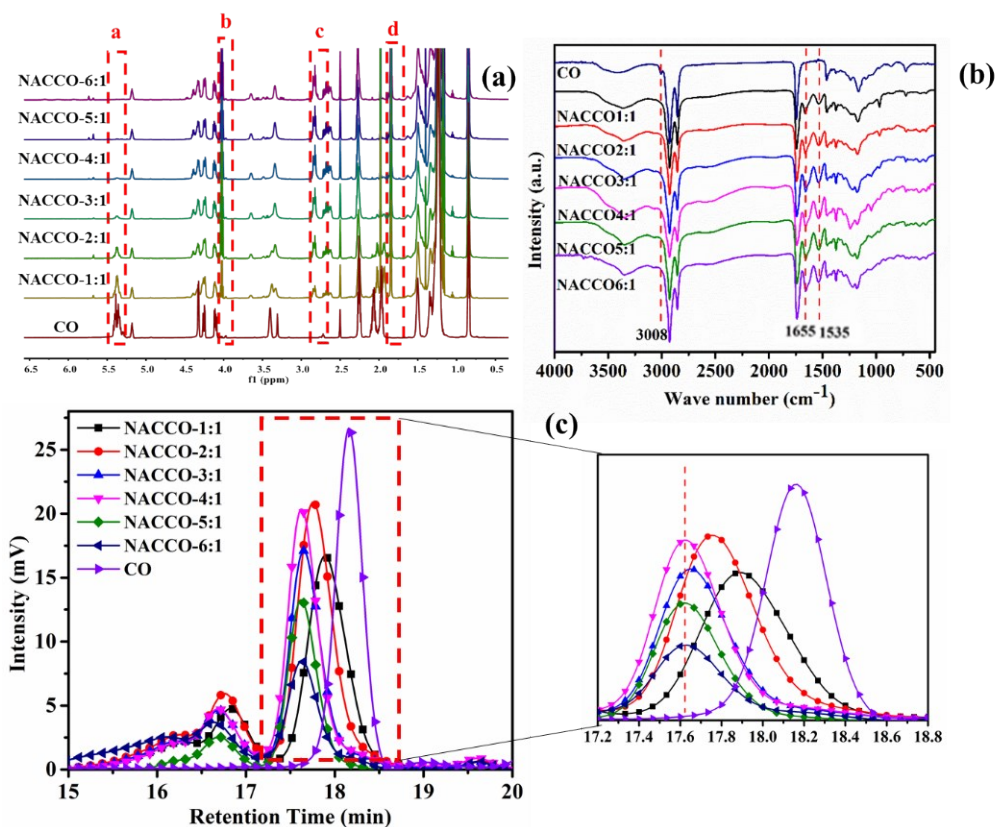
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 2 **Figure S3.** FTIR spectra of castor oil-based internal emulsifiers prepared with and without
 3 photoinitiator.



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 5 **Figure S4.** ¹H NMR (a) and FTIR (b) spectra, and GPC curves (c) of castor oil-based internal
 6 emulsifiers with different reaction times.



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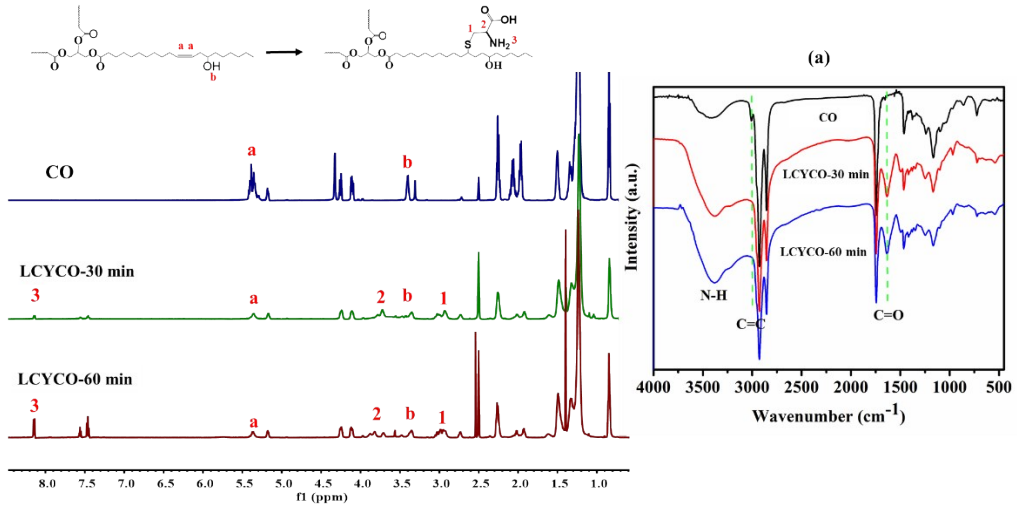
2 **Figure S5.** ¹H NMR (a) and FTIR (b) spectra, and GPC curves (c) of castor oil-based internal
 3 emulsifiers with different SH:C=C molar ratios.

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5 **Synthesis of comparative samples with different thiols**

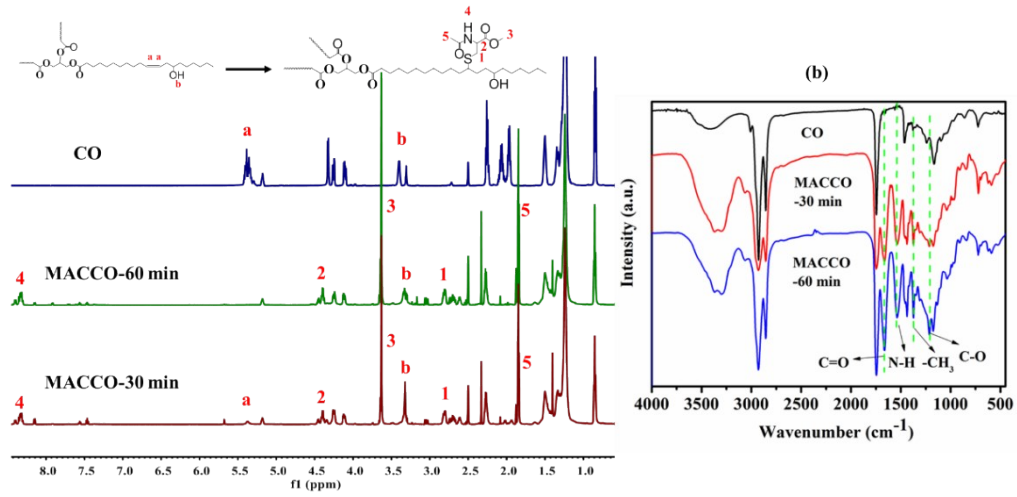
6 For investigating the mechanism of different thiols and castor oil, five thiols (CEEH, MAC, LCY, ME
 7 and MP) were selected. The preparation process is the same already described and the resulting
 8 products were named CEEHCO, MACCO, LCYCO, MECO, and MPCO, respectively. The conversion
 9 rates of carbon-carbon double bonds were monitored for two specific reaction times (30 min and
 10 60 min).

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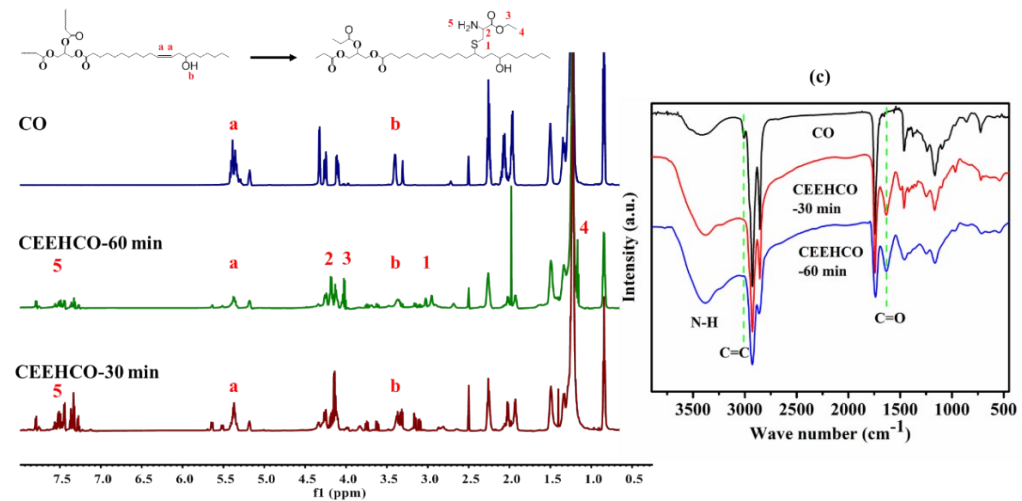
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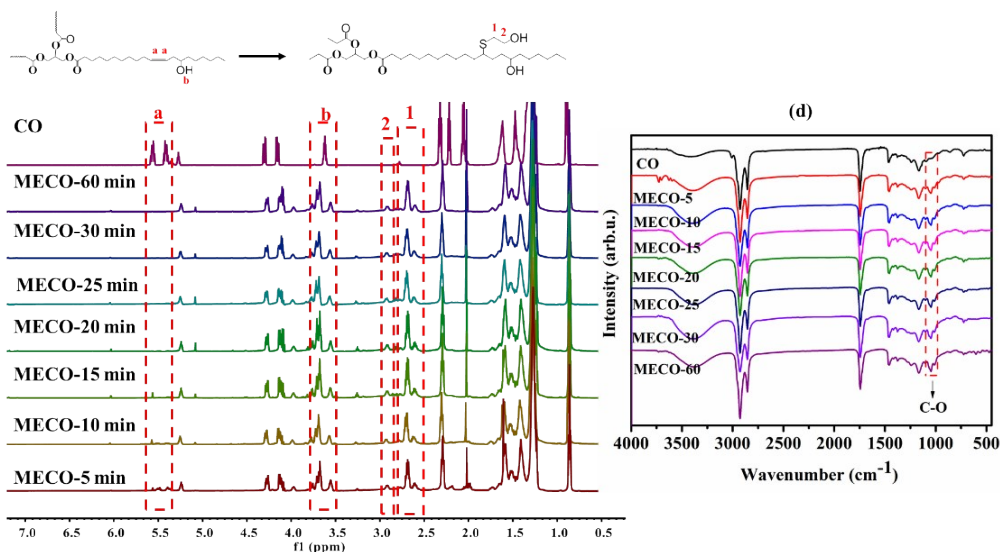
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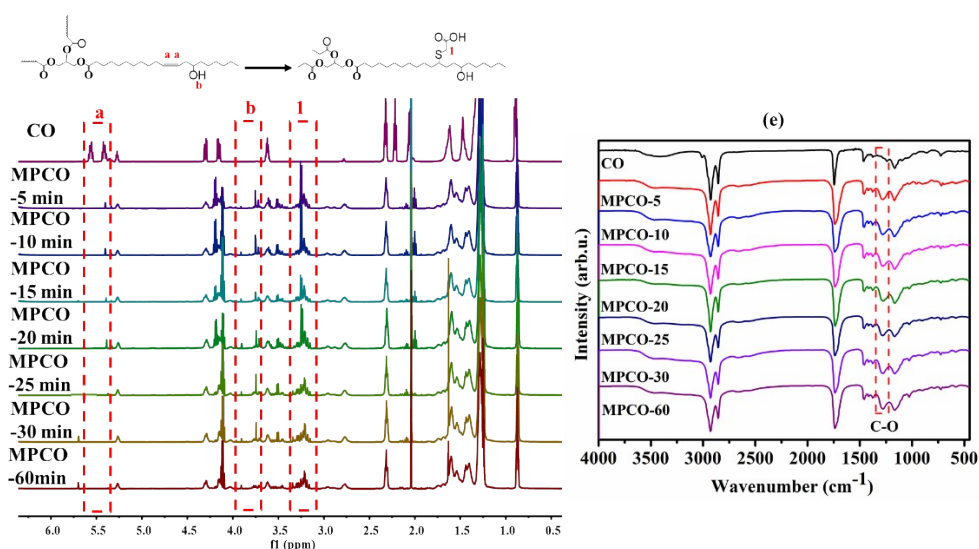
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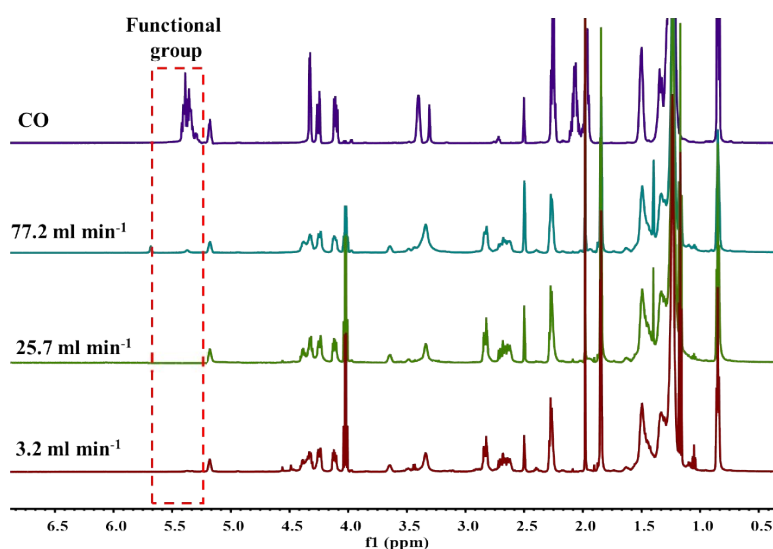
4 **Figure S6.** ^1H NMR and FTIR spectra of (a) LCYCO, (b) MACCO, (c) CEEHCO, (d) MECO, and (e)
 5 MPCO with different reaction times.

6

7 **Table S2.** The first-principles calculations of NAC and ME.

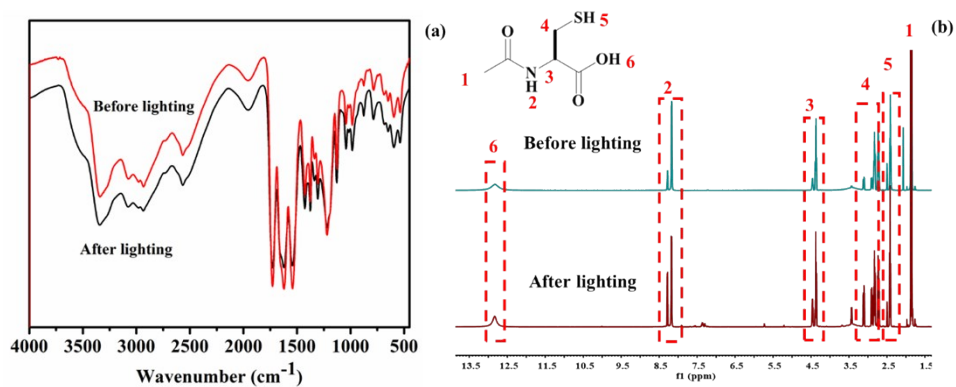
| | E0/hartree | E/hartree | H/hartree | G/hartree |
|-------------------|-----------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Castor oil | -3146.1 | -3146.0 | -3146.0 | -3146.3 |
| NAC | -873.8 | -873.8 | -873.8 | -873.9 |
| 2-Mercaptoethanol | -552.5 | -552.5 | -552.5 | -552.6 |
| Reaction 1 | -5769.5 | -5769.4 | -5769.4 | -5769.8 |
| Reaction 2 | -4805.6 | -4805.5 | -4805.5 | -4805.8 |
| H | -0.5 | -0.5 | -0.5 | -0.5 |
| | $\Delta E_0/(\text{kJ mol}^{-1})$ | $\Delta E/(\text{kJ mol}^{-1})$ | $\Delta H/(\text{kJ mol}^{-1})$ | $\Delta G/(\text{kJ mol}^{-1})$ |
| path1 | -3767.3 | -3763.5 | -3773.4 | -3567.5 |
| path2 | -3801.2 | -3799.8 | -3809.7 | -3610.0 |

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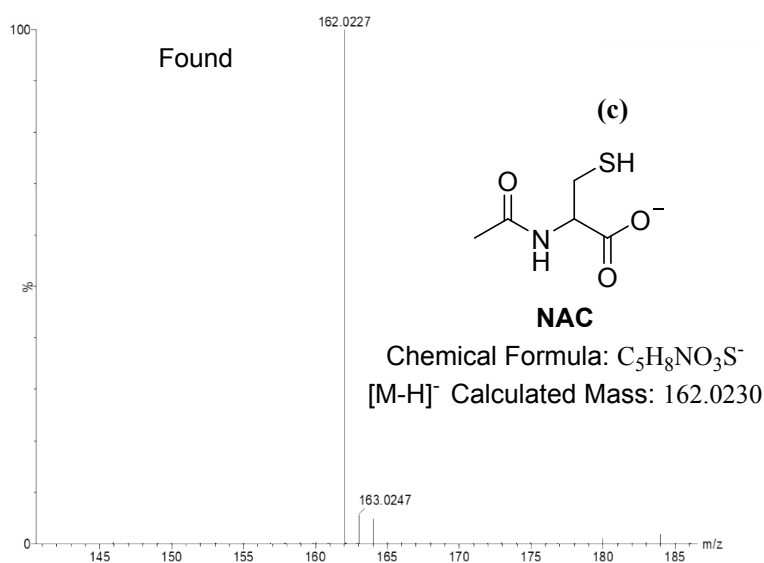


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3 **Figure S7.** ^1H NMR spectra of new chain-extender from flow chemistry prepared with different
4 flow rates.



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6

7 **Figure S8.** (a) FTIR spectra of NAC before and after being illuminated by UV light, and (b) ^1H NMR
8 spectra of NAC before and after being illuminated by UV light, and (c) Mass spectrum of NAC

1 after being subjected to UV irradiation.

2 **Continuous-flow reaction**

3 A simple continuous-flow device was equipped with an autosampler (50.0 ml), a quartz spiral
4 tube, a cooling device and an ultraviolet lamp (500 W, $\lambda = 362$ nm). The reactant solution was
5 injected at different speeds through the autosampler and was reacted under the irradiation of
6 the ultraviolet lamp when flow through the quartz spiral tube. The reaction mixture could
7 directly flow out from the end of the quartz tube, which was extracted with ethyl acetate and
8 washed by distilled water repeatedly. The extracts were dried with anhydrous magnesium
9 sulfate, filtered and subjected to rotary evaporation to remove ethyl acetate. The residue was
10 dried at 45 °C under vacuum overnight to give internal emulsifier NACCO.

11

12

13 **Synthesis of bio-based waterborne polyurethane dispersion**

14 Firstly, the polyols (PPG, PCDL, CO, and castor oil derivative) and IPDI were added to a double-
15 necked flask equipped with mechanical stirring and mixed for 10 min at 78 °C. Then, the DBTDL
16 catalyst (1.0 wt. % of the polyol) was fed into the mixture and the reaction proceeded for 10-30
17 min. Subsequently, NACCO internal emulsifier was dissolved in MEK and added dropwise to the
18 mixture for approximately 1 h. The molar ratios of the OH groups of NACCO, the NCO groups of
19 IPDI, and the OH groups of polyols are shown in **Table S3**. After the reaction, an additional 5.0-
20 10.0 mL of MEK was added to the mixture to decrease the viscosity of the system. After reaction
21 for 2 h until the NCO content reduced to less than 10.0 % as determined by back titration, the
22 system was neutralized with TEA for about 30 min and let cool down to room temperature.
23 Finally, the mixture was emulsified with distilled water at the speed of 400-500 rpm for 2 h, and
24 excess MEK was removed by rotary evaporation to obtain the waterborne polyurethane (PU)
25 with a solid content of 15.0 %. The PUs prepared were named PU-p, where p designates the
26 different polyols used. **Scheme S1** and **Table S3** show the representative synthesis and
27 composition of waterborne polyurethane dispersions prepared.

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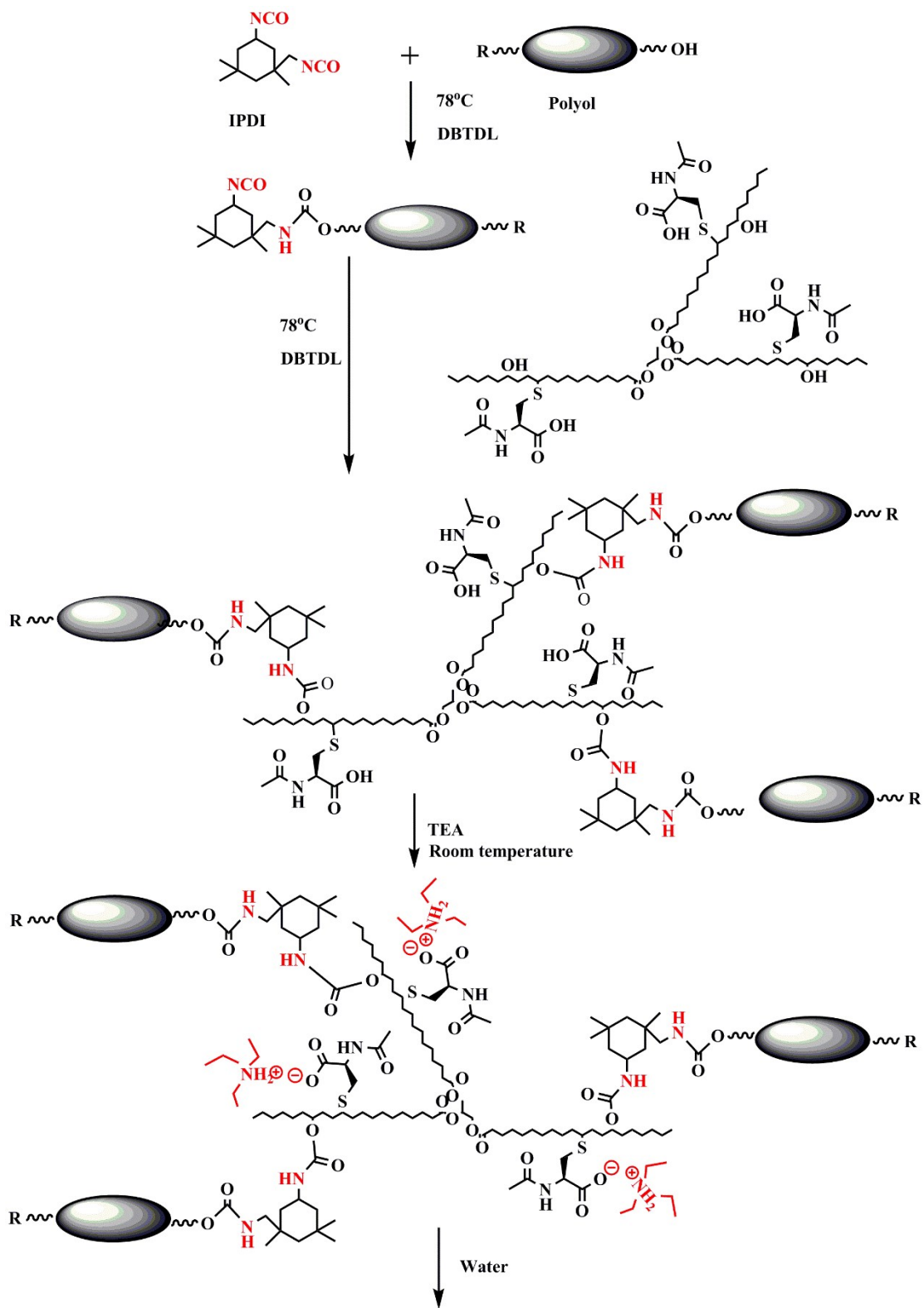
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2 **Table S3.** The composition of waterborne polyurethane dispersion^a

| Sample | OH number of the polyols (mg KOH g ⁻¹) | Emulsifier content (%) | Molar ratio |
|-------------|---|---------------------------|--|
| | | | OH ^b : NCO: OH ^c |
| PU-CO164 | 164 | 15.0 | 1:2:0.99 |
| PU-CO208 | 208 | 15.0 | 1:2:0.99 |
| PU-PPG800 | 152 | 15.0 | 1:2:0.99 |
| PU-PPG400 | 284 | 15.0 | 1:2:0.99 |
| PU-PCDL500 | 224 | 15.0 | 1:2:0.99 |
| PU-PCDL1000 | 112 | 15.0 | 1:2:0.99 |
| PU-SCP | 149 | 15.0 | 1:2:0.99 |

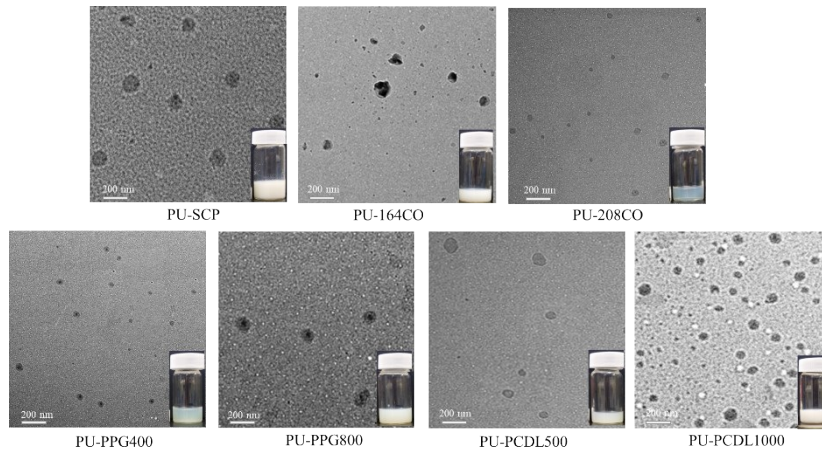
3 ^aThe results were obtained from the average values of at least four replicates of each
4 independently prepared sample. ^b Hydroxyl mol equivalent of polyol, ^c Hydroxyl mol equivalent
5 of NACCO.



1

2 **Scheme S1.** Representative synthesis of waterborne polyurethane dispersion with polyols and
 3 the new internal emulsifier.

4

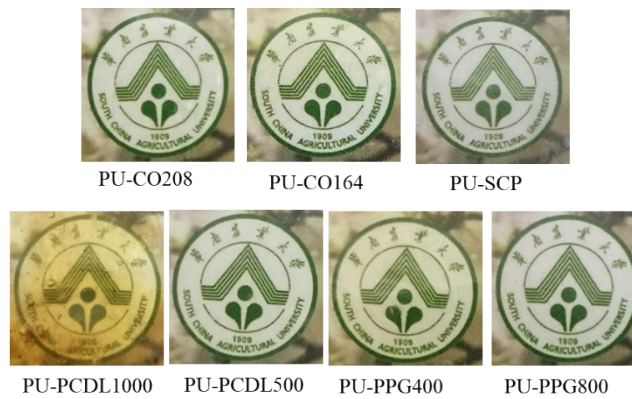


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2 **Figure S9.** The TEM image of the waterborne polyurethane dispersions

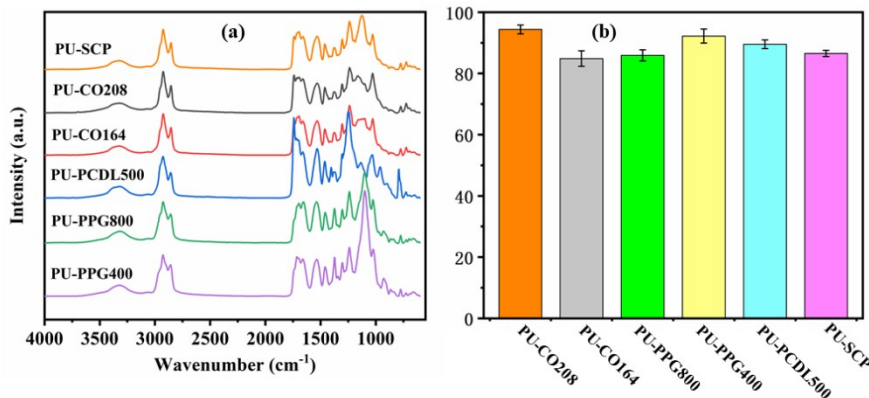
3 **Synthesis of waterborne polyurethane films**

4 The waterborne polyurethane dispersions prepared were poured into a silicon mold and dried at
 5 room temperature to obtain PU films for further testing. All samples were dried at 45 °C for more
 6 than 24 h before the test.



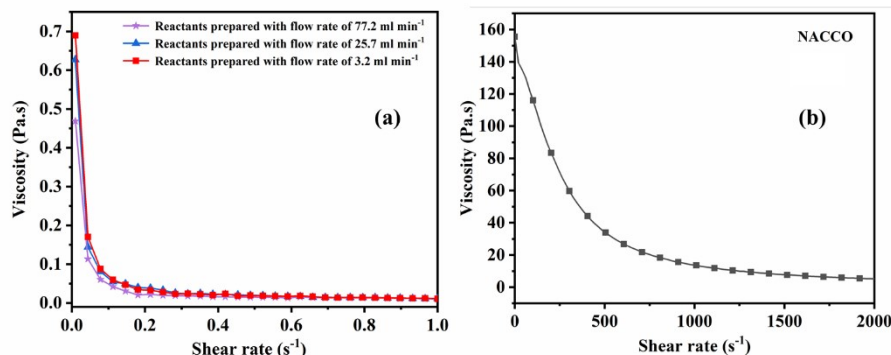
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8 **Figure S10.** The appearance of the waterborne polyurethane films prepared with different
 9 polyols and the new internal emulsifier.



10

11 **Figure S11.** The FT-IR spectra and gel fraction of the waterborne polyurethane



1

2 **Figure S12.** The viscosity of the internal emulsifier reacted with different flow rates

3

4 Table S4. Viscosity at the end of the reactions with different flow rates when shear rate
5 was 0.6 s^{-1}

| flow rates (ml min^{-1}) | Viscosity of the sample (Pa. s) |
|-------------------------------------|---------------------------------|
| 77.2 | 0.008 |
| 25.7 | 0.013 |
| 3.2 | 0.016 |

6 The viscosity of the internal emulsion was 7.2 Pa. s at the shear rate of 1500 s^{-1}

7

8 **Characterization**

9 The ^1H NMR spectra were obtained with a Bruker AV 600 spectrometer operating at 600 MHz.

10 The samples were dissolved in dimethyl sulfoxide- D_6 (D , 99.9 %) + 0.03 % V/V TMS). The

11 conversion rates (C) of the carbon-carbon double bonds was calculated using the following

12 formula:¹

$$C = \frac{d' - 1}{(1 - d - 1)} \times 100 \% \quad (1)$$

13 Where d and d' correspond to the areas of the H-C=C signal (5.1-6.4 ppm) in the ^1H NMR spectra.

14 The mass spectrum (LC-MS) (AB Sciex API 3200) analysis was performed using electrospray ion

15 source (ESI), and ESI source was negative ion mode. CH_3OH was used as the solvent to dissolve

16 the recovered NAC.

17 Fourier transform infrared spectroscopy (FTIR) was recorded on a Thermo-Nicolet Nexus 670 FT-

18 IR spectrometer scanning wavenumbers from 450 cm^{-1} to 4000 cm^{-1} .

19 The molecular weight of the internal emulsifiers was measured by THF-eluted GPC (Waters

20 e2695), equipped with a 2414 RI detector and Styragel HR2 and Styragel HR1 columns. The

21 column flow rate was 0.3 mL min^{-1} at a temperature of $35 \text{ }^\circ\text{C}$. The instrument was calibrated with

1 polystyrene standards.

2 Electron spin resonance (ESR) spectra were obtained on a Bruker A300 ESR spectrometer. ESR
3 was used to detect sulfur radicals (\bullet SR) from NAC or 2-mercaptoethanol under UV light
4 irradiation and in the presence of photoinitiator, with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO)
5 as the radical trapper. DMPO/C₂H₅OH was prepared by dissolving 0.05 g of DMPO in 4.0 mL of
6 absolute ethanol and performing ultrasonic irradiation for 3 min. This led to solution A. After the
7 designated reaction time, 200 μ L of the reaction solution is mixed with 200 μ L of solution A,
8 becoming then solution B. Solution B was used for the detection of sulfur radicals.

9 The hydroxyl value of the internal emulsifiers was measured by the Unilever method and the acid
10 value was determined by the AOCS Office Method Te 1a-64. The results and errors were
11 obtained from the average values of at least four replicates of each independently prepared
12 sample.

13 The rheological behavior at the end of the reaction was measured by a Kinexus Prorotational
14 rheometer. The viscosity of the products was tested at a shear rate ranging from 0.1-1.0 s⁻¹ at
15 room temperature.

16 The residual NCO content was measured by the common method. Specifically, the prepolymer
17 was diluted with MEK and then dissolved in the mixture solution of standard dibutylamine and
18 toluene to consume the residual NCO. The bromocresol green was used as an indicator, and
19 isopropanol was dropped to improve the coloration of bromophenol. The sample was back
20 titrated with KOH solution (0.5 mol L⁻¹). Moreover, a black titration was required without
21 prepolymer.

22 Morphology of particles was observed by transmission electron microscopy (TEM -Tecnai 12,
23 Netherlands FEI). The dispersions were diluted to 0.1 wt. % with deionized water. The results and
24 errors were obtained from the average values of at least four replicates of each independently
25 prepared sample.

26 The zeta potential and particle size of the waterborne polyurethane dispersions were
27 determined with a Zeta-seizer Nano ZSE (Malvern Instruments, United Kingdom). The dispersion
28 was diluted to 0.01 wt. % before testing. The results and errors were obtained from the average
29 values of at least four replicates of each independently prepared sample.

30 The gel fraction of the WPU was measured by immersing the films in acetone at room

1 temperature for 72 h, and the acetone was changed every 12 hours. The films were dried and
2 weighted after finished immersion. The gel content was calculated as the following equation:

$$3 \quad \text{Gel content (\%)} = (m_0 - m_1) / m_0 \times 100\% \quad (2)$$

4 Where m_0 and m_1 are the film mass before and after immersing. The results and errors were
5 obtained from the average values of at least four replicates of each independently prepared
6 sample.

7 TGA of the PU films was performed on a TRIOS Discovery TGA 550 from 30 °C to 700 °C with a
8 heating rate of 10 °C min⁻¹, under the nitrogen atmosphere. Samples of 5.0-10.0 mg were used
9 for the analysis.

10 A Netzsch DMA 242C dynamic mechanical analyzer (Germany) was used for dynamic mechanical
11 analysis (DMA) with temperatures ranging from -60 °C to 140 °C, under the tensile mode,
12 frequency of 1Hz, and heating rate of 5 °C min⁻¹. The PU film dimensions were 25 mm × 5 mm
13 (length × width). The maximum peak of Tan δ was considered as the glass transition temperature
14 (T_g) of the films.

15 T_g of the PU films was also obtained by differential scanning calorimetry using a DSC 214 Polyma
16 calorimeter (Germany) under the nitrogen atmosphere (40.0 mL min⁻¹ flow rate). The dynamic
17 temperatures were 30-100 °C at a heating rate of 10.0 K min⁻¹, 100-60 °C at a cooling rate of 10.0
18 K min⁻¹, and -60-100 °C at a heating rate of 5.0 K min⁻¹.

19 Tensile tests were conducted on a Shimadzu AGS-X electronic universal testing machine (Japan)
20 with an extension rate of 100.0 mm min⁻¹. The film dimensions were 30 mm × 10 mm (length ×
21 width). The results and errors were obtained from the average values of at least four replicates
22 of each independently prepared sample.

23

24 1. Liang, H. Y.; Feng, Y. C.; Lu, J. Y.; Liu, L. X.; Yang, Z. H.; Luo, Y.; Zhang, Y.; Zhang, C. Q., Bio-based
25 cationic waterborne polyurethanes dispersions prepared from different vegetable oils. *Ind Crop Prod*
26 **2018**, 122, 448-455.

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