Supporting Information For:

Effect of the Ratio of Acetylacetate Groups on the Properties of a Novel Plant-Based Dual-Cure Coating System

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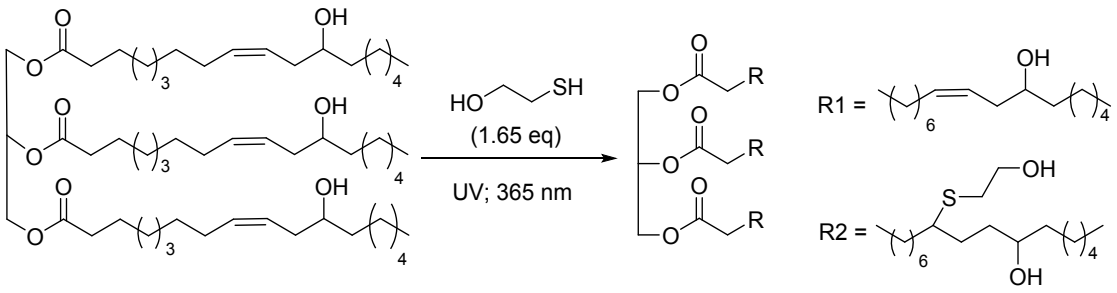
1 Synthesis of modified acetoacetylated castor oil

Castor oil (a1) was obtained from Sigma Aldrich (China). **Acetoacetylated castor oil (b1) was** reported by our previous work[1].

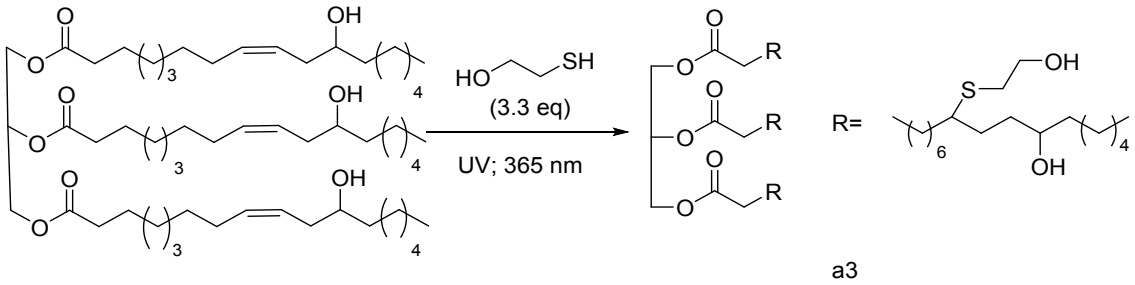
1. 1 Synthesis of part modified castor oil (a2)



a2 : R = R1 or R2

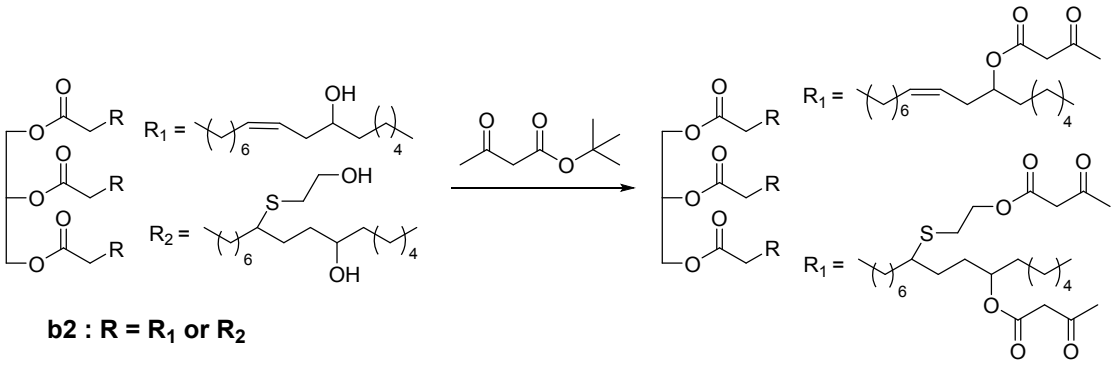
Castor oil **a1** (14 g, 0.015 mol), 2-hydroxy-2-methylpropheone (5 *wt* %) and 2-mercaptoethanol (1.934 g, 0.02475 mol) in DCM (40 mL) were thoroughly mixed in a round-bottomed flask under nitrogen for 10 min. Then, the reactants were irradiated by UV-light irradiation (8 mW, 365 nm) for 5 h. The dichloromethane was removed via rotary evaporation after the reaction, and then the excess 2-mercaptoethanol was removed by vacuum distillation at 100-110 °C, finally, yellow oil of **a2** was obtained in yield of 49.17 % (calculation method by ^{1}H NMR in **Figure S2**). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 5.49-5.41(m, 6H), 5.25 (m, 1H), 4.31-4.14 (m, 4H), 3.67-3.56 (m, 4H), 2.67-2.31 (m, 2H), 2.18-2.01 (m, 8H), 1.61 (m, 8H), 1.42-1.29 (m, 32H), 0.88 (m, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ(ppm) = 173.08, 133.61, 126.08, 70.86, 68.81, 61.96, 61.41, 61.19, 40.60, 37.85, 37.45, 37.11, 36.49, 34.02, 33.84, 32.52, 31.77, 29.54, 29.27, 28.88, 27.25, 26.59, 25.51, 24.66, 22.54, 14.03. Viscosity: 11.77 Pa.s. GPC (theoretical formula weight = 1053); Mn = 990, Mw = 1079, PDI = 1.09.

1. 2 Synthesis of modified castor oil (a3)



Castor oil **a1** (14 g, 0.015 mol), 2-hydroxy-2-methylpropheone (5 *wt* %) and 2-mercaptoethanol (3.868 g, 0.0495 mol) in DCM (40 mL) were thoroughly mixed in a round-bottomed flask under nitrogen for 10 min. Then, the reactants were irradiated by UV-light irradiation (8 mW, 365 nm) for 5 h. The dichloromethane was removed via rotary evaporation after the reaction, and then the excess 2-mercaptoethanol was removed by vacuum distillation at 100-110 °C, finally, yellow oil of **a3** was obtained in yield of 93.33 % (calculation method by ^{1}H NMR in **Figure S3**). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 5.26 (m, 1H), 4.29-4.14 (m, 4H), 3.77-3.69 (m, 6H), 2.93-2.71 (m, 9H), 2.33-2.30 (m, 6H), 1.61-1.29 (m, 69H), 0.88-0.86 (m, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ(ppm) = 173.25, 172.84, 71.54, 70.19, 68.83, 61.96, 61.92, 61.43, 61.24, 45.91, 45.78, 42.89, 42.21, 37.87, 37.49, 37.21, 34.96, 34.82, 34.11, 33.95, 33.71, 33.11, 32.94, 32.70, 31.79, 30.71, 29.56, 29.36, 29.13, 28.95, 26.67, 26.44, 25.71, 25.64, 25.47, 24.74, 22.59, 14.09. Viscosity: 19.15 Pa.s. GPC (theoretical formula weight = 1170); Mn = 1081, Mw = 1192, PDI = 1.10.

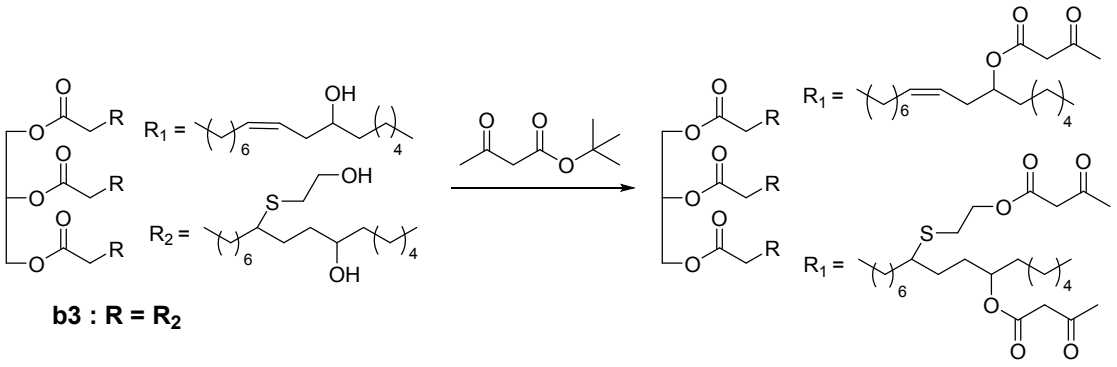
1. 3 Synthesis of part modified acetoacetylated castor oil (b2)



b2 : R = R_1 or R_2

Tert-butylacetoacetate (10.678 g, 0.0675 mol) and toluene (30 mL) were added to the modified castor oil **a2** (15.81 g, 0.015 mol) in a 250 mL round-bottomed flask, and the solution was heated to 130 °C with stirring for 6 h and stopped when no more liquid evolved and then the excess *t*-butyl acetoacetate was removed by vacuum distillation at 130-140 °C, finally, a yellow oil was obtained **b2** with a yield of 95.37 % (calculation method by ^{1}H NMR in **Figure S4**). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 5.44-5.35 (m, 3H), 5.25 (m, 1H), 4.95-4.88 (m, 2H), 4.29-4.14 (m, 4H), 3.47-3.42 (m, 4H), 2.30-2.23 (m, 14H), 1.98-1.92 (m, 4H), 1.59-1.55 (m, 10H), 1.28 (m, 33H), 0.87-0.6 (m, 6H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ(ppm) = 200.15, 172.73, 172.38, 133.69, 124.66, 74.70, 73.15, 68.78, 64.12, 61.85, 50.11, 49.63, 32.73, 37.09, 33.89, 33.74, 33.19, 32.16, 31.52, 29.85, 29.12, 28.92, 24.98, 24.66, 22.41, 13.94. Viscosity: 2.26 Pa.s. GPC (theoretical formula weight = 1432); Mn = 1359, Mw = 1492, PDI = 1.10.

1. 4 Synthesis of modified acetoacetylated castor oil (b3)



b3 : R = R_2

Tert-butylacetoacetate (14.24 g, 0.09 mol) and toluene (30 mL) were added to the modified castor oil **a3** (17.56 g, 0.015 mol) in a 250 mL round-bottomed flask, and the solution was heated to 130 °C with stirring for 6 h and stopped when no more liquid evolved and then the excess *t*-butyl acetoacetate was removed by vacuum distillation at 130-140 °C, finally, a yellow oil was obtained **b3** with a yield of 91.20 % (calculation method by ^{1}H NMR in **Figure S5**). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 5.17 (m, 1H), 4.16-4.07 (m, 6H), 3.59-3.28 (m, 6H), 2.67-2.56 (m, 4H), 2.24-1.86 (m, 12H), 1.53-1.22 (m, 42H), 0.80 (m, 6H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ(ppm) = 200.38, 172.71, 172.53, 163.53, 75.16, 74.95, 73.33, 68.81, 64.36, 64.28, 64.15, 61.93, 50.12, 49.73, 45.88, 42.73, 39.63, 36.33, 34.84, 34.57, 34.29, 34.06, 33.81, 31.56, 30.83, 29.98, 29.55, 29.22, 28.98, 28.43, 28.17, 26.59, 26.39, 26.28, 25.06, 24.91, 24.68, 22.43, 21.06, 13.98. Viscosity: 3.24 Pa.s. GPC (theoretical formula weight = 1675); Mn = 1486, Mw = 1661, PDI = 1.12.

2. GPC characterization of acetoacetate-modified castor oil

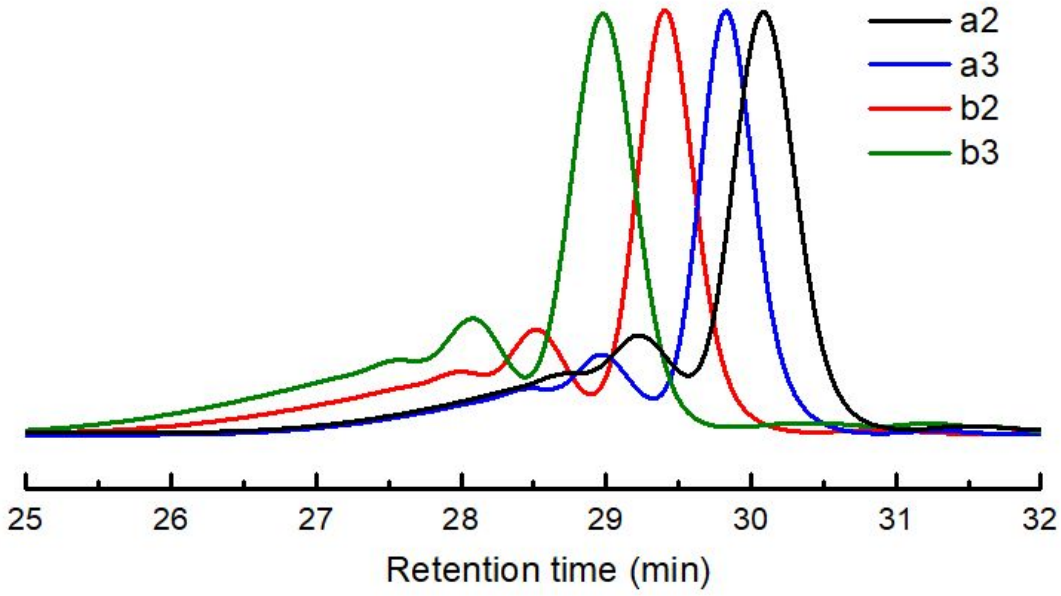


Figure S1 GPC characterization of acetoacetate-modified castor oil

3 Calculate the yield of modified acetoacetylated castor oil

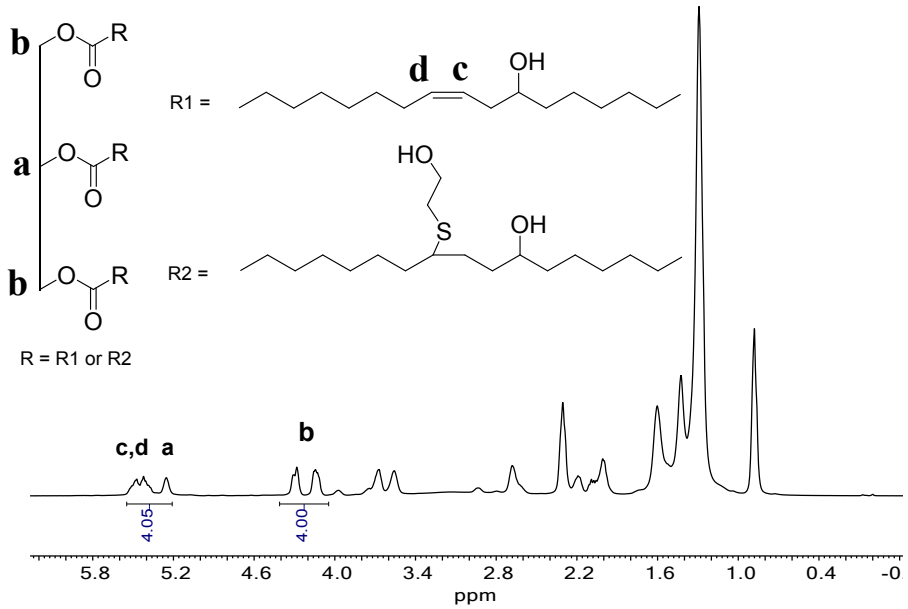


Figure S2 ^{1}H NMR spectra of part modified castor oil (**a2**)

From the **Figure S2**, we can see that the ^{1}H NMR spectra peak areas ratio are corresponding to the structure, and the yield of part modified castor oil was calculated using the equation: (A2) = [A(d+c)-A(d'+c')]/A(d+c) = [(7-1)-(4.05-1)]/(7-1)=0.4917

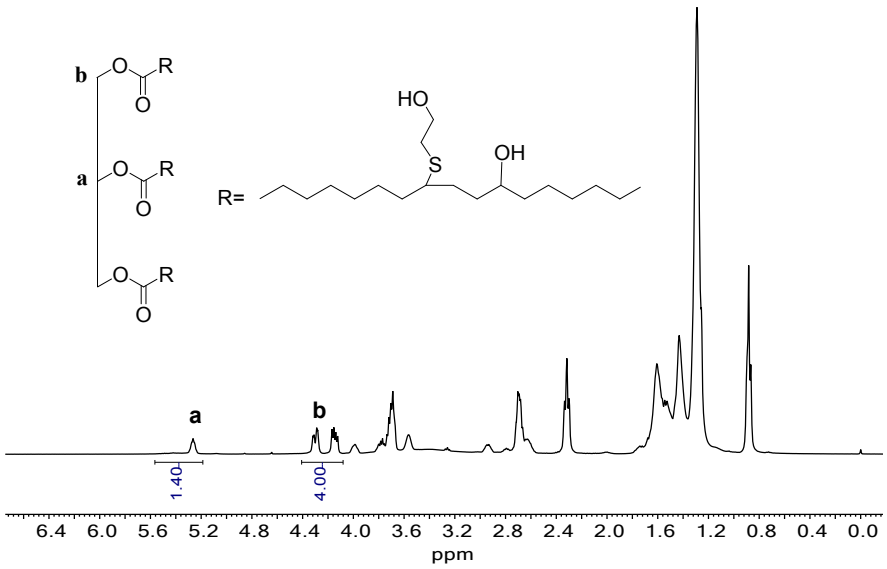


Figure S3 ^{1}H NMR spectra of modified castor oil (**a3**)

W (a3) = [(7-1)-(1.40-1)]/(7-1)=0.9333

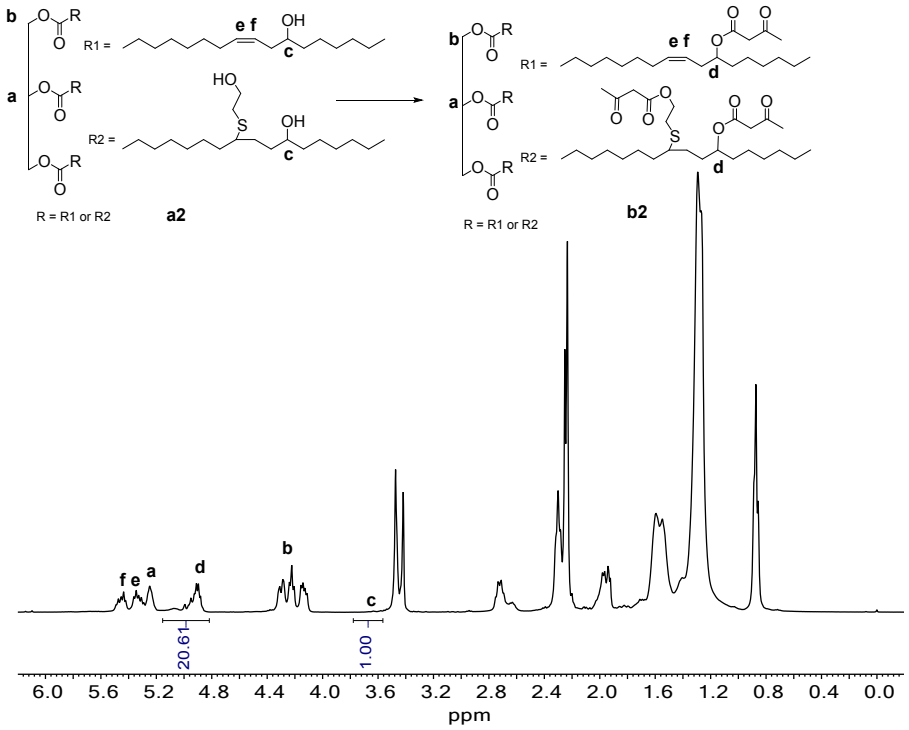


Figure S4 ^{1}H NMR spectra of part modified acetoacetylated castor oil (**b2**)

W(b2)=A(d)/[A(d)+A(c)]=20.61/21.61=0.9537

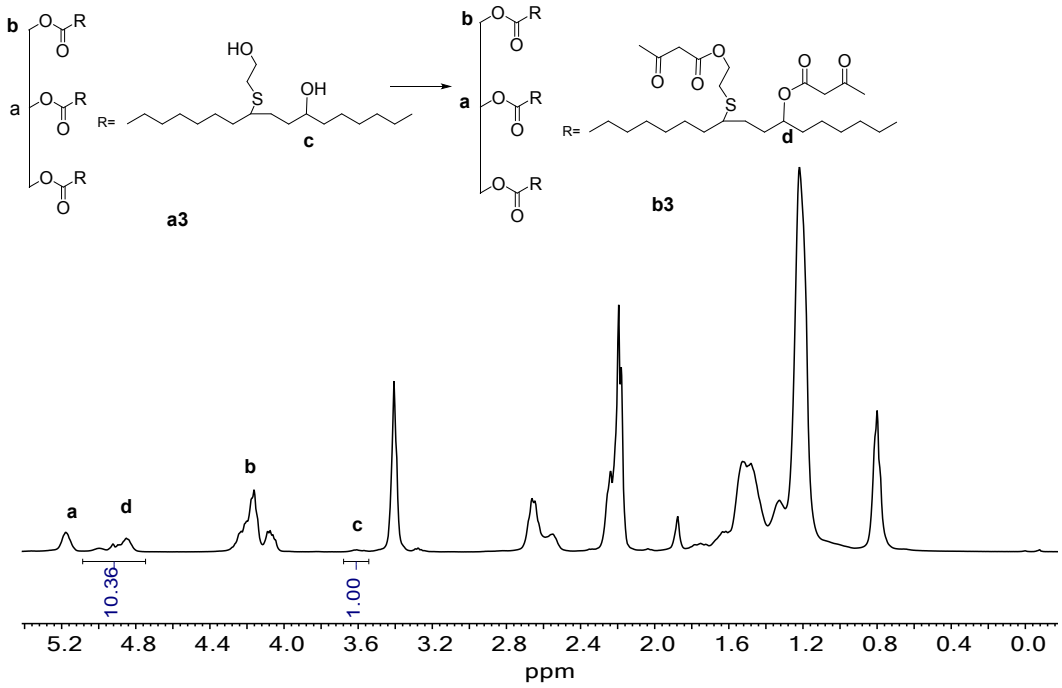


Figure S5 ^{1}H NMR spectra of modified acetoacetylated castor oil (**b3**)

W(b3)=A(d)/[A(d)+A(c)]=10.36/11.36=0.912

4 The Viscosity of modified acetoacetylated castor oil

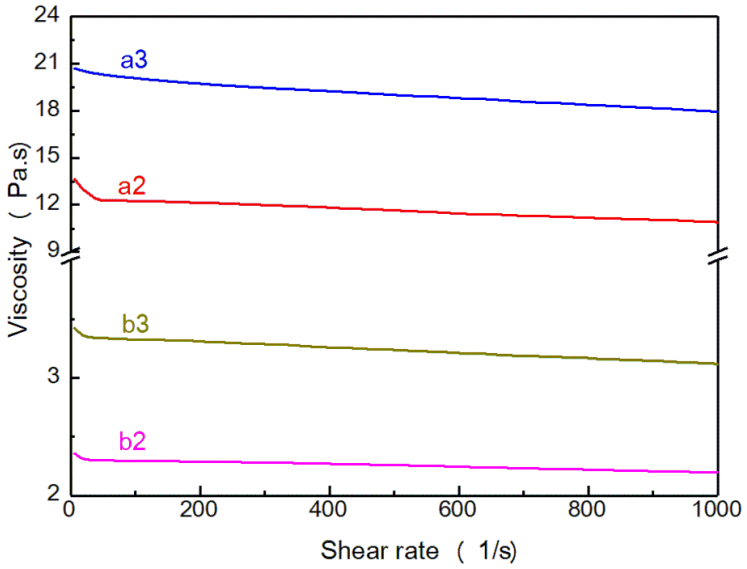


Figure S6 the viscosity of modified acetoacetylated castor oil

5 The DSC curves indicating glass transition of the three films

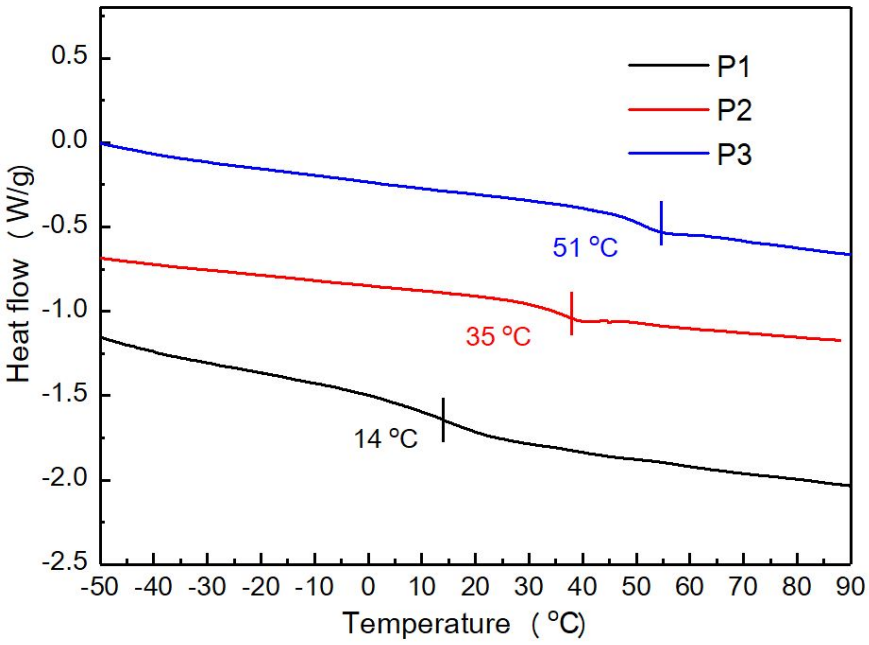


Figure S7 The DSC curves indicating glass transition of the three films.

6 The NMR spectra of modified acetoacetylated castor oil

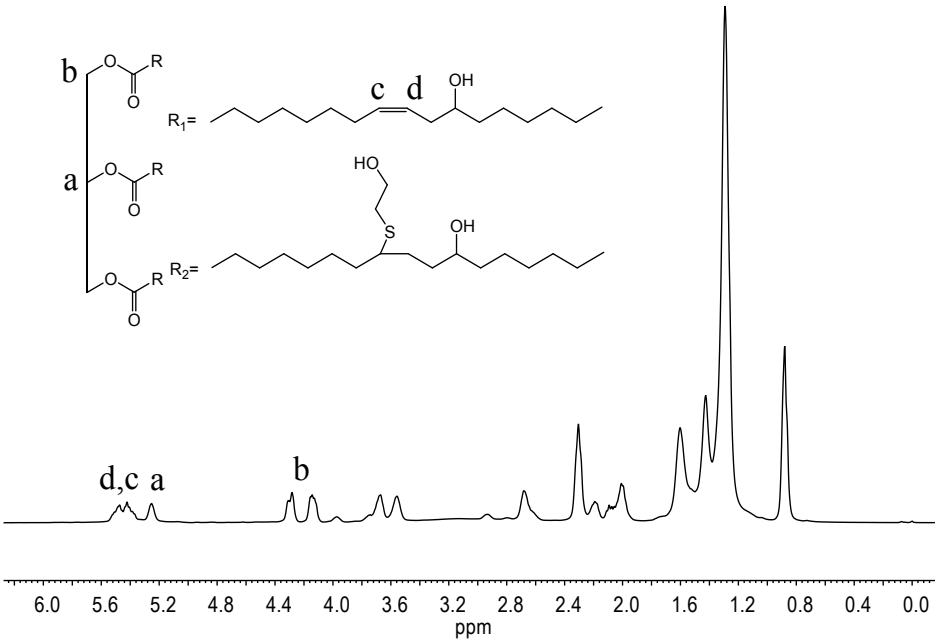


Figure S8 ^{1}H NMR spectra of modified castor oil **(a2)**

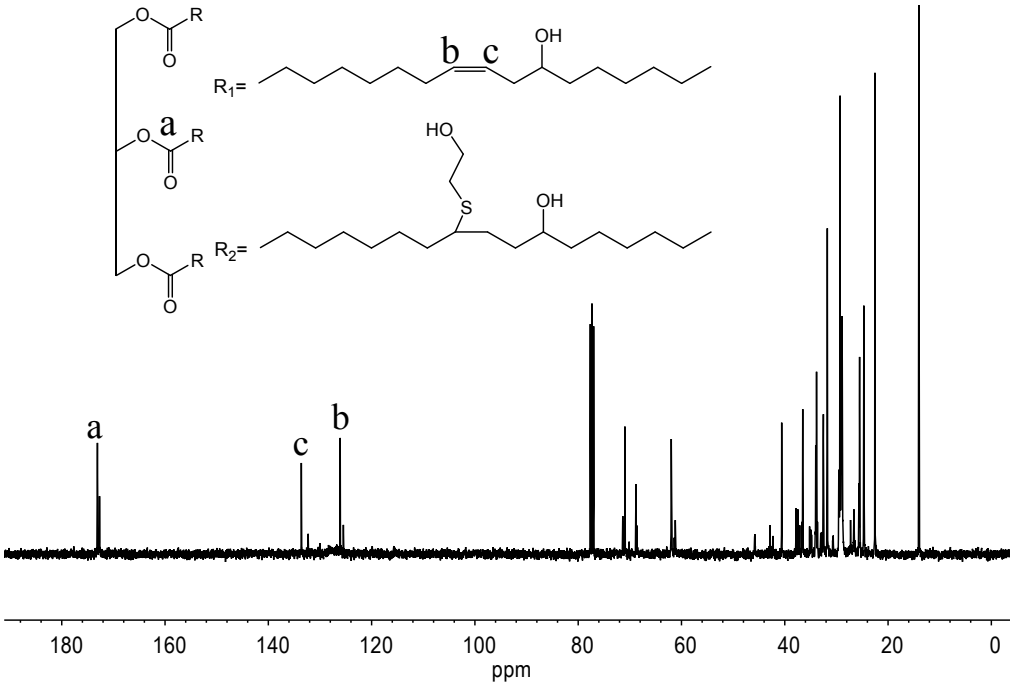


Figure S9 ^{13}C NMR spectra of modified castor oil (**a2**)

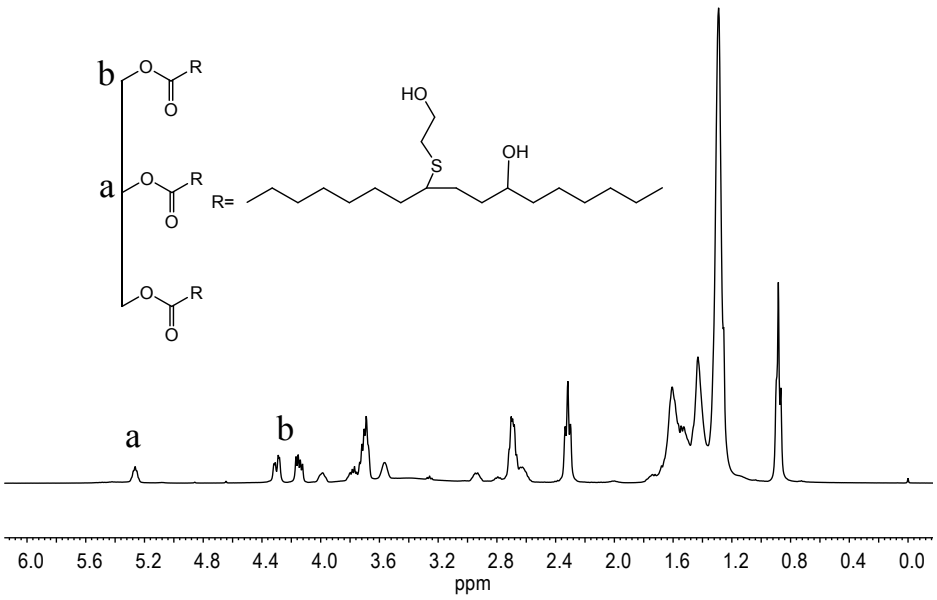


Figure S10 ^{1}H NMR spectra of modified castor oil (**a3**)

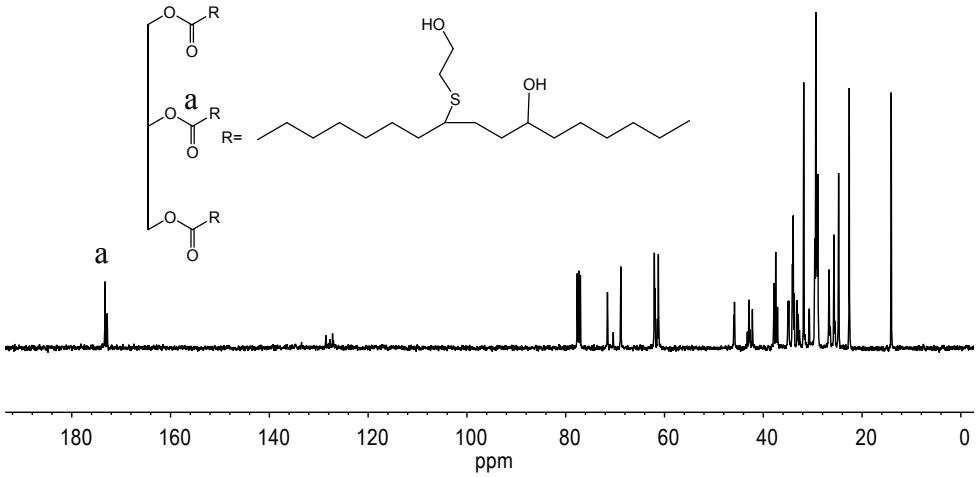


Figure S11 ^{13}C NMR spectra of modified castor oil (**a3**)

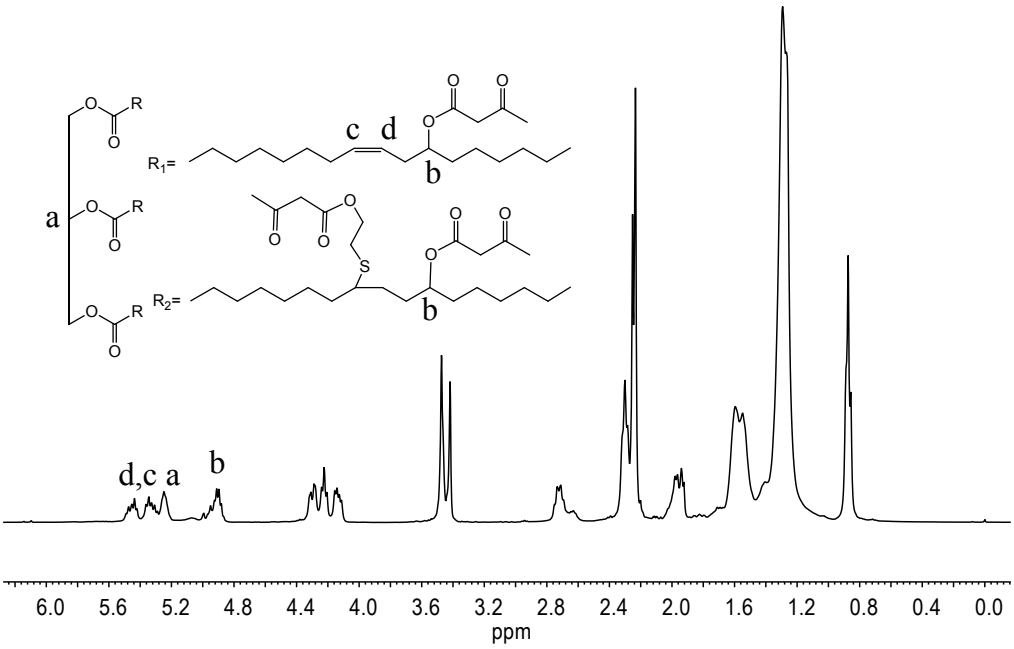


Figure S12 ^{1}H NMR spectra of modified acetoacetylated castor oil (**b2**)

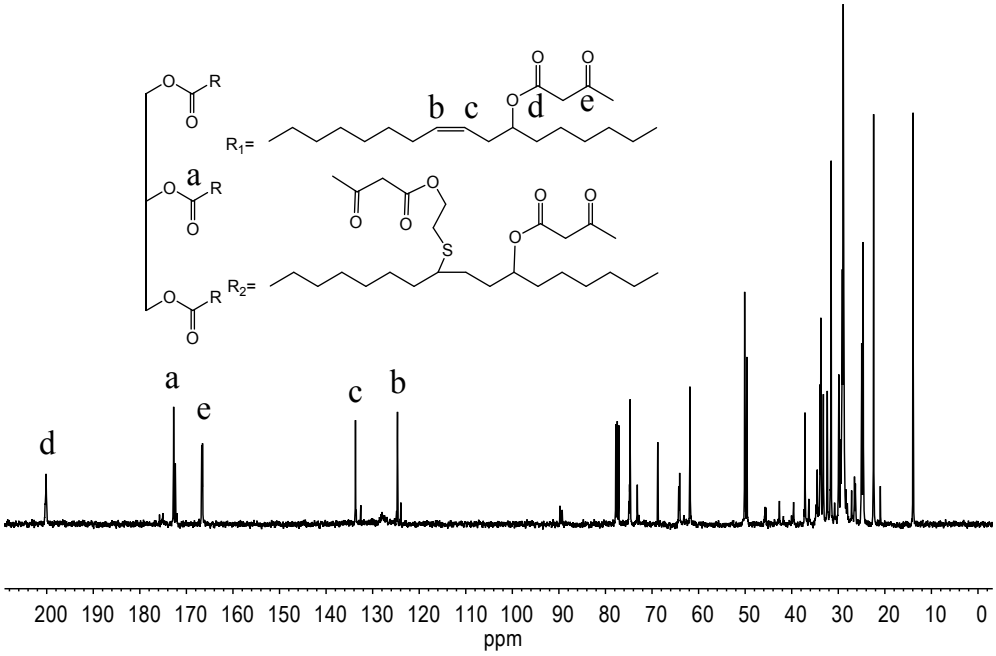


Figure S13 ^{13}C NMR spectra of modified acetoacetylated castor oil (**b2**)

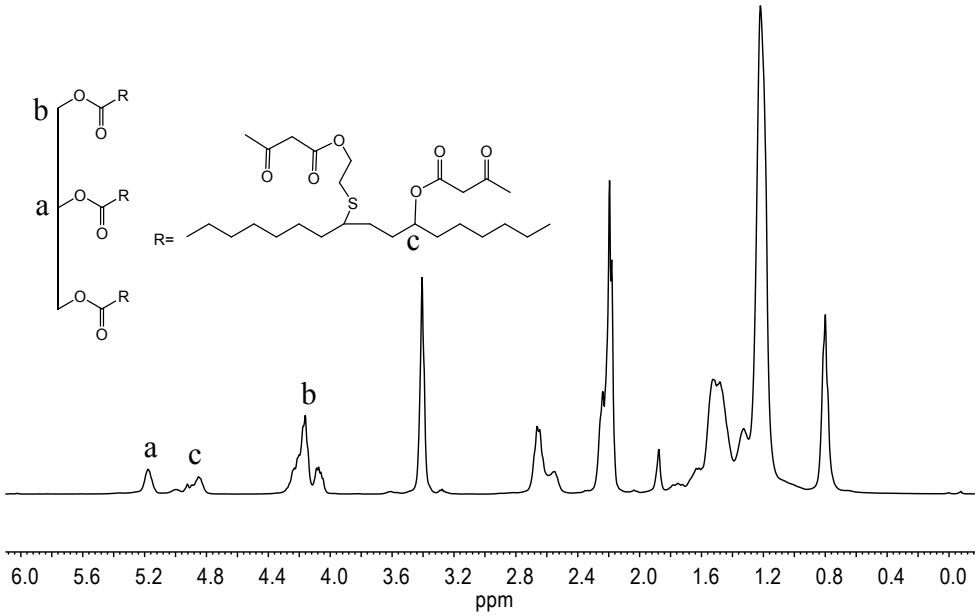


Figure S14 ^{1}H NMR spectra of modified acetoacetylated castor oil (**b3**)

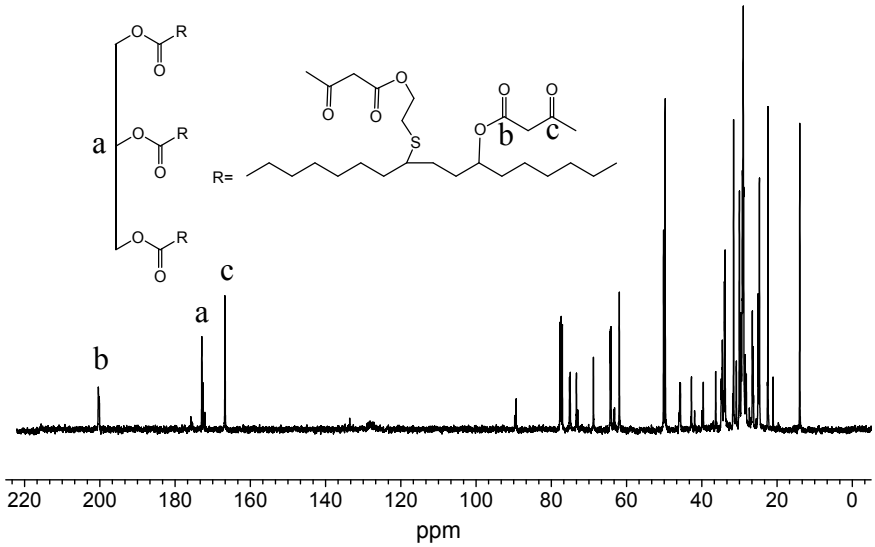


Figure S15 ^{13}C NMR spectra of modified acetoacetylated castor oil (**b3**)

1. X. He, J. Zhong, Z. Cao, J. Wang, F. Gao, D. Xu and L. Shen, *Progress in Organic Coatings*, 2019, **129**, 21-25.