Supporting Information

Silk Fibroin-Based Multiple-Shape-Memory Organohydrogels

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Table S1. Gel fraction W_g and equilibrium water content *EWC* of OHGs

wt. % of the hydrophobic components in OHGs						W_g	EWC
PC18A	$C_{14}H_{30}$	$C_{18}H_{38}$	$C_{22}H_{46}$	$C_{22}H_{46}O$	$C_{32}H_{66}$		
25	0	75	0	0	0	1.1 ± 0.1	50%
50	0	50	0	0	0	1.1 ± 0.2	50%
12.5	0	37.5	0	0	50	0.46 ± 0.05	77%
33.33	0	33.33	0	0	33.33	1.0 ± 0.1	50%
37.5	0	37.5	0	0	25	1.1 ± 0.1	41%
12.5	50	12.5	0	0	25	0.73 ± 0.04	66 ± 1 %
25	25	25	0	0	25	0.9 ± 0.1	62 ± 3 %
37.5	12.5	37.5	0	0	12.5	1.1 ± 0.1	52 ± 2 %

Table S2. Synthesis conditions of PC18A/n-docosane (Doco) blends at various compositions. Irgacure was used at 0.2 mol% of C18A monomer.

Sample No	*C18A* (g)	*Doco* (g)	Irgacure (mg)	Doco wt. %	Doco mol %
1	3	1	4.1	25	25.8
2	2.8	1.2	3.9	30	30.9
3	2.6	1.4	3.6	35	36.0
4	2.4	1.6	3.3	40	41.1
5	2.2	1.8	3	45	46.1
6	2	2	2.8	50	51.1
7	1.8	2.2	2.5	55	56.1
8	1	3	1.4	75	75.8

Table S3. Synthesis conditions of PC18A/n-octadecane (Octa) blends at various compositions. Irgacure was used at 0.2 mol% of C18A monomer.

Sample No	*C18A* (g)	*Octa* (g)	Irgacure (mg)	Octa wt. %	Octa mol %
9	3	1	4.1	25	29.8
10	2.8	1.2	3.9	30	35.3
11	2.6	1.4	3.6	35	40.7
12	2.4	1.6	3.3	40	46.0
13	2.2	1.8	3	45	51.1
14	2	2	2.8	50	56.0
15	1.8	2.2	2.5	55	60.9
16	1	3	1.4	75	79.3

Table S4. Synthesis conditions of PC18A/n-dotriacontane (Dotria) blends at various compositions. Irgacure was used at 0.2 mol% of C18A monomer.

Sample No	*C18A* (g)	*Dotria* (g)	Irgacure (mg)	Dotria wt. %	Dotria mol %
17	3	1	4.1	25	19.4
18	2.8	1.2	3.9	30	23.6
19	2.6	1.4	3.6	35	27.9
20	2.4	1.6	3.3	40	32.4
21	2.2	1.8	3	45	37.1
22	2	2	2.8	50	41.9
23	1.8	2.2	2.5	55	46.8
24	1	3	1.4	75	68.3

Table S5. Synthesis conditions of PC18A/n-tetradecane (Tetra) blends at various compositions. Irgacure was used at 0.2 mol% of C18A monomer.

Sample No	*C18A* (g)	*Tetra* (g)	Irgacure (mg)	Tetra wt%	Tetra mol %
25	3	1	4.1	25	35.3
26	2.8	1.2	3.9	30	41.2
27	2.6	1.4	3.6	35	46.8
28	2.4	1.6	3.3	40	52.2
29	2.2	1.8	3	45	57.2
30	2	2	2.8	50	62.1
31	1.8	2.2	2.5	55	66.7
32	1	3	1.4	75	83.1

Table S6. Synthesis conditions of PC18A/n-octadecane/n-docosane blends.

Sample No	*Octa* (g)	*Doco* (g)	*C18A* (g)	Irgacure (mg)	Octa wt%	Doco wt%	C18A wt%	Octa mol %	Doco mol %	C18A mol %
33	1	2	1	1.4	25	50	25	17.5	28.6	53.9
34	0.5	3	0.5	0.7	12.5	75	12.5	11.1	54.6	34.2
35	1.2	1.2	1.6	2.2	30	30	40	20.4	16.7	62.9
36	1.4	2	0.6	0.8	35	50	15	19.0	22.3	58.7
37	1.4	0.2	2.4	3.3	35	5	60	23.8	2.8	73.4
38	1.4	1.6	1	1.4	35	40	25	19.9	18.7	61.4
39	1.6	1	1.4	1.9	40	25	35	21.8	11.1	67.1
40	1.6	2	0.4	0.6	40	50	10	19.6	20.1	60.4
41	1.8	1.5	0.7	1	45	37.5	17.5	21.0	14.3	64.7
42	3	0.6	0.4	0.6	75	15	10	23.6	3.9	72.6

Table S7.

Synthesis conditions of OHGs with PC18A and n-octadecane in the oil phase.

Phases	**Raw Materials**	**OHG-1**	**OHG-2**
Water Phase (∑5 mL)	SF (9.5 *w/v*%)	3.421 mL	
	Distilled Water	0.355 mL	
	Ethanol	0.835 mL	
	DMAA	0.389 mL	
	BAAm	5.83 mg	
	Irgacure 2959	1.69 mg	
Oil Phase (∑5 mL)	C18A	2 g	1 g
	n-octadecane	2 g	3 g
	Irgacure	2.8 mg	1.4 mg
	Octadecane wt. %	50	75

Table S8. Synthesis conditions of OHGs with PC18A, n-octadecane, and/or n-docosane in the oil phase.

Phases	Raw Materials	OHG-3	OHG-4	OHG-5
Water Phase (∑5 mL)	SF (9.5 w/v%)		3.421 mL	
	Distilled Water		0.355 mL	
	Ethanol		0.835 mL	
	DMAA		0.389 mL	
	BAAm		5.83 mg	
	Irgacure		1.7 mg	
Oil Phase (∑5 mL)	C18A	3.5 g	3.5 g	3.5 g
	n-octadecane	0.5 g	-	0.25 g
	n-docosane	-	0.5 g	0.25 g
	Irgacure 2959	4.8 mg	4.8mg	4.8 mg
	Octadecane wt. %	12.5	0	6.25
	Docasane wt. %	0	12.5	6.25
	C18A wt. %	87.5	87.5	87.5

Table S9. Synthesis conditions of OHGs with PC18A, n-octadecane, and/or n- dotriacontane in the oil phase.

Phases	Raw Materials	OHG-6	OHG-7	OHG-8
Water Phase (∑5 mL)	SF (9.5 w/v%)		3.421 mL	
	Distilled Water		0.355 mL	
	Ethanol		0.835 mL	
	DMAA		0.389 mL	
	BAAm		5.83 mg	
	Irgacure		1.7 mg	
Oil Phase (∑5 mL)	C18A	0.5 g	1.33 g	1.5 g
	n-octadecane	1.5 g	1.33 g	1.5 g
	n-dotriacontane	2 g	1.33 g	1 g
	Irgacure 2959	0.7 mg	1.8 mg	2.1 mg
	Octadecane wt. %	37.5	33.3	37.5
	Dotriacontane wt. %	50	33.3	25
	C18A wt. %	12.5	33.3	37.5

Table S10. Synthesis conditions of OHGs with PC18A, n-octadecane, n- dotriacontane, and n-tetradecane in the oil phase.

Phases	Raw Materials	OHG-9	OHG-10	OHG-11
Water Phase (∑5 mL)	SF (9.5 w/v%)		3.421 mL	
	Distilled Water		0.355 mL	
	Ethanol		0.835 mL	
	DMAA		0.389 mL	
	BAAm		5.83 mg	
	Irgacure		1.7 mg	
Oil Phase (∑5 mL)	C18A	1.5 g	1 g	1.5 g
	n-octadecane	0.5 g	1 g	1.5 g
	n-dotriacontane	1 g	1 g	0.5 g
	n-tetradecane	1 g	1 g	0.5 g
	Irgacure 2959	2.1 mg	1.4 mg	2.1 mg
	Octadecane wt. %	12.5	25	37.5
	Dotriacontane wt. %	25	25	12.5
	Tetradecane wt. %	25	25	12.5
	C18A wt. %	37.5	25	37.5

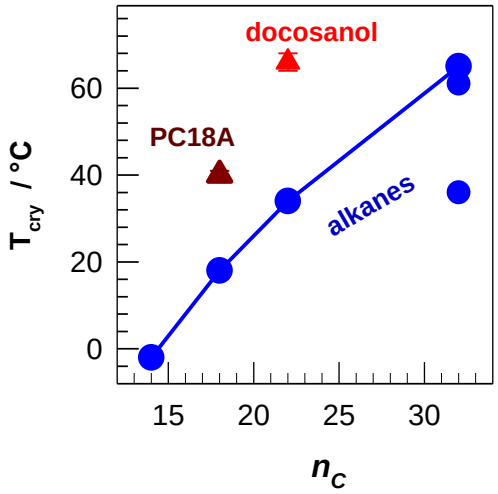

Figure S1. Crystallization temperature T_{cry} of neat PC18A and HCs plotted against the number of carbon atoms n_C.

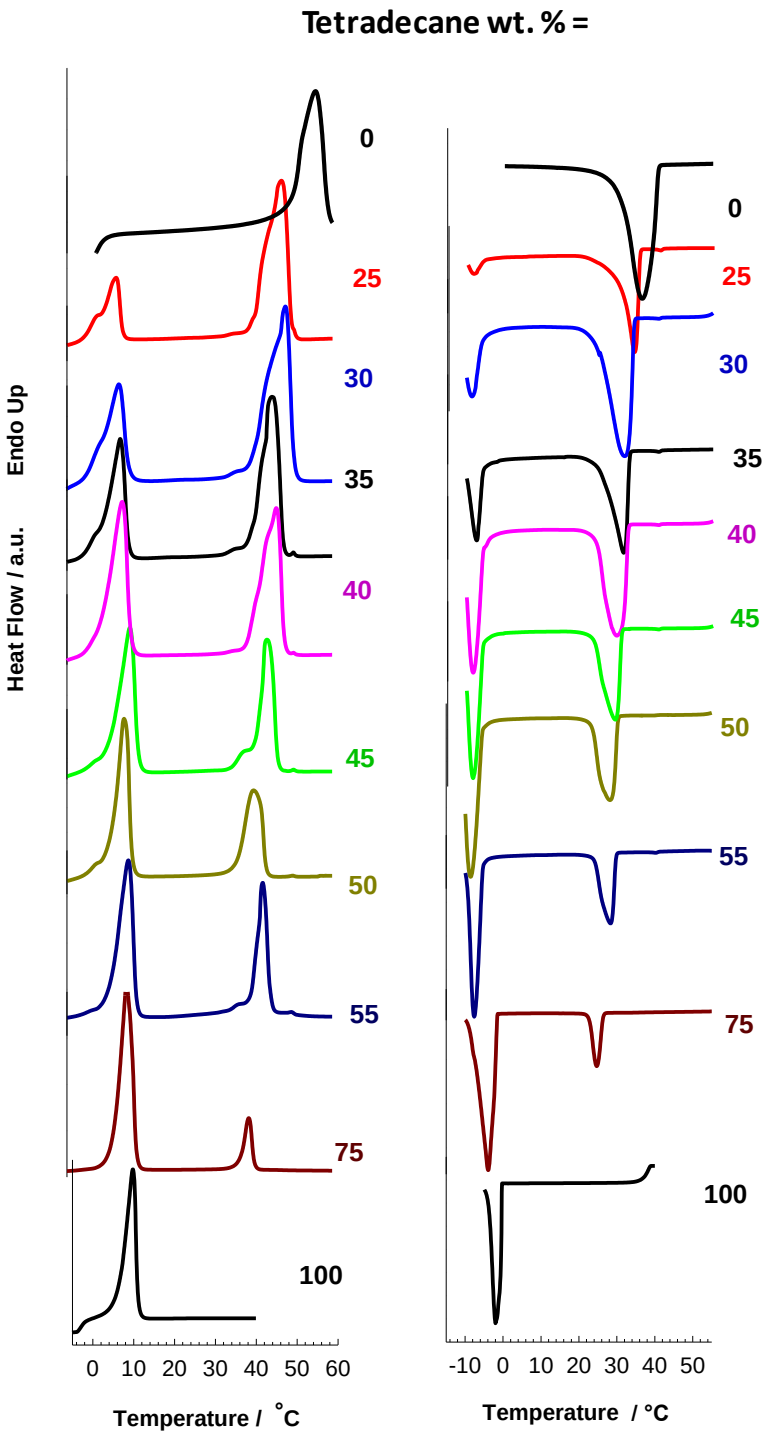

Figure S2a. Heating and cooling DSC scans of dimer combinations of in-situ formed PC18A and tetradecane at various combinations.

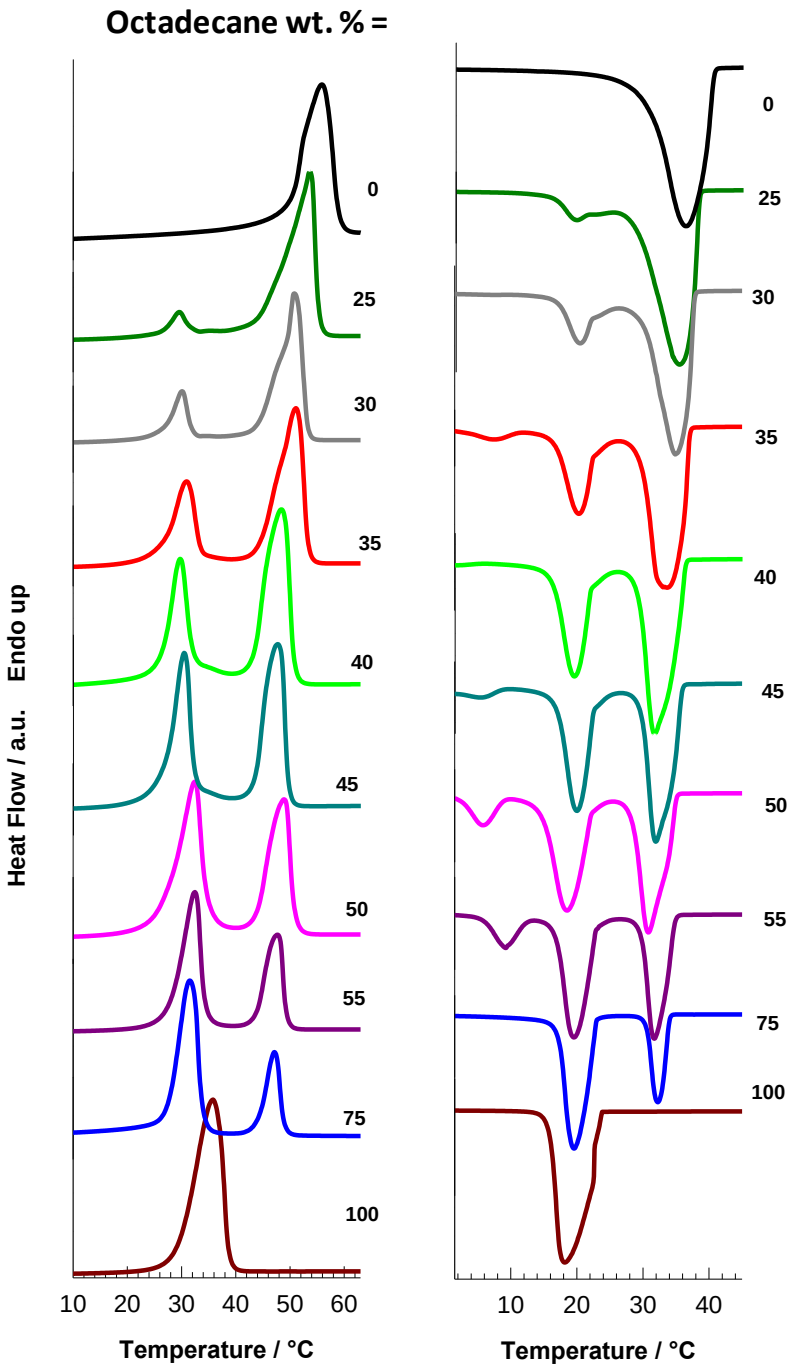

Figure S2b. Heating and cooling DSC scans of dimer combinations of in-situ formed PC18A and octadecane at various combinations.

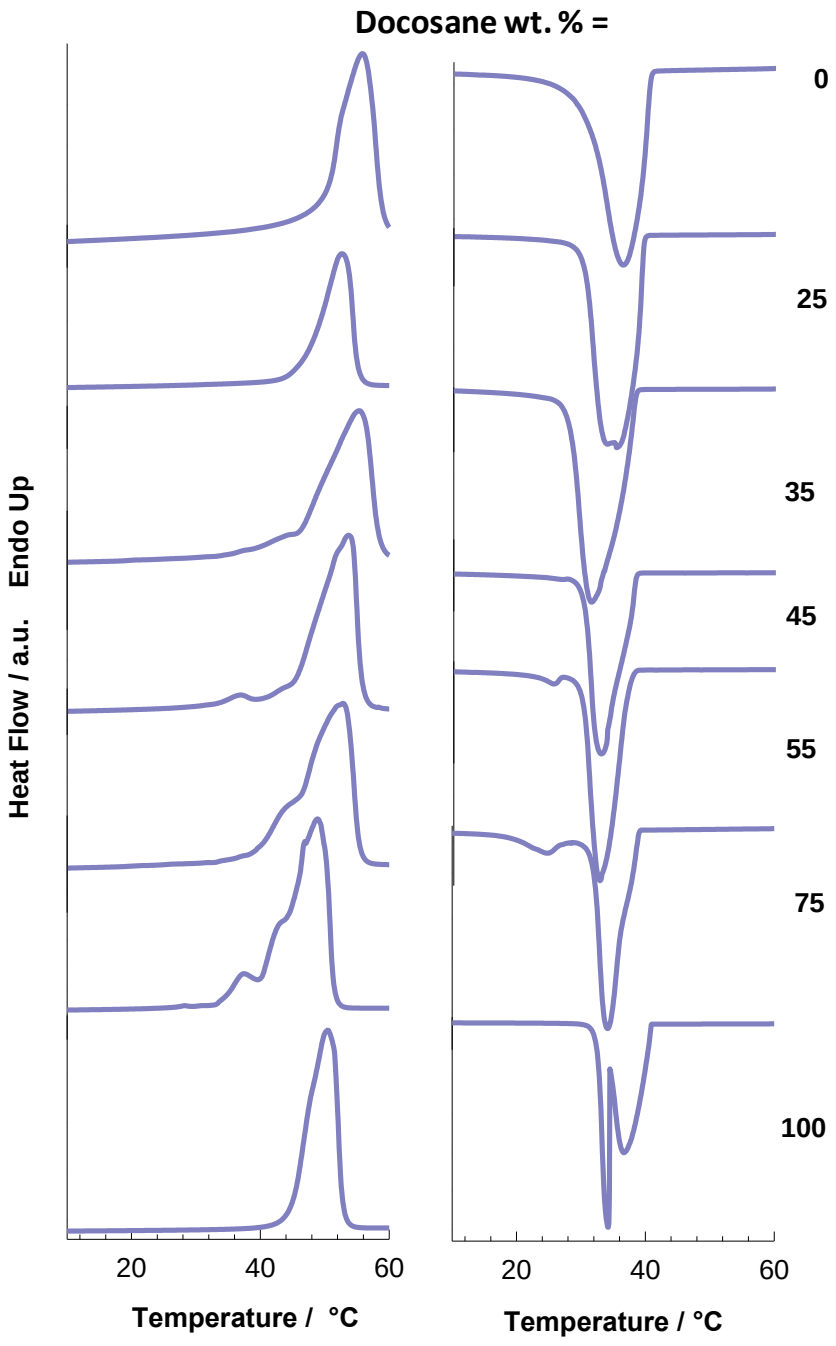

Figure S2c. Heating and cooling DSC scans of dimer combinations of in-situ formed PC18A and docosane at various combinations.

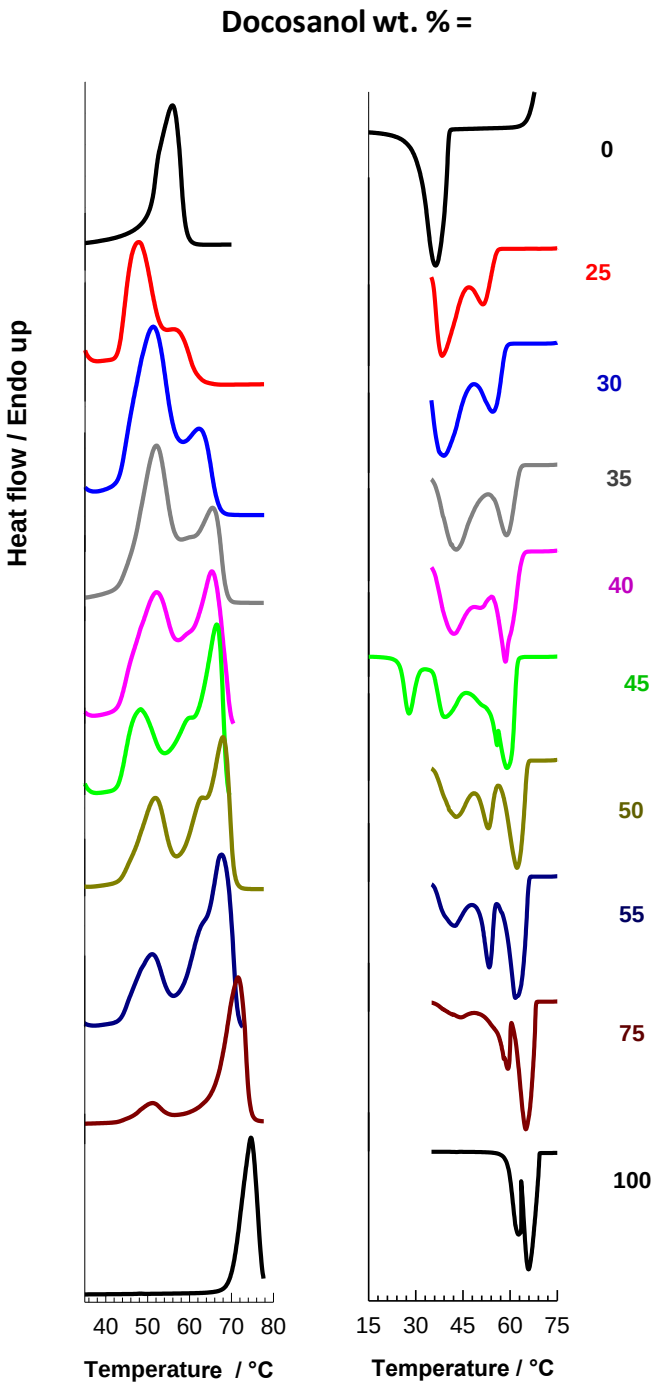

Figure S2d. Heating and cooling DSC scans of dimer combinations of in-situ formed PC18A and docosanol at various combinations.

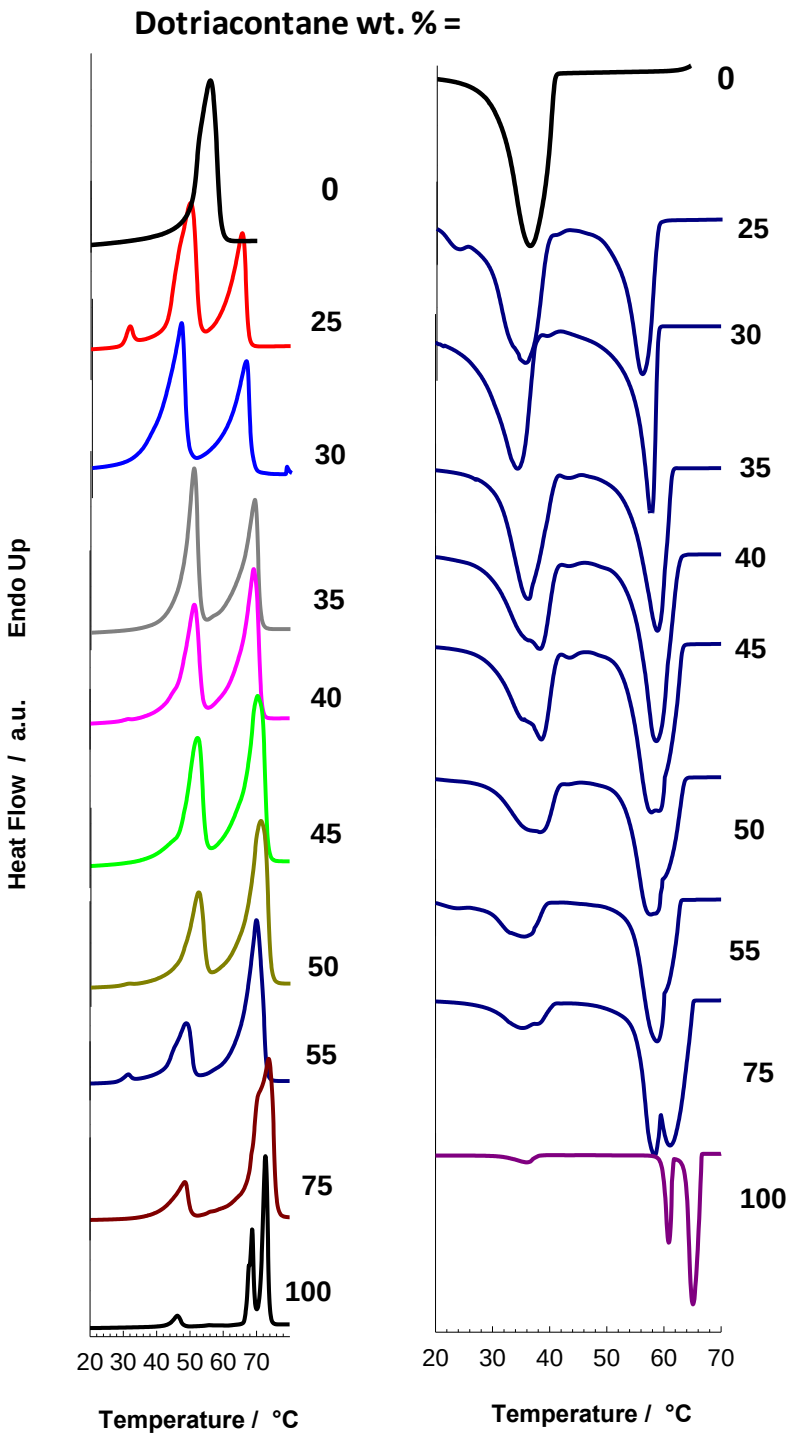

Figure S2e. Heating and cooling DSC scans of dimer combinations of in-situ formed PC18A and dotriacontane at various combinations.

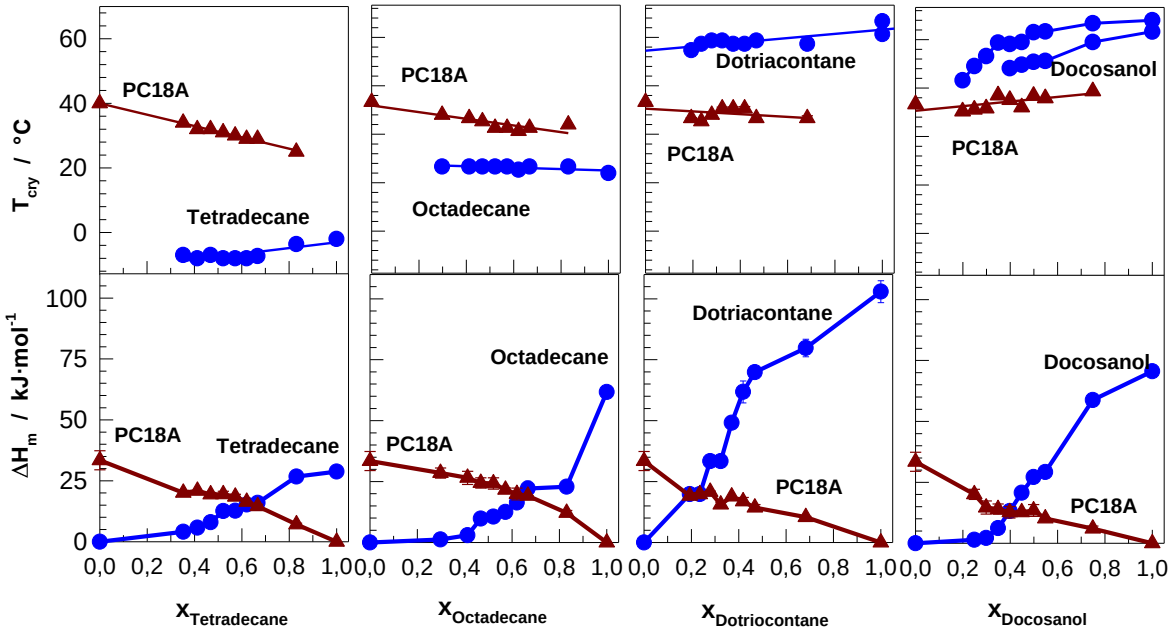

Figure S3. Crystallization temperature (T_{cry}), and melting enthalpy (ΔH_m) of dimer combinations of in-situ formed PC18A/HC blends plotted against the hydrophobe mole fraction in the blends.

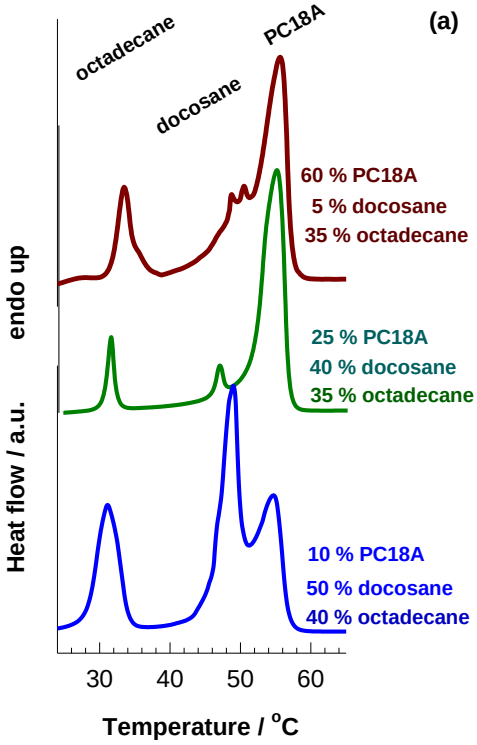

Figure S4. DSC scans of ternary alkane blends (PC18A/$C_{18}H_{38}$/$C_{22}H_{46}$) at various combinations as indicated by wt. %.

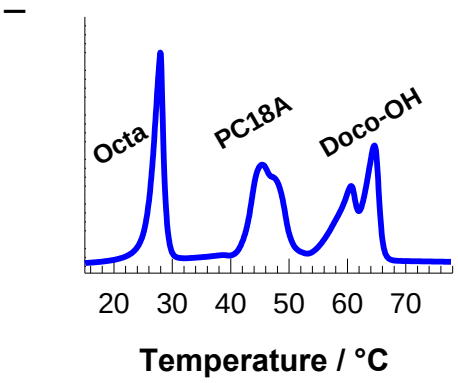

Figure S5. DSC scans of ternary alkane blends containing equal amounts of PC18A, $C_{18}H_{38}$ and $C_{22}H_{46}O$ (Doco-OH)

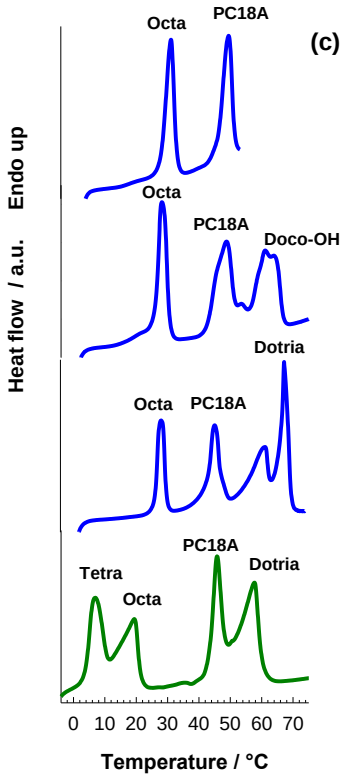

Figure S6. DSC scans of OHGs containing dimer, trimer, and quadruple combinations of equal amounts of alkanes and PC18A in the microinclusions.

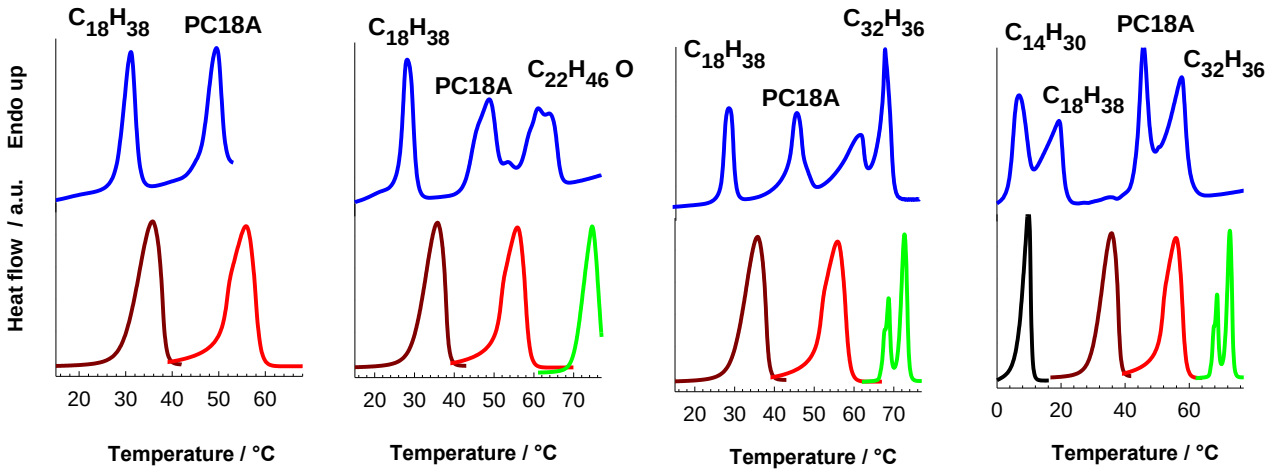

Figure S7. DSC scans of OHGs with equal amounts of blend components in the microinclusions (upper panel), and of the neat hydrophobes (bottom panel).

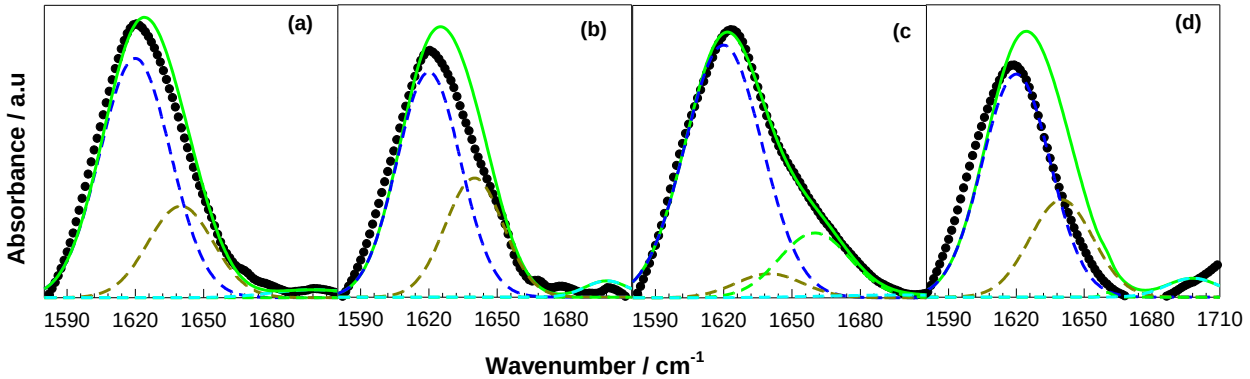

Figure S8. Amide I region of FTIR spectra for OHGs. The original data are shown by the filled circles while the results of curve fitting for the original spectrum and hidden peaks are shown by the solid and dashed curves, respectively. Composition of the microinclusions are: PC18A/ $C_{18}H_{38}$ microinclusions with 75 (a) and 50 wt. % $C_{18}H_{38}$ (b). PC18A/ $C_{18}H_{38}$ / $C_{32}H_{66}$ at weight ratios 37.5 / 37.5 / 25 (c). PC18A/ $C_{14}H_{30}$ /$C_{18}H_{38}$ / $C_{32}H_{66}$ at equal weight ratios (d).

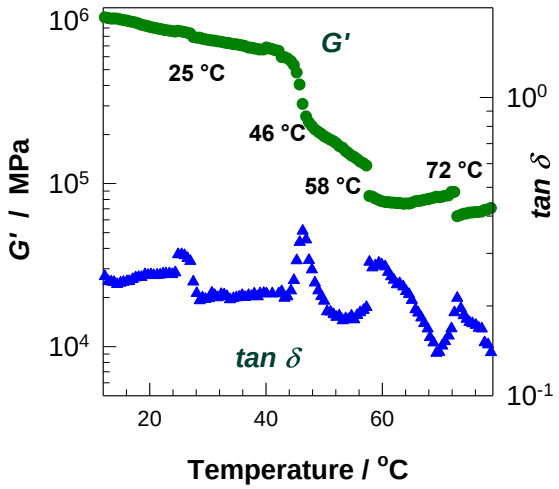

Figure S9. Storage modulus *G'* (circle) and loss factor *tan* δ (triangle) of an OHG specimen containing PC18A/$C_{18}H_{38}$/$C_{32}H_{66}$ at a weight ratio of 37.5/37.5/25 shown as a function of temperature. ω = 1 rad·s^{-1}. Heating rate = 1 °C·min^{-1}. Three of four transitions at 46, 58, and 72 °C are observable in *G'* vs. temperature plot. Although the transition at the lowest temperature of 25 °C is not seen, the peak in *tan* δ at this temperature reveals its existence.