Lubricating and waxy esters, II: Synthesis, crystallization, and melt behavior of branched monoesters

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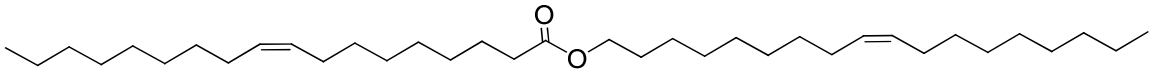
TITLE RUNNING HEAD: Lubricating and waxy esters, II: Branched monoesters.

ABSTRACT. A comprehensive study of branched derivatives of four pure jojoba wax-like esters (JLEs), having 36, 40 (two isomers) and 44 carbons was conducted to elucidate their crystallization and melting behavior. Crystallization and melting characteristics depended strongly on the number of branches, molar mass and symmetry. The derivatives demonstrated a very strong tendency to form glassy liquids rather than crystal phases and remain liquid-like at very low temperatures. As the number of branches increased, their crystallinity decreased drastically while their glassy phase increased concomitantly with the depression of the onset of crystallization and/or glass transition temperature. A variety of possible transformation paths, ranging from very little polymorphic activity to extremely polymorphic behavior, depending on number of branches, mass and symmetry were revealed. It is shown that asymmetry plays a large role in the low temperature behavior, rendering the branched derivatives of the asymmetrical JLEs much better candidates for lubricant formulations.

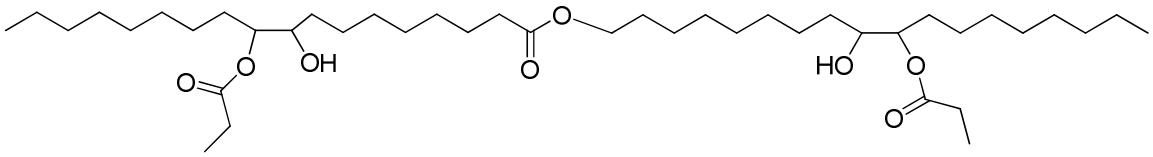
KEY WORDS. Branched jojoba wax esters; Differential scanning calorimetry; Crystallization; Melting; Solid fat content; Lubricants; Waxes.

Scheme S1: Structure of the Jojoba-Like mono-Esters (JLE) and their branched derivatives.

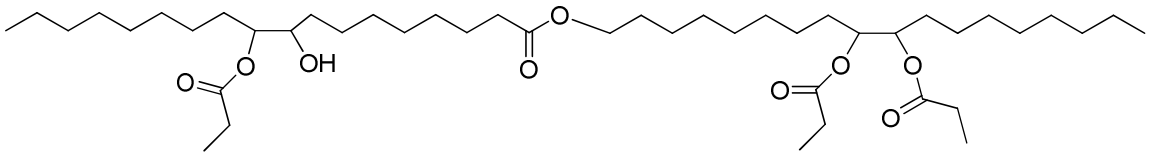
a- Octadec-9-enyl octadec-9-enoate (JLE-36S)



b- 9(10)-hydroxy-10(9)-(propionyloxy)octadecyl 9(10)-hydroxy-10(9)-(propionyloxy)octadecanoate (JLE-36S-2)



c- 1-(9(10)-hydroxy-10(9)-(propionyloxy)octadecanoyloxy) octadecane-9,10-diyldipropionate or 1-(9(10)-hydroxy-10(9)-(propionyloxy)octadecyloxy)-1-oxooctadecane-9,10-diyl dipropionate (JLE-36S-3)



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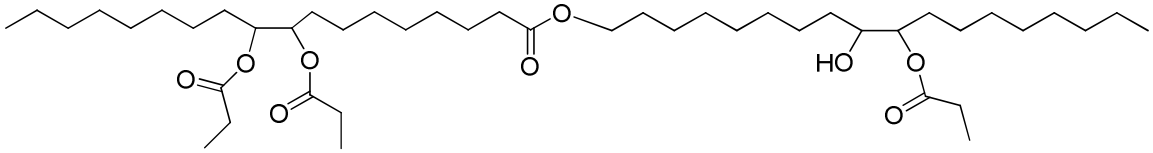
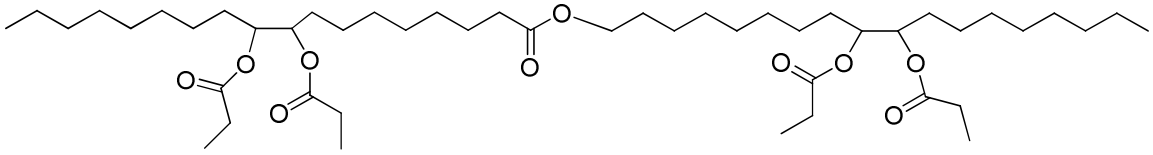
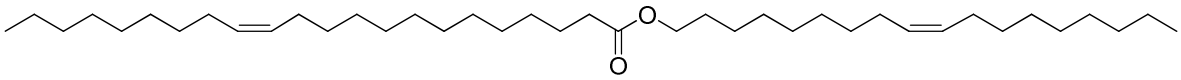


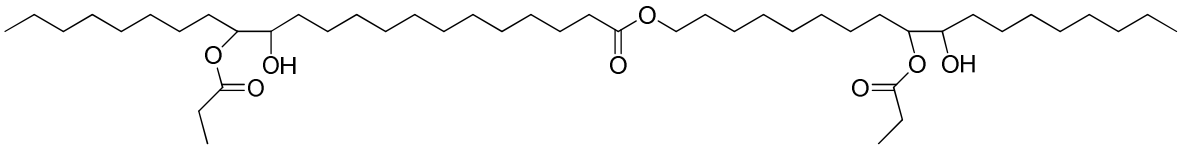
d- 1-(9,10-bis(propionyloxy)octadecanoyloxy)octadecane-9,10-diyl dipropionate (JLE-36S-4)



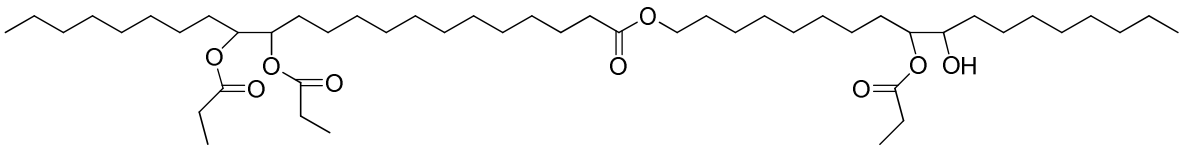
e- Octadec-9-enyl docos-13-enoate (JLE-40S)



f- 10(9)-hydroxy-9(10)-(propionyloxy)octadecyl 13(14)-hydroxy-14(13)-(propionyloxy)docosanoate (JLE-40S-2)



g- 22-(10(9)-hydroxy-9(10)-(propionyloxy)octadecyloxy)-22-oxodocosane-9,10-diyl dipropionate or 1-(13(14)-hydroxy-14(13)-(propionyloxy)docosanoyloxy) octadecane -9,10-diyl dipropionate (JLE-40S-3)



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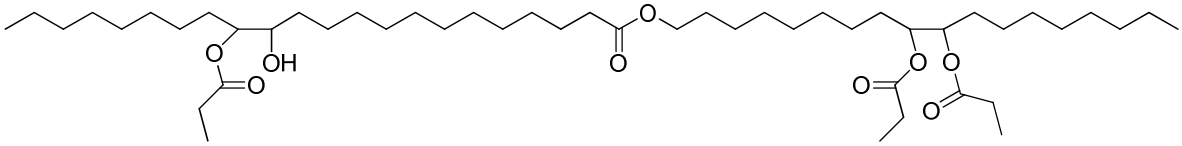
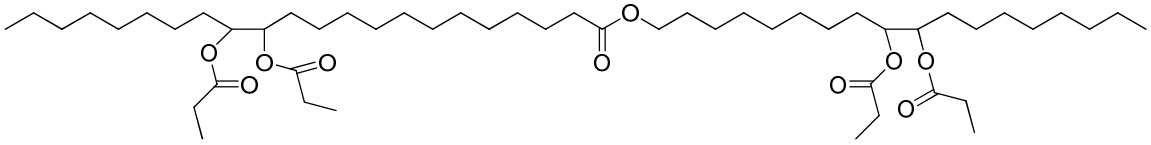
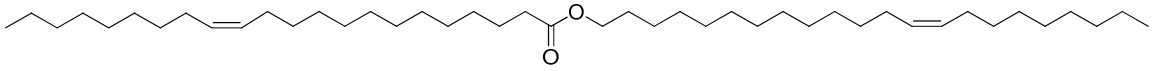


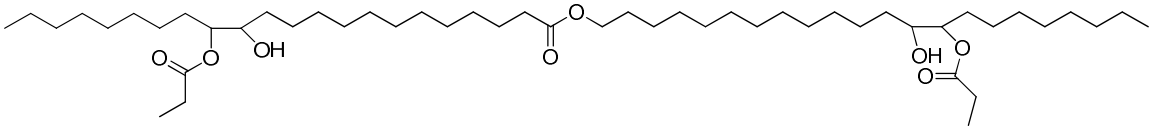
h- 1-(13,14-bis(propionyloxy)docosanoyloxy)octadecane-9,10-diyl dipropionate (JLE-40S-4)



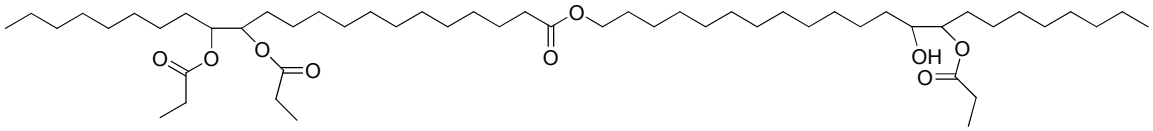
i- Docos-13-enyl docos-13-enoate (JLE-44S)



j- 13(14)-hydroxy-14(13)-(propionyloxy)docosyl 13(14)-hydroxy-14(13)-(propionyloxy)docosanoate (JLE-44S-2)



k- 22-(13(14)-hydroxy-14(13)-(propionyloxy)docosyloxy)-22-oxodocosane-9,10-diyl dipropionate or 22-(13(14)-hydroxy-14(13)-(propionyloxy) docosanoyloxy) docosane-9,10-diyl dipropionate (JLE-44S-3)



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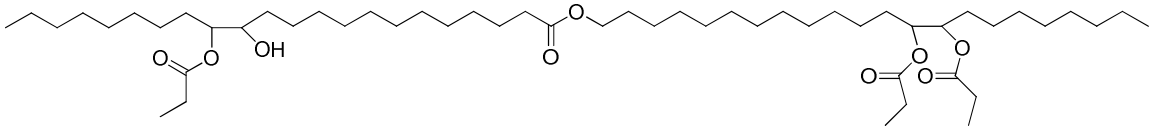
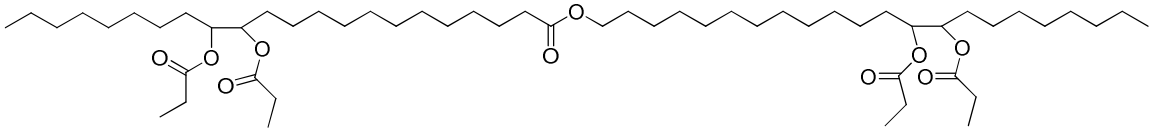
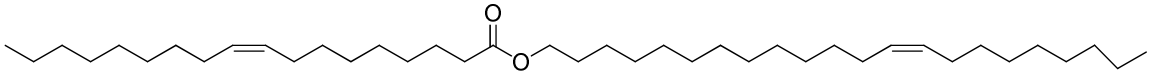


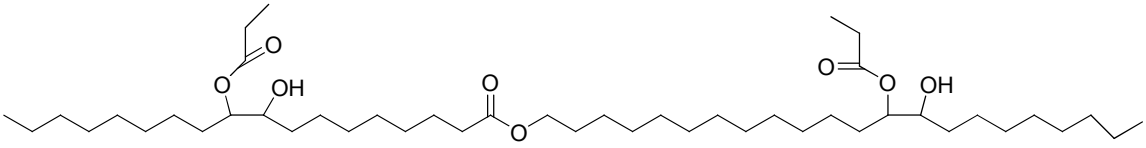
l- 22-(13,14-bis(propionyloxy)docosanoyloxy)docosane-9,10-diyl dipropionate (JLE-44S-4)



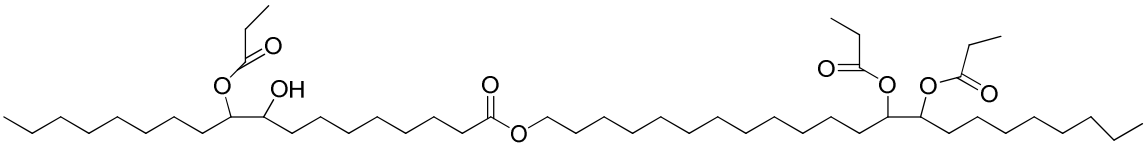
m- Docos-13-enyl octadec-9-enoate (JLE-40A)



n- 14(13)-hydroxy-13(14)-(propionyloxy)docosyl 9(10)-hydroxy-10(9)-(propionyloxy)octadecanoate (JLE-40A-2)



o- 22-(9(10)-hydroxy-10(9)-(propionyloxy)octadecanoyloxy) docosane-9,10-diyl dipropionate or 1-(14(13)-hydroxy-13(14)-(propionyloxy)docosyloxy)-1-oxooctadecane-9,10-diyl dipropionate (JLE-40A-3)



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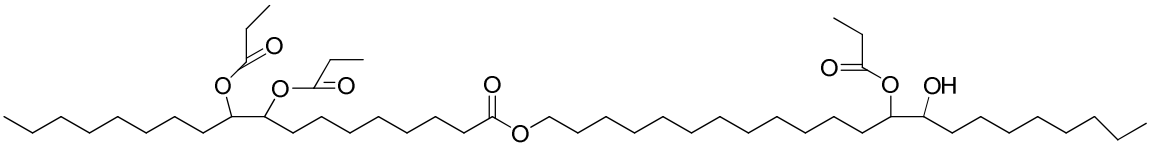

p- 1-(13,14-bis(propionyloxy)docosyloxy)-1-oxooctadecane-9,10-diyl dipropionate (JLE-40A-4)

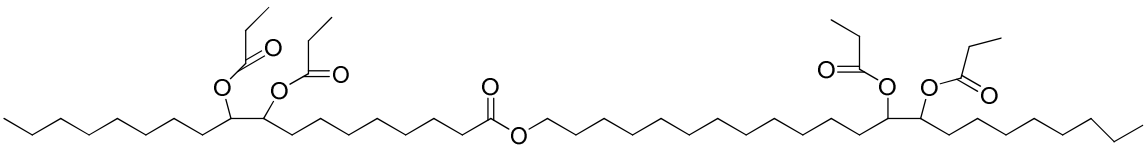

Table S1: Nomenclature used for the Jojoba-Like mono-Esters (JLE) and their branched derivatives prepared in this work. The column headed "Structure" refers to the generalized structures shown in Scheme S1.

Compound	IUPAC Name	Structure
JLE-36S	Octadec-9-enyl octadec-9-enoate	n1=n2=8 m1=m2=5

JLE-36S-2	9(10)-hydroxy-10(9)-(propionyloxy)octadecyl 9(10)-hydroxy-10(9)-(propionyloxy)octadecanoate	n1=n2=8 m1=m2=5 R=C_2H_5
JLE-36S-3	1-(9(10)-hydroxy-10(9)-(propionyloxy)octadecanoyloxy) octadecane-9,10-diyldipropionate or/and 1-(9(10)-hydroxy-10(9)-(propionyloxy)octadecyloxy)-1-oxooctadecane-9,10-diyl dipropionate	n1=n2=8 m1=m2=5 R=C_2H_5
JLE-36S-4	1-(9,10-bis(propionyloxy)octadecanoyloxy)octadecane-9,10-diyl dipropionate	n1=n2=8 m1=m2=5 R=C_2H_5
JLE-40S	Octadec-9-enyl docos-13-enoate	n1=n2=8 m1=9;m2=5
JLE-40S-2	10(9)-hydroxy-9(10)-(propionyloxy)octadecyl 13(14)-hydroxy-14(13)-(propionyloxy)docosanoate	n1=n2=8 m1=9;m2=5 R=C_2H_5
JLE-40S-3	22-(10(9)-hydroxy-9(10)-(propionyloxy)octadecyloxy)-22-oxodocosane-9,10-diyl dipropionate or/and 1-(13(14)-hydroxy-14(13)-(propionyloxy)docosanoyloxy)octadecane-9,10-diyl dipropionate	n1=n2=8 m1=9;m2=5 R=C_2H_5
JLE-40S-4	1-(13,14-bis(propionyloxy)docosanoyloxy)octadecane-9,10-diyl dipropionate	n1=n2=8 m1=9;m2=5 R=C_2H_5
JLE-44S	Docos-13-enyl docos-13-enoate	n1=n2=8 m1=m2=9
JLE-44S-2	13(14)-hydroxy-14(13)-(propionyloxy)docosyl 13(14)-hydroxy-14(13)-(propionyloxy)docosanoate	n1=n2=8 m1=m2=9 R=C_2H_5
JLE-44S-3	22-(13(14)-hydroxy-14(13)-(propionyloxy)docosyloxy)-22-oxodocosane-9,10-diyl dipropionate or/and 22-(13(14)-hydroxy-14(13)-(propionyloxy)docosanoyloxy)docosane-9,10-diyl dipropionate	n1=n2=8 m1=m2=9 R=C_2H_5
JLE-44S-4	22-(13,14-bis(propionyloxy)docosanoyloxy)docosane-9,10-diyl dipropionate	n1=n2=8 m1=m2=9 R=C_2H_5
JLE-40A	Docos-13-enyl octadec-9-enoate	n1=n2=8 m1=5;m2=9
JLE-40A-2	14(13)-hydroxy-13(14)-(propionyloxy)docosyl 9(10)-hydroxy-10(9)-(propionyloxy)octadecanoate	n1=n2=8 m1=5;m2=9 R=C_2H_5
JLE-40A-3	22-(9(10)-hydroxy-10(9)-(propionyloxy)octadecanoyloxy) docosane-9,10-diyl dipropionate or/and 1-(14(13)-hydroxy-13(14)-(propionyloxy)docosyloxy)-1-oxooctadecane-9,10-diyl dipropionate	n1=n2=8 m1=5;m2=9 R=C_2H_5
JLE-40A-4	1-(13,14-bis(propionyloxy)docosyloxy)-1-oxooctadecane-9,10-diyl dipropionate	n1=n2=8 m1=5;m2=9 R=C_2H_5

Table S2: Synthesis and ^{1}H-NMR characterization data of the epoxides of JLE-36S: 8-(3-octyloxiran-2-yl)octyl 8-(3-octyloxiran-2-yl)octanoate, JLE-40S: 8-(3-octyloxiran-2-yl)octyl 12-(3-octyloxiran-2-yl)dodecanoate, JLE-44S: 12-(3-octyloxiran-2-yl)dodecyl 12-(3-octyloxiran-2-yl)dodecanoate and JLE-40A: 12-(3-octyloxiran-2-yl)dodecyl 8-(3-octyloxiran-2-yl)octanoate. EA/HE: Ethyl Acetate/Hexane.

Epoxides of	EA/HE	Yield/%	^{1}H-NMR in $CDCl_3$ δ (ppm)
JLE-36S	1:30	70	4.1 (2, t),2.9(4, br), 2.3 (2, t), 2.1-2.0 (8, m), 1.7-1.6 (4, m), 1.5-1.20 (42, m), 0.86-0.76 (6, t)
JLE-40S	1:20	75	4.1 (2, t), 2.9 (4, br), 2.3 (2, t), 2.1-2.0 (8, m), 1.7-1.56 (4, m), 1.44-1.20 (50, m), 0.86-0.76 (6, t)
JLE-44S	1:20	73	4.1(2, t),2.9 (4, br), 2.3(2, t), 2.1-2.0(8, m), 1.7-1.56 (4,m), 1.44-1.20 (58, m), 0.86-0.76(6, t)
JLE-40A	1:30	72.7	4.1(2, t), 2.9 (4, br), 2.3(2, t), 2.1-2.0(8, m), 1.7-1.56 (4,m), 1.44-1.20 (50, m), 0.86-0.76(6, t)

Table S3: Synthesis and ^{1}H-NMR characterization data of the branched derivatives of JLEs. EA/HE: Ethyl Acetate/Hexane. The structure and nomenclature of branched derivatives of JLEs are presented in the supporting information Scheme S1 and Table S1.

Sample	EA/HE	Yield	^{1}H-NMR in $CDCl_3$ δ (ppm)
JLE-36S-2	1:10	89.5%	4.8 (2, m), 4.1 (2, t), 3.7-3.5 (2,m), 2.4-2.2 (6, m), 1.5-1.2 (46, m), 1.1 (6, t), 0.8 (6, t)
JLE-36S-3	1:6	30.6% JLE-36S -4 + 38. 2% JLE-36S -3 at 120 °C	5.0 (2, m), 4.8 (1, m), 4.0 (2, t), 3.6 (1, m), 2.4-2.2 (8, m), 1.8-1.2 (55, m), 1.1 (9, t), 0.8 (6, t)
JLE-36S-4	1:10	30.6% JLE-36S -4 + 38. 2% JLE-36S -3 at 120 °C	5.0 (4, m), 4.0 (2, t), 2.4-2.2 (10, m), 1.7-1.5 (6, m), 1.4-1.2 (48, m), 1.1 (12, t), 0.8 (6, t)
JLE-40S-2	1:8	47.8% JLE-40S -2 + 29% JLE-40S -3 at 95 °C; 46% JLE-40S -2 + 35.7% JLE-40S -3 +11.3% JLE-40S -4 at 120 °C	4.8 (2, m), 4.0 (2, t), 3.6 (2, br), 2.3 (4, q), 2.2 (2, t), 1.8-1.5 (10, m), 1.5-1.2 (56, m), 1.1 (6, t), 0.8 (6, t)

JLE-40S-3	1:10	47.8% JLE-40S -2 + 29% JLE-40S -3 at 95 °C; 46% JLE-40S -2 +35.7% JLE-40S -3 +11.3% JLE-40S -4 at 120 °C	5.0 (2, m), 4.8 (1, m), 4.0 (2, t), 3.6 (1, br), 2.4-2.2 (8, m), 1.7-1.2 (63, m), 1.1 (9, t), 0.8 (6, t)
JLE-40S-4	1:10	46% JLE-40S -2 + 35.7% JLE-40S -3 +11.3% JLE-40S -4 at 120 °C	4.8 (4, m), 3.6 (2, t), 2.2-2.0 (10, m), 1.4-1.2 (12, br), 1.1-0.9 (50, m), 0.8 (12, t), 0.6 (6, t)
JLE-44S-2	1:8	71.6 % JLE-44S -2 and 17.9% JLE-44S -3 at 95 °C	4.8 (2, m), 4.1 (2, t), 3.6 (2, br), 2.4 (4, q), 2.3 (2, t), 1.6 (10, br), 1.5-1.2 (62, m), 1.1 (6, t), 0.9 (6, t)
JLE-44S-3	1:10	71.6 % JLE-44S -2 and 17.9% JLE-44S -3 at 95 °C, 44.8% JLE-44S -4+39.7% JLE-44S -3 at 120 °C	5.0 (2, m), 4.8 (1, m), 4.0 (2, t), 3.5 (1, br), 2.4-.22 (8, m), 1.6-1.2 (71,m), 1.1 (9, t), 0.8 (6, t)
JLE-44S-4	1:10	44.8% JLE-44S -4+39.7% JLE-44S -3 at 120 °C	5.0 (4, m) , 4.0 (2, t), 2.4-2.2 (10, m), 1.6-1.4 (12, br), 1.4-1.2 (58, m), 1.1 (12, t), 0.8 (6, t)
JLE-40A-2	1:8	77.8% JLE-40A -2 + 9.5% JLE-40A -3 at 95 °C	4.8 (2, m), 4.0 (2, t), 3.6 (2, br), 2.3 (4, q), 2.2 (2, t), 1.8-1.5 (10, m), 1.5-1.2 (54, m), 1.1 (6, t), 0.8 (6, t)
JLE-40A-3	1:10	77.8% JLE-40A -2 + 9.5% JLE-40A -3 at 95 °C, 42.8 % JLE-40A -4 + 48.5% JLE-40A -3 at 120 °C	5.0 (2, m), 4.8 (1, m), 4.0 (2, t), 3.6 (1, br), 2.4-2.2 (8, m), 1.7-1.2 (63, m), 1.1 (9, t), 0.8 (6, t)
JLE-40A-4	1:10	42.8 % JLE-40A -4 + 48.5% JLE-40A -3 at 120 °C	4.8 (4, m), 3.6 (2, t), 2.2-2.0 (10, m), 1.4-1.2 (12, br), 1.1-0.9 (50, m), 0.8 (12, t), 0.6 (6, t)

Table S4: Enthalpy of crystallization and melting of the branched derivatives of JLEs.

Sample	# of carbons	2-Branches	3-Branches	4-Branches
			Crystallization	
JLE36S	36	10.7 ± 1.1	3.8 ± 0.9	1.5 ± 1.3
JLE40S	40	36.5 ± 2.0	19.6 ± 2.3	3.4 ± 2.2
JLE44S	44	60.8 ± 2.7	45.5 ± 3.4	6.7 ± 1.3
			Melting	
JLE36S	36	11.8 ± 0.2	11.8 ± 2.0	9.4 ± 0.3
JLE40S	40	40.0 ± 5.0	12.0 ± 3.1	0.5 ± 0.4
JLE44S	44	52.6 ± 1.7	39.2 ± 2.7	11.1 ± 1.1