The Relationship Between the Structure of Monoalkyl Branched Saturated Triacylglycerols and Some Physical Properties

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ABSTRACT: Three different physical properties, the gel point ("solidification point"), the refractive index and the density, were determined and related to the structure of the branched triacylglycerols. A four-factor central composite face-centered design was constructed where the four variables were the length of the main chain, the branching position, the length of the side chain, and the number of branched fatty acyl groups attached to the glycerol backbone. Second-order models were calculated in which the three physical properties were related to the structure. Four additional branched triacylglycerols were analyzed in order to confirm the validity of each model. Contour plots are shown in order to visualize the prediction equations which were obtained.

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Triacylglycerols containing branched fatty acids occur sparingly in nature. They are known components of, e.g., human sebum (1,2) and adipose tissue of lambs (3–5). At least in human sebum, the branched fatty acids occur more frequently in the 2-position than in the 1- and 3-positions (1). One important property of the branched triacylglycerols in human sebum seems to be its porosity for water vapor (6). Branched fatty acids also have been found in milk (7). The crystal structures of both branched saturated fatty acids and triacylglycerols have been described in the literature (8). Furthermore, esters between branched fatty acids and polyols, often others than glycerol, have found use in, e.g., lubricants, owing to excellent lubricity, stability toward oxidation, and low-temperature properties (9,10).

The physical properties of branched triacylglycerols have been investigated previously by Aydin *et al*. (11), who synthesized both the 1-monoacylglycerols and the homotriacylglycerols of nine different α-monoalkyl branched saturated fatty acids. The physical properties investigated were the refractive index (at 20°C), the dielectric constant, and the dipole moment.

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Abbreviation: ANOVA, analysis of variance.

However, no other systematic investigation has been carried out relating the physical properties of triacylglycerols containing monoalkyl branched saturated fatty acyl groups to their structure. In the present study the gel point ("solidification point"), the refractive index (at 60°C), and the density are related to the structure of such triacylglycerols. A chemometrical approach was applied to the problem resulting in a four-factor central composite face-centered design. The aim has been to cover all possible triglyceride structures with "normal" chain lengths (main chain between 6 and 18 carbons). This approach has required the syntheses of a number of new compounds (12). In the case of the gel point, any polymorphic properties which the triacylglycerols may have were not taken into consideration.

MATERIALS AND METHODS

Materials. All triacylglycerols have been synthesized (12). The objective has been to obtain high purities in order to minimize the effects of impurities on, e.g., the nucleation. The purity of the triacylglycerols was found to be >98% by gas–liquid chromatography and/or high-performance liquid chromatography. All compounds synthesized are racemic.

Measurements. The gel points were determined on a Bohlin VOR Rheometer (Lund, Sweden) used in the oscillation mode. The samples were placed between a cone and a plate with diameters of 25 mm and a gap size of 0.15 mm. The gap was adjusted at 0°C for the samples with high gel points (>−10°C) and at −25°C for the samples with low gel points (<−10°C). The torsion bar used had a torque constant of 92.3 gcm. The samples were subjected to an oscillation (frequency 0.500 s^{-1}) in autostrain mode. This means that the strain was adjusted according to the measured torque in such a way that increased torque leads to a decrease in strain. The strain amplitude varied between 0.002 and 0.2. The measurements were performed in a standard low-temperature cell cooled by liquid nitrogen. The samples were cooled from −10 to −100°C (10 to −10°C for the triacylglycerols with high gel points) with a temperature gradient of −0.5°C/15 s. The results were recorded every 6 s.

The gel points were determined by means of the tangent to the sharply increasing storage modulus (G′). This indicates an increase in the elastic component of the sample. The results are strongly dependent on the temperature gradient chosen, owing to the fact that the triacylglycerols show different polymorphic behavior and nucleation rates. This method of determining the gel point is a modification of the method of Bohlin *et al.* (13).

The gel points of the triacylglycerols with very high gel points (>10°C) were determined simply by agitating 2 g of the triacylglycerol contained in a small bottle with a thermometer using the same frequency as in the rheometer. The samples were cooled by the surrounding air and when necessary with an ice-water mixture. The cooling was carried out in such a way as to achieve the same gradient as with the rheometer (–2°C/min).

Both methods of determining the gel point ("solidification point") described above have in common that any polymorphic properties, if present, are not considered. This should be taken into account when looking at the results. One of the triacylglycerols in the present study, which had a gel point of 10°C, was a liquid at room temperature for more than 1 wk before crystallizing. As is the case with all methods concerning crystallization and melting (e.g., differential scanning calorimetry and rheology), the results depend on the exact method used and how the results are evaluated.

The refractive indices were determined at 60°C with an Abbé refractometer (Carl Zeiss, Jena, Germany), model A.

The densities were determined at 60°C with an Anton Paar Precision density meter (Instrument AB Lambda, Sollentuna, Sweden), OMA 02C.

Experimental design. The structures of the monoalkyl branched saturated triacylglycerols were chosen according to a four-factor central composite design. The four factors are the length of the main chain (X_1), the branching position (X_2), the length of the side chain (X_3), and the number of branched fatty acyl groups attached to the glycerol (X_4). As can be seen in Table 1, the different levels of variable X_2 are defined as functions of variable X_1. In a similar way, the levels of variable X_3 are defined as functions of variables X_1 and X_2. This is due to the fact that, in the case of the branching position, level +1 represents a carbon atom near the end of the main chain. Depending on the length of the main chain, the number of the carbon atom to which the branch is affixed will vary. In the same way, the length of the branch has an upper limit. If this limit is passed, the branch has become the main chain. In the case of the branching position, level +1 has been chosen as a position two carbons away from the end of the main chain to be able to vary the length of the branch.

TABLE 1
Factor Levels of the Experimental Design

	Level		
Factor	–1	0	+1
Length of main chain (X_1)	6	12	18
Branching position (X_2)	2	$X_1/2$	$X_1 - 2$
Length of side chain (X_3)	0	$(X_1 - X_2 + 1)/2$	$X_1 - X_2$
Number of branched acyl groups (X_4)	1	2	3

The complete experimental design, including four control substances, is shown in Table 2. As can be seen, the axial points have been placed 1 unit away from the center instead of the ideal distance of 2 units. This variant of the central composite design is called central composite face-centered design.

The straight chain acid (which is present when there are fewer than three branched fatty acids present in the triacylglycerol) has been chosen to be dodecanoic acid for the axial and center points and hexanoic or octadecanoic acid (half of each) for the remaining triacylglycerols (this is also the way the straight chain acid would have been chosen if the length of the straight chain had been treated as a fifth variable in a fractional factorial design). This way of designing the experiment is based on the idea that the branched fatty acid to a great extent determines the behavior of the entire triacylglycerol.

Statistical analyses. The evaluation of the results was made with the help of the software MODDE for Windows, version 3.0 (Umetri AB, Umeå, Sweden). All measurements were done in a randomized order. Measurements in the center point of the design were repeated twice. MODDE uses multiple linear regression to calculate a prediction equation for each response:

$$Y_p = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 \quad [1]$$

The estimated coefficients are then rejected or retained depending on their probability. The test is performed at a significance level of $\alpha = 0.05$. The significant coefficients are then reestimated to give the final prediction equation. Outliers, identified by normal probability plots of the residuals (14), are excluded from the multiple linear regression. The fact that a compound has been identified as an outlier means that it does not fit into the mathematical description of a particular physical property. It does not mean that the measurements are incorrect or that the wrong substance has been synthesized. The subject has been described in a recent review article (15).

RESULTS AND DISCUSSION

Gel point. The coefficients of the final prediction equation of the gel point are shown in Table 3 with the corresponding probabilities and 95% confidence intervals. Four triacylglycerols have been identified as outliers (by the technique of normal probability plots) and are consequently excluded from the regression calculations. The four compounds are the triacylglycerols with hexanoyl groups in two positions and a branched fatty acyl group in the remaining position (all marked in Table 4). The two control triacylglycerols with deviating gel points both have two stearoyl groups attached to the glycerol. This could explain why their gel points are high compared to their predicted values (in contrast to the other

TABLE 2
Experimental Design Including Four Control Substances

Branched triacylglycerol	Length of main chain (X_1)	Branching position (X_2)	Length of side chain (X_3)	Number of branched acyl groups (X_4)
Triacylglycerols included in the design				
1-(2-Methylhexanoyl)-2,3-dioctadecanoyl-glycerol	−1	−1	−1	−1
1,2-Dihexanoyl-3-(2-methyloctadecanoyl)-glycerol	+1	−1	−1	−1
1,2-Dihexanoyl-3-(4-methylhexanoyl)-glycerol	−1	+1	−1	−1
1-(16-Methyloctadecanoyl)-2,3-dioctadecanoyl-glycerol	+1	+1	−1	−1
1-(2-Butylhexanoyl)-2,3-dihexanoyl-glycerol	−1	−1	+1	−1
1-(2-Hexadecyloctadecanoyl)-2,3-dioctadecanoyl-glycerol	+1	−1	+1	−1
1-(4-Ethylhexanoyl)-2,3-dioctadecanoyl-glycerol	−1	+1	+1	−1
1-(16-Ethyloctadecanoyl)-2,3-dihexanoyl-glycerol	+1	+1	+1	−1
Tris(2-methylhexanoyl)-glycerol	−1	−1	−1	+1
Tris(2-methyloctadecanoyl)-glycerol	+1	−1	−1	+1
Tris(4-methylhexanoyl)-glycerol	−1	+1	−1	+1
Tris(16-methyloctadecanoyl)-glycerol	+1	+1	−1	+1
Tris(2-butylhexanoyl)-glycerol	−1	−1	+1	+1
Tris(2-hexadecyloctadecanoyl)-glycerol[a]	+1	−1	+1	+1
Tris(4-ethylhexanoyl)-glycerol	−1	+1	+1	+1
Tris(16-ethyloctadecanoyl)-glycerol	+1	+1	+1	+1
1-Dodecanoyl-2,3-bis(6-propyldodecanoyl)-glycerol	0	0	−0.2	0
1-Dodecanoyl-2,3-bis(3-ethylhexanoyl)-glycerol	−1	0	0	0
1-Dodecanoyl-2,3-bis(9-pentyloctadecanoyl)-glycerol	+1	0	0	0
1-Dodecanoyl-2,3-bis(2-pentyldodecanoyl)-glycerol	0	−1	−0.111	0
1-Dodecanoyl-2,3-bis(10-methyldodecanoyl)-glycerol	0	+1	−1	0
1-Dodecanoyl-2,3-bis(6-methyldodecanoyl)-glycerol	0	0	−1	0
1-Dodecanoyl-2,3-bis(6-hexyldodecanoyl)-glycerol	0	0	+1	0
1,2-Didodecanoyl-3-(6-propyldodecanoyl)-glycerol	0	0	−0.2	−1
Tris(6-propyldodecanoyl)-glycerol	0	0	−0.2	+1
Control triacylglycerols				
1-Hexanoyl-2,3-bis(6-propyldodecanoyl)-glycerol	0	0	−0.2	0
1-Octadecanoyl-2,3-bis(6-propyldodecanoyl)-glycerol	0	0	−0.2	0
1,2-Didodecanoyl-3-(16-methyloctadecanoyl)-glycerol	+1	+1	−1	−1
1,2-Dioctadecanoyl-3-(6-propyldodecanoyl)-glycerol	0	0	−0.2	−1

[a]This compound was not synthesized in sufficient amounts to perform measurements.

outliers which have short main chains and correspondingly low gel points). The resulting equation is:

$$Y_{p,\text{ gel point}} = -57 + 23\,X_1 - 1.0\,X_2 - 30\,X_4 + 20\,X_1X_4 + 48\,X_2^2 + 16\,X_4^2 \quad [2]$$

The length of the side chain (X_3) is the only factor which does not have an influence on the response. Figure 1 shows a contour plot of the response surface for triacylglycerols having three branched fatty acyl groups attached to the glycerol skeleton. The response surfaces for the other types of triacylglycerols (having one or two branched fatty acids) have the same appearance. It can be seen that the lowest gel points are obtained when the branch is situated on the middle of the main chain. This result is analogous to a previous investigation on the branched fatty acids themselves (16).

The observed and the predicted gel points are compared in Table 4. An analysis of variance (ANOVA) scheme is shown in Table 5. The coefficient of multiple determination is R^2 = 0.961.

Refractive index (60°C). Four compounds have been identified as outliers, three of which are the same as for the gel point prediction equation. All outliers are marked in Table 4. The calculated response function (the parameters of which

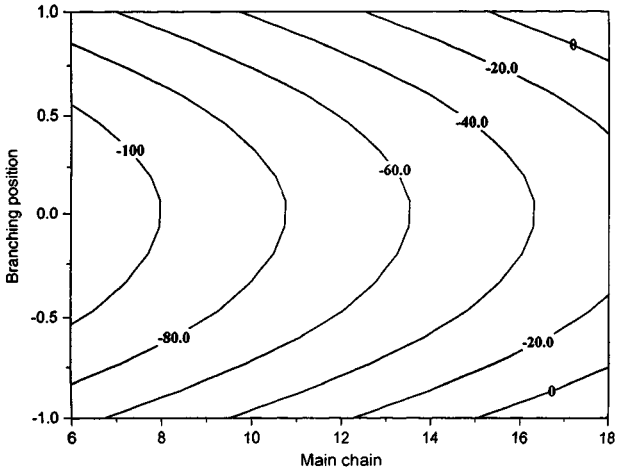

FIG. 1. Contour plot showing the gel point as a function of the structure for monoalkyl branched saturated homotriacylglycerols. The length of the main chain (X_1) is given as the number of carbons (6 to 18) while the branching position (X_2) is given as coded values (−1 to +1).

TABLE 3
Coefficients from the Final Prediction Equations of the Gel Point, the Refractive Index, and the Density

Term	Coefficient[a]	Probability[b]
Gel point		
Constant	−57 ± 8	0.00
Main chain (X_1)	23 ± 6	0.00
Branching position (X_2)	−1.0 ± 6	0.75
Number of branches (X_4)	−30 ± 6	0.00
Main chain × number of branches (X_1X_4)	20 ± 7	0.00
(branching position)^2 (X_2^2)	48 ± 12	0.00
(number of branches)^2 (X_4^2)	16 ± 12	0.01
Refractive index		
Constant	1.4432 ± 0.0008	0.00
Main chain (X_1)	0.0046 ± 0.0010	0.00
Branching position (X_2)	0.0003 ± 0.0010	0.50
Side chain (X_3)	0.0010 ± 0.0010	0.06
Number of branches (X_4)	−0.0018 ± 0.0010	0.00
Main chain × branching position (X_1X_2)	−0.0018 ± 0.0011	0.01
Main chain × number of branches (X_1X_4)	0.0038 ± 0.0012	0.00
Branching position × side chain (X_2X_3)	-0.0014 ± 0.0011	0.02
Side chain × number of branches (X_3X_4)	0.0025 ± 0.0011	0.00
Density		
Constant	0.8906 ± 0.0037	0.00
Main chain (X_1)	−0.0145 ± 0.0047	0.00
Branching position (X_2)	0.0108 ± 0.0050	0.00
Side chain (X_3)	−0.0090 ± 0.0051	0.00
Number of branches (X_4)	0.0012 ± 0.0049	0.62
Main chain × number of branches (X_1X_4)	−0.0189 ± 0.0053	0.00

[a]Values are given with 95% confidence intervals. [b]The probability that a coefficient is equal to zero.

can also be found in Table 3 together with 95% confidence intervals and values of probability) is:

$$Y_{p,\text{ refractive index (60°C)}} = 1.4432 + 0.0046\ X_1 + 0.0003\ X_2 + 0.0010\ X_3 - 0.0018\ X_4 - 0.0018\ X_1X_2 + 0.0038\ X_1X_4 - 0.0014\ X_2X_3 + 0.0025\ X_3X_4 \quad [3]$$

All four factors are important to the response, which means that two factors must be set to a fixed value in order to make a contour plot possible. Since the branching position is the least important factor, it has been set to $X_2 = 0$, i.e., a branching in the middle of the main chain. In this way it is possible to visualize the response function (Fig. 2). Also in this case the homotriacylglycerols have been chosen for the figure. One conclusion is that the longer the main chain the higher the refractive index. This is also similar to the properties of the branched fatty acids themselves (16). The observed and the predicted values are compared in Table 4. An ANOVA scheme is shown in Table 5. The coefficient of multiple determination is $R^2 = 0.950$.

Density (60°C). In addition to the three compounds for which the density could not be measured, two more triacylglycerols were excluded from the regression calculations (Table 4). The obtained prediction equation is:

$$Y_{p,\text{ density (60°C)}} = 0.8906 - 0.0145\ X_1 + 0.0108\ X_2 - 0.0090\ X_3 + 0.0012\ X_4 - 0.0189\ X_1X_4 \quad [4]$$

As in the refractive index case, it is not possible to show the response function in a single picture. All four factors are important. Just to give the reader some idea of the appearance of the response surfaces, one of them is shown in Figure 3. This picture of the homotriacylglycerols demonstrates the decreasing effect of a longer side chain and the increasing ef-

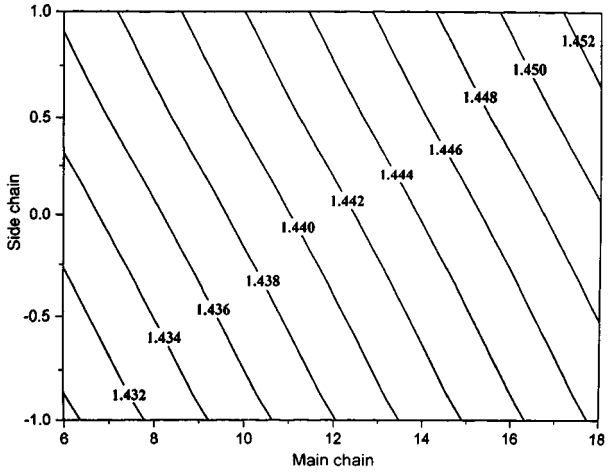

FIG. 2. Contour plot showing the refractive index (at 60°C) as a function of the structure for monoalkyl branched saturated homotriacylglycerols. The length of the main chain (X_1) is given as the number of carbons (6 to 18), and the length of the side chain (X_3) is given as coded values (−1 to +1). In this plot the branching position is set to a medium position ($X_2 = 0$).

TABLE 4
Gel Points, Refractive Indices, and Densities of Monoalkyl Branched Triacylglycerols

Branched triacylglycerol	Gel point			Refractive index (60°C)			Density (60°C)		
	Observed (°C)	Predicted[a] (°C)	Residual (°C)	Observed	Predicted[a]	Residual	Observed	Predicted[a]	Residual
Triacylglycerols included in the design									
1-(2-Methylhexanoyl)-2,3-dioctadecanoyl-glycerol	32	34 ± 16	2	1.4429	1.4422 ± 0.0028	0.0007	0.8841	0.8833 ± 0.0114	0.0008
1,2-Dihexanoyl-3-(2-methyloctadecanoyl)-glycerol[b,c]	–16	40 ± 15	56	1.4350	1.4474 ± 0.0043	–0.0124	0.8989	0.8921 ± 0.0108	0.0068
1,2-Dihexanoyl-3-(4-methylhexanoyl)-glycerol[b,c,d]	–71	32 ± 16	103	1.4300	1.4493 ± 0.0035	0.0193	0.9458	0.9048 ± 0.0126	0.0410
1-(16-Methyloctadecanoyl)-2,3-dioctadecanoyl-glycerol	43	38 ± 16	5	1.4490	1.4473 ± 0.0027	0.0017	—[e]	0.9136 ± 0.0136	—
1-(2-Butylhexanoyl)-2,3-dihexanoyl-glycerol[b,c,d]	–67	34 ± 16	101	1.4305	1.4421 ± 0.0044	–0.0116	0.9280	0.8654 ± 0.0129	0.0626
1-(2-Hexadecyloctadecanoyl)-2,3-dioctadecanoyl-glycerol	50	40 ± 16	10	1.4485	1.4472 ± 0.0028	0.0013	0.8642	0.8742 ± 0.0101	–0.0100
1-(4-Ethylhexanoyl)-2,3-dioctadecanoyl-glycerol	32	32 ± 16	±0	1.4442	1.4434 ± 0.0029	0.0008	0.8865	0.8869 ± 0.0116	-0.0004
1-(16-Ethyloctadecanoyl)-2,3-dihexanoyl-glycerol[b]	–41	38 ± 16	–79	1.4395	1.4414 ± 0.0030	–0.0019	0.9053	0.8957 ± 0.0106	0.0096
Tris(2-methylhexanoyl)-glycerol	–70	–65 ± 12	–5	1.4271	1.4260 ± 0.0029	0.0012	0.9269	0.9234 ± 0.0096	0.0035
Tris(2-methyloctadecanoyl)-glycerol	28	21 ± 15	7	1.4452	1.4464 ± 0.0028	–0.0012	0.8704	0.8566 ± 0.0109	0.0138
Tris(4-methylhexanoyl)-glycerol	–70	–67 ± 12	–3	1.4325	1.4330 ± 0.0025	–0.0005	0.9390	0.9449 ± 0.0112	–0.0059
Tris(16-methyloctadecanoyl)-glycerol	30	19 ± 13	11	1.4478	1.4463 ± 0.0028	0.0015	0.8749	0.8781 ± 0.0111	–0.0032
Tris(2-butylhexanoyl)-glycerol	–58	–65 ± 12	7	1.4343	1.4357 ± 0.0029	–0.0014	0.9026	0.9055 ± 0.0108	–0.0029
Tris(4-ethylhexanoyl)-glycerol	–76	–67 ± 12	–9	1.4380	1.4370 ± 0.0029	0.0010	0.9367	0.9270 ± 0.0096	0.0097
Tris(16-ethyloctadecanoyl)-glycerol	10	19 ± 13	–9	1.4499	1.4503 ± 0.0027	–0.0004	—[e]	0.8602 ± 0.0136	—
1-Dodecanoyl-2,3-bis(6-propyldodecanoyl)-glycerol	–56	-57 ± 8	1	1.4431	1.4430 ± 0.0008	0.0001	0.8884	0.8924 ± 0.0036	–0.0040
	–55	–57 ± 8	2	1.4431	1.4430 ± 0.0008	0.0001	0.8885	0.8924 ± 0.0036	–0.0039
	–58	–57 ± 8	–1	1.4431	1.4430 ± 0.0008	0.0001	0.8883	0.8924 ± 0.0036	–0.0041
1-Dodecanoyl-2,3-bis(3-ethylhexanoyl)-glycerol	–64	–81 ± 10	17	1.4372	1.4386 ± 0.0013	–0.0014	0.9152	0.9051 ± 0.0057	0.0101
1-Dodecanoyl-2,3-bis(9-pentyloctadecanoyl)-glycerol	–51	–34 ± 10	–17	1.4471	1.4478 ± 0.0013	–0.0007	0.8741	0.8761 ± 0.0061	–0.0020
1-Dodecanoyl-2,3-bis(2-pentyldodecanoyl)-glycerol	–25	-8 ± 14	–17	1.4420	1.4426 ± 0.0013	–0.0006	0.8786	0.8809 ± 0.0058	–0.0023
1-Dodecanoyl-2,3-bis(10-methyldodecanoyl)-glycerol	–4	–10 ± 13	6	1.4416	1.4440 ± 0.0017	–0.0024	—[e]	0.9103 ± 0.0087	—
1-Dodecanoyl-2,3-bis(6-methyldodecanoyl)-glycerol	–52	–57 ± 8	5	1.4410	1.4422 ± 0.0012	–0.0012	0.8935	0.8996 ± 0.0058	–0.0061
1-Dodecanoyl-2,3-bis(6-hexyldodecanoyl)-glycerol	–55	-57 ± 8	2	1.4448	1.4441 ± 0.0013	0.0007	0.8809	0.8817 ± 0.0067	–0.0008
1,2-Didodecanoyl-3-(6-propyldodecanoyl)-glycerol[c]	–24	–12 ± 14	–12	1.4420	1.4453 ± 0.0015	–0.0033	0.8910	0.8913 ± 0.0063	–0.0003
Tris(6-propyldodecanoyl)-glycerol	–70	–71 ± 13	1	1.4431	1.4407 ± 0.0011	0.0024	0.8851	0.8936 ± 0.0058	–0.0085
Control triacylglycerols									
1-Hexanoyl-2,3-bis-(6-propyldodecanoyl)-glycerol	–60	–57 ± 8	–3	1.4410	1.4430 ± 0.0008	–0.0020	0.8979	0.8924 ± 0.0036	0.0055
1-Octadecanoyl-2,3-bis-(6-propyldodecanoyl)-glycerol	–19	–57 ± 8	38	1.4450	1.4430 ± 0.0008	0.0020	0.8816	0.8924 ± 0.0036	–0.0108
1,2-Didodecanoyl-3-(16-methyloctadecanoyl)-glycerol	25	38 ± 16	–13	1.4390	1.4473 ± 0.0027	–0.0083	0.8686	0.9136 ± 0.0136	–0.0450
1,2-Dioctadecanoyl-3-(6-propyldodecanoyl)-glycerol	29	–12 ± 14	41	1.4459	1.4453 ± 0.0015	0.0006	0.8781	0.8913 ± 0.0063	–0.0132

[a]Values are given together with their 95% confidence intervals. [b]Outlier in the gel point evaluation. [c]Outlier in the refractive index evaluation. [d]Outlier in the density evaluation. [e]Insufficient material to perform the measurements.

TABLE 5
Analysis of Variance Scheme and Residual Sum of Squares Breakdown for the Three Prediction Equations

	Gel point			Refractive index			Density		
Source of variation	Sum of squares	Degrees of freedom	Mean square	Sum of squares	Degrees of freedom	Mean square	Sum of squares	Degrees of freedom	Mean square
Constant	14 408	1	14 408	45.7489	1	45.7489	16.7823	1	16.7823
Model terms	39 190	6	6 532	6.38×10^{-4}	8	7.97×10^{-5}	0.0077	5	0.0015
Residuals	1 592	15	106	3.39×10^{-5}	13	2.61×10^{-6}	0.0009	15	0.0001
Total	55 189	22	2 509	45.7496	22	2.0795	16.7909	21	0.7996
Residual sum of squares breakdown									
Pure error	4.7	2	2.3	0	2	0	8.65×10^{-8}	2	4.33×10^{-8}
Lack of fit	1 587	13	122	3.39×10^{-5}	11	3.08×10^{-6}	8.59×10^{-4}	13	6.61×10^{-5}

fect of a branch far out on the main chain. A longer main chain gives a higher density only when there are two or three branched fatty acyl groups attached to the glycerol. The ANOVA scheme is shown in Table 5. The coefficient of multiple determination is $R^2 = 0.900$. The density prediction equation is the least accurate of the three prediction equations.

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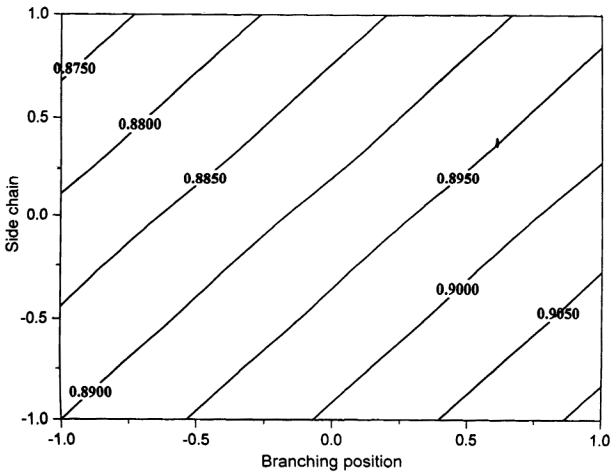

FIG. 3. Contour plot showing the density (at 60°C) as a function of the structure for monoalkyl branched saturated homotriacylglycerols. Both the branching position (X_2) and the length of the side chain (X_3) are given as coded values (–1 to +1). The length of the main chain (X_1) is fixed at a medium position ($X_1 = 12$).

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