Viscosity and Its Relationship to Crystallization in a Binary System of Saturated Triacylglycerides and Sesame Seed Oil

Jorge F. Toro-Vazquez[a],* and Alberto Gallegos-Infante[b]

[a]Centro de Investigación y de Estudios de Posgrado, Facultad de Ciencias Químicas; Universidad Autónoma de San Luis Potosí, Zona Universitaria, 78210, San Luis Potosi, México and [b]Facultad de Químicas-DIPA-PROPAC, Universidad Autónoma de Querétaro, Cerro de las Campanas, Circuito Universitario, Querétaro, México

ABSTRACT: This paper describes the relationship of viscosity with the crystallization process in a binary system formed by sesame oil and different concentrations of tripalmitin (TP) and tristearin (TS) (0.0, 0.032, 0.098, 0.18, 0.26, 0.344 g/dL). The behavior of the reduced viscosity (η_{red}) indicated that TP and TS affected the native bilayer lamellar organization of sesame oil triacylglycerides. The behavior of η_{red} at TP or TS concentrations ≤0.098 g/dL suggested that, as a result of intermolecular interactions between the saturated triacylglyceride and the unsaturated triacylglycerides of sesame oil, the oil solution developed lamellar structures with a smaller size than the native structures in sesame oil. At TP or TS concentrations >0.098 g/dL, the behavior of η_{red} indicated that TP or TS segregated out of the lamellar structure as the temperature was decreased. The kinetics of the segregation phenomenon was a function of the concentration of saturated triacylglyceride and the type of triacylglyceride (i.e., TP or TS), and was favored by an increase in the shear rate. In all situations, the temperature of nucleation was achieved when η_{red} = 0, which may represent the point at which the interfacial energy between sesame oil and the developing nuclei achieved its maximum value. The higher the intermolecular interaction between the TP or TS and the triacylglyceride structure of the sesame oil, the lower the temperature at which η_{red} = 0 in the oil solutions. As a result, the diffusion term (i.e., viscosity of the liquid phase) became a limiting factor for crystal growth rate, especially at TP and TS concentrations ≤0.18 g/dL.
JAOCS 73, 1237–1246 (1996).

KEY WORDS: Crystallization, nucleation, reduced viscosity, sesame oil, tripalmitin, tristearin.

In general, physical properties are associated with parameters that describe the shape and organization of the molecules in the system. The nature of such relationships for oil viscosity and protein interfacial properties has been established (1–3).

Triacylglycerides have several physical properties that determine processing conditions of fats and oils and the stability and organoleptic properties of the food they constitute. The phase changes of pure triacylglycerides, i.e., polymorphic transformations and melting and crystallization temperatures are physical properties that determine some of the functional properties of lipids in food systems (i.e., texture). Structural parameters, such as degree of unsaturation, length of the hydrocarbon chain of the fatty acids, and the positional distribution of the fatty acids esterified to the glycerol (i.e., stereospecific distribution) all determine the phase changes of triacylglycerides (4). The cooling/heating rate and time–temperature history (i.e., thermal cycles) applied to the system are additional variables that affect the molecular organization of triacylglycerides and, therefore, the phase change properties (4,5).

Fats and oils are a mixture of different triacylglycerides; as a result, specific melting and solidification temperatures are not observed. Rather, melting and solidification temperature profiles are observed. Thus, when oils are cooled, the triacylglyceride family with the highest melting temperature is the first to crystallize and develop a solid in a liquid phase. These systems, generally known as plastic fats (4,6), have a fractal organization (7) that significantly affect the melting properties and spreadability of food systems, such as butter and margarine (5).

Triacylglyceride crystallization is utilized as a process to achieve any of three objectives: (i) to eliminate small quantities of high-melting compounds from an oil, so it remains clear at low ambient temperature; (ii) to obtain oil/fat fractions with particular phase change properties; and (iii) to develop or modify the texture of food systems. Although achievement of these objectives is certainly crucial in oil and fats processing, considerable work is still required to completely control these processes.

The relation between the structural organization of molecules in the liquid state (i.e., melt) or in solution (i.e., solute in a solvent) and the crystallization process have been recognized for a long time (8). However, for triacylglycerides, the nature of such relationships has not been established. In the melt, triacylglycerides are organized in bilayer lamellar structures (4). The shape and size of the lamellar structures change with the diffusion rate of the molecules (i.e., temperature) (Fig. 1) (4,9), which determines the change of viscosity with the temperature of the system. Thus, oil viscosity is an indi-
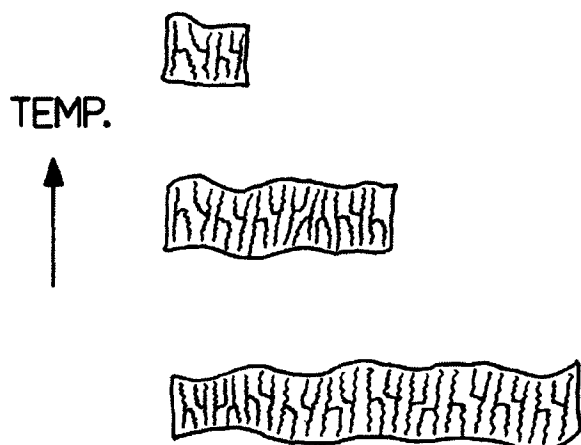
TEMP.

FIG. 1. Proposed bilayer lamellar structure of triacylglycerides in the liquid state as described by Hernqvist (Ref. 9).

rect measurement of the degree of structure of the triacylglycerides in the liquid state. Within this framework, this paper describes the crystallization process of triacylglycerides, from the structural organization of the molecules in the melt to the nucleation stage, by means of reduced viscosity measurements and crystallization curves. The model system utilized was a mixture of sesame seed oil with different proportions of tripalmitin (TP) or tristearin (TS). Considering the high concentration of unsaturated fatty acids in the triacylglycerides of sesame seed oil (10), the mixture of TP or TS with sesame oil was considered as a binary system, formed by unsaturated and saturated triacylglycerides. In a pure binary system, formed by TP and TS, Ng (11) observed that, during constant supercooling, interaction of triolein molecules at the tripalmitin crystal/solution interface decreased the interfacial free energy and, subsequently, the activation free energy for TP nucleation. The saturated mono-triacylglycerides, TP and TS, may modify the native bilayer lamellar structures of the unsaturated triacylglycerides of sesame oil. The measurement of oil viscosity at supercooling conditions might provide information about the changes in triacylglyceride organization in the liquid state and its possible relationship with the process of crystallization of TP and TS in sesame oil.

Sesame seed oil is obtained from the seeds of *Sesamum indicum* L., and it is sold as a gourmet oil with high natural oxidative stability and unique flavor. Mexico is one of the main producers of this oil. The fatty acid composition, triacylglyceride distribution, and concentration of sterols, tocopherols, and lignins have been studied in sesame oil (10,12,13). However, there are no studies regarding its physicochemical properties and interactions with other lipid systems that might eventually support the development of value-added products based on sesame oil (i.e., spreads).

EXPERIMENTAL PROCEDURES

Materials. Refined sesame seed oil (Aceitera San Juan, S.A., Salvatierra, Gto., México) was stored at 4°C in the dark under nitrogen atmosphere. The same batch of oil was used in all experiments. TP and TS, more than 99% pure (experimentally confirmed by gas chromatography and differential scanning calorimetry), were obtained from Sigma Chemical Co. (St. Louis, MO).

Physical and chemical analysis. The fatty acid composition of sesame oil was determined by gas chromatography, following the methodology of Bannon *et al.* (14), with a Shimadzu chromatograph GC-9A (Shimadzu Corp., Kyoto, Japan) with flame-ionization detector and a Shimadzu C-R1B Chromopac integrator. A glass column (2.6 × 2.1 mm) packed with GP 10% SP 2330 on Chromosorb 100/120 (Supelco, Bellefonte, PA) was utilized, with helium as the carrier gas (20 mL/min). The temperature in the column was 200°C and the injection port was held at 215°C. The fatty acid composition was determined with the GLC-10 mixture of methyl fatty acids from Supelco as standards, after normalization of the chromatogram areas according to the method of Ackman and Sipos (15).

A DuPont differential scanning calorimeter (DuPont Co., Wilmington, DE) was utilized to obtain melting curves for TP and TS in the interval between 10 and 80°C at a heating rate of 1.0°C/min. The equipment was calibrated with Indium, and an empty aluminum pan was utilized as the reference.

Crystallization curves. TP and TS solutions in sesame seed oil were prepared at different concentrations (0.0, 0.032, 0.098, 0.18, 0.26, and 0.344 g/dL). Complete dissolution of TP and TS in the oil was achieved by heating the dispersion for 30 min at 80°C with constant stirring. The solutions were stored in the dark at 4°C until their use (<8 d).

Dynamic (e.g., nonisothermal) crystallization curves of the TP and TS solutions were obtained by measuring the absorbance (600 nm) of the solutions as a function of the temperature. A double-beam spectrophotometer (Shimadzu UV-2101PC; Shimadzu Corp.) with temperature control (Brookfield TC-200; Brookfield Instruments; Stroughton, MA) and a cooling system (Brookfield TC-350) was utilized. After destroying the "memory" of crystallization of the solution by heating (80°C for 60 min), the system was cooled at a rate of 1.0°C/min until a temperature of −2°C was reached. During cooling, the absorbance of the solutions was recorded each 12 s with a data acquisition system (UV-2101/3101PC Personal Spectroscopy; Shimadzu Corp.). Calibration of the spectrophotometer was done with the liquid fraction obtained by filtration of sesame seed oil after storage at 4°C for 15 d and 1 h at −20°C. Crystallization curves for pure TP and TS were determined under the same conditions after melting the triacylglyceride (80°C for 60 min). Two independent crystallization curves were obtained for all samples, and the mean of the absorbance as a function of temperature was used in further calculations (Fig. 2). The variation coefficient of absorbance in the linear part of the crystallization curve (see next paragraph) was between 2 to 3%.

Based on the relationship between the amount of light absorbed and dispersed for a solution with suspended particles (16), the temperature of nucleation onset (T_N) was calculated

(Fig. 2). The statistical parameter utilized for the T_N calculation was the cumulative summation of deviations (CUSUM) (17), where CUSUM = $\Sigma(A_s-A_B)$ from temperature = 80°C to temperature = -2°C. Thus, the first temperature at which the absorbance of the oil solution (A_s) was significantly higher than the absorbance of the oil utilized as the blank (A_B) in the calibration of the spectrophotometer $(A_B = 0)$ was considered T_N. Likewise, the slope in the linear part of the crystallization curve was determined by linear regression (Fig. 2), and its value was considered the overall crystallization rate, associated with the process of massive nucleation mixed with crystal growth (V_{Cr}). The units of V_{Cr} were expressed in terms of the increment in absorbance when the temperature was decreased 1°C at a cooling rate of 1.0°C/min ($\Delta A/-\Delta°C$).

Measurements of shear stress and reduced viscosity. The shear stress (τ) of the TP and TS solutions was determined as a function of temperature at different shear rate (γ) with a Brookfield DV-II viscosimeter (Brookfield Intruments) by using the small-sample adapter (Brookfield 13R) and spindle SC4-18. The temperature of the sample was controlled with a Brookfield TC-200 temperature controller connected to a cooling system (Brookfield TC-350). The volume of sample was always 8 mL.

To measure the shear stress of the oil solutions under conditions as close as possible to those utilized in the crystallization curves (i.e., nonstirring conditions), τ was measured at designated temperatures while decreasing the temperature from 80 to -2°C at a cooling rate of 1.0°C/min. The oil solutions were only stirred during τ measurement. Thus, the solution in the sample container of the viscosimeter was initially

heated (80°C for 60 min) to destroy the "memory" of crystallization. Afterwards, the system was cooled (1.0°C/min), and once the temperature of 60°C was reached, τ of the solution was determined by increasing the shear rate from 0.396 to 79.2 s^{-1}; the equilibrium time for recording the shear stress at each shear rate was 25 s. The system was again cooled (1.0°C/min), and τ of the solution was measured at 5°C intervals until the temperature of 10°C was achieved, and then at 2.5°C intervals until -5°C. Two independent determinations of τ were performed at each temperature and utilized in further analysis.

For calculation of the reduced viscosity, the oil solutions were considered as binary mixtures, where the solvent was the sesame oil and the solute was TP or TS. Thus, from τ of the solutions, the reduced viscosity (η_{red}) was calculated as a function of shear rate and temperature with Equation 1:

$$\eta_{red} = [(\tau_{So}-\tau_{Se})/\tau_{Se}](1/C) \qquad [1]$$

where τ_{Se} is the shear stress of sesame oil, τ_{So} is the shear stress of the TP or TS solution, and C is the concentration of TP or TS in the solution. Variations in η_{red} are associated with changes in the molecular conformation of solute molecules as well as with changes in the intermolecular interactions between solute molecules and between solute and solvent molecules. Thus, the effect of TP or TS addition on the triacylglyceride organization in sesame oil, and its possible association to crystallization, was evaluated by plotting η_{red} of the oil solutions as function of temperature, TP or TS con-
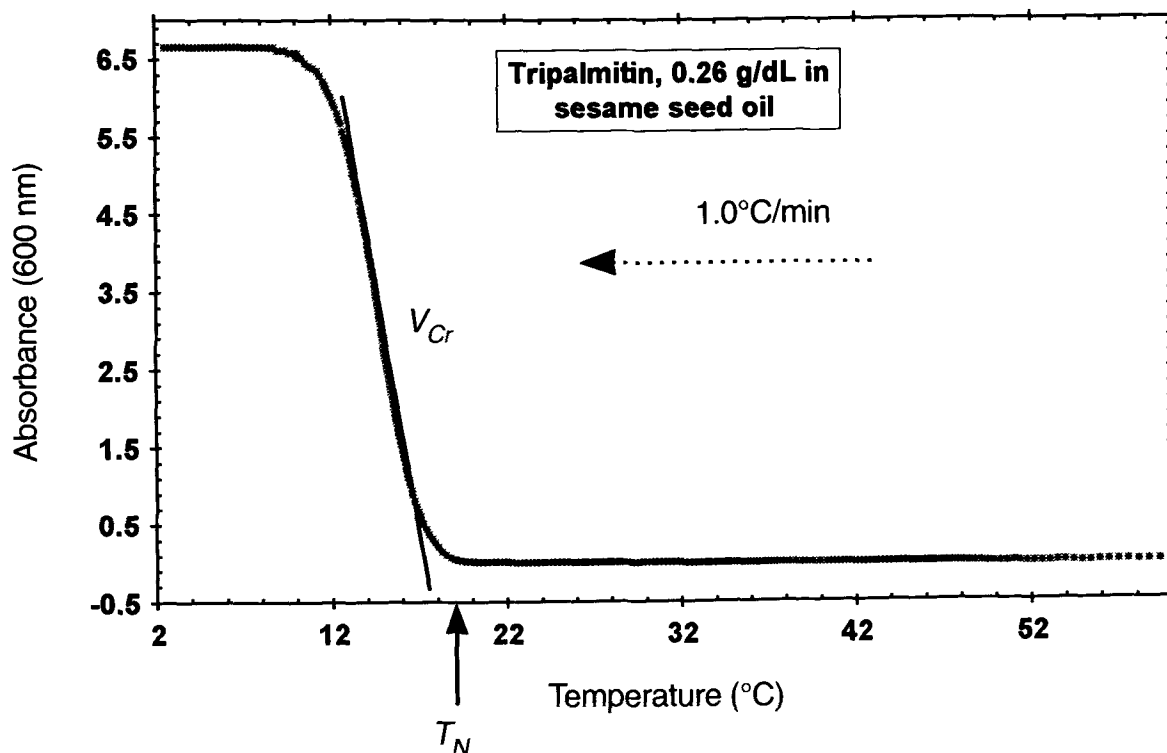

FIG. 2. Nonisothermal crystallization curve showing the rate of crystallization (V_{Cr}) and the temperature of nucleation (T_N).

centration, and shear rate. The overall experimental error for η_{red} (i.e., independent of temperature, TP or TS concentration, and shear rate), calculated through analysis of variance, was 0.035 for TS solutions and 0.071 for TP solutions.

RESULTS AND DISCUSSION

Several authors have used absorbance measurements to characterize the different stages of isothermal crystallization in lipid systems (16,18). In general, in a system under isothermal crystallization, the amount of light that is dispersed and absorbed is proportional to the concentration of crystals and the average area of the crystal distribution (16). There are no restrictions that limit the use of this relationship to nonisothermal crystallization process. Thus, in the crystallization curves, determined by absorbance measurements, T_N was associated with the temperature of onset of nucleation, while V_{Cr} was associated with the process of massive nucleation mixed with crystal growth (Fig. 2).

Pure TS started to nucleate at higher temperature (T_N = 48.59°C) and crystallized at a higher rate (V_{Cr} = 3.639 ΔA/Δ°C) than TP (T_N = 41.81°C, V_{Cr} = 2.833 ΔA/Δ°C). This was the result of a higher gradient of supercooling (i.e., the driving force for crystallization) achieved for TS because of the more elevated melting temperature of TS [72.11°C, obtained in this study by differential scanning calorimetry, and 72.5°C, reported by Norton et al. (19)] in comparison to TP [65.67°C, obtained in this study by differential scanning calorimetry, and 65.3°C, reported by Norton et al. (19)]. The

difference in the magnitude of the values of T_N and V_{Cr} between TP and TS was also present in the oil solutions at all concentrations of saturated triacylglyceride utilized (Figs. 3 and 4). Under nonisothermal conditions, the kinetic induction time for crystallization (e.g., value associated to the temperature when nucleation begins, T_N) and the relative crystallinity (e.g., value that represents the percentage of solid/crystal formation during nucleation and crystal growth and associated with V_{Cr}) decreases as the cooling rate increases (20). In this investigation, the cooling rate was kept constant in all experiments (1.0°C/min). Therefore, the differences in V_{Cr} and T_N among the systems studies depended only on the differences in structural/physicochemical properties of the triacylglyceride in the oil solutions (i.e., TP vs. TS solutions) and/or the different concentration of saturated mono-triacylglyceride in the sesame oil. Variation in the concentrations of diacylglycerides and/or free fatty acids could affect the magnitude of V_{Cr} and T_N. However, in this research, the same batch of sesame oil was utilized in all experiments.

The crystallization rate showed a maximum at a TP and TS concentration of 0.18 g/dL (Fig. 4); at concentrations <0.18 g/dL, where a substantial lower temperature was needed to achieve nucleation (Fig. 3), V_{Cr} decreased significantly. Under these conditions, the viscosity (i.e., shear stress) of the oil solutions was significantly higher than at TP and TS concentrations ≥0.18 g/dL (Fig. 5). When crystallization occurs from the melt, the activation free energy for diffusion of the molecules in the melt plays an essential role in the kinetics of crystal growth (8). Thus, whereas growth rate is proportional
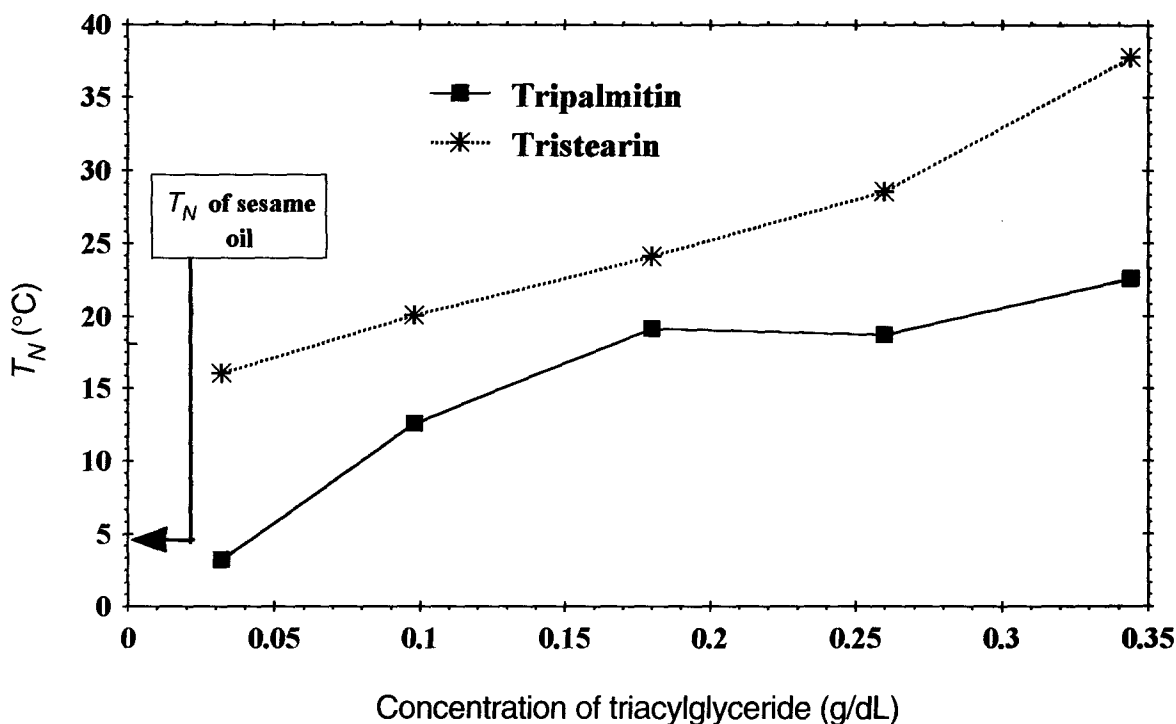

FIG. 3. Temperature of nucleation (T_N) of oil solutions at different concentrations of tripalmitin and tristearin. The arrow indicates the temperature of nucleation of sesame oil (4.25°C).
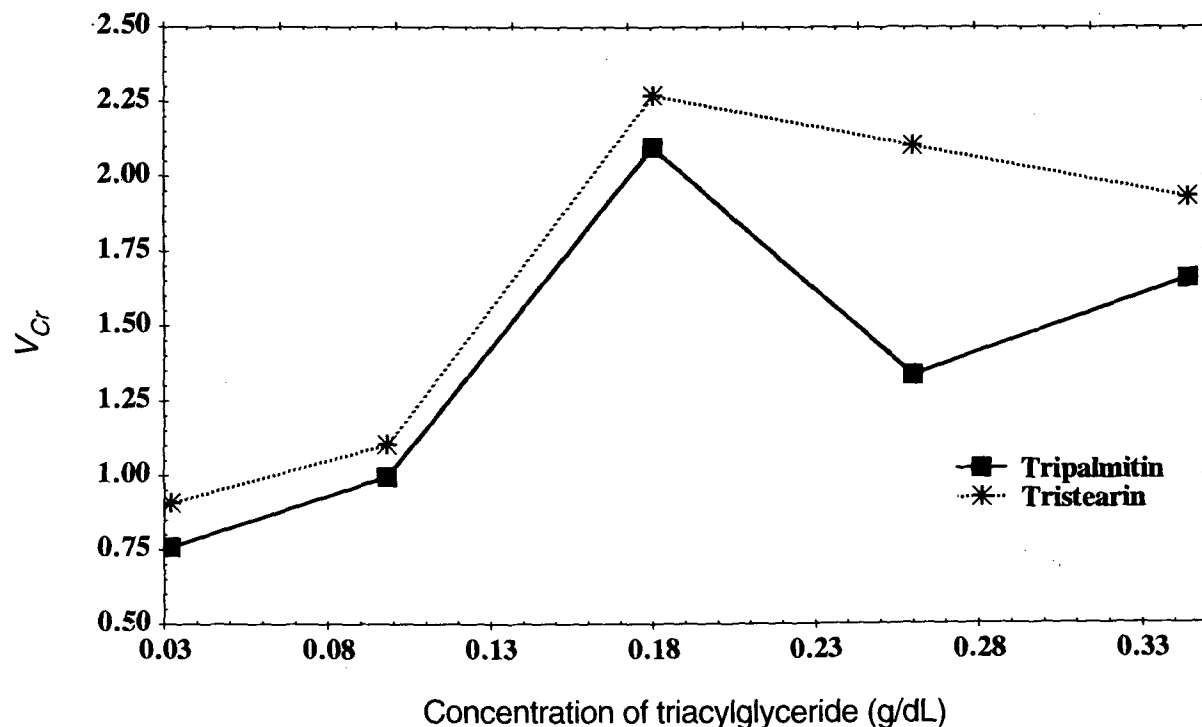
FIG. 4. Rate of crystallization (V_{Cr}) for tripalmitin and tristearin in sesame seed oil.

to supercooling, it is inversely proportional to viscosity (21). These results indicated that, at TP and TS concentrations ≥0.18 g/dL, the crystallization process was balanced by the effect of supercooling and molecular diffusion. However, at TP and TS concentrations <0.18 g/dL, the diffusion term became the rate-determining step of crystallization.

In particular for T_N, its magnitude decreased as the proportion of unsaturated triacylglycerides (i.e., sesame oil) increased in the system (Fig. 3). The fatty acid profile of sesame oil (% w/w) was the following: palmitic acid 9.5%, stearic acid 5.42%, oleic acid 39.7%, linoleic acid 43.75%, palmitoleic acid 0.29%, linolenic acid 0.6%, unidentified fatty acids 0.5%. The fatty acid composition was in close agreement with the results obtained by Kamal-Eldin and Appelqvist (10). Sesame seed oil showed a high degree of unsaturation (14.92% of saturated fatty acids, 39.99% of monounsaturated fatty acids, and 44.5% of polyunsaturated fatty acids). Thus, solutions of TP or TS in sesame oil might be considered binary systems formed by saturated and unsaturated triacylglycerides. Within this framework, the T_N behavior (Fig. 3) might be explained based on the results of Ng (11) for pure binary systems of triacylglycerides with high and low melting temperatures (i.e., saturated and unsaturated triacylglycerides). Thus, the unsaturated triacylglyceride molecules of sesame oil interacted, through polar or dispersive forces, with the saturated triacylglyceride at the interphase between the oil solution and the developing nucleus of TP or TS. As a result of the molecular interaction, the component with the higher melting temperature (T_M) decreased its T_M. The degree of reduction in T_M was an inverse function of the concentration of TP or TS in sesame oil. Thus, the supercool-

ing gradient, T_M-T_N, required to induce TP or TS nucleation in sesame oil, needed a lower temperature (i.e., a lower T_N) as a function of the decrease in T_M. However, an additional explanation, based on the effect that TP and TS had on the organization of the unsaturated triacylglycerides of sesame oil, might also apply.

The development of molecular organization in the liquid state is a requirement to produce crystallization (8). However, the development of a nucleus (i.e., the critical number of molecules in achieving a solid phase) must be associated with evolution in the organization of the triacylglyceride molecules in the liquid state (i.e., bilayer lamellar structures, Fig. 1) as the temperature approaches the degree of supercooling required to achieve nucleation. In fact, the change of oil viscosity with temperature of the system is determined by the shape and size of the triacylglyceride lamellar structures (Fig. 1). Figure 6 shows, according to the Arrhenius equation, the τ profile at different shear rates (7.92–79.2 s^{-1}) of the solutions of TP and TS at 0.098 g/dL. The τ profile of sesame oil was also included in the plot to show the contribution of TP and TS to the shear stress of the oil solution as the temperature of the system approached T_N. The τ values at shear rates ≤3.96 s^{-1} were not considered because of the low sensitivity of the viscosimeter at such shear rates. On the other side, due to the shear rate applied during the τ measurements, the onset of crystallization might have occurred at a different temperature than that determined under nonstirring conditions. However, the oil solutions were just stirred during τ measurement, and therefore, the shear rate effect on crystallization was considered limited.
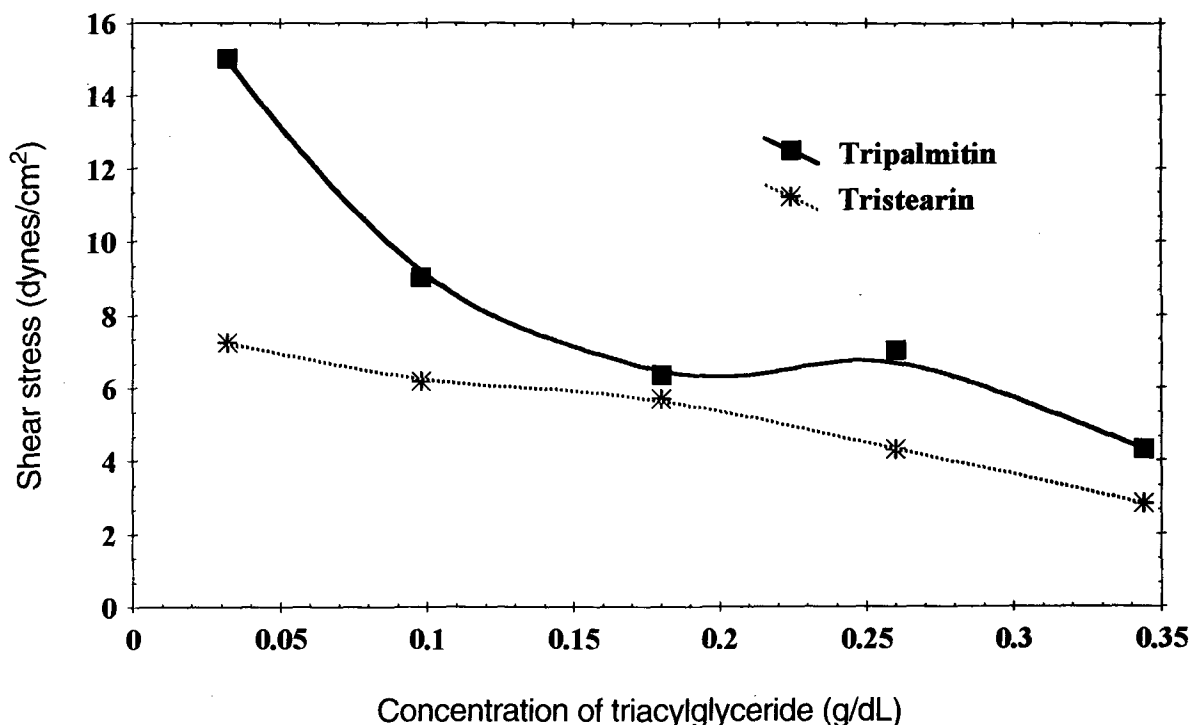
FIG. 5. Shear stress values (shear rate = 7.92 s^{-1}) of oil solutions at the temperature where the reduced viscosity equals zero (η_{red} = 0). The temperature of viscosity measurement was T_N (Fig. 3).

Before and after T_N, there was a difference in τ of the TP and TS solutions with respect to τ of sesame oil (Fig. 6). At temperatures $<T_N$, supercooling favored the development of crystals; thus the difference between the τ profiles showed the effect of the volumetric fraction of crystals on the viscosity of the liquid phase. In the vicinity of a critical temperature or critical solute concentration at which phase separation occurs, binary liquid systems present large concentration fluctuations (22). As a result, the viscosity of binary liquid mixtures shows strong temperature and concentration dependence as some critical solution temperature is approached (i.e., T_N) (22). At temperatures $>T_N$, there were no conditions to produce crystallization; thus the difference in the τ profiles indicated the effect of the saturated triacylglyceride on the molecular organization, in the liquid state, of the triacylglycerides of sesame oil. This effect depended on the shear rate applied to the system (Fig. 6). Whereas sesame oil showed a linear behavior in the Arrhenius model up to temperatures $<T_N$ (4.25°C) at all shear rates utilized, the shear stress profile of the TP and TS solutions was not linear (Fig. 6). However, as the shear rate was increased, τ of the oil solutions became more linear and approached the τ profile of sesame oil (Fig. 6). These results suggest that, as the shear rates increased, the original lamellar organization of the unsaturated triacylglyceride in sesame oil was achieved. This event may be associated with segregation of the saturated triacylglyceride from the sesame oil phase due to the exclusion of incompatible molecules by the steric nature of the cis unsaturation. This process was promoted as the shear rate increased. Nevertheless, under the shear rate effect, crystallization of the segregated molecules did not occur because supercooling had not been achieved. With differential scanning calorimetry, nuclear magnetic resonance, and X-ray diffraction, Norton et al. (19) showed that the solubility of TP and TS in triolein was significantly lower than that established for ideal solutions. These authors suggested than, even in the liquid state at nonstirring conditions, saturated triacylglyceride may be segregated from the triolein phase due to the steric nature of the cis unsaturation (19).

The shear stress data were utilized to calculate η_{red} of the oil solutions to obtain additional information on the triacylglyceride organization of the solutions at temperatures $>T_N$. In general, the η_{red} of a binary system follows a linear relationship with the concentration of solute in the solvent. The extrapolation of η_{red}, when the concentration of the solute is zero, is known as the intrinsic viscosity of the solute, a value that is associated with the effective hydrodynamic volumes of separate, noninteracting molecules that make up a gram of solute (22). In this investigation, a linear relationship was not observed between η_{red} and the concentration of TP or TS in the oil (data not shown), mainly because the solute and the solvent molecules shared structural characteristics and physicochemical properties. Besides, departures from linearity are common in systems under conditions of phase separation and transition, and in liquid crystalline systems, which show a strong temperature and concentration dependence as some critical temperature is approached (i.e., T_N) (22).

The η_{red} of the oil solutions, plotted as a function of the temperature at two different shear rates, is shown in Figures 7
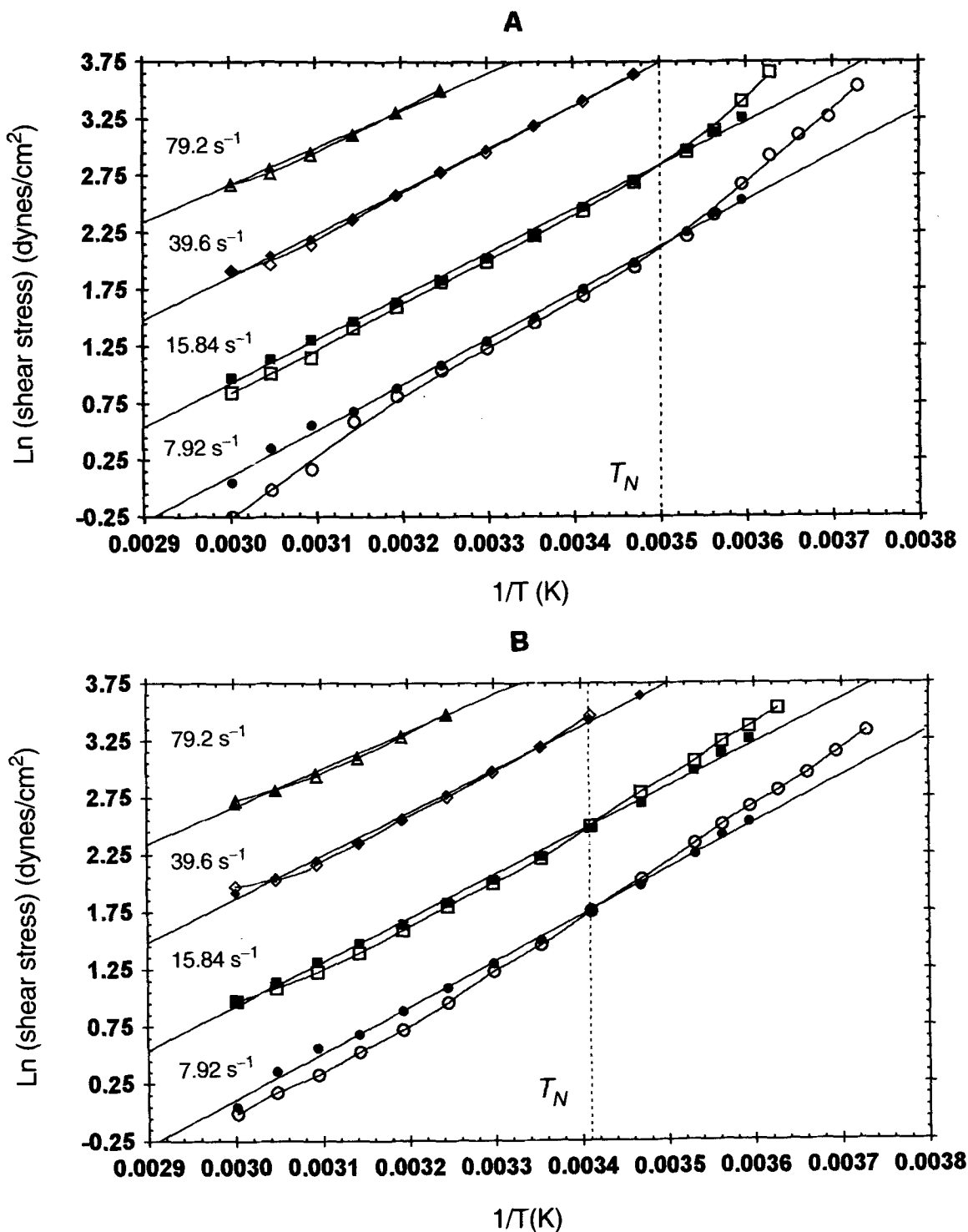
FIG. 6. Shear stress profiles at different shear rates for tripalmitin (A) and tristearin (B) at 0.098 g/dL in sesame seed oil. Solid legend belongs to sesame oil and empty legend belongs to tripalmitin and tristearin solutions.

and 8 for the different TP or TS concentrations investigated. The η_{red} measurements indicate changes in the molecular conformation of solute molecules (i.e., intramolecular phenomena) as well as changes in the intermolecular interactions (e.g., association, dissociation, etc.) between solute molecules

and between solute and solvent molecules (22). However, the chemical nature of the triacylglyceride molecules limited the contribution of conformational changes to the magnitude of η_{red}. Therefore, before nucleation occurred, η_{red} showed the effect of the intermolecular interactions between the saturated
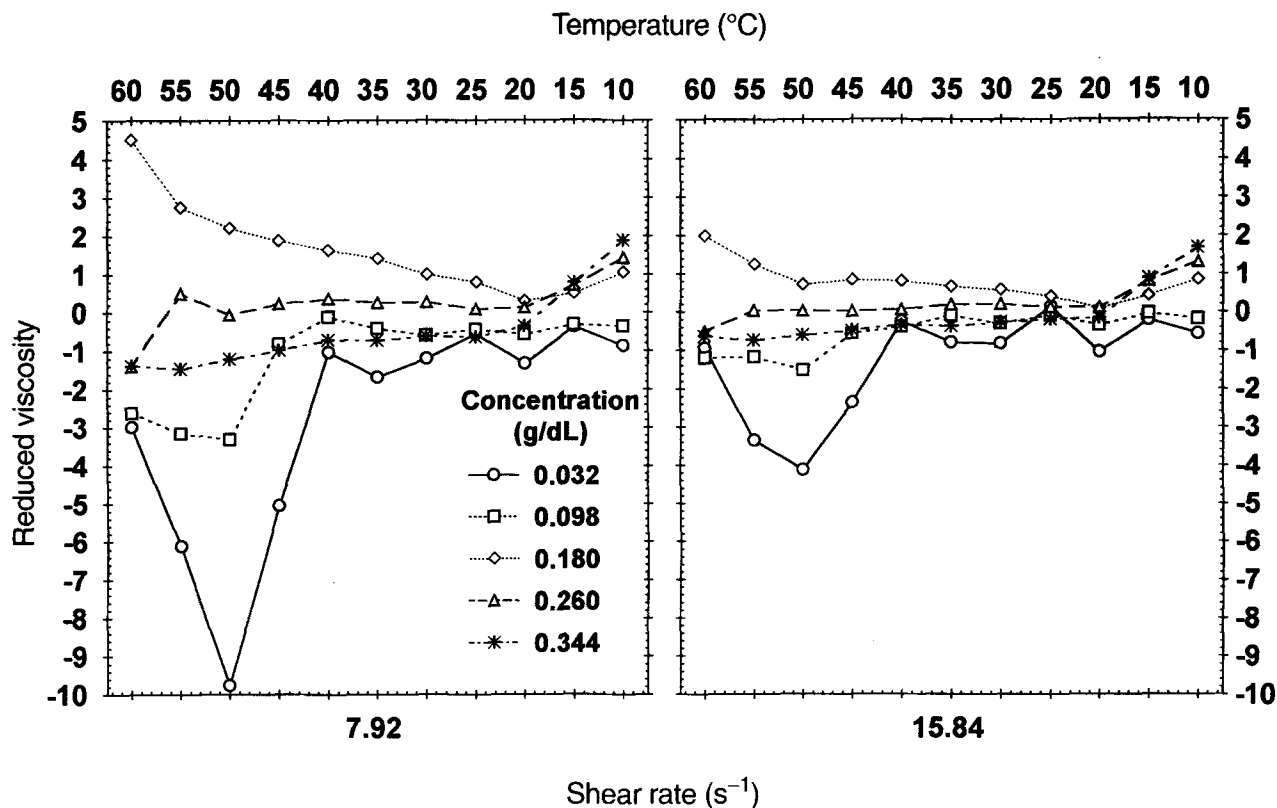
FIG. 7. Reduced viscosity of tripalmitin solutions as a function of tripalmitin concentration in sesame oil and temperature at two shear rates: A, 7.92 s^{-1}; B, 15.84 s^{-1}.

triacylglyceride and the native organization of the unsaturated triacylglycerides of sesame oil. Ongoing studies with TP–sesame oil solutions by differential scanning calorimetry and polarized microscopy (Dibildox-A.E., and Toro-V.J.F., unpublished results) show that, at TP concentrations ≤0.098 g/dL, mixed crystal formation occurs between a triacylglyceride fraction of sesame oil and TP. However, at TP concentrations >0.098 g/dL, TP crystallizes independently. These results suggest that, before nucleation occurred, the negative values of η_{red} at TP or TS concentrations ≤0.098 g/dL indicated that, as a result of the intermolecular interactions between the saturated triacylglyceride and the unsaturated triacylglycerides of sesame oil, the oil solution developed lamellar structures with a smaller size than the native structures in sesame oil. This triacylglyceride structure in the liquid state may be responsible for the mixed crystal formation. In the other side, at TP or TS concentrations >0.098 g/dL, the change in η_{red} as a function of temperature showed the rate of TP or TS segregation out of the lamellar structure as the system approached T_N. In other words, the increase in interfacial energy between the bilayer lamellar structure of TP or TS and the lamellar organization of unsaturated triacylglyceride of sesame oil is described by the change in η_{red} as the temperature is decreased. The results shown in Figures 7 and 8 indicate that the kinetics of the segregation phenomenon that occurred at TP or TS concentrations >0.098 g/dL was a

function of the concentration of saturated triacylglyceride and the type of triacylglyceride (i.e., TP or TS), and that it was favored by an increase in the shear rate.

Independent of the saturated triacylglyceride concentration and shear rate applied, T_N was always achieved right after $\eta_{red} = 0$, which represents the point where the interfacial energy between the sesame oil and the developing nucleus in the sesame oil accomplished its maximum value (i.e., minimum solubility of the crystal developed in sesame oil). Thus, the higher the intermolecular interaction between the saturated triacylglycerides and the unsaturated triacylglycerides of sesame oil, the lower the temperature needed to accomplish the point where $\eta_{red} = 0$ in the oil solutions. The results obtained indicate that the lower the concentration of saturated triacylglyceride in the sesame oil, the higher the intermolecular interaction with the unsaturated triacylglyceride of the solvent (Figs. 7 and 8) and the lower the temperature needed to achieve $\eta_{red} = 0$ (Fig. 3). As a result, the viscosity of the liquid phase becomes the limiting factor for crystal growth rate, especially at TP and TS concentrations <0.18 g/dL (Fig. 5). Thus, in binary systems, such as the one investigated here, the degree of intermolecular interaction between the triacylglyceride structures determines the development of mixed crystal formation or the segregation rate of the molecules with the highest melting temperature, which in turn determines the nucleation temperature of the system. In conclusion, TP and TS
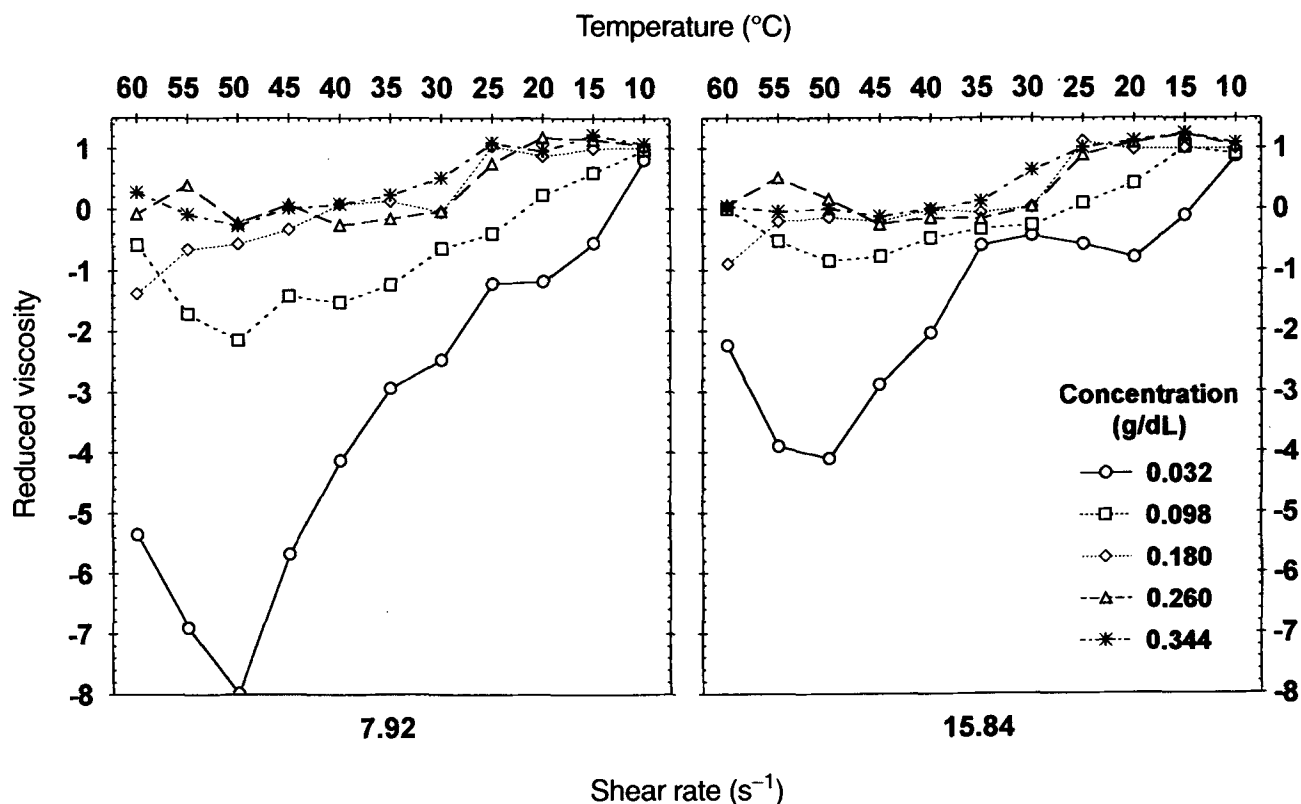
FIG. 8. Reduced viscosity of tristearin solutions as a function of tristearin concentration in sesame oil and temperature at two shear rates: A, 7.92; B, 15.84.

nucleation was more difficult in sesame oil solutions than in their own melt, which implies that a higher overall free energy of nucleation was needed to crystallize TP and TS in sesame oil than in their own melt.

ACKNOWLEDGMENT

REFERENCES

1. Toro-Vazquez, J.F., and R. Infante-Guerrero, Regressional Models That Describe Oil Absolute Viscosity, *J. Am. Oil Chem. Soc. 70*:1115–1119 (1993).
2. Dutt, N.V.K., and D.H.L., Prasad, Inter-Relationship Among the Properties of Fatty Oils, *Ibid. 66*:701–703 (1989).
3. Kato, A., and S. Nakai, Hydrophobicity Determined by a Fluorescence Probe Method and Its Correlation with Surface Properties of Proteins, *Biochem. Biophys. Acta 624*:13–20 (1980).
4. Larsson, K., *Lipids-Molecular Organization, Physical Functions and Technical Applications*, The Oily Press, Scotland, 1994.
5. Bornaz, S., J. Fanni, and M. Parmentier, Heat Treatment of Cream: A Model of the Butter Texture Response in Relation with Triglyceride Composition. *J. Am. Oil Chem. Soc. 72*:163–169 (1994).
6. Drewnowski, A., Fats and Food Texture: Sensory and Hedonic Evaluations, in *Food Texture*, edited by H.R. Moskowitz, Marcel Dekker, New York, 1987, pp. 251–253.

7. Vreeker, R., L.L. Hoekstra, D.C. den Boer, and W.G.M. Agterof, The Fractal Nature of Fat Crystals Networks, in *Food Colloids and Polymers: Stability and Mechanical Properties*, edited by E. Dickinson and P. Walstra, The Royal Society of Chemistry, Cambridge, 1993, pp. 16–22.
8. Hartel, R.W., Solid-Liquid Equilibrium: Crystallization in Foods, in *Physical Chemistry of Foods*, edited by H.G. Schwartzber and R.W. Hartel, Marcel Dekker, Inc. New York, 1992, pp. 47–81.
9. Hernqvist, L., Crystal Structures of Fats and Fatty Acids, in *Crystallization and Polymorphism of Fats and Fatty Acids*, edited by N. Garti and K. Sato, Marcel Dekker, Inc. New York, 1988, pp. 97–137.
10. Kamal-Eldin, A., and L.A. Appelqvist, Variation in Fatty Acid Composition of the Different Acyl Lipids in Seed Oils From Four Sesamum Species, *J. Am. Oil Chem., Soc. 71*:135–139 (1994).
11. Ng, W.L., Nucleation Behavior of Tripalmitin from a Triolein Solution, *Ibid. 66*:1103–1106 (1989).
12. Kamal-Eldin, A., and L.A. Appelqvist, Variation in Composition of Sterols, Tocopherols and Lignans in Seed Oils from Four *Sesamum* Species, *Ibid. 71*:149–156 (1994).
13. Kamal-Eldin, A., L.A. Appelqvist, and G. Yousif, Lignan Analysis in Seed Oils from Four *Sesamum* Species: Comparison of Different Chromatographic Methods, *Ibid. 71*:141–147 (1994).
14. Bannon, C.D., J.D. Craske, Ngo Trong Hai, N.L. Harper, and K.L. O'Rourke, Analysis of Fatty Acids Methyl Esters with Accuracy and Reliability, *J. Chrom. 247*:63–69 (1982).
15. Ackman, R.G., and J.C. Sipos, Application of Specific Response Factors in the Gas Chromatographic Analysis of Methyl Esters

of Fatty Acids with Flame-Ionization Detectors, *J. Am. Oil Chem. Soc. 41*:377 (1964).

16. Grall, D.S., and R.W. Hartel, Kinetics of Butterfat Crystalliza-tion, *Ibid. 69*:741–747 (1992).

17. *Statistica User's Guide*, Statistica for Windows, Version 4.3 StatSoft, Tulsa, OK, 1994.

18. Davis, T.R., and P.S. Dimick, Isolation and Thermal Characteri-zation of High-Melting Seed Crystal Formed During Cocoa But-ter Solidification, *J. Am. Oil Chem. Soc. 66*:1488–1493 (1989).

19. Norton, I.T., C.D. Lee-Tuffnell, S. Ablett, and S.M. Bociek, Calorimetric, NMR and X-ray Diffraction Study of the Melting Behavior of Tripalmitin and Tristearin and Their Mixing Behav-ior with Triolein, *Ibid. 62*:1237–1244 (1985).

20. Chan, T.W., and A.I. Isayev, Quiescent Polymer Crystallization: Modeling and Measurements, *Poly. Eng. Sci. 34*:461–471 (1994).

21. Boistelle, R., Fundamentals of Nucleation and Crystal Growth, in *Crystallization and Polymorphism of Fats and Fatty Acids*, edited by N. Garti and K. Sato, Marcel Dekker, New York, 1988, pp. 189–226.

22. Bohdanecký, M., and J. Kovàr, *Viscosity of Polymer Solutions*, Elsevier Scientific Publishing Co., New York, 1982.