Physical Characterization of Lard Partial Acylglycerols and Their Effects on Melting and Crystallization Properties of Blends with Rapeseed Oil

LING-ZHI CHEONG,[†] HONG ZHANG,[†,#] YUAN XU,[§,⊥] AND XUEBING XU*,[†]

[†]Department of Molecular Biology, Aarhus University, DK-8000 Aarhus, Denmark, and [§]National Food Institute, Technical University of Denmark, DK-2800 Lyngby, Denmark. [#]Present address: Innovation Centre Brabrand, Arla Foods, DK-8220 Brabrand, Denmark. [⊥]Present address: Department of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark

This work attempted to examine the effects of lard partial acylglycerols on the melting and crystallization properties of blends with lard and rapeseed oil (LR). Partial acylglycerols [lard-monoacylglycerols (lard-MAG) and lard-DAG] were found to result in different melting and crystallization properties of LR. Lard-MAG exerted slight inhibitory effect on crystallization of LR. Nevertheless, it was not statistically significant ($P > 0.05$). In fact, the presence of lard-MAG did not change the solid fat content (SFC) of LR. Lard-DAG, on the other hand, exerted different effects on the crystallization of LR depending on its concentration and degree of supercooling. The presence of a low concentration of lard-DAG was found to significantly ($P < 0.05$) delay nucleation and crystal growth velocity of LR at low degree of supercooling, which was reflected by a reduced Avrami constant (k) and SFC and increased half-time of crystallization ($t_{1/2}$). Meanwhile, a high concentration of lard-DAG was found to promote nucleation and crystal growth in LR at low degrees of supercooling with increased k and SFC and decreased $t_{1/2}$. The characteristics of the blends may have correlations with their properties in potential meat applications.

KEYWORDS: Lard; diacylglycerol; Avrami equation; crystallization; enzymatic glycerolysis; short-path distillation

INTRODUCTION

Lard has exceptional properties compared to other vegetable oils such as wider plastic ranges and special flavor values. It has total production reaching 2.5 million pounds per year. Since 1925, lard has lost its significance to numerous substitutes such as hydrogenated cottonseed and soybean oil (*1*). Available substitutes coupled with negative nutritional values such as low digestibility, high calories, and saturated fatty acids (SFA) content have brought about vastly diminished usage of lard in the food industry. Many studies have demonstrated the link of SFA to cardiovascular disease (*2, 3*), which consequently reduced use in the food industry. Nonetheless, lard remains a major player in the meat product industry due to its positive contributions in flavor and texture (*1*).

To improve the nutritional values of lard, attempts have been made to blend lard with vegetable oils such as olive (*4, 5*), soybean (*6*), and extra virgin olive oil (*7*). Physical blending of lard with vegetable oils may not be a good solution as the end products often demonstrate reduced stability. Blending of lard with olive oil, for example, was found to result in end products with considerable dripping during ripening (*4*). To increase product

stability, lard can be interesterified with other vegetable oils such as rapeseed, high-oleic sunflower (*8*), and perilla seed oils (*9*). These studies focused mainly on changing the fatty acid (FA) contents, particularly reducing the percentage of SFA in lard (*4−9*). Another area worth studying is the changing of the acylglycerol structure in lard.

Diacylglycerols (DAG) emerged in the late 1990s as a healthier form of oil. With only two FAs attached to the glycerol structure, DAG have been proven to be metabolized in a manner that reduces postprandial lipid levels (*10−12*) and prevents weight gain (*13, 14*). To date, DAG have been produced from numerous plant oils including rapeseed (*15*), palm (*16*), and blends of soybean and rapeseed oils (*17*). Nevertheless, few studies have been done on the production of DAG from animal-based fat such as lard. Hence, it is timely to investigate the possibilities of producing lard-DAG for potential applications in the meat industry.

Production of DAG usually results in a mixture containing monoacylglycerols (MAG), DAG, and triacylglycerols (TAG). Hence, a purification step is an essential process (*18*). In fact, from an economic point of view, it is advantageous to use the mixture for applications. Nevertheless, careful consideration should be given to the amount of partial acylglycerols to produce edible fat products with desirable melting and crystallization properties. So far, quite a number of studies have been made to investigate the effect of partial acylglycerols on the melting and

*Address correspondence to this author at the Department of Molecular Biology, Aarhus University, Gustav Wieds Vej 10, DK-8000 Aarhus C, Denmark (telephone +45 8942 5089; fax +45 86123178; E-mail: xu@mb.au.dk).

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crystallization properties of TAG (*19–23*). Each of these studies reported different effects depending on the type and amount of partial acylglycerols present. As in the production process, effects of lard-DAG on the melting and crystallization properties of TAG have not been evaluated.

Therefore, this work aims to investigate the effects of lard partial acylglycerols on melting and crystallization properties of blends of lard with rapeseed oil (LR). Lard-DAG was first produced through enzymatic glycerolysis. It was then purified through short-path distillation (SPD) to obtain the different acylglycerol fractions, namely, lard-MAG, lard-DAG, and lard-TAG fractions. The partial acylglycerol fractions (lard-MAG and lard-DAG) were then added at different concentrations to blends of lard and rapeseed oil (1:1 wt %). The effects of partial acylglycerols on the melting and crystallization properties of LR were thus examined.

MATERIALS AND METHODS

Materials. Lard was supplied by Danish Crown AmbA (Horsens, Denmark); rapeseed oil was supplied by Aarhus Karlshamn AB (Aarhus, Denmark). Glycerol with a purity of 99.5 wt % was purchased from VWR International Ltd., Albertslund, Denmark. Novozym 435, a commercially available *Candida antarctica* lipase B (CALB) immobilized by physical adsorption onto a macroporous hydrophobic polymethyl methacrylate (PMMA) matrix, was donated by Novozymes A/S (Bagsvared, Denmark). All other reagents and solvents used were of analytical grade.

Enzymatic Glycerolysis of Lard. Enzymatic glycerolysis of lard was carried out using the 1 kg batch scale reactor as described previously by Zhang et al. (*24*). Two batch productions were carried out. The process was carried out under slightly reduced pressure (≥0.5 bar) filled with nitrogen. Lard and glycerol at a substrate ratio of 9:1 was first equilibrated to 65 °C. Once the reaction mixture was sufficiently heated, enzyme Novozym 435 (7 wt % of oil mass) was added and distributed homogenously throughout the system using an impeller stirrer at 400–500 rpm. After 18 h of reaction, the reaction mixture was filtered by vacuum filtration at 1.5–2 bar to separate the enzyme and product. The product was then stored at −20 °C for further purification.

Purification of Acylglycerol Fractions. Purification of acylglycerol fractions was carried out using a KD4 system (UIC, Alzenau-Hoerstein, Germany) similar to the KD6 system previously described by Xu et al. (*18*). The nonvarying conditions were as follows: evaporator and degasser vacuum, 0.1 at Pa; feed tank temperature, 60 °C; and roller speed, 400 rpm. The varying distillation conditions are listed in **Table 1**.

Blends Preparation. Lard was first heated at a temperature of 65 °C. Once completely melted, lard was blended with rapeseed oil at a ratio of 1:1 (wt %). The blend of lard and rapeseed oil (LR) produced was then added with purified lard-MAG and lard-DAG at various concentrations to produce different blends with a final total weight of 500 g. Four different blends were produced from LR and lard-MAG (0.1, 0.5, 1, and 2 wt % of final total weight), and five different blends were produced from LR and lard-DAG (1, 5, 10, 20, and 50 wt % of final total weight). Blends of LR with added partial acylglycerols were produced in duplicate and stored at −20 °C for further analysis.

Analysis of Acylglycerol Composition. The acylglycerol composition was analyzed using a Hitachi-Merck HPLC series 7000 (Hitachi-Merck, Tokyo, Japan) conjugated with a PL-ELS 2100 evaporative light scattering detector (ELSD) (Polymer Laboratories, Shropshire, U.K.). The operating conditions of the ELSD were 70 °C evaporating

Table 1. Varying Distillation Conditions in Short-Path Distillation for Purification of Acylglycerol Fractions

	feed rate (mL/h)	evaporation temperature (°C)	condenser temperature (°C)
removal of FFA and glycerol	200	120	50
removal of MAG	150	170	60
removal of DAG	150	230	60

temperature, 50 °C nebulizing temperature, and 1.6 mL/min gas flow. Separation of the different acylglycerol components was performed using a reverse phase Supelcosil LC-18, 5 μm column (250 mm × 4.6 mm) (Supelcosil Inc., Bellefonte, PA). A binary solvent system of acetonitrile (solvent A) and isopropanol/hexane (2:1) (solvent B) under gradient elution was used. Beginning with 70% solvent A and 30% solvent B, solvent A was reduced to 40% and solvent B was increased to 60% at 40 min. The composition of 40% solvent A and 60% solvent B was maintained for 10 min before reverting back to 70% solvent A and 30% solvent B for another 6 min. The flow rate of the solvent was at a constant 1.0 mL/min. Eluted peaks were identified by comparison of retention times with TAG standards. TAG standards were obtained from Sigma-Aldrich (Denmark). The acylglycerol composition was expressed as weight percent of the total weight of the sample. MAG was expressed as the sum of isomers, whereas DAG was expressed as 1,2 DAG or 1,3 DAG. Double determinations were performed.

Determination of Fatty Acid Composition. The samples were first dissolved in 1 mL of heptane and methylated with 60 μL of 2 M methanolic potassium hydroxide. The mixtures were then added with sodium sulfate anhydrous and centrifuged at 4000 rpm for 10 min. One hundred microliters of the supernatant was added to 1 mL of heptane and analyzed for fatty acid composition. Fatty acid composition was determined using a Hewlett-Packard 5890 GC system equipped with a flame ionization detector, a HP automatic sampler, and a Supelco SP-2380 fused silica capillary column (60 m × 0.25 m × 0.2 μm). Helium was used as a carrier gas at a flow rate of 40 mL/min. The injector and detector temperatures were set at 260 and 280 °C, respectively. The oven temperature was initiated at 70 °C for 2 min. Then, the temperature was increased to 160 at 15 °C/min and to 200 at 1.5 °C/min. The temperature was maintained at 200 °C for 15 min before increasing to 225 at 25 °C/min and held for 10 min. The total run time was 59 min. The peaks were identified by comparison of retention time with fatty acid methyl ester (FAME) standards. FAME standards (C10:0, C12:0, C14:0, C16:0, C16:1, C17:0, C18:0, C18:1, C18:2, C18:3, C20:0, C20:1, C20:2, C22:1) were obtained from Sigma-Aldrich. All measurements were conducted in duplicate.

Melting and Crystallization Profiles. Melting and crystallization profiles were analyzed using a PerkinElmer Pyris 6 DSC (PerkinElmer, Boston, MA). Samples weighed between 6 and 10 mg and were sealed in aluminum pans. The prepared pans were first heated to 80 °C for 15 min to ensure no residual nuclei remained. To obtain the crystallization curve, the samples were then cooled from melt (80 °C) at 5 °C/min to −60 °C. To obtain the melting curve, the samples were equilibrated at −60 °C for 15 min before they were heated to 80 at 5 °C/min. The samples were analyzed in duplicates.

Solid Fat Content (SFC) Profile. SFC as a function of temperature was determined using a Bruker Minispec mq 20 pulse nuclear magnetic resonance (pMNR). The samples were first heated at 70 °C for 30 min to destroy any crystal history, followed by chilling at 0 °C for 60 min, and then kept at the desired temperatures for 30 min prior to measurements. The melting, chilling, and holding of the samples were carried out in pre-equilibrated thermostated baths. SFC was measured within the temperatures ranges from 0 to 40 °C in 5 °C increments. Double determinations were performed.

Crystallization Kinetics. Crystallization kinetics was determined using the method described by Wright et al. (*23*). SFC as a function of time was first determined using Bruker Minispec mq 20 pulse nuclear magnetic resonance (pMNR). Samples were heated at 70 °C for 30 min to destroy any crystal history. Duplicates for each sample were placed in a thermostated water bath, and SFC readings were taken at appropriate time intervals. Static crystallization was performed at high (5 and 10 °C) and low degrees of supercooling (20 and 25 °C). Induction times of crystallization were determined from curves of SFC as a function of time by extrapolating back to the onset of the linear SFC increase. Crystallization kinetics was quantified by fitting the data from SFC as a function of time into the Avrami equation. The general form of the Avrami equation is

$$X(t) = 1 - \exp(-Kt^n) \qquad (1)$$

where *K* is the crystallization rate constant involving both nucleation and growth rate parameters under isothermal conditions; *n*, sometimes

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Table 2. Values for the Avrami Exponent, *n*, for Different Types of Nucleation and Growth

n	types of crystal growth and nucleation expected
3 + 1 = 4	spherulitic growth from sporadic nuclei
3 + 0 = 3	spherulitic growth from instantaneous nuclei
2 + 1 = 3	disk-like growth from sporadic nuclei
2 + 0 = 2	disk-like growth from instantaneous nuclei
1 + 1 = 2	rod-like growth from sporadic nuclei
1 + 0 = 1	rod-like growth from instantaneous nuclei

referred to as an index of crystallization, indicates the nucleation and crystal growth mechanism. Equation 1 can also be rewritten as follows:

$$\log\{-\ln[1 - X(t)]\} = n \log t + \log K \quad (2)$$

On the basis of the value of *n*, the nucleation mechanism can be described as instantaneous, where nuclei appear all at once early in the process, or sporadic, where the number of nuclei increases linearly with time. As for crystal growth mechanism, it can occur either as rods, disks, or spherulites (*25*). **Table 2** shows the values of *n* for different types of nucleation and crystal growth mechanisms. The half-time of crystallization, $t_{1/2}$, which reflects the magnitudes of the crystallization rate constants, can be obtained as follows:

$$t_{1/2} = \left[\frac{\ln(2)}{k}\right]^{1/n} \quad (3)$$

Statistical Analysis. The data were subjected to analysis of variance (ANOVA) using Minitab 12 statistical software (Minitab Inc., State College, PA). The significance level being tested was α = 0.05. Differences with a significance level of 5% ($P < 0.05$) were considered to be significant.

RESULTS AND DISCUSSION

Acylglycerol Profile and FAC. Table 3 shows the acylglycerol profile and FAC of lard, glycerolyzed lard, and the different acylglycerol (lard-MAG, lard-DAG, and lard-TAG) fractions obtained from SPD. Following enzymatic glycerolysis, glycerolyzed lard had significant increments in MAG (9.1%) and DAG (47.9%) composition, which corresponded with a decrement in TAG (43.0%) composition. One can also see from the acylglycerol profile that SPD is able to purify the different acylglycerol fractions to a purity of at least 90%. In terms of FAC, enzymatic glycerolysis did not result in significant ($P > 0.05$) changes in FAC of lard. In fact, lard, glycerolyzed lard, and the different acylglycerol fractions had very similar FACs with oleic (35.4−37.3%), palmitic (25.6−28.3%), and stearic (15.8%−17.4%) acids as their dominant FAs. Hence, one can assume the changes in melting and crystallization are due to changes in acylglycerol structure rather than FA composition. For the glycerolysis reaction in this work, the central concern was to prepare the products for following studies. There have been a number of approaches developed by the authors (*15, 16, 26*). In certain systems, more than 60% DAG yields could be achieved. Pilot productions have been also evaluated in terms of production stability. More than 50% yields were obtained for more than five batches (*27*). Obviously, in this production protocol, the method was used simply to obtain certain amounts of products without optimization.

Melting and Crystallization Profile. Figure 1A shows DSC melting curves of lard, glycerolyzed lard, and the different acylglycerol fractions obtained from SPD. The melting profile of lard changed considerably following glycerolysis. Lard contained four distinct melting peaks, namely, one in the low-melting fraction (LMF) (peak I), two in the medium-melting fraction (MMF) (peaks II and III), and another one in the high-melting fraction (HMF) (peak IV). Glycerolyzed lard also contained four melting peaks. However, these peaks are wide and less

Table 3. Acylglycerol Profile and FAC of Lard, Glycerolyzed Lard, and the Different Acylglycerol Fractions Obtained from SPD

	lard	glycerolyzed lard	lard-MAG fraction	lard-DAG fraction	lard-TAG fraction
Acylglycerol Profile					
MAG (wt %)	0.0	9.1	91.6	1.5	1.1
1,2 DAG (wt %)	1.1	13.6	2.7	21.2	2.7
1,3 DAG (wt %)	1.0	34.3	5.7	74.6	6.4
TAG (wt %)	97.9	43.0	0.0	2.7	89.8
FAC					
C10:0	0	0	0	0	0
C12:0	0	0	0	0	0
C14:0	1.5	1.4	1.3	1.6	1.3
C16:0	27.3	26.7	26.3	28.3	25.6
C16:1	2.3	2.3	2.1	2.4	2.1
C17:0	0.4	0.4	0.4	0.4	0.4
C18:0	16.6	16.4	17.3	15.8	17.4
C18:1	36.6	37.1	37.1	35.4	37.3
C18:2	9.4	9.5	9.5	9.1	9.5
C18:3	0.7	1.0	0.9	0.7	0.9
C20:0	0.2	0.2	0.2	0.2	0.3
C20:1	0.6	0.6	0.7	0.7	0.8
C20:2	0.4	0.4	0.4	0.3	0.4
C22:1	0.2	0.2	0.1	0.2	0.2
others[a]	3.7	3.7	3.7	5.0	3.7

[a] "Others" refers to other fatty acids such as C8:0 that may be present in the blends but not identified by the FAME standards.

pronounced. Similar observations were found in the DSC crystallization curves in which glycerolyzed lard showed wider and less pronounced crystallization peaks than lard (**Figure 1B**). Wider melting and crystallization peaks in glycerolyzed lard imply the existence of inhibitors to nucleation and crystal growth (*26*), which in the present case may most probably be the partial acylglycerols. Smith et al. (*19*) postulated that most nucleation and crystal growth occur at specific hotspots where there is a highly defected surface structure. As the partial acylglycerols (MAG and DAG) and TAG in glycerolyzed lard had similar chemical compositions and structures, they tend to cocrystallize into partial acylglycerols, incorporating their chains into the growing TAG crystals and leaving their head groups at the defecting surface structure. These blocked or poisoned the specific hotspots and subsequently slowed the velocity of crystal growth. Consequently, glycerolyzed lard may have initiated new nucleation sites and grown from a large number of "types" of nuclei over a wide time span (*19, 26*).

The presence of partial acylglycerols has been shown to affect crystallization behavior of a number of different fats and oils. Rapeseed-DAG, for example, was found to cocrystallize with rapeseed-TAG, resulting in delay in polymorphic transformation from β' to β crystals (*21*). Siew and Ng (*20*) found different palm-DAGs had different effects on crystallization of palm oil, with dipalmitoylglycerol enhancing crystallization, palmitoyloleoylglycerol retarding crystallization, and dioleoylglycerol having no significant effect. Meanwhile, Wright et al. (*23*) found the presence of milk fat-DAG delayed the onset of crystallization at low degrees of supercooling.

Purified acylglycerol fractions had respective distinct melting and crystallization profiles that were different from those of lard and glycerolyzed lard. Of the three purified acylglycerol fractions,
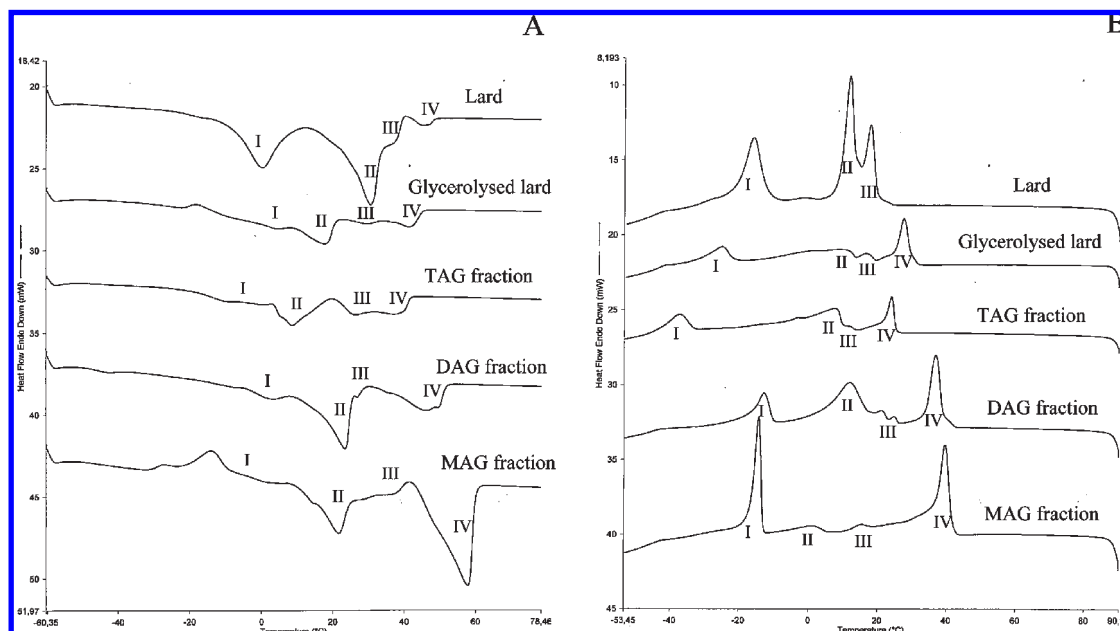
Figure 1. DSC melting curves (**A**) and DSC crystallization curves (**B**) of lard, glycerolyzed lard, and the different acylglycerol fractions obtained from SPD.
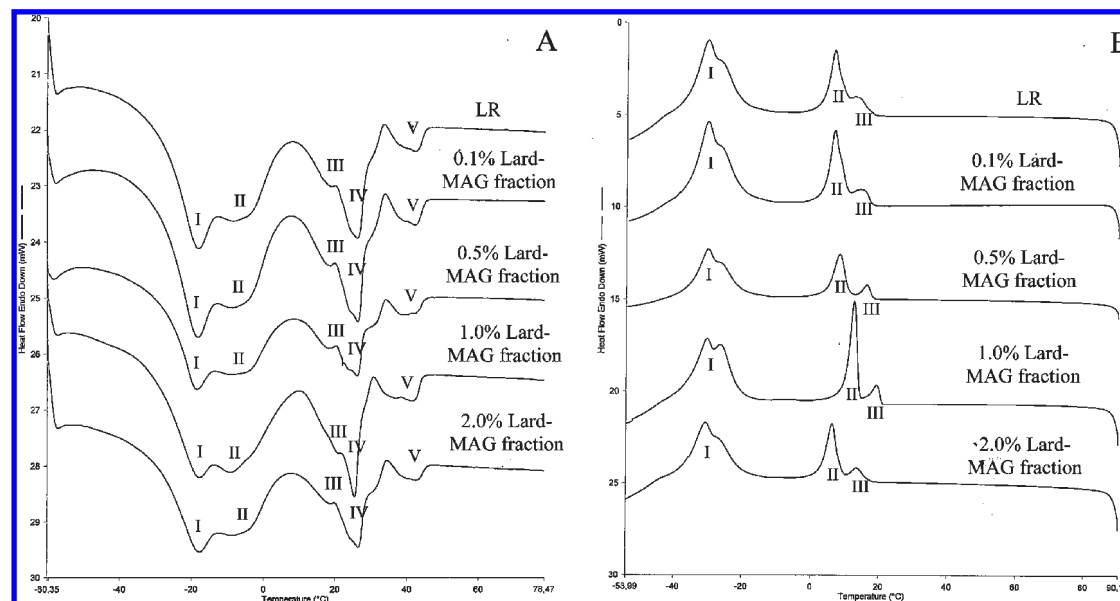

Figure 2. DSC melting curves (**A**) and DSC crystallization curves (**B**) of blends of lard and rapeseed oil (LR) with added lard-MAG fraction.

the lard-MAG fraction had the sharpest crystallization peaks with steepest onset to peaks (**Figure 1B**). This indicates that initial nucleation and subsequent crystallization growth in lard-MAG fraction occurred simultaneously over a short period of time, presumably forming a single molecular compound with large crystal structures in the lard-MAG fraction (*26*). Formation of large crystal structures suggests the lard MAG-fraction may have had the highest melting temperature among the acylglycerol fractions, which was clearly reflected in the DSC melting curves (**Figure 1A**). Similar observations were also found in butterfat-MAG by Yang et al. (*27*).

When added in various concentrations to a blend of lard with rapeseed oil (LR), purified acylglycerol fractions exerted different effects on the melting and crystallization profiles. **Figure 2** shows LR contained five melting peaks, namely two in the LMF (peaks I and II), two in the MMF (peaks III and IV), and another one in the HMF (peak V). Addition of a low concentration of lard-MAG (0.1−2%) to LR had little if any effects on melting

(**Figure 2A**) and crystallization (**Figure 2B**) profiles of LR. Nevertheless, it is worth noting that with the addition of greater than 1% of lard-MAG, there was insignificant (*P* > 0.05) delay in the onset of crystallization peak temperatures. This indicates that lard-MAG may have a slight inhibitory effect on the crystallization of LR, but this effect was not statistically significant.

Although not shown in DSC crystallization curves (**Figure 3B**), one can see from the DSC melting curves (**Figure 3A**) that lard-DAG had different effects on the crystallization of LR depending on the concentration. With the addition of low concentrations of 5−10% of lard-DAG, LR exhibited broad melting peaks and disappearance of peaks in LMF and MMF. This indicates that the presence of low concentrations of lard-DAG inhibits nucleation and crystal growth in LR. Meanwhile, addition of 20−50% of lard-DAG was found to promote nucleation and crystal growth in LR. Sharper and new melting peaks can be observed in melting curves of LR with 20−50% of added lard-DAG. Instead of inhibiting crystallization by blocking the specific
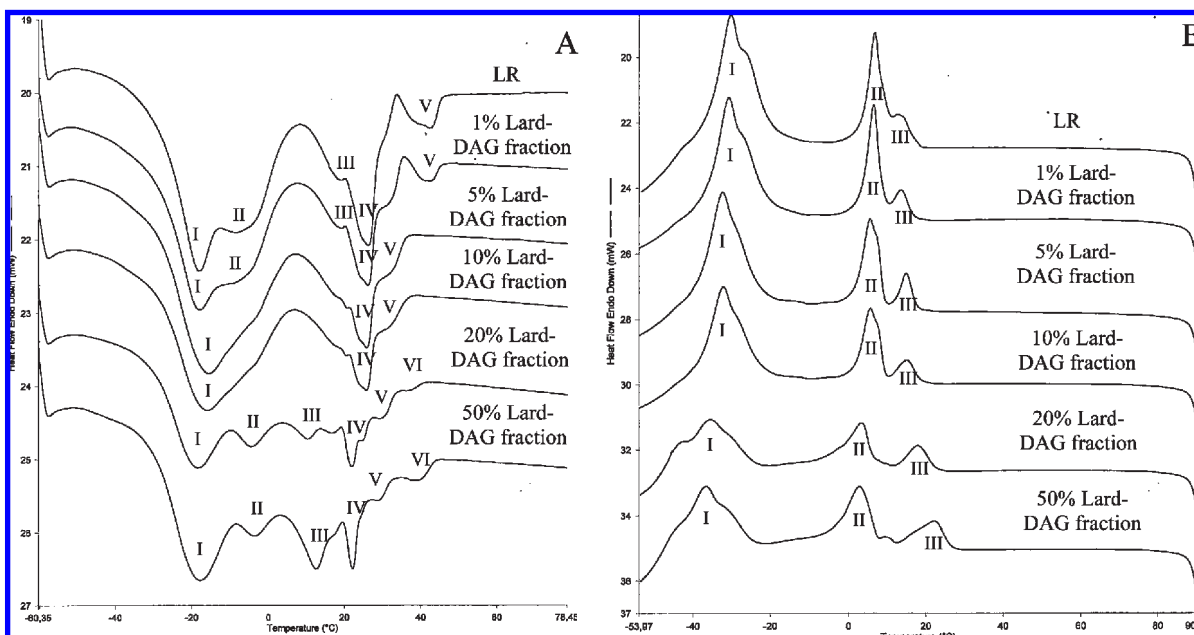
Figure 3. DSC melting curves (**A**) and DSC crystallization curves (**B**) of blends of lard and rapeseed oil (LR) with added lard-DAG fraction.

hotspots on TAG crystals for nucleation and crystal growth, high concentrations of lard-DAG may have promoted crystallization through initiation of new nucleation sites and crystal growth among the DAG molecules.

The different effects exerted by the addition of lard-MAG and DAG on the melting and crystallization profile of LR may due to differences in their molecular structures. MAG had smaller molecules and are less similar to TAG as compared to DAG. Hence, they are expected to bind less strongly and for shorter residence time to TAG crystals as compared to DAG. Nevertheless, once bound on TAG crystals, MAG are expected to block or poison the specific hotspot more effectively than DAG due to the greater difference in MAG structure as compared to TAG (*19*). Therefore, it is impossible to draw unambiguous conclusions about the abilities of partial acylglycerols to affect the melting and crystallization properties of TAG. In the present case, it seems the longer residence time of DAG outweighed the stronger blocking ability of MAG in affecting melting and crystallization properties of TAG.

Solid Fat Content (SFC) Profile. SFC as a function of temperature profiles for lard, glycerolyzed lard, and partial acylglycerols fractions are shown in **Figure 4A**. SFC profiles for lard changed considerably following enzymatic glycerolysis. The presence of partial acylglycerols in glycerolyzed lard significantly ($P < 0.05$) reduced its SFC at temperatures below 35 °C. Partial acylglycerols have changed the crystallization thermodynamics by acting as inhibitors to crystallization which delay the velocity of crystal growth, hence reducing the SFC. This is also reflected earlier in the wider and less pronounced DSC melting curves of glycerolyzed lard (**Figure 1A**). Purified partial acylglycerols, particularly the lard-MAG fraction, also had altered crystallization thermodynamics. The lard-MAG fraction had significantly ($P < 0.05$) higher SFC at all temperatures below 40 °C. This result is in agreement with the melting and crystallization profiles of the lard-MAG fraction, which suggests lard-MAG had a large crystal structure from simultaneous nucleation and crystal growth over a short time span. Meanwhile, lard-DAG and -TAG fractions showed smaller but significant ($P < 0.05$) SFC increment and decrement, respectively.

The purified lard-MAG fraction may have higher crystal growth velocity as suggested by SFC and melting and crystal-

lization profiles; however, it did not change the crystal growth velocity of LR when added in various concentrations to LR. Addition of 0.1−2% of lard-MAG had no significant ($P > 0.05$) effect on SFC of LR (**Figure 4B**). Purified lard-DAG, on the other hand, had different effects on SFC of LR depending on their concentration (**Figure 4C**). Addition of low concentrations of 5−10% of lard-DAG suppressed the SFC of LR. Although the SFC suppression is not statistically significant ($P > 0.05$), it agreed with the DSC melting curves that the resence of a small amount of lard-DAG delayed crystal growth velocity. At a concentration of 20−50% of lard-DAG, SFC of LR increased significantly ($P < 0.05$).

Crystallization Kinetics. Unlike lard-MAG, the presence of lard-DAG in LR had significant ($P < 0.05$) effects on SFC and the melting and crystallization profiles of LR. As the effects varied with lard-DAG concentration, LR with low (1%) and high concentrations (50%) of added lard-DAG were studied in terms of crystallization kinetics at different degrees of supercooling. **Figure 5** shows SFC as a function of time during static crystallization at 5.0, 10.0, 20.0, and 25.0 °C. At high degrees of supercooling (5 and 10 °C), the presence of low concentrations of lard-DAG had no significant ($P > 0.05$) effects on SFC of LR. Both LR and LR with 1% of added lard-DAG displayed identical crystallization kinetics and reached the same final SFC. Nevertheless, when subjected to higher crystallization temperatures of 20 and 25 °C, effects of low concentrations of lard-DAG became more apparent, with the crystallization curves becoming more sigmoidal. Although the presence of low concentrations of lard-DAG at low degrees of supercooling had an inhibitory effect on crystallization, the final amounts of SFC attained are similar. The inhibitory effects altered only the crystallization kinetics as there was no significant ($P > 0.05$) difference in terms of induction time for crystallization at 25 °C (**Table 4**). This is contrary to findings by Wright et al. (*23*), who found that the presence of minor components such as DAG delayed onset of crystallization at low degrees of supercooling.

Addition of high concentrations of lard-DAG, on the other hand, resulted in LR starting to crystallize earlier and having higher final SFC regardless of the degree of supercooling. In fact, a high concentration of lard-DAG was found to enhance crystallization by having low induction time (**Table 4**) even at static
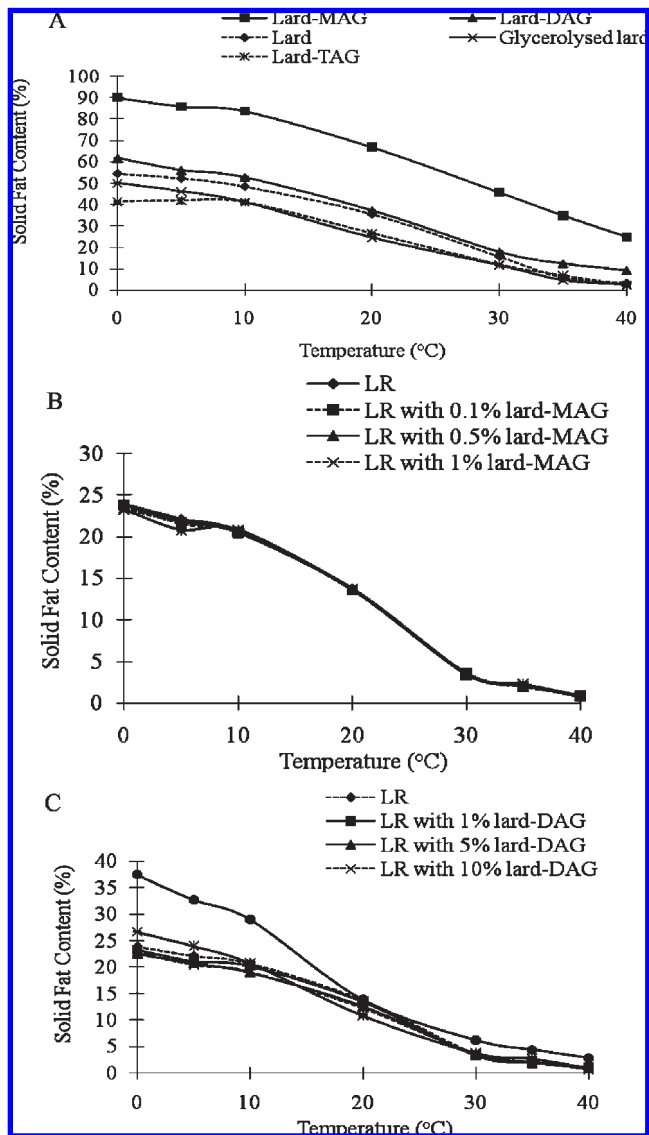
Figure 4. Solid fat content (%) as a function of temperature (°C) for lard, glycerolyzed lard and partial acylglycerol fractions (lard-MAG fraction, lard-DAG fraction, lard-TAG fraction) (**A**), for blends of lard and rapeseed oil (LR) with added lard-MAG fraction (0.1% lard-MAG, 0.5% lard-MAG, 1.0% lard-MAG, 2.0% lard-MAG) (**B**), and for blends of lard and rapeseed oil (LR) with added lard-DAG fraction (1% lard-DAG, 5% lard-DAG, 10% lard-DAG, 20% lard-DAG, 50% lard-DAG) (**C**).

crystallization of 25 °C. This corresponded well with earlier findings that a high concentration of added lard-DAG promoted crystallization by initiating more nucleation sites but also elevating crystal growth.

As high degrees of supercooling had no apparent effects on the crystallization kinetics of LR with added lard-DAG, quantification of crystallization kinetics was only done for low degrees of supercooling at a temperature of 25 °C. Data from SFC as a function of time for LR and LR with 1 and 50% added lard-DAG at 25 °C were very well fitted into the Avrami equation, which yielded straight lines with high correlation coefficients, R^2, of 0.999. **Table 5** shows the Avrami constants (k), half-time of crystallization ($t_{1/2}$), Avrami exponents (n), and R^2 of LR and LR with added lard-DAG. In coherence with previously elucidated findings, the presence of low concentrations of lard-DAG blocked the specific nucleation hotspots and delayed crystallization kinetics of LR at low degrees of supercooling. ANOVA showed LR with 1% added lard-DAG had significantly
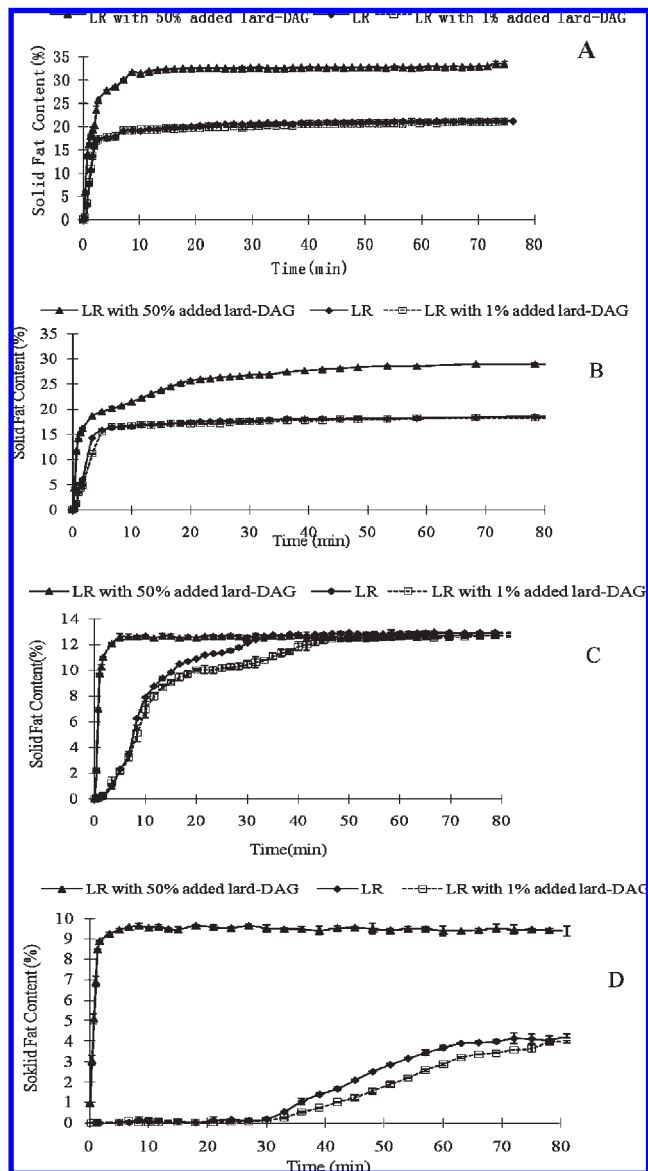

Figure 5. Solid fat content as a function of time (min) for LR, LR with 1.0% of added lard-DAG, and LR with 50.0% of added lard-DAG during static crystallization at 5.0°C (**A**), 10.0°C (**B**), 20.0°C (**C**), and 25.0 °C (**D**).

Table 4. Induction Time for Crystallization in Blends of Lard and Rapeseed with Added Lard-DAG

temperature (°C)	induction time[a] (min)		
	LR	LR with 1% added lard-DAG	LR with 50% added lard-DAG
5.0	0.00 ± 0.00 a	0.00 ± 0.00 a	0.00 ± 0.00 a
10.0	0.00 ± 0.00 a	0.00 ± 0.00 a	0.00 ± 0.00 a
20.0	1.67 ± 0.00 a	1.17 ± 0.70 a	0.00 ± 0.00 a
25.0	31.50 ± 2.12 b	31.50 ± 2.12 b	0.00 ± 0.00 a

[a] Mean value of two replicates ± standard deviation of the mean. Different letters (a, b) indicate significant differences ($P < 0.05$).

($P < 0.05$) lower k and higher $t_{1/2}$ as compared to LR. The presence of high concentrations of lard-DAG, on the other hand, enhanced crystallization with significantly ($P < 0.05$) higher k and lower $t_{1/2}$.

Both LR and LR with 1% added lard-DAG had no significant ($P > 0.05$) difference in n. Although the presence of a low concentration of lard-DAG was found to delay the crystallization

Table 5. Avrami Constants, *k*, Half-Times of Crystallization, $t_{1/2}$, Avrami Exponents, *n*, and Correlation Coefficients, R^2, of LR and LR with Added Lard-DAG[a]

	k (t^{-k})	$t_{1/2}$ (min)	n	R^2
LR	$(3.54 \pm 0.20) \times 10^{-7}$ a	45.52 ± 0.20 d	3.79 ± 0.01 g	0.999 j
LR (1% added lard-DAG)	$(5.04 \pm 0.25) \times 10^{-8}$ b	53.41 ± 0.69 e	4.13 ± 0.01 g	0.999 j
LR (50% added lard-DAG)	$(7.30 \pm 0.50) \times 10^{-1}$ c	0.97 ± 0.20 f	1.80 ± 0.00 i	0.999 j

[a] Mean value of two replicates $\pm$ standard deviation of the mean. Different letters indicate significant differences ($P < 0.05$).

kinetics of LR, both LR and LR with 1% of added lard-DAG crystallized in similar manners. This is not surprising as lard-DAG had probably cocrystallized with lard-TAG, forming a single crystal form. A high concentration of 50% of added lard-DAG resulted in significantly smaller *n*, which indicates different modes of crystal growth. It is possible that instead of cocrystallizing with lard-TAG, lard-DAG may have crystallized among them, leading to the formation of different crystal growth modes and polymorphism.

In conclusion, partial acylglycerols were found to have different abilities in affecting the melting and crystallization properties of TAG. In comparison to lard-MAG, lard-DAG, which had higher similarity in terms of acylglycerol structure to LR, was found to significantly ($P < 0.05$) affect crystallization kinetics and modes of crystal growth in LR. Although low concentrations of lard-DAG did not change the modes of crystal growth in LR, it significantly delayed nucleation and crystal growth velocity of LR. High concentrations of lard-DAG, on the other hand, not only promoted nucleation but also changed the modes of crystal growth in LR. With regard to the potential applications of partial lard acylglycerols in the meat industry, the meaning of the above characteristics is not yet fully known. Applications of such lard partial acylglycerols in meat products are under way. The correlations between the characteristics and the meat product quality will greatly spur potential applications in industry.

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