Photopyroelectric Determination of Thermophysical Parameters and Detection of Phase Transitions in Fatty Acids and Triglycerides. Part II: Temperature Dependence of Thermophysical Parameters

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ABSTRACT: The photopyroelectric (PPE) technique was used to detect solid-to-liquid phase transitions in saturated [C6:0, C10:0, C12:0, C16:0 palmitic acid (P), C18:0 stearic acid (S)] and unsaturated (C18:2) fatty acids and some triglycerides (PSP, PPS). By using the standard PPE configuration with a thermally thin and optically opaque sample and a thermally thick sensor (a1.1); the temperature behavior of the volume-specific heat in a temperature range that includes the melting points for C10:0, C12:0, C16:0, and C18:0 was obtained. When the standard PPE configuration, with sample and sensor both being thermally thick and the sample being optically opaque (a1.2), was used, the information contained in the phase of the PPE signal allowed direct measurement of the thermal diffusivity for C10:0, C12:0, and PSP. The inverse configuration with a thermally thick sample and thermally thin sensor (b1.2) or a semitransparent thermally thick sensor (b2) was used to obtain critical behavior of the thermal effusivity for C10:0 and C12:0, respectively. Critical behavior of the thermal conductivity for same samples was computed from information obtained from amplitude and phase measurements (a1.2), or by combining a1.1 and b1.2 data. The history (age, storage conditions, annealing) of the samples affects the critical behavior of thermal parameters. *JAOCS 72*, 281–287 (1995).

KEY WORDS: Fatty acids, melting points, phase transitions, photopyroelectric spectroscopy, thermophysical parameters, triglycerides.

Thermophysical properties of fats and edible oils are the subject of intensive research efforts carried out both in industry and academic institutions. Once known and understood, such properties may be used to benefit industrial manufacturers by improving specific applications in food products and production processes as well as the stability and shelf life of the products. Due to their composition and intrinsic inhomogeneity, food samples are generally difficult to analyze thermally. As already mentioned in Part I of this paper (1), the methods most frequently used in practice are differential scanning calorimetry, thermogravimetry, and thermomechanical analysis. In addition, steady-state and transient methods were developed and adopted to measure the static (specific heat) and dynamic (thermal diffusivity, thermal conductivity, and thermal effusivity) thermophysical parameters.

Despite advances (test methods and analytical procedures have been introduced) made in the technology of oils and fats and science of nutrition that have led to a need for much greater awareness of composition and structure of dietary lipids, there still is a lack of data on thermophysical properties of products.

The photopyroelectric (PPE) technique (a pyroelectric sensor measures the temperature variation of a sample exposed to modulated radiation), introduced in Part I (1) as a novel candidate method for detection of phase transitions, is fast, sensitive, reproducible, and nondestructive; the result of a PPE measurement (i.e., PPE voltage) is related to the thermophysical parameters of the sample.

In this paper, the feasibility of the PPE method for determining the temperature dependence of the thermophysical parameters of saturated and unsaturated fatty acids and triglycerides is demonstrated. Samples were provided by Unilever Research Laboratory (Vlaardingen, The Netherlands). The saturated fatty acids contain more than 90% of the designated component; the purity of linoleic acid and the triglyceride samples exceeded 98%.

CALIBRATION PROCEDURES

In Part I of this paper, we have shown that the critical behavior of thermal parameters of some lipid samples can be studied by using various PPE configurations, provided that (i) requirements imposed by these special experimental conditions

are fulfilled, and (ii) an appropriate calibration for each configuration was performed.

The PPE technique is capable of measuring the absolute value of thermal diffusivity (Part I, Eq. 9). Concerning the remaining thermophysical parameters, literature values for the volume-specific heat can be used. Whenever possible, the use of substances (water, for example) with well-known thermal parameters is recommended for calibration purposes. Likewise, it is suggested that a range of operating temperatures is selected far from the critical points (preferably where the temperature dependence of a specific thermal parameter is not pronounced).

Configuration a1.1. In this configuration, values of volume-specific heat at room temperature (2) were used for calibration. Due to the fact that the thickness of the sample is not precisely known, it is necessary to check (experimentally) the invariability of the phase (Part I, Eq. 5) to make sure that the criterion for a thermally thin regime is satisfied. A plot of the amplitude of the PPE signal vs. one of its components is displayed for two (0.2 and 8 Hz) chopping frequencies in Figure 1. Figure 2 contains the experimental results obtained with C16:0. As expected from the theory, the sample is thermally thin at 0.2 Hz, while at 8 Hz it is considered to be in the intermediate region (i.e., close to the critical frequency). Consequently, the 0.2 Hz frequency was used in this configuration.

Configuration a1.2. As mentioned above, an absolute calibration can be achieved here when working with a calibrated cell (Part I, Eqs. 7 and 9). To select the proper modulation, a frequency scan was made. The amplitude and phase of the PPE signal for three samples [C10:0, C12:0, PSP (P = palmitic acid, S = stearic acid)] are shown in Figures 3 and 4. The frequency scan was performed for the samples in a solid [C12:0, 1,3 dipalmitoyl-2 stearoyl-glycerol (PSP)] and liquid (C10:0) state. Figures 3 and 4 exhibit similar results (same
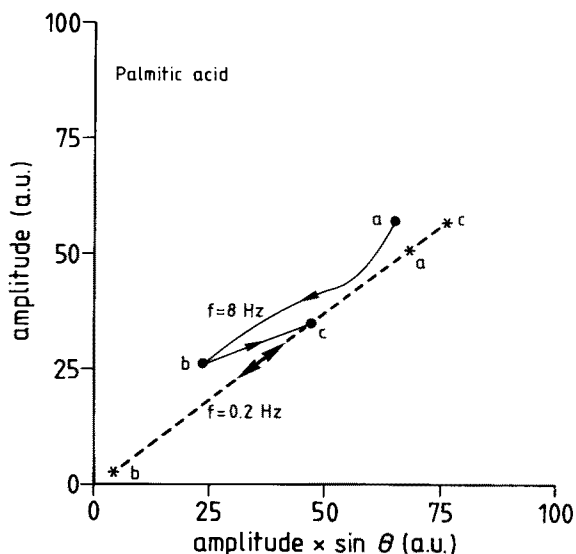

FIG. 2. The amplitude of photopyroelectric (PPE) signal as a function of temperature in the vicinity of the melting point for palmitic (C16:0) acid at two chopping frequencies. The meaning of a, b, and c is the same as specified in Figure 1.

slopes) obtained from phase and amplitude data. As indicated in Equations 7 and 8 of Part I, these slopes are $-(\pi/\alpha_s)^{1/2} L_s$. For chopping frequencies exceeding 25 Hz, all investigated samples are thermally thick, and consequently, 78 Hz was considered as suitable for this experiment.

FIG. 1. Amplitude of photopyroelectric signal plotted vs. the quadrature (amplitude × sin ϕ) component of the lock-in amplifier for palmitic (C16:0) acid. Letters a, b, and c refer to the initial, critical, and final points of the measurements.
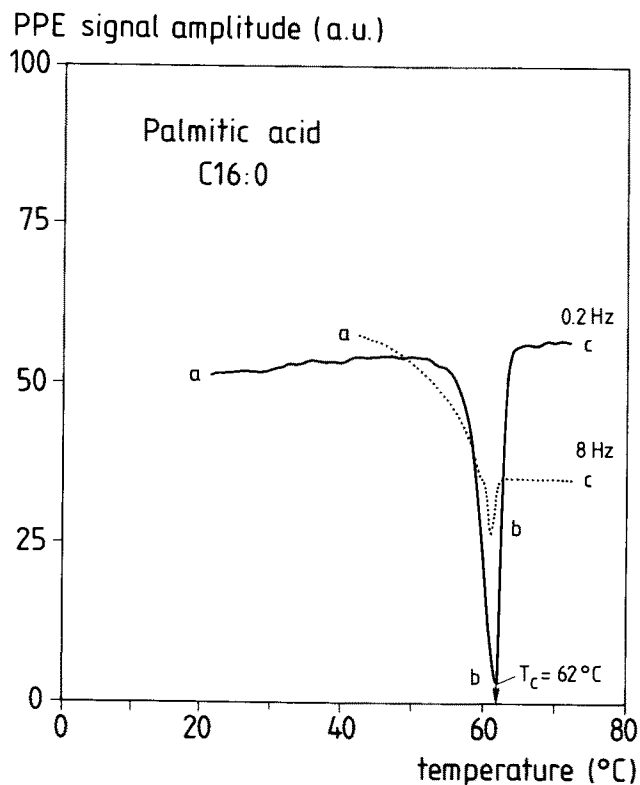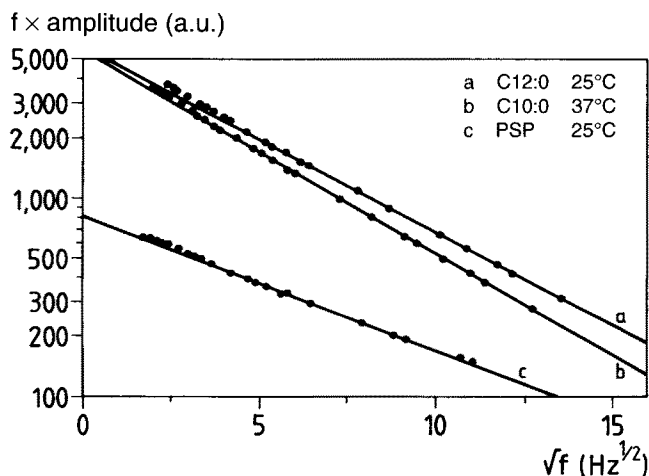

FIG. 3. Frequency scan for amplitude of the photopyroelectric signal obtained for C10:0, C12:0, and 1,3 dipalmitoyl-2 stearoyl-glycerol (PSP) samples. The product of amplitude and frequency plotted vs. square root of frequency must be linear in a thermally thick regime (for the sample).
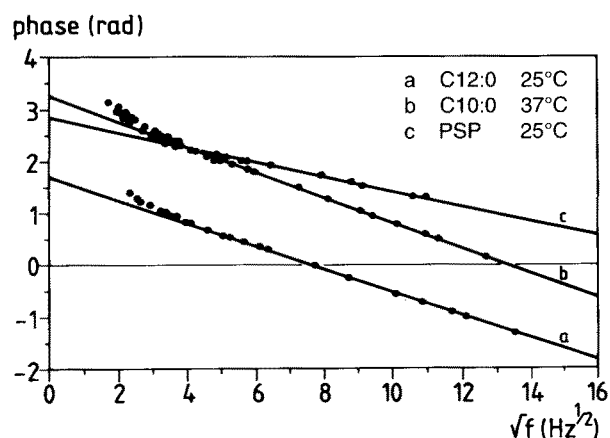
phase (rad)

a	C12:0	25°C
b	C10:0	37°C
c	PSP	25°C

$\sqrt{f}$ (Hz$^{1/2}$)

FIG. 4. Same as Figure 3 but for the phase of the photopyroelectric signal.

volume specific (10^6 • J/Km^3)

temperature (°C)

FIG. 5. The critical behavior of volume-specific heat for some saturated fatty acids with even number of carbon atoms. The calibration values were taken from Reference 2.

Configuration b1.2. In this configuration, the calculated critical frequencies for sensor and sample [thermal effusivity of about 500Ws$^{1/2}$/m^2 K is typical for fatty acid (unpublished data, Dadarlat, D., H. Visser and D. Bicanic)] are 200 and 0.01 Hz, respectively. The frequency of 0.1 Hz was used consistently throughout this experiment to satisfy Equation 12. The ratio $b_{sp}/a_p L_p$ is 46 at 0.1 Hz, and the simplified form of Equation 12 applies with an accuracy of *ca.* 2% (unpublished data, Dadarlat, D., H. Visser and D. Bicanic). Pure water with a thermal effusivity of 1580 Ws$^{1/2}$/m^2 K at room temperature (3,4) was used to calibrate the measurement.

Configuration b2. To calibrate this configuration, a value of effusivity at some temperature far from the melting point is required. Consequently, this configuration depends in a certain way on the results obtained in former configurations. The calibration value can be obtained by performing either an experiment of type b1.2 (at room temperature) or by combining a1.1 and a1.2 data. As already demonstrated, at 78 Hz the restrictions imposed by this configuration are fulfilled.

RESULTS

Volume-specific heat. The temperature dependence of the volume-specific heat for some even saturated fatty acids is displayed in Figure 5 for the temperature range that encompasses their melting points. Sharp positive peaks are observed in the critical region; outside this region the volume-specific heat depends only slightly on the temperature, which is in agreement with the literature data (2). The phase diagram shows good agreement with previously reported values (2) as well.

With configuration a1.1, the solid-to-liquid phase transitions in triglyceride samples PPS (1,2 dipalmitoyl-3-stearoyl-glycerol) and PSP were detected; results are presented in Figures 6 and 7. Surprising is the presence of two anomalies for the PPS specimen. The anomaly observed at the higher temperature appears susceptible to the thermal treatment of the sample. Repeated heating cycles (up to 75°C) led to a gradual decrease of the anomaly's amplitude, and after three cycles the anomaly vanished completely. The occurrence of two
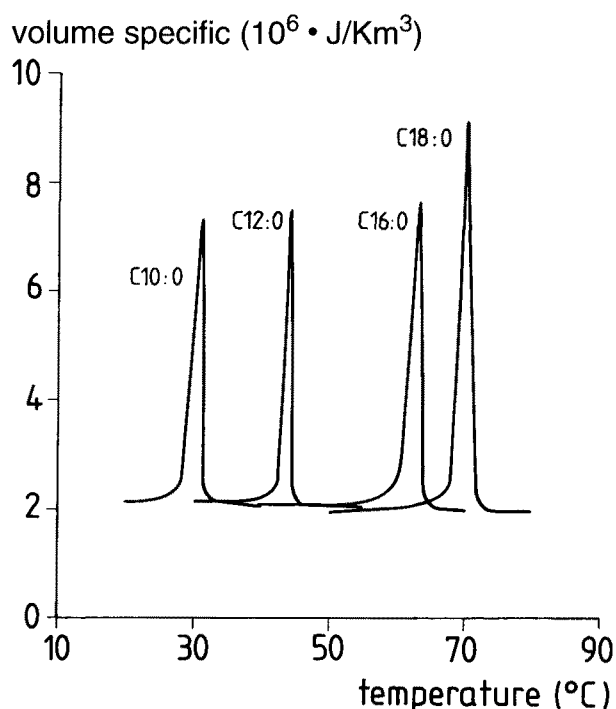
anomalies observed in the PPS sample can be explained in terms of molecular asymmetry. During the process of crystallization, the molecules can associate in two different ways (PPS–PPS and PPS–SPP), thereby giving rise to two crys-
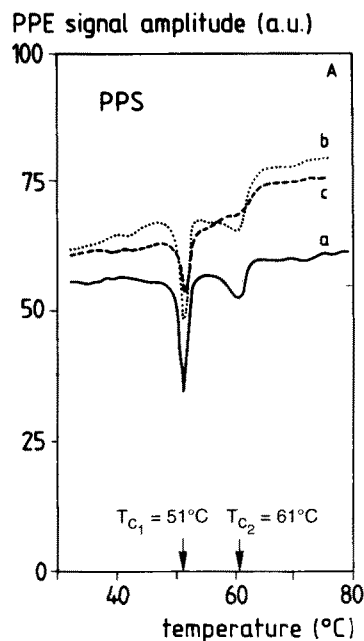

PPE signal amplitude (a.u.)

$T_{c_1} = 51°C$ $T_{c_2} = 61°C$

temperature (°C)

FIG. 6. Amplitude of photopyroelectric (PPE) signal as a function of temperature for 1,2 dipalmitoyl-3 stearoyl–glycerol (PPS) in a temperature range that includes two critical points. Letters a, b, and c indicate the first, second, and third temperature cycle, respectively.
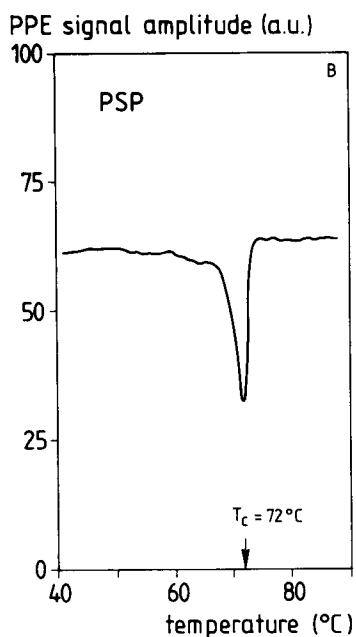
FIG. 7. The amplitude of PPE signal vs. temperature for PSP near the melting point. See Figures 3 and 6 for abbreviations.
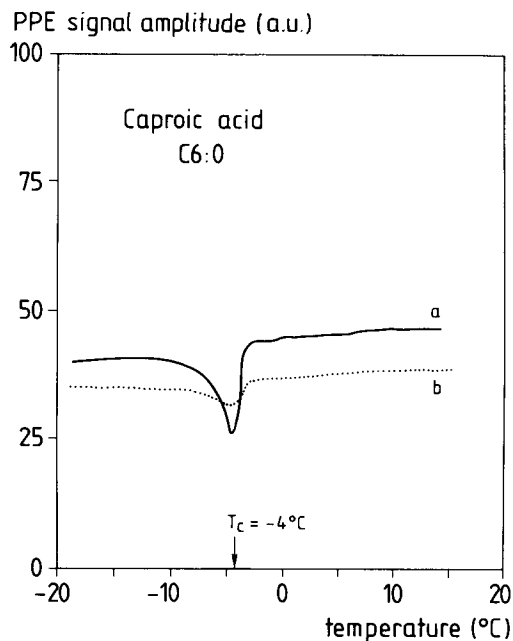

FIG. 8. Critical behavior of the amplitude of the PPE signal for caproic acid: one-year-old sample kept in refrigerator (a) and one-year-old sample stored at room temperature (b). See Figure 6 for abbreviation.

talline phases that are initially detected. Repeated recrystallizations suggest a preference of the sample for one of the two phases, which eventually becomes the only crystalline phase of the material.

Similar measurements (same configuration but with the cold finger) were performed on C6:0 and C18:2 specimens that had various histories and were stored under different conditions; the results are presented in Figures 8 and 9. It appears that a sample's history influences the critical behavior of specific heat: For samples that were either old or stored at elevated temperatures, the critical anomaly is smeared out (C6:0) or disappears completely (C18:2). At the same time, the unsaturated fatty acids appear less stable than the saturated ones.

Thermal diffusivity. High-resolution measurements in the a1.2 configuration have been performed for C10:0, C12:0, and PSP; plots showing the temperature dependence of the phase of the PPE signals are presented in Figures 10, 11, and 12. The sign of the phase can be positive or negative, depending on the thermal and geometrical properties of the sample but also on the initial phase of the lock-in amplifier, which is adjustable. For the purpose of phase transition investigations, only the relative critical variation is important. The corresponding behavior of thermal diffusivity α is displayed in Figures 13, 14 and 15. A discontinuity was observed in the critical region for the investigated samples. Due to a rigorously controlled temperature variation rate, slow heating–cooling cycles were possible. A hysteresis, characteristic for a first-order phase transition and associated with the latent heat, was observed for all samples. For C10:0 and C12:0, the hysteresis loop is not closed, a fact that suggests poor stability of the selected samples to heating–cooling cycles. Oxida-

tion processes and/or other chemical reactions (that might contaminate the sample) probably occur during these cycles.

Thermal effusivity. By using the b1.2 (with C12:0) and b2 (with C10:0) configurations, the temperature dependence of thermal effusivity near the melting point was recorded (Figs. 16 and 17). When heating, a sharp peak was observed in the critical region (C12:0). High-resolution measurements performed with C10:0 indicate the presence of a small positive
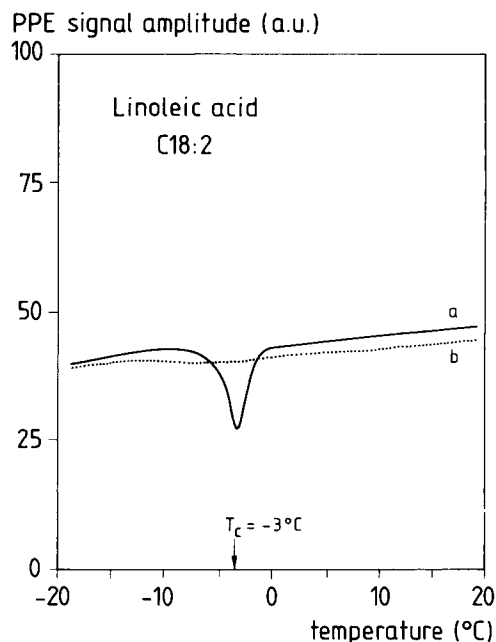

FIG. 9. Same as Figure 8 but for linoleic acid: one-year-(a) and eight-year-(b) old specimens stored in refrigerator.
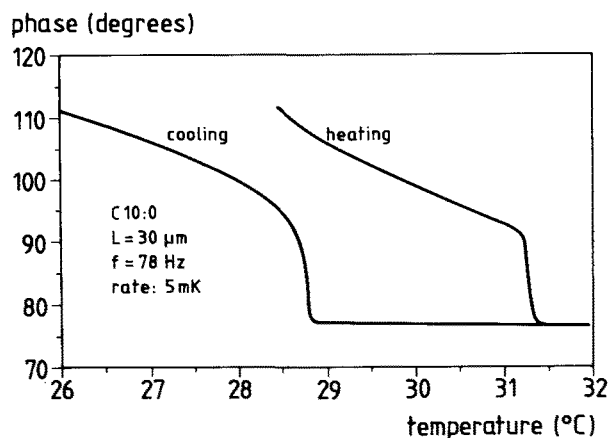
FIG. 10. The temperature behavior of the phase of the photopyroelectric signal (for C10:0) in the vicinity of the melting point.
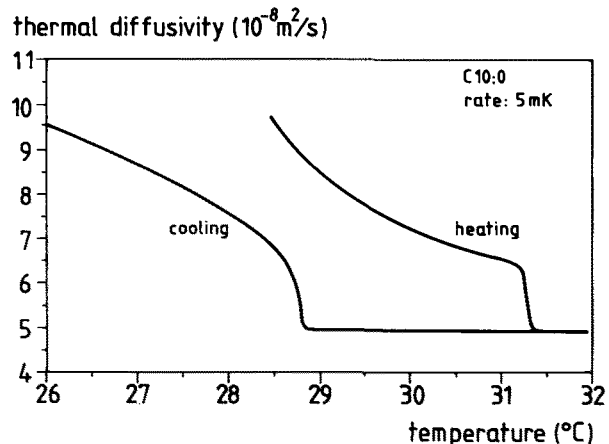

FIG. 13. The critical behavior of thermal diffusivity for C10:0.
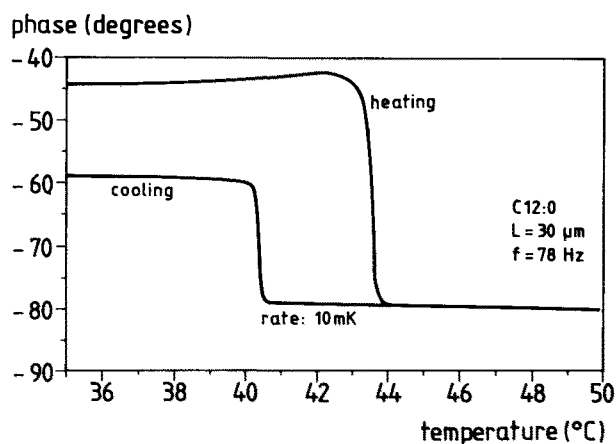

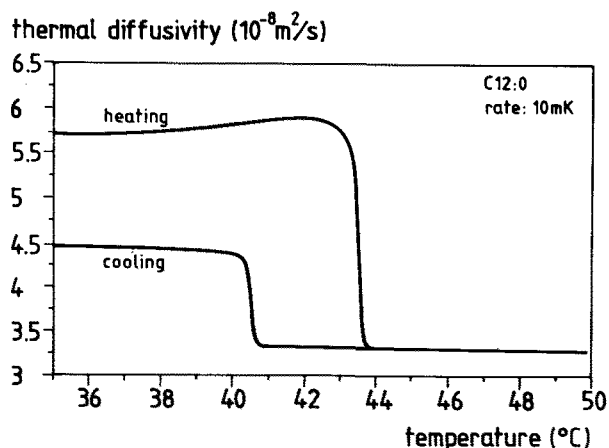FIG. 11. Same as Figure 10 but for C12:0.
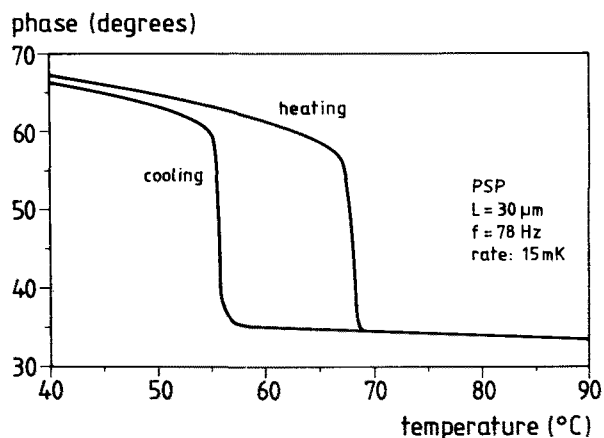

FIG. 14. Same as Figure 13 but for C12:0.

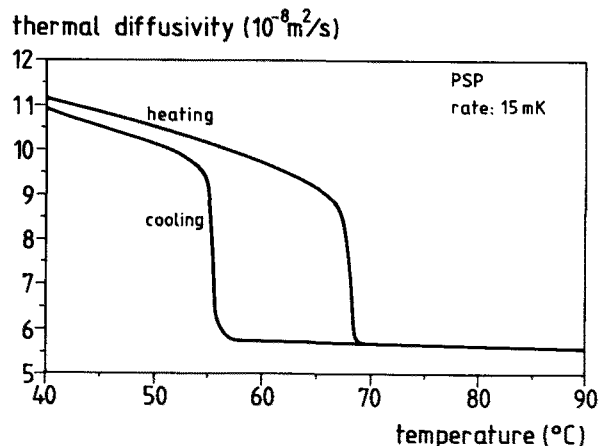FIG. 12. Same as Figure 10 but for PSP. See Figure 3 for abbreviation.

FIG. 15. Same as Figure 13 but for PSP. See Figure 3 for abbreviation.

peak in the plot of the thermal effusivity when heating and only discontinuity when cooling. A hysteresis similar to that observed for other thermal parameters during the heating–cooling process was present here as well. To test the ef-

fects of age on the thermal properties of fatty acids, the same sample (C12:0) was measured in the b2 configuration after being kept in a closed flask for about six months at room temperature. The results shown in Figure 18 suggest the presence
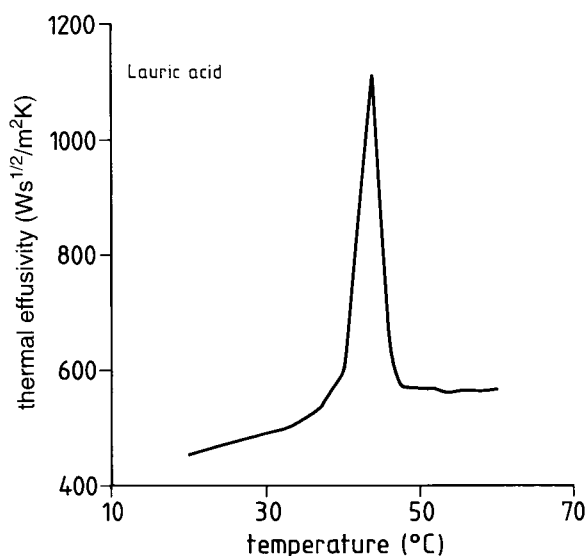
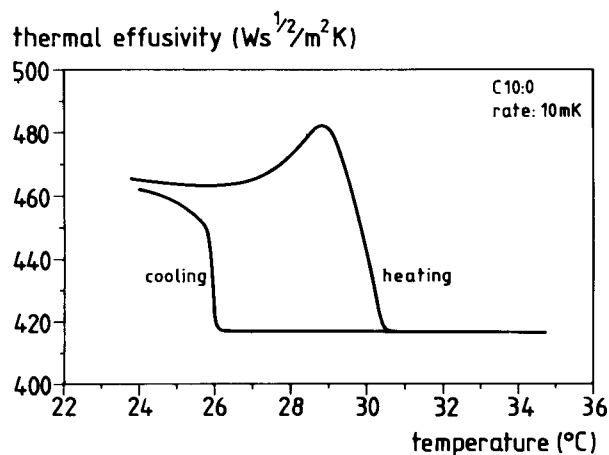FIG. 16. The critical behavior of thermal effusivity for C12:0.

FIG. 18. The critical behavior of thermal effusivity for C12:0, maintained at room temperature for six months.

FIG. 17. Same as Figure 16 but for C10:0.

FIG. 19. The critical behavior of thermal conductivity of C12:0, calculated with experimental data obtained in a1.1 and b1.2 configurations.

of a smaller critical anomaly for thermal effusivity, as observed before for the specific heat of C6:0 and C18:2.

Thermal conductivity. Thermal conductivity is the only thermal parameter of lipids that cannot be measured directly by the PPE technique. It can, however, be derived from well-known relationships between thermal parameters (Part I, Eq. 2) and by combining experimental data of two abovementioned special configurations. Figure 19 shows such an example, namely, the temperature dependence of thermal conductivity for C12:0 as obtained by combining a1.1 and b1.2 configurations. Alternatively, one can use the information contained in the amplitude and phase of the PPE signal (a1.2); an example (for C10:0) is displayed in Figure 20. As shown in Figures 19 and 20, the thermal conductivity of the fatty acid features a positive "jump" in the critical region; for C10:0 this is associated with an additional small dip.

The temperature dependence of static (volume-specific heat) and dynamic (thermal diffusivity, thermal effusivity, and thermal conductivity) thermophysical parameters of several
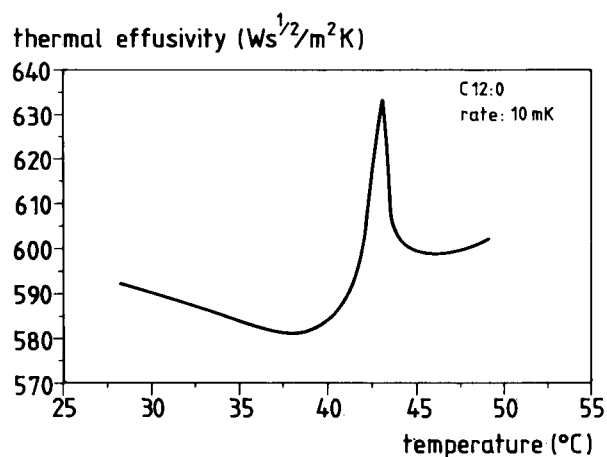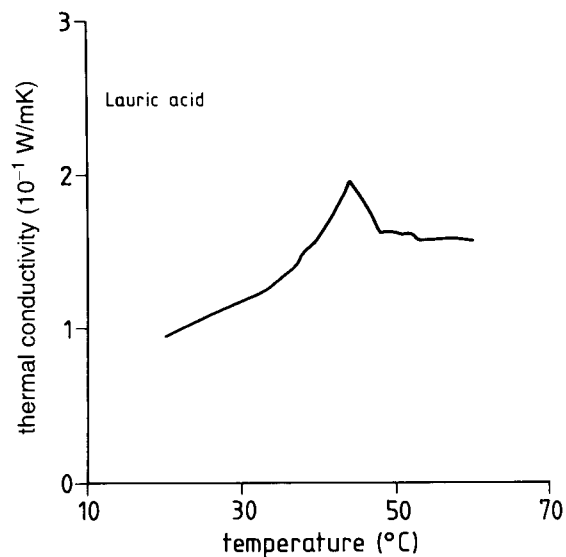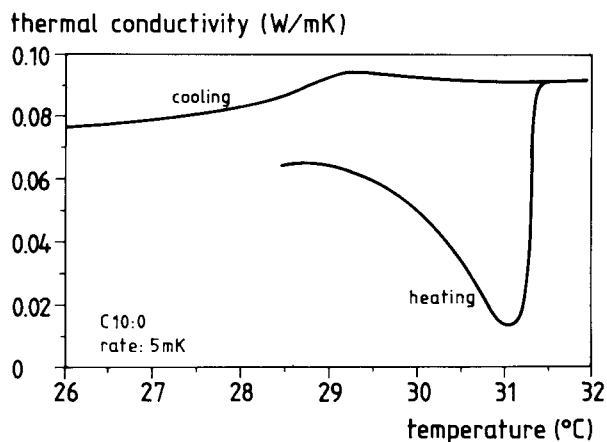

FIG. 20. The critical behavior of thermal conductivity for C10:0, calculated with data contained in amplitude of the photopyroelectric signal (a1.2).

even fatty acids and triglycerides has been measured for the first time by the PPE method. The temperature range included the critical region of solid-to-liquid phase transition. All thermal parameters exhibited sharp anomalies in the critical region; these are characteristic for first-order phase transitions. Investigated samples were shown susceptible to heating–cooling cycles and sensitive to storage conditions. The magnitude and the "width" of the anomaly in a critical region for various thermal parameters seem to be related to the purity and age of the samples. A hysteresis was observed whenever high-resolution heating–cooling cycles were performed at a low temperature variation rate. The phase transition was apparently always sharper during cooling; this is probably due to a supercooled liquid to solid phase transition. Unfortunately, due to a general lack of experimental data on the critical behavior of the thermophysical parameters of lipids, it is not possible to make direct comparisons of our results. However, quantitative literature data (2) (especially for specific heat and outside the critical region) agree well with our results. Values of critical temperatures obtained by the PPE method are also in good agreement with previously reported values.

We have also initiated a photoacoustic study of phase transitions in some odd and higher (number of C atoms in the chain above 18) even fatty acids. Likewise, direct measurements of thermal conductivity of liquid fatty acids by a novel method, based on analysis of the temporal profile of the thermal lens signal induced in the sample, are currently in progress.

ACKNOWLEDGMENTS

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