Aging of Tristearin: Comparison of DSC and Positron Lifetime Results

William W. Walker
Department of Physics and Astronomy, The University of Alabama, Tuscaloosa, AL 35487

Physical aging of tristearin that has been solidified from the melt has been investigated by two techniques: differential scanning calorimetry and positron lifetime measurements. In particular, the α- to β-phase transformation was studied as a function of the annealing temperature.

Triglycerides are known to exist in three major polymorphic forms: α, β' and β. These correspond to hexagonal, orthorhombic and triclinic lattices with melting points of 55, 63 and 73 C, respectively. Of these three, only the β form is stable. When the α phase is produced, it gradually transforms to the stable β phase. The process is referred to as aging. The rate of aging is a function of the temperature at which the α form is maintained, i.e., the annealing temperature.

Few investigations of the kinetics of phase transformations of triglycerides have been reported. The most comprehensive of these has been the work of Whittam and Rosano (1), who used differential thermal analysis, X-ray, nuclear magnetic resonance, infrared and visual techniques. Dafler (2) has also reported on the effects of annealing on the phase transformations of tristearin.

This paper reports on the use of positron lifetime measurements to study the effect of annealing temperature on the α-to-β transformation rate in tristearin. The positron data have been correlated with results obtained by differential scanning calorimetry (DSC).

A positron injected into an organic material can annihilate while free or can capture an electron to form positronium (Ps) in either the singlet (p-Ps) or the triplet (o-Ps) state. The lifetime of the o-Ps state in organic materials is typically 1-3 ns, which is an order of magnitude longer than the lifetime of free positrons or p-Ps. Thus the longest-lived component in the positron lifetime spectrum is identified as the o-Ps lifetime. Because the spectra obtained in this work were analyzed into three lifetime components, the o-Ps lifetime is referred to as τ_3. It has long been recognized that observation of the o-Ps lifetime can serve as a useful tool in phase transformation investigations, since its value strongly depends on the electron density in the Ps atom's environment (3).

EXPERIMENTAL PROCEDURES

The tristearin sample was obtained from Sigma Chemical Co. (St. Louis, Missouri) and had a stated purity of 99%. The differential scanning calorimeter used was a Perkin-Elmer DSC-1B. The sample holder atmosphere was purged with dry nitrogen gas flowing at 20 ml/min. Sample weights were of the order of 20 mg. Heating rate and sensitivity were 10 C/min and 16, respectively.

Positron lifetime measurements were made with a conventional apparatus consisting of Amperex XP1021 photomultipliers, Naton 136 plastic scintillators, Ortec 583 Constant Fraction Differential Discriminators, Ortec 467 Time to Pulse Height Converter and Nuclear Data ND66 Multichannel Analyzer. The positron source was 10 μCi of ^{22}Na deposited between sheets of 1/4 mil Mylar®. The source was surrounded by about 3 g of tristearin in an aluminum holder, which fit snugly in a large aluminum block in which cartridge heaters were embedded. A Hewlett-Packard Model 220 Temperature Controller maintained the sample at the selected temperature. Positron data were analyzed using the program Positronfit Extended (4).

The experimental procedure consisted of producing a sample of tristearin in the α form by rapid cooling from the melt and holding the sample at a selected temperature for an extended period. During this annealing time, periodic measurements were made by both positron and DSC techniques.

The sample was melted on a hot plate inside a glove box with a dry nitrogen atmosphere. Rapid cooling was achieved by placing the holder containing the molten sample on a copper bar cooled by liquid nitrogen. The sample was allowed to warm to room temperature before being removed from the glove box. Subsequently, the sample was continuously held at the selected annealing temperature inside the heating block except for very brief intervals when DSC samples were removed.

RESULTS AND DISCUSSION

Figure 1 shows τ_3 plotted as a function of annealing time for a sample held at 44.5 C. Three other annealing temperatures (44.0, 45.0 and 46.0 C) were used, and in each case the shape of the τ_3 vs annealing time curve

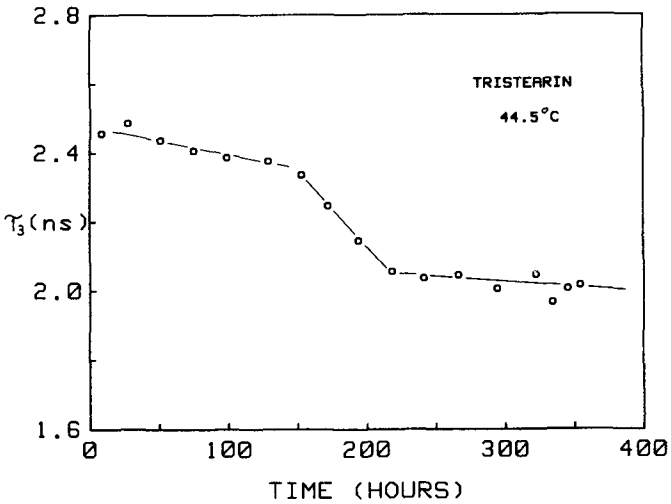

FIG. 1. The long-lived positron lifetime component (τ_3) as a function of annealing time for tristearin held at 44.5 C.

DSC point. In Figure 3 it is seen that at ca. 220 hr of annealing time the α-to-β transition ceases to appear in the DSC measurements. This same annealing time corresponds to the end of the second region of the positron measurements of Figure 1. This behavior was observed for all four annealing temperatures used. This correlation allows one to interpret the end of region two of the positron data as the annealing time required to totally convert α to β. Figure 4 shows the logarithm of the annealing time required to reach the end of region two of the positron measurements for each of the four annealing temperatures used.

Dafler (2), using x-ray diffractometry, explained his data for aging of the α form of tristearin in the following way: He suggeted that the α form made a very rapid transition to the β' form, followed by conversion of β' to β by two separate mechanisms, each having a different rate constant. Since our DSC studies did not show any evidence of the β' form being present, our results require a different interpretation. To be consistent with our DSC data, we propose that the first two regions of the positron lifetime data represent two different mechanisms for α-to-β conversion and that region three corresponds to aging of the β form by an additional mechanism. The nature of these mechanisms, of course, cannot be determined from these experiments. However, these results demonstrate that positron lifetime measurements can serve as a convenient probe to monitor aging processes in the triglycerides.

REFERENCES

1. Whittam, J.H., and H.L. Rosano, *J. Am. Oil Chem. Soc. 52*:128 (1975).
2. Dafler, J.R., *Ibid. 54* :249 (1977).
3. *Positronium and Muonium Chemistry*, edited by H.J. Ache, Advances in Chemistry Series, No. 175, American Chemical Society, Washington, DC, 1979.
4. Kirkegaard, P., and M. Eldrup, *Comp. Phys. Commun. 7*:401 (1974).

[Received September 15, 1986]