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THERMAL STUDY OF DIPALMITOYL 1,2 DIGLYCERIDE TRANSITIONS

by

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ABSTRACT

The enthalpy of the phase transitions of purified dipalmitoyl 1,2 glyceride, including the melting of two of the phases, have been measured by differential thermal analysis. The special procedures required for measurement of some of the phases are described. The results of measurements of similar transitions of nonadecane of lower purity are also given. Values obtained are discussed in relation to the structures of the phases and the study of phospholipids.

Key-words: Diglycerides; Phase transitions; Thermal analysis.

INTRODUCTION

The polymorphism of dipalmitoyl 1,2 glyceride (DPG) was studied in detail by Craievich et al. (1). This compound is of special interest because of the close relation with the natural phospholipids. A comparison of the phases and transitions of these compounds is useful. Measurements of heats of transition for all the DPG phases are reported here together with further details of the transitions involving the low temperature phase.

Several different systems of nomenclature have been used for the many phases formed by glycerides and phospholipids and have often led to confusion. For this reason, a brief description of each phase will be used here rather than symbols. Highly purified DPG forms large single crystals from solution with a melting point of 69.6°C in which the chains are packed in an $O_{\perp}$ subcell and tilted in the molecular layers. This phase was designated crystalline C in reference 1. There is another phase formed by cooling the melt which has a melting point of 51.4°C and in which the chains are packed in an hexagonal subcell. This was called $L_{\beta'}$ and L_{β} in 1. In $L\beta$, above 26°C, the chains are perpendicular to the stacking plans and in $L\beta'$, below 26°C, the chains became progressively tilted[1]. Finally, yet another phase is formed by keeping the hexagonal phase at lower temperatures (in our case at 15°C) which transforms before melting and has a rectangular subcell with parameters close to hexagonal. This was termed L_{γ} in reference 1.

EXPERIMENTAL

The sample used was the same as used in the previous study (1), it was purified by repeated slow crystallization from benzene and freed from traces of solvent and water. There was no evidence of degradation after several cycles at 75°C. A Mettler T.A. 2000 diferential thermal analysis apparatus was used and samples were weighed into aluminium capsules which were then sealed.

Typical scans obtained by the procedures described are shown in Figure 1, which is derived from Figure 4 of reference 1 by the addition of the heating scan for the pure low temperature phase. As the thermal peaks are large and reproducible, the enthalpies are readily obtained by standard procedures. However, samples cooled below about 30°C show, by heating, a simultaneous melting of the hexagonal phase and crystallization of the high melting point phase leading to a complex endo-exothermic DTA peak (Fig. 1c). Therefore to obtain the correct value for the hexagonal phase, the sample was melted by heating to about 75°C and then cooled until the hexagonal phase is formed, but keeping the temperature above 30°C to avoid nucleation of the high melting point phase. After the sample had completely solidified it was heated to scan the single endothermic peak at 51.4°C (Fig. 1e).

For measurement of the enthalpy of the low temperature phase, the sample was melted as before, cooled until the hexagonal phase is obtained and then stored at 15°C, for 40 days. On heating after this time there was an exothermic transition

at 50°C. This involves a direct transition from the low temperature form to the high melting phase. On further heating the peak for the high melting phase was also scanned. The samples were observed during the heating and cooling cycles to ensure that the desired phase was obtained. One sample was found to supercool so that the hexagonal phase did not appear and on storage the stable high melting point phase was obtained.

Measurements were also made with a sample of nonadecane of approximately 99% purity for the transition to the hexagonal phase and for the melting of this phase.

These experiments gave the results listed in Table 1. Values for the transition temperatures and the observed positions of the peak maxima were recorded at a heating rate of 0.5°C/minute. They differ slightly from those given in reference 1 because of a lower heating rate and the absence of an endothermic peak, due to crystal growth of the high melting point phase, from the melting peak of the hexagonal phase.

DISCUSSION

The present results show that the phase relations given in reference 1 are better described as follows:

$$\text{Hexagonal } (L\beta') \xleftrightarrow{T_3 = 26^\circ C} \text{Hexagonal } (L\beta) \xleftrightarrow{T_2 = 51{,}4^\circ C} \text{Liquid}$$

$$\underset{\text{phase } (L\gamma)}{\text{Low Temperature}} \xrightarrow{T_2 = 50^\circ C} \underset{\text{phase } (C)}{\text{High Melting}} \xrightarrow{T_1 = 69{,}6^\circ C} \text{Liquid}$$

The formation of the high melting point phase during melting of the hexagonal phase is due to the transformation of nuclei of the low temperature phase, formed below 30°C., into nuclei of the high melting point phase and growth of these nuclei. Nucleation of the high melting point phase from the melt occurs at a very low rate.

Comparison between the transitions observed in hydrocarbons, glycerides and especially DPG and phospholipids is of value, although the complexity due to interactions of water with the latter precludes a full discussion here.

The structure of the low temperature form of nonadecane can be deduced from the work of Smith (2), the chains are in a planar zigzag conformation and perpendicular to the molecular layers. A study of n-hexatriacontane ($C_{36}H_{74}$) by Vand (3) showed that at room temperature a phase exists with chain axes perpendicular to the layers and packed in the common $0\underline{1}$ subcell. As the crystals are heated to the transition temperature of 76°C. the lattice expands in an assymetric manner until the parameters are close to those of the hexagonal phase. The chains are again in the planar zigzag and this phase is slightly less stable than another form with the same subcell and titled chains. Structural determinations of these two forms were made by Shearer and Vand[4] and by Teare (5).

The results of Vand (3), Larsson (6) and Doucet et al. (7) show that in the hexagonal form* of the hydrocarbons studied, the chain axes are perpendicular to the molecular layers. Further, during the transition there is only a small shift in chain positions so that the enthalpy must arise mainly from changes

*Hexagonal phases are called "rotator" phases in ref. 8 and 9.

in molecular motion and/or conformation. As a matter of fact a significant increase in molecular motion and conformational defects has been detected by small angle x-ray diffraction in odd numbered hydrocarbons C_nH_{2n+2}, at the transition from crystaline to hexagonal phases (8).

The spacings for the low temperature and hexagonal phases of DPG(1) are virtually identical with those of the hydrocarbon phases at corresponding temperatures so that the chain packing is probably similar. There are therefore three observed phases of DPG and of hydrocarbons with similar chain packing and relative stability. However, as demonstrated in reference 1, there is a continuous development of a small chain tilt in the hexagonal phase of DPG at lower temperatures A similar observation has been made in some phospholpid phases so that this feature may be associated with the presence of the glycero-ester groups in these molecules.

To compare the enthalpies on the two studied systems we roughly estimate $\Delta H/CH_2$ (enthalpy per unit CH_2 group) by using the factor 19 for nonadecane and 32 for DPG. The values obtained for the several transformations are listed in Table II. $\Delta H/CH_2$ gives a lower value for DPG for the lower transition and a higher value for the melting of the hexagonal phases. As no allowance has been made for differences in structure of the carboxy-ester and end groups the values are in reasonable correspondance. A close agreement is observed between the values of $\Delta H/CH_2$ associated with the transition from the low temperature phase to liquid. A possible source of the divergences is the lower purity of the nonadecane.

CONCLUSIONS

Quantitative study of the transitions of DPG requires special procedures to ensure that only the phases desired are present. Measurement of the metastable hexagonal phase are particularly liable to error because of recrystallization of the high melting phase or the formation of another stable phase on long storage. Similar complexities are probable in studies of phospholipid transitions.

The hydrocarbons and glycerides and especially DPG form several phases and undergo transitions which are similar to those of the phospholipids. Because of the simpler chemistry and absence of interactions with water these can be more readily studied with precise physical methods.

FIGURE CAPTIONS

Differential thermal analysis curves for dipalmitoyl 1,2 glyceride

a) Heating of crystalline sample.

b) First cooling, formation of hexagonal phase. Heating curves after melting and cooling the sample to different temperatures.

c) $T = 20^{0}C$.

d) $T = 30^{0}C$ and

e) $T = 40^{0}C$.

f) Heating of the phase obtained by storage of hexagonal phase for 40 days at $15^{0}C$.

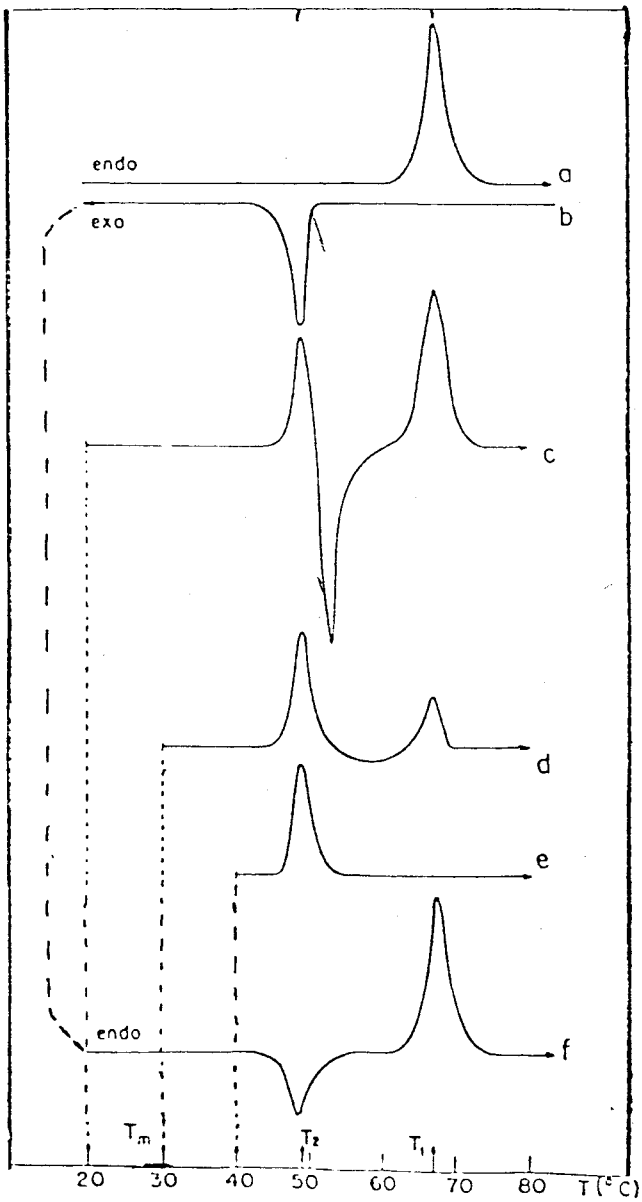
endo
a
exo
b
c
d
e
endo
f
T_m
T_2
T_1
20
30
40
50
60
70
80
T(°C)

Table I

Thermal data for dipalmitoyl 1,2 glyceride and nonadecane

System	Phase transition	T°C	ΔH[kcals mol^{-1}]
DPG	High melting --- Liquid	69.6	22.98
	Hexagonal --- Liquid	51.4	12.41
	Low Temperature --- High melting	50	- 4.7
	By calculation:		
	Low Temperature --- Liquid	-	18.3
	Low Temperature --- Hexagonal	-	5.9
Nonadecane $C_{19}H_{40}$	Low Temperature --- Hexagonal	21.5	2.31
	Hexagonal --- Liquid	33.6	8.40
	By calculation:		
	Low Temperature --- Liquid	-	10.71

Table II

Comparison between DPG and nonadecane

	ΔH[cals/CH_2]	
	DPG	$C_{19}H_{40}$
Low Temperature --- Hexagonal	184	122
Hexagonal --- Liquid	388	442
Low Temperature --- Liquid	572	564

REFERENCES

1. A.F. Craievich, A.M. Levelut, M. Lambert and N. Albon, J. Physique 39, 377 (1978).

2. A.E. Smith, J. Chem. Phys. 21, 2229 (1953).

3. V. Vand, Acta Cryst. 6, 797 (1953).

4. H.M.M. Shearer and V. Vand. Acta Cryst. 9, 379 (1956).

5. P.W. Teare, Acta Cryst. 12, 294 (1959).

6. K. Larsson, Nature 213, 383 (1967).

7. J. Doucet, I. Denicolo, A.F. Craievich, J. Chem. Phys. 75, 1523 (1981).

8. A.F. Craievich, I. Denicolo & J. Doucet, Phys. Rev. B (1984) In the press.