Clarification of Propylene Glycol Monoester Polymorphism

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ABSTRACT

A minor revision based on new data is reported for the polymorphism of 1-propylene glycol monopalmitate and monostearate. Metastable Form I is now found to be intermediate in melting level between α and stable Form II. Form III as previously reported transforms to α below the α mp. For the 80:20 mix of 1-propylene glycol monostearate-2-propylene glycol monostearate, the approximate equilibrium mixture, it is again observed that Form II is stable, melting a little above α; and Form I transforms to α slightly below the α mp; and Form III is missing.

INTRODUCTION

Thermal data on polymorphic states of propylene glycol monoesters were first reported by Kuhrt et al. (1). Further details were added by Martin and Lutton (2) who identified four polymorphic states for pure 1-monoesters. Later observations, while confirming most of the earlier findings, have led to different conclusions with regard to melting level of the metastable Form I.

EXPERIMENTAL PROCEDURES

The esters were prepared by direct esterification of pure fatty acid (>99%) with an excess of propylene glycol and essentially total recovery of monoester by crystallization from hexane, essentially as previously described (2).

Repeated crystallization of mixed monoester isomers, from highly purified palmitic acid, in 10 volumes hexane at 10 C, then 16 C, gave a 28% yield of purified 1-propylene glycol monopalmitate (1-PGMP). The crystals were Form II.

Similar repeated crystallization of mixed stearate isomers from 7 volumes hexane at 16 C and 21 C gave a 33% yield of purified 1-propylene glycol monostearate (1-PGMS). The fact that the crystals were Form I of 52 C mp stimulated the present investigation.

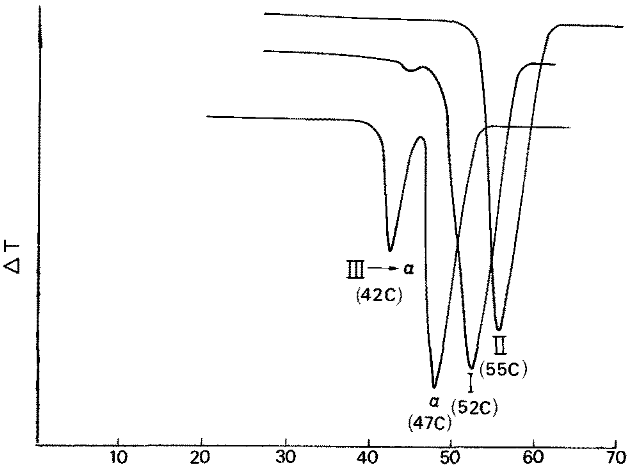

FIG. 1. Differential thermal analysis of 1-propylene glycol monostearate (1-PGMS).

X-ray diffraction data and melting points were obtained as described previously (2).

Differential thermal analysis (DTA) was carried out with a DuPont 900 instrument which gave significantly superior results, sharper peaks, and better resolution than the apparatus employed earlier (2). The solvent crystallized sample was ground with mortar and pestle and packed into standard DTA capillaries (2 mm OD) to a height of 3-4 mm (ca. 3 mg). Chromel-alumel thermocouples were inserted in the sample, and in glass beads in similar capillaries for reference and temperature programing. The assembly was heated in a silver block at 10 C/min to complete melting to confirm melting level of the crystals from solvent. A cooling curve was obtained with N_2 flowing through the channel provided. A heating curve on sample cooled from the melt was then normally obtained to explore metastable states. Heating curves for 1-PGMS, starting in the three solid states known at 25 C, are shown in Figure 1. Each peak is labeled with the approximate finally accepted thermal value for the relevant phase change. Melting and transformation data for palmitate and stearate are summarized in Table I.

DISCUSSION

Present observations call for little change with respect to earlier description of Forms II, III and α. It is now seen, however, for both palmitate and stearate 1-monoester, that Form I, contrary to earlier indications (2), actually melts between α and Form II melting points.

Form II is obtained by slow solvent crystallization. For PGMP it has been obtained, without seeding, from hexane at 16 C. For PGMS it has been obtained in two ways: (a) with seeding, from hexane at 21 C, and (b) by evaporation of hexane from solution at 38 C.

Form I is obtained by more rapid crystallization from solvent. For PGMS a crystallization from hexane at 21 C or evaporation of dilute hexane solution at the same temperature produces Form I. PGMP is a little harder to obtain as Form I, but by evaporation of 5-10 ml solvent per 1 g at 10 C, the phase is formed.

Form III is formed easily by melting and rapidly chilling to 0 C, and α is obtained by heating Form III above its transformation point.

In the light of the new observations on Form I melting level, some earlier work was repeated on the mix 1-PGMS/2-PGMS 80:20, that mixture being of the equilibrium proportion formed in monoesters prepared by interesterification.

TABLE I

Tabulation of Thermal Data
for 1-Propylene Glycol Monoesters

	Trans point, C	Melting point, C		
Ester	III → α	α	I	II
P	31.0(28.5)[a]	37.5(37)	42.0	47.8(45)
S	42.0(38.5)	47.2(47.1)	52.5	55.3(55.9)

[a] Data of Martin and Lutton (2).

Earlier experiments (2) showed that when 1-PGMS/2-PGMS 80:20 was solidified from melt, Form I was obtained which transformed to α giving an α diffraction pattern at 42 C, 3 C below the α mp. This behavior has been confirmed. It has also been observed that the same 80:20 composition, crystallized from 15 volumes hexane evaporated at 21 C, gives Form II, according to diffraction patterns obtained at 25 C and at 42 C. Form II is thus the stable form for both pure 1-PGMS and for the 80:20 equilibrium isomeric mixture. Form I, melting between α and Form II for pure PGMS transforms to α slightly below the α mp for the 80:20 mixture. Form III, transforming to α below the α mp for pure PGMS, is still not observed for the 80:20 mixture.

REFERENCES

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