SHORT COMMUNICATION

The Effect of Partial Glycerides on Trilaurin Crystallization

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ABSTRACT: The effects of partial glycerides of fatty acid chainlength from C_{10} to C_{18} on trilaurin crystal growth rate were investigated. Glycerides of particular form were found to have similar effects. Free fatty acids or monoglycerides either had little effect or slightly increased growth rates, whereas diglycerides, especially 1,3-diglycerides reduced them. If a particular glyceride has shorter chainlengths than trilaurin, the inhibition of crystallization is extremely small. For slightly longer chainlengths, a significant reduction of crystallization rate is seen, although smaller than with the addition of partial laurates. Maximum inhibition occurs with chainlength matching, and the magnitude decreases with increasing difference between host and guest chainlength.
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KEY WORDS: Crystallization, glyceride, habit, microscopy, modification, triglyceride, trilaurin.

Guest glycerides can greatly affect the crystal growth and polymorphic behavior of many commercial fat systems. As impurities, they can have deleterious effects on a system's properties, or as additives they can control the crystallization (e.g., by stabilizing a particular polymorph). However, there is little understanding of the effect of an individual glyceride on a pure triglyceride, let alone complex impurities, on industrial systems. In our previous work (1), we initiated addressing this problem. We showed that monolaurin and lauric acid increase the trilaurin crystal growth rate but decrease facet and crystal size. However, the addition of dilaurates caused a significant decrease in the growth rate. The crystal morphology was also altered, and the relative stability of the less stable phases increased. 1,3-Dilaurin retarded the growth rate by a greater amount than 1,2-dilaurin. It was shown that the varying effects were caused by the varying shapes and sizes of the additive molecules.

The results presented here develop this work by investigating the effect of glyceride side-chainlength on trilaurin crystallization, in particular by considering the effect of caprates (C_{10}), myristates (C_{14}), palmitates (C_{16}) and stearates (C_{18}).

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EXPERIMENTAL PROCEDURES

Materials. All glycerides were obtained from Sigma Chemical Co. (Poole, Dorset, United Kingdom) at better than 99% pure. The trilaurin was analyzed and found to be 99.9% pure with a trace of diglyceride.

Methods. Mixtures of 1, 2, and 5% (by weight) of each additive in trilaurin were prepared. Samples with 3 molar% of each additive were also made, and a control sample of trilaurin was prepared. Samples were heated to approximately 80°C to ensure complete dissolution of the additive.

Temperature gradient microscopy. A temperature gradient microscope stage has been designed and built after the manner of Hunt *et al.* (2) and Whittam and Rosano (3). It was operated as described previously (1). Crystallization was monitored at forced cooling rates between 10 and 100°C per hour.

RESULTS

Trilaurin crystallization was monitored at all slide movement rates. At slower rates, long, thin, lath-like β crystals were formed and grew into the melt. At faster rates, these were soon outgrown by finer β and then by β′ crystals as described before (1).

The effects of the different groups of additives will be described below in turn.

Caprates. Photographs of crystals of trilaurin plus monocaprin and 1,3-dicaprin grown at a slide movement rate of 1 mm/h are illustrated in Figure 1. Crystal form is similar to that of pure trilaurin at the same growth rate. Plots of growth distance against time for caprates at a slide movement rate of 1 mm/h are illustrated in Figure 2. All additives retard the growth by some amount. Varying the additive concentration had little effect.

Investigation of the effect of undercooling on growth rate was made at the slide movement rate of 5 mm/h. There was little difference in behavior from the control. Thus, crystal growth mechanisms are unaltered by the addition of caprates to trilaurin.

Myristates. Photographs of crystals of trilaurin plus monomyristin and 1,3-dimyristin at 1 mm/h are shown in Figure 3. Plots of growth against time at a slide movement rate of 1 mm/h are illustrated in Figure 4.

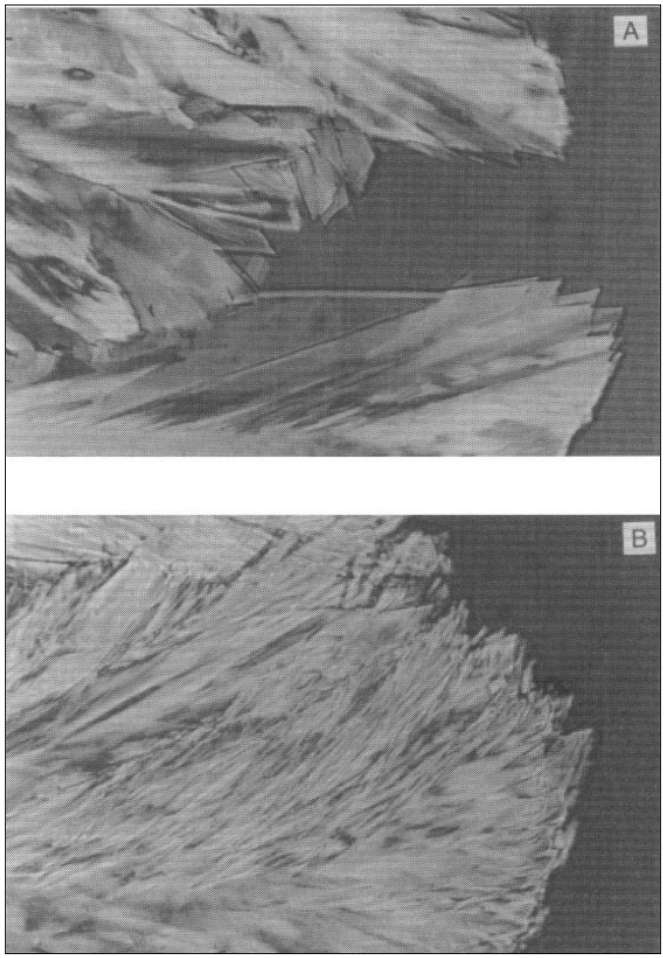

FIG. 1. A: Crystals of trilaurin plus 1% monocaprin after 2 h at 1 mm/h; B: Crystals of trilaurin plus 1% 1,3-dicaprin after 2 h at 1 mm/h.

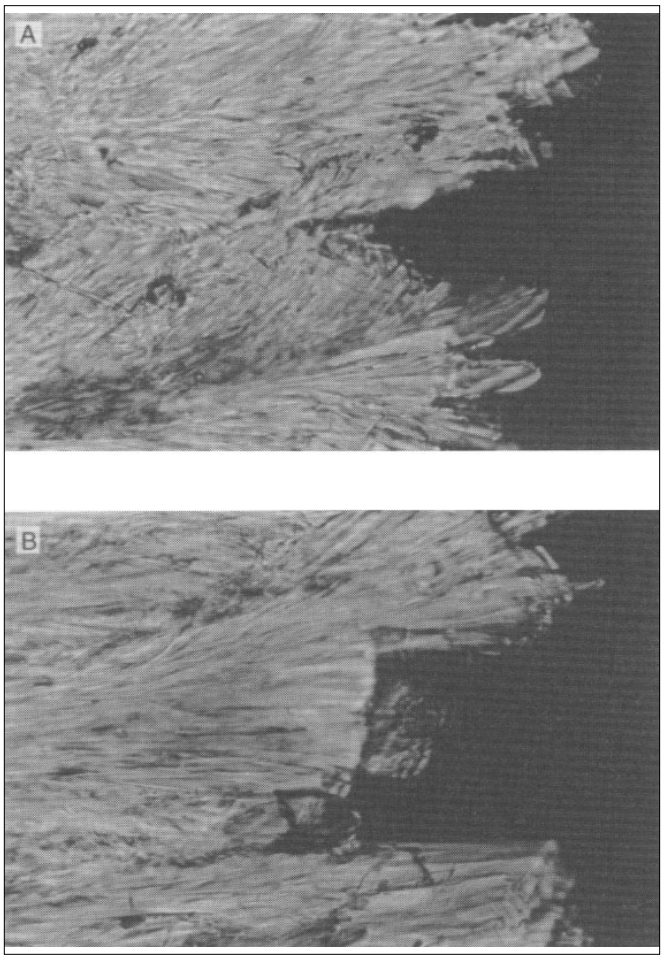

FIG. 3. A: Crystals of trilaurin plus 1% monomyristin after 2 h at 1 mm/h; B: Crystals of trilaurin plus 1% 1,3-dimyristin after 2 h at 1 mm/h.

The effects are again smaller than those of the corresponding laurate. However, they are greater than those caused by the addition of the corresponding caprate. The free fatty acid appears to promote growth, and the monomyristate has little effect. The diglycerides decrease the rate significantly, with the 1,3-isomer having a particularly large effect. Trimyristin also has a large retardation effect. The 1,3-diglyceride isomer reduces growth rates by approximately one-third. This is significant, but it is a smaller effect than that caused by the 1,3-dilaurin, where the retardation is over twice as great. At 3 molar % additive, the ratio of the effects is similar. Increasing additive concentration increases the overall effect.

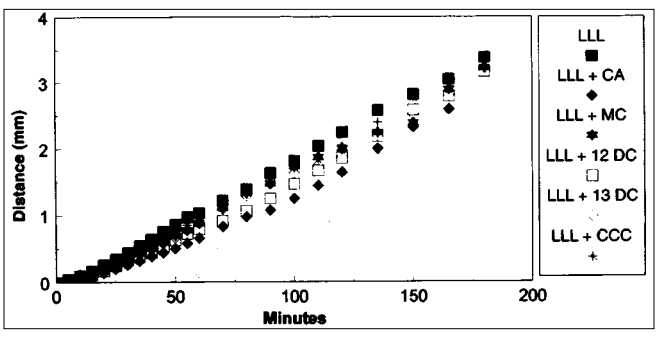

FIG. 2. Growth distance vs. time for caprates, at a slide movement rate of 1 mm/h. LLL, trilaurin; CA, capric acid; MC, monocaprin; DC, dicaprin; CCC, tricaprin. ■, LLL; ♦, LLL + CA; ★, LLL + MC; □, LLL + 12DC; ◇, LLL + 13DC; ✳, LLL + CCC.

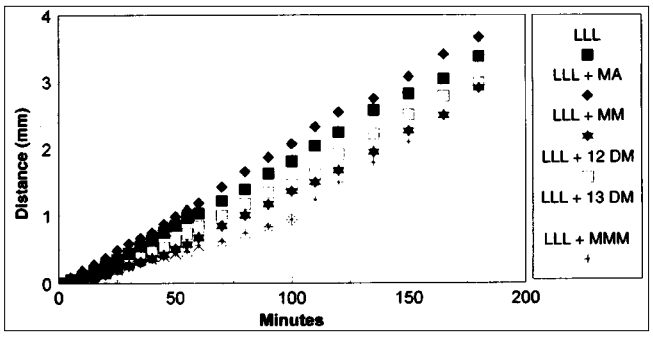

FIG. 4. Growth distance vs. time for myristates, at a slide movement rate of 1 mm/h. LLL, trilaurin; MA, myristic acid; MM, monomyristin; DM, dimyristin; MMM, trimyristin. ■, LLL; ♦, LLL + MA; ★, LLL + MM; □, LLL + 12DM; ◇, LLL + 13DM; ✳, LLL + MMM.

Growth rate dependence on undercooling is again similar to pure trilaurin. Additives do not affect the crystal growth mechanisms, merely the overall rate.

Palmitates. These had a similar but smaller effect than the corresponding myristates.

Stearates. Monostearin was not soluble in trilaurin, and no further work was performed.

DISCUSSION

Glycerides dissimilar from the host have minimal effects on crystal growth. Those with shorter chainlength than the host have small effects. The effect appears to be maximal when the chainlength is that of the host, and then decreases with further increasing chainlength. The effect therefore varies as in Figure 5, with a strong peak corresponding to chain matching between additive and substrate. This is in agreement with the earlier results on monoglycerides in the limited study of Sambuc *et al*. (4).

The caprates have a small but significant effect on crystal growth. The interference is qualitatively similar to that caused by the corresponding laurate molecule. Probably, the dicaprates affect growth rates by interfering with the interface structure and preventing further molecules from joining. In this case, monocaprin and capric acid also decrease the growth rate.

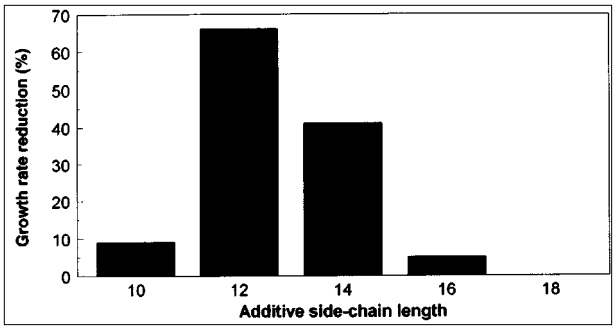

FIG. 5. The effect of 1,3-diglyceride side-chainlength on the crystal growth of trilaurin.

Overall, the effects of caprates are much less than those of the partial laurates. For an additive to have an appreciable effect upon the crystal growth of a triglyceride, there appears to be a critical minimum chainlength, which is the same as that of the host triglyceride. Molecules with shorter chainlengths than this have minimal effect.

The myristates have similar but smaller effects than the laurates. The effects are, however, much greater than those of the caprates.

The shape of the curves in all series of experiments is regular, and the rate of growth tends toward a final rate, presumably determined by the slide movement rate. The linear nature of the bulk of the curve shows that growth of one particular phase (β) is occurring, and never is there any polymorphic transformation at a slide movement rate of 1 mm/h.

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