



# Crystallization behavior of monoacylglycerols in a hydrophobic and a hydrophilic solvent



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## ABSTRACT

Systems containing monoacylglycerols (MAGs) in both a hydrophobic solvent (liquid oil) and a hydrophilic solvent (water) can be used for the development of calorie-reduced food products. In this study, the crystallization behavior of MAGs in a hydrophobic solvent (rapeseed oil) and a hydrophilic solvent (water) was studied and compared. Pure monopalmitin (MP) and a commercial MAG containing MP were used for this study. Differential scanning calorimetry (DSC) data were coupled with X-ray diffraction (XRD) data obtained using synchrotron radiation and cryo-scanning electron microscopy (cryo-SEM) images were recorded to illustrate the microstructural characteristics of the systems. Although the polymorphic behavior of the MAGs was found to be the same in both solvents, the crystallization onset temperature was found to be concentration-dependent in the systems with liquid oil as solvent, in contrast to the systems with water as solvent. On the other hand, the temperature of the polymorphic transition from the  $\alpha$  to the sub- $\alpha$  polymorph was constant in both systems. Differences in microstructure could be attributed to the inherent properties of the hydrophobic or hydrophilic solvent.

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## 1. Introduction

The addition of MAGs to liquid oil is interesting from a practical point of view as they represent a strategy to structure oil without using solid fat, which implicates health advantages (Pernetti, van Malssen, Flöter, & Bot, 2007; Rogers, 2009). However, the behavior of MAGs in liquid oil is scarcely documented in literature. In fact, most authors assume that the phase behavior of MAGs in liquid oil is similar to that in water.

A characteristic feature of MAGs in water, which is abundantly described in literature, is their ability to form lyotropic mesophases or liquid crystals. MAGs crystallize in bilayers and are normally insoluble in water. However, when a mixture of MAGs and water is heated, the hydrocarbon chains become liquid at a certain temperature while at the same time water penetrates between the bilayers along the plane of the glycerol head groups. This results in the formation of liquid crystalline phases. The introduction of the liquid chain concept by Chapman (1958) was an important step towards the elucidation of these phases. He demonstrated the phenomenon of the melting of hydrocarbon chains. This occurs because the van der Waals forces between hydrocarbon chains are weaker than the hydrogen bonding between the polar head groups (Nawar, 1996). Only a few years later, Luzzati, Mustacchi, Skoulios, and Husson (1960) revealed the structure of the most common liquid crystalline phases.

Several types of liquid crystalline phases are possible dependent on the MAG/water ratio and the temperature. Just above the melting

point of the MAG, a lamellar mesophase is formed. This rather fluid mesophase consists of lipid bilayers alternated by water layers. This is schematically shown in Fig. 1A. If the water content is raised above the swelling limit of the lamellar mesophase, a transformation into spherical multilamellar vesicles (liposomes) occurs, also called a lamellar dispersion (Stauffer, 2005). The formation of closed vesicles with preserved lamellar structure avoids direct contact between bulk water molecules and water molecules associated with the lipid bilayers (Krog, 1997). At higher temperatures, a cubic mesophase and a hexagonal mesophase are formed.

The interlayer spacing in the lamellar phase of non-ionic MAGs ( $d_w$  in Fig. 1A) is determined by the balance between the long-range van der Waals forces and the osmotic repulsion between the lipid bilayers. In this way, a water layer thickness of about 20 Å is reached in various systems (Larsson & Krog, 1973). As investigated by Van de Walle, Goossens, and Dewettinck (2008), introducing charged groups on the surface of the lipid bilayers leads to an increased swelling (thicker water layers), a higher temperature stability of the lamellar phase (the transition to the cubic phase is shifted to higher temperatures) and an expansion of the lamellar phase into the higher water content region. This is due to the creation of electrical repulsive forces (Van de Walle et al., 2008).

If the lamellar phase or dispersion is cooled, a gel phase is formed with an ointment-like consistency (Heertje, Roijers, & Hendrickx, 1998). The gel phase is called the  $\alpha$ -gel as it is the hydrated form of the  $\alpha$  polymorph. The  $\alpha$ -gel also has a lamellar structure but the hydrocarbon chains are now in a crystalline state, as schematically shown in Fig. 1B. The gel consistency of this phase is due to the possibility of the lipid bilayers to slide in relation to one another (Larsson, 1967). The

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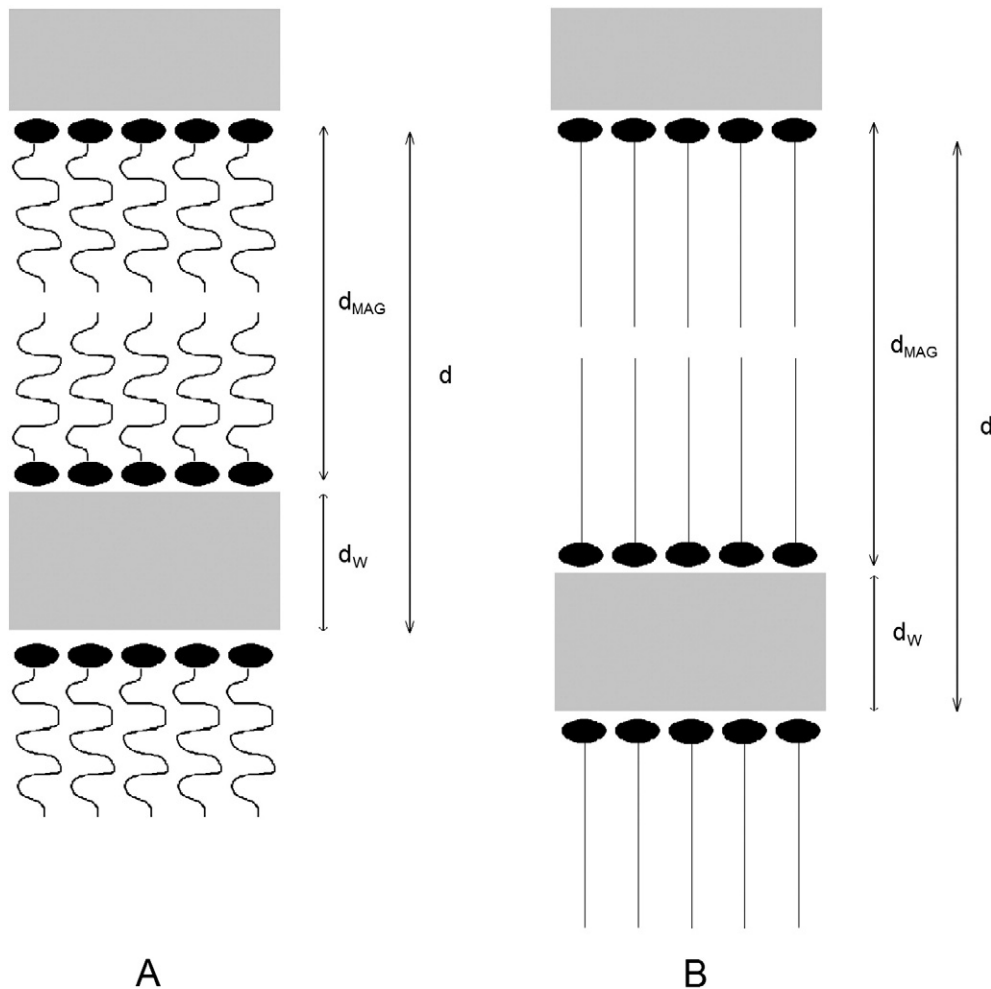


Fig. 1. Schematic representation of (A) the lamellar mesophase and (B) the  $\alpha$ -gel phase of a MAG/water mixture.

transition temperature from lamellar to gel phase is called the Krafft temperature.

Phases of MAG/water systems can find use as main components in low-calorie food products (Heertje et al., 1998). Similarly, MAGs added to liquid oil can aid in calorie reduction of food products (Pernetti et al., 2007; Rogers, 2009). Most authors assume that the phase behavior of MAGs in liquid oil is similar to that in water. Surprisingly, only a limited number of authors have investigated MAG/liquid oil systems in detail. Ojijo, Neeman, Eger, and Shimoni (2004) reported the possible use of MAG/liquid oil systems as a healthy substitute for margarine and butter due to the formation of a gel network upon cooling. This gel network was assumed to be an  $\alpha$ -crystalline gel, similar to aqueous systems. Moreover, a liquid crystalline lamellar phase was assumed to exist before gel formation during cooling. A coagel mesophase was found to form during storage (Ojijo, Kesselman, et al., 2004). Chen, Van Damme, and Terentjev (2009) conducted a more detailed investigation of the phase behavior of a commercial C18 MAG in hazelnut oil. Their proposed phase diagram displays three phases. On cooling the well-mixed liquid isotropic phase, an inverse lamellar phase is formed with the hydrophobic head groups now situated in the middle of the bilayer. This is schematically shown in Fig. 2 which shows the bilayer structure in both liquid oil and water. This phase rheologically behaves like an elastic gel, as opposed to the fluid behavior of the aqueous lamellar phase but similar to the aqueous  $\alpha$ -gel known at lower temperatures. Based on WAXD measurements, it was deduced that the glycerol heads are packed in a hexagonal manner in the inverse lamellar bilayer. The second phase transition from inverse-lamellar to a

crystalline phase includes the crystallization of the aliphatic chains in a sub- $\alpha$  form with an orthorhombic packing. This phase retains the mechanical properties of the gel phase.

MAG/water systems and MAG/liquid oil systems are both promising blends for the development of calorie-reduced food products. Although the behavior of both systems is often said to be comparable, a lot of uncertainty still remains in this matter. This paper seeks to redress the

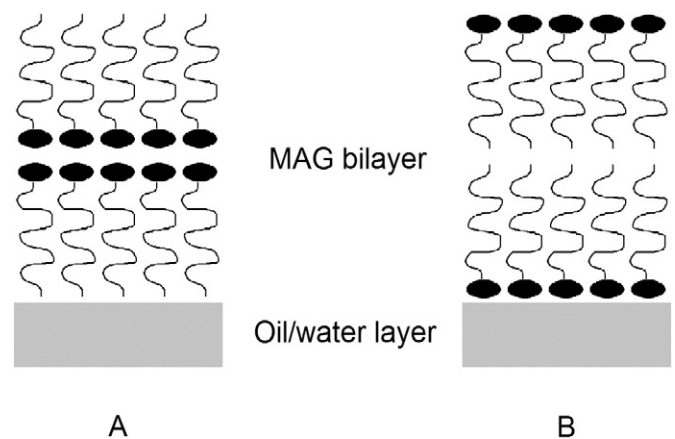


Fig. 2. Schematic representation of the bilayer structure of MAGs blended with (A) liquid oil and (B) water.

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