Binary Phase Behavior of Saturated-Unsaturated Mixed-Acid Triacylglycerols—A Review
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Abstract: Most natural lipids contain a complex mixture of individual triacylglycerols (TAGs). An in-depth knowledge of the mixing behavior of TAGs is necessary for the rational design and engineering of food materials. The binary phase diagram of TAGs is a simplified model that can be explored to help foster an understanding of the phase behavior of complex fats and oils. This article reviews recent research on the binary phase behavior of saturated-unsaturated mixed-acid TAGs, with special emphasis on the stearic-unsaturated and palmitic-unsaturated diacid TAGs. The occurrence of polymorphic forms and mutual solubility of TAG mixtures are strongly related to the glycerol conformation of the saturated-oleic diacid TAGs; it appears to be most influenced by the chain-length mismatch in saturated-elaidic diacid TAGs. In addition, the polymorphism of pure enantiomers and racemic mixture of chiral TAGs was also reviewed, while the effect of chirality on mixing behavior was discussed.

Key words: phase behavior, triacylglycerols, polymorphism, unsaturated fatty acid

1 INTRODUCTION
Most functions of lipids in foods, pharmaceuticals, and cosmetics depend on their physicochemical properties, which can partly be attributed to the physical properties of their major component, triacylglycerols (TAGs), and largely to the phase behavior of various TAGs1,2.

The mixing behavior of TAGs is affected by multiple factors3, such as the types of fatty acid moieties (e.g., chain length, saturated or unsaturated, cis or trans double bond configuration), positions of carbon atoms of the glycerol groups in which various fatty acid chains are connected, polymorphism of the component TAGs, and external factors (e.g., thermal treatment, additives, application of shear, sonication, and pressure)4,5.

Triacylglycerols can be divided into two categories on the basis of their fatty acid compositions. The TAGs that have only one type of fatty acids are called monoaic TAGs (e.g., trilaurin LLL; tripalmitin PPP; triolein OOO), while those that have two or three types of fatty acids are called mixed-acid TAGs (e.g., 1,2-dipalmitoyl-3-stearoyl-glycerol PPS; 1-palmitoyl-2-oleoyl-3-stearoyl-glycerol POS)6. Saturated-unsaturated mixed-acid TAGs are commonly present in nature and employed in industrial applications7. For example, cocoa butter has more than 80% Sat-O-Sat type TAGs (Sat: saturated fatty acid; O: Oleic acid)8. However, the polymorphic behavior of saturated-unsaturated mixed-acid TAGs is more complicated than that of monoaic TAGs, since the molecular interactions of the aliphatic chains, methyl end stacking, and glycerol conformation of mixed-acid TAGs are modified, as opposed to those of monoaic TAGs7,8. As a consequence, the relative stability of multiple polymorphic forms and their mutual solubility are modified7,9,10.

From an industrial viewpoint, in order to explore the possibility of engineering the nanostructure of fats to target specific functionalities, an in-depth knowledge of the TAG structure-mixing behavior relationship is required10.

Since most of the fats present in nature and employed in industrial applications contain different types of mixed-acid TAGs11, their binary phase behavior needs to be studied as a basic model of complex fats and oils.

This article reviews recent research on the binary phase behavior of saturated-unsaturated mixed-acid TAGs, with
special emphasis on TAGs that contain palmitic acid and stearic acids—the most abundant saturated fatty acids. The effects of glycerol conformation, cis and trans configuration of double bonds, chain-length mismatch, and chirality of asymmetric TAGs on polymorphism and binary phase behavior are discussed.

2 Binary phase behavior of saturated-unsaturated mixed-acid TAGs that contain cis-unsaturated fatty acids

Three typical mixing phases have been reported for the binary systems of TAGs:\(3\): (i) solid solution phase, (ii) eutectic phase, and (iii) molecular compound (MC) formation. A solid solution phase is defined as two components being miscible at all concentration ratios in both the liquid and solid phases. A solid solution phase is formed when two component TAG molecules exhibit structural similarity and affinitive molecular interactions, such that the component molecules randomly occupy the same crystallographic positions. On the contrary, when two component molecules are immiscible, eutectic equilibrium is obtained. When the eutectic point shifts along the solidus to an endpoint, the resulting phase is said to be monotectic. The formation of a MC is a very special case, as it is only formed at clearly defined compositions through specific molecular interactions among the component TAG molecules.

The formation of MCs was observed in binary mixtures between symmetric saturated-oleic diacid TAGs, such as SOS/OSO\(^{12, 13}\) and POP/OPO\(^{14}\) (SOS: 1,3-di-stearoyl-2-oleoyl-glycerol; OSO: 1,3-dioleoyl-2-stearoyl-glycerol; POP: 1,3-dipalmitoyl-2-oleoyl-glycerol; OPO: 1,3-dioleoyl-2-palmitoyl-glycerol). Phase diagrams of the SOS/OSO and POP/OPO binary mixtures are shown in Fig. 1(a) and (b). In each mixture, the MC was formed at a concentration ratio of 1:1\(^{12, 13}\). The most stable form of MC was the \(\beta\) form, represented as \(\beta_c\) in the phase diagrams. The phase diagram of the SOS/OSO mixture revealed two monotectic juxtaposed phases of \(\beta_{SSO}/\beta_c\) and \(\beta_c/\beta_{SSO}\) (Fig. 1(a))\(^{13}\). The phase diagram of the POP/OPO mixture also exhibited two monotectic phases, \(\beta_{POP}/\beta_c\) and \(\beta_c/\beta_{POP}\) (Fig. 1(b))\(^{14}\).

The formation of MCs was also observed in some binary mixtures between symmetric and asymmetric saturated-oleic diacid TAGs, such as SOS/SSO\(^{15}\) and POP/PPO\(^{16}\) (SSO: 1,2-di-stearoyl-3-oleoyl-rac-glycerol; PPO: 1,2-di-palmitoyl-3-oleoyl-rac-glycerol). The most stable form for symmetric SOS and POP was the \(\beta\) form, while it was the \(\beta’\) form for asymmetric SSO and PPO\(^{15, 16}\). As shown in Fig. 1(c) and (d), the phase diagram of the POP/PPO mixture exhibited two monotectic phases of \(\beta’_{POPO}/\beta_c\) and \(\beta_c/\beta’_{POP}\). Two eutectic phases of \(\beta’_{POPO}/\beta_c\) and \(\beta_c/\beta_{POPO}\) were observed in the diagram of the SOS/SSO mixtures in the most stable form, along with two monotectic phases of \(\alpha’_{SSO}/\alpha_c\) and \(\alpha_c/\alpha_{SSO}\).

![Fig. 1](image)

Fig. 1  (a) Phase diagrams of SOS/OSO\(^{12, 13}\), (b) POP/OPO\(^{14}\), (c) SOS/rac-SSO\(^{15}\), (d) POP/rac-PPO\(^{16}\). (P: palmitic acid, O: oleic acid, S: stearic acid)
TAGs POP, OPO, PPO, SOS, SSO and OSO formations of TAG crystals were tuning fork and chair structure was converted from triple in the TAGs that form MCs. Interestingly, the chain-length type, as shown in Fig. 2. White circles, black circles, and zigzag lines represent oxygen atoms, glycerol carbon atoms, and hydrocarbon chains, respectively. Mechelen et al. solved the $\beta_a$ and $\beta_2$ crystal structure models of POP and SOS from high-resolution synchrotron powder diffraction data using the direct-space parallel tempering program FOX and refining with the Rietveld module GSAS. The symmetric POP and SOS revealed the tuning fork-type glycerol conformation and a triple chain-length structure that consists of an unsaturated zone in between two saturated ones. By contrast, due to the asymmetry in the fatty acid structures of PPO, the glycerol conformation was depicted as chair-type.

Since the solvent molecules could potentially alter the formation of MC crystals, it is necessary to observe the MC crystals in solution phase. In fact, it is of practical significance for the fractionation procedure in dry and solvent methods. Ikeda et al. analyzed the phase behavior of the binary mixtures of POP/OPO and POP/PPO, including a model solvent of n-dodecane. The $\beta$ form of the MC was always observed in solutions (50\%, 20\%), even in a dilute solution including 2\% POP + OPO (POP + PPO) and 98\% n-dodecane. These results indicate that specific molecular interactions must occur between POP and OPO and between POP and PPO molecules to create the MC crystals, even under the influence of solvent molecules.

To determine the molecular-based driving force for MC formation, studying the phase behavior of another binary mixture, Sat-O-Sat/O-O-Sat (Sat: saturated fatty acid; O: oleic acid), has attracted significant attention. The binary phase behavior of POP/rac-OOP (1,2-dioleoyl-3-palmitoyl-rac-glycerol) has been studied by Zhang et al. In addition, noting that most of the previous studies have been conducted using racemic asymmetric mixed-acid TAGs, the mixture of SOS/sn-OS (1,2-dioleoyl-3-stearoyl-sn-glycerol; sn: stereo-specifically numbered), in which sn-OS is optically active, was also examined and compared. However, no MC formation was observed in either of the mixtures. The phase diagrams are shown in Fig. 3. It is clear that both the two mixtures POP/rac-OOP and SOS/sn-OS are immiscible, except for the concentration ranges for each component of less than 20–30\%, where either minor component is incorporated as an impurity in crystalline phases of the major component. The phase behavior of the SOS/sn-OS mixtures in Fig. 3(b) was quite similar to that of POP/rac-OOP in Fig. 3(a), and was characterized as peritectic.

The potential MC structure models of POP/OPO, POP/PPO, and POP/OOP, with double chain-length structures, are depicted in Fig. 4. As indicated by the arrow in Fig. 4, the significance of a parallel direction for the glycerol groups was evidenced in the MC formation of POP/OPO and POP/PPO. Furthermore, the MC conformation of POP/OPO enables the oleoyl and palmitoyl chains to create sep-

### Table 1 Polyomorphc forms of some major saturated-unsaturated mixed-acid triacylglycerols and molecular compounds.

| Saturated-unsaturated mixed-acid Triacylglycerols$^a$ | Polymorphic forms |
|-----------------------------------------------------|------------------|
| POP                                                 | $\alpha$-2, $\gamma$-3, $\delta$-3, $\beta'$-2, $\beta$-3 |
| PPO                                                 | $\alpha$-3, $\beta'$-2, $\beta$-3 |
| OPO                                                 | $\alpha$-2, $\beta'$-2, $\beta$-3 |
| OOP                                                 | $\alpha$-2, $\beta$-3 |
| SOS                                                 | $\alpha$-2, $\gamma$-3, $\beta'$-3, $\beta$-3 |
| SSO                                                 | $\alpha$-3, $\beta$-3 |
| OSO                                                 | $\alpha$-2, $\beta'$-2, $\beta$-3 |
| sn-OOS                                              | $\alpha$-3, $\beta$-3 |
| sn-PPO (sn-OOP)                                     | $\alpha$-2, $\beta'$-3 |
| POS                                                 | $\alpha$-2, $\delta$-3, $\beta'$-3, $\beta$-3 |
| SLS                                                 | $\alpha$-2, $\gamma$-3 |
| SRS                                                 | $\alpha$-2, $\gamma$-3, $\beta'$-3 |
| SES                                                 | $\alpha$-2, $\beta'$-2, $\beta$-2 |
| SSE                                                 | $\alpha$-2, $\beta'$-2, $\beta$-2 |
| SEE                                                 | $\alpha$-2, $\beta'$-2, $\beta$-2 |
| PEE                                                 | $\alpha$-2, $\beta'$-2 |
| PEP                                                 | $\alpha$-2, $\beta'$-2 |
| PPE                                                 | $\alpha$-2, $\beta'$-2 |
| EPE                                                 | $\alpha$-2, $\beta'$-2, $\beta$-2 |

Molecular Compound
- MC of POP/OPO: $\alpha$-2, $\beta'$-2, $\beta$-2
- MC of POP/PPO: $\alpha$-2, $\beta'$-2, $\beta$-2
- MC of SOS/OSO: $\alpha$-2, $\beta'$-2, $\beta$-2
- MC of SOS/SOS: $\alpha$-2, $\beta'$-2, $\beta$-2

For simplicity, multiple $\beta'$ and $\beta$ forms ($\beta_2$, $\beta_2'$, $\beta_3$, $\beta_3'$) are represented by $\beta'$ and $\beta$. Polymorphic forms with double or triple chain-length structure are presented as $\alpha$-2, $\gamma$-3, $\beta'$-2.

$^a$ P: palmitoyl, S: stearoyl, O: oleoyl, R: ricinoleoyl, L: linoleoyl, E: elaidoyl (data based on previous research)\(^{2,15\text{--}25}\).

$^{15}$ $\beta_{\text{SOS}}$. In each mixture, the MC was formed at a concentra-

tion ratio of 1:1. The presence of oleic acid moieties is commonly observed in the TAGs that form MCs. Interestingly, the chain-length structure was converted from triple (for the component TAGs POP, OPO, PPO, SOS, SSO and OSO) to double (for molecular compound)\(^{15\text{--}16}\).

The potential structural models of $\beta_{\text{POP}}$, $\beta_{\text{OPO}}$, and $\beta_{\text{PPO}}$ are depicted in Fig. 2. The two typical glycerol conformations of TAG crystals were tuning fork and chair type, as shown in Fig. 2. White circles, black circles, and zigzag lines represent oxygen atoms, glycerol carbon atoms, and hydrocarbon chains, respectively. Mechelen et al. solved the $\beta_a$ and $\beta_2$ crystal structure models of POP and SOS from high-resolution synchrotron powder diffraction data using the direct-space parallel tempering program FOX and refining with the Rietveld module GSAS\(^{26\text{,}27}\).

The symmetric POP and SOS revealed the tuning fork-type glycerol conformation and a triple chain-length structure that consists of an unsaturated zone in between two saturated ones. By contrast, due to the asymmetry in the fatty acid structures of PPO, the glycerol conformation was depicted as chair-type\(^{16}\).

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To determine the molecular-based driving force for MC formation, studying the phase behavior of another binary mixture, Sat-O-Sat/O-O-Sat (Sat: saturated fatty acid; O: oleic acid), has attracted significant attention. The binary phase behavior of POP/rac-OOP (1,2-dioleoyl-3-palmitoyl-rac-glycerol) has been studied by Zhang et al.\(^{24}\) In addition, noting that most of the previous studies have been conducted using racemic asymmetric mixed-acid TAGs, the mixture of SOS/sn-OS (1,2-dioleoyl-3-stearoyl-sn-glycerol; sn: stereo-specifically numbered), in which sn-OS is optically active, was also examined and compared. However, no MC formation was observed in either of the mixtures. The phase diagrams are shown in Fig. 3. It is clear that both the two mixtures POP/rac-OOP and SOS/sn-OS are immiscible, except for the concentration ranges for each component of less than 20–30\%, where either minor component is incorporated as an impurity in crystalline phases of the major component. The phase behavior of the SOS/sn-OS mixtures in Fig. 3 (b) was quite similar to that of POP/rac-OOP in Fig. 3 (a), and was characterized as peritectic.

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arate leaflets, with stabilized aliphatic chain-chain interactions. With regard to POP/OOP, in case 1, it causes destabilization due to the coexistence of oleoyl and palmitoyl chains in both the leaflets. This differs from POP/PPO, in which the coexistence of oleoyl and palmitoyl chains are limited to one leaflet (case 1 and case 2). In case 2 of POP/OOP, the oleoyl and palmitoyl chains are placed in separate leaflets. However, this model could cause additional destabilization of the glycerol conformation and methyl end stacking. Therefore, the MC formation of POP/PPO and POP/OPO mixtures appears to be the most influenced by the contribution of glycerol conformation. The fact that the SOS/sn-OOS mixture was immiscible, being unable to form an MC like the SOS/OSO and SOS/SSO mixtures, can be explained by the same mechanism.  

With a basic understanding of the MC formation mechanism, the phase behaviors of the binary mixtures of OPO, PPO, and OOP were recently examined systematically by Bayés-García et al. It should be noted that OPO, PPO, and OOP are the counterpart TAGs of POP, OOP, and PPO, in which the positions of palmitic acid and oleic acid interchanged.

The possible molecular compound models of these mixtures are presented in Fig. 5. Eutectic behavior was ob-
served in OPO/PPO, as predicted by the model, which is similar to POP/OOP. MC crystals were formed in the mixtures of OPO/OOP and PPO/OOP. However, the MC crystals of OPO/OOP and PPO/OOP occurred only under metastable conditions, tending to separate into their component TAGs to form eutectic mixture systems.

Taking into account the proposed model of the MC, it can be assumed that the glycerol conformation of OPO/OOP was probably converted from the less stable chair-type OPO to the more stable tuning fork-type during stabilization (case 1), or from the less stable tuning fork-type of OOP to the more stable chair-type (case 2).

The proposed structural model of the PPO/OOP MC is depicted with the chair conformation of the glycerol groups and separate chain packing of the palmitoyl and oleoyl chains, which may increase the packing coefficient. However, experimental results indicate the metastability of the MC PPO/OOP. Bayés-García et al. suggested that the metastability is probably due to the racemicity of PPO and OOP. The importance of chirality for understanding their mixing behaviors was thus evidenced.

In addition, solid solution phase was also observed in some binary mixtures of saturated-unsaturated mixed acid TAGs. Roussset et al. studied the binary system of two major cocoa butter-component TAGs, POS and SOS. The phase behaviors of various polymorphic forms of sub-α, intermediate forms, and stable β forms were examined. The phase diagram illustrated in Fig. 6(a) indicates a solid solution between POS in β-3 form and SOS in β1-3 form with complete miscibility.

Takeuchi et al. studied the binary mixture of SLS/SOS (SLS: 1,3-distearoyl-2-linoleoyl-sn-glycerol). As shown in Fig. 6(b), the solid solution phases were observed in the metastable α and γ forms in all concentration ranges. However, an α-melt-mediated transformation into β and β2 resulted in the formation of immiscible phases in the concentration ranges of SLS below 30%.

### 3 Polymorphism and mixing behavior of enantiopure and racemic TAGs

The chirality of TAGs is important for understanding the mixing behavior of saturated-unsaturated mixed-acid TAGs. However, few studies have compared the structural properties of enantiomers and racemic mixtures of chiral TAGs. Schlenk crystallized racemic POS, as well as the antipodes, and found that the former yielded β crystals, while the pure enantiomers crystallized in the β′ form instead of the β form. Craven et al. reported that the enantiopure 1,2-bisdecanoyl-3-palmitoyl-sn-glycerol is β′-stable and the racemic bisdecanoyl-1(3)-palmitoyl-rac-glycerol TAG is β-stable, while the compound formed was racemic (with a unit cell containing equal quantities of both

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*J. Oleo Sci. 67, (6) 679-687 (2018)*
the enantiomers.\textsuperscript{33} The mixture of enantiomers and racemic compound was eutectic. According to Craven, a model was proposed wherein each unit cell of the $\beta'$ form contained one enantiomer, while that of the $\beta$ form contained both enantiomers. The $\beta'$ form of enantiomers and the $\beta$ form of racemic mixture were eventually concluded to be a stereochemical phenomenon.

Recently, the crystallization and polymorphism of enantiopure 1-oleoyl-2,3-dipalmitoyl-sn-glycerol (S-OPP), 1,2-dipalmitoyl-3-oleoyl-sn-glycerol (R-PPO), and their binary mixtures were studied by Mizobe et al.\textsuperscript{23}. A basic feature of the mixture systems of S-OPP and R-PPO is its eutectic nature, due to the different polymorphic structures of the two enantiomers and the racemic compound of rac-PPO (shown in Fig. 7). Polymorphic forms of S-OPP and R-PPO had $\alpha$-2 and $\beta'$-3 forms, whereas rac-PPO contained $\alpha_{r}$-3, $\beta_{r}$-2, and $\beta'$-3. The melting point of pure enantiomers, $\beta'_{r}$-3 and $\beta_{r}$-3, was higher than that of racemic $\beta_{r}$-3 by 3°C. In all cases (pure enantiomers and racemic compound), the most stable form was found to be $\beta$-3, while $\beta$ was not crystallized, which is fairly different from POS and 1,2-bisdecanoyl-3-palmitoyl-glycerol\textsuperscript{23, 32, 33}. More experimental and modeling work is required to clarify the complicated crystal behavior of enantiomers and racemic compounds, with the driving force of racemic compound formation being the biggest concern. However, all of these results demonstrate the importance of the relationship between glycerol conformation and subcell packing.

Furthermore, as mentioned above, the phase behavior of SOS/sn-OOS was not significantly different from that of POP/rac-OOP due to its eutectic nature\textsuperscript{25}. However, the phase behavior of MC-forming mixtures, in which the racemic TAG is replaced by one enantiomer, are worth studying. For example, we can speculate that some differences exist between POP/Sn-PPO and POP/rac-PPO, as well as OPO/sn-OOP and OPO/rac-OOP. In the case of MCs in which both component TAGs are chiral, e.g. PPO/OOP, one possible explanation for their metastability could be the racemic compound formation of R-PPO/S-PPO and R-OOP/S-OOP, which is preferred over the $\beta$-form of PPO/OOP MC\textsuperscript{30}.

### 4 Polymorphism and mixing behavior of saturated-unsaturated mixed-acid TAGs that contain elaidic acid

As summarized in Table 1, the double bond configuration (trans or cis) of TAG plays an important role in the occurrence of polymorphic forms. The symmetric SES, PEP, and EPE, as well as the asymmetric ones (PEE, SEE, SSE, PEE), are packed in a double chain-length structure, similar to the trisaturated monoacid TAGs. In the series of TAGs containing elaidic acid chain, the replacement of stearic acid with palmitic acid shows a drastic conversion with respect to the relative stabilization of $\beta'$ and $\beta$. As reported by Elisabetti et al., $\beta'$ is the most stable in PEP (1,3-dipalmitoyl,2-oleoyl-rac-glycerol), EPP (1,3-oleoyl-2,3-dipalmitoyl-rac-glycerol), and PEE (1-palmitoyl-2,3,dielaidoyl-rac-glycerol), whereas $\beta$ is the most stable in SES (1,3-distearoyl-2-oleoyl-rac-glycerols), ESS (1,3-distearoyl-2,3-dielaidoyl-rac-glycerols), and SEE (1-stearoyl-2,3-dielaidoyl-rac-glycerols)\textsuperscript{22}. However, in the series of TAGs containing oleic acid chain, the replacement of stearic acid with palmitic acid did not show a drastic conversion with respect to relative stabilization. For example, the $\beta$ form was the most stable in both, symmetric SOS and POP, while the $\beta'$ form was most stable in asymmetric SSO, OOS, POP, and OOP.

It is interesting to note that the symmetric PEP had a stable $\beta'$ form, while SES had a stable $\beta$ form\textsuperscript{21}. The $\beta$-2 and $\beta'$-2 form structures of a series of mono-unsaturated TAGs were solved and compared with the corresponding fully saturated TAGs by Mechelen et al.\textsuperscript{34, 35}. It should be noted that the $\beta$-2 form of PEP (stable $\beta'$ form) is difficult to obtain, with the potential methods being through crystallization from a solvent, as reported by Lutton\textsuperscript{21}. According to the resolved $\beta$-2 structure of PEP and SES, the different chain lengths of PEP and SES lead to differences in the methyl end-plane shapes, as represented by the dotted
line in Fig. 8. Mechelen et al. suggested that the stepped methyl end-plane may explain the unusually lower melting point of β-2 PEP. According to the structural solution, all the β-2 forms (PEP, SES, PPE, SSE) crystallized in a tuning fork conformation, whereas all the β'-2 phase of these TAGs had chair conformations. Interestingly, β-2 form has been observed to be the most stable form of EPE (present work, unpublished). The results indicate that the occurrence of polymorphic forms of saturated-elaidic diacid TAGs appears to be the most influenced by the contribution of the chain length. More experimental and modeling work is required to understand the mechanism.

Binary phase behaviors of various saturated-unsaturated mixed-acid TAGs are summarized in Table 2. Understanding the phase behavior of these binary mixtures have high significance for the separation of high-melting and low-melting fractions of vegetable fats and oils, and for texture control of fat-based food products such as margarine and chocolate. Few mixtures of TAGs containing elaidic acid chain have been examined due to the adverse health effects of trans fatty acids. But in fact, clarifying the phase behavior of TAGs containing elaidic acid chain is important for the development of substitute for trans fat. Grootscholten et al. reported the solid solution phase of the SES/SSE mixture. However, the binary phase behavior of palmitic-elaidic diacid TAGs are yet to be verified. Taking into account the differences observed in polymorphism, we can assume a different mixing behavior between palmitic-elaidic diacid TAG mixtures and stearic-elaidic diacid TAG mixtures. Even small differences in the total chain length (e.g., PEP and SES), or a simple rearrangement of the chain position (e.g., PEE and EPE) have a significant effect on the polymorphism and mutual solubility of saturated-unsaturated mixed-acid TAGs.

Table 2  Binary phase behavior of saturated-unsaturated mixed-acid Triacylglycerols.

| Binary mixtures | Phase behavior                                      |
|-----------------|-----------------------------------------------------|
| POP/OPO         | Molecular compound                                  |
| POP/PPO         | Molecular compound                                  |
| POP/OOP         | Eutectic                                            |
| SOS/OSO         | Molecular compound                                  |
| SOS/SSO         | Molecular compound                                  |
| SOS/αn-OOS      | Eutectic                                            |
| SOS/SLS         | Solid Solution (α and γ) Eutectic (β’ and β)        |
| SES/SSE         | Solid solution                                      |
| OPO/OOP         | Molecular compound only in metastable state         |
| OPO/PPO         | Eutectic                                            |
| OOP/PPO         | Molecular compound only in meta stable state        |
| PEP/EPE         | –                                                   |
| PEP/PPE         | –                                                   |
| POS/SOS         | Solid solution                                      |
| SOS/POP         | SOS>50% eutectic, SOS ≤ 50% solid solution          |

Data based on previous research 6, 9, 11–16, 20, 24, 25, 30

Fig. 8  Methyl end-plane of (a) PEP and (b) SES. Step planes and steps at the methyl end-plane are marked by a dotted line.
5 CONCLUSIONS

The binary phase behavior of TAGs can be explored to help foster an understanding of the mixing behavior of complex fats and oils. In this review, recent research efforts on the crystal structure and binary phase behavior of saturated-unsaturated mixed-acid TAGs were summarized, with special emphasis on the stearic-unsaturated and palmitic-unsaturated diacid TAGs. The correlation between the molecular structure and mixing behavior of TAGs was discussed in order to explore the possibilities for engineering the nanostructures of fats and developing structured lipids.

The results indicate that intramolecular and intermolecular interactions are largely affected by the variation in molecular shape of the fatty acid moieties and their positions. The binary phase behavior of saturated-oleic diacid TAGs appears to be most influenced by glycerol conformation, whereas the binary phase behavior of saturated-elaidic diacid TAGs appears to be most influenced by the chain-length mismatch. The effect of chirality on the crystal structure and mixing behavior was evidenced. However, there remains much uncertainty, especially with regard to the structure of racemic compounds.

We expect that any future work will be carried out in the following areas. (1) Structural solution of chiral TAGs, racemic mixtures, and MCs in different polymorphic forms; (2) In situ observation of the transformation pathways and mixing behavior of enantiopure and racemic compound TAGs; (3) Research on the influence of external factors on mixing behavior (e.g. thermal treatment, additives, and application of shear).

ACKNOWLEDGMENTS

This work was supported by a grant from the National Natural Science Foundation of China (No. 31401661), Doctoral foundation of ZZULI, and Scientific Research Foundation for Returned Scholars, Ministry of Education of China.

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