Polymorphic Behavior of Gondoic Acid and Phase Behavior of Its Binary Mixtures with Asclepic Acid and Oleic Acid

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ABSTRACT: Molecular properties of polymorphic forms of gondoic acid [*cis*-$C_{20:1}\Delta 11\omega 9$ (GOA)] have been studied by X-ray diffraction (XRD), differential scanning calorimetry (DSC), optical microscopy, and Raman scattering, in comparison to those of six principal unsaturated fatty acids: oleic acid [*cis*-$C_{18:1}\Delta 9\omega 9$ (OA)], erucic acid [*cis*-$C_{22:1}\Delta 13\omega 9$ (ERA)], petroselinic acid [*cis*-$C_{18:1}\Delta 6\omega 12$ (PSA)], asclepic acid [*cis*-$C_{18:1}\Delta 11\omega 7$ (APA)], palmitoleic acid [*cis*-$C_{16:1}\Delta 9\omega 7$ (POA)], and elaidic acid [*trans*-$C_{18:1}\Delta 9\omega 9$ (ELA)]. In addition, phase behavior of binary mixtures of GOA and APA and OA was examined by XRD and DSC. The polymorphic structures of GOA are quite similar to those of APA, ERA, POA, and partly to OA. In particular, DSC and Raman scattering studies have shown that gondoic acid exhibits conformational disordering on heating at the ω-chain, a chain segment between the double bond and CH_3 group, as a transition from all-*trans* (γ form) to *gauche*-rich (α form) conformations. A miscible mixing phase was observed in the mixture of GOA and APA, yet eutectic phases were observed in the GOA and OA mixtures. This is a remarkable contrast because the binary mixture systems of varying combinations of *cis*-unsaturated fatty acids examined so far exhibited either eutectic nature or molecular compound formation. It is expected that specific molecular interactions between GOA and APA that originate from the equivalence of the length of the Δ-chain, the chain segment between the *cis*-double bond and COOH group, and also from the presence of the γ–α order–disorder transformation would be operating to form the miscible mixing phase.

JAOCS 74, 1153–1159 (1997).

KEY WORDS: Asclepic acid, differential scanning calorimetry, gondoic acid, oleic acid, phase behavior of binary mixtures, polymorphism in unsaturated fatty acids, X-ray diffraction.

Unsaturated fatty acids are important lipid molecules that play critical roles in functional activities of biological organisms, and also in fatty products (1). They occupy about one-half of all acyl chains in biomembrane phospholipids, promoting fluidity and permeability of the membrane through conformational flexibility of the acyl chains. Hence, the study of physical and chemical properties of unsaturated fatty acids has attracted much attention in biophysical sciences. The major factors that influence the physical and chemical properties of unsaturated fats and lipids are the number, position, and configuration of double bonds. Hence, it must be of the highest importance to elucidate molecular-level understanding of structure–function relationships of the unsaturated fatty acids. The authors have studied thermal and structural properties of principal unsaturated acids over the past 10 yr, dealing with single phases of oleic acid [*cis*-$C_{18:1}\Delta 9\omega 9$ (OA)] (2–5), erucic acid [*cis*-$C_{22:1}\Delta 13\omega 9$ (ERA)] (6–10), petroselinic acid [*cis*-$C_{18:1}\Delta 6\omega 12$ (PSA)] (11–13), asclepic acid [*cis*-$C_{18:1}\Delta 11\omega 7$ (APA)] (7,14), palmitoleic acid [*cis*-$C_{16:1}\Delta 9\omega 7$ (POA)] (9,15), elaidic acid [*trans*-$C_{18:1}\Delta 9\omega 9$ (ELA)] (16), and with binary mixture phases of OA/PSA, OA/APA (17), POA/APA (18), OA/ELA (16), OA/POA, and OA/myristoleic acid [*cis*-$C_{14:1}\Delta 9\omega 5$ (MOA)] (19).

Table 1 summarizes the molecular properties of six unsaturated fatty acids involving *trans*-type elaidic acid, together with thermal data of phase transitions. Several remarks are pertinent (20): (i) Two forms, called γ and α, are commonly present in POA, OA, APA, and ERA. The γ and α forms exhibit a reversible transformation, where aliphatic conformation of the ω chain transforms from ordered (γ) to disordered (α) on heating. Yet, the ordered conformation of the Δ-chain does not change, keeping an $O'_{//}$ subcell unchanged (10). Here, the ω- and Δ-chains refer to the segments of the aliphatic chains between a methyl end group and the double bond and the segment be-

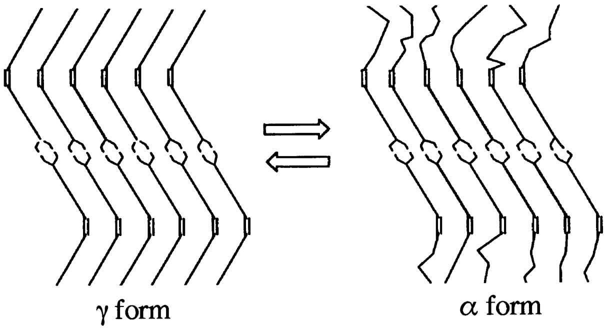

FIG. 1. A molecular model of γ–α transformation observed in oleic acid, erucic acid, asclepic acid, and palmitoleic acid.

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TABLE 1
Molecular Properties of Polymorphism in Principal *cis*-Monounsaturated Fatty Acids and Elaidic Acid

				Phase transformation			
Fatty acid	Form	Olefinic conformation[a]	Subcell	form	T_{tr}(°C)	Δ_{tr}(kJ/mol)	References
Palmitoleic	γ	S-C-S′	$O'_{//}$	$\rightarrow \alpha$	−18.4	7.5	9,15
	α	S-C-T	$O'_{//} + O_{\perp}$-like	Melting	2.0	32.1	
Asclepic	γ	S-C-S′	$O'_{//}$	$\rightarrow \alpha$	−15.4	7.8	7,14
	α	S-C-T	$O'_{//} + O_{\perp}$-like	Melting	13.8	39.8	
Oleic	γ	S-C-S′	$O'_{//}$	$\rightarrow \alpha$	−2.2	8.8	2–5
	α	S-C-T	$O'_{//} + O_{\perp}$-like	Melting	13.3	39.6	
	β_2	Unclear	// type	Melting	16.0	48.9	
	β_1	T-C-T	$T_{//}$	Melting	16.3	57.9	
Petroselinic	LM	Unique[b]	$O_{\perp}$	Melting[c]	—	—	11–13
	HM	S-C-S	$O_{\perp}$-like + $M_{//}$	Melting	30.5	47.5	
Erucic	γ	S-C-S′	$O'_{//}$	$\rightarrow \alpha$	−1.0	8.8	6–10
	α	S-C-T	$O'_{//} + O_{\perp}$-like	$\rightarrow \alpha_1$	31.2	5.4	
	γ_1	S-C-S	$T_{//}$	$\rightarrow \alpha_1$	9.0	8.9	
	α_1	S-C-S	$T_{//}$	Melting	34.0	54.0	
Elaidic	I	*trans*	$O_{\perp}$	Melting	44.5	53.6	16

[a] S-C-S′, *skew-cis-skew′*; S-C-S, *skew-cis-skew*; T-C-T, *trans-cis-trans*: S-C-T, *skew-cis-trans*.
[b] Torsion angles (157°, *cis*, −160°).
[c] Melt-mediated transformation to high-melting (HM) form; LM, low melting.

tween the double bond and a COOH group, respectively. Accordingly, transition temperature (T_{tr}) and enthalpy (ΔH_{tr}) decrease with decreasing length of the ω chain. Figure 1 illustrates a molecular model of the $\gamma \rightarrow \alpha$ transformation. (ii) Tight-packing forms, called β forms, appear singly in OA. X-ray structural analysis (21) has shown that β_1 reveals peculiar olefinic conformation *trans-skew-trans* and crystal packing, which are not present in other unsaturated fatty acids. (iii) Subcell structures with parallel arrangements are often present in the *cis*-unsaturated acids. This fact is reasonable because the parallel side-by-side packing is stable for molecules with a *cis*-configuration of the double bonds. However, peculiar subcells are present in PSA, whose *cis* double bond is placed closer to the polar COOH group. The LM form, with lower melting point, reveals the $O_{\perp}$ subcell, and thereby this form exhibits a curious olefinic conformation that is far different from the usual type of *skew-cis-skew′* (11,12). The overall structural properties of the LM form of PSA are identical to the B form of stearic acid. In the high-melting (HM) form, the subcell structure is $O_{\perp}$-like for the Δ chain, yet the ω chain has the subcell of $M_{//}$ (13). (iv) ELA has a single form with the $O_{\perp}$ subcell and has lost polymorphic diversity (16). This form again reveals the same crystal morphology as that of the B form of stearic acid. (v) The binary mixture systems of OA/PSA, OA/APA, POA/APA, and OA/ELA revealed eutectic phase behavior (17,18), yet the OA/POA and OA/MOA showed formation of molecular compounds (19). No mixture system that exhibits a miscible solid-solution phase has been observed.

The present work aims at analyzing molecular properties of polymorphic forms of gondoic acid [*cis*-$C_{20:1}\Delta 11\omega 9$ (GOA)] in comparison to those of the six unsaturated fatty acids displayed in Table 1. In addition, the phase behavior of the binary mixture of GOA and APA was examined. It may be worth referring to a concluding remark here that the polymorphic structures of GOA are quite similar to those of APA, ERA, POA and partly to OA, and that miscible mixing behavior was observed in the mixture of GOA and APA for the first time. Because the mixture systems of GOA with the other fatty acids were all of eutectic nature, it is expected that specific molecular interactions are operating between GOA and APA as elaborated in this study.

MATERIALS AND METHODS

The samples (>99.9% purity) were supplied by NOF Corporation (Amagasaki, Japan). Their purity was determined by the methods as fully described in previous reports.

As for the single-phase properties of GOA, melting and transformation were examined by differential scanning calorimetry (DSC) (Rigaku 8150, Tokyo, Japan). X-ray diffraction (XRD) patterns (Cu-Kα; $\lambda = 0.1542$ nm, Ni filter) were employed to obtain short- and long-spacing values (Rigaku). Raman spectra of the GOA crystals were measured with a Jasco R500 double monochromator (Jasco, Tokyo, Japan) with the 514.5 nm line (Ar^+ laser) as excitation. The scattered light was collected at right angles to the incident beam.

The crystallization from neat liquid with DSC was performed by melting the samples (*ca.* 10–20 mg) at 80°C over 10 min, so that no structure was retained in the melt phase. Then cooling was done with DSC computer programs at the rates of 2°C/min for heating, of 50°C/min for quenching, and of 2°C/min for slow cooling. The temperature of transformation or melting was defined as a crossing point of a heating base line and the maximal slope of an initial endothermic line (onset temperature). Crystallization from solution was done to obtain single crystals, with acetonitrile and decane as solvents. The crystals were grown at controlled temperatures below 0°C, so that thermodynamic equilibration was achieved uniquely for different polymorphic forms.

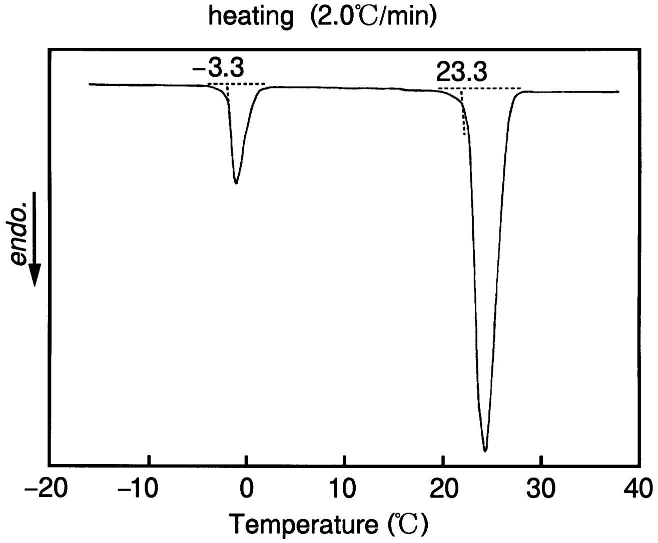

FIG. 2. A differential scanning calorimetry heating thermogram of gondoic acid.

As for the mixture systems, heating DSC thermograms were taken for different mixing concentration ratios, after melting of the mixtures at 80°C and quenching to –100°C. XRD spectra were also taken for the mixtures on heating at a rate of 2°C/min after quenching of the molten mixtures from 80 to –100°C.

RESULTS AND DISCUSSION

Polymorphic behavior of GOA. Figure 2 shows the heating DSC thermogram of GOA taken at a heating rate of 2°C/min. A small endothermic peak at –3.2°C and a large endothermic peak at 23.3°C correspond to transformations from a low-temperature form to a high-temperature form, and to melting of the high-temperature form, respectively. The enthalpy values of the two peaks were 9.0 and 49.7 kJ/mol. No other forms were detectable after thermal fluctuation below and above 23.3°C.

The XRD patterns and single crystal morphology observed below and above –3.2°C were quite different, as shown in Figures 3 and 4, respectively. The high-temperature form showed strong short-spacing peaks at 0.408, 0.388, and 0.369 nm and three weak peaks. The long-spacing value (001) was 4.41 nm. The strong peaks of the low-temperature form were 0.467, 0.397, 0.388, and 0.368 nm, and the long-spacing value (001) was 4.47 nm. The crystal morphology, as shown in Figure 4, of the high-temperature form, taken at 3°C in acetonitrile solution, was of truncated lozenge shape with interplanar angles of 130 and 115°. The low-temperature form, observed at –5°C in decane solution, revealed a rectangular shape. All data of DSC, XRD, and crystal morphology have evidenced that the low-temperature and high-temperature forms of GOA represent γ and α forms, respectively, both of which were also observed in OA (2), ERA (6), APA (14), and POA (15).

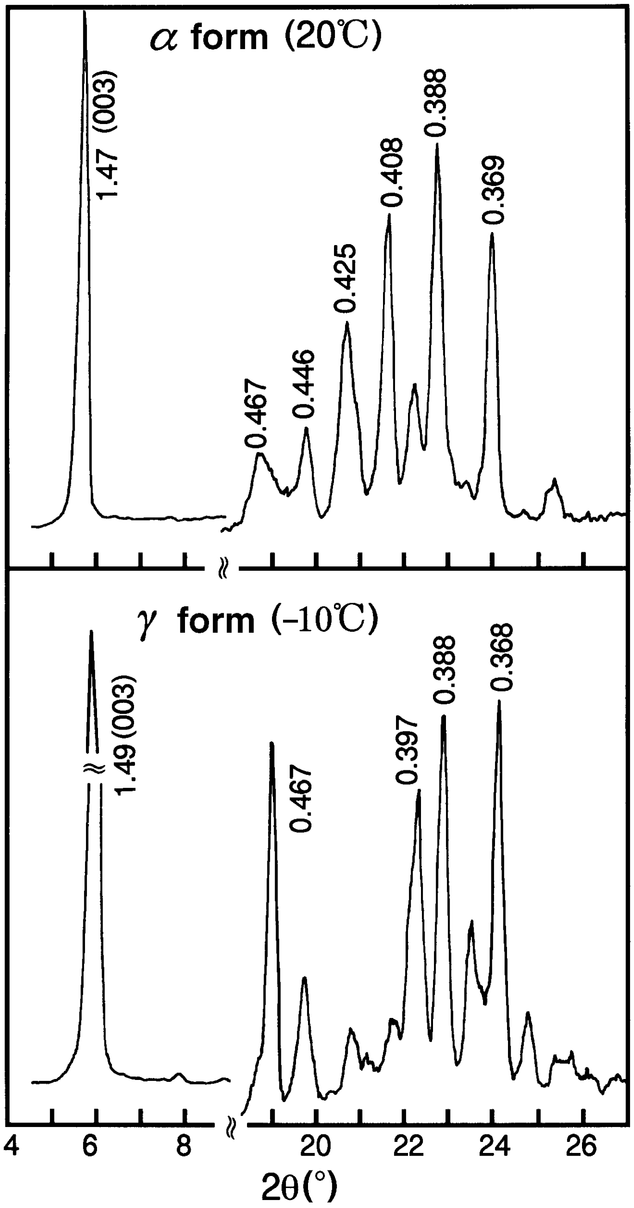

FIG. 3. X-ray diffraction spectra of α form and γ form of gondoic acid (unit, nm).

Figure 5 shows Raman scattering spectra around 1050–1150 cm^{-1}, taken at 4 and –10°C. Three strong scattering bands are revealed. Careful attention was paid to two bands of symmetric C-C stretching modes, νs, of the two forms shown by asterisks. These bands are sensitive to conformational ordering or disordering of the ω-chain and the Δ-chain of the unsaturated fatty acids. The third spectrum at 1066 cm^{-1} is due to asymmetric C-C stretching modes of the ω-chain and Δ-chain, which are less sensitive to the chain conformation.

Previous studies on OA (4), ERA (9,10), and POA (9,22) showed that the two bands denoted by arrows are due to νs (C-C) bands of the ω-chain at the higher frequency and Δ-chain at the lower frequency. The transformation from γ to α

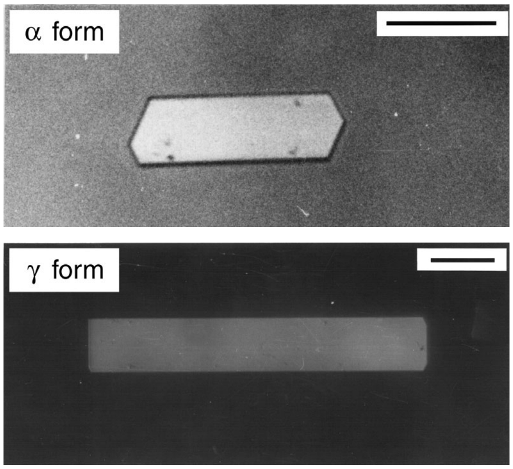

FIG. 4. Single-crystal morphology of α form and γ form of gondoic acid (scale bar, 100 mm).

resulted in a reduction in intensity of the νs (C-C) band of the ω-chain, keeping the intensity of the νs (C-C) band of the Δ-chain unchanged, because of the disordering at the ω-chain illustrated in Figure 1. The present study also showed the same result, that the νs (C-C) band of the ω-chain at 1125 cm^{-1} decreased in intensity by increasing the temperature from −10 to 4°C, while the band at 1108 cm^{-1} was not altered. For OA (4), the νs (C-C) bands of the ω-chain and the Δ-chain appeared at 1125 and 1095 cm^{-1}, respectively. The νs (C-C) bands of the ω-chain of GOA and OA appeared at the same frequency, while the νs (C-C) band of the Δ-chain of GOA is shifted toward a higher region by 13 cm^{-1} compared to OA. This is attributed to the difference in the length of the Δ-chain, which is longer in GOA than in OA by two CH_2 units. For further comparison, the corresponding spectra of ERA, having 13 and 9 carbon atoms in the Δ- and ω-chains, appeared at 111 8 cm^{-1} (Δ-chain) and 1125 cm^{-1} (ω-chain).

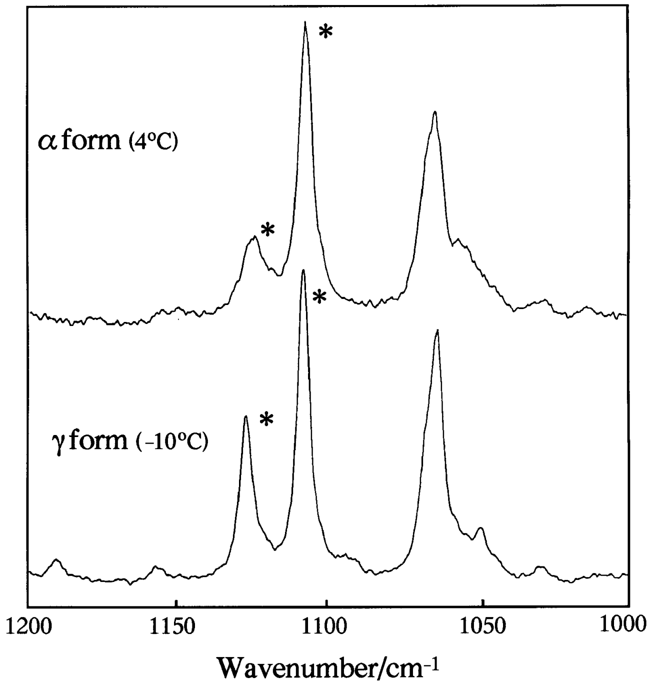

FIG. 5. Raman scattering C-C stretching bands of α form and γ form of gondoic acid.

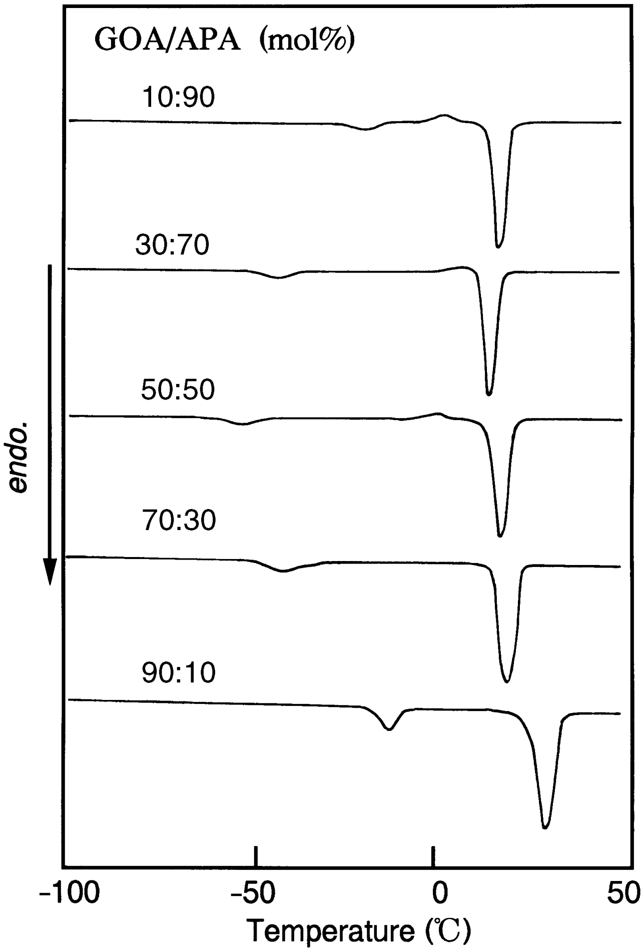

FIG. 6. Differential scanning calorimetry heating thermograms of gondoic acid (GOA)/asclepic acid (APA) mixtures.

From these results, we concluded that GOA reveals a typical polymorphic transformation in which the conformational disordering occurs at the ω-chain segment from all-*trans* (γ form) to *gauche*-rich (α form) hydrocarbon conformations. The values of T_{tr} (−3.2°C) and ΔH_{tr} (9.0 kJ/mol) are in good agreement with those of the transformations occurring in *cis*-unsaturated fatty acids with the same Δ-chain length as that of GOA (Table 1). It is quite interesting and indicative that the γ–α transformation occurs singly in the *cis*-unsaturated fatty acids where the numbers of hydrocarbon atoms of the ω-chain are odd, and are the same or shorter than those of the Δ-chains.

Phase behavior of binary mixtures of GOA/APA and GOA/OA. The heating DSC thermograms of the mixtures of GOA/APA with mol% ratios of 90:10, 70:30, 50:50, 30:70, and 10:90 are shown in Figure 6. As for the single phase of APA, T_{tr} (γ–α) and melting point of the α form are −15.4 and

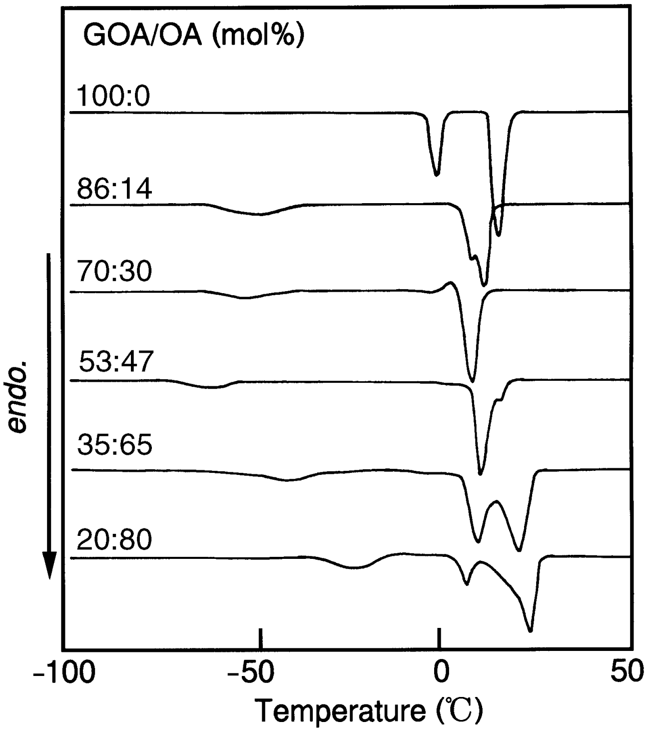

FIG. 7. Differential scanning calorimetry heating thermograms of GOA/OA mixtures. See Figure 6 for abbreviations.

13.8°C, respectively, as shown in Table 1. There are two endothermic peaks in each mixture. The higher-temperature peak, which corresponds to melting, slightly decreased with an increasing amount of GOA until GOA/APA = 30:70, yet it increased above the GOA concentration of 50 mol%. The small endothermic peak also decreased first and then increased, with an increasing amount of GOA, yet its variations are quite large compared to those of the melting peaks. There are some small exothermic peaks below the melting points, e.g., around 2°C, in the mixtures of GOA/APA = 10:90 and 50:50. The details of these peaks were not clear.

Figure 7 shows the DSC heating thermograms of mixtures of GOA and OA. Unlike Figure 6, large high-temperature peaks were split into two with increasing amounts of GOA, except for the mixture of GOA/OA = 70:30. The small low-temperature peak decreased first and then increased with an increasing amount of GOA, as also exhibited in Figure 6. The DSC behavior of Figure 7, involving the high-temperature and low-temperature peaks, was quite similar to that of eutectic mixtures of OA/PSA and OA/APA.

Figure 8 shows phase diagrams of the mixtures of (A) GOA/APA and (B) GOA/OA, which are based on the DSC thermograms of Figures 6 and 7. The remarkable difference between the two diagrams is revealed in the single melting behavior in the GOA/APA mixture. It shows the miscible nature of mixing of the two fatty acids, which was observed for the first time in a series of varying binary mixtures of principal unsaturated fatty acids. By contrast, the duplicated melting points of the GOA/OA mixtures, except for the eutectic point at GOA/OA = 70:30, show the eutectic nature of mixing, which has also been observed in OA/PSA, OA/APA, and OA/ELA.

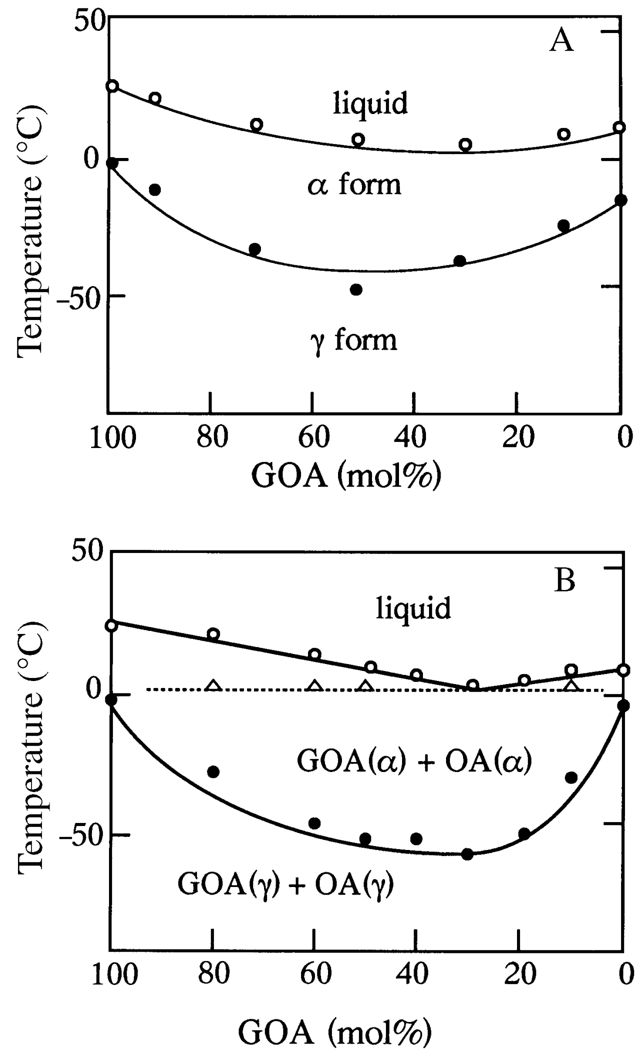

FIG. 8. Phase diagrams of the mixtures of (A) GOA/APA and (B) GOA/OA. See Figure 6 for abbreviations.

The miscible nature of the GOA/APA mixture was reinforced by the XRD patterns, as shown for the mixture of GOA/APA = 50:50 in Figure 9. Single peaks of the long-spacing spectra were detectable at −100 and −20°C. This is in remarkable contrast to the eutectic phase, which revealed two separated long-spacing spectra, as evidenced in OA/PSA and OA/APA (17). The long- and short-spacing spectra changed on heating around −50°C, where the γ–α transformation occurred in the mixed crystal of GOA and APA. The long-spacing values were 4.29 nm at −100°C and 4.35 nm at −20°C. The two values are almost equal to the average values of long spacings of the γ forms of GOA (4.42 nm) and APA (4.08 nm), and those of the α forms of GOA (4.49 nm) and APA (4.08 nm). The short-spacing patterns of γ and α forms of the mixed crystal are slightly different from those of GOA (Fig. 3). This may be ascribed to distortions in the subcell structures of the two forms in the mixed crystals, although no de-

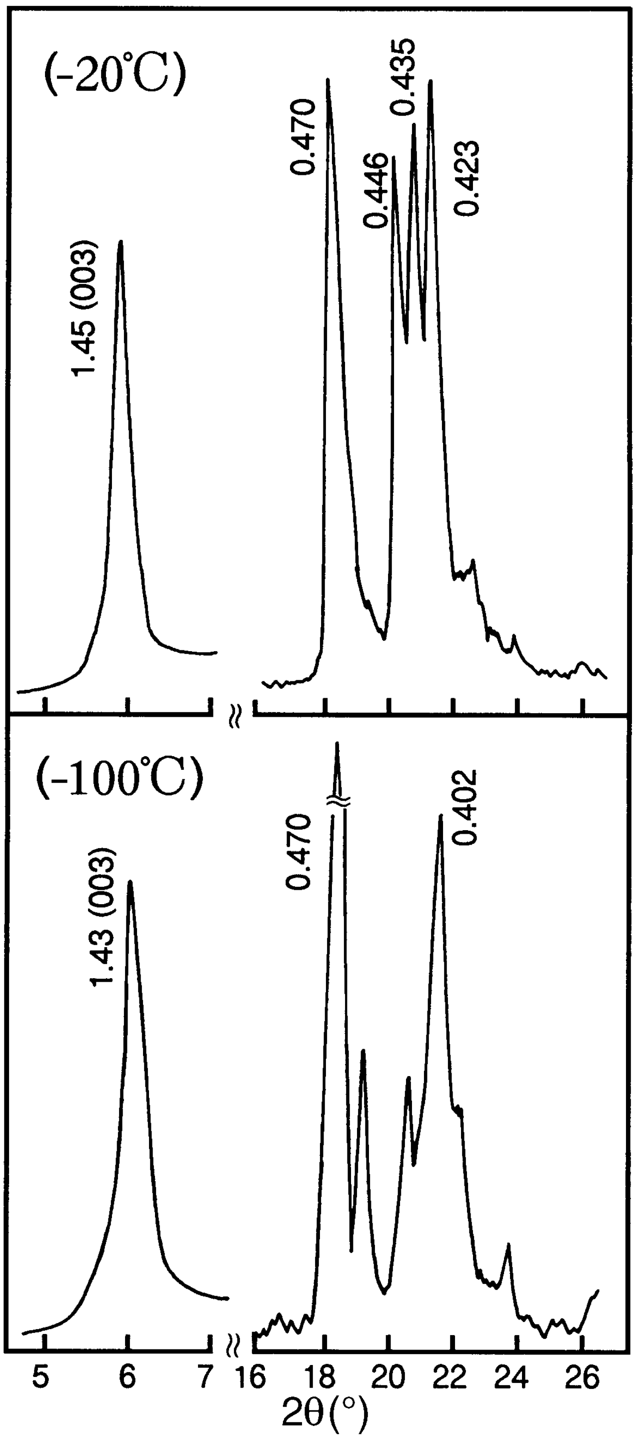

FIG. 9. X-ray diffraction spectra of mixtures of GOA/APA = 50:50 (unit, nm). See Figure 6 for abbreviations.

tails were available in the present study.

The miscible nature of the GOA/APA mixture is ascribed to specific molecular interactions that involve two aspects, the mutual length of the Δ-chain having 11 hydrocarbon atoms and the identical polymorphic structures in the low-temperature γ form and the high-temperature α form. As for the first aspect, the mixture of GOA/OA shares the same length of the ω-chain and the occurrence of the γ–α transformation. However, no miscible phase was revealed. In addition, the mixture of OA/APA, whose two components have the same whole chainlength and the γ–α transformation, also exhibited the eutectic property. This again suggests the importance of the equivalence of the Δ-chain length. Based on the structure model of the γ–α transformation depicted in Figure 1, one may deduce that the miscible GOA/APA mixed crystal might be formed by strong van der Waals lateral interactions in the interior portion of the dimer units in the crystal. The enthalpic deficit due to the difference in the ω-chain length may be minimized by the presence of the α form, where the ω-chain is conformationally disordered.

However, the importance of Δ-chain matching and the occurrence of the γ–α transformation contradict the experimental findings of the formation of molecular compounds observed in the mixture of POA/OA. This is because the mixture system of POA/OA exhibits various types of molecular compounds, although the POA and OA have the same Δ-chainlength and the same polymorphic γ–α transitions. The DSC study revealed the formation of the molecular compounds of OA_3POA_2 and of OA_1POA_2 in the α form and γ form, respectively (19). Therefore, further elucidation is necessary to interpret the complicated molecular interactions revealed in the phase behavior of the binary mixtures of *cis*-monounsaturated fatty acids.

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[Received October 1, 1996; accepted May 6, 1997]