The Influence of Polymorphic Form on Oxygen and Water Vapor Transmission through Lipid Films

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Fully-hydrogenated soybean and rapeseed oil was blended 2:1, layered on a filter paper support, adjusted to the desired polymorphic form and tested for resistance to transmission to oxygen and water vapor. Resistance to oxygen transport decreased upon conversion from α to the β' form and then increased substantially upon conversion to the β polymorph. This was attributed to the greater solid-state density of the β form, which likely affects resistance to gas flux by lowering the oxygen diffusion constant through the film. Resistance to water vapor transmission also decreased following the α to β' transition and then increased somewhat upon conversion to the β form. However, resistance of the β form did not exceed that of the α form at any of the temperatures tested. Moisture sorption characteristics of the various polymorphic forms apparently caused relative resistance values for water vapor flux to differ somewhat from those for oxygen flux.

Although lipid films are generally quite resistant to transmission of oxygen and water vapor, they differ greatly in their barrier properties. These differences are based on several factors (1,2). Of considerable importance are solid-state morphological characteristics, including crystal size, shape and intra- and intercrystalline arrangements; and, for water vapor transport, the relative polarity of the lipid molecule. The point of interest in this study is intracrystalline arrangement, commonly known as polymorphism.

In the solid-state, triacylglycerol molecules arrange themselves in bimolecular layers with hydrocarbon chains aligned in a parallel manner allowing interchain Van der Waals' interactions to be maximal. Molecules of monoacid triacylglycerols exist in a double chain-length, modified tuning-fork, or chair conformation with acyl chains in the #1 and #3 positions of a given molecule pointing in an opposite direction to the #2 acyl chain of the same molecule (3).

It is generally accepted that triacylglycerols can exist in three basic polymorphic states—designed alpha (α), beta prime (β'), and beta (β)—although multiple forms within these major classes have been reported (4-6). The polymorphic forms differ from one another in physical and thermodynamic properties, however, melting leads to identical liquid phases. Specifically, the polymorphs differ in melting point, density, heat of fusion, free energy, thermodynamic stability, and crystalline structure.

There are only two reports in the literature concerning the relationship between polymorphic form and transmission of water vapor through lipid films (7,8). We were unable to find any reports on 0_2-barrier properties of different lipid polymorphs. Lovegren and Feuge (8) evaluated the water vapor permeability of acetylated monostearin films that were solidified from the melt. Permeability was high initially, but decreased more than 100-fold after storage for 2 weeks at room temperature. The authors postulated that the reduction in permeability resulted from a polymorphic change in the lipid structure; however, this was not confirmed.

Landmann *et al.* (7) studied water vapor transmission through cocoa butter coatings. They also found that rapidly solidified cocoa butter was more permeable than cocoa butter which had been tempered. After 1 week of storage at room temperature, water vapor permeability decreased approximately 15-fold. This change was attributed to conversion of the cocoa butter to a more stable polymorphic state. Once again, specific polymorphic forms of the lipid were not unequivocally identified and the occurrence of polymorphic transitions was not positively confirmed.

Thus, carefully executed studies to conclusively elucidate the relationship between polymorphic form of a lipid and resistance to transmission of gases and vapors have not been performed, and it is the objective of this study to explore these relationships. Based on the behavior of synthetic polymer films, one might predict that the barrier properties of lipids would improve in the order of increasing stability and density, i.e., $\alpha \rightarrow \beta' \rightarrow \beta$ (9 11). Presumably, the α-polymorph would be least resistant to gas and vapor flux because acyl chain packing density is lower, and molecular mobility is greater, than in the β'- and β-polymorphs. As will be shown, this prediction is not accurate.

MATERIALS AND METHODS

The lipid material chosen for study was a 2:1 (w/w) blend of fully-hydrogenated soybean and rapeseed oils (Procter and Gamble, Cincinnati, OH), hereafter referred to simply as fully-hydrogenated oil (FHO). The iodine value was 0.33 and the fatty acid composition of the component tricylglycerols is presented in Table 1.

Film fabrication and establishment of the desired polymorphic form. A lipid film was prepared as described in a previous article (1), using Whatman No. 50 (W50) filter paper as a supporting matrix for the FHO. The finished FHO-W50 films contained 4.0 ± 0.2 mg lipid/cm^2 of film area ($\overline{X}$ ±SD). Approximately 75% of the FHO was embedded within the W50 filter matrix and the remainder was on one surface. Lipid content per unit film area was determined by weighing W50 filter discs before and after lipid application. The thickness of the FHO-W50 films was 0.11-0.12 mm.

To produce the α-polymorphic form, molten FHO was quenched at room temperature. To achieve the β' form, α films were tempered for 24 hours at 53 ± 1C. To produce the β form, β' films were tempered for 336 hours at 58 ± 1C. Films were maintained in a flat, horizontal position during tempering.

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TABLE 1

Fatty acid composition of a fully-hydrogenated blend of soybean and rapeseed oils (2:1).

Fatty acid type	% (w/w)
16:0[a]	7.5
18:0	71.3
20:0	3.4
22:0	16.8
24:0	0.6
others	0.4

[a]Fatty acid chain length:number of double bonds. Data from Procter and Gamble, Cincinnati, OH.

Differential scanning calorimetry (DSC). Lipid samples were accurately weighed (2-4 mg) into aluminum pans, which were then hermetically sealed. A thermal analysis was performed with a Perkins Elmer DSC and a heating rate of 5C/min was used. An empty aluminum pan was used as a reference and indium was used for calibration. Following completion of the heating curve, molten FHO was maintained at 87C for 10 minutes and the cooled to 27C at a rate of 5C/min.

X-ray diffraction. The polymorphic form of FHO was determined by powder x-ray diffraction. Solidified lipid was scraped off W50 filter supports and finely powdered for analysis. Copper K_α radiation (λ=1.5418 A) was generated by a Norelco x-ray diffractometer (Phillips Electronic Instruments, Mt. Vernon, NY) utilizing an accelerating voltage of 40 kv and a current of 30 mamp. A diffracted angle range of 15-18° 2θ was scanned at a rate of 1 deg/min.

Scanning electron microscopy (SEM). Surface appearance of FHO-W50 films was observed with a JEOL JSM-35C electron microscope (JEOL Ltd., Tokyo). Film pieces were mounted on aluminum stubs and coated with gold-palladium alloy (15 nm). A 10 kv accelerating voltage was utilized, with the electron beam directed at a 45° angle to the film surface.

Measurement of resistance to oxygen and water vapor transmission. Determination of oxygen and water vapor transmission rates through FHO-W50 films and calculation of resistances to oxygen [$r(O_2)$] and water vapor [$r(H_2O)$] transmission were performed as previously described (1,2). Units of resistance are $sec \cdot m^{-1}$.

Diffusion of O_2 through films generally obeys Fick's first law, i.e., the rate of transport is directly proportional to the O_2 partial pressure differential across the film and O_2 diffusivity is constant. However, when water vapor is diffusing through polar film matrices deviation from Fick's first law is common (2). Consequently, it is appropriate to report moisture barrier properties of FHO-W50 films as "effective" resistance [eff $r(H_2O)$], which is accurate under the environmental conditions employed (i.e., % of relative humidity, temperature). Similarly, temperature dependence of eff $r(H_2O)$ is expressed as an "apparent" activation energy (E_{app}) (2).

Seven replicates of each polymorphic form of FHO-W50 films were evaluated for $r(O_2)$ at 25, 30, 25, and 40C. Ten or more replicates of each film type were tested for eff $r(H_2O)$ at the same temperatures. To confirm the absence of polymorphic transitions during the determination, x-ray diffraction of the α and β' FHO films was performed before and after determination of O_2 and water vapor transmission rates at temperatures above 25C. Water vapor transmission data for the α-polymorph at 40C is not reported because partial transition to the β' form occurred during the time necessary to reestablish an equilibrium vapor flux (ca 5-10 hr.). This was not a problem for the determining $r(O_2)$ of the α-polymorph at 40C because the time required for equilibration was sufficiently short (ca 1 hr.).

The student's t-distribution was used to calculate 95% confidence intervals for $r(O_2)$ and eff $r(H_2O)$, and to evaluate the statistical significance ($P \leq 0.05$) between calculated activation energies of O_2 and H_2O transport (12).

RESULTS AND DISCUSSION

A fully-hydrogenated blend of soybean and rapeseed oil (FHO) was selected for study because of the ease with which all three polymorphic states could be initially formed and then retained under the time-temperature conditions used to measure oxygen and water vapor flux. Attempts were made to utilize relatively pure triacylglycerol samples, such as 90% tripalmitin and 90% tristearin, however, it was difficult to obtain the intermediate β' polymorph by tempering the α form. Exposure to elevated temperature resulted in direct conversion of the α form to the β form. Other investigators have reported this behavior with relatively pure triacylglycerols (13-15).

It is well known that the α and β' crystal states are more stable in mixed triacylglycerol preparations (13,15). The α and β' polymorphs of FHO were both stable for months at room temperature. Stabilities were sufficient to enable oxygen transmission rates for both polymorphs to be evaluated at temperatures up to 40C, and water vapor transmission rates of β' and α polymorphs to be determined up to 40 and 35C, respectively.

Cooling and heating DSC curves of FHO are presented in Figure 1. Cooling from the molten state yielded an exothermic minimum at 52.6C. The heating curve of the α-polymorph displayed three distinct endothermic peaks with maximums at 55.3, 60.7, and 63.5C. It was on the basis of the DSC heating curve that tempering conditions were selected for promoting polymorphic transformations. The $\alpha \rightarrow \beta'$ transition was performed at 53C, just below the endotherm corresponding to melting of the α-polymorph. The transformation of β' to β was accomplished at 58C, just below the second endotherm corresponding to melting of the β'-polymorph.

Powder x-ray diffraction patterns of the three polymorphic forms of FHO are shown in Figure 2. The patterns conform to the criteria established by Larsson (14) for identification of triacylglycerol polymorphs and are qualitatively identical to patterns of the α, β' and β crystal forms of fully-hydrogenated soybean oil reported by Dafler (16). The α form, obtained by rapid quenching of molten FHO at room temperature, displays a single, strong diffraction spacing at 4.13 A. Tempering of powdered α FHO at 53C for 2 hours yileded the β' form, distinguished by a pair of spacings at 3.82 and 4.21 A. Further tempering at 58C for 168 hours produced the stable β-

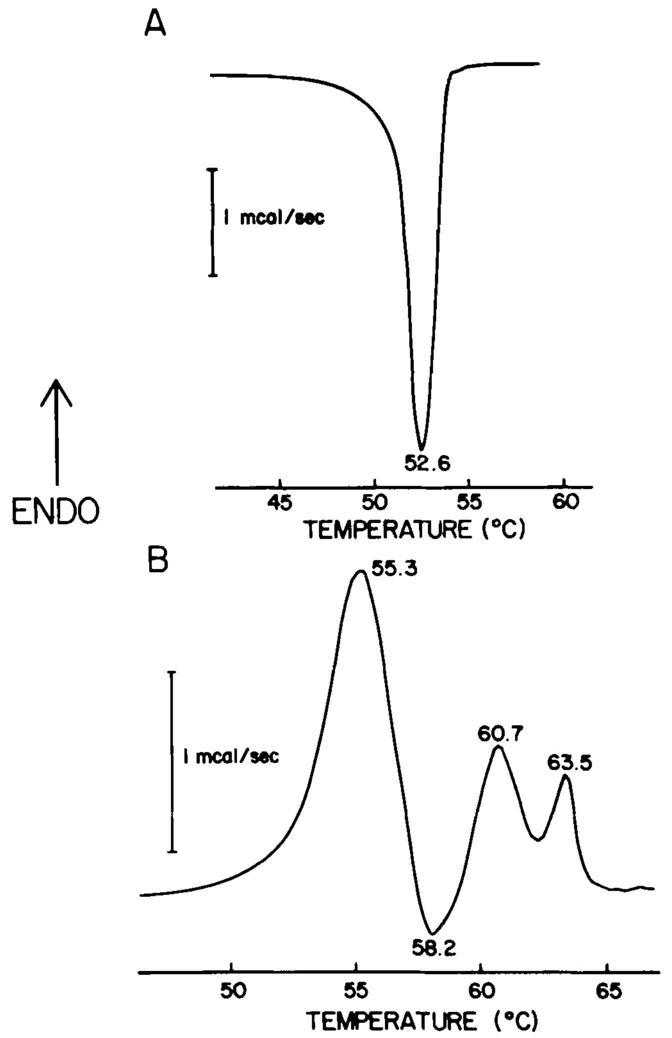

FIG. 1. DSC thermograms of FHO, a fully-hydrogenated blend of soybean and rapeseed oils (2:1). A. Cooling curve from molten lipid (rate=5C/min). B. Heating curve of the α-polymorph obtained following quenching of molten lipid at room temperature (rate=5C/min).

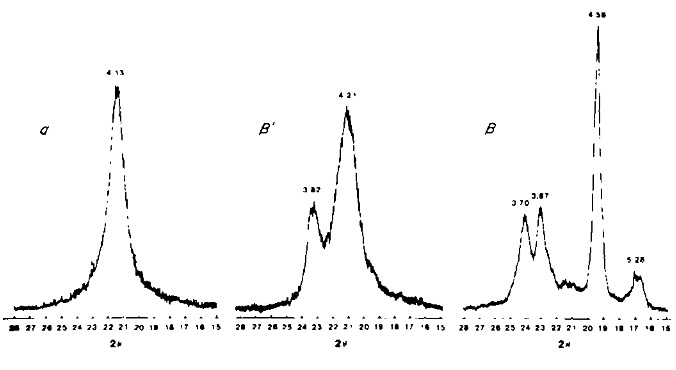

FIG. 2. Powder x-ray diffraction patterns of α, β', and β polymorphic forms of a fully-hydrogenated blend of soybean and rapeseed oils (2:1). The x-axis is the Bragg diffraction angle. Diffraction spacings are in units of Ångstroms.

polymorph, with diffraction spacings at 3.70, 3.87, 4.58, and 5.28 A.

Interestingly, the rate of polymorphic transformation was slower when FHO was coated on W50 filter supports than when it was tempered in powdered form. While powdered α FHO converted completely to the β' form in 2 hours at 53C (Fig. 2), FHO scraped from W50 filter paper (after subjecting the α FHO-W50 film to an identical tempering regime) remained in the α form, as idicated by the single diffraction spacing at 4.14A (Figure 3). After 12 hours at 53C, a diffraction pattern characteristic of the β' form was developing, but this development was not complete until 24 hours had passed (Fig. 3).

A similar phenomenon was observed for the β'→β transition. Tempering of powdered β' FHO for 60 hours at 58C yielded the characteristic β phase pattern, and transformation was complete after 168 hours (7 days) (Fig. 2). When coated on W50 filter paper, however, a tempering time approximately twice as long was required for the characteristic β-polymorph x-ray diffraction pattern to fully develop (Fig. 4).

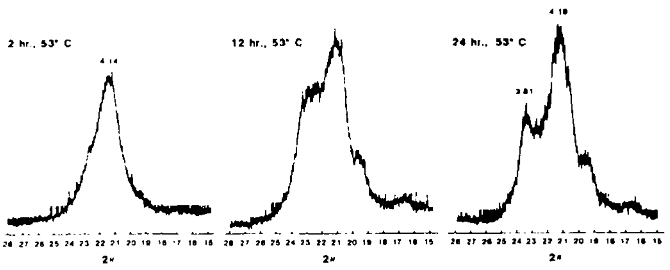

FIG. 3. Powder x-ray diffraction patterns of a fully-hydrogenated blend of soybean and rapeseed oils (2:1) scraped from W50 filters after tempering the lipid-W50 films at 53 ± 1C for 2, 12, and 24 hours. The lipid was in the α polymorphic form prior to tempering. The x-axis is the Bragg diffraction angle. Diffraction spacings are in units of Ångstroms.

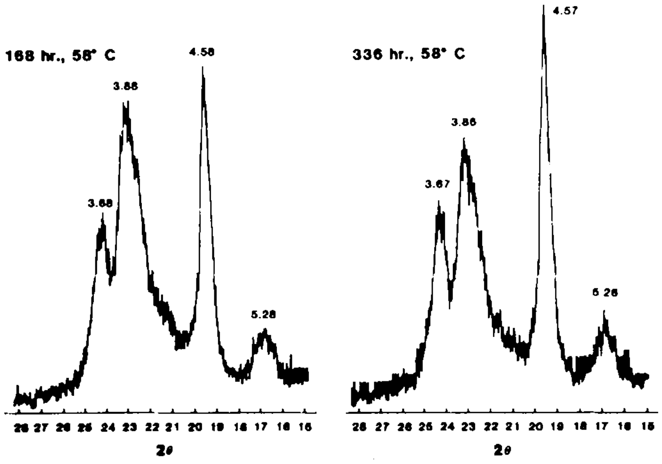

FIG. 4. Powder x-ray diffraction patterns of a fully-hydrogenated blend of soybean and rapeseed oils (2:1) scraped from W50 filters after tempering the lipid-W50 films at 58 ± 1C for 168 and 336 hours. The lipid was in the β'-polymorphic form prior to tempering. The x-axis is the Bragg diffraction angle. Diffraction spacings are in units of Ångstroms.

Evidently, the W50 filter matrix stabilized the lower-melting polymorphic forms of FHO. Enhanced stability against fracture was reported previously when lipids were embedded in a W50 filter matrix, as opposed to deposition on the surface (2). Fibers of the W50 filter paper interact sufficiently with the lipid to substantially increase resistance to fracturing, and this interaction may also hinder crystalline transformations by promoting increased rigidity of the lipid crystal structure.

Scanning electron microscopy (SEM). Surface structures of FHO-W50 films were observed with SEM. The α-polymorph film had a dimpled appearance with relatively large needle-like crystals scattered over the surface (Fig. 5). This surface appearance has been reported for other triacylglycerols, such as for a tristearin-W50 film (1). Why the needle-like crystals exist on the surface is not known conclusively; however, we suspect that this condition may represent incipient polymorphic transformation to the β' crystalline state. After tempering FHO-W50 films at 53C for 24 hours to convert α crystals to β', the number and size of needle-like crystals protruding from the surface was observed to increase substantially.

Oxygen barrier properties. Arrhenius plots illustrating the temperature dependence of r(O_2) of FHO-W50 films as influenced by polymorphic form are presented in Figure 6. Linear regression parameters and calculated activation energies of O_2 transport are listed in Table 2.

At 25C, the α FHO film yielded a r(O_2) of 74.1 x 10^7 sec·m^{-1}. The β' FHO-W50 film displayed a significantly lower r(O_2) of 64.9 x 10^7 sec·m^{-1} at 25C. This was somewhat suprising because the orthorhombic arrangement of acyl chains in the β' form is molecularly more dense than the hexagonal arrangement of the α form. Furthermore, acyl chain mobility is less in the β' form than in the α form (14,17). Resistance to gas and vapor transmission through synthetic polymer films increases as film density increases and chain mobility is reduced (9-11). Evidently, the slight increase in density and the cessation of acyl chain oscillatory movement that occur upon conversion of the lipid crystal state from α to β' are outweighed by other factors that influence O_2 transmission. Furthermore, a recent nuclear magnetic resonance study by Norton *et al.* (18) indicates that acyl chain mobility in the α-polymorph may be less than previously believed. Their results showed that only 10-20% of the triacylglycerol molecule actually retains rotational freedom in the α-polymorphic state. A mechanistic hypothesis explaining the lower r(O_2) of the β' film relative to the α will be proposed shortly.

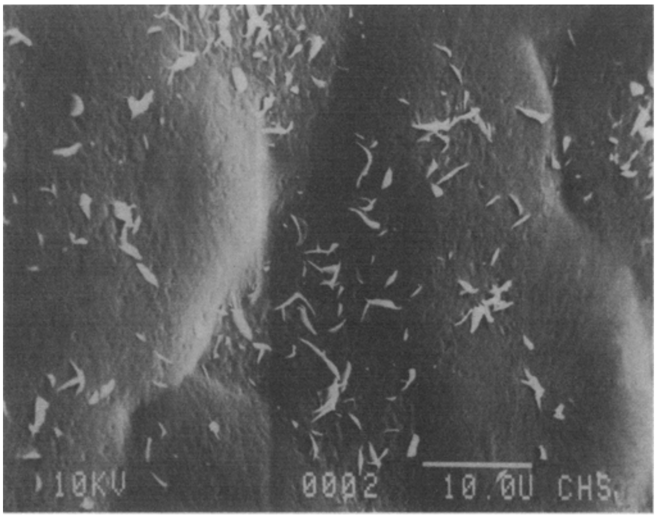

FIG. 5. SEM micrograph of the lipid surface of an α FHO[a]-W50 film. Amount of lipid per unit area of film was 4.0 mg/cm^2. Micrograph was taken at a 45° angle to the film surface. The white bar is a 10μm in length.

[a]Fully-hydrogenated blend of soybean and rapeseed oils (2:1).

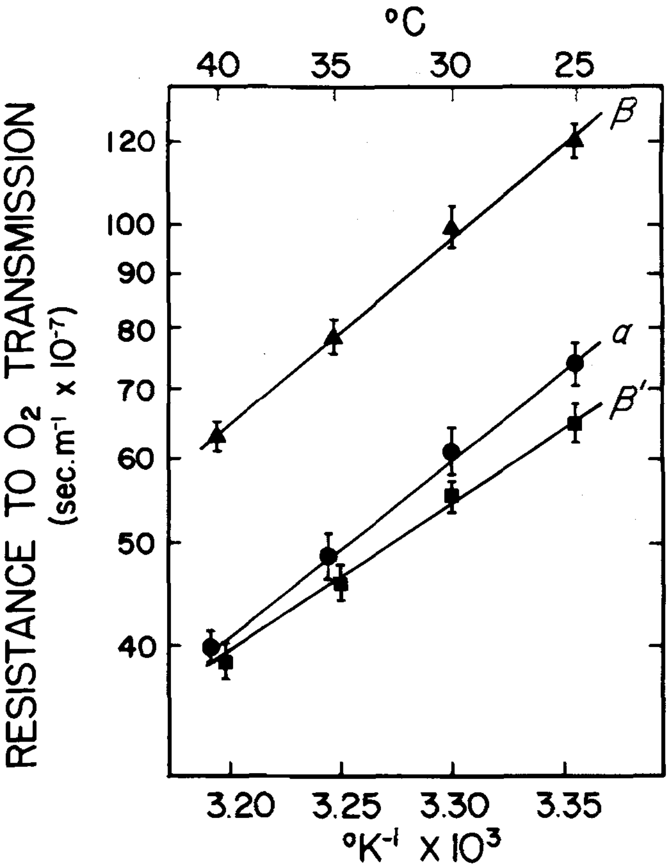

FIG. 6. Temperature dependence of the resistance to oxygen transmission [r(O_2)] of FHO[a]-W50 films as influenced by polymorphic form of the lipid: α (●), β' (■), and β (▲) polymorphic forms. Numerals on ordinate have been reduced by a factor of 1 x 10^7. Amount of lipid per unit area of film was 4.0 ± 0.2 mg/cm^2 ($\bar{X}$ ± SD). Each data point is the average of seven replicates. Vertical bars represent 95% confidence intervals for resistance. Least squares regression lines are drawn throughout each set of data. See Table 2 for regression equations and correlation coefficients.

[a]Fully-hydrogenated blend of soybean and rapeseed oils (2:1).

Resistance to O_2 transmission increased greatly following the transformation from β' to the stable β-polymorph (Fig. 6). The r(O_2) of β FHO-W50 at 25C was 120 x 10^7 sec·m^{-1}, approximately 60 and 85% greater, respectively, than the resistance of the α and β' forms.

Calculated activation energies (E) for O_2 transmission through FHO-W50 films increased in the order β'→α→β (Table 2), the same order as the increase in absolute resistance to gas flux. Thus, for O_2 transport through the various polymorphic forms of FHO, it appears that the

TABLE 2

Activation energies and parameters of regression equations for resistance of FHO-W50 films to oxygen and water vapor transmission as affected by temperature and polymorphic form[a]

Resistance[b] (sec·m^{-1})	Polymorphic form	Regression[c] constant	Regression[c] coefficient	Correlation coefficient	Activation energy[d]
					(E)
	α	3.21	1688.10	0.9992	7.7±0.3^{A}
r(O_2)	β'	4.05	1419.02	0.9985	6.5±0.2^{B}
	β	3.18	1759.83	0.9981	8.1+0.2^{C}
					(E_{app})
	α	11.45	-2045.34	0.9726	-9.1±1.9^{A}
eff r(H_20)	β'	9.44	1476.79	-0.9995	-6.7+0.7^{B}
	β	8.68	1221.03	-0.9990	-5.5+0.6^{C}

[a] FHO is a fully-hydrogenated blend of soybean and rapeseed oils (2:1), W50 is Whatman 50 filter paper. Lipid coverage was 4.0 ± 0.2 mg ($\bar{X} \pm$ SD)/cm^2 of W50 filter paper.

[b] Resistance to water vapor transmission is expressed in terms of effective resistance [eff r(H_2O)] and oxygen transmission is simply r(O_2).

[c] Regression equation is log r=b (1/T) + a. Regression lines are plotted in Figs. 6 and 7.

[d] Units of E for resistance to oxygen transmission and E_{app} (apparent activation energy) for resistance to water vapor transmission are kcal/mole; data are means ± SD; within each group (i.e., O_2 or H_2O), values with different superscript letters are significantly different ($P \leq 0.05$).

measured E can be interpreted as an energy barrier to O_2 permeation.

Water vapor barrier properties. Arrhenius plots indicating the temperature dependence of eff r(H_2O) of FHO-W50 films as influenced by polymorphic form are presented in Figure 7. Regression equations and apparent activation energies (E_{app}) of water vapor transport are listed in Table 2.

The α FHO film displayed an eff r(H_2O) of 40.2 x 10^3 sec·m^{-1} at 25C. Upon polymorphic transition from α to β', eff r(H_2O) of FHO-W50 films decreased significantly (Fig. 7), a result similar to that observed for r(O_2). The eff r(H_2O) of β' FHO-W50 films was 30.6 x 10^3 sec·m^{-1} at 25C, approximately 25% lower than that of the α-polymorph.

Transformation of β' to the β-polymorph significantly increased eff r(H_2O) of the FHO films, but to a lesser extent than was observed for r(O_2). The eff r(H_2O) of β FHO-W50 films was 38.7 x 10^3 sec·m^{-1} at 25C, a resistance not significantly different from that of the α films.

The negative slopes of the Arrhenius plots for eff r(H_2O) of FHO-W50 films (Fig. 7) have previously been ascribed to the moisture sorption behavior of the polar filter support (2). These slopes are responsible for the negative "apparent" activation energies (E_{app}) for the transport process (Table 2). While the negative E_{app} values are attributable to the W50 supporting matrix, the differences in magnitude of the E_{app} values for the three polymorphs must be a consequence of the lipid polymorphic form. In particular, the α FHO-W50 film displayed a substantially larger E_{app} (-9.1 ± 1.9 kcal/mole) than those of the β' and β films, meaning that eff r(H_2O) increased more rapidly with elevation of temperature. This result may be due to the healing of minor film defects or imperfections during the time period needed to reestablish an equilibrium vapor flux at each temperature above 25C (ca 5-10 hrs.). The α-polymorph has a slightly more flexible, plastic structure than the β' or β forms, which, presumably, would render the α films more receptive to healing of minor flaws at elevated temperatures. The plasticity of the α-polymorph is a consequence of the hexagonal packing mode, which enables fatty acid acyl chains to exhibit torsional mobility (19).

Mechanistic considerations relating to barrier properties of α, β', β polymorphs. One can specualte as to why the various polymorphic forms of the FHO films differed in resistance to oxygen and water vapor. There was a slight, but statistically significant, decrease in r(O_2) at 25C upon conversion of the α form to β' (Figure 6.) According to Bailey and Singleton (20), the β' polymorphic form of triacylglycerols has only a slightly greater density than that of the α polymorphic form; 1.017 and 1.014 g/cm^3 for the β' and α forms of tristearin, respectively. Therefore, the α to β' conversion is one of transition from a plastic, relatively flexible state to a nonplastic, rigid conformation of similar density. This loss of plasticity conceivably could render the film susceptible to formation of localized crystal and crystal boundary defects attendant with the polymorphic phase change. An increase in such crystalline imperfections would reduce r(O_2) by elevating slightly the O_2 diffusion constant through the β' triacylglycerol film. Furthermore, the time (24 hr) for the α to β' transition was almost certainly insufficient for tempering to have a significant bearing on the change in resistance (21).

A large increase in r(O_2) occurred during transition from the β' polymorphic form to β (Figure 6). This finding is in accord with initial expectations. The density of the β form of triacylglycerols (1.043 g/cm^3 for tristearin, ref. 20) is significantly greater than that of either the β' or α forms, and this property would tend to increase r(O_2) by decreasing the oxygen diffusion constant through the β film. Furthermore, the rate of the β' to β transformation was quite slow (336 hr at 58C) which would help minimize development of crystal defects during the polymor-

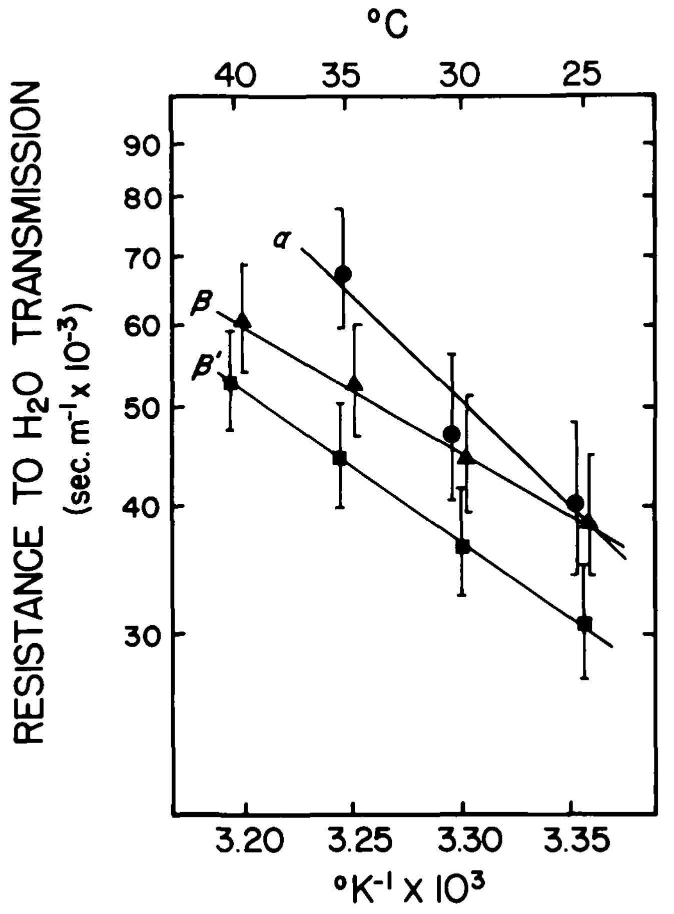

FIG. 7. Temperature dependence of the effective resistance to water vapor transmission [eff r(H_2O)] of FHO[a]-W50 films as influenced by polymorphic form of the lipid: α (●), β' (■), and β (▲) polymorphic forms.* Amount of lipid per unit area of film was 4.0 ± 0.2 mg/cm² ($\bar{X}$ ± SD). Each datum point is the average of at least 10 replicates. Vertical bars represent 95% confidence intervals for resistance. Least squares regression lines are drawn through each set of data. See Table 2 for regression equations and correlation coefficients.

[a]Fully-hydrogenated blend of soybean and rapeseed oils (2:1).

***Numerals on ordinate have been reduced by a factor of 1 x 10^3.**

phic transition and would also tend to heal minor defects that may have existed previously.

As was the case for oxygen transport, the eff r(H_2O) decreased significantly following conversion from the α form to β' (Figure 7). It is reasonable to invoke the same explanation for this change in eff r(H_2O) that was just proposed for the change in r(O_2) during the same transition.

Transition of the β' form to the stable β form caused the eff r(H_2O) to increase, but at any given temperature over the range 25-40C the resistance value for β never exceeded that of the α polymorph (Figure7). This result is contrary to the oxygen transport data and to initial expectations. The greater density of the β polymorph, as compared to those of the α and β' polymorphs, would lead one to suspect that the β polymorph would be most resistant of all polymorphs to vapor flux. This is logical since greater density would tend to be associated with a smaller diffusion constant for vapor flux. Furthermore, tempering effects would likely be significant during the β' to β conversion (336 hr at 58C to complete the conversion) and this would also tend to improve resistance of the film to vapor flux (21). Since the increase in resistance was far less than expected, it is likely that the hydration capacities (i.e., solubility coefficients) of the various polymorphs had an important bearing on the results obtained, with the α polymorph apparently being most resistant to hydration. It is well known that resistance to vapor flux is inversely related to solubility of the vapor in the film (2). We should mention, however, that one author (22) has suggested that the α polymorph should exhibit the greatest hydration capacity of the various polymorphs. This issue obviously cannot be resolved without measuring the actual moisture sorption properties of the various polymorphs.

Comparison of our results with those of Lovegren and Feuge (8) and Landmann *et al.* (7) reveal some important contrasts. These investigators both reported very large decreases in water vapor permeability (15 to 100-fold) through lipid films during tempering. The authors attributed this to polymorphic changes. However, this assumption was not confirmed experimentally. In light of our results, the reductions in apparent water vapor permeability reported in the aforementioned studies are far too large to be caused by polymorphic changes. Other factors, such as a simple healing of gross defects in the films, is a more likely explanation. In addition, the study by Lovegren and Feuge (8) involved films of acetylated monostearin, and this lipid absorbs appreciable quantities of water. Permeability was determined by the cup-method, in which films are sealed over a dish containing desiccant and the assembly is placed in an environment of controlled humidity. Weight gain of the dish is monitored and used to calculate water vapor permeability. It is probable that the high apparent water vapor permeability determined initially for the acetylated monostearin film was, at least in part, attributable to moisture sorption by the film rather than to transmission of water vapor.

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