Properties of 2-Oleodipalmitin, 2-Elaidodipalmitin and Some of Their Mixtures[1]

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ABSTRACT

The glycerides 2-oleodipalmitin (POP) and 2-elaidodipalmitin (PEP) were synthesized and their melting behavior and dilatometric properties were determined. Three mixtures of POP with PEP were examined. Five polymorphs of POP and four of PEP were identified by x-ray diffraction patterns. Rates of transformation of the lower melting polymorphs were, in general, quite rapid at temperatures just below their melting points. But transformation of unseeded POP to its highest melting form was slow and required several days at a temperature just below melting. Coefficients of expansion were determined for the highest melting polymorph and the liquid form of each triglyceride. Melting dilation was determined for the highest melting polymorph. Mixtures of POP with PEP exhibited different melting ranges depending on the tempering procedures and the composition, but even quickly-solidified mixtures tempered without melting to the highest melting range as they were slowly heated over a period of 2 hr. Slow cooling from the melt essentially segregated the components.

INTRODUCTION

The physical properties of 2-oleodipalmitin (POP) and 2-elaidodipalmitin (PEP) have been investigated by others. Jackson et al. (1), who prepared POP from trityl glycerol and acid chlorides, reported melting points. This same sample was used both by Daubert and Clarke (2), who concluded, on the basis of heating and cooling curves, that POP could exist in four polymorphs, and by Filer et al. (3), who obtained x-ray diffraction patterns of two polymorphs. Malkin and Wilson (4) examined POP and PEP prepared by the acylation of 1,3-dipalmitin and found five polymorphs of POP and four of PEP. Their melting points for POP agreed generally with those found by Daubert and Clarke, except that an additional, higher-melting polymorph was found. Lutton and Jackson (5) examined several POP samples and found on the basis of x-ray diffraction and thermal data four polymorphs of each sample, but the melting points differed somewhat from those reported by Malkin and Wilson and by Daubert and Clarke. Crowe and Smyth (6) reported on the basis of dielectric properties four polymorphs of POP. Their findings agreed with those of Lutton and Jackson, except that the melting point of their highest melting polymorph was 2.1 C lower. Craig et al. (7,8) determined the dilatometric properties of one form of POP. Kerridge (9) and Moran (10) determined the phase behaviors of mixtures containing POP. Lavery (11) examined the melting characteristics and polymorphism of POP by differential thermal analysis and x-ray powder photography. Minor and Lutton (12) found three polymorphs of PEP, only one of which corresponded with one of the four found by Malkin and Wilson.

The purpose of the current investigation was to synthesize pure POP and PEP and to determine their physical properties as well as those of several of their mixtures.

SYNTHESIS

Preparation of Intermediates

Technical-grade palmitic acid was esterified to obtain methyl palmitate, which was purified by distillation through a high efficiency column. No impurities could be detected in the final product by gas liquid chromatography (GLC).

1,3-Dipalmitin was synthesized by a modification of the directed interesterification procedure of Baur and Lange (13). Dry, powdered sodium methoxide was substituted for the xylene suspension, and methyl palmitate was substituted for the tripalmitin. The reacting mixture was main-

TABLE I

Interplanar Spacings of 2-Oleodipalmitin[a] Diffraction Pattern (Fig. 3)

A	B	C	D	E	F
16.05 W	46.1 S	36.9 VS	44.1 VVS	44.1 S^{-}	46.5 VW
4.13 VS	37.4 S^{+}	24.2 VW	22.6 VVW	31.5 VS	31.5 VS
3.97 VW	23.9 VW	14.13 W^{+}	14.60 M^{+}	21.5 VW	21.5 VVW
3.70 VVW	14.24 W	5.32 W	4.95 VW	14.36 W	12.44 W
3.49 VVW	5.27 W	4.78 S	4.31 VS	12.35 W^{+}	10.39 VW
	4.77 M	4.60 M[b]	4.00 VS	10.27 W	8.18 VW
	4.55 M[b]	4.55 M[b]		8.18 VW	6.86 VVW
	4.37 M[b]	3.95 VS		7.08 VVW	5.50 W^{+}
	4.23 M[b]	3.66 W		6.80 VW	5.24 W
	3.93 S	2.56 VVW		5.50 W	4.62 VS
	3.64 W			5.15 VW	4.09 M
	2.56 VVW			4.62 VS	3.98 M
				4.31 W	3.85 M
				4.07 M	3.75 S
				3.83 W	3.65 VW
				3.73 M^{+}	3.32 VVW
				2.60 VVW	2.60 VVW
					2.28 VVW

[a] Spacings in angstroms and relative intensity; VS, very strong; S, strong; M, moderate; W, weak; VW, very weak; VVW, very, very weak.

[b] High points of a broad band.

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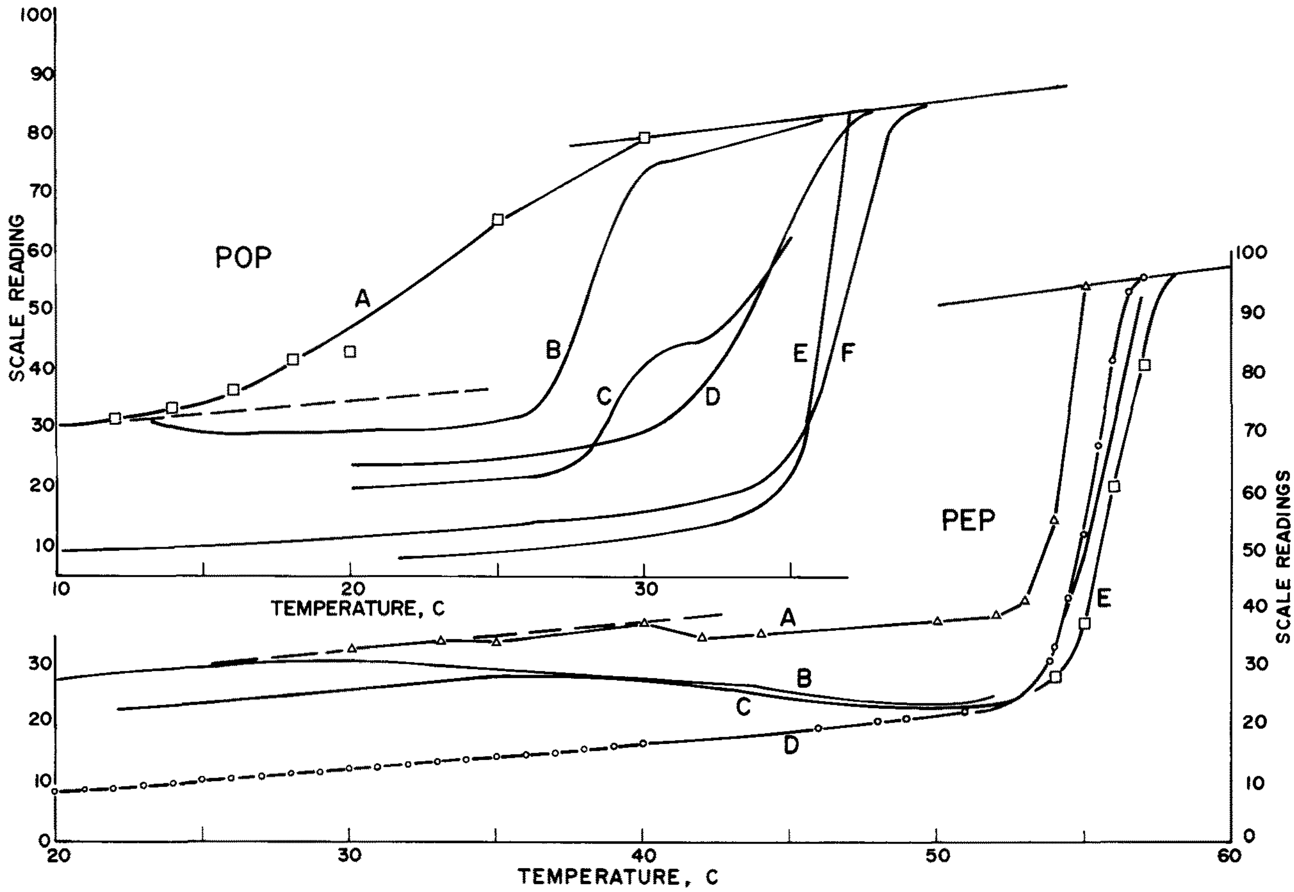

FIG. 1. Heating curves obtained with volumetric dilatometer. POP: A, solidified at 0 C, "thrust in" technique employed; B, solidified at 0 C, not tempered; C, solidified at 0 C and tempered one day at about 23 C; D, solidified at 0 C and tempered several days at about 23 C; E, solidified by slow cooling from 35 C, stepwise heating in melting range of curve; and F, solidified by slow cooling from 35 C, curve obtained by heating at a uniform rate of 0.33 deg/min. PEP: A, solidified at 0 C, thrust in technique employed; B, solidified at 0 C, not tempered; C, solidified at 0 C, tempered five days at about 23 C; D, solidified by slow cooling from 52 C; and E, solidified by slow cooling from 57 C.

tained at 50 C for 1 hr and then cooled slowly to room temperature. The following day the catalyst was deactivated with 1% glacial acetic acid in *n*-hexane. The 1,3-dipalmitin was purified by cooling a 10% solution in a mixture of *n*-hexane and ethanol (1:1 v/v) to 27, 10 and 0 C, successively, and removing the precipitate formed at each temperature. The fractions were analyzed by thin layer chromatography (TLC) employing silicic acid (Adsorbosil-1, Applied Science Laboratory, Inc.) and a developing solvent consisting of ethyl ether-petroleum ether-acetic acid (40:60:1 v/v), which gave excellent separation of the 1,3- and 1,2-diglycerides. The 27 and 10 C fractions were pure 1,3-dipalmitin, while the 0 C fraction contained only a small amount of 1,2-dipalmitin.

Methyl oleate of about 97% purity was derived from olive oil essentially by the method of Wheeler and Riemenschneider (14) and a portion was converted into oleic acid. Another portion was elaidinized with selenium and fractionally crystallized to obtain methyl elaidate of 92% purity. The methyl elaidate was converted into elaidic acid and further purified by fractional crystallization.

Oleoyl and elaidoyl chlorides were prepared by proven procedures employing oxalyl chloride.

Preparation of 2-Oleo- and 2-Elaidodipalmitin

1,3-Dipalmitin in a chloroform-pyridine solution was treated with a chloroform solution of the freshly prepared acid chloride (oleoyl or elaidoyl) using a modification of a procedure described previously (15). The esterification was started at room temperature. Then the temperature was increased gradually to 75-85 C, and the reaction was continued for about 3 hr. After removal of the byproducts and solvent, the triglyceride was purified by three crystallizations from acetone, 0 C for POP and 23 C for PEP. The 2-oleodipalmitin, which still contained color bodies, was further purified by bleaching in a hexane solution with neutral, activated clay, followed by passing the hexane solution through a silicic acid-diatomaceous earth column and another crystallization of the fat from acetone at 0 C.

Analysis of the purified POP and PEP by TLC revealed the complete absence of free fatty acids, monoglycerides and diglycerides. GLC analyses for fatty acid composition of the two triglycerides revealed that stearic acid was the only impurity, the fatty acids from POP containing 0.1% and those from PEP, 0.5%. The purities of the POP and PEP were concluded to be approximately 99.7% and 98.5%, respectively.

DILATOMETRIC MEASUREMENTS

A gravimetric dilatometer (16,17) was used to determine coefficients of expansion of the most stable polymorph and the liquid state and to determine melting dilation of the most stable polymorph.

A volumetric dilatometer (18) was used to establish the number of polymorphs and their rates of transformation. Three procedures were used. The first or "thrust in" procedure, which was used for transient forms, consisted of a rapid solidification of the sample, and sometimes a special tempering, just before the dilatometer was thrust into a

TABLE II

Polymorphs of 2-Oleodipalmitin and 2-Elaidodipalmitin From X-Ray Diffraction Patterns

POP Pattern, (Fig. 3)	Polymorph	Corresponding form
A	5	Alpha
B	3 and 4	Beta double prime, Lutton; beta prime, Malkin
C	3	Beta double prime, Malkin, Lavery
D	2	Beta prime-2, Lutton, Lavery
E	1, some 2	---
F	1	Beta
PEP Pattern, (Fig. 4)		
A	4	Alpha
B	3 and 4	---
C	3	Beta prime, Malkin, Lutton
D	2	Beta prime, Malkin, Lutton
E	1	Beta, Malkin

bath at a set temperature. Readings were taken at convenient intervals. In the second procedure, the dilatometer was placed in the bath which was heated at a uniform rate (ca. 0.33 deg/min). The dilatometer reading was recorded at one-degree intervals. This procedure gave good values for melting range when the range was not too narrow. The third procedure, useful when sharp melting was encountered, consisted of raising the temperature stepwise and waiting at each step until the dilatometer reading became constant.

Six dilatometric curves for POP are recorded in Figure 1. Curve A was obtained by the "thrust in" technique. For each point the sample was melted and then solidified in ice for 10 min before being placed in the constant temperature bath. Maximum expansion occurred within about 1 to 4 min. Apparently, the sample consisted of Forms 4 and 5 (see x-ray data). Some evidence of a very *transient melting* point around 12 C was obtained. When the untempered POP was placed in a bath held at about 12 C, expansion after about 1 min was higher than that represented by the solid line, followed by immediate contraction. This indicated a partial melting and resolidification. At 25 C or above, partial melting also occurred but resolidification was much slower.

Curve B was obtained by solidifying the melted sample in ice for 0.5 hr and then heating it at 0.33 deg/min. At 12 to 15 C the sample converted to a different solid form. This conversion was very rapid at 16 to 20 C when the thrust in technique was used, being essentially complete in 3 min. After conversion the POP melted over the range of 26-30 C (Form 3). Under the conditions used, a small amount was converted to the higher melting Form 2, as indicated by an unmelted portion above 30 C. Curve C, which indicated a mixture of Forms 2 and 3, resulted when the melted POP was solidified in ice and then tempered for one day at 22 C before the dilatometric curve was run at a uniform rate of heating (0.33 deg/min). Form 2, Curve D, was obtained on tempering for several days at room temperature.

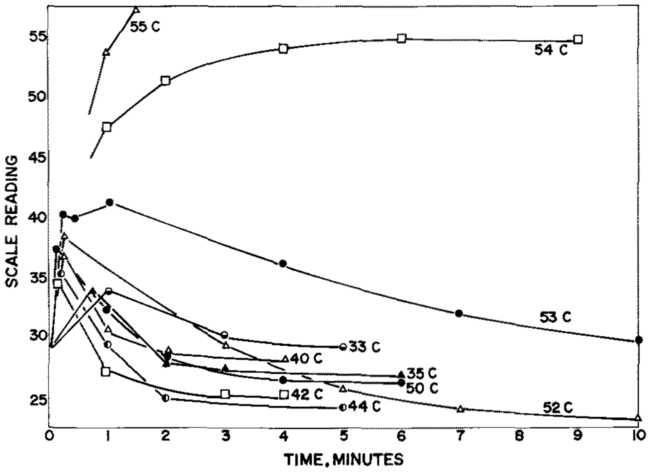

FIG. 2. Dilatometric curves of PEP quickly solidified at 0 C and thrust into a constant temperature bath at the indicated temperatures.

Curve F was produced on solidifying the POP slowly by allowing the bath to cool from 35 C and then heating the sample at a constant rate. The same cooling technique plus heating in a stepwise manner with equilibrium attained at each step produced Curve E.

The following values for POP were determined with the gravimetric dilatometer: melting dilation at 37.5 C, 0.0971 ml/g; coefficient of expansion, solid, -38 to 15 C, 0.000357 ml/(g)(C); coefficient of expansion, liquid, 40 to 50 C, 0.000833 ml/(g)(C).

Dilatometrically, the quickly solidified form of PEP appeared to be stable up to 27 C (Fig. 1). Heating above this temperature resulted in rapid conversion to the next-to-highest melting polymorph. Conversion to Forms 2 and 3 occurred without dilatometric evidence of melting; that is, the solid lines for Curves B and C never rose above the solid line for Curve A. Melting of Form 2 began at about 54 C.

The following values for PEP were determined with the gravimetric dilatometer: melting dilation at 55.4 C; 0.1239 ml/g; coefficient of expansion, solid, -38 to 0 C, 0.000394 ml/(g)(C); coefficient of expansion, liquid, 57 to 60 C, 0.000870 ml/(g)(C).

TABLE III

Interplanar Spacings of 2-Oleodipalmitin[a] Diffraction Pattern (Fig. 4)

A	B	C	D	E
51.9 VS	47.8 VS	44.8 VS	44.1 VS+	40.1 VS+
15.49 VW	14.97 W	14.72 W	22.1 VVW	22.9 W
4.22 VS	4.23 VS	4.35 W	14.72 M	14.59 VS+
	3.88 W	4.23 VS	8.75 VVW	11.04 VVW
		3.86 M	7.25 VVW	8.66 W
			4.36 S	7.19 W
			4.22 VS+	5.37 VW
			4.06 M	4.23 M
			3.83 S-	4.06 VW
			3.17 VVW	3.81 VS

[a] Spacings in angstroms and relative intensity; VS, very strong; S, strong, W, weak; VW, very weak; VVW, very, very weak.

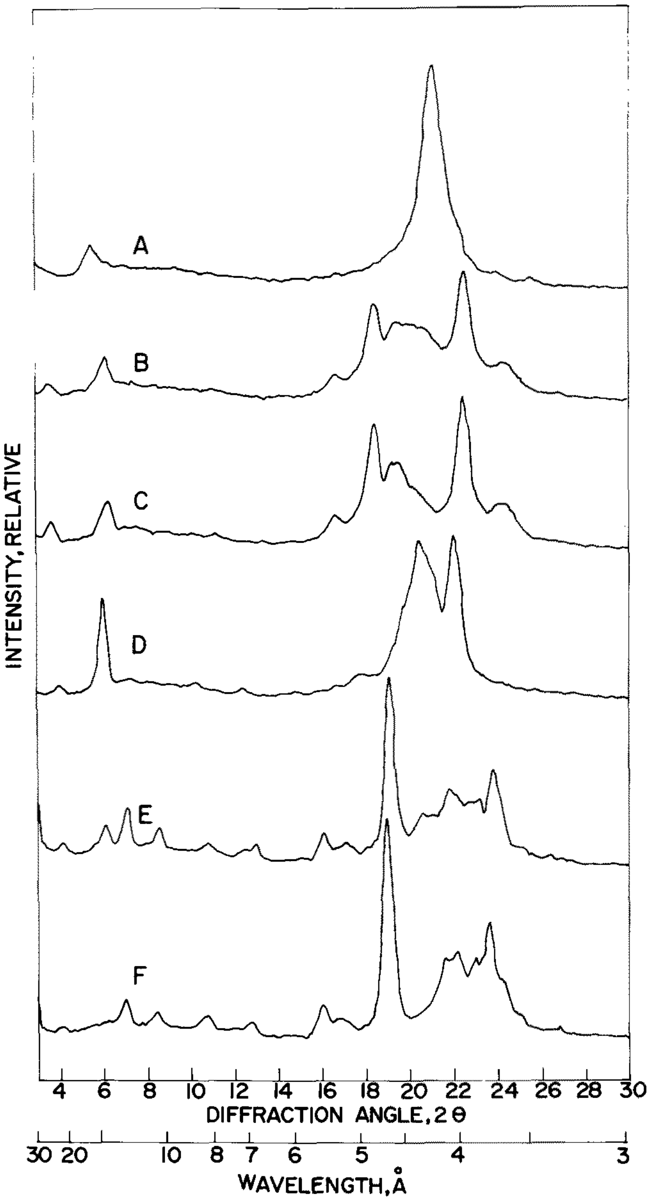

FIG. 3. X-ray diffraction patterns of POP: A, solidified below 5 C; B, tempered 10 min at 16 C; C, further tempered, 1 hr at 25 C; D, further tempered, 3 days at about 23 C; E, further tempered, several hr at 35 C; F, crystallized from acetone at 0 C.

The rate of transformation for the several polymorphs of PEP is indicated in Figure 2. The curves were obtained by the thrust in technique after solidifying the sample in ice water, and sometimes after holding it for a few minutes at 20 C. At temperatures of 33 and 35 C, expansion of the polymorph obtained on solidification at 0 C and conversion to a higher melting polymorph required less than 5 min. At 40 to 50 C, the appearance of a third polymorph is not definitely established. But at 52 C, a third polymorph has definitely appeared. While the temperature was increased, which speeds any given polymorphic transformation, the time to resolidify and contract to a more dense form increased to over 10 min and the density at 10 min was well below that of the next-lower polymorph. At 53 C evidence of a fourth polymorph appeared. The initial expansion at 53 C occurred in 15 sec, which was followed by a slight contraction over a period of 10 sec, a further expansion for 40 sec, and then a very slow contraction. At 54 C the PEP melted and then resolidified very slowly, indicating formation of the most stable polymorph.

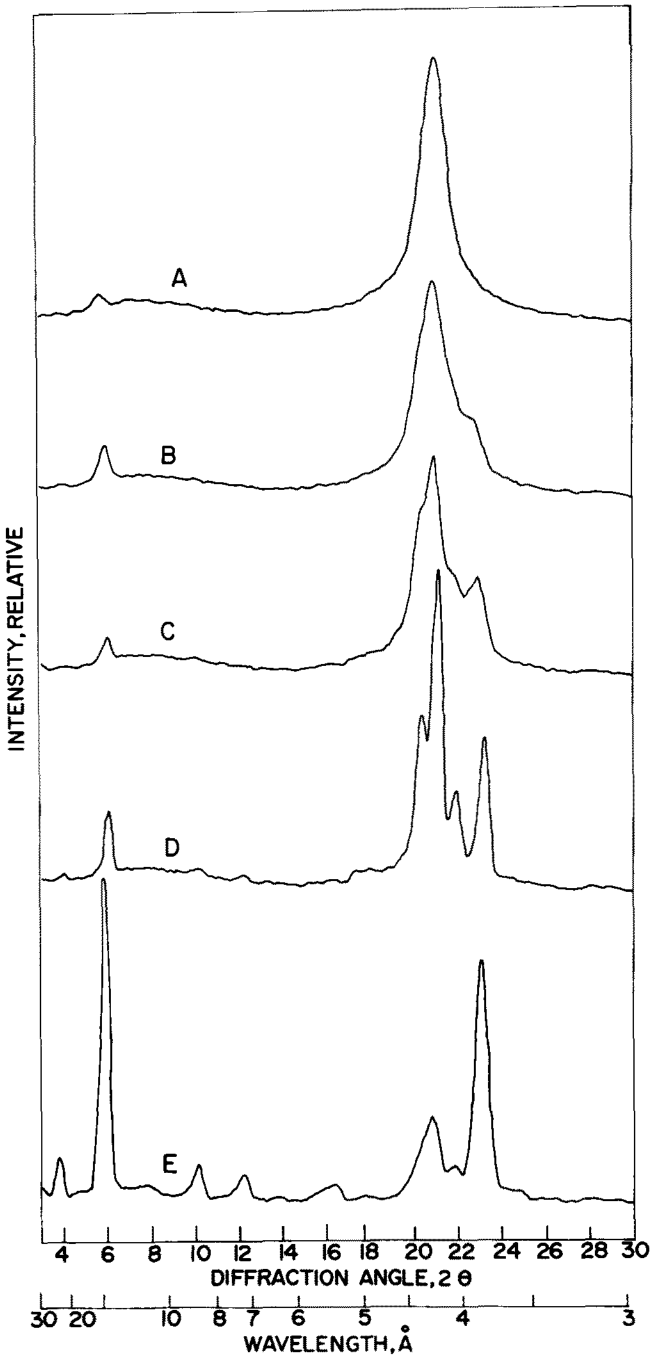

FIG. 4. X-ray diffraction patterns of PEP: A, solidified in ice water; B, tempered 10 min at 35 C; C, further tempered, 10 min at 42 C; D, further tempered, 2 hr at 52 C; E, crystallized from acetone at 23 C.

CAPILLARY MELTING POINTS

The capillary tube melting point of Form 1 of POP, obtained after crystallization of the compound from acetone at 0 C, was 37.2 C. A reproducible melting point for Form 2 could not be obtained. Depending upon the tempering procedure employed, the melting points ranged from 33.2 C to just below 37.0 C. The capillary melting point of Form 3, 29.4 C, was obtained after solidifying the POP in ice water and then holding it for a few minutes at 23 C. The melting point of Form 4, 20.8 C, was obtained by solidifying the POP in ice water and then plunging the capillary tube in a constant temperature bath. Also, the existence of Form 4 was indicated by an abrupt change in the rate of solidification. The melt in the capillary tube solidified in less than 10 sec at 20 C, but over 30 sec was necessary at 23 C.

PEP crystallized from acetone at 23 C, melted at 56.5 C (Form 1). Slow solidification from the melt resulted in a melting point at 56.0 C (mostly Form 2). Quick solidification in ice water and determination of the melting point by the thrust in technique gave a melting point at 53.5 C (Form 3). Thin films of quickly solidified PEP, such as the meniscus portion in the capillary tube, were found to melt and quickly resolidify at temperatures between about 41.6 and 52.6 C. According to the dilatometric data, quickly solidified PEP readily underwent a polymorph transformation at about 35 C without melting. Marked changes in the solidification rate in capillary tubes occurred at about 33 C indicating the existence of a polymorphic transformation at this temperature.

MIXTURES OF POP AND PEP

Three mixtures of POP and PEP (1:3, 1:1 and 3:1, by weight) were examined in volumetric dilatometers. Each of the mixtures exhibited three melting ranges. The lowest range was obtained immediately after solidification of the mixture in ice water. The crystal forms giving this lowest range were stable only below 15 C. The intermediate melting range was obtained after rapid solidification of the melt and tempering of the solid for 16 to 72 hr at room temperature, about 23 C. To obtain the highest melting range, the quickly solidified mixture was heated to incipient melting and slowly cooled; or the mixture was heated slowly (over 2 hr) to incipient melting. Actually, the mixtures containing 50% and 75% PEP, tempered to the highest melting range far more rapidly than indicated, only 2 or 3 min at a temperature just below incipient melting being required. The highest melting range for each of the POP-PEP ratios was found to be approximately as follows: 3:1, 31-47 C; 1:1, 38-51 C; 1:3, 44-54 C.

The mixtures appeared to melt at a more or less uniform rate over the melting range, provided the tempering was accomplished without melting. Slow cooling of a partially melted mixture promoted segregation of the components by the formation of relatively large and pure crystals of the compounds. Subsequent heating resulted in significantly independent melting of each component.

X-RAY DIFFRACTION PATTERNS

X-Ray diffraction data for POP and the interpretation have been reported heretofore (3-5,11), but there has been some disagreement. Lutton (19) suggested that triglyceride polymorphs be characterized by their short spacings, which are determined by cross-sectional structure, in the following way: alpha, 4.15, single strong line; beta prime, 4.2 and 3.8, two strong lines, sometimes more; beta, 4.6, strong line, usually strongest. "Sub" was used to identify the lower melting of two polymorphs having essentially the same short spacings.

Our x-ray diffraction patterns of POP were obtained with a sample crystallized from solvent and with a single sample tempered stepwise using the conditions developed in the dilatometric study. Melted POP was poured into the sample holder, covered with a microscope slide and an aluminum block containing dry ice was placed in contact with the glass slide. The solidified sample was kept below 5 C before and during exposure to the x-rays. Total elapsed time from solidification to completion of the x-ray exposure was about 1 hr. This quickly solidified polymorph had a single short spacing at 4.13 A and no long spacing below 51.9 A, the largest long spacing observable with the instrument used (Fig. 3 and Tables I and II). This polymorph corresponded with the alpha form reported by Lutton and Lavery, except that they found long spacings of 45 and 47 A, respectively. When the POP sample was tempered for 10 min at 16 C and then cooled again, the x-ray diffraction pattern had two long spacings, 46.1 and 37.4 A, and several short spacings appeared or intensified. Apparently, at this point the sample was a mixture of a transient form and the form obtained subsequently on further tempering for 1 hr at 25 C. The latter had no long spacing at 46.1 A and an intensified spacing at 37 A. Also, several short spacings decreased in intensity. The short spacings at 3.95 and 4.78 A were intensified by the two tempering steps. Our Form 3, dilatometric melting range, 26-30 C, yielded an x-ray pattern resembling that obtained by Malkin and Lavery for the beta double prime form. Additional tempering for 3 days at about 23 C yielded the polymorph, Form 2, corresponding to Lutton's beta prime-2 form. Further tempering at 35 C for several hours converted the POP mostly to the highest melting polymorph, whose pure state is represented by x-ray diffraction pattern F, Figure 3, obtained by crystallization from solvent.

X-ray diffraction and other relevant data for PEP are reproduced in Figure 4 and Tables II and III. The quickly solidified sample, which was stable for a short time at temperatures up to 33 C, gave the x-ray pattern of the alpha form obtained by Lutton, except that the long spacing was 51.9 A instead of the 45.5 A obtained by Lutton. Tempering this sample for 10 min at 35 C changed both the long and short spacings. Further changes occurred on additional tempering for 10 min at 42 C. Polymorph 3, pattern C of Figure 4, is believed not to be identical with either of the main polymorphs represented by patterns B or D. For example, the diffraction at 3.83 A, pattern D, is not the same as the diffraction at 3.86 A, pattern C, or 3.88 A, pattern B. Also, the intensity of the lines at approximately 14.7 A decreases in going from pattern B to C and then increases in going from pattern C to D, indicating changes in type of polymorph rather than changes in proportion. From the limited data given by Malkin and by Lutton, it was concluded that their beta prime polymorph corresponded with our polymorph 2 or 3. Malkin's beta polymorph could correspond with our polymorph 1, with some 2 present. No x-ray pattern similar to that of Lutton's beta form was found.

When the PEP sample giving x-ray pattern C, Figure 4, was tempered for 2 hr at 52 C a pattern with four sharp peaks in the short spacing region was obtained. This pattern was quite different from that given by the solvent-crystallized PEP, pattern E.

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J.J. Creely obtained the x-ray diffraction patterns.

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