[CONTRIBUTION FROM THE PROCTER & GAMBLE COMPANY, IVORYDALE, OHIO]

The Polymorphism of 2-Myristyldistearin, 2-Myristyldipalmitin, 1-Stearyldimyristin and 1-Palmityldimyristin

BY F. L. JACKSON AND E. S. LUTTON

In describing the polymorphism of the four mixed triglycerides of palmitic and stearic acids, Lutton, Jackson and Quimby[1] reported corrections of earlier work by Malkin and associates.[2] They showed, for instance, that 2-stearyldipalmitin has two and not four polymorphic forms, called alpha and beta prime according to a nomenclature based on X-ray pattern type.[3]

In the present paper are described the results of the re-examination of another small group of mixed glycerides previously reported by Malkin, *et al*,[2,4] The present group includes 2-myristyldistearin (SMS), 2-myristyldipalmitin (PMP), 1-stearyldimyristin (SMM) and 1-palmityldimyristin (PMM). These glycerides, besides being interesting in themselves, shed sidelights on SPS and SPP of the previously reported group of palmitic–stearic glycerides[1] and contribute to the general picture of the polymorphism of triglycerides.

For PMP, SMM and PMM only three forms have been found instead of the four reported by Malkin. The fourth, Malkin's vitreous state, could not be confirmed. The reporting here of four forms for SMS results from the discovery of a new beta prime-4 form. Such a structure was found by Malkin for other glycerides but not for SMS.

Experimental

The four mixed triglycerides were prepared from the corresponding mono- and diglycerides by reaction with myristyl chloride according to established methods of

TABLE I

ANALYTICAL CONSTANTS OF STARTING MATERIALS AND PRODUCTS

	I. V.	Saponification value		Hydroxyl value		% Mono-	M. p., °C.		
	Exp.	Exp.	Theory	Exp.	Theory	glyceride[5]	Exp.	Lit.	Ref.
Myristic acid	0.6	243.6	245				[a]		
1-Monopalmitin	.0	169	169.6			98.4	76.5	77	6
1-Monostearin	.1	156.3	156.4			101.9	81.5	81.5	6
1,3-Dipalmitin	.0	197.4	197.3	99	98	0.5	72.4	72.5	7
1,3-Distearin	.1	179.4	179.7	92	90	0.4	78.2	78	7
SMS		202.8	201.5				63.8	62.5	4a
								63.5	8
PMP		218.2	216.3				60.3	60.0	2a
SMM		215.8	216.3				56.4	56.0	4b
PMM		225.4	224.0				54.4	54 0	2b

[a] Myristic acid setting point, 53.93°; lit. value,[9] 53.65°.

TABLE II

DETAILED d/n VALUES FOR SMS, PMP, SMM, AND PMM

Long Spacings

	SMS				PMP		
(*hkl*)	*Alpha*-2	*Beta* Prime-2	*Beta* Prime-4	*Beta*-3	*Alpha*-2	*Beta* Prime-2	*Beta*-2
001	47.20 VS	43.8 VS		(62) VS	44.2 VS	43.7 VS	39.2 VS
002	23.9 VVW		42.5 VS	32.7 S+	22.3 VW	21.5 VS	19.75 W
003	15.92 S	14.5 M	28.1 W	22.1 M−	14.9 S	14.4 S	13.11 M
004			21.5 W	16.7 M			
005	9.57 VW			13.3 M			
006			14.2 M		7.46 VW		6.49 VW
007			12.1 W	9.40 VW			
008							
009			9.45 VW	7.44 VW			
0010			8.53 VW				
0011			7.70 VW	6.00 VW			
Average d.	47.6	43.7	85.0	66.3	44.6	43.3	39.2

---

(1) Lutton, Jackson and Quimby, THIS JOURNAL, **70**, 2441 (1948).

(2) (a) Malkin and Meara, *J. Chem. Soc.*, 103 (1939); (b) Carter and Malkin, *ibid.*, 577 (1939).

(3) Lutton, THIS JOURNAL, **70**, 248 (1948).

(4) (a) Malkin and Meara, *J. Chem. Soc.*, 1141 (1939); (b) Carter and Malkin, *ibid.*, 1518 (1939).

(5) Handschumacher and Linteris, *J. Am. Oil Chem. Soc.*, **24**, 143 (1947).

(6) Malkin, *et al.*, *J. Chem. Soc.*, 1628 (1936).

(7) Malkin, *et al.*, *ibid.*, 1409 (1937).

(8) Robinson, Roche and King, THIS JOURNAL, **54**, 705 (1932)

(9) Francis and Piper, *ibid.*, **61**, 578 (1939).

TABLE II (*Continued*)

	SMS				PMP		
(*hkl*)	*Alpha*-2	*Beta* Prime-2	*Beta* Prime-4	*Beta*-3	*Alpha*-2	*Beta* Prime-2	*Beta*-2
Short Spacings	4.13 VS		5.80 W	5.24 W	4.14 VS	5.40 W	5.28 W
	2.40 VW	4.25 S	4.33 S	4.61 S	2.40 VW	4.13 VS	4.59 VS
		4.11 S	4.03 S+	4.27 W		3.75 S	4.44 M
		3.78 M	3.77 VS	3.83 S		3.46 VW	4.02 M
		3.42 W	3.44 W	2.76 VW		3.08 VW	3.84 S[a]
		2.80 VW	3.24 W+	2.50 W+		2.80 VW	3.74 S[a]
		2.54 W	2.78 VW	2.38 W		2.54 W	3.59 W
		2.32 VW	2.53 W	2.28 W			3.42 VW
			2.47 VW	2.09 W			3.34 VW
			2.32 VW	1.90 VW			2.92 W
			2.22 VW				2.82 VW
							2.66 VW
							2.55 M
							2.42 M−
							2.31 VW
							2.10 VW
							1.93 VW

Long Spacings	SMM			PMM		
(*hkl*)	*Alpha*-2	*Beta* Prime-3	*Beta*-3	*Alpha*-2	*Beta* Prime-2	*Beta*-2
001	44.2 VS	41.2 VS	61.2 VS	42.8 VS	39.2 VS	37.9 VS
002	22.4 VW	20.8 W	31.25 S			18.55 W
003	14.9 S	13.74 M	20.6 M	14.45 S	12.96 M	12.37 M
						(10.65 VW)
004	11.05 VW		15.63 M	10.85 W		9.33 M
005		8.25 W	12.38 M			7.50 W
						(6.92 VW)
006				7.15 W		6.30 W
007					5.53 VW	
008			7.70 W+			
009						
0010			6.22 VW			
Average d.	44.5	41.3	61.7	43.1	38.9	37.5
Short Spacings	4.14 VS	5.72 W	5.27 W	4.14 VS	4.77 W	5.31 M
	2.40 VVW	4.88 VW	4.78 VW	2.41 VW	4.14 VS	4.93 VW
		4.33 S[a]	4.58 S		4.00 W	4.59 VS
		4.19 S[a]	4.24 W+		3.72 S	4.43 VW
		3.81 S	3.78 VS		3.06 VW	3.99 W
		3.51 W	3.38 VW		2.74 VW	3.83 S
		3.13 W+	3.23 W		2.48 VW	3.68 S
		2.84 VW	2.78 W		2.23 W	3.56 M
		2.56 W+	2.51 W+			3.41 W
		2.32 W+	2.47 W+			3.22 W
		2.20 M−	2.35 W			3.09 VW
			2.26 W			2.97 W
			2.10 M			2.81 W
			1.90 W−			2.60 VW
			1.84 VW			2.57 W+
						2.39 W+
						2.31 W
						2.21 W−
						2.06 W
						1.95 W
						1.86 VW
						1.78 VW

[a] Resolved on 0.05 slit pattern, 10-cm. film distance.

synthesis. The mono- and diglycerides were made by directed rearrangement.[10] Myristic acid was purified by methyl ester distillation and repeated solvent crystallization. Myristyl chloride was prepared by reaction of the acid with excess thionyl chloride and vacuum distillation.

---

(10) Eckey and Formo, *J. Am. Oil Chem. Soc.*, in press.

After synthesis the triglycerides were crystallized four to six times from solvents—acetone, isopropyl alcohol, or alcohol-ether mixtures.

Constants for the starting materials and the resultant triglycerides are given in Table I.

While procedures for studying triglyceride polymorphism have been described in earlier papers from this and other laboratories, it seems advisable to give in brief detail the course followed with SMS. The alpha form was obtained by melting and chilling to 30° or lower. The beta prime-2 form was prepared by holding alpha near its m. p. of 44.2°, but was best obtained by crystallizing from the melt at 0.5 to 1° above the alpha m. p. The beta prime-4 form appeared on holding the beta prime-2 form three to five minutes at its m. p., 56.6°. It was also accidentally obtained in an excellent state of crystallinity by solvent crystallization (1:10 in Skellysolve B). The beta-3 form was obtained via alpha or beta prime by 10-15 days storage at 50-60°. It was also the normal result of solvent crystallization, *e. g.*, from acetone, ether or isopropyl alcohol. The beta-2 forms encountered with PMP and PMM were obtained by procedures comparable to those described for the beta-3 form of SMS. Detailed X-ray and melting point data are recorded in Tables II and III, respectively. The recorded melting point values correspond to the "rapid c. m. p." for alpha and beta prime forms as previously described[1] and to "solvent c. m. p." for beta forms.

TABLE III

CHARACTERISTIC THERMAL AND X-RAY DATA

	SMS	PMP	SMM	PMM
	Melting Points, °C			
Alpha	44.2	40.1	35.9	35.6
Beta prime-2	56.6	47.0	46.5	46.5
Beta prime-4	59.3			
Beta	63.8	60.3	56.4	54.4
	X-Ray Data: Long Spacings, Å			
Alpha	47.6	44.6	44.5	43.1
Beta prime-2	43.7	43.3	41.3	38.9
Beta prime-4	85.0			
Beta	66.3	39.2	61.7	37.5
	Short Spacings, Å			
Alpha	4.13 VS	4.14 VS	4.14 VS	4.14 VS
Beta prime-2	4.25 S	4.13 VS	4.33 S	4.14 VS
	4.11 S	3.75 S	4.19 S	3.72 S
	3.78 M		3.81 S	
Beta prime-4	4.33 S			
	4.03 S+			
	3.77 VS			
	3.24 W+			
Beta	4.61 S	4.59 S	4.58 S	4.59 S
	3.83 S+	3.84 S	3.78 VS	3.83 S
		3.74 S		3.68 S

Discussion

The lowest melting forms of SMS, PMP, SMM, and PMM are alpha forms each having a single strong short spacing and definite long spacings. No glassy forms such as have been reported by Malkin and associates for these glycerides and for tristearin, etc.,[11] were found in spite of careful search. This is in agreement with previous findings from this and other laboratories.[12,13,14] To answer in detail the objections of Clarkson and Malkin[15] to these corrections of their earlier work does not seem constructive. Perhaps it is sufficient to describe again typical behavior of a lowest melting form claimed by Malkin to be vitreous. After melting and chilling to temperatures of 35 to −50°, a sample of PMP, for example, in a 1-mm. glass capillary gives a typical alpha diffraction pattern at room temperature. On thrusting the sample, after X-ray exposure, into a bath at 43° (alpha m. p. 40.1°, as here reported), it melts with only a slight cloud of higher melting polymorph developing. This temperature is 3° below Malkin's reported alpha m. p. of 46°.[4a] Within a few minutes at 43° the sample resolidifies in a more stable form. Any interpretation denying that the alpha pattern and the lowest melting point are truly associated seems unduly strained.

As alpha is the lowest melting form for each of these glycerides so a typical beta prime-2 form, in Lutton's[3] nomenclature, was the next higher melting form.

The glycerides PMP and PMM show a third and highest melting form which is beta-2 in each case. Only such double-chain-length structures are to be expected where chain length differences do not exceed two carbons.

The third and highest melting form of SMM is beta-3 in agreement with the data of Malkin, whose long spacing values for related glycerides indicate that beta-3 structure is typical for stable forms of $C_nC_{n-4}C_{n-4}$ glycerides.[3]

Thus three of these triglycerides—PMP, SMM and PMM—have three forms, each with a distinct melting point. In this respect they resemble tristearin (SSS) and the forms are the same as for SSS except for the stable form of SMM which is beta-3 instead of beta-2. Malkin, *et al.*,[2,4,6] have reported the same forms and one other, a supposed vitreous form, not found in this study. Comparative data are shown in Table IV.

In all three instances Malkin's "beta prime m. p." is an extra m. p. and does not appear to the present authors to be characteristically associated with any recognized diffraction pattern. The ensuing discussion, concerning SMS, illuminates the situation.

As has been said, SMS also shows alpha and beta prime-2 forms. Like SMM, its highest melting form is beta-3. But unlike any of the other glycerides here reported, it has a hitherto unreported beta prime-4 form, a fourth crystal modification intervening in melting level between beta prime-2 and beta-3. Such a form, named merely "beta prime," by Malkin has been reported for 2-lauryl dipalmitin, another $C_nC_{n-4}C_n$ glyceride, and for certain other glycerides.[3] This is the first time, however, that both beta prime-2 and beta prime-4 forms have been reported for a single triglyceride. The four distinct patterns for SMS appear in Plate I (data in Table II) where it is seen

---

(11) Clarkson and Malkin, *J. Chem. Soc.*, 666 (1934).

(12) Bailey, *et al.*, *Oil and Soap*, **22**, 10 (1945).

(13) Lutton, THIS JOURNAL, **67**, 524 (1945).

(14) Filer, *et al.*, *ibid.*, **68**, 168 (1946).

(15) Clarkson and Malkin, *J. Chem. Soc.*, 985 (1948).

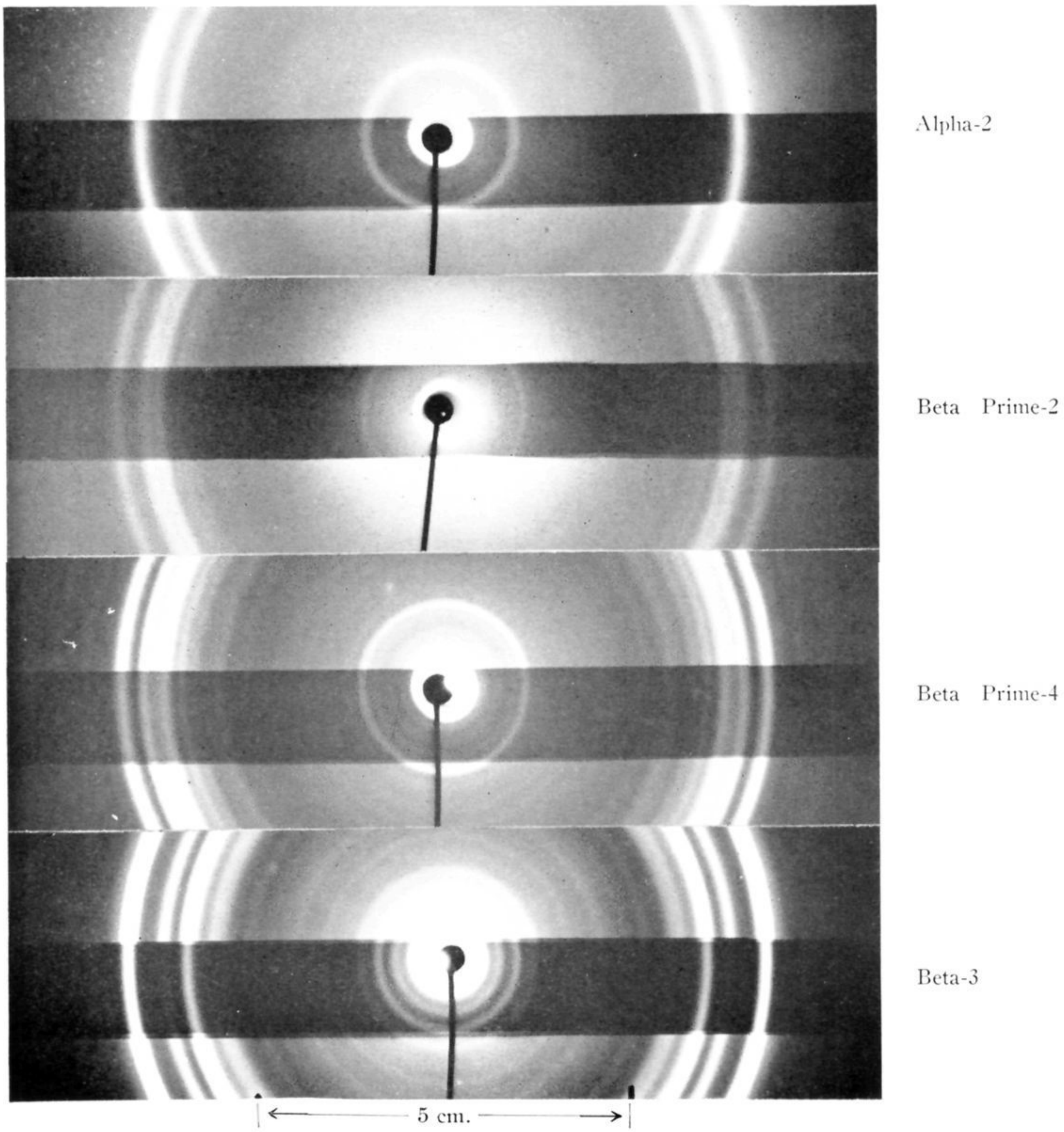

Fig. 1.—X-Ray diffraction patterns of the four forms of 2-myristyldistearin The pattern strips are printed from flat film taken with a strip of nickel foil to eliminate CuKβ radiation. Sample to film distance is 10 cm.

TABLE IV

COMPARATIVE DATA FOR PMP, SMM AND PMM

	PMP				SMM				PMM			
	M. p., °C.		L. S., Å.		M. p., °C.		L. S., Å.		M. p., °C.		L. S., Å.	
Form	J and L	M and M[2a]	J and L	M and M[2a]	J and L	C and M[4b]	J and L	C and M[4b]	J and L	C and M[2b]	J and L	C and M[2b]
Vitreous		37				36				34		
Alpha	40.1	46	44.6	44.4	35.9	46	44.5	46.4	35.6	45.5	43.1	42.8
Beta prime	47.0	55	43.3	42.4	46.5	52	41.3	41.7	46.5	50.5	38.9	39.5
Beta	60.3	60	39.2	39.0	56.4	56	61.7	61.4	54.4	54	37.5	37.7

that beta prime-2 and beta prime-4 are distinguished by both short and long spacings. (For some reason, beta prime-2 appears to give a consistently weak pattern.) A comparison of the present data for SMS with those of Malkin appears in Table V.

TABLE V

COMPARATIVE DATA FOR SMS

	M. p., °C.		L. S., Å.	
Form	J and L	M and M[4a]	J and L	M and M[4a]
Vitreous		47		
Alpha	44.2	56	47.6	49.5
Beta prime-2	56.6		43.7	44.7
Beta prime-4	59.3	59	85.0	
Beta-3	63.8	62.5	66.3	65.8

SMS is the second case among saturated triglycerides where four distinct forms other than the supposed vitreous form have been found to be approximately associated with the four melting points given by Malkin, *et al.* The other case was that of 1-stearyldilaurin where alpha-2, beta prime-2, beta prime-3 (unreported by Carter and Malkin[4b]) and beta-3 forms were found.[3] At this stage it is a reasonable expectation that other undiscovered triglyceride forms will in some cases justify the existence of four melting points as reported by Malkin, *et al.* In many cases, however, the next to highest m. p. appears to be but a necessary accompaniment of the unjustified assumption of the existence of a vitreous form supposedly melting at the actual alpha m. p. level.

Except for the presence of a beta prime-4 long spacing for SMS and the absence of thermal points corresponding to Malkin's "beta prime m. p.s" of PMP, SMM and PMM, the present actual numerical values for long spacings and thermal points are in reasonably good agreement with those of Malkin. Perhaps five cases deserve separate mention. The present beta m. p. for SMS is 1.3° higher and in good agreement with another earlier value.[9] The lowest (alpha) m. p.s for SMS and PMP are respectively 2.8° lower and 3.1° higher than those of Malkin. The alpha long spacings for SMS and SMM are each 1.9 Å. lower than Malkin's values and in better keeping with the general experience that long spacing for a given type of form is, to a first approximation, a function of molecular weight; thus, in the present set of data the alpha long spacings of PMP and SMM (same molecular weight) are very nearly equal.

Relative Stabilities of Metastable Forms.—While it is true that symmetrical glycerides show better crystallinity than unsymmetrical glycerides upon crystallization from solvent, it is not a safe generalization that symmetrical glycerides show more rapid transformation to stable forms. Thus the three metastable forms of SMS all have moderate stability and the alpha form of PMP has rather high stability although the intermediate beta prime-2 form is fleeting. The two metastable forms of SMM and PMM show moderate but not rapid rates of transformation.

Comparison with Closely Related Homologs.—In comparing individual glycerides with closely related homologues previously studied in this laboratory it is seen that PMM is very similar in general behavior to 1-stearyldipalmitin (SPP), also of the $C_nC_{n-2}C_{n-2}$ group, except for lower corresponding melting points and more rapid rate of transformation, in keeping with the lower molecular weight. PMP differs from 2-palmityldistearin (SPS) in exhibiting a beta prime form, which, as has been said, is rather fleeting. These two glycerides are similar, however, in their rather high alpha stability and in the closeness of the two strong beta short spacings in the 3.8 Å. region.

Acknowledgment.—The authors wish to express their appreciation to Mr. R. G. Folzenlogen for the synthesis of the triglycerides and to others of this laboratory for experimental assistance and constructive discussions in the preparation of this paper.

Summary

In a re-examination of the four saturated diacid triglycerides—SMS, PMP, SMM and PMM—in each case three of the four diffraction patterns of Malkin, *et al.*, were observed. These patterns were (1) alpha-2, (2) beta prime-2, and (3) beta-2 for PMP and PMM, beta-3 for SMS and SMM; they are properly associated with Malkin's first (lowest), second and fourth m. p.s, respectively, and not as he has reported with his second, third, and fourth m. p.s. Once again careful search has failed to reveal a pattern for the "vitreous" form of Malkin supposedly associated with the lowest m. p. level (actually the alpha m. p.).

For SMS an additional (fourth) form was identified through its distinctive beta prime-4 pattern. This form is associated with Malkin's third m. p.

From somewhat limited evidence it appears that most saturated diacid triglycerides have three

polymorphic forms each with a characteristic melting point. (Some, *e. g.*, 2-stearyldipalmitin, have only two.) Where, as in the case of SMS, four forms actually do occur to correspond with Malkin's four published m. p. values, new patterns should be expected, since only three of Malkin's four patterns appear to be authentic.

IVORYDALE, OHIO RECEIVED JANUARY 3, 1949

[CONTRIBUTION NO. 89 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Infrared Studies of 1,2- and *trans* 1,4-Structure of Polybutadiene and Butadiene–Styrene Copolymers Polymerized at Various Temperatures[1]

BY E. J. HART[2] AND A. W. MEYER

One of the major improvements in the quality of synthetic butadiene rubbers has resulted from the use of low temperatures of polymerization. In particular, tensile strength, resilience, flex life, abrasion resistance and processing properties of tire tread stocks have been favorably affected.[3]

It is of great importance to determine the reasons for improvements in the physical properties of low temperature polymers in order to expedite future research. Comparison of the physical properties of Hevea rubber with isomerized rubber or synthetic polyisoprene illustrates the point that crystallizable polymers are required for high tensile strengths, particularly in gum vulcanizates. From the low tensile strengths obtained on isomerized rubber it may be concluded that the existence of random sequence of *cis–trans* configurations is sufficient to prevent crystallization during stretching of the rubber. Also in synthetic polyisoprene, polybutadiene and GR-S, appreciable quantities of 1,2-addition are found and become the source of further irregularities in the chain structure of the polymer. 1,2- and *cis–trans* 1,4-additions in random sequence may be considered as the major structural variations leading to noncrystallizable and inferior polymers. In order to determine the relative importance of 1,2- and *cis–trans* 1,4- addition, it is necessary to develop analytical methods for these isomeric units present in butadiene polymers.

Several methods have been employed in the determination of the amount of 1,2- addition in polybutadiene and butadiene–styrene copolymers. In emulsion polymers it has been reported that 78% of the butadiene addition is in the 1,4- configuration and the remainder in the 1,2- configuration.[4] Therefore, 78% of the butadiene is present as *cis–trans* isomers of the 1,4- addition product arranged in random sequence. From the results on isomerized rubber it would be expected that even if the 1,2- addition could be reduced to negligible values, inferior products would still result because of the presence of the large amount of *cis-trans* isomers in random sequence.

Beu, Reynolds, Fryling and Murry[5] reported that crystallization can be developed in polybutadiene prepared at 20° and lower. Further, they deduced from their X-ray work that the partially crystallized rubber corresponded to the *trans*-configuration. However, it is difficult to measure the *trans*-isomeric content of the polymer quantitatively or even relatively by X-ray methods. Ozonization,[6] perbenzoic acid[7] and infrared[8] methods have been applied to the measurement of the per cent. 1,2-addition in butadiene polymers. Of these methods the perbenzoic acid and infrared methods are in fair agreement.

The present paper shows that the infrared spectrometer is admirably suited not only to the measurement of 1,2-addition but also to the measurement of *trans*-1,4-addition in polybutadiene and butadiene–styrene copolymers. It is the purpose of this paper to describe briefly the 1,2- and *trans*-1,4-addition analytical methods and also to report results on the effect of temperature of polymerization and styrene content on 1,2- and *trans*-1,4-addition in butadiene polymerization and copolymerization.

Experimental

Materials.—Emulsion polymers used in this study are listed in Table I. These were secured from the following sources; the 14R and 26E series[9] were obtained from the Synthetic Rubber Laboratories, University of Akron; the J888-J949 series was obtained from the Synthetic Rubber Division, United States Rubber Company, Naugatuck, Connecticut; GR-S and GR-S10 were regular commercial materials.

Purification of Polymers.—Since it is desirable to use carbon disulfide solutions of the polymers for the infrared analysis, the following

---

[1] This paper was presented before the High Polymer Forum at the St. Louis Meeting of the American Chemical Society, September 7, 1948.

[2] Present address: Argonne National Laboratory, Chicago, Ill.

[3] W. A. Schultze, W. B. Reynolds, C. F. Fryling, L. R. Sperberg and J. E. Troyan, *India Rubber World*, **117**, 739 (1948).

[4] R. F. Dunbrook, *ibid.*, **117**, 617 (1948).

[5] K. E. Beu, W. B. Reynolds, C.F. Fryling and H. L. Murry, *J. Polymer Sci.*, **3**, 465 (1948).

[6] Rabjohn, Bryan, Inskeep, Johnson and Lawson, THIS JOURNAL, **69**, 314 (1947).

[7] I. M. Kolthoff and T. S. Lee, *J. Polymer Sci.*, **2**, 206 (1947); I. M. Kolthoff, T. S. Lee and M. S. Mairs, *ibid.*, **2**, 220 (1947).

[8] J. E. Field and D. E. Woodford, private communication to Office of Rubber Reserve, October, 1945.

[9] W. K. Taft, private communication to Office of Rubber Reserve, January, 1948.