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Thermodynamics of Crystallization in High Polymers: Gutta Percha^{1,2}

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The melting temperatures of two of the crystalline modifications of gutta percha and their mixtures with either methyl oleate or tetradecane as diluent were determined by X-ray diffraction and dilatometric methods. It was found that the melting temperatures of the two forms in the pure polymer were 64 and 74°, respectively. From these studies the heat of fusion per repeating unit of the high melting form was deduced to be 3070 ± 250 cal./mole, while the heat of fusion for the low melting modification was found to be about one-half to three-fourths this value. An analysis indicates the low melting form is a metastable one. The heats and entropies of fusion of each of the forms of gutta percha are appreciably greater than those of the monomorphous *cis*-hydrocarbon, natural rubber. The difference in the entropies of fusion of the two polymers persists even when allowance is made for the significant contribution due to the volume change accompanying fusion.

Introduction

Statistical and thermodynamic methods describing the fusion process of semi-crystalline polymers have been developed in recent years³⁻⁵ and the major deductions of the theory have been substantiated by experiment.⁵ The theoretical analysis has indicated that, due to the nature of a semi-crystalline polymer, the significant thermodynamic parameters are those which are characteristic of the structural repeating unit. Thus an equilibrium melting temperature T_m^0 is defined as that at which the most perfect crystallites are unstable relative to the pure polymeric liquid and is representative of the melting temperature of a macroscopic perfect crystal. Similarly, it is of great utility to consider the heat and entropy of fusion characteristic of the transformation of polymer repeating units from the crystalline to liquid state rather than the quantities applicable to the transformation of the entire semi-crystalline polymers. These latter quantities will obviously depend on the relative amounts of crystalline and non-crystalline material in the system. To determine melting temperatures which are of thermodynamic significance it is necessary to employ slow heating rates⁶⁻⁸ so that sufficient time is allowed for the formation of the more perfect crystallites.

The thermodynamic parameters governing the crystallization behavior of natural rubber, *cis*-polyisoprene, have recently been deduced⁸ and it is of interest to compare these results with those for gutta percha, the *trans*-polyisoprene. A study of the crystallization behavior of gutta percha is complicated by the existence of several crystalline modifications. Two of them occur without the application of any external stress⁹⁻¹⁴ while a third re-

cently discovered polymorph occurs only when the polymer is deformed.¹⁵ The polymorphism of gutta percha together with the usual difficulties of establishing equilibrium conditions in a semi-crystalline polymer have made past interpretation of the volume-temperature relations difficult.¹⁶⁻¹⁸ However, since it has been deduced from studies on other polymers that equilibrium conditions can be approached using slow heating rates, the adoption of this procedure has aided in clarifying the analyses of the data for gutta percha. Furthermore, an analysis of the melting of each of the forms can help establish thermodynamic criteria for their relative stability without recourse to kinetic observations as has been necessary in the past.^{10,14} We shall be concerned solely with the two crystalline modifications which can occur without the application of external stress. To avoid confusion in their identification we shall term them the low melting form (LMF) and the high melting form (HMF) which correspond to the β - and γ -forms, respectively, in Fisher's terminology.¹⁵

Experimental

A cake of gutta percha was received in a vacuum tin from the Tjipeti Rubber Plantation in the Netherlands Indies and was stored in a Dry Ice chest prior to use. Since a preliminary analysis indicated the sample to contain only about 94% hydrocarbon, further purification was deemed advisable. A portion of the sample was passed through a dry wash-mill several times in order to form a sheet, and then about 80 g. of the gutta percha was extracted with freshly distilled acetone for about 135 hours. The extraction process was conducted in the absence of light, as much as feasible, and periodically interrupted to replace the acetone. About 60 g. of the extracted gutta percha was dissolved in 8 liters of toluene to which 0.6 g. of phenyl- β -naphthylamine had been added. The dissolution of the gutta percha and its subsequent precipitation were conducted in an atmosphere of nitrogen and the sample was protected from direct light. After the resulting solution was passed through a coarse sintered glass filter, the gutta percha was reprecipitated by the slow addition of 10 liters of distilled ethanol containing 0.4 g. of phenyl- β -naphthylamine. The precipitate was collected on sintered glass filters, washed with ethanol and dried *in vacuo* at 35 to 45° for over 30 hours. The gutta percha purified in this manner was sealed with nitrogen in tubes, each tube containing about 3-5 g. of the sample, and stored at Dry Ice temperatures. These latter precautions are necessary, for otherwise rather extensive degradation will occur in a relatively short time. Chemical analyses¹⁹ show that the gutta percha purified in

(1) A portion of this work was supported by the Office of Naval Research.

(2) Presented in part before the 125th and 127th Meetings of the American Chemical Society.

(3) P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).

(4) P. J. Flory, R. R. Garrett, S. Newman and L. Mandelkern, *J. Polymer Sci.*, **12**, 97 (1954).

(5) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 563.

(6) R. D. Evans, H. R. Mighon and P. J. Flory, *THIS JOURNAL*, **72**, 2018 (1950).

(7) P. J. Flory, L. Mandelkern and H. K. Hall, *ibid.*, **73**, 2532 (1951).

(8) D. E. Roberts and L. Mandelkern, *ibid.*, **77**, 781 (1955).

(9) H. Hopf and G. von Susich, *Kautschuk*, **6**, 234 (1930).

(10) E. A. Hauser and G. von Susich, *ibid.*, **7**, 120, 125, 145 (1931).

(11) C. S. Fuller, *Ind. Eng. Chem.*, **28**, 907 (1936).

(12) G. Bruni and G. Natta, *Atti. Accad. Naz. Lincei*, **19**, 206 (1934).

(13) K. H. Storks, *THIS JOURNAL*, **60**, 1753 (1938).

(14) C. W. Bunn, *Proc. Roy. Soc. (London)*, **A180**, 40 (1942).

(15) D. Fisher, *Proc. Phys. Soc.*, **B66**, 7 (1953).

(16) J. N. Dean, *Trans. Inst. Rubber Ind.*, **8**, 25 (1932).

(17) W. Saffoti, *Tech. Bull. No. 9, Instituto Agronomico do Norte, Belen, Para, Brazil*, Dec. 1946.

(18) H. M. Leeper and W. Schlesinger, *J. Polymer Sci.*, **11**, 307 (1953).

(19) We are indebted to Mrs. Rachel J. Fanning of the National Bureau of Standards for the chemical analyses.

this manner contained 98% hydrocarbon, 0.5% acetone-soluble material, 0.05% protein, 0.12% insoluble material and 0.29% ash. The intrinsic viscosity of the polymer in benzene at 30° was 1.14. An extrapolation of the results of Wagner and Flory²⁰ indicate that the polymer had a viscosity-average molecular weight of about 70,000.

The diluents used in this study, *n*-tetradecane and methyl oleate (Eastman Kodak Co.), were of technical grade and were used as received. Their densities were measured at two widely different temperatures and a linear variation between these temperatures was assumed. The gutta percha-diluent mixtures were prepared in a manner identical to that used for the rubber-diluent mixtures in the previous investigation.⁸ Compositions were computed at the melting temperatures of the mixtures.

The dilatometric methods^{7,21} previously described in detail were followed in the present work, the dilatometers being immersed in a constant temperature bath regulated to within $\pm 0.1^\circ$. The density of gutta percha was determined at 0 and 25° using the method of hydrostatic weighings.²²

The X-ray diffraction powder patterns were taken using a Geiger counter X-ray diffractometer with Cu K α radiation, operating at 40 kv. and 20 ma. The X-ray diffraction patterns at elevated temperatures were obtained using a camera of the type designed by Mauer and Boltz.²³ Temperature control was achieved through the circulation of water from a slowly heated bath set at a predetermined maximum temperature, through the coils originally intended to act as cooling coils for this high temperature camera.²³ The temperature of the specimen was recorded by means of an iron-constantan thermocouple placed next to it and is regarded as accurate to $\pm 0.5^\circ$.

Results and Discussion

Pure Gutta Percha.—Below the melting temperature of the LMF, the crystalline forms observed will depend on the previous thermal history of the sample. At the outset it is important to establish conditions for the formation of each of the modifications so that the properties studied can be properly attributed. If a sample of gutta percha, after being held at an elevated temperature sufficiently long for all crystallinity to disappear, is rapidly transferred to a thermostat maintained at 0° and allowed to crystallize isothermally at this temperature, a characteristic X-ray diffraction pattern is obtained (at room temperature) indicated by the dotted lines of Fig. 1. The observed Bragg spacings can be identified with β -gutta percha as defined by Fisher,¹⁵ for which an orthorhombic unit cell of dimensions $a = 7.84 \text{ \AA}$, $b = 11.87 \text{ \AA}$, and $c = 4.75 \text{ \AA}$, and a density of 1.04 g./cc. has been proposed. Similarly, if the same sample is crystallized at 55° from the melt, to a pseudo equilibrium value of the degree of crystallinity then at room temperature the X-ray diffraction pattern indicated by the solid lines of Fig. 1 is observed. The Bragg spacings are in agreement with that previously observed for γ -gutta percha for which a monoclinic unit cell of dimensions $a = 5.9 \text{ \AA}$, $b = 7.9 \text{ \AA}$, $c = 9.2 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 94^\circ$ and a density of 1.05 g./cc. has been proposed. The patterns in Fig. 1 illustrate quite clearly the fact that at least two different crystal structures can be achieved. Though the two patterns are quite distinct the spacings characteristic of the LMF have very similar counterparts in the HMF; the HMF on the other hand has several spacings which are unique to it.

(20) H. L. Wagner and P. J. Flory, *THIS JOURNAL*, **74**, 195 (1952).

(21) L. Mandelkern and P. J. Flory, *ibid.*, **73**, 3206 (1951).

(22) L. A. Wood, N. Bekkedahl and F. L. Roth, *J. Research Natl. Bur. Standards*, **29**, 391 (1942); *Ind. Eng. Chem.*, **34**, 1291 (1942).

(23) F. A. Mauer and L. H. Boltz, private communication.

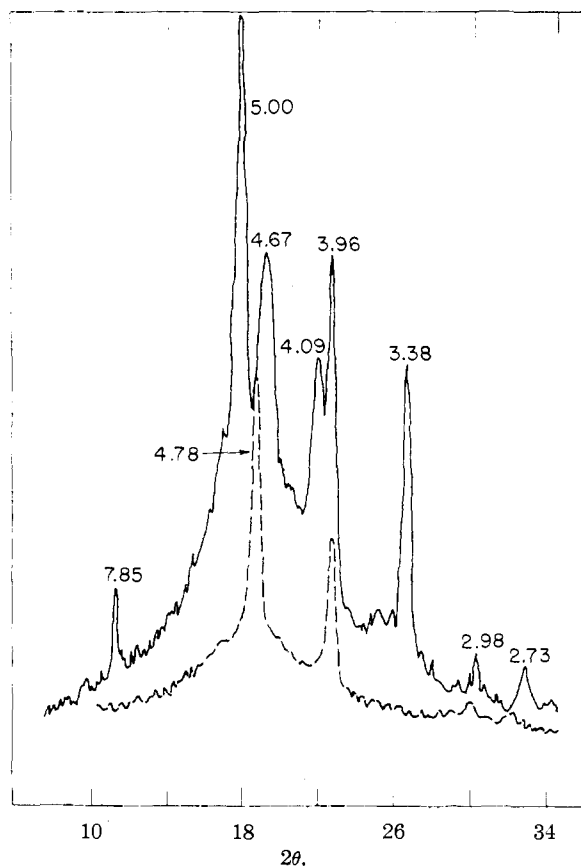


Fig. 1.—X-Ray diffraction patterns for two crystalline modifications of gutta percha at 25°: dotted line is for LMF; solid line, for HMF. Bragg spacings are indicated.

To determine the melting temperatures, T_m^0 , of each of the forms, the dependence of the specific volume on temperature was investigated following the crystallization of a given polymorph. For T_m^0 to be of thermodynamic significance slow heating rates must be employed, to allow for the attainment of a more perfectly crystalline array. Thus up to about 10° below T_m^0 the temperature was increased in a stepwise manner at a rate of about 1°/12–24 hr., while above this temperature the heating rate was decreased to about half this value. At a given temperature the volume increased at first, then decreased, reaching a constant value within the observed time. Behavior of this sort is typical of polymeric systems and has recently been reported for gutta percha.¹⁸ The results of these observations are illustrated in Fig. 2 where the final observed specific volumes are plotted against temperature. The open circles represent observations after crystallization from the melt at 60°, crystallization conditions which allow only the formation of the HMF. On subsequent heating the volume followed the path indicated by the open circles and the melting of this polymorph occurs at 74°. The course of the dilatometric observations after crystallization at 0°, where only the LMF occurs, is indicated by the closed circles of Fig. 2. The high volumes observed in the range 0–50°, and previously reported by Leeper and Schlesinger,¹⁸ would appear to be artifacts of the experimental observa-

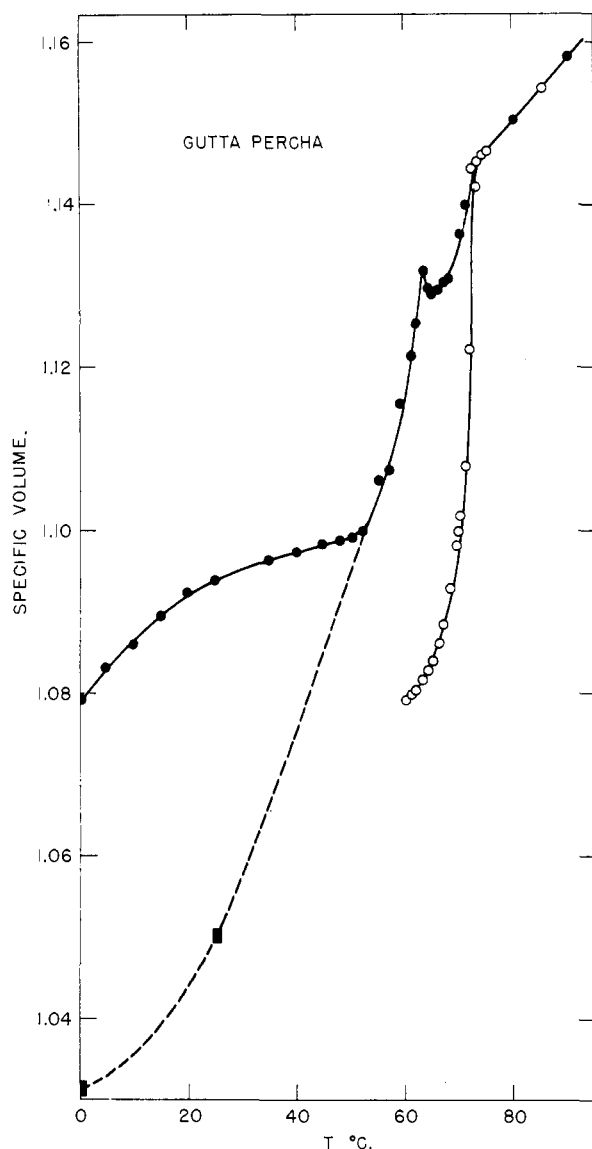


Fig. 2.—Specific volume of gutta percha as a function of temperature: after crystallization at 0°, ●; after crystallization at 60°, ○; by the method of hydrostatic weighings, ■.

tion, since independent measurements of the specific volume, by the method of hydrostatic weighings, give values indicated by the solid squares. The dotted curve is thus probably a truer representation of the melting behavior of the LMF. The higher volumes observed dilatometrically could be caused by the fact that the rather rapid crystallization may prevent the mercury from completely penetrating the interior of the sample. This situation will, of course, become alleviated as the temperature is increased. The rather large increase of specific volume is terminated at 64°, where X-ray diffraction patterns indicate the disappearance of spacings attributable to the LMF. This temperature, 64°, is then taken as the melting temperature of the LMF. During the heating process some HMF is developed and its fusion is indicated by the solid circles in the temperature range 64–74°. The

observed melting temperatures of the respective forms are appreciably higher than some of the values reported in the literature.^{10,18,14,24} This is, undoubtedly, a consequence of the slow heating rates employed in the present investigation; similar behavior has been noted with many other polymers studied.

Polymer-Diluent Mixtures.—When a low molecular weight diluent is added to a semi-crystalline polymer, its melting temperature is depressed in accordance with the thermodynamic principles of phase equilibria. For polymer-diluent systems it has been shown that³⁻⁵

$$1/T_m - 1/T_m^0 = (R/\Delta H_u)(V_u/V_1)(v_1 - \chi_1 v_1^2) \quad (1)$$

where T_m is the melting temperature of the polymer-diluent mixture, R the gas constant, ΔH_u the heat of fusion per mole of repeating unit, V_u the molar volume of the repeating unit, V_1 the molar volume of the diluent, v_1 the volume fraction of the diluent and χ_1 is a thermodynamic interaction parameter, which can be written as $\chi_1 = BV_1/RT_m$ where B is the molar free energy change brought about by first neighbor interactions. Equation 1 is analogous to the classical expression for the depression of the freezing point of a liquid. It is applicable to both polymorphs of gutta percha, when the appropriate values of T_m^0 and ΔH_u are used, since the liquid state and thus the thermodynamic interaction parameter are identical in both cases. By rearranging equation 1 a form more convenient for

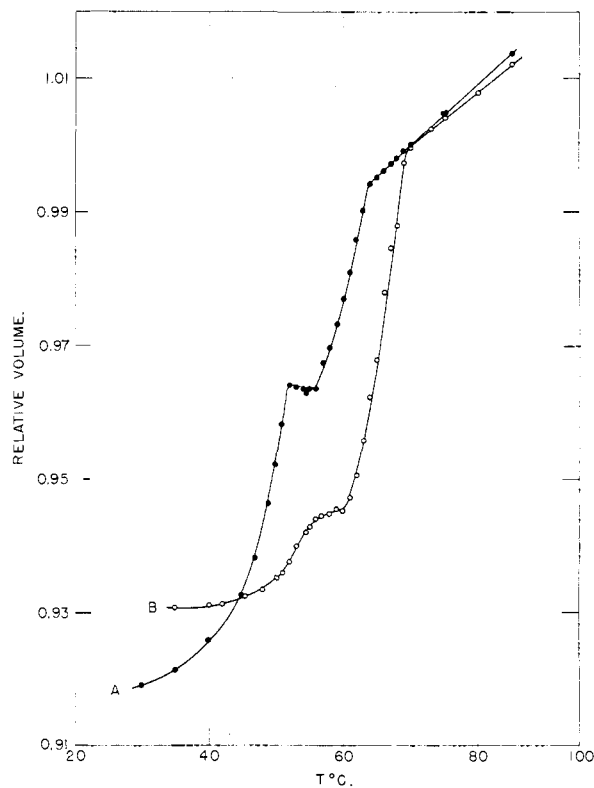


Fig. 3.—Relative volume for gutta percha-diluent mixtures as a function of temperature: curve A with tetradecane $v_1 = 0.446$; curve B with methyl oleate $v_1 = 0.277$.

(24) K. H. Meyer, *Naturwissenschaften*, **26**, 199 (1938).

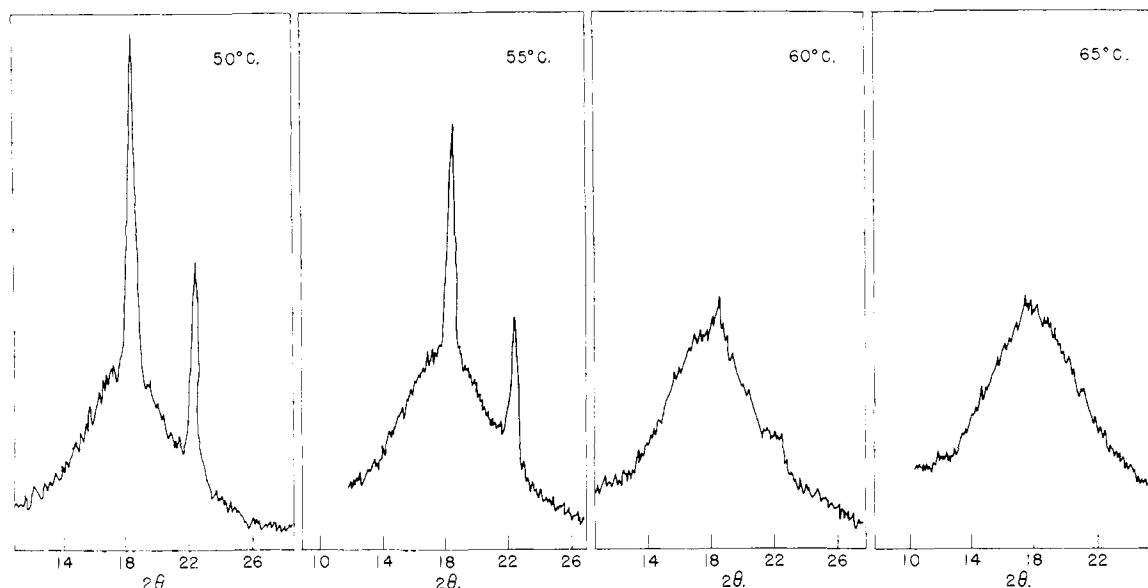


Fig. 4.—X-Ray diffraction patterns of the low melting form of pure gutta percha at various temperatures.

the analysis of experimental data is obtained. Thus

$$[1/T_m - 1/T_m^0]/v_1 = (R/\Delta H_u)(V_u/V_1)[1 - (BV_1/R)v_1/T_m] \quad (2)$$

Thus, by studying the dependence of the melting temperature of each of the forms on diluent concentration, the respective values of ΔH_u can be obtained, and by making use of the appropriate melting temperatures the free energy of fusion per repeating unit of each of the forms can be calculated.

The melting temperature of the HMF in mixtures with either tetradecane or methyl oleate as diluent can be determined unambiguously by dilatometric means. The heating rates employed were similar to those followed for the bulk polymer and similar variations of the volume with time under isothermal conditions were observed. Typical results of the volume-temperature behavior of two of the diluent mixtures are given in Fig. 3. Curve A is for a mixture containing tetradecane with a volume fraction of 0.446, while curve B is for a mixture containing methyl oleate with a volume fraction of 0.277. The melting temperature of the HMF is clearly discernible. The melting temperatures of the HMF of all the mixtures studied are given in Table I and have been plotted according to the method suggested by equation 2. The plots are well represented by straight lines, the slopes of which are sufficiently close to zero so that within the experimental error $B = 0$ for either of the diluent mixtures. From the intercepts of these plots ΔH_u is found to be 3145 ± 235 cal./mole of repeating unit using methyl oleate as diluent, and 2990 ± 110 with tetradecane. The average value of ΔH_u for the HMF is then 3070 ± 130 cal./mole of repeating unit.

The melting temperature of the LMF in the diluent mixtures is not so easily discerned by dilatometric methods. This is due to the fact that the volume change on melting is relatively diffuse and cannot easily be distinguished from the usual recrystallization phenomena that occur. As a consequence of this, the melting temperatures of the LMF were determined by heating the sample in an

X-ray diffraction unit, and observing the resulting pattern at temperature intervals. The temperature at which the pattern characteristic of the LMF disappeared was taken as the melting temperature. The reliability of the melting point as determined by the X-ray method was first investigated using the undiluted polymer. In Fig. 4 X-ray diffraction patterns of the pure polymer, crystallized under conditions so that only the LMF occurred, were obtained at four different temperatures. From the resulting patterns it can be deduced that melting occurred in the range of 60–65° which is in excellent agreement with the dilatometric observations. About eight hours elapsed in heating the sample from 50–65°. This is admittedly a rapid heating rate but apparently in this system sufficient annealing can occur even in this relatively short time. Polymer-diluent mixtures give similar results as is illustrated in Fig. 5 where the diffraction patterns, at different temperatures, for a gutta percha-methyl oleate mixture with $v_1 = 0.168$, are given. At 55° the characteristic pattern of the LMF persists while at 59° it has disappeared. Hence, this mixture has been assigned a T_m of 56–59°. The melting temperatures of the LMF as determined by the X-ray method are also given in Table I. With the X-ray results as a guide, a re-examination of the dilatometric data indicated in most cases where the melting occurred. For example, in Fig. 3 the gradual rise in volume in the vicinity of 50° and its subsequent levelling off can now be identified with the melting of the LMF.

The rather large uncertainties in the T_m of the LMF in these mixtures precludes a detailed analysis of the data by means of equations 1 and 2 and hence an accurate determination of ΔH_u for this crystalline form. However, a reasonable estimate of ΔH_u can be obtained. In Fig. 6 the melting temperatures of the gutta percha-methyl oleate mixtures are plotted against composition. The upper curve, appropriate to the HMF, is calculated

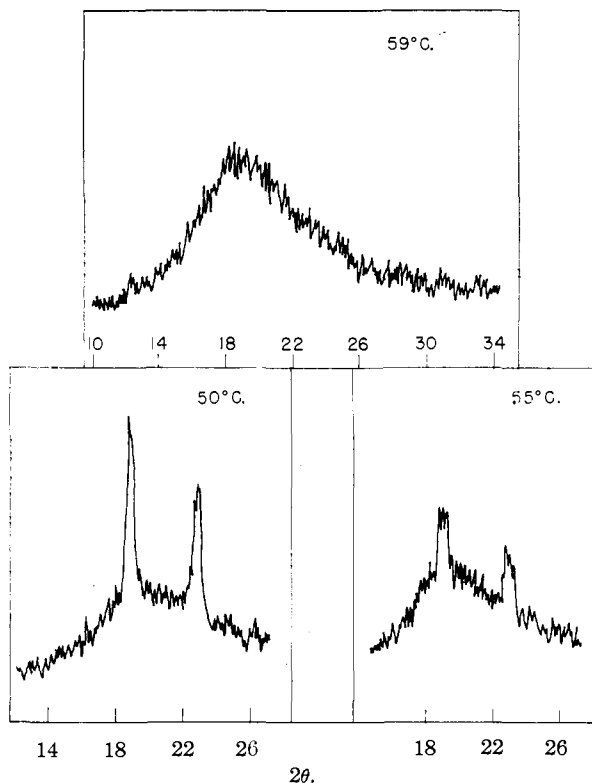


Fig. 5.—X-Ray diffraction patterns of the low melting form of gutta percha when mixed with methyl oleate $v_1 = 0.168$.

TABLE I
MELTING TEMPERATURES OF GUTTA PERCHA-DILUENT MIXTURES

v_1	T_m (HMF), °C.		T_m (LMF), °C.	
	Dilatometer	X-Ray	Dilatometer	X-Ray
With methyl oleate				
0.000	74		64	60-65
.106	72		59-60	
.168	71-71.5			56-59
.266	69.5-70			
.277	69		56-57	55-58
.333	68.5-69			55-58
.422	66-67			53-55
.573	63.5-64			50-53
With tetradecane				
0.000	74		64	60-65
.195	69-69.5			
.195	70	68-70	57.5-58	54-58
.287	67-67.5		53.5-54	
.331	66.5-67		53-53.5	53-56
.446	63.5-64		51-52	51-53
.570	61.5-62		49-50	44-47
.696	58.5-59	55-57	45	39-46

from equation 1 using the parameters just deduced, and the experimental points are indicated by closed circles. The lower three curves are theoretical ones appropriate to the LMF, calculated from equation 1, using $B = 0$ which is characteristic of the liquid state of the polymer, and values of ΔH_u equal to all of, three-fourths of and one-half that of the HMF. The melting points of the LMF determined by the X-ray diffraction methods are given by the verti-

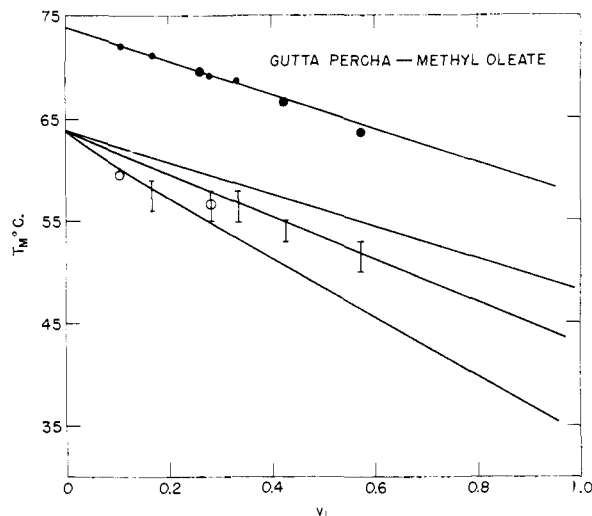


Fig. 6.—Plot of melting temperatures of gutta percha-methyl oleate mixtures *vs.* volume fraction of methyl oleate: upper curve for HMF, $\Delta H_u = 3140$ cal./mole; lower three curves for LMF, $\Delta H_u = 3140, 2355$ and 1570 cal./mole, respectively; T_m of HMF, dilatometric method, ●; T_m of LMF, dilatometric method, ○; T_m of LMF, X-ray method, I.

cal lines, those by the dilatometric methods, by the open circles. This plot indicates that the ΔH_u appropriate to the LMF is less than that of the HMF and is probably between one-half and three-fourths of it. A similar plot is given in Fig. 7 for the data obtained with tetradecane as diluent. The results are concordant with those obtained with methyl oleate, and again indicate that ΔH_u for the LMF is between one-half and three-fourths that of the HMF. This estimation of the ΔH_u for the LMF is adequate enough to allow a discussion of the thermodynamic stability of the two forms.

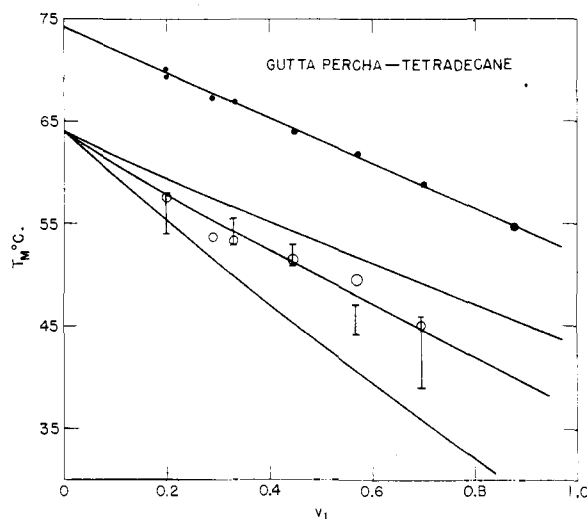


Fig. 7.—Plot of melting temperatures of gutta percha-tetradecane mixtures *vs.* volume fraction of tetradecane: upper curve for HMF, $\Delta H_u = 2990$ cal./mole; lower three curves for LMF, $\Delta H_u = 2990, 2240$ and 1495 cal./mole, respectively; T_m of HMF, dilatometric method, ●; T_m of LMF, dilatometric method, ○; T_m of LMF, X-ray method, I.

Thermodynamic Parameters.—The stability of polymorphs can be discussed in terms of their respective free energies of fusion per repeating unit. As with polymorphs of low molecular weight crystals at a given temperature, the crystal form which has the lower free energy (relative to a standard state) is the more stable one. Taking the completely liquid polymer as our standard state, the crystalline modification having the greater free energy of fusion per repeating unit should be the more stable one. Thus, if at a temperature T below its melting temperature, the LMF should be the more stable one, then

$$\Delta f_u^{\text{LMF}} > \Delta f_u^{\text{HMF}} \quad (3)$$

where Δf_u is the free energy of fusion per repeating unit. Since $\Delta f_u = \Delta H_u(1 - T/T_m^0)$ the condition for stability would be that

$$\Delta H_u^{\text{LMF}} > \Delta H_u^{\text{HMF}} ([1 - T/T_m^{0,\text{LMF}}]/[1 - T/T_m^{0,\text{HMF}}]) \quad (4)$$

Since $T_m^{\text{HMF}} > T_m^{\text{LMF}}$, a minimum requirement for the stability of the LMF is that its heat of fusion per repeating unit be greater than that of HMF. Although ΔH_u^{LMF} could not be determined precisely, as was already mentioned, it was found nevertheless to be appreciably less than ΔH_u^{HMF} . It is therefore concluded that the LMF is a metastable modification in the temperature interval studied, in agreement with the earlier surmises^{10,14,15} based solely on kinetic observations.²⁵

It thus appears that the thermodynamics of the polymorphism in semi-crystalline polymers can be described in a manner similar to the methods used for low molecular weight materials. A third polymorph of gutta percha, predicted by Fuller¹¹ and by Bunn¹⁴ and recently discovered by Fischer,¹⁵ occurs only when the sample is stretched. The stretching process increases the free energy of the pure liquid and thus, under these conditions, this modification may become thermodynamically favored. Alternatively, prior to deformation this modification may be thermodynamically favored, the deformation process only serving to favor its crystallization kinetics. This question must remain unresolved until the free energy of fusion of this form is evaluated.

The heat of fusion of the HMF is appreciably greater than for natural rubber, the *cis*-polyisoprene for which a value of 1050 cal./mole has been reported.⁸ For low molecular weight hydrocarbons the heats of fusion for the isomers in the *trans* configuration are greater than those for the *cis* configuration. However, the differences in the heat of fusion of the two low molecular weight isomers are not as great as is observed here for the two polymeric hydrocarbons. A possible reason for the large difference in ΔH_u may reside in the crystal structures of natural rubber and the HMF of gutta percha. According to Bunn¹⁴ the unit cell of natural rubber has four chains passing through it but two are right-handed chains and two are left-handed chains. On the other hand, the unit cell of gutta percha is composed entirely of either right- or left-handed molecules. Thus, the greater asym-

metry of the long chain *cis*-hydrocarbon and its effect in the packing of the crystal might contribute to its lower heat of fusion.

The entropy of fusion of the HMF is calculated to be 8.8 cal./deg./repeating unit or 2.93 cal./deg./single bond. For the LMF the entropy of fusion is calculated to be 7.0 cal./deg./repeating unit or 2.34 cal./deg./single bond. These are appreciably larger than for natural rubber⁸ where the entropies of fusion for the single crystal form observed are 3.46 cal./deg./repeating unit and 1.15 cal./deg./single bond, respectively, and for other polymers⁵ where the entropy of fusion per single bond has been found to be in the order of R .

Although it has been tacitly assumed that the major contribution to the entropy of fusion is the configurational freedom gained by the chain units in the liquid state, it is also necessary to consider the entropy change which arises from the volume increase which occurs on melting. This contribution to the entropy of fusion can be calculated^{26,27} from the well known relation

$$(\partial S/\partial V)_T = -\alpha/\beta \quad (5)$$

where α is the volume-temperature coefficient at constant pressure and β is the volume-pressure coefficient at constant temperature. Thus

$$\Delta S_v = -(\alpha/\beta)\Delta V_u \quad (6)$$

where ΔS_v is that portion of the entropy change per repeating unit due to ΔV_u , the volume increase per repeating unit on melting; α and β are evaluated for either the crystalline or liquid phases at the melting point. The entropy of fusion, ΔS_u , can be considered to be approximately the sum of ΔS_v and ΔS_c , where ΔS_c is the increase in configurational entropy on fusion. To evaluate ΔS_v , the volume-temperature coefficient, the volume-pressure coefficient, and the specific volumes of the liquid and the all-crystalline polymer at the melting temperature must be known. For amorphous natural rubber at its melting temperature $\alpha = 7.42 \times 10^{-4}$ cm.³/g./deg.,²⁸ $\beta = 60 \times 10^{-6}$ cm.³/g./bar²⁹ and $\Delta V_u = 0.098$ cm.³/g.^{8,14} so that $\Delta S_v = 1.8$ cal./deg./mole of repeating unit, which is an appreciable portion of the observed ΔS_u . The gain of the configurational entropy on fusion is then 1.7 cal./deg./mole of repeating unit. Not all the quantities entering equation 6 are known for gutta percha so only an approximate calculation can be made for ΔS_v . Taking 1.05 g./cc. as the density of the unit cell of the HMF at 20°¹⁵ and assuming that its volume-temperature coefficient is 2×10^{-4} cm.³/g./deg. one finds ΔV_u at 74° to be 0.182 cm.³/g. of repeating unit. From the data in Fig. 2, the volume-temperature coefficient of the amorphous gutta percha is 7.5×10^{-5} cm.³/g./deg. and we assume that the volume-pressure coefficient at 74° is 60×10^{-6} cm.³/g./bar, the same as for natural rubber. Since the volume-pressure coefficient of amorphous gutta percha has not been measured, the calculated value of ΔS_v will be in error because

(26) J. C. Slater, "Introduction to Chemical Physics," McGraw-Hill Book Co., New York, N. Y., 1939, p. 261.

(27) R. A. Oriani, *J. Chem. Physics*, **19**, 93 (1951).

(28) N. Bekkedahl, *J. Research Natl. Bur. Standards*, **13**, 411 (1934).

(29) A. H. Scott, *ibid.*, **14**, 99 (1935).

(25) K. H. Meyer, "Natural and Synthetic High Polymers," Interscience Publishers, Inc., New York, N. Y., 1942, p. 134.

of uncertainty in the value assumed. From equation 6 ΔS_v for the HMF of gutta percha is then 3.7 cal./mole/deg., giving 5.1 cal./mole/deg. for the configurational contribution to the entropy of fusion. Thus the volume change on melting makes a significant contribution to the observed entropy of fusion both for natural rubber and gutta percha and presumably for other semi-crystalline polymers as well. In fact, similar contributions have been observed in metals²⁷ and more recently in low molecular weight hydrocarbons³⁰ so that they appear to be quite general.

The configurational entropy change per HMF unit of gutta percha is still about three times that of natural rubber at their respective melting temperatures. According to the lattice treatment of polymer configurations³¹⁻³³ the entropy of disorientation per mole of segments at constant volume is given by

$$\Delta S = R \ln [(Z - 1)/e] \quad (7)$$

where Z is the lattice coordination number. A segment is defined as the size of a unit in the corresponding freely jointed chain. This is a chain which matches the contour length and the unperturbed root-mean-square displacement length of the actual chain molecule. Unfortunately, from the experimentally determined ΔS_u we calculate the disorientation entropy per repeating unit so a direct comparison with equation 7 cannot be made. However, from equation 7 we can expect that the disorientation entropy should be greater for the more flexible chain, and for a chain having a higher value of Z , that is the more disordered the packing in the liquid state. Thus, if the packing in the liquid state is the same for both rubber and gutta percha, the results for the configurational entropy of fusion indicate that the gutta percha molecule is more flexible in the liquid state. Conversely, if the two chain molecules possessed the same flexibility the liquid packing in gutta percha would appear to be the more disordered. According to Wall's³⁴ calculations a freely rotating gutta percha molecule, wherein the normal bond distances and valence angles are maintained, will have a greater extension in space than the corresponding rubber molecules. However, the investigations of Wagner and Flory²⁰ indicate that, in the unperturbed state, *i.e.*, in the absence of the effect of solvent, the natural rubber molecule has a greater extension relative to its size calculated by assuming free rotation. They find that the values of the ratio of the unperturbed end-to-end distance to that for free rotation are 1.71 and 1.46 for natural rubber and gutta percha, respectively. Thus steric effects and the potentials

hindering rotation about the single bonds are obviously different in the two cases and allow the molecule in the *trans* configuration to be the more compact one. The greater flexibility of gutta percha in the liquid state would then contribute to the larger value observed for the change in configurational entropy on melting.

Crystallization Kinetics.—When a sample of gutta percha is brought from a temperature above the melting temperature of the HMF to any temperature below, crystallinity develops in a well-defined, reproducible manner when care is taken to start with a completely melted sample. The isotherms which result when the specific volume is plotted against time display the characteristic sigmoidal shape that has been observed for a wide variety of polymer systems.^{35,36} In the temperature range of 20-60° the isotherms at the various temperatures are superposable merely by rescaling the time, which again is in agreement with observations on many polymers.³⁶ The rate of crystallization depends very strongly on the temperature as is indicated in Table II where τ_i , the time at which crystallinity is first observed, is given at various temperatures. τ_i will depend on the over-all crystallization rate, *i.e.*, the nucleation and growth rates as well as the sensitivity of the crystallinity detector. Thus its variation with temperature can be taken as a relative measure of the temperature coefficient of the crystallization rate constant.

TABLE II
TIME FOR DETECTION OF CRYSTALLINITY AT VARIOUS CRYSTALLIZATION TEMPERATURES

T, °C.	τ_i (min.)	T, °C.	τ_i (min.)
0	<3	51	60
20	<3	53	80
35	3-5	55	160
40	7-10	57	340
45	20	59	500-1700
49	43		

An examination of the data in Table II as well as the isotherms, indicates that the crystallization rate constant is a smoothly varying function of temperature despite the fact that the X-ray diffraction analysis indicates that at different temperatures different polymorphs are occurring. For example, when crystallinity develops from the melt at 55° and higher temperatures, only the HMF occurs; at 50 and 40° both the HMF and LMF form; while below 40° only the LMF occurs. One concludes, therefore, that the crystallization rate is independent of the form of the polymorph which results.

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(35) L. A. Wood and N. Bekkedahl, *J. Appl. Physics*, **17**, 362 (1946); *J. Research National Bureau of Standards*, **36**, 489 (1946).

(36) L. Mandelkern, F. A. Quinn, Jr., and P. J. Flory, *J. Appl. Physics*, **25**, 830 (1954).

(30) J. D. Hoffman, private communication.

(31) M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942); *Ann. N. Y. Acad. Sci.*, **41**, 1 (1942).

(32) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(33) Ref. 5, pp. 497 and 574.

(34) F. T. Wall, *J. Chem. Phys.*, **11**, 67 (1943).