[CONTRIBUTION FROM THE RUBBER SECTION, NATIONAL BUREAU OF STANDARDS]

Thermodynamics of Crystallization in High Polymers: Natural Rubber[1,2]

BY DONALD E. ROBERTS AND LEO MANDELKERN

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The existence of an equilibrium melting temperature, T^0_m, at 28 ± 1°, for unstretched natural rubber has been established. using dilatometric methods. The lower melting temperatures previously observed are a consequence of the low temperatures of crystallization and the rapid heating rates employed. From melting point studies of mixtures of the polymer with low molecular weight diluents, the heat of fusion per repeating unit, ΔH_u has been evaluated as 15.3 ± 0.5 cal./g. The values of ΔH_u and T^0_m have then been combined with data of other workers to obtain the following information concerning natural rubber: (1) The variation of melting temperature with applied hydrostatic pressure has been calculated from the Clapeyron equation to be 0.0465 °C./atm. (2) The degree of crystallinity resulting from maintaining a sample at 0° until the rate of crystallization is negligible has been calculated, by three independent methods, to be in the range 26 to 31%. (3) Analysis of the stress–strain–temperature relationship has indicated that crystallization is the cause of the large internal energy changes that are observed at relatively high elongations.

Introduction

In various crystalline polymers the degrees of crystallinity range up to 90% and the sizes of the crystallites are such that a given molecule can participate in more than one crystallite. A crystalline polymer that is not subjected to any external stresses can be considered to consist of a collection of connected, but randomly oriented crystallites which are imbedded in an amorphous matrix. It might appear that for systems possessing such a complex morphology the possibility of any quantitative description of its behavior is precluded. However, it has been demonstrated[3a–e] that when many crystalline polymers are heated slowly the temperature at which the last traces of crystallinity disappear is well-defined, reproducible, and independent of any previous thermal history of the sample. This temperature is the one of thermodynamic significance, for it is the temperature at which the most perfect crystallites are unstable relative to the pure polymeric liquid and hence can be identified with the equilibrium melting temperature, T^0_m of the polymer. Slow heating is of the utmost importance since conditions are then fulfilled to yield ultimately only the more perfect crystallites; the imperfect crystallites will melt at temperatures well below T^0_m. If the heating is conducted rapidly, as is customary for low molecular weight materials, then the melting temperature that is observed,[3a,3b,4,5] depends on the previous thermal history of the sample, and is of uncertain thermodynamic significance. In particular, this melting temperature will depend on the temperature of the crystallization or the manner in which the crystallization was induced. For polyesters[3a] and polyamides[3b] such behavior has been clearly demonstrated to be a consequence of fast heating; when slow heating rates are employed an equilibrium melting temperature has been shown to exist.

The establishment of T^0_m has allowed the application of a thermodynamic analysis to the melting process.[6–8] Thus, the effect of extraneous ingredients as low molecular weight diluents on lowering T^0_m can be predicted and assessed by appropriate experiment. For natural rubber, Wood and Bekkedahl[4] have shown that the melting temperature on fast heating varies from about 0° to 30° depending on the crystallization temperature. The seeming lack of an equilibrium melting temperature in this polymer has led to the opinion that its fusion process cannot be described by a thermodynamic analysis.

Since thermodynamic analysis has contributed greatly to an understanding of the crystallization behavior of other polymers, it is important to inquire as to whether an equilibrium melting temperature does exist for natural rubber. This question can best be answered by experiments in which, for the reasons mentioned above, the melting process must be carried out extremely slowly.

Experimental

Materials.—Three samples of natural rubber were used in this study. Two of the samples were molecular weight fractions and were identical to two of those used by Wagner and Flory[9] in their study of the molecular configuration of natural rubber. The number average molecular weights of these samples were 119,000 and 280,000, respectively. The third sample, though heterogeneous in regard to molecular weight, had been subject to an extensive purification procedure following the method of McPherson.[10,11] This purified sample consisted of 98.7% rubber hydrocarbon, 0.44% protein, and 0.18% ash. To this sample 1.00% of phenyl-β-naphthylamine was added as antioxidant.

The diluents, methyl oleate (Eastman Kodak Co.), *n*-dodecane (The Matheson Co.) and *n*-tetradecane (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 rubber–diluent mixtures were prepared by dissolving about 3 g. of the polymer together with an appropriate amount of diluent in 30 ml. of benzene. The solution was frozen at the temperature of an ice–water mixture and the benzene removed by subliming for 24 hours. The polymer–

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[1] A portion of this work was supported by the Office of Naval Research, Washington, D. C.

[2] Presented in part before the 125th Meeting of the American Chemical Society, Kansas City, Mo., March, 1954.

[3] (a) R. D. Evans, H. R. Mighton and P. J. Flory, THIS JOURNAL, **72**, 2018 (1950); (b) P. J. Flory, L. Mandelkern and H. K. Hall, *ibid.*, **73**, 2532 (1951); (c) L. Mandelkern and P. J. Flory, *ibid.*, **73**, 3206 (1951); (d) L. Mandelkern, R. R. Garrett and P. J. Flory, *ibid.*, **74**, 3949 (1952); (e) L. Mandelkern, M. Hellman, D. W. Brown, D. E. Roberts and F. A. Quinn, Jr., *ibid.*, **75**, 4093 (1953).

[4] L. A. Wood and N. Bekkedahl, *J. Appl. Phys.*, **17**, 362 (1946); *J. Research Natl. Bur. Standards*, **36**, 489 (1946).

[5] J. T. Maynard and W. E. Mochel, *J. Polymer Sci.*, **13**, 235 (1954).

[6] P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).

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

[8] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 568ff.

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

[10] A. T. McPherson, *J. Research Natl. Bur. Standards*, **8**, 751 (1932).

[11] We are indebted to Mrs. Rachel Fanning of the National Bureau of Standards for the purification and subsequent analysis of the rubber hydrocarbon.

diluent mixture was then weighed and the amount of diluent which remained was computed. The volume fractions of the two components were computed at the melting temperature of the mixture.

The dilatometric methods[3b,3c] previously described in great detail were followed in the present work, the dilatometers being immersed in a constant temperature bath where temperature was regulated to within ±0.1° in the range studied.

Results and Discussion

Pure Natural Rubber.—The dependence of the specific volume on temperature for a molecular weight fraction of natural rubber for four different crystallization temperatures, T_c, is shown in Fig. 1.

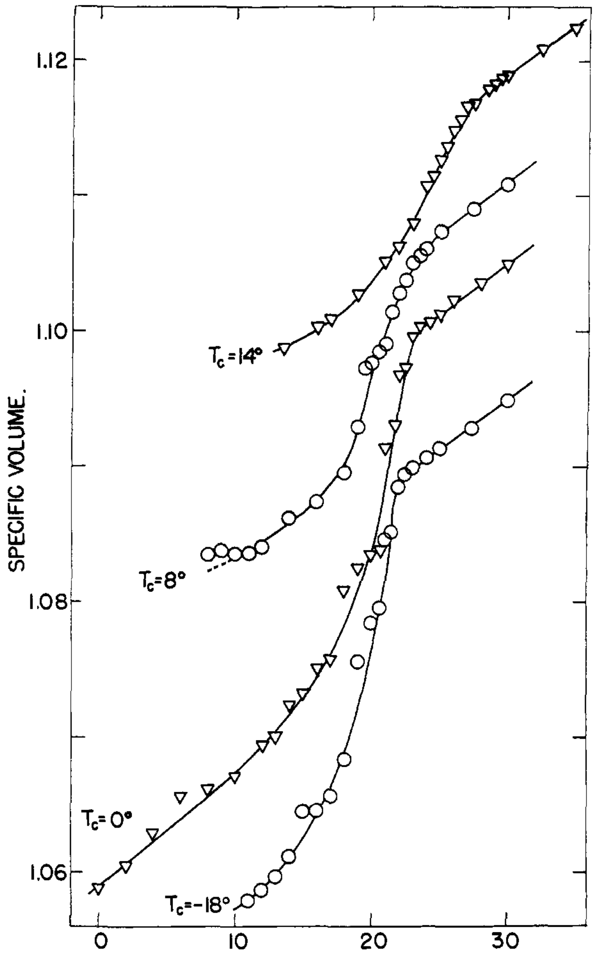

Fig. 1.—Specific volume as a function of temperature for a molecular weight fraction of natural rubber, $\overline{M}_n$ = 119,000. Each curve represents heating cycle subsequent to crystallization at the indicated temperatures, and all are arbitrarily displaced along ordinate. For actual specific volumes add 0.004 cm.^{3}/g. to the −18° crystallization curve; subtract 0.006 from the 0° curve; subtract 0.012 from the +8° curve; subtract 0.020 from the +14° curve.

For clarity in presentation, the curves have been arbitrarily displaced along the ordinate. This plot is typical of the observations for the other two samples of natural rubber studied. The significant thermal history of the samples consisted in the transfer from a temperature above the melting point to the predetermined crystallization temperature. After sufficient crystallinity had developed the dilatometric observations were made in the order of ascending temperature, employing slow heating rates. Up to 15° the temperature was increased at the rate of about 1°/12–24 hours, and at each temperature the volume first increased for about 6 to 12 hours then decreased reaching a constant value within the prescribed time. This behavior is typical of the melting process in polymers[3a-e,12,13] and is apparently due to the partial melting of imperfect crystallites and the subsequent formation of more perfectly ordered regions. Above 15° the heating rate was decreased to about 1°/24–48 hours, and a similar behavior was observed in the volume–time relation, though at temperatures within 3–5° of the melting temperature the subsequent decrease in volume was absent. The variations of the specific volume with time at a fixed temperature as just described are applicable to the melting process subsequent to crystallization at −18, 0 and +8°. At 14° approximately 100 days were required for the development of sufficient crystallinity to permit satisfactory observations. In this case the variations of the volume with time, at any given temperature on subsequent heating, were much less than that observed after crystallization at the other temperatures.

The specific volume–temperature plot of Fig. 1 indicates quite clearly the temperature at which the last traces of crystallinity disappear, and these values are listed in Table I. The results for the crystallization at −18, 0 and +8° are, within experimental error, independent of both the crystallization temperature and the individual samples. On fast heating,[4] the variation in the temperature at which melting was complete is about 20°, ranging from +2° for crystallization at −18 to 22° for crystallization at +8°. For crystallization at +14°, we observe on slow heating a melting temperature 5–6° higher than for the lower crystallization temperatures. This is a reflection of the more perfect degree of order that is achieved by a slow crystallization process, which is also manifested in the small changes observed in the volume–time relations. The melting temperature following 14° crystallization, namely, 28 ± 1°, must then be close to the true equilibrium melting temperature.

TABLE I

MELTING TEMPERATURES OF NATURAL RUBBER SAMPLES AFTER CRYSTALLIZATION AT THE INDICATED TEMPERATURE

Crystn. temp., (Tc), °C.	M.t. (Tm), °C. Sample I $\overline{M}_n$ = 119,000	Sample II $\overline{M}_n$ = 200,000	Sample III Purified rubber
−18	22 −22.5	21 −21.5	21 −22
0	22.5–23	21.5–22	22.5–23.5
+ 8	23.5–24	21.5–22	22.5–23
+14	27 −28	25.5–26	28 −29

There are many reports of types of natural rubber whose melting temperatures appear to be much greater than 28° and this phenomenon also needs explanation in the light of the assignment of 28° as T^0_m for natural rubber. Rubber which has been

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(12) M. Dole, A. E. Worthington and Paul Marx, Abstracts 125th Meeting of the American Chemical Society, 1954.

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

stretched beyond its normal limit can be given a large set by cooling. Such rubber is termed "racked rubber" and its X-ray diffraction patterns show that it is composed of highly oriented crystallites.[14] On subsequent heating the crystallites disappear in the vicinity of 35 to 40° and the melting process is accompanied by a large retraction.[15,16] Since the crystallites are oriented, the connecting amorphous regions must necessarily be deformed from their statistically more probable configuration (though no external stresses are maintained), and it is then expected that the crystallites will be stable at higher temperatures compared to the undeformed system. Another variety of natural rubber is "stark rubber"[4] which is normally found crystalline at room temperature, and whose melting temperature is in the range 35 to 45°. Recent X-ray diffraction investigations[17] of several different varieties of "stark rubber" indicates that its crystallites are also oriented.

When these anomalies are accounted for, natural rubber displays a melting behavior that is typical of polymeric materials. The low melting points can be attributed to the low temperature of crystallization and the subsequent rapid heating rates employed. The abnormally high melting points of "racked" and "stark" rubber are due to the internal stresses and orientation of the amorphous regions caused by the orientation of the crystallites.

Polymer–Diluent Mixtures.—The addition of a lower molecular weight diluent to a semi-crystalline polymer lowers the equilibrium melting temperature in a manner similar to the depression of the melting temperature of a low molecular weight crystal. By the application of the thermodynamic principles governing the melting in binary systems it has been shown that[7,8]

$$1/T_{\mathrm{m}} - 1/T^0_{\mathrm{m}} = (R/\Delta H_{\mathrm{u}})(V_{\mathrm{u}}/V_1)(v_1 - \chi_1 v_1^2) \quad (1)$$

where T_{m} is the melting temperature of the polymer–diluent mixture, R is the gas constant, ΔH_{u} the heat of fusion per mole of repeating unit, V_{u} is the molar volume of the repeating unit, V_1 the molar volume of the diluent, v_1 is the volume fraction of the diluent, and χ_1 is a thermodynamic interaction parameter[18] which can be written as $\chi_1 = BV_1/RT_{\mathrm{m}}$ where B is the molar free energy change brought about by first neighbor interactions. A form of equation 1 more convenient for the analysis of experimental data is

$$[1/T_{\mathrm{m}} - 1/T^0_{\mathrm{m}}]/v_1 = (R/\Delta H_{\mathrm{u}})(V_{\mathrm{u}}/V_1)\left[1 - \left(\frac{BV_1}{R}\right) v_1/T_{\mathrm{m}}\right] \quad (2)$$

Thus, from measurements of the melting temperature as a function of diluent concentration there can be obtained the value of ΔH_{u}, one of the fundamental molecular parameters of crystalline polymers and one of great utility.

The melting temperatures of mixtures of the purified rubber hydrocarbon with each of the three diluents were determined dilatometrically. The heating rates employed were similar to those described for the pure polymers and similar variations of the volume with time were observed. The crystallization was induced by maintaining the original amorphous mixtures at temperatures where the crystallization rate was comparable to that of the bulk rubber at 0°, so that appreciable crystallization developed after 48 hours. Because of the lengthy time intervals required it is quite impractical to conduct the crystallization at temperatures more conducive to the formation of the most perfect crystallites. To correspond with actual experimental conditions. T^0_{m} was therefore approximated by 296°K. (23°C.) for these studies, which introduces a slight error in the subsequent analysis. The melting temperatures of the mixtures, which covered a range of concentrations from about $v_1 = 0.10$ to 0.40, are given in Table II. In Fig. 2, as suggested by equation 2, $(1/T_{\mathrm{m}} - 1/T_{\mathrm{m}}{}^0)/v_1$ is plotted against V_1/T_{m} for each of the diluents used.

TABLE II

MELTING TEMPERATURES OF NATURAL RUBBER–DILUENT MIXTURES

v_1	T_{m}, °C.	ΔH_{u}, cal./mole of repeating unit[a]	BV_1/R
With tetradecane			
0.122	17	1040 ± 80	1.07
.153	16		
.215	14–15		
.240	13		
.288	11–12		
.296	11		
.394	7–8		
With methyl oleate			
0.157	17–18	980 ± 30	1.49
.170	16–17		
.210	16–17		
.292	14		
.297	13–14		
.364	11–12		
.370	12–13		
With dodecane			
0.165	15–16	1100 ± 60	1.18
.220	13–14		
.256	12–13		
.356	8–9		
.360	8–9		

[a] The uncertainty in ΔH_{u} is estimated from the intercepts of the slightly different straight lines to which the data in Fig. 2 can be fitted.

The data of Fig. 2 can be represented by straight lines, and from the slopes and intercepts of the plots ΔH_{u} and BV_1/R are obtained; these values are also given in Table II. Employing these parameters and making use of equation 1 the dependence of T_{m} on composition can be computed; these calculated results are represented in Fig. 3 by the solid lines. The plotted points represent the experimental observations, and good agreement is achieved. The deviations from linearity observed in Fig. 2 are merely reflections of the extreme sensitivity of this type plot when the depressions of T^0_{m} are small. Concordant values of ΔH_{u} are obtained as expected, since it is a property of the

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(14) E. A. Hauser and P. Rosbaud, *Kautschuk*, **3**, 17 (1927).

(15) L. R. G. Treloar, *Trans. Faraday Soc.*, **36**, 538 (1940).

(16) H. Feuchter and E. A. Hauser, *Kautschuk*, **5**, 194, 218, 245, 276 (1929).

(17) D. E. Roberts and L. Mandelkern, in preparation.

(18) Ref. 8, page 507ff.

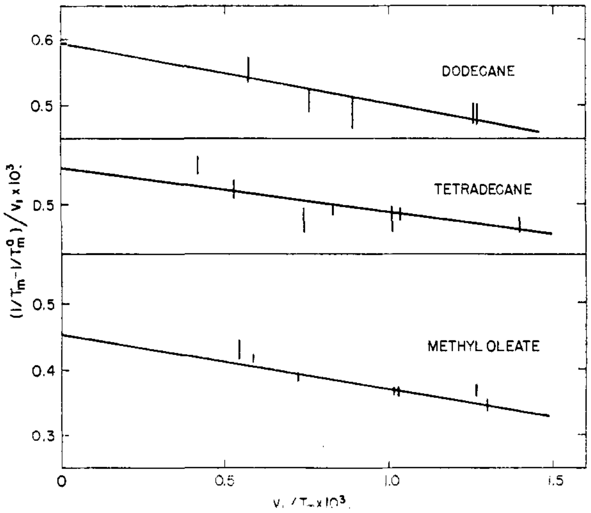

Fig. 2.—Plot of $(1/T_m - 1/T^\circ_m)/v_1$ *vs.* v_1/T_m for natural rubber mixed with the indicated diluents.

repeating unit and is independent of the nature of the diluent or its interaction with polymer. The average value of ΔH_u is 1040 ± 35 cal. per mole of repeating unit, or 15.3 cal. per gram of polymer. If natural rubber could be made completely crystalline, a situation presumably never relizable, the heat of fusion that would be observed from calorimetric measurements would be ΔH_u. The entropy of fusion is calculated to be 3.46 cal. per repeating unit or 1.15 cal. per deg. per single bond that can "rotate freely" when in the amorphous state. This value is somewhat smaller than has been observed for other polymers[7,8]; however, this is not too rational a basis of comparison since at a minimum the entropies of fusion of various polymers should be compared at constant volume.

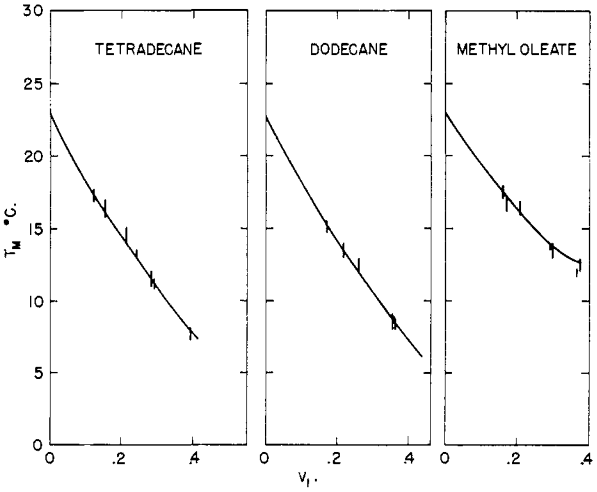

Fig. 3.—Plot of melting temperature, T_m, of natural rubber–diluent mixtures against volume fraction of diluent, v_1. Solid lines are calculated.

The value of ΔH_u can also be obtained from appropriate experiments where the crystallization is induced by stretching rather than by cooling. If T_m is measured as a function of the elongation at high elongation, then by the application of an equation developed by Flory[19] ΔH_u can be deduced. Experiments of this type are much more difficult to perform and interpret than those reported here. The results of Arlman and Goppel[20] and Fox, Flory and Marshall[21] give values of ΔH_u of 1030 and 800 cal. per mole, respectively, which are in fair accord with the value based on the diluent studies, particularly when due regard is given to the difficulties of the stretching experiments and the differences in the materials used.

The volume change per repeating unit on melting, Δv_u, can be estimated for natural rubber from data available in the literature. The specific volume of the completely amorphous polymer is given by Wood and Bekkedahl[4] as 1.099 cm.^{3}/g. at 28°. Bunn[22] and Fisher[23] have reported a value of 1.00 g./cm.^{3} as the density of the unit cell of the rubber crystallites at 20°. At 28° the specific volume of the crystal can be estimated quite accurately to be 1.001 cm.^{3}/g. by assuming that the rate of change of specific volume with temperature is 2×10^{-4} cm.^{3}/g./deg.[24] Δv_u then is 0.098 cm.^{3}/g. The variation of the melting temperature with applied hydrostatic pressure, P, is given by the Clapeyron equation as

$$dT^0_m/dP = T^0_m \, \Delta v_u/\Delta H_u = 0.0465 \text{ deg./atm.} \quad (3)$$

when T^0_m is taken as 301°K. at 1 atmosphere. The melting temperature at 1230 atmospheres has been observed by Dow[25] to be 77.5°, and calculated from equation 3 to be 84°. The difference between calculated and observed is certainly within the experimental error and illustrates again the validity of the application of thermodynamic principles to the melting of crystalline polymers, in this case for a one component system.

Polymers in general and natural rubber in particular are only partially crystalline even at equilibrium. Since many of the physical and mechanical properties of polymers are dependent on the amount of crystallinity it is quite important to determine this quantity reliably. It has been already pointed out that on heating, subsequent to crystallization, marked variations in the amount of crystallinity occur in polymeric materials before apparent equilibrium is attained at a given temperature. Also if crystallization is occurring from the supercooled liquid the rate of crystallization, and consequently the time for the equilibrium degree of crystallization to be attained, is extremely temperature sensitive,[26] and can vary from minutes to days depending on the temperature. Thus any statements about the degree of crystallinity must be accompanied by a definite thermal history. Since the degree of crystallinity can be determined by a variety of methods, if a comparison between the different methods is to be made it is of the utmost importance that the polymer receive

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(19) P. J. Flory, *J. Chem. Phys.*, **15**, 397 (1947).

(20) J. J. Arlman and J. M. Goppel, *Applied Sci. Res.*, **A2**, 1 (1949).

(21) T. G. Fox, Jr., P. J. Flory and R. E. Marshall, *J. Chem. Phys.*, **17**, 704 (1949).

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

(23) D. Fisher, *Proc. Phys. Soc.*, **60**, 99 (1948).

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

(25) R. B. Dow, *J. Chem. Phys.*, **7**, 201 (1939).

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

the same thermal history. Prior to the measurement of the degree of crystallinity of natural rubber a convenient thermal history to follow is that of crystallization from the supercooled liquid at 0° for a sufficient period of time so that equilibrium is practically attained.

For natural rubber which had received this thermal treatment, Bekkedahl and Matheson[27] found that the heat of fusion as determined calorimetrically, ΔH^*_u, is 4.00 cal./g. Since ΔH_u, the heat of fusion per repeating unit, has been determined from the present work to be 15.3 cal./g., the ratio $\Delta H^*_u/\Delta H_u$ is equal to 0.262; this is the fraction of the material that is crystalline. This quantity can also be determined from density measurements since λ, the degree of crystallinity, is equal to the ratio $(\bar{V}_a - \bar{V})/(\bar{V}_a - \bar{V}_c)$ where $\bar{V}_a$ is the specific volume of the amorphous or liquid polymer at the temperature under consideration, $\bar{V}_c$ the specific volume of the all-crystalline polymer at this temperature, and $\bar{V}$ the specific volume of the semi-crystalline polymer. At 0° $\bar{V}_a$ and $\bar{V}$ are 1.080 and 1.054 cm.^{3}/g., respectively[4]; a value at 0° of $\bar{V}_c$ of 0.996 cm.^{3}/g. is determined from the density of the crystal unit cell[22,23] assuming that $d\bar{V}_c/dT$ is 2×10^{-4} cm.^{3}/g./deg. C. The degree of crystallinity is then calculated to be 0.31 ± 0.04.

The rate of change of specific volume with temperature of a substance in the glassy state $d\bar{V}_g/dT$ is known to be the same as $d\bar{V}_c/dT$, the rate of change of specific volume with temperature of a substance in the crystalline state.[28] It would be expected, then, that for natural rubber $d\bar{V}_g/dT$ would be independent of the degree of crystallinity and equal to $d\bar{V}_c/dT$. It has been verified by Bekkedahl[24] and by Work[29] that $d\bar{V}_g/dT$ for natural rubber is independent of the degree of crystallinity. Thus λ should equal the ratio of $(d\bar{V}_a/dT - d\bar{V}/dT)/(d\bar{V}_a/dT - d\bar{V}_g/dT)$. From Bekkedahl's work[24] it is found that $d\bar{V}_a/dT$ equals 7.42×10^{-4} cm.^{3}/g./deg. C., $d\bar{V}/dT$ equals 5.72×10^{-4} cm.^{3}/g./deg. C., and $d\bar{V}_c/dT$ equals 2×10^{-4} cm.^{3}/g./deg. C., so that λ becomes equal to 0.31 ± 0.04.

These independent methods give excellent agreement for the fraction of the natural rubber which is crystalline and are in accord with the much earlier estimates of Parks.[30] Determinations of the degree of crystallinity by means of X-ray methods are unfortunately not available for natural rubber undergoing the specified thermal treatment. However, from the work of Goppel and Arlman[31] on unstretched natural rubber it can be reliably estimated that the degree of crystallinity resulting from the specified thermal treatment would be about 0.30 to 0.35. Thus, good agreement is obtained for the degree of crystallinity of natural rubber regardless of the method used in its determination. This appears not to be the case for some other polymers, notably polyethylene,[32,33] which has been extensively studied. However, for any rational comparison to be made the same thermal history must be maintained and it is not at all clear that this has been done for the other polymers investigated.

An expression for the retractive force f of stretched vulcanized (cross-linked) natural rubber can be given from general thermodynamic considerations as[34]

$$f = (\partial E/\partial L)_{T,V} + T(\partial f/\partial T)_{p,\alpha} \qquad (4)$$

where

$$(\partial f/\partial T)_{p,\alpha} = -(\partial S/\partial L)_{T,V}$$

and E is the internal energy, S the entropy, L the stretched length, and α the ratio of the stretched to the unstretched length at the given temperature. By maintaining the pressure p and the elongation α constant and determining the variation of the retractive force with temperature, the contributions to the retractive force of both the internal energy changes and the entropy changes can be assessed.

It is found[35,36] that up to elongations of about 200 to 300% (α = 3–4), $(\partial E/\partial L)_{T,V}$ is effectively equal to zero so that the change in entropy with length of the entire amorphous material is entirely responsible for the retractive force. At slightly higher elongations $(\partial E/\partial L)_{T,V}$ begins to decrease very rapidly and assumes large negative values on subsequent elongations. It is well known from X-ray[31,37] and density[31,38] measurements that this is a region where the crystallization of rubber commences. The isothermal stress–strain curve at this point shows an abrupt and continual rise due to the accelerated decrease of entropy with length on further elongation.[19]

The total internal energy change ΔE in stretching the rubber from $\alpha = 1$ to a given elongation α can be obtained, as has been indicated by Boonstra,[39] by graphically determining the value of

$$\int_{\alpha=1}^{\alpha} (\partial E/\partial L)_{T,V}\, d\alpha$$

Boonstra[39] suggested that if the decrease in internal energy on stretching were due entirely to crystallization, the ratio of $\Delta E/\Delta H_u$ should equal the fraction of the material crystalline. Using a value of ΔH_u determined in a somewhat arbitrary manner, though remarkably close to the value reported here, he was able to demonstrate that almost all the internal energy change was indeed due to crystallization. The results of repeating the calculations based on Boonstra's original data but using ΔH_u equal to 15.3 cal./g. are given in Table III. Two different rubber vulcanizates designated as sample S and T, respectively, were used and the degree of crystallinity was independently deter-

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(30) G. S. Parks, *J. Chem. Phys.*, **4**, 459 (1936).

(31) J. M. Goppel and J. J. Arlman, *Appl. Sci. Research*, **A1**, 462 (1949).

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(37) J. E. Field, *ibid.*, **12**, 23 (1941).

(38) W. L. Holt and A. T. McPherson, *J. Research Natl. Bur. Standards*, **17**, 657 (1936).

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TABLE III

DEGREE OF CRYSTALLINITY OF NATURAL RUBBER ON STRETCHING (FROM BOONSTRA)[39]

ΔH_u = 15.3 cal /g. of unit.

Elongation:	300%			400%			500%		
	ΔE, cal./g.	$\Delta E/\Delta H_u$	λ (X-ray)	ΔE, cal./g.	$\Delta E/\Delta H_u$	λ (X-ray)	ΔE, cal./g.	$\Delta E/\Delta H_u$	λ (X-ray)
Sample S	0.394	0.026	0.04	1.845	0.12	0.15	3.46	0.23	0.30
Sample T	.398	.026	.05	1.44	.095	.105	2.93	.19	0.19–0.22

mined by the X-ray method.[31] Quantitative agreement is obtained between $\Delta E/\Delta H_u$ and the degree of crystallinity, which strongly suggests that the crystallization process is the cause of the large internal energy changes that are observed. This conclusion is based solely on a thermodynamic analysis of the experimental facts without recourse to any molecular interpretation as to the nature of the retractive force. A quantitative molecular interpretation of the upsweep of the stress-strain curve which sets in at about $\alpha = 3$ naturally will have to take into account the phase change that is occurring. It cannot be explained solely on the basis of the entropy change that occurs in deforming a completely amorphous material.[40,41]

Acknowledgment.—The authors wish to acknowledge many interesting discussions on this subject with L. A. Wood and N. Bekkedahl and thank them for making available many of their original data.

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WASHINGTON, D. C.

[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY, TULANE UNIVERSITY]

The Rate of Reaction of Ethyllithium and Anisole

BY T. F. FAGLEY AND ELIAS KLEIN

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The reaction of ethyllithium with anisole in benzene solutions was found to follow, at 30 and 40°, the rate law, $dV/dt = k(V_\infty - V)^2b^2/(V_\infty a)$, where V is the volume of ethane at time t, b and a are the initial concentrations of anisole and ethyllithium, respectively. The presence of the $(V_\infty a)$ term is interpreted. Dielectric constant measurements are correlated with the change in rate with anisole concentration.

In the extensive investigations of the reaction of alkyl and aryl alkali compounds with such compounds as anisole, thianaphthene and alkyl benzenes, hydrogen–alkali interchange has been interpreted to involve coördination of the organometallic reagent with the electronegative atom or with the pi electrons in the aromatic nucleus. Bryce-Smith[1] has suggested that the reactions are not nucleophilic, since the aromatic nucleus retains the electrons of the original carbon–hydrogen bond. He considered the reaction to involve a protophilic attack in which the alkali compound possibly functions as an ion-pair. Roberts and Curtin[2] stated that the predominantly *ortho* orientation observed with the substituents F, OCH_3, CF_3 in the benzene ring is best accounted for by assuming that the reaction involves an initial coördination of the metallic atom of the metalating agent with an unshared electron-pair of the substituent group followed by the removal of an *o*-hydrogen by the anion of the metalating agent.

In this Laboratory a kinetic study of the reaction of ethyllithium with anisole in benzene solutions has been made. The difficulty of preparing pure ethyllithium in peroxide-free ethers and the possibility of cleavage of the ether in concentrated solutions at and above room temperatures discouraged attempts at measurements in such media. The lithiation of thianaphthene in benzene was discarded because of precipitation of the product and evidence of catalytic effect of the solid. The reaction of ethyllithium, prepared in benzene, with benzene solutions of anisole was finally chosen for study. Considerable care was taken in the preparation of the reagents to eliminate ambiguities resulting from contamination by peroxides, ethoxides and colloidal lithium. The reaction was followed by measuring the volume of ethane collected over mercury, at constant pressure, as a function of time. The solubility of ethane in benzene–anisole mixtures necessitated using small volumes (5 milliliters) of relatively concentrated solutions. Further, since the reaction was extremely slow in solutions less concentrated than 1 molar in anisole (even in 1.667 *M* anisole the rate of evolution was 5 ml. per hour), and concentrated solutions of ethyllithium in benzene were not possible because of the limited solubility of ethyllithium in benzene, high concentrations of anisole were required. This presented the additional problem of "medium effect" on the kinetics. An attempt to evaluate this effect was made in terms of dielectric constant measurements of some anisole–benzene solutions.

Experimental

Materials.—The anisole was an Eastman White Label product. It was dried with metallic sodium and then fractionally distilled through a Vigreux column. The refractive index at 25° was 1.5144 for the sodium D-line. It was stored over sodium and a stream of oxygen-free dry nitrogen passed through it to displace any dissolved oxygen. The benzene used as solvent was Reagent Grade "Baker Analyzed"; it was fractionally crystallized, distilled and dried

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(1) D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954).

(2) J. D. Roberts and P. Y. Curtin, THIS JOURNAL, **73**, 810 (1951).